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A theoretical approach to aromatic-radical interaction

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A Theoretical Approach to Aromatic-Radical Interaction

By

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A thesis submitted to the University of Wales in the candidature

for the degree of Philosophiae Doctor

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Abstract

This thesis describes work conducted towards the design and implementation of suitable models to describe accurately aromatic radical systems and the stabilising non covalent interaction with the radical. The DFT methodologies, B3LYP, BH&HLYP and B3PW91 have been implemented throughout this work as a result of an extensive trail.

A key finding was the identification and elucidation of the C_6H_6/Cl^{-1} radical complex its properties and thermochemical data. The most stable structure of this complex was identified as a hybridised intermediate σ - π -complex. This non covalent complex possesses charge transfer character, where the Cl⁻ is positioned approximately 2.5Å from the aromatic ring.

The optimised model for this structure was further employed as a blueprint model for the design and analysis of other aromatic-radical systems. Throughout the analysis of other Ar-radical complexes theoretical DFT calculations predict the most stable geometry is one which mirrors the $C_6H_6/C1$ radical complex.

The solvent effect on the C_6H_6/Cl radical complex in the hydrogen abstraction reaction of alkanes has also been examined. These processes are currently not widely understood. Methane, ethane, propane and *t*-butane have been modelled with the reaction of the C_6H_6/Cl complex and the un-complexed chlorine radical. DFT calculations predict an endothermic pathway for the reaction of Cl with primary hydrogens. An exothermic pathway is predicted for the reaction with secondary and tertiary hydrogens. The predicted stabilities of the transition states from these reactions in the presence of the aromatic moiety are greatly enhanced. It is clearly seen that the presence of the benzene moiety distinctly facilitates the selectivity of tertiary hydrogen abstraction.

Introduction

Radicals are highly reactive intermediates that play an important role in a wide variety of synthetic, ¹⁻³ biological^{4,5} and atmospheric⁶ processes, to name a few. In general, radicals are very unstable and are regarded as highly reactive, short-lived intermediates, in the same class as carbocations (R_3C^+), carbanions (R_3C^-) and carbenes, (R_2C :). Radicals are specifically defined as atoms or compounds containing at least one unpaired electron. Simple examples include hydroxyl and chlorine radicals ('OH and Cl'), which have one unpaired electron in their outer valance shell, resulting in an overall neutral, electron-deficient species. The high reactivity of radicals can therefore be rationalised by the desire of the unpaired electron to pair with a second electron in order to produce a filled outer shell, forming a two-electron, covalent bond.

The lifetime of different radicals can vary significantly and relies on both thermodynamic and kinetic factors, namely the stability conferred by delocalisation of the unpaired spin and steric hindrance. Typically, the short lifetimes of radicals mean that their isolation and long term study is challenging under normal laboratory conditions. As a result, whilst the concept of a radical was already well established by the 1800's,⁷ the first solid experimental evidence for the presence of an organic radical was not made until 1900 by Moses Gomberg.³ Gomberg³ reacted triphenylmethylbromide **1** with silver in the absence of oxygen and observed a yellow solution which he attributed to the presence of the delocalised radical **2** (Figure i.1). It was possible for Gomberg to observe this radical as it reacted slowly due to the steric hindrance at the triphenylmethyl centre precluding rapid dimerisation. This is a clear example of radical persistence through steric factors.



Figure i.1. Reaction of triphenyl methyl bromide 1 to form the triphenyl methyl radical 2.³

In many radical reactions, thermodynamic stability is a controlling factor where radical formation is the rate determining step, *eg.* hydrogen abstraction reactions. The more stable the radical intermediate, the more likely it is to form, thus it is less reactive in subsequent reactions, relative to a less stable radical. Radical stability is reflected in the magnitude of the bond dissociation energy (BDE), with more readily formed radicals having smaller BDEs than those that are more difficult to form (Table i.1).

	BDE
Compound	kJ mol ⁻¹
F ₂	158
Cl ₂	242
Br ₂	192
I ₂	151
Me-H	435
<i>i</i> - Pr	410
t-Bu-H	385
Benzyl-H	368

Table i.1. Bond Dissociation Energies.8

Radical stability is influenced mainly by electronic factors, including the electronegativity of the atom holding the unpaired spin, hyperconjugation, conjugation, and the electron-donating and electron-withdrawing influence of adjacent functional groups. In the case of the halogen radicals, chlorine, bromine and iodine, the BDE of the corresponding diatomic halides generally increases with electronegativity of the atomic species (Table i.1).⁸ Consequently, chlorine radicals are more reactive in hydrogen abstraction reactions than bromine radicals, which are in turn more reactive than iodine radicals.

The phenomenon of hyperconjugation can be used to explain the relative reactivity of C-H bonds. For a typical alkane, the rates of hydrogen abstraction increase in the order, primary < secondary < tertiary. This corresponds to BDEs of 435, 410 and 385 kJ mol⁻¹, respectively,⁸ as shown in Table i.1. As can be seen, the tertiary C-H bonds are the weakest and consequently these hydrogens are abstracted at the fastest rates.

Hyperconjugation affords additional stabilisation in a radical centre. This effect arises from an interaction between the p orbital of the radical with the pair of electrons from a neighbouring σ bond, similar to the effect of delocalisation known to exist in the π -electron cloud in benzene. A simple example of hyperconjugation can be seen in the ethyl radical **3**, Figure i.2.⁸



Figure i.2. Hyperconjugation in the ethyl radical 3.

Greater stabilisation is achieved when the radical centre is surrounded by additional alkyl groups or other substituents which are electron donating, with inductive effects stabilising the radical. Resonance effects also lead to an increase in stabilisation due to electron delocalisation, however the interaction is between the electron in the p orbital of the radical and a lone pair of electrons or a neighbouring π -bond. A typical example of resonance can be seen in the benzyl radical **4**.



Figure i.3. Resonance in the benzyl radical.

The effects of resonance (or mesomerism) by either electron-donating or electronwithdrawing groups can also influence radical stability.⁸ Overlapping of the orbitals between the heteroatom and the p-orbital of the radical leads to three-electron bonding. In aromatic systems, substituents may give rise to a perturbation that is greater at the *para* position than at the *meta* position. This effect is characteristic of the conjugative charge, which is transmitted to alternate atoms. For heteroatoms which are electron-donating (O, N) the radical stability is enhanced, where conversely, electron-withdrawing heteroatoms (F) afford little radical stabilisation. A substituent may be therefore characterised as electron-donating (+R) or electron withdrawing (-R) (Figure i.4).



Figure i.4. Resonance effects.

For those molecules which contain both electron-withdrawing and electron-donating substituents, the radical has increased stability from captodative effects. The stability of the radical is more pronounced from the combined effect of the two substituents. The effectiveness of this type of interaction leads to the additional stability associated with the ability of the unfilled orbital to transmit charge between the electron-withdrawing and electron-donating groups. A simple example of captodative stabilisation may seen in the glycine radical (Figure i.5).⁷



Figure i.5. Captodative stabilisation in the glycine radical.

To enquire as to the effects of different substituents on an aromatic compound, a linear free energy relationship may be inferred by use of the Hammett equation,^{9,10} (i.1) which has been derived from the acidities of aromatic acids.^{9,10}

$$\log K_i / K_H = \rho \sigma_i \tag{i.1}$$

A correlation of this type is clear evidence that the changes in structure produce proportional changes in the activation energy.

 K_i represents the equilibrium constant of substituent *I*, compared with that of an unsubstituted compound (H). The substituent constant σ is a number characteristic of the substituent. The sign and magnitude of σ for a given substituent is a measure of its capacity to electronically perturb its environment. A negative σ value signifies an electron-donating group (+R) where a positive σ value signifies an electron withdrawing group (-R). The slope of a Hammett plot of K_i versus σ is the reaction constant, ρ . This is a measure of the sensitivity of a reaction to the effects of electronic perturbation. The magnitude of ρ gives a measure of the degree to which the reaction responds to different substituents. This measure is a logarithmic scale so a change of 1 indicates a tenfold change in rate constant for unit change in σ .⁸⁻¹⁰ A positive value for ρ signifies that the electron donating (-R) substituent. A negative value of ρ signifies that the electron donating (-R) substituent facilitates in stabilising the developing positive charge, which is situated in close proximity to the aromatic ring.

Russell¹¹ demonstrated that the plot of the relative rates *versus* σ^{8-10} for the hydrogen abstraction from toluene gives a reasonably linear Hammett correlation. This linear relationship with radicals produces the ρ values that are typically low and negative, as is shown in Table i.2.

Reaction	°C	ρ
$ArCH_3 + R^{\bullet} \rightarrow ArCH_2 + RH$		
$\mathbf{R}' = \mathbf{B}\mathbf{r}'$	80	-1.4
$R' = CCl_3'$	55	-1.5
R' = ROO'	30	-0.6
R = t-BuO'	40	-0.4

Table i.2. Linear free energy relationships for hydrogen abstraction reactions from toluene.¹¹

The correlations of reaction rates with σ^{8-10} do not always produce linear Hammett plots. Strong conjugatative interaction from +R groups (*eg.* lone pairs) in the *para* position may develop to a greater extent (than that measured in the dissociation of benzoic acids), which therefore produces a deviation from linearity in the Hammett plot. Thus, the +R effect is also dependant on the reaction in addition to the effect of the substituent. Different sets of substituent constants have been generated for groups which express enhanced resonance properties *via* the +R groups (*eg.* lone pairs) and the –R groups (*eg.* NO₂), which are expressed as the σ^{+12-14} and σ^{-12-14} scales respectively. For radical reactions a scale of substituent effects σ^{*15} has been derived from the thermal decomposition of dibenzylmercury derivatives. All of the values for σ^{*15} are positive which infers that any group is more effective than hydrogen in stabilising the radical centre.

Radical interactions between neutral species occur between the singly occupied molecular orbital (SOMO) of the radical and the frontier orbitals of the other reagent. A lowering of energy within the system will result from bonding interactions with the highest occupied molecular orbital (HOMO) (or the lowest unoccupied molecular orbital LUMO) with the SOMO of the radical. Thus, either the adjacent electron pair, π -, or vacant orbital has the ability to stabilise the radical centre. Interaction of the frontier orbitals is illustrated in Figure i.6. The radical is said to display nucleophilic character if the SOMO-LUMO interaction dominates. However, if the SOMO-HOMO interaction is more pronounced then the radical is said to display electrophilic character. Hydrogen abstraction by chlorine radical is an example of the chlorine atom behaving as an electrophilic radical.



Figure i.6. Frontier orbital interaction of a radical with the HOMO and LUMO.

Hydrogen abstraction reactions by highly reactive chlorine radicals are known to be exothermic.⁸ This implies an "early" transition state along the reaction coordinate. Hammond's postulate^{8,16} states that the transition state of an exothermic reaction is reactant-like. The radical character in the "early" transition state is distributed from the chlorine atom to the carbon atom. However, reaction at the tertiary hydrogen will produce a more stable intermediate than reaction at the primary position. Therefore the activation energy required for reaction at the tertiary hydrogen will be less than that required for the primary position, resulting in a faster reaction rate for tertiary hydrogen abstraction. However, due to the highly reactive nature of the chlorine radical, hydrogen abstraction reactions conducted in the absence of certain solvents are notoriously unselective.¹⁷

Radical reactions usually proceed through a chain-reaction process.⁸ This involves a mechanism that proceeds by generation of the radicals through initiation. This step is the initial reaction, which begins a cycle of chain-propagation reactions that are in competition with the termination step, where two radicals must combine to give a non-radical product. The classical example of a chain-reaction process is that of radical halogenation.

The mechanism for free radical halogenation of alkanes was first suggested in 1930 by Schwab and Heyde.¹⁸ These chain reactions are of particular importance as they provide an effective method for introducing functionality into alkanes, thus making more useful precursors for use in many chemical reactions.

Typical industrial examples include the pesticides lindane,⁷ (benzene hexachloride) **5** and 1,1,1-trichloro-2,-bis(*p*-chlorophenyl)ethane (DDT), **6**.⁸



Figure i.7. The pesticides Lindane 5 and DDT 6.^{7,8}

The general mechanism described for halogenation *via* a chain reaction in Scheme i.1 may be applied to each of fluorine, chlorine, bromine and iodine, but the reactions show important differences due to the relative reactivities of the halogen atoms and consequent differences in selectivity in hydrogen abstraction from similar substrates.



Scheme i.1. General scheme for free radical halogenation of an alkane RH by halogen X.

Organofluorine compounds are of importance because they have unique and desirable properties. As such, the elucidation of the chemical properties and synthesis of bioactive organofluorine compounds is a rapidly developing area of research because of their importance in biochemical and medicinal applications.¹⁹ Thus, radical fluorination processes have attracted a great deal of interest.¹⁹⁻²¹

Fluorine is the most electronegative and chemically reactive of all the elements, thus the reaction with fluorine *via* the proposed reaction mechanism in Scheme i.1 is highly exothermic and controlled direct fluorination is difficult to accomplish. The exothermicity is explained by the low BDE of diatomic fluorine of 158 kJ mol⁻¹,⁸ combined with the formation of extremely strong C-F and H-F bonds of *ca*. 460 kJ mol⁻¹ and 565 kJ mol⁻¹,⁸ respectively, in the product. The transition state of the hydrogen abstraction reaction is more "reactant-like" which results in a very early transition state.¹⁶ In this case, the bond breaking processes have not proceeded very far at the transition state and the rate of reaction is less sensitive to the exact nature and strength of the bond being broken. The result is low selectivity for such reactions, with a mixture of products often being formed.

Controlling the heat evolved by the reaction is often accomplished by dilution of fluorine with an inert gas. Selective direct fluorination at saturated carbon sites has demonstrated that tertiary C-H sites may be fluorinated using elemental fluorine in a reaction medium of CHCl₃/CFCl₃ at -78° C.²⁰ These reaction conditions limit the scale-up reaction of direct fluorination reactions however, indirect fluorination, using acetonitrile as a solvent has recently afforded selective fluorination of both secondary and tertiary C-H sites.²¹ The reactions are carried out by passing fluorine gas (diluted to 10% in nitrogen) through a mixture consisting of the substrate and acetonitrile, cooled to 0 °C..

Radical iodination reactions represent the opposite end of the reactivity spectrum. Hydrogen abstraction by iodine radicals is appreciably endothermic and iodine radicals do not react well with alkanes or alkenes at moderate temperatures, *i.e.* 60°C.²² The formation of iodine radicals may be achieved by photo-dissociation of iodine containing compounds²³ with a relatively low BDE of 151 kJ mol⁻¹.⁸ The radical thus formed can then either react rapidly with another iodine radical or with a carbon-centred radical species at a diffusion controlled rate.²⁴ However, the energy afforded from formation of H-I and C-I bonds, as measured by BDEs of 297 and 239 kJ mol⁻¹, respectively,⁸ is not adequate to maintain the process where a C-H bond with a BDE of *ca* 400 kJ mol⁻¹ must be broken.⁸

The chlorination and bromination of alkanes *via* the general mechanism illustrated in scheme i.1 is a significant process used industrially in the preparation of alkyl chlorides and bromides.⁸ Simple alkyl chlorides are commonly used as solvents for example, carbontetrachloride.⁸ The compound Halothane, CF₃CHClBr, is an important anaesthetic because of its effectiveness and non-toxic properties.⁸

Radical bromination of alkanes is more selective than the corresponding fluorination reaction, due to its less reactive properties of Br[•]. This leads to a reaction that is only slightly exothermic, where the transition state is more "product like" and therefore the thermodynamic stability of the intermediate carbon-based radical is much more important in the overall product distribution. Controlled radical selectivity may therefore be achieved in these reactions and they have been used in the regiochemical synthesis of valines⁴ and glycines.⁵

Chlorination reactions of alkanes are of intermediate selectivity relative to fluorination and bromination reactions. These reactions often produce a mixture of mono-chlorinated products in substrates with fairly long carbon chains.²⁵ This limited control of selectivity is attributable to the reasonably high reactivity of the chlorine radical.

The reactivity and thus selectivity of radical reactions can be modulated by external factors. In particular, solvents have been found to influence the outcome of free radical hydrogen abstraction reactions in ways that are not typically observed in reactions of either nucleophiles or electrophiles. The effects of solvent on radical reactivity were first reported by Russell and Brown,^{17,26-29} where they demonstrated that the use of either aromatic or aliphatic solvent in the hydrogen abstraction reaction of 2,3-dimethylbutane, (2,3-DMB), influenced the product distribution in different ways.^{17,26-29} A greater selectivity toward tertiary hydrogen abstraction, relative to primary hydrogen abstraction, was observed when the reaction was conducted in an aromatic solvent (than when it was conducted in an aliphatic solvent) such as benzene^{17,26-29} (Scheme i.2). These solvent

effects prompted a significant amount of scientific interest³⁰⁻⁴⁰ and the initial findings of Russell^{17,26-29} were soon confirmed by Walling and Mayahi among others.³⁰



Scheme i.2. Reaction product ratios of hydrogen abstraction from 2,3-DMB. (Note: $r(3^{\circ}/1^{\circ}) = (Yield 3^{\circ} RCl/Yield 1^{\circ} RCl) x 6)$

Specifically, reactions within an aliphatic solvent gave a primary (1°) hydrogen abstraction to tertiary (3°) hydrogen abstraction product ratio of 60:40. However, the same reaction conducted within an aromatic solvent gave a primary to tertiary hydrogen abstraction product ratio of 10:90. The hydrogen atoms at the tertiary position are more reactive toward abstraction than the primary because the corresponding tertiary radical is much more stable than the primary radical. The increased selectivity towards the more reactive tertiary hydrogen atom abstraction in the aromatic solvent was attributed by Russell to a less reactive halogenating agent than Cl^{*} itself being present in this mixture.^{17,26-29}

Most radicals are described as "free radicals" since they exist independently, free from any support from another species. However "complexed" radicals may also exist, where the radical interacts with another species without the formation of a formal bond.^{11,17,26-29} This situation is directly analogous to carbene chemistry where the distinction is made between a free carbene and a carbenoid, the latter of which arises from complexation

with another species, usually a metal.⁸ Similar chemistry is observed with both species, but carbenoids are generally less reactive and more selective than the free carbene. For a "complexed" radical, the radical reactivity may be reduced relative to the "free" species, as the radical can be stabilised by non-covalent interactions, such as hyperconjugation, in the interaction with the complexing entity.

In the free radical halogenations reported by Russell,^{17,26-29} other than the substrate and chlorine, the only other species present was the solvent. It could be assumed that the free radical can interact with the solvent, resulting in the formation of a transient species that retains the general chemical characteristics of the "free" radical, *i.e.* formation of the same radical intermediates and products, with no solvent molecules incorporated into the products. Moreover, because this transient species is more stable than the "free" radical, lower reactivity and enhanced selectivity would be observed.

This reasoning led to the proposal that a complex between Cl^{*} and benzene was the highly selective hydrogen abstractor in the hydrogen abstraction reaction of DMB. A hexahapto π -complex (7) and a 6-chlorocyclohexadienyl σ -type complex, (8), were the two possible extreme structures proposed initially by Russell to rationalise his observations.^{17,26-29}



Figure i.8. Proposed η_6 (7) and cyclohexadienyl (8) structures for the highly selective H abstractor.

The reactivity of the Cl[•] is reliant on its electron deficient nature. Therefore, the proposed complexes 7 and 8 were reasoned as being less reactive than Cl[•] due to interaction of the π -electrons of the aromatic molecule with the semi-occupied p-orbital of the radical, thus generating a more selective, electron rich species. The decrease in reactivity affords a preferentially more selective abstracting species to react with the

more reactive tertiary hydrogens. By measuring the kinetics of chlorination, only two abstracting species were shown to be present in the photochlorination reaction, namely the Cl[•] and the Ar-Cl[•] complex species.^{17,26-29} To further investigate the solvent effect, the reaction of sixteen other aliphatic compounds towards a chlorine atom, in the presence of aliphatic, aromatic and polar solvents were studied.²⁸ In these cases, aliphatic solvents did not affect the selectivity of chlorination, as illustrated by the product ratios presented in Table i.3. Reactions in polar and aromatic solvents, however, show a significant increase in preference for hydrogen abstraction from the more substituted carbon atoms, as opposed to primary carbon atoms.²⁸

Table i.3. The relative reactivities at 25 $^{\circ}$ C of hydrogen abstraction of the alkanes using different solvent media.²⁸

		Solvent			
	Hydrogen	Aliphatic	C_6H_6	$C_{6}H_{6}(CH_{3})_{3}$	CS_2
2 3-DMB	1°	4	1	1	1^a
2,5 DMD	3°	2	20	35	225
u nontono	1°	0	0.97	0.92	0.86
<i>n</i> -pentane	2°	3	4.6	6.2	25

^aAssumed

Russell's modified mechanism for free radical chlorination in aromatic solvents is summarised in Scheme i.3.²⁸

Cl' + PhH
$$\xrightarrow{k_{Cl}}$$
 PhH/Cl'complex
Cl' + 2,3-DMB $\xrightarrow{k_1}$ 1° Radical' + HCl
Cl' + 2,3-DMB $\xrightarrow{k_3}$ 3° Radical' + HCl
PhH/Cl' $\xrightarrow{k'_1}$ 1° Radical' + PhH + HCl
PhH/Cl' $\xrightarrow{k'_3}$ 3° Radical' + PhH + HCl
1° Radical' + Cl₂ \xrightarrow{FAST} 1° RCl + Cl'
3° Radical' + Cl₂ \xrightarrow{FAST} 3° RCl + Cl'

Scheme i.3. Reaction scheme of chlorination of 2,3-DMB in aromatic solvent.²⁸

The kinetic expression for selectivity as a function of rate constants and the concentrations of pertinent species can be expressed as shown in Equation i.2:

$$r(3^{\circ}/1^{\circ}) = 6 \left[\frac{\frac{k_{3}}{k_{1}} \left\{ \left(1 + \frac{k'_{3} + k'_{1}}{k_{-CI}} \left[2, 3 - DMB\right]\right) + \frac{k'_{3}}{k_{-CI}} \frac{k_{CI}}{k_{1}} \left[PhH\right] \right\} \right]}{\left(1 + \frac{k'_{3} + k'_{1}}{k_{-CI}} \left[2, 3 - DMB\right]\right) + \frac{k'_{1}}{k_{-CI}} \frac{k_{CI}}{k_{1}} \left[PhH\right] \right\}} \right]$$
(Equation i.2)

The suggestion that the highly selective abstracting species in the chlorination of 2,3-DMB was a η_6 -type complex was challenged by Skell and Taylor in 1983.⁴¹ They argued that the alternative, 6-chlorocyclohexadienyl radical had traditionally been invoked to account for other chemistry in the benzene/chlorine reaction, specifically in the formation of hexachlorocyclohexane, as shown in scheme i.4, and the formation of adducts with maleic anhydride, illustrated in scheme i.5.²



Scheme i.4. Chlorination of benzene to form hexachlorocyclohexane.¹



Scheme i.5. Reaction of maleic anhydride in the presence of chlorine, benzene and light to afford chlorinated products.²

Skell and co-workers^{41,42} went on to suggest that the actual abstracting species was that of the 6-chlorocyclohexadienyl radical, which they termed the σ -complex. This claim was supported by the rationale that, with solely a η_6 -complex as the abstracting species, no difference in product ratios would be expected with a change in the concentration of substrate. As there would be no change in the concentration of benzene or chlorine radical, the π -complexation equilibrium should not be altered since it is assumed to be rapidly established. Conversely, the experiments of Skell *et al.*⁴¹ did in fact show a marked increase in selectivity when the substrate concentration reaction approached that of a chlorine free radical. This is consistent with equation i.1 where, at higher alkane concentrations, the [2,3-DMB] terms become increasingly important. The selectivity approaches that of a free Cl^{*} because this species reacts with 2,3-DMB before the Cl^{*}/PhH complex can be formed.

At very low 2,3-DMB concentrations, the selectivity was almost invariant with the concentration of 2,3-DMB. Skell *et al.*⁴¹ argued that as the time for encounter of the abstractor and substrate was lengthened, this allowed the concentration of a new and more selective abstractor to increase. Because σ -bond formation would require significant geometric changes, *i.e.* re-hybridisation, which would take longer than π -complexation where no substantial reorganisation is necessary, it would be more likely that this new abstractor was the σ -complex. This argument was further supported by the rate of disappearance of benzene in the presence of chlorine, and thus assumed rate of σ -complex formation, being measured at *ca* 10⁻⁹ Lmol⁻¹s⁻¹, which was consistent with the

difference in timescales expected between encounters with the abstracting species in 1 M alkane, estimated at 10^{-10} s, and 0.01 M alkane, estimated at 10^{-8} s. The flaw in this argument was highlighted by Ingold *et al.*,⁴³ in that the relative time frames for σ -*versus* π -complex formation are insignificant since all the reactions of Cl[•] are diffusion controlled.

The case for the σ -complex as the major hydrogen abstractor was further examined by Ingold et al.43 in 1998, where laser flash photolytic techniques for the detection of a single C₆H₆/Cl[•] abstracting complex was reported. A UV/Visible spectrum recorded absorptions at 320 and 490nm and an equilibrium constant of $K_{CI} = 200 \text{ M}^{-1}$ was proposed for the formation of the C₆H₆/Cl[•] complex.⁴³ From the spectroscopic evidence, Ingold *et al.*⁴³ tentatively concluded that the absorptions were more consistent with the π complex (7), due to the charge transfer band exhibited at 490nm, which is directly analogous to I_2/C_6H_6 and Br_2/C_6H_6 π -complexes.^{43,44} The formation of intensely-coloured charge-transfer complexes, otherwise known as donor-acceptor complexes, in non-polar solvents was first theoretically inferred by Mulliken.⁴⁵ The condition for the formation of a charge transfer complex, from two components, requires that one system is an electron donor, *i.e.* a low ionisation potential, and the other a good electron acceptor, *i.e.* with a high electron affinity. Such complexes are well studied in the literature.^{44,46-48} The solid state structures of Cl_2/C_6H_6 and Br_2/C_6H_6 have been shown to be hexahapto geometry by X-ray analysis, as illustrated in Figure i.9.49,50 In contrast, detailed theoretical studies on the iodine benzene charge transfer complex have shown that the most stable geometry for the complex is predicted to be a π -complex, where the I₂ is positioned at the above-bond and the above-carbon conformations.⁵¹



Figure i.9. The hexahapto geometry of halogen-benzene complexes has been confirmed by X-ray spectroscopy for both X=Cl and Br.

In 1996, Skell *et al.*⁴² argued that the work by Ingold *et al.*⁴³ did not discount structure **8** as the major abstracting species, by reasoning that the charge transfer band at 490nm and the absorption at 320nm were consistent with other cyclohexadienyl radicals because of substantial spin density at Cl^{*} arising from hyperconjugation with the aromatic ring, as depicted in Figure i.10.



Figure i.10. Hyperconjugation of the radical with the aromatic ring.

The existence of Br atom and I atom π -complexes with arenes is well documented^{44,52} and the existence of a 6-fluorocyclohexadienyl radical had been spectroscopically confirmed.⁵³

In light of these observations Skell *et al.*⁴² suggested that halogen-aromatic complexes, in the halogen series $I \rightarrow F$, displayed a graduation from weak interactions characterised by π -complexation, *i.e.* I'/arene π -complex, to a stronger covalent interaction characterised by cyclohexadienyl radical formation, *i.e.* F'/arene σ -complex. In this case, the transition from π - to σ - was suggested to be accompanied by (i) an alteration of the angle between the C-X bond and the plane of the benzene ring, from 90° (when X=I) to 120° (when X=F) and (ii) a decrease in the C-X bond length. Given the transient nature of these complexes, confirmation of this hypothesis would be best accessed through theoretical models.⁴²

Prior to this hypothesis from Skell *et al.*,⁴² however, Sergeev *et al.*⁵⁴ examined the PhH/Cl[•] complex with ESR spectroscopy and interpreted their results as providing evidence for Cl[•] forming a complex, intermediate in structure to that of the $\eta_6 \pi$ complex and a chlorocyclohexadienyl radical (Figure i.11). Sergeev *et al.*⁵⁴ believed that this structure provides optimum overlap of the LUMO of the chlorine and the HOMO of

the aromatic system, therefore the interaction should be stronger than a simple π complex. However, the conclusions from this work appear to have been largely ignored
in the mainstream literature.



Figure i.11. Postulated structure from ESR experiment.54

The prolonged debate in the literature as to the exact structure and related properties of the Cl[•]-Ar complex inspires the examination of an appropriate model of this system that will allow the structural and electronic properties to be elucidated. Moreover, since short lived systems of this type are difficult to study experimentally, theoretical modelling affords the easiest access to species of this type.

Computational methodology is increasingly employed to complement experimental data, especially for radicals and other reactive intermediates. Effective use of calculations can yield both thermodynamic and kinetic data and thus helps alleviate the associated difficulties in isolating such highly reactive species. Moderately sized molecules, such as aromatic hydrocarbons, are now accessible using computational methods, but can readily take up a large amount of computational resources if the theoretical methods are not carefully chosen. In addition, the theoretical modelling of radicals needs to be treated with particular caution, since effects like spin contamination can dramatically alter the calculated results.

Spin contamination can occur in open shell systems, which are those containing an unpaired electron, such as radicals and delocalised systems. Open shell calculations are required to use separate spatial orbitals for the spin up (α) and spin down (β) electrons. A spin unrestricted wave function treats the alpha and beta orbitals independently, as illustrated in Figure i.12.



Figure i.12. The separate orbitals of electrons in an unrestricted open shell system.

A difficulty arises when the unrestricted wave functions are not necessarily eigenfunctions of the total spin, $\langle S^2 \rangle$, and can thus be contaminated by states of higher multiplicity. As a result, the wavefunctions of doublet, or spin-unpaired systems, such as radicals, may be spin contaminated by mixtures of quartet, sextet, and higher spin states. This spin contamination manifests itself in estimated vales of the total spin, $\langle S^2 \rangle$. Spin contamination results in wavefunctions that appear to be the desired spin state, but have a small amount of another spin state mixed in. This occasionally results in a slight lowering of the computed total energy due to the molecule having added degrees of freedom. More often, the result is a slightly increased total energy since a higher energy state is being mixed in. However, this change is an artefact of an incorrect wave function. Since this is not a systematic error, the difference in energy between states will be adversely affected. A high spin contamination can affect the geometry, population analysis and significantly affect the spin density of the molecule in question.

There have been a variety of solutions to the problem of spin contamination, namely spin restricted open shell models, typically defined by the RO prefix. Spin restricted models force the spatial parts of the doubly-occupied orbitals to be the same. This ensures that the wave function is a pure spin state and thus an eigenfunction of the total spin, denoted by the $\langle S^2 \rangle$ operator.⁵⁵ However, the spin densities predicted by the RO technique are often incorrect and suffer from an unrealistic spin localisation in a radical.⁵⁶ This is

because, in the RO framework, any spin polarisation of the electrons, in doubly-occupied orbitals, can only be in the same direction as the unpaired electrons α . ESR studies have shown that there are many open-shell systems where regions of the molecule have an excess β spin density.⁵⁷ This implies that the RO technique is qualitatively incorrect with respect to spin polarisation.

The introduction of high levels of electron correlation can help to minimise the effects of spin contamination by introducing spin projected energy corrections for spin contaminated systems. Such methods that incorporate electron correlation include Møller-Plesset perturbation theory (MPn), quadratic configuration interaction (QCISD), and coupled cluster theory, (CCSD). Prior to the widespread use of methods based on density functional theory (DFT), which will be discussed later, the MP2 method was one of the least expensive ways to improve on Hartree-Fock theory. Hartree-Fock theory is very useful for providing initial, first level predictions for many systems, however, its neglect of electron correlation makes it unsuitable for systems which are likely to become spin contaminated, such as open shell, radical systems, and unsuitable for proper modelling of the energetics of reactions and bond dissociation energies. OCISD and CCSD methods represent some of the highest levels for the treatment of electron correlation, usually providing great accuracy. For treatment of molecular systems of particular interest, such as aromatic-radical complexes, these higher-level theoretical methods would not be practical. In contrast, density functional theory, (DFT), achieves significantly greater accuracy than Hartree-Fock at only a modest increase in computational cost,⁵⁸ for medium and larger sized molecular systems. Density functional methods achieve this by including some of the effects of electron correlation much less expensively than other methods, eg. QCISD and CCSD.

DFT methods compute electron correlation *via* general functionals of the electron density. In DFT, functionals are defined as functions of the electron density, itself a function of co-ordinates in real space, and the electronic energy is partitioned into several components that are computed separately. The kinetic energy, the nuclear-electron interaction, the coulomb repulsion, and an exchange correlation term, each account for

the remainder of the electron-electron interaction, which itself is divided into separate exchange and correlation components.

Kohn and Sham⁵⁹ showed that the approximate functionals employed by current DFT methods may be written as:

$$E_{\text{exact}} = E^{T}(\rho) + E^{V}(\rho) + E^{J}(\rho) + E^{XC}(\rho)$$
 (Equation i.3)

The exact ground-state electronic energy (E_{exact}) is completely determined by the electron density (ρ). E^{T} is the kinetic energy term arising from the motion of electron, E^{V} includes terms describing the potential energy of the nuclear attraction and of the repulsion between pairs of nuclei, whilst E^{J} is the electron-electron repulsion term. E^{XC} is known as the exchange-correlation term and, by definition, contains all contributions not accounted for by the first three terms, including the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motions of individual electrons.

A variety of functionals within DFT methods have been defined and are distinguished by the way that the exchange and correlation components are treated. Local exchange and correlation functionals involve only the values of the electron spin densities. For example, the local spin density treatment of Vosko, Wilk and Nusair,⁶⁰ known as VWN, is a widely-used local correlation functional. Gradient corrected functionals involve both the values of the electron spin and their gradients. Such functionals are also known as non-local. One of the most popular gradient corrected exchange functionals, BLYP, is a combination of two forms of functionals, the one proposed by Becke⁶¹ and in addition a gradient corrected correlation functional of Lee, Yang and Parr, LYP.⁶² There are also several hybrid functionals which define the exchange functional as a linear combination of Hartree-Fock, local and gradient corrected exchange terms. This exchange functional is then combined with a local and/or gradient corrected correlation functional.

Different functionals may be constructed by varying the component functionals, *eg.* by substituting the Perdew-Wang 1991⁶³ (PW91) functional for LYP, in combination with the B3 parameter hybrid. One of the best-known hybrid functionals is Becke's three parameter hybrid, the B3- method,⁶⁴ which he combined with the Perdew-Wang 1991 correlation functional in his original work.⁶³ It is generally recognised that hybrid methods perform the best to reproduce experimental enthalpies of formation, as recently shown in a theoretical assessment involving 148 molecules of various categories, for which the B3LYP method has an average deviation from the experimental energies of only 12.5 kJ mol^{-1.65-67} The BH&HLYP method is another hybrid functional. Although less popular than the three parameter hybrids, it includes 50% Hartree-Fock exchange, 50% Slater exchange and the additional correlation effect of the LYP functional.⁶⁸

With numerous methods available, the selection of an appropriate theoretical method for the calculation of any molecular property becomes important. It is generally the case that high levels of theory and large basis sets provide results that are in better agreement with experimental values due to a better description of the molecule in question. Larger basis sets more accurately describe the orbitals by imposing fewer constraints on the location of electrons in space. However, the larger basis sets correspondingly require more computational resources.⁵⁸ For larger systems, especially those containing either radicals or significant delocalisation such as the aromatic-radical complex, is therefore appropriate to choose a basis set that accurately describes complex accurately without a significant compromise neither on resources nor on the quality of calculated results.

The basis set is the mathematical description of the orbitals within the system, and it is these orbitals that, in turn, combine to approximate the total electronic wavefunction, Ψ^2 , used to perform the calculation.⁵⁸ Standard basis sets use linear combinations of Gaussian functions to form the orbitals. Split valence double-zeta basis sets, *eg.* 4-31G, have two sizes of basis functions for each valance orbital. For example, with the 4-31G basis set, there would be a total of 20 primitive Gaussian functions needed for the calculation of one carbon atom (Figure i.13). Therefore, even for moderately sized systems, such as the aromatic-Cl complex, the number of basis functions increases rapidly with a larger basis set and can put a significant demand on computational resources.

C Core			Valence		
4-31G	$1s^2$	$2s^2$	2p _x	2p _v	2p _z
	(4G)	(3G)(1G)	(3G)(1G)	(3G)(1G)	(3G)(1G)

Figure i.13. Number of functions needed to calculate carbon with a 4-31G basis set.

Split valance basis sets allow orbitals to change size, but not shape. Polarised basis sets, eg. 6-31G(d), synonymous with $6-31G^*$, remove this limitation by adding orbitals with high angular momentum beyond that which is required for the ground state description of each atom.⁵⁸ For example, adding a single polarization function to a triple zeta basis set, 6-311G, *i.e.* to form $6-311G^*$, will result in one d function for first and second row atoms and one f function for first transition row atoms, since d functions are already present for the valence electrons in the latter. It has been shown that basis sets including polarisation functions are able to accurately predict the thermodynamic and kinetic parameters for the reactions between fluorine atoms and halomethanes and the results are in good agreement with the experimental data.⁶⁹

Diffuse functions, denoted by +, are large versions of s- and p-type functions, as opposed to the standard valence type functions and they also allow the orbitals to occupy a greater region of space.⁵⁸ Similarly, adding a diffuse function to the 6-311G basis set, *i.e.* 6-311+G will produce one s, one p, and one d diffuse function for third-row atoms. Addition of d functions to first row atoms, such as carbon, is beneficial when one considers hybridisation. For example, sp³ orbitals are formed on carbon by mixing filled 2s orbitals and partially filled 2p orbitals. A natural extension to this is to allow some small contribution from filled 3d orbitals as well. Similarly, diffuse functions can be considered as the mixing in of 3s orbitals.⁵⁸

Basis sets with diffuse functions are important for systems in which electrons are relatively far from the nucleus, and for molecules with occupied p-orbitals such as radical systems, anions or other systems with a significant negative charge. For example, inclusion of diffuse functions within a basis set has been shown to significantly improve the reproducibility of experimental data for the calculation of non-covalent interactions in phosphate complexes.⁷⁰ Diffuse functions have also shown to be effective in reducing the effects of Basis Set Superposition Error (BSSE) in the calculations for the reactions of haloethanes with hydroxyl radicals.⁷¹

Other types of basis sets are available within computational chemistry programs in order to calculate molecular properties. A series of basis sets for correlated calculations has been developed by Dunning.⁷² These basis sets are referred to as correlation consistent (prefix cc) and are designed such that a base set of s and p functions is combined with correlation functions. The smallest member of this series, and thus often the starting point for correlated calculations, is the correlation consistent polarized double zeta basis set designated cc-pVDZ.⁷³ Other varients include, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z, (triple, quadruple, quintuple-zeta and sextuple-zeta, respectively).^{72,74-76} These basis sets include polarisation functions by definition, as shown in Table i.4, and are cited to be considerably economical since these basis sets have had redundant functions removed and have been rotated in order to increase computational efficiency.⁷⁷

Table i.4. A list of the valence polarisation functions for the various atoms included in the Dunnings basis sets.

Atoms	cc-pVDZ	cc-pVDZ	cc-pVQZ
Н	2s,1p	3s,2p,1d	4s,3p,2d,1f
He	2s,1p	3s,2p,1d	4s,3p,2d,1f
B-Ne	3s,2p,1d	4s,3p,2d,1f	5s,4p,3d,2f,1g

The calculations using the Dunnings basis sets can afford good accuracy and can dramatically reduce the computational cost. For example, the MP2 optimisation of benzene carried out using the cc-pVDZ basis set took approximately half the time than that taken by the original uncontracted Dunnings correlation consistent basis set and showed a better consistency within the calculated energies.⁷⁸

When examing systems such as complexes, effects such as basis set superposition error (BSSE) may emerge. This is a problem when calculating the interactions between two species using *ab initio* calculations.⁷⁹ This error occurs because the energy of each unit within an associated complex will be lowered by the basis functions of the other.⁷⁹ BSSE introduces a non physical attraction between the two units. The counterpoise correction (CP) method is the most effective means of correcting for BSSE.⁸⁰ The CP method calculates each of the units with the basis functions of the other, but without nuclei or electrons, using ghost orbitals. Such corrections have shown noticeable improvements in optimised geometries of organic transition states with relatively small basis sets.⁷⁹

The geometries of transition states may be confirmed by performing a frequency analysis calculation, the number of imaginary frequencies indicates whether the optimised geometry is a stable minimum, transition sate, or higher order saddle point. In addition, Zero-Point Energy (ZPE) corrections can also be obtained from frequency analysis. The ZPE is a correction to the electronic energy of the molecule to account for the effects of molecular vibrations. The ZPE must always be combined with the appropriate scaling factor when calculating final predicted energies. The scale factor is applied to eliminate systematic errors in calculated frequencies and varies by basis set.⁸¹

The utility of theoretical calculations to look at the structure and properties of aromatichalogen radical complexes has already been exploited by a selection of workers.⁸²⁻⁸⁷ Some of the theoretical studies have used both DFT and relatively high level *ab initio* methods.^{82-84,87} During the course of this work, the potential surface for (halogen) X'benzene interaction was calculated by Tsao *et al.*⁸² as a function of C-X distance for η_1 , η_2 and η_6 complexes.

They deduced that a distorted σ geometry, similar to 9 Figure i.11, was the most stable representation for the C₆H₆/Cl[•], C₆H₆/Br[•] and C₆H₆/l[•] complexes. The cyclohexadienyl radical 8 was also deduced as the most stable representation for the Ar-F[•] complex. Jarzeba *et al.*⁸⁷ also concluded that 9 may be the best representation for the Ar-Cl[•] complex. However, Berho *et al.*⁸³ obtained a C-Cl[•] distance of 2.57Å for the Ar-Cl[•]

complex B3LYP calculations but discounted these structures as erroneous. Theoretical values in the range of -25^{82} to -43^{83} kJ mol⁻¹ have been quoted for the energy of formation for the C₆H₆/Cl[•] complex, where an experimental value of -34 kJ mol⁻¹ has been obtained.^{43,88} However, in both theoretical and experimental studies of C₆H₆/Cl[•] complexes, there has been no consensus on the exact structure of this species.

Theoretical calculations can be used in parallel with experiment to verify calculated energies and to examine intermediate structural geometries. The unresolved question of the structure of the C₆H₆/ Cl[•] complex is therefore accessible by the use of an appropriate method. Only recently have good quality theoretical methods been accessible for systems where non-covalent interactions predominate. Thus Chapter One of this thesis describes an assessment study of a number of methods with the aim of establishing an appropriate method to examine the C₆H₆/Cl[•] species. By careful comparison with experimental data, it is expected that this method should be general for other radical-aromatic complexes. Additionally, an accurate theoretical model may be able to solve the debate over whether π - or σ - intermediates are more probable as abstractors in free radical chlorinations.

Systems related to the aromatic-halogen complexes have also been well-studied in the literature. These aromatic-radical complexes are often studied using either laser flash photolysis or pulse radiolysis techniques to measure the kinetics of the reactions of the radical and the aromatic. These experiments are often coupled with FTIR or UV spectrophotometers in order to detect the products of reaction.^{89,90}

Cyclohexadienyl-type radicals are resonance-stabilised radicals resulting from the addition of an atom or radical X and can be represented by the two following resonance structures (Figure i.8). The cyclohexadienyl radical itself (X=H, Figure i.14) has been isolated and studied in the gas phase and its UV spectra recorded. The stability of the C_6H_7 radical has been experimentally determined by laser flash photolysis methods at both -92⁹¹ and -88 kJ mol^{-1.83}



Figure i.14. Resonance structures of cyclohexadienyl type radicals.

Cyclohexadienyl radicals are reported to absorb characteristically within the region of 270-320nm.^{43,83} The reaction products of the cyclohexadienyl radical in the gas phase have been reported⁸³ and both the association and disproportionation reaction pathways have been observed to occur. The association pathway yields the two different possible isomers, as illustrated in Figure i.15. The disproportionation pathway yields essentially 1,4-cyclohexadiene (and small amounts of 1,3-cyclohexadiene) along with benzene.



Figure i.15. The disproportionation pathway of the cyclohexadienyl radical.

In general, however, very few other aromatic adducts have been isolated^{1,2,53,83,92} and available experimental data on the stabilities of cyclohexadienyl-type radicals are scarce, presumably due to their low stabilities and associated short lifetimes. The most prevalent reports are those regarding the hydroxycyclohexadienyl radical because of its implied involvement in atmospheric chemistry and the reaction of OH radicals with anthropogenic aromatic compounds.^{6,84,83,89,90,93-108}

The formation of a radical-aromatic complex or adduct within some reaction mechanisms is very important, especially in the gas phase chemistry of the 'OH radical.^{6,84,83,89,90,93-108} The 'OH radical can act as a scavenger by initiating tropospheric oxidation of anthropogenic pollutants. The role of the 'OH radical in the removal of aromatic hydrocarbons is particularly important, due to the extensive environmental and health hazards presented by aromatic pollutants.⁹⁰ Although compounds such as benzene, toluene and the xylenes may reside in the atmosphere at low ppb levels, it has been

estimated that their oxidation reactions may be responsible for 30% of photochemically produced tropospheric ozone.⁸⁴

The complete degradation mechanism for aromatic compounds is initiated by reaction with 'OH radicals, and has been reported as involving radical stabilisation by addition of these radicals to the ring, so forming a hydroxycyclohexadienyl-type radical.^{89,90} Reports in the literature support the concept of a reaction pathway initiated by addition of 'OH to benzene to form a chemically active pre-reactive complex,^{84,102} which then proceeds to generate the hydroxycyclohexadienyl radical,^{6,84,83,89,90,93-108} as depicted in Figure i.16.



Figure i.16. Formation and degradation of the 'C₆H₆/'OH radical adduct

The fates of the C₆H₆/OH complexes are somewhat different to the C₆H₆/Cl[•] radical complexes. For example, C₆H₆/Cl[•] adducts decompose to regenerate the reactants in a very short time period, *ca* 10⁻⁸ s.⁹⁴ In contrast, the C₆H₅F-OH adduct is stable over a time scale of at least 10⁻² s. This is consistent with bond dissociation energies of 69 ± 6 kJ mol⁻¹ measured for the C₆H₆/OH complexes,¹⁰⁹ indicating that these complexes would be much more stable than the equivalent chlorine complexes where bond dissociation energies of 30 ± 10 kJ mol⁻¹,^{83,110} 34 ± 8 kJ mol⁻¹ and 38 ± 2.5 kJ mol⁻¹ have been reported.^{88,43}

The lower bond dissociation energy of the benzene-Cl[•] complex, relative to that of the benzene-[•]OH complex, indicates a complex that is more reactive and less stable. This can be rationalised by considering the difference in nature of the [•]OH and Cl[•] radicals. Hydroxyl radicals are one of the most highly-reactive oxygen-centred radicals known and consequently they are also short lived,⁷ like the chlorine radical. The increase in stabilisation observed for hydroxycyclohexadienyl radical relative to the equivalent

chloro complex can be attributed to the presence of the lone pairs of electrons on the oxygen that are available for hyperconjugation, in addition to the interaction of the single electron of the SOMO with the HOMO of the aromatic moiety.⁷ The chlorine radical however, has only one unpaired electron in the SOMO which is available for interaction with the HOMO of the aromatic species.⁷

Due to the unstable nature of these radical complexes, theoretical calculations are increasingly being introduced to complement kinetic analysis of reactions where the formation of a radical adduct is likely.^{3,4,6,84,86,90} Theoretical calculations performed by Berho *et al.*,⁸³ using the B3LYP/6-31G(d) and BAC-MP4 levels of theory, were employed for a series of cyclohexadienyl type radicals with the objective to establish a scale of stability as a function of the nature of radical X. All of the predicted energies for the C₆H₆/X[•] complexes studied by Berho *et al.*⁸³ were found to be lower than the sum of the radical species and benzene at infinite separation, indicating that complex formation would be thermodynamically favourable.^{82,83} Berho *et al.*⁸³ examined the radicals, F[•], Cl[•], Br[•], H[•], OH and [•]CH₃ in their calculations and the results are presented in Table i.5.

$\Delta H^{\circ}_{298}/\text{kJ mol}^{-1}$			
Х	B3LYP	BAC-MP4	Expt.
Br	a-16.7 ⁸²	a	n/a
C1	-43.3	-30.1	-3438
CH_3	-41.3	-41.9	n/a
OH	-70.2	-73.7	69
H	-99.4	-88.7	-9288
F	-150.2	-138.9	-82.84^{82}

Table i.5. Comparison between theoretical and experimental results.⁸³

^aBerho et al.⁸³ did not calculate this value using this method

The calculated results show a reasonably good agreement with experimental data. For all of the structures a typical cyclohexadienyl geometry was obtained (Figure i.1, 2). Interestingly, Berho *et al.*⁸³ reported that the B3LYP calculations led to an incorrect geometry, since a C-Cl bond length of 2.57Å was obtained. When the C-Cl bond length was 1.92Å, spin contamination was also reported to be a significant problem for the B3LYP geometries. Re-optimisation by Berho *et al.*⁸³ of the C₆H₆/Cl[•] radical with the BH&HLYP functional gave what they identified as the correct geometry, whilst spin

contamination was reported to be low and ΔH° using this method was reported as -20.1 kJ mol^{-1.83} The principle conclusion made by Berho *et al.*⁸³ was that neither Cl, Br, or the CH₃ radical can add efficiently to the aromatic ring as a result of the low stability of the incipient cyclohexadienyl-type radical.

A recent and more detailed computational study on the addition of halogen radicals to benzene was published during the course of the work for this thesis.⁸² For all of the halogens except fluorine, the calculations predicted an intermediate geometry (Figure i.4) was the most stable structure to represent the X-cyclohexadienyl radical. It was also reported that all of these structures exhibited a charge transfer band in the calculated UV spectra.⁸² The σ -type geometry was not found to a global minimum on the potential energy surface for these structures with the exception of the fluorocyclohexadienyl radical where $\Delta H^{\circ} = -120-129$ kJ mol⁻¹ was predicted for σ -complex with BH&HLYP methodology.

In light of the experimental data of Sergeev *et al.*,⁵⁴ it is worth reconsidering the conclusions arising from the work of Berho *et al.*⁸³ Chapter Two of this thesis examines in detail the complex formation between F', Br', I', 'OH and 'CH₃ radicals with benzene and compares the theoretical predictions with available experimental data.

Whilst there appear to be significant differences in binding energies when radicals of different properties are complexed to benzene, within Aromatic-Cl[•] complexes there can be substantial variation in binding energy when the nature of the aromatic is altered by substituents. Russell found that the selectivity observed in 2,3-DMB abstraction reactions was reduced when solvents containing electron-withdrawing substituents, such as nitrobenzene, benzoyl chloride and trifluoromethane were used, but increased when aromatics containing electron-donating substituents were used,²⁷ as illustrated in Table i.6.
	Selectivity
Solvent	3° vs 1°
Anisole	18.4
Toluene	15.4
Fluorobenzene	10.3
Chlorobenzene	10.2
Nitrobenzene	4.9

Table i.6. Experimental effects of solvents on the selectivity of hydrogen abstraction from 2,3-DMB.²⁷

Electron-donating substituents afford an improved stabilisation of the radical species, either through resonance delocalisation or inductive effects, over the corresponding unsubstituted aromatic. A concomitant decrease in reactivity of the aromatic-radical complex relative to that of the C_6H_6/Cl complex is observed, thus further enhancing selectivity of hydrogen abstraction. In direct contrast, the electron-withdrawing substituents of the aromatic are unable to properly stabilise the electron deficient radical centre and the selectivity in hydrogen abstraction reactions approaches that of the free chlorine radical. The effect of solvent on hydrogen abstraction has been found to parallel the basicity of the solvent.²⁷

Similarly, Bunce *et al.*¹¹¹ looked at the effects of fluorinated benzenes on the selectivity of hydrogen abstraction by Cl radical from 2,3-DMB. They found a decrease in the selectivity on increasing fluorination of the solvent. In this case, reactions carried out in C_6H_6 were the most selective, then those carried out in C_6H_5F , then $C_6H_4F_2$, with those in $C_6H_3F_3$ the least selective. Selectivity had disappeared completely when C_6F_6 was used as the solvation medium. These effects are consistent with the electronegativity of fluorine making the π -cloud of the aromatic less available for complexation. This has a two-fold effect, lowering the selectivity of the complexed species, and enhancing the dissociative process so that a lesser complexed species is available for hydrogen abstraction.

Related to the solvent effect observed in radical chlorination reactions, the formation of an Ar-OH complex has been suggested in the mechanism of the reactions of 'OH with toluene,^{98,105,112} aniline,^{95,109} bromobenzene^{95,109} and fluorobenzene,⁹⁴ iodobenzene,¹¹³

phenol,⁹³ aniline and p- and m-xylenes.¹¹⁴ The general opinion in the mainstream literature is that the dominant fate of the Ar-OH adducts is their decomposition back to reactants without further participation in hydrogen abstraction reactions. The bond dissociation energies of the benzene-OH, aniline-OH and bromobenzene-OH have been determined at 69 ± 6 , 77 ± 9 , and 58 ± 6 kJ mol⁻¹, respectively.¹⁰⁹ In the case of aniline, the strongly electron donating NH₂ group affords a more stable complex than that with benzene. The least stable complex is that which contains the electron withdrawing bromine atom, as reflected by the relative BDE's of the complexes. One would therefore expect to observe a solvent effect. In contrast, this is not seen experimentally since the measurements for BDE are made in solution, and differs from those measured in the gasphase as a result of hydrogen bonding with solvent molecules.¹¹⁵⁻¹¹⁷ Typically, hydrogen bonding by the substrate (eg. phenol) is observed,¹¹⁶ however, in phenols containing OH or NH₂ groups, hydrogen bonding of the radical is more dominant because of the electron-withdrawing effect of the radical oxygen, which increases acidity and is therefore more available to give H-bonds, the OH or NH₂ groups..¹¹⁷

Russell extended his studies to the reactions of *t*-butoxy radicals, since their reactivity is quite similar to that of chlorine atoms.¹¹⁸ It was found that the solvent effect in the reactions of *t*-butoxy radicals at 130°C is considerably less than that observed in photochlorination reactions at 20-55°C.¹¹⁸ This effect was attributed to the increased temperature driving extensive dissociation of the *t*-butoxy radical- π -complex.¹¹⁸ Moreover, the driving force for the formation of a complex within this reaction was said to be considerably less for the *t*-butoxy radical than for a chlorine atom, since the desire of a *t*-butoxy radical for an electron is considerably less than that of a chlorine atom.¹¹⁸ Consequently, the *t*-butoxy radical may be expected to form a weaker π -complex with benzene than the complex formed with a chlorine atom.¹¹⁸

The group of Aver'ynov and co-workers³¹⁻³⁸ have produced a significant body of experimental work relating to solvent effects on many different radical reactions. Like Walling, they agree that the electron donating properties of each solvent influences the observed selectivity. They have also developed selectivity models, the parameters of

which describe the ability of solvents to form complexes and the relative reactivities of the C-H bonds towards attack by such complexes. These parameters vary directly with the electronic properties of the solvent.³¹

Whilst the selectivity of hydrogen abstraction is able to be predicted from known experimental data, where the nature of the aromatic may be unknown it would be useful to have a predictive theoretical model. It is also important to confirm that it is the stability of the aromatic-Cl^{*} complex that is the major contributor to the observed effect, as other factors may play a role. Chapter Three explores how aromatic substituents affect the electronic properties of the corresponding aromatic-Cl^{*} complex and how these properties relate to the observed solvent effect in chlorination reactions. The majority of theoretical calculations, including many described in this thesis, are performed in the gas phase and although gas phase predictions are appropriate for many purposes, they do not properly describe the characteristics of molecules in solution. One theoretical model for probing solvent effects is referred to as the Self-Consistent Reaction Field (SRCF) method. This method models the solvent as a continuum of uniform dielectric constant, *i.e.* the reaction field. The solute is placed in a cavity within the solvent. The cavity may be defined by different approaches, the simplest of which is the Onsager reaction field model.¹¹⁹

A net stabilisation is achieved in the system by the dipole of the molecule of interest inducing a dipole in the medium. Thus, the electric field applied by the solvent dipole interacts with the molecular dipole and can alter properties such as minimum energy geometries and stabilisation energies. The cavity within the polarised continuum (PCM) model¹²⁰ is defined as a union of interlocking spheres and the isodensity PCM (IPCM) model^{120,121} defines the cavity as an isodensity surface of the molecule. Solvation effects computed with benzene as a solvent found that the presence of a dielectric field generally tends to stabilise all of the predicted stable complexes.⁸² Therefore to properly account for the selectivity observed in radical chlorinations, it is important to see whether this selectivity is solely modulated by complex formation, or whether there is further

contribution from the bulk solvent. The use of solvent continuum models with aromatic-Cl[•] complexes is thus explored in Chapter Three.

Where radical reactions are under thermodynamic control, the relative stabilities of the radical intermediates, as measured by the BDEs of the associated C-H bonds, are the major contributing factor towards the observed selectivity. A direct solvent effect on the transition state of a reaction is another way in which the outcome may be affected. Solvent effects where the solvent polarity affects the rate of reaction, for instance, have been reported in a number free radical reactions.¹ Thus a solvent interaction with the transition state, rather than the starting complex, may provide either an alternative or additional contributor to the changes in selectivity observed in radical chlorinations.

A recent study has used DFT to investigate the chemical reactivity of the S=C=S····Cl complex toward 2,3-DMB. The reaction was compared to the corresponding reaction of Cl with 2,3-DMB. Wang *et al.*¹²² found that the calculated reaction of Cl with 2,3-DMB, in the absence of CS₂, was exothermic for both primary and tertiary hydrogen abstraction, with very similar barriers for the rate-determining step. This observation implies very little tertiary selectivity, which is in agreement with experiments conducted in an inert solvent.²⁷

The reaction of the S=C=S····Cl complex with 2,3-DMB showed notably different behaviour with the primary abstraction becoming endothermic by 24.6 kJ mol⁻¹, whilst the tertiary abstraction was still exothermic by 5.4 kJ mol⁻¹.¹²² These values suggest that the primary reaction path will be noticeably slower than the tertiary abstraction channel in the presence of CS₂. Additionally, the reaction profiles for abstraction are significantly different in the presence of the CS₂, relative to those where free chlorine is the abstracting species.¹²²

Despite the differences in reaction profile, it was reported that the optimised geometries for the transition states show that the C-H and H-Cl bond lengths for each transition structure do not differ greatly. Bond lengths of the order 1.4-1.5Å were predicted, which would appear to show that hydrogen is shared between the C and Cl^{.122} The low electron density found on the shared proton for all of the transition states would appear to characterise C^{...}H^{...}Cl bonding.^{123,124} The charge on the shared proton was found to increase slightly on the transition states of the S=C=S....Cl complex with 2,3-DMB, indicating that these intermediates are stabilised less than the transition states for the equivalent primary structures.¹²² This can be characterised by the higher energies predicted for the tertiary transition states for the S=C=S....Cl complex reaction than the Cl' reaction. It was concluded by Wang et al.¹²² that the structures and reaction vectors corresponding to the vibrational mode of hydrogen abstraction indicates that the CS₂ moiety perturbs the transition structure of tertiary abstraction by the S=C=S····Cl complex to be more product-like. This would account for the prediction of a structure that is lower in energy and hence more stable than the primary transition structure. The transition structure for the primary hydrogen abstraction by the S=C=S....Cl complex was predicted to be perturbed by the CS₂ moiety to produce a structure which is more reactant-like, thus resulting in a higher energy structure than the tertiary equivalent.¹²²

The structure of transition states where aromatics such as benzene participate as part of an aromatic-chlorine complex have not yet been examined, even though the reactions themselves are experimentally well characterised. Clearly there is some effect in the transition-state, beyond the inherent reactivities of the complex, as the reaction of 2-deuterio-2-methyl propane exhibits a deuterium isotope effect, which is larger in the presence of aromatic solvent.²⁷ This isotope effect indicates that the transition state where an aromatic solvent is present should be later than that for abstraction by a free chlorine atom, with a greater degree of bond-cleavage. Since this is an observation can be tested theoretically, as illustrated by the work on CS_2 -Cl complexes, Chapter Four examines the direct effects of solvent complexation on the transition state of the hydrogen abstraction reaction from both primary and tertiary centres.

Chapter 1

Radical reactions are extremely important both industrially and biochemically. Therefore it is important to have a solid understanding of the factors that influence them and especially how external factors, such as solvent, might be used to mediate more selective processes. This study focuses on free radical chlorination as a specific example, as this reaction is well-studied experimentally, 26,29,30-37,39,122,125-128 and exhibits the clearest example of aromatic solvent effects of any radical reaction so far reported in the literature. As discussed in the introduction, two possible structures were considered by Russell^{17,26-29} as the selective abstracting agent when chlorinations were carried out in the presence of aromatics, namely a hexahapto, π complex 12 and a σ chlorocyclohexadienyl radical 13. Experimental data indicate that for related halogen-aromatic complexes, F-Ar is best represented by a cyclohexadienyl radical^{53,92} while I'-Ar is a hexahapto, π complex.^{51,134} It has been suggested that for X[•]-Ar complexes there is continuum of structures in the series I \rightarrow Br \rightarrow Cl \rightarrow F going from $\eta_6 \rightarrow \eta_2 \rightarrow \eta_1$ geometries.¹ Identification of the correct structure using computational methods is one of the first steps to accurately modelling radical chlorinations in the presence of aromatic solvent. This chapter aims to assess which theoretical models are able to accurately reproduce the observed thermochemistry for the C₆H₆Cl[•] complex, such that this level of theory can be used with other related complexes in subsequent chapters. Through this study, the chapter will also address, by examining a series of model complexes, which structure may best represent the C_6H_6/Cl° complex.

Results

Standard *ab initio* molecular orbital theory and density functional (DFT) calculations were performed using the GAUSSIAN 94/98^{129,130} suite of programs.

Preliminary low level *ab initio* calculations were performed using restricted open shell (signified with an RO prefix) calculations. The low level ROHF/4-31G(d) method was used in order to construct the appropriate geometries for the model complexes illustrated in Figure 1.1. These consist of a monohapto (η_1) complex **10** with the chlorine radical positioned directly over a single carbon atom in the benzene ring with C_s symmetry, a dihapto (η_2) complex **11** with the chlorine radical positioned over the centre of a carbon-carbon bond of the benzene ring with C_s symmetry, and a hexahapto (η_6) complex **12** where the chlorine radial is positioned over the centre of the benzene ring with C_{6v} symmetry.



Figure 1.1. Model complexes used to identify the structure of the C_6H_6/Cl^2 complex.

Complexation enthalpies (ΔH°_{298}) for the formation of the C₆H₆/Cl[•] complexes were calculated using the reaction shown below in Scheme 1.1:

 $Cl' + C_6H_6 \implies C_6H_6Cl'$ Scheme 1.1

The relative complexation enthalpies thus calculated from the reaction in Scheme 1.1 represent the difference in the calculated energies of the complexed product species and the sum of the radical and aromatic species at infinite separation.

To ensure good starting geometries, the three model complexes were re-optimised using the ROHF and the ROB3LYP methodologies, in conjunction with the 6-31G(d) basis set, prior to further calculation. To gain an understanding of the molecular surface, the potential energy curves of the three model complexes were calculated at the ROHF/6-31G(d) and the ROB3LYP/6-31G(d) levels of theory, as a function of the chlorine-benzene distance. Molecular symmetry was initially maintained for each of the model complexes by imposing geometric constraints on the fully constrained (C) models.



Figure 1.2. Potential energy curve calculated at ROHF/6-31G(d) and ROB3LYP/6-31G(d) for the η_1 model, **10**, page 37. ZPE corrections have not been included. Relative energy in kJ mol⁻¹.



Figure 1.3. Potential energy curve calculated at ROHF/6-31G(d) and ROB3LYP/6-31G(d) for the η_2 model, **11** page 10. ZPE corrections have not been included. Relative energy in kJ mol⁻¹.



Figure 1.4. Potential energy curve calculated at ROHF/6-31G(d) and ROB3LYP/6-31G(d) for the η_6 model, **12** page 10. ZPE corrections have not been included. Relative energy in kJ mol⁻¹.

The minimum point on each potential surface was further optimised at the ROHF/6-31G(d) and ROB3LYP/6-31G(d) methods while maintaining molecular symmetry. Vibrational frequency calculations were performed, where specified, on the optimised geometries that were of the lowest energies on the potential curve in order to analyse the nature of the complexes. The frequencies thus obtained were used to calculate the zero-point vibrational energy (ZPE) correction, which was applied with the appropriate scaling factor^{58,81} in order to obtain the energy at zero Kelvin for each species. These results are presented in Tables 1.1-1.3. In each case, the optimisation calculations yielded complexation energies that indicate the C₆H₆/Cl[•] complex is more stable than benzene and chlorine radical at infinite separation.

Table 1.1. Complexation energies for the calculated minima of the model complexes.[†] The number of calculated negative frequencies is given in parentheses. Molecular symmetry was maintained for each of the fully constrained model complexes. ZPE corrections are included. (Hartree/Particle)

6-31 G(d)	η_1 complex		η_2	complex	η_6 complex		
14 - 14 1	dCl (Å)	ΔH° kJ mol ⁻¹	dCl (Å)	ΔH° kJ mol ⁻¹	dCl (Å)	ΔH° kJ mol ⁻¹	
ROHF	3.1	-2.9 (1)	3.4	-1.8 (1)	3.1	-0.9 (3)	
ZPE		0.107851		0.107941		0.107686	
ROB3LYP	2.7	-42.8 (0)	2.8	-34.3 (1)	3.3	-2.5 (0)	
ZPE		0.101384		0.101079		0.101653	

All calculations were examined for the effects of spin contamination, with $\langle S^2 \rangle \leq 0.75$, indicative of no or negligible spin contamination. The wavefunction stability for the ROHF method was tested and was found to be unstable. The wavefunction for the ROB3LYP method was stable.

To improve the complexation energies of the minimum energy geometries, higher level single point energy calculations were performed on the optimised DFT geometries at the

[†] Scale factors for 6-31G(d) basis set.^{58,81}

B3LYP = 0.9084, HF = 0.9135.

restricted open shell second order Møller-Plesset (ROMP2) level in conjunction with the 6-31G(d) basis set. These results are summarised in Table 1.2.

Table 1.2. Complexation energies of ROB3LYP minima at ROMP2/6-31 G(d) single point calculation. Models are fully constrained.

6-31G(d)	η_1 complex		η_2	complex	η_6 complex		
	dCl (Å)	ΔH° kJ mol ⁻¹	dCl (Å)	ΔH° kJ mol ⁻¹	dCl(Å)	ΔH° kJ mol ⁻¹	
ROMP2	2.7	-13.9	2.8	-13.9	3.3	0.5	

The counterpoise correction method (CP) was used to examine the effects of basis set supposition error (BSSE). The ROB3LYP/6-31G(d) minima were further optimised at the ROMP2/6-31G(d) level of theory with the inclusion of the CP method. CP correction calculations optimised the three minima at 3Å, 3.8Å and 3Å for the η_1 , η_2 and η_6 complexes **10-12**, respectively. The corrected energies are presented in Table 1.3. The wavefunction at the ROMP2 level of theory was found to be unstable.

Table 1.3. Relative energies of minima optimised at ROMP2 with incorporation of counterpoise correction method. Molecular symmetry was maintained for each of the fully constrained model complexes.

6-31G(d)	η_1 complex		η_2	complex	η_6 complex		
	dCl (Å)	ΔH° kJ mol ⁻¹	dCl (Å)	ΔH° kJ mol ⁻¹	dCl(Å)	ΔH° kJ mol ⁻¹	
ROMP2	2.7	-0.71	2.8	-0.14	3.3	5.45	

An assessment of basis set effects was undertaken where the model complexes at the minimum geometries of the surface scans were re-optimised with the larger basis sets. The ROB3LYP method was used in conjunction with larger basis sets namely, 6-31G(d,p), 6-311G(d,p), 6-311+G(d), 6-311+G(d,p) and 6-31++G(d). Molecular symmetry was not maintained within these calculations (optimisations of the C-C, C-H and C-Cl bonds were included). The calculated energies of the semi-constrained (S) models were compared to fully-constrained (C) models. These calculated energies are presented in Table 1.4. In the fully-constrained models all of the bonds and angles were specified as constants, not allowing for optimisation of these definitions. *i.e.* molecular symmetry was maintained.

	η_1 geometry	η_2 geometry	η_6 geometry
Basis Set	ΔH° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)
dC-Cl	2.7Å	2.7Å	3.2Å
6-31G(d)	-38.9 (1)	-35.9 (1)	Ь
6-31G(d,p)	-38.6	-35.6	-9.7 (2)
6-31+G(d)	-38.2	-34.9	-45.4 ^c
6-311G(d,p)	-38.0	-35.1	Ь
6-311+G(d,p)	-35.1	-32.2	-40.5^{c}
6-311+G(d)	-36.1 ^a	-31.4 ^a	-41.0^{c}
6-31++G(d)	-34.4 ^a	-31.6 ^{<i>a</i>}	-43.0^{c}

Table 1.4. Effects of basis set on the relative complexation energies of the semi-constrained models with ROB3LYP.

The numbers of calculated negative frequencies are in parentheses. ZPE corrections have not been included. $\langle S^2 \rangle = 0.75$ for all results in Table 1.4. "Result from single point calculation." No result due to convergence failure. "The optimised geometry resulted in the structure similar to the η_1 complex.

All wavefunctions from the optimised energies in Table 1.4 were found to be stable, with the exception of the η_6 geometry 12, where an unstable wavefunction was detected at the 6-31G(d), 6-31G(d,p) basis sets. The wavefunction for the 6-31+G(d) single point calculation on the constrained geometry was also found to be unstable.

The optimised bond lengths from the semi-constrained geometries are presented in Table A1.1, Appendix 1. The importance of comparing several methods of calculation simultaneously has been stressed, especially when examining radical-molecule interactions.¹³¹ Different methods may be more reliable, and/or efficient for different types of systems. It would appear that a choice can be made for a specific family of reactions. However, it is necessary to try a few logically chosen methods first. In order to assess the performance of the various levels of theory for the calculation of relative complexation energies, it is necessary either to compare the results with reliable experimental data and/or with the results of a benchmark theoretical procedure.

The use of other theoretical methods was therefore extended to include B3PW91 and BH&HLYP. Except where indicated, unrestricted open shell wavefunctions (*i.e.* UB3LYP) were utilised and the "U" is typically dropped for simplicity. These levels of

theory have been examined with the following range of basis sets: 6-31G(d), 6-31+G(d) and aug-cc-pVDZ.

The σ -type semi-constrained model **13** is shown below in Figure 1.5. The constraints were imperative in this model, as the σ -complex geometry **13** was only obtainable when the angles associated with the chlorine atom were fixed.



Figure 1.5. The σ geometry complex.

Table 1.5. Results of DFT calculation on σ complex 13.

6-31G(d)	B3LYP	B3PW91	BH&HLYP
ΔH° (kJ mol ⁻¹)	-5.4 (0)	-94.5 (0)	-85.2 (0)
ZPE	0.10017	0.10051	0.10374
d1(C ₆ -Cl)/Å	1.96	1.92	1.89
$(C_3-C_6-Cl)/^\circ$	129	129	129
$(H_1 - C_6 - C_3)/^{\circ}$	130	130	130
NImag	0	0	0

ZPE corrections are included in ΔH° . $\langle S^2 \rangle = 0.75$ for B3LYP and B3PW91. $\langle S^2 \rangle = 0.85$ for BH&HLYP. Re-optimisation at B3PW91/6-31+G(d) resulted in $\Delta H^\circ = -19.4$ kJ mol⁻¹.

The optimised lengths of the C-Cl bond were calculated at 2.8Å, 2.7Å and 2.6Å for the η_1 **10**, η_2 **11** and σ semi-constrained **13** models, respectively. The energies for these geometries are presented in Table 1.6.

	$\eta_1 \text{ complex}$ $\Delta H^\circ \text{ (kJ mol}^{-1} \text{)}$		$\eta_2 \text{ complex} \ \Delta H^{\circ} \text{ (kJ mol}^{-1} \text{)}$		$\eta_6 \text{ complex} \ \Delta H^\circ \ (\text{kJ mol}^{-1})$		σ complex ΔH° (kJ mol ⁻¹)	
	Basis Set							
Level of theory	6-31+G(d)	aug-cc-pVDZ	6-31+G(d)	aug-cc-pVDZ	6-31+G(d)	aug-cc-pVDZ	6-31+G(d)	aug-cc-pVDZ
ROB3LYP	-38.2	-35.7 ^a	-35.9	-111.2	b	b	-45.7 (0) ^c	249.7 ^{<i>a,e</i>}
UB3LYP	-34.6(1)	-35.5 ^a	-31.4(2)	-110.8	-7.2 ^a	-85.5 ^a	$-40.3(0)^{c}$	224.6 ^{<i>a</i>,<i>e</i>}
ROB3PW91	-43.5(1)	-35.6 ^a	-30.4(2)	-112.1	b	-84.2 ^a	$-39.2(0)^{c}$	219.5 ^{<i>a</i>,<i>e</i>}
UB3PW91	-33.3(1)	-35.2^{a}	-29.9(2)	-111.5	-3.6 ^a	-83.6 ^a	$-39.8(0)^{c}$	213.7 ^{<i>a</i>,<i>e</i>}
ROBH&HLYP	-109.0	-18.3 ^a	-105.0	-104.4	-86.3 ^a	-85.1 ^a	-90.4 (0) ^f	248.5 ^{<i>a,e</i>}
UBH&HLYP	-108.4	-19.7 ^a	-106.8	-105.0	-86.9^{a}	-85.2^{a}	$-105.1(0)^{f,e}$	232.3 ^{<i>a,e</i>}

Table 1.6. Effects of differing DFT methods and basis set on the relative energies for the semi-constrained (S) model complexes.

The numbers of calculated negative frequencies are in parentheses where applicable. ZPE corrections have not been included. ^{*a*}Result from single point calculation. ^{*b*}No result due to convergence failure. ^{*c*}C-Cl bond calculated at 2.5Å. ^{*d*}Not calculated with this method. ^{*e*}Spin contaminated. ^{*f*}dC-Cl=1.9Å. It was envisaged that constrained models would produce a systematic procedure for theoretically studying the potential surface of the C₆H₆/Cl⁺ complexes by incorporating the structures **10-13** as originally postulated by the experimentalists. However, obtaining consistent energies, stable wavefunctions and consistent frequency analyses for the constrained and semi-constrained model complexes proved difficult. Geometric constraints within the models led to difficulties within the optimisation procedures, where the convergence criteria, needed for successful computation, could not be met. Hence, the semi-constrained (S) models were abandoned and all the constraints were relaxed to afford totally unconstrained (U) models to obtain minimum energy structures. The fully relaxed geometries of the four model complexes were optimised using the unrestricted open shell DFT methodologies (UB3LYP, UB3PW91 and UBH&HLYP) in conjunction with the 6-31G(d) basis set. When η_1 **10**, η_6 **12** and σ type **13** complexes were all fully optimised, the same stationary point, structure **14**, was obtained, as illustrated in Figure 1.6. Structure **15** was obtained from optimisation of the η_2 starting geometry **11**. A summary of the calculated relative energies and geometric parameters is presented in Table 1.7.



Figure 1.6. The optimised structure from the fully relaxed geometries (U) from the η_1 , η_6 and σ complexes, 14. The fully relaxed geometry from the η_2 complex, 15.

								121				
		Starting B3LYP/	Geometry 6-31G(d)			Starting (B3PW91/	Geometry /6-31G(d)			Starting BH&HLY	Geometry P/6-31G(d)	
	η_1	η_2	η_6	σ	η_1	η_2	η_6	σ	η_1	η_2	η_6	σ
Resultant structure	14	15	14	14	14	15	14	14	14	15	14	14
ΔH° (kJ mol ⁻¹)	-35.1	-33.4	-35.3	-35.1	-112.3	-109.8	-112.5	-95.4	-105.1	-103.1	-105.2	-105.1
ZPE correction	0.10132	0.10129	0.10132	0.9084	0.10151	0.10152	0.10151	0.10810	0.10495	0.10499	0.10494	0.10494
d1(C ₆ -Cl)/Å	2.60	2.76	2.58	2.59	2.60	2.62	2.50	2.51	2.60	2.76	2.59	2.60
a1(C ₃ -C ₆ -Cl)	97.16	85.4 ^{<i>a</i>}	97.3	104.7	105.3	86.2 ^{<i>a</i>}	105.5	105.6	96.54	86.4 ^{<i>a</i>}	96.1	103.1
a2 (<i>ipso</i> hydrogen)	173.0	177.0	173.0	172.8	171.3	177.4	171.2	171.1	174.0	178.0	174.0	173.9
NImag	0	1	0	0	0	1	0	0	0	1	0	0

Table 1.7. Calculated relative energies and geometric properties for structures optimised from 10, 11 and 12, Figure 1.1, page 37.

Bond distances (d1) and bond angles (a1) are shown in angstroms and degrees, respectively. NImag denotes the number of imaginary frequencies. All energies include ZPE and the appropriate scaling factor.[†] $S^2 = 0.85$ for BH&HLYP. $S^2 = 0.75$ for B3LYP and B3PW91.

Re-optimisation of 14 and 15 at B3PW91/6-31+G(d) afforded $\Delta H^{\circ} = -39$ and -36 kJ mol⁻¹, respectively. No spin contamination was observed.

Re-optimisation of 14 and 15 at BH&HLYP/6-31+G(d) afforded $\Delta H^{\circ} = 113$ and -110 kJ mol⁻¹, respectively. $\langle S^2 \rangle = 0.88$ for BH&HLYP.

^{*a*}definition of this angle: C_1 - C_1 - H_2 . [†]Scale factors for the 6-31 G(d) basis set. B3LYP = 0.904, B3PW91 = 0.9772, BH&HLYP = 0.99^{58,81}

The atomic spin densities for the optimised structures 13, 14, and 15 were calculated at each DFT method with the 6-31G(d) basis set, and are presented in Table 1.8.

13	B3LYP	B3PW91	BH&HLYP
ortho	42%	40%	38%
para	12%	10%	12%
ipso	2%	4%	4%
C1	3%	6%	8%
14			
ortho	12%	14%	18%
para	15%	20%	20%
ipso	9%	4%	2%
C1	66%	62%	71%
15			
ortho	5%	3%	3%
para	6%	6%	4%
ipso	11%	12%	9%
C1	67%	67%	75%

Table 1.8. Positive spin densities for structures 13-15.

The SOMO's were calculated using Spartan (03^{132}) at the B3LYP/6-31G(d) level of theory and are illustrated in Figure 1.7, below.

Figure 1.7. Illustrations of the SOMO for optimised geometries 13-15.





15

TD-DFT (Time dependant density functional theory) calculations were performed on the structures **13-15** to obtain UV-visible spectral information, using the geometries optimised by the three DFT methodologies in conjunction with the 6-31G(d) basis set (Table 1.9). The equivalent B3LYP/6-31G(d) calculation was performed on the η_6 complex **12** (Table 1.10) for comparison.

Vibrational frequency analysis shows that the η_1 and η_6 complexes, **10** and **12**, respectively, are high-energy structures (Table 1.4) and these are unlikely to be observed by UV-visible experimentally. The data are in Table 1.10 for the η_6 complex **12** is included for comparative purposes only since this complex was originally proposed by Russell.

13	$\lambda_{max} nm$	f	14	$\lambda_{max} nm$	f	15	$\lambda_{max} nm$	f
B3LYP	464.9	0.0019	B3LYP	645.1	0.0017	B3LYP	578.8	0.0021
	323.1	0.0087		444.7	0.1804		460.9	0.1148
	246.9	0.1075		305.4	0.0290		327.0	0.0240
B3PW91	460.3	0.0018	B3PW91	635.1	0.0017	B3PW91	568.0	0.0022
	320.3	0.0075		445.2	0.1810		460.0	0.1166
	306.4	0.0444		310.9	0.0311		333.8	0.0271
BH&HLYP	394.8	0.0024	BH&HLYP	494.1	0.0026	BH&HLYP	468.8	0.0033
	292.6	0.0109		443.7	0.2092		438.3	0.1425
	272.2	0.0403		341.2	0.0757		379.1	0.0189

Table 1.9. DFT methods on the UV-visible absorption maxima and oscillator strengths for structures 13-15.

Table 1.10. UV-visible absorption maxima and oscillator strengths for constrained η_6 complex 12.

η_6	$\lambda_{max} nm$	f
B3LYP	3882.6	0.0000
	3881.6	0.0001
	485.41	0.0000

Figure 1.8. UV-visible spectrum of at B3LYP/6-31G(d).[†]



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 $^{^{\}dagger}$ The spectrum was generated by Spartan '03. 132

Discussion

Selection of the appropriate theoretical method for the calculation of molecular properties is of particular importance. High levels of theory combined with a large basis set accurately describe the electronic structure of the molecule in question, which in turn, often provides results in excellent agreement with experimental values. Medium sized molecules, such as those containing a benzene moiety, can readily take up significant computational resources, particularly when the molecular size, and hence the number of electrons, increases. Limitations on resources require that the choice in theoretical accuracy is pursued with care and without greatly compromising the accuracy of results.

As an initial probe into the interaction of chlorine radical with benzene, four representative models were selected **10-13**. This would allow four different environments on approach to the ring to be assessed, one electron deficient (**10**) and corresponding to the initial π -complex proposed by Russell, two where interactions directly with the π -cloud are possible (**11** and **12**), and one where the structure corresponds to the cyclohexadienyl derivative **13**. This approach has been successfully used to probe carbocation- π interactions,¹³³ with a similar approach used in the theoretical study of the interaction of molecular chlorine with aromatics.¹³⁴ Jarzeba *et al.*⁴⁸ have used a similar strategy for their calculations involving C₆H₆/Cl[•] complexes.⁸⁷

By looking at the range of energies as the chlorine approaches the aromatic ring it is possible to assess at what point the radical becomes meaningfully stabilised and how this stabilisation varies at different points on the ring. That is, whilst one of the complexes may not be the minimum energy structure, it may have a binding energy comparable to the gas-phase minimum energy complex and thus could contribute to the overall selectivity in solution. A number of closely-related structures with low barriers to interconversion could account for the difficulty in assigning a specific structure to the abstracting complex in experimental studies.¹³⁵

Although the C_6H_6/Cl° complex had been explored theoretically, it is worth re-examining this system, since early work was mostly done with a very small basis set and did not

examine DFT methods.⁸⁷ In addition, the conclusions from other works contained a number of assumptions,^{83,110} which did not necessarily support the findings in the experimental literature.^{54,135} Furthermore, little theoretical work has been published which details the solvent effect with substituted aromatics, so is it thus favourable to establish effective methods on which future work can be reliably based.

Two main levels of theory were initially tested in order to find an appropriate description of radical open shell systems, namely the restricted open shell (RO) HF and the restricted open shell density functional method, B3LYP. The B3LYP method was chosen based upon increasing support in the literature for its use on radical systems¹³⁶ and because of the inclusion of electron correlation. In general, DFT optimised geometries have been shown to be an improvement on the equivalent *ab initio* geometries, obtained at similar computational expense.¹³¹ However, the calculated energies are often less accurate, when using DFT, than those calculated by *ab initio* methods.¹³¹

The potential energy surfaces calculated for structures **10-12** (page 37) at both the ROHF/6-31G(d) and ROB3LYP/6-31G(d) levels, are depicted in Figures 1.2-1.4. On close inspection of the ROHF curves, only the η_1 structure **10** and η_2 structure **11** display a minimum that could correspond to a complex with small stabilisations of -3.4 kJ mol⁻¹ and -1.6 kJ mol⁻¹, respectively, whereas no such minimum is observed for the η_6 model **12**. This is consistent with the hypothesis that the most stable complex may be a σ -complex.

For the ROB3LYP curves in Figures 1.2-1.4, clear minima are visible at around 2.7Å for the η_1 and η_2 structures **10** and **11**, though there appears to be significant interaction even as far as 3.5 Å. This suggests that it will be important to include a large enough basis set in subsequent calculations to ensure that these long-distance interactions are properly treated. For the η_6 structure **12**, the stabilisation at around 3Å is of a smaller magnitude than for the other two structures **10** and **11**, and does not appear to diminish as rapidly as the chlorine atom gets further from the ring. The absolute magnitude is consistent with the calculations of Sokolov *et al.*¹¹⁰ where the stabilisation of the π -complex was estimated at less than 12 kJ mol⁻¹. The magnitude of the stabilisation at a distance further than 3.5 Å seems for the η_6 structure **12** to be consistent with that of the other two models **10** and **11**. This perhaps suggests that at this distance there is a less-well defined interaction, which as the chlorine atom gets closer to the aromatic ring, is localised to the periphery, where the majority of the electron density is located.

It can be seen from Figures 1.2-1.4 and Table 1.1 that DFT provides energies that are more comparable to the experimental energies reported in the literature^{43,83,88,110} of \approx 34 kJ mol⁻¹, than the energies obtained by HF. In particular, Benson⁸⁸ estimated ΔH° for Cl[•] + C₆H₆ \rightarrow C₆H₆/Cl[•] *via* a thermodynamic cycle and derived the value, $\Delta H^{\circ} = -34 \pm$ 8 kJ mol⁻¹, consistent with that derived by Ingold *et al.*⁴³ of $\Delta H^{\circ} = -38 \pm 25$ kJ mol⁻¹. Gas phase flash photolysis studies for the reaction of Cl[•] and C₆H₆ detect the exothermic formation of an C₆H₆/Cl[•].¹¹⁰ The equilibrium constant for the Cl[•] + C₆H₆ \rightarrow C₆H₆/Cl[•] reaction was estimated to be of the order of 1-2 x 10⁻¹⁸ cm³ molecule⁻¹ ($\Delta H^{\circ} = -32-34$ kJ mol⁻¹).

From the potential surface calculations, it is straight-forward to identify good starting points for better optimised structures. These were achieved by keeping the systems constrained to maintain symmetry, but to reach a lower-energy minimum. The results from Table 1.1 illustrate that the complexes thus obtained have a relatively large Cl⁻ aromatic bond distance suggesting that there is at least some π -character associated with the complex, but that the η_6 structure is not a good description, despite being a local minimum at ROB3LYP/6-31G(d).

The restricted MP2 method provides a good compromise between accuracy and expense in the calculation of reliable energies for some radical systems.¹³¹ The MP*x* methods are referred to as post-SCF methods because they add correlation corrections to the basic HF model. ROMP2 calculations were performed as above, but the constraints implicit in the models meant that convergence could not always be achieved for each increment of C-Cl distance, resulting in a failed calculation.

ROMP2/6-31G(d) single point energy calculations, performed on minimum energy ROB3LYP/6-31G(d) geometries for comparison (Table 1.2, page 41) afforded - 13 kJ mol⁻¹ for the η_1 , η_2 geometries **10** and **11**, and 0.4 kJ mol⁻¹ for η_6 geometry **12**. The higher level ROMP2 method does not improve the ROB3LYP obtained energies, relative to the experimental energy of *ca*. -34 kJ mol⁻¹.^{43,88,110} This may be attributed to the handling of electron spin. A spin restricted wavefunction (RO) contains doubly occupied molecular orbitals plus one or more singly occupied orbitals. These wavefunctions are eigenfunctions of the spin squared operator $\langle S^2 \rangle$ and thus yield pure doublet states, (or triplets etc.) However, the spin restricted wavefunctions may suffer from unrealistic spin localisation in a radical.^{56,137} A spin unrestricted wavefunction treats alpha and beta orbitals independently, as shown in Figure 1.9.

Figure 1.9. The description of the electronic orbitals in an unrestricted wavefunction.

The unrestricted approach affords lower energies than the restricted procedure since there is greater flexibility in describing the electronic structure. In particular, it typically results in a more realistic description of the electron distribution in an open shell species. Spin unrestricted wavefunctions are also known to be less computationally demanding than spin restricted methods.¹⁵⁵ However, spin contamination can occur in states of higher multiplicity in spin unrestricted wavefunctions since these are not necessarily eigenfunctions of the total spin <S²>.

The spin contamination manifests itself in values for $\langle S^2 \rangle$ that are no longer those of pure spin states. The spin contaminated $\langle S^2 \rangle$ values are greater than 0.75 for doublets and greater than 2.0 for triplets *etc.*¹³⁷

The effects of spin contamination are problematic when calculating reliable energies for radicals. Spin contamination can distort the potential energy surface and the resultant optimised geometries and energies are highly inaccurate. To check for the presence of spin contamination, most programs will print out the expectation value of the total spin, $\langle S^2 \rangle$. If there is no spin contamination, then $\langle S^2 \rangle$ should equal s(s+1), where s equals 0.5 multiplied with the number of unpaired electrons. As a guideline, it is accepted that the spin contamination is negligible if the value of $\langle S^2 \rangle$ differs from s(s+1) by less than 10%.

Although this affords a quick test, the results should be compared against experimental evidence or more rigorous calculations.

Within *ab initio* methods, basis set superposition error, BSSE, is a recognised problem⁷⁹ when calculating the interactions between two or more species. The error occurs because the energy of each unit within an associated complex will be lowered by the overlapping basis functions of the other. The counterpoise correction method (CP) was introduced to identify BSSE and correct for these energy differences.⁸⁰ The counterpoise correction method calculates each of the molecular units with the basis functions of the other (but without the nuclei or electrons) using ghost orbitals. The counterpoise correction of

BSSE makes intermolecular complexes less stable with longer intermolecular distances than is apparent from the normally optimised structure. Such corrections have shown noticeable improvements in optimised transition state geometries with relatively small basis sets.⁷⁹

Counterpoise energy correction calculations were performed at ROMP2/6-31G(d)//UB3LYP/6-31G(d), and the results are presented in Table 1.3. The energy corrections did not have a significant improvement on the energies relative to those obtained after using DFT or those available experimentally.^{43,83,88,110} The inadequacy of MP2 methodology on the model systems in question is likely to be attributable to the wavefunction instabilities found in the optimised structures.

As reflected in the above results, the HF method is limited as there is no full treatment of the effects of electron correlation. Although HF theory automatically includes the major correlation effects arising from pairs of electrons with the same spin, termed the exchange correlation, the motion of electrons with opposite spin, remains uncorrelated. As such, it is a good base-level theory, but neglect of electron correlation makes it unsuitable for the accurate modelling of the energetics of reactions and bond dissociation.⁵⁸ Therefore, this explains why HF results are unsatisfactory for accurately modelling the C₆H₆/Cl[•] complex. DFT, however, has been shown to provide accurate results for systems with two-centre/three electron interactions, due to its inclusion of electron correlation.^{104,138} In addition, inclusion of electron correlation makes DFT particularly suitable for systems that are likely to become spin contaminated, such as open shell radical systems.⁵⁸

Typically, the more unusual the electronic structure of a given system, the higher level of theory is needed to model it accurately. Where MP2 and HF methods have been used in the literature, a method of a higher level has superseded it to improve the calculated energies.^{131,137,139,140} In contrast, DFT is a more economical procedure as it computes the electron correlation *via* general functions of the electron density. Inclusion of electron

correlation by DFT functionals partitions the electronic energy into several components that are computed separately. Thus the performance of the density functional methods was explored further.

The effect of increasing the basis set on calculated energies was examined on semiconstrained models using the restricted MO approach, the results of which were compared to the effects of unrestricted *versus* restricted MO theory. The effects of increasing the size of basis set were examined at the ROB3LYP level by optimisation of the minimum energy ROB3LYP/6-31G(d) η_1 , η_2 and η_6 optimised geometries. The energies obtained from differing basis sets are presented in Table 1.4 (page 42). Since open shell radical systems are known to suffer from the effects of spin contamination,^{58,131,139} the electron spin was restricted for the basis set assessment.

Where the optimisation procedure failed, a single point energy (SP) calculation was employed on a previously optimised ROB3LYP/6-31G(d) geometry. Failed optimisations mainly occurred for the 6-311+G(d) and 6-31++G(d) basis sets. The comparison of geometries obtained with different basis sets validates the calculation of single point energies. Single point calculations afford the wavefunction and energy for a given system with a well-specified geometric structure, which as Appendix A shows, are all very similar with variations only in the order of 0.1Å. Single point calculations on such geometries provide a prediction of the energy. However, since the optimisation failed it provides only a comparison. Problems were encountered specifically with the η_6 complex. In order to maintain the geometries during optimisation, constraints within the model had to be applied. These constraints meant that convergence could not always be achieved within the optimisation and the calculation would fail on this basis. In addition the wavefunction for the η_6 geometry was found to be unstable. The instability within the calculation is also likely to contribute to problems with convergence. Stable minima were found for the constrained η_6 model geometry at the 6-31G(d) and 6-31G(d,p) but in these cases the wavefunctions were found to be unstable. Complexation energies of these minima were calculated for the η_6 geometry at -2.4 and -4.5 kJ mol⁻¹, similar to values originally postulated by Russell.^{17,27,28}

Jarzeba *et al.*⁸⁷ reported that on constraining the geometry, a C_{6v} geometry structure was calculated and the position of the chlorine radical was 3.7Å above the centre of the benzene ring. This geometry was reported not to be a stable minimum, but a second order saddle point.⁸⁷ This is consistent with the second order saddle point calculated (at ROB3LYP/6-31G(d,p)) in this work (Table 1.4) for the constrained η_6 geometry, where the CI was instead calculated at 3.2Å above the centre of the benzene ring. Sokolov *et al.*¹¹⁰ were unable to characterise a stable π complex experimentally. From their theoretical calculations, the bonding in such a complex would be less than 12 kJ mol⁻¹ which implies that such a species would not survive more than a few picoseconds at ambient temperature and would therefore be too short-lived to play any role in the hydrogen abstraction reaction. It was on this basis that Sokolov *et al.*¹¹⁰ assigned their results to a σ complex.

Other theoretical studies have calculated a minimum η_6 geometry using BH&HLYP and B3LYP methods.⁸² However, the wavefunction for these calculations were also found to be unstable, consistent with data obtained from this work. Tsao et al.⁸² estimated a complexation energy of -5 kJ mol⁻¹ for the η_6 geometry and calculated two imaginary frequencies. These results⁸² are consistent with data obtained in this work (Table 1.4). With larger basis sets, optimisation calculations from this work, afforded a structure resembling the η_1 geometry obtained from the initial η_6 model. This observation, coupled with the subsequent failure of the calculations for the η_6 geometry indicates a very weak interaction in an unstable complex. Recent research in the literature failed to experimentally characterise a stable π complex between a chlorine atom and benzene. The prediction of >12 kJ mol⁻¹ for the binding energy in the η_6 complex¹¹⁰ correlates with the low energies obtained in this work for a structure of such geometry (Table 1.4). This axial structure is inconsistent with the principle of maximum overlap of the HOMO and LUMO, and it is doubtful that such a structure of benzene and chlorine would exhibit properties consistent with the ESR data that have been reported, for example Sergeev et al.⁵⁴

The relative accuracies of a variety of model chemistries may be examined by their relative performance against the compound G2 molecule set.⁵⁸ Table 1.11 lists some model chemistries with the mean absolute deviation from experiment (MAD), the standard deviation and the largest positive and negative deviations from experiment for each model chemistry.

Table 1.11. The deviations of some model chemistries.⁵⁸ Energies in kJ mol⁻¹.

Model chemistry	MAD	StdDay	Largest Errors		
Widder enemistry	MAD	StuDev	Positive	Negative	
B3LYP/6-311+G(3df,2df,2p)//B3LYP/6-31 G(d)	11.2	10.8	52.3	-38.9	
B3LYP/6-311+G(2d,p)//B3LYP/6-31 G(d)	13.3	12.5	56.9	-84.0	
B3LYP/6-31+G(d,p)// B3LYP/6-31 G(d)	16.7	17.5	73.6	-141.8	
B3LYP/6-31 G(d)//HF/3-21 G(d)	33.4	39.3	39.3	-226.7	

Large maximum errors are often observed, however, many model chemistries are inaccurate at predicting thermochemical data.⁵⁸ It is due to these short-comings of existing methods that compound methods such as the complete basis set (CBS) and Gaussian-n methods were introduced.⁵⁸ However, these values (in Table 1.11) do not imply that such a method may be unreliable for modelling other properties of molecular systems. For example, DFT can be quite accurate at predicting vibrational frequencies, a variety of relative energy values, energy differences to similar models and reaction energies.⁵⁸ The most computationally demanding methods are not necessarily the best. The most accurate method seems to be the B3LYP/6-311+G(3df,2df,2p)//B3LYP/6-31G(d) which is not the most expensive.⁵⁸ It has been recommended that B3LYP/6-31G(d) should be used for geometries and zeropoint corrections followed by an optimisation using B3LYP with the largest practical basis set, for energy calculations.⁵⁸

With the 6-311+G(d,p) and 6-31++G(d) basis set, the energies obtained (in Table 1.4),

-35.1 and -34.4 kJ mol⁻¹, respectively, for the semi-constrained η_1 model show a good correlation with experimental value of -34 kJ mol⁻¹.^{43,88} The energies obtained with the other basis sets are presented in Table 1.4 are also within 4.5 kJ mol⁻¹, indicating consistency for this method. From this basis set assessment, it can be concluded that the use of additional functions, while increasing the size of the basis set, provides only a

limited improvement, for a relatively high computational cost, upon the energies and structures obtained, and that smaller basis sets may be entirely adequate to provide reasonable energies for larger models.

For all geometries, vibrational frequency analyses (seen in Table 1.4) were performed only at the smaller basis sets, due to the additional time needed to complete these calculations. One imaginary frequency was calculated for the η_2 model, which indicates that this geometry is the transition structure of the η_1 model. Animation of this negative vibrational mode reveals the chlorine atom as rocking from one side to the other, directly above the C=C bond. The magnitude of this negative frequency was calculated to be -85 cm⁻¹. For the semi-constrained η_1 model, one imaginary frequency was calculated. This is attributable to the optimisation of the bonds without optimisation of the angles within the system, especially of those about the C-Cl bond. Indeed, animation of this vibrational mode reveals the chlorine atom rocking in a similar fashion as was found for the negative vibrational mode from the η_2 model. The magnitude of this negative frequency was calculated to be -62 cm⁻¹.

In addition to an assessment of different basis sets, a trial of DFT methodologies was introduced. BH&HLYP was chosen since it has been cited as improving the molecular description of two centre/three electron bonding.¹³⁸ B3PW91 has been used in studies examining binding energies,¹⁴¹ therefore a comparison of these functionals with B3LYP could be made. Table 1.6 summaries the calculated energies. Of the three DFT methods, B3PW91 and B3LYP appear to provide results that best reflect those obtained experimentally.

During the course of this work Tsao *et al.*⁸² published calculations on halogen atombenzene complexes, η_1 , η_2 and η_6 , using B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels of theory, which mirrors our selection. Inclusion of larger basis sets and theoretical methods were incorporated in their study to improve the accuracy involved in the calculation of relative energies. The findings of Tsao *et al.*⁸² correspond closely with the results produced in this work. The potential surface, for Cl⁺-benzene interaction, was calculated by Tsao *et al.*⁸² as a function of C-Cl distance. The η_1 model obtained by Tsao *et al.*⁸² was a stable minimum with a Cl⁺-benzene distance of 2.6Å when calculated with both B3LYP/6-31G(d) and BH&HLYP/6-31G(d) methodologies. Inspection of Table 1.7 shows that the findings by Tsao *et al.*⁸² are similar to the results presented herein. It was reported that wavefunction instability was also found in the η_6 calculations. They did also report that the η_6 structure was not a stable minimum. The η_2 structure was found to be a transition structure, between η_1 minima, which was 2 kJ mol⁻¹ less stable than the η_1 geometry and exhibited a C-Cl bond length of 2.8Å. Similarly, for the σ geometry, a structure consistent with this work was obtained with BH&HLYP. However, Tsao *et al.*⁸² did not identify a stable σ structure with the B3LYP level of theory and they concluded that a structure identical to **14** (Figure 1.6, page 45) was the most stable representation for the C₆H₆/Cl⁺ complex, consistent with the calculations presented herein.

As an additional comparison, and extension to the basis-set assessment, the Dunning's basis set was trialled.^{77,78} These basis sets have had redundant functions removed in order to improve computational efficiency.^{77,78} In addition, such basis sets have reportedly performed well in the analysis of weakly bound molecular complexes.¹⁴² It was envisaged that, due to the economic benefits, additional functions could be introduced into the calculation. Optimisation of the semi-constrained models with different DFT methods afforded energies that were greatly overestimated (Table 1.6, page 44). Dunning's basis set to be computationally more, taking up triple the time compared to using a standard split valance basis set. Moreover, frequency analysis calculations using the Dunning's basis set were extremely costly computationally and unviable. Inspection of the calculated energies for the η_1 complex (Table 1.6) shows that the Dunning's basis set reasonably predicts the complexation energies only with the B3LYP and B3PW91 methods.

The Dunning's optimised geometries were near identical to the optimised DFT structures. It was therefore assumed valid to perform single point energy calculations with this basis set due to the significant computational cost associated with full optimisation. It is apparent that the Dunning's basis set does not consistently provide C_6H_6/Cl' complexes with an adequate electronic description during the optimisation procedure.

On inspection of the energies presented in Table 1.6, it can be noted that the spin unrestricted methods, combined with the split valence basis set, generally correlate more strongly with the estimated experimental value for the C_6H_6/Cl° complex of ≈ -34 kJ mol⁻ ^{1,88,111} than the energies calculated with the spin restricted and the Dunning's basis set SP energies. As previously mentioned, spin-restricted wavefunctions may suffer from unrealistic spin-localisation in a radical.⁵⁶ Therefore, the apparent overestimation of some energies may be attributable to this effect. Overestimation, relative to the experimental^{88,111} values of \approx -34 kJ mol⁻¹, is also seen in BH&HLYP. Although they are consistent with one another at RO and U methodology, the energies are not consistent with the experimental findings. The single point Dunning's calculations on the σ complexes, with d(C-Cl) constrained to 1.9Å, are spin contaminated. The total spin was found to be $S^2 = 0.86$, thus the calculated energies indicate that this method is inappropriate for these systems and the obtained energies should be treated as unreliable. Spin contamination was also observed, $\langle S^2 \rangle = 0.85$, for the BH&HLYP calculation for the σ complex, also consistent with an inappropriate molecular description, as reflected by the energies. This can be seen in Table 1.5, page 43.

Successful optimisations employing the split valance basis set were only obtained for the η_1 , η_2 and σ models. Difficulties were encountered with the η_6 model for reasons previously explained. The model has been included because this structure was one of the originally postulated C₆H₆/Cl[•] complexes.^{17,26,27}

Full optimisation of the η_1 , η_2 , η_6 and σ models resulted in the two stationary structures **14** and **15**, depicted in Figure 1.6, page 45. The η_1 , η_6 and σ type complexes all fully optimised to the same stationary point, as would be expected, since they are all near the same local minimum on the potential surface. The minimum geometries of the C₆H₆/Cl[•] complexes **14** and **15** are obtained when derived when using any of the three DFT methods with the 6-31G(d) basis set, and both the structures **14** and **15** present as a

distorted cyclohexadienyl complex. Negligible differences within the benzene framework were observed, only the positions of the *ipso* hydrogens and the chlorine radical showing slight distortion. Frequency analyses showed that structures **14** and **15** were a stable minimum and transition state geometry, respectively. Animation of the negative frequency of structure **15** reveals the chlorine atom rocking from one side to another, above the plane of the C=C bond. The magnitude of the negative frequency was calculated at -59 cm⁻¹, and is similar in action to that observed in the constrained η_2 structure. The transition state allows the chlorine atom to migrate around the benzene ring and the energy difference corresponds to this process.

Of the calculated structures (Figure 1.6, page 45) structure **14** is of the lowest energy when calculated with any DFT method with the 6-31G(d) basis set. The complexation energies (Table 1.7) calculated at B3LYP/6-31G(d) basis set affords complexation energies for **14** and **15** which are in excellent agreement within 2-3 kJ mol⁻¹ to the experimental^{88,111} values of -34 kJ mol⁻¹. No η_6 structure could be identified using the unconstrained model systems. The B3LYP/6-31G(d) method provides a good estimation in terms of geometry and energies without substantial computational cost and provides results comparable to the high accuracy BAC-MP4 results obtained by Sokolov *et al.*¹¹⁰ With respect to the structural nature of the C₆H₆Cl^{*} complex, all optimisations that are not spin contaminated, predict a C-Cl length of 2.6Å.

The stabilisation energies for 14 and 15, calculated with both BH&HLYP and B3PW91 methods, as shown in Table 1.7, are significantly lower than the experimental value^{88,111} of -34 kJ mol⁻¹. Re-optimisation of the model complexes at B3PW91/6-31+G(d) affords the energies of -39 and -36 kJ mol⁻¹ for structures 14 and 15, respectively. Re-optimisation using BH&HLYP/6-31+G(d) afforded an energy at -113 and -110 kJ mol⁻¹ for structures 14 and 15, respectively. Re-optimisation using BH&HLYP/6-31+G(d) afforded an energy at -113 and -110 kJ mol⁻¹ for structures 14 and 15, respectively. This overestimation in the BH&HLYP is attributable to the effects of spin contamination, $\langle S^2 \rangle = 0.88$. The re-optimisations, using the B3PW91/6-31+G(d) method, describes the Ar-Cl^{*} complex moderately, but with an

associated increase in computational cost. It is clear that the BH&HLYP method is unsuitable for describing the C_6H_6/Cl° system.

The BH&HLYP method (Table 1.7) overestimates energies in the work by approximately 70 kJ mol⁻¹. This functional includes 50% Hartree-Fock exchange, 50% Slater exchange in addition to the additional correlation effects of the LYP functional.⁶⁸ The B3PW91 and B3LYP methods are three parameter hybrid functionals that incorporate a mixture of gradient corrected correlation functionals with the Becke exchange and the exact Hartree-Fock exchange.⁶⁴ It has been reported that the use of BH&HLYP, while providing good results for two centre/three electron bonding systems, has shown to produce an overestimation relative to experimental energies in some two-centre/three electron radical systems.¹⁵⁵ The overestimation from the BH&HLYP method (Table 1.6) suggests that the C_6H_6/Cl' complex is not a classical two/centre – three/electron system. Consequently, BH&HLYP should not be relied upon to produce accurate energies for these types of complexes. However, closer inspection of the calculated structures, (14 and 15) shows the existence of a two centre/three electron type interaction. Such situations are favourable for radicals with high electron affinities (*i.e.* Cl^{\cdot}, EA – 3.62eV) and molecules with low ionisation energies (*i.e.* C_6H_6 , IE 9.25eV).⁸ The formation of a relatively weak bond has little impact on the ipso C=C bonds within structure 14, but appears to perturb the ortho C=C bonds by 0.02Å and the ipso C=C bond in structure 15 by 0.01Å. This suggests that structures 14 and 15 have both some σ and π bonding character for the Cl^{*} interaction with benzene and little electronic reorganisation is required to form the complexes as the *ipso* C=C bonds remain sp² hybridised.

Full optimisation of the η_1 and η_2 model complexes using the B3LYP, B3PW91 and BH&HLYP methods (Table 1.6) calculate dC-Cl ≥ 2.5 Å, irrespective of the handling of electron spin, *i.e.* RO *versus* U. This suggests that structure **14** is a real minimum and is required to be seriously considered as a possible structure for the hydrogen abstraction species in chlorination reactions in aromatic solvent, contrary to Berho *et al.*⁸³ Reliable single point energy estimations were not obtained for the η_6 model as successful optimisations were difficult to achieve. Moreover, the few successful optimisations were found to have an unstable wavefunction.

Optimisation from the σ complex starting geometry (from the energies in Table 1.6) resulted in η_1 geometry where the C-Cl distance was calculated as approximately 2.5Å using all methods, with exception of BH&HLYP. Although the BH&HLYP calculations had optimised a 'correct' σ geometry, the spin unrestricted calculations were found to be severely spin contaminated, ($\langle S^2 \rangle = 0.88$). It is probable that that, due to the spin contamination and the problems associated with the RO approach (as previously described) the BH&HLYP stationary points are unrealistic.

The BH&HLYP optimised geometry derived from the σ starting structure 13 affords a structure with the *ipso* carbon with sp^2 hybridisation, inconsistent with a formal σ geometry. These findings are inconsistent with those obtained by Berho et al.⁸³ They reported the use of BH&HLYP to afford structures that are not spin contaminated but with a calculated C-Cl length of 1.9Å ($\Delta H^{\circ} = -20.1 \text{ kJ mol}^{-1}$). It was claimed on this basis that the B3LYP calculations generate an erroneous geometry for the C₆H₆/Cl[•] complex, since the C-Cl distance was calculated as 2.57Å ($\Delta H^{\circ} = -43.4 \text{ kJ mol}^{-1}$).⁸³ Structurally, there are small changes in the aromatic component that reflect complexation of the chlorine in both the semi-constrained and fully unconstrained models. For instance, in the optimisation of the semi-constrained models, the planarity of the benzene ring is maintained. However, a slight shortening is observed in certain areas within the C=C framework, thus reflecting a stronger C=C double bond character. Shortening was observed in the C₄-C₅ and C₁-C₂ bonds of the η_1 complex (d = 1.38Å), compared to the typical C-C bond length in benzene length (d = 1.40). Similar shortening was observed for the C₃-C₄ bond in the η_2 complex, although a slight lengthening was observed (d =1.41Å) at C1-C2. All of the C-H bonds are calculated at 1.086Å. Geometries for the semi-constrained η_6 complex were only obtained at the 6-31G(d,p) basis set, where no geometric changes were observed. However, a structure with two imaginary frequencies was obtained. The optimised bond lengths for all the models are shown in Appendix 1. The geometries do not show a significant difference on increasing basis set. Choice of a suitable basis was therefore made based on the resources available without comprising greatly on the quality of the calculated energies. In Figure 1.10, the C₄-C₅ and C₆-H bonds of the η_1 geometry were calculated as showing slight shortening. The C₄-C₃ C₂-H and C₂-H bonds of the η_2 geometry showed a slight shortening. Only the C₂-C₁ bond in the η_2 geometry showed a slight lengthening. Comparison of these structural observations with those obtained by Berho *et al.*⁸³ show similar distortions about the benzene ring. Optimisations of both the unconstrained and semi-constrained models from this work show that the approach of the chlorine atom, at 2.5Å, perturbs the C-C bonds.



Figure 1.10. Optimised bond lengths

The C-C bonds *ipso* to the chlorine in the optimised structures **14** and **15** from this work do not show significant change in length, unlike the lengthening to 1.5Å observed for the σ -complex (Figure 1.11) described by Berho *et al.*⁸³ This is due the carbon atom not being sp³ hybridised as the equivalent atom in the cyclohexadienyl structure. This therefore confirms that no formal bond is acquired in the complex structures proposed in this work compared with the optimised geometries of the σ -complex (Figure 1.11). Berho *et al.*⁸³ also calculated C-C bond lengths slightly shorter (1.37Å) than the typical C-C bonds in benzene (1.40Å) in bonds C₂-C₃ and C₅-C₆ with slight lengthening (1.42Å) reported for bonds C₃-C₄ and C₄-C₅.



Figure 1.11. Atom numbering of the σ Ar-Cl[•] complex.

It was also noted by Berho *et al.*⁸³ that geometry optimisation using the B3LYP method afforded a C-Cl bond length of 2.6 Å and that geometries with a shorter C-Cl bond length were spin contaminated. The long C-Cl bond and the spin contamination prompted Berho *et al.*⁸³ to use the BH&HLYP functional. Using this functional, the C-Cl distance was calculated at 1.9 Å and no spin contamination was reported.⁸³

All geometry optimisations using B3LYP from this work calculate a C-Cl bond length of 2.6Å, with the exception of optimisation of the semi-constrained σ model **13** in Figure 1.5, which affords a C-Cl bond length of 1.9 Å. The only occurrence of spin contamination arising from optimisation was observed in this BH&HLYP-calculated σ geometry **13**. Similarly, spin contamination was observed in the stationary point of the σ complex optimised at HF/3-21G(d) by Jarzeba *et al.*⁸⁷ Their spin density analysis indicated that the unpaired electron is mostly confined to the sp² carbons of the aromatic ring and very little spin density is located on the chlorine. Identical observations regarding the location of the spin density and the spin contamination were found in the calculation of the σ geometry **13** from this work. The distribution of the spin density in the complexes is presented in Table 1.8 and Figures 1.7.

Jarzeba *et al.*⁸⁷ reported a stabilisation energy of -30 kJ mol⁻¹ for the σ complex. This value agrees with the experimental^{88,111} findings and with the magnitude of the energies obtained from this work for the intermediate σ - π -complexs, **14** and **15**, Table 1.7. However, the accuracy of the value obtained for the energy of this σ -complex is questionable due to the high level of spin contamination reported for this species reported by Jarzeba *et al.*⁸⁷ In addition, Berho *et al.*⁸³ have estimated that the σ complex should be unstable and therefore of high energy, and calculated an energy of -20kJ mol⁻¹ for this
species. Jarzeba *et al.*⁸⁷ also reported a stable minimum (optimised from a relaxed C_{6v} geometry at HF/3-21G(d)) of -17 kJ mol⁻¹ for an intermediate σ - π -species corresponding to structure **15** from this work (Figure 1.6, page 45). A distance of 2.7Å was reported for the position of the chlorine atom above the centre of a C=C bond and no spin contamination was observed for this complex. These geometry observations are reasonably consistent with structure **15** from this work.

Inspection of the B3LYP/6-31G(d) and B3PW91/6-31+G(d) energies for the σ complex **13** (Table 1.5, page 43) clearly shows that this structure is approximately 30 kJ mol⁻¹ less stable than structures **14** and **15** and does not reflect the energies obtained from experimental data (\approx 34 kJ mol⁻¹).^{43,88,111} The experimental value of \approx 35 kJ mol⁻¹ for the BDE for the chlorocyclohexadienyl radical, or σ complex, has only been estimated from the experimentally-determined equilibrium constant.¹¹⁰ This value is inconsistent with the theoretical DFT value of -20 kJ mol⁻¹, recorded by Berho *et al.*⁸³ and the B3PW91 and B3LYP energies obtained in Table 1.5 of this work. Clearly these observations do not agree with the rationale presented by Berho *et al.*⁸³ who argues that the σ cyclohexadienyl radical must be the only correct geometry for the Ar-Cl' species because their values correlate with those presented by Sokolov *et al.*¹¹⁰

Sergeev *et al.*⁵⁴ used results from ESR spectroscopy to propose that Cl[•] forms a structural intermediate between that of a hexahapto π -complex (η_6), and a chlorocyclohexadienyl radical (Figure 1.12). It was argued that this structure provides optimum overlap of the LUMO of the chlorine and the HOMO of the aromatic system, and so the interaction should be stronger than for a π -complex. Considerable spin density was also observed on the chlorine atom, suggestive of a complex between benzene and chlorine rather than a covalently bound system where the unpaired spin density is delocalised to the aromatic ring. A comparison of the distribution of spin density in complexes **13**, **14** and **15** can be seen in Table 1.9.



Figure 1.12. Postulated structure from ESR experiments.⁵⁴

In light of the present calculations, the proposal of the σ - π hybrid intermediate structure, by Sergeev *et al.*⁵⁴ (Figure 1.12), would appear to be the most logical structure for the abstracting entity. The theoretical prediction for the complexation energies of the C_6H_6/Cl^{-1} species are approximately -30 kJ mol⁻¹, which satisfactorily agree with the experimental values.^{43,88,111} Early arguments were based around whether the structure was a π or a σ type complex. However, since the advent of computational chemistry and its growing reliability, a few publications have re-ignited the interest in this complex and in prediction of its electronic and geometrical structure.^{82,83,110} Where DFT has previously been used to calculate the energy of the chlorocyclohexadienyl structure,⁸³ the B3LYP functional was reported to afford a C-Cl bond length of 2.57Å. This is inconsistent with the σ geometry, yet the authors dismissed this as error.

One of the other pieces of evidence used to argue for specific structures has been the presence of charge transfer bands in the experimental UV-visible spectra. Charge transfer complexes are characterised by one component that is electron rich (the donor, *i.e* benzene) and another component that is strongly electron attracting (the acceptor, *i.e* halogen); hence they are also known as donor-acceptor complexes.

$$[D: A \leftrightarrow D^+ A^-] \qquad \qquad \text{Scheme 1.2}$$

The charge-transfer structure, D^+ A⁻, makes only a small contribution to the total electronic structure of such complexes and provides the interaction that holds the components together.¹⁴³ The energy involved in the charge transfer interaction is typically only tens of kJ mol⁻¹.¹⁵⁵ The donors have a high energy HOMO, in which the electrons are loosely held, *i.e.* they have low ionisation energy. The acceptors

correspondingly have a low lying LUMO. In such a complex there is often some overlap of the HOMO of the donor with the LUMO of the acceptor that results in transfer of some electron density between donor and acceptor. Aromatics and halogen molecules are well known to interact and form charge transfer complexes.¹⁴⁴⁻¹⁴⁸ Examples have been examined by solution phase UV-visible spectra for the iodine benzene complex.^{51,145} and also aromatic complexes with bromine and chlorine.^{135,147}

Charge transfer complexes are characterised by large dipole moments. The magnitudes of the dipole moments will depend on the polarisability of the complex species. The ability of an aromatic system to interact with the lone electron from the chlorine radical results in high polarisability of the resulting complex. For comparison, a value of 0.25 Debye is predicted for a benzene molecule. Values of 4.04 and 3.85 Debye were calculated for structures 14 and 15, respectively. The dipole moments of the σ and the η_6 complex were calculated at 3.00 and 0.584 Debye, respectively. Moreover, the confirmations of the dipole moments for complexes 14 and 15 correlate with the predicted charge transfer bands for these species. Due to the hyperconjugation of Cl[•] with the aromatic system, substantial spin density arises on the chlorine. It is this spin density which gives rise to the observed charge transfer band.

The calculated UV-visible spectra, presented in Table 1.9-10 and Figure 1.8 (pages 48 and 49) predict an intense charge transfer band at approximately 440nm for **14** and 460nm for **15** arising from the substantial spin density of approximately 66% at the chlorine atom for both **14** and **15**. No such spin density is predicted for the σ bonded structure, **13**, where positive spin density of 3-8% in the chlorine region was calculated. Tsao *et al.*⁸² reported the spin density on Cl[•] to be 70% with 30% transferred to the ring when calculated with BH&HLYP. Their paper⁸² agrees with the observations from UV-visible, ESR, kinetic and product studies in addition to the results emanating from this work.

From the calculated UV spectrum in Figure 1.8 and the data in Table 1.11, no charge transfer bands exist for either the η_6 or the σ -species. These data are inconsistent with the experimental UV data presented by Ingold *et al.*,¹³⁵ who favoured the η_6 species, and Skell *et al.*^{41,42} who favoured the σ species. Therefore, it seems unlikely that the η_6 and σ structures are the species postulated as the highly selective H-abstractor. The predicted UV spectrum (Figure 1.8) and the calculated data reported here, all support the calculated structures **14** and **15** as being the most consistent with the structure postulated following the ESR experiment conducted by Sergeev *et al.*⁵⁴

The different basis sets and methods used by Jarzeba *et al.*⁸⁷ (HF/3-21G(d) and PMP2/6-31+G(d)) would account for the differences in energy from the B3PW91 and B3LYP results from this work, shown in Tables 1.5 and 1.7. However, single point energy calculations require a well-specified geometry in order to obtain energies of reasonable comparison with experimental data. The excited states of structures identical to **13** and **15** (Figures 1.5 and 1.6, respectively) were calculated at the CIS/6-31+G(d) level by Jarzeba *et al.*⁸⁷ A charge transfer band, calculated by this method was assigned to the intermediate π complex, resembling **15**, but no such absorptions were found in calculations for the σ complex. Jarzeba *et al.*⁸⁷ showed that the non-detection of a charge-transfer band indicates the absence of any appreciable spin density on the chlorine atom of the σ complex. These observations correlate with the calculated spin density analysis (Table 1.8) and UV-visible data (Table 1.9) that is observed from this study.

A transition energy geometry was afforded in this work for **15**, and not a stable minimum as obtained by Jarzeba *et al.*⁸⁷ This discrepancy could be attributable to the lower level of theory (MP2 3-21G(d)) of the geometry optimisations performed by Jarzeba *et al.*⁸⁷

Comparisons of the UV-visible spectra for 13, 14 and 15 are presented in Table 1.9. Weak absorptions were predicted (Table 1.9 and Figure 1.8) between 305-310nm indicative of a π - π^* band for structures 14 and 15. These spectroscopic predictions are in good agreement with the experimental UV data recorded in the literature,⁴³ (λ_{max} 320 and 490nm). The absorptions larger than 450nm predicted for 14 and 15 indicate that

substantial spin density exists within the molecule. The weaker absorptions, between 305-310nm and the charge transfer band at 450nm, for 14 and 15 confirm that these structures are not a true σ -geometry. It can be noted that no significant absorptions (Table 1.10) are calculated for the η_6 geometry 12, confirming that this structure was not that observed by the experimentalists.

The UV-visible spectrum of the chlorination reaction affords absorptions of λ_{max} 320 and 490nm.⁴³ On irradiation of neat CCl₄, a similar absorption spectrum to the C₆H₆/Cl[•] complex is observed, exhibiting bands with maxima at 340 and 480nm.⁴⁰ The kinetic measurements of the C₆H₆/Cl[•] complexes were carried out at 500nm since the lifetime of CCl₄ is less than 100 ns, which is shorter than that of the UV band.⁴⁰ Yields and decay rates of the C₆H₆/Cl[•] complex were reported to be dependent upon experimental conditions such as irradiation doses, the concentration of benzene and the presence of oxygen.⁴⁰

The predictions of Skell *et al.*⁴² require that appreciable spin density should exist at the chlorine atom and agree with the calculated spin densities from this work. However, the proposal of appreciable spin density at Cl[•] is inconsistent with the σ -complex 13. It is evident from the SOMOs (Figure 1.7) of structures 13, 14 and 15 that the unpaired electron is mainly distributed in the Cl region in 14 and 15. It may be seen in 13, (Figure 1.7) that the distribution of the unpaired electron is mainly delocalised within the benzene ring, with only a small percentage (*ca.* 3-8 %) distributed on the chlorine. The unpaired electron in the SOMO can be approximately represented in the 2p_x (C6), 2p_z 3p_z (C5, C1, C3) and the 3p_x (Cl) orbitals of structure 14. Description of the α electron in the SOMO of structure 15 can be approximated in the 2p_x, 2p_z (C1, C2, C3), 2p_z (C5) and 3p_x (Cl) orbitals. It is also evident that there exists π (in-phase) conjugation in the C₆H₆Cl[•] complex between the second highest and second lowest HOMO and LUMO orbitals (Figure 1.13) signifying an "allowed" interaction between the Cl[•] and the benzene moiety.



Figure 1.13. Depiction of the orbitals for the minimum complex 14 and transition state 15.

The other direct spectroscopic evidence of the C_6H_6/Cl° complex lies in the ESR data provided by Sergeev *et al.*⁵⁴ In this case a structure strongly resembling the minimum identified as **14**, was postulated by Sergeev *et al.*⁵⁴ A good test to whether this complex does indeed satisfy experimental observations, would be to calculate the ESR spectrum directly. Unfortunately, this was not possible using Gaussian 94/98^{129,130} as the methodology for calculating the ESR as not yet been parameterised for chlorine.

The results presented in this chapter demonstrate the variation between different levels of theory. While hybrid functionals are the most popular it is evident that the variation in definition of functionals can lead to dramatic differences in the calculated energies for difficult systems such as the C_6H_6/Cl° complex. The B3LYP method with a modest basis set provides a description of the C_6H_6/Cl° system consistent with available experimental data^{43,88,} and is typically known from the literature to give reliable geometries.^{83,131,} As a result, it appears that this will be an appropriate and cost-effective method for looking at a wider subset of substituted aromatic/halogen complexes.

The controversy regarding whether the abstracting species in radical chlorinations is either a π - or σ -complex additionally appears to be resolved. For all density functional methods, the σ - π -hybrid structure is the minimum energy on the potential surface. Additionally, this structure appears to best account for all of the experimental data, not only in terms of energy, but also in terms of the ESR⁵⁴ and UV-visible data.¹³⁵

The Study of the Non-bonding Interactions between Benzene and other Radicals

In the previous chapter non-bonding interactions between chlorine radical and benzene were examined. The results indicated that these interactions afford a complex that is more stable than the individual species at infinite separation, consistent with experimental observations. It is therefore likely that non-bonding interactions can also exist between other radical-aromatic species. The degree of complexation of such radicals it not only of synthetic interest, but also has important implications for the reactions of radicals within biological and atmospheric processes. As identified in Chapter One, the B3LYP/6-31G(d) level of theory appears to provide a reasonable description of aromatic-radical interaction, whilst being sufficiently economic for calculating the properties of these complexes.

F', Br' and I' radicals have been selected to give an overview of the halogen series and thus afford parameters for a wide range of radical selectivity. The 'OH radical is extremely important in atmospheric chemistry^{6,84,89,90,93,96,98,100,102,149} and in oxidative systems, especially as a by-product of superoxide generation.^{108,150} The 'CH₃ radical acts as a model for the general class of carbon-based radical, some of which are generated as biological intermediates, such as in the reactions of RNR.¹⁵¹ Moreover, alkyl radicals ('CH₃) are important intermediates in many reactions including hydrogen abstraction.

Results

Standard DFT calculations were performed with the 6-31G(d) basis set using the methodologies established in Chapter One. Potential energy surface scans were performed at the B3LYP/6-31G(d) level of theory, as a function of radical-benzene distance. For calculation of the iodine radical, the Los Alamos effective core potentials (ECP), denoted as LanL2MB/DZ, were used.¹⁵²⁻¹⁵⁴ Vibrational frequency calculations were performed, where specified, on the optimised geometries that were of the lowest energies on the potential curve in order to analyse the nature of the complexes. The

frequencies thus obtained were used to calculate the zero-point vibrational energy (ZPE) correction. The ZPE correction was applied with the appropriate scaling factors to the energy of each species.^{58,81} All calculations were examined for the effects of spin contamination. Wavefunction stability calculations were performed on all minima.

Complexation enthalpies of formation (ΔH°) of C₆H₆X[•] were calculated based on the reaction (Scheme 2.1) shown below:



Figure 2.1. Reversible complexation of the radical, X, to benzene.

The calculated relative energies and radical-benzene bond lengths are summarised in Table 2.1. The location of the unpaired α electron in the singly-occupied molecular orbital (SOMO) for each species is graphically represented in Figure 2.2. Areas of positive electron density are summarised in Table 2.2.

6-31 G(d)		AH ^o (kI mol ⁻¹)		dC-X/Å	
X	B3LYP	B3PW91	BH&HLYP	B3LYP	B3PW91	BH&HLYP
16a F m	-51.45(1)	-64.55(1)	-100.18(1)	2.1	2.1	2.1
ZPE	0.100997	0.101208	0.104788	(77873)		
19a F σ	-133.3(0)	-155.2(0)	-197.5(0)	1.4	1.4	1.4
ZPE	0.101754	0.102004	0.105394			
16b Br η_1	-32.75(0)	-53.73(0)	-108.59(0)	2.7	2.6	2.7
ZPE	0.101199	0.101404	0.104849			
17b Br η ₂	-31.52(1)	-51.68(1)	-106.83(1)	2.9	2.8	2.9
ZPE	0.101104	0.101322	0.104783			
	h	r.		2.2		
18b Br η_6	$4.30(0)^{b}$	$-26.14(1)^{o}$	-91.74(2)	3.3	3.3	3.3
ZPE	0.103955	0.098615	0.104559			
16.1	14.09(0)	14.17(0)	8.01(0)	2.2	2.0	2.2
16C I η_1	-14.08(0)	-14.1/(0)	-8.21(0)	3.2	3.0	5.5
ZPE	0.101705	0.10221	0.103483			
17c I m	-13.66(1)	-13.67(1)	-7.96(1)	33	3.2	34
	0.101614	0.102114	0 105419	5.5	5.2	5.1
	0.101011	0.102111	0.105 115			
18c I n6	-2.37(2)	-1.70(2)	-0.48 ^c	4.1	4.1	4.1 ^c
ZPE	0.101347	0.101851				
19d OH σ anti	-42.30 (0)	-87.30(0)	$-136.09(0)^{a}$	1.4	1.4	1.4
ZPE	0.113992	0.114359	0.118155			
19d OH	-30.89(0)	-75.45(0)	$-125.57(0)^{a}$	14	14	14
σ eclipse	50.05(0)	(0)	120.07(0)	A.C. 1		***
ZPE	0.113344	0.113696	0.117554			
10.011	20.05(0)	50 1 ((0)	102.02/024	1.5	1.5	1.5
THE CH ₃ O	-29.95(0)	-39.10(0)	-123.93(0)"	1.5	1.5	1.5
ZFE	0.13/301	0.15/04/	0.142248			

Table 2.1. Calculated complexation enthalpies and C-X distances for C_6H_6X complexes. The numbers of imaginary frequencies are in parenthesis. All energies have been scaled.[†]

ZPE's in units of Hartree/Particle. ^aSpin contaminated. ^bWavefunction instability. ^cObtained from a single point energy calculation.

[†] DFT Scale Factors at the 6-31 G(d) basis set.^{58,81}

 $B_{3LYP} = 0.9084, B_{3PW91} = 0.9772, BH&HLYP = 0.99.$





Calculated at the B3LYP/6-31G(d) level in Spartan '03.¹³² No successful calculation for the η^6 I complex was obtained.

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	B3LYP	B3PW91	BH&HLYP		B3LYP	B3PW91	BH&HLYP
19a				16c			
<i>ipso</i> H	4%	4%	2%	Ipso C	5%	3%	2%
ortho	49%	52%	52%	Ortho	4%	8%	3%
para	43%	40%	44%	Para	7%	6%	3%
F	5%	4%	2%	Ι	84%	83%	92%
17a				17c			
ipso C's	41%	42%	40%	ipso C's	10%	12%	6%
para C's	55%	53%	58%	para C's	6%	4%	2%
F	4%	5%	2%	Ī	84%	84%	92%
				18c			
16b				Ring C's	0.6%	0.6%	- (
ipso	4%	3%	1%	Ĩ	99.4%	99.4%	<u>05</u>
ortho	10%	12%	14%				
para	14%	15%	6%	19d			
Br	72%	70%	79%	<i>ipso</i> H	4%	6%	5%
				Ortho	40%	36%	41%
17b				Para	55%	55%	51%
ipso C's	14%	15%	11%	0	1%	3%	3%
para C's	12%	12%	8%				
Br	74%	73%	81%	19e			
				<i>ipso</i> H	5%	4%	5%
18b				Ortho	40%	45%	44%
Ring C's	3%	12%	6%	Para	51%	47%	47%
Br	97%	88%	94%	Methyl C	4%	4%	4%

Table 2.2. Spin Densities for C₆H₆X' complexes.

Time-dependant DFT CIS calculations were performed using the three DFT methods (B3LYP, B3PW91 and BH&HLYP) with the 6-31G(d) basis set. UV-visible spectra were calculated at the B3LYP/6-31G(d) level of theory using Spartan 2003^{132} software. Graphical representations of the UV-visible spectra are shown in Appendix 2. UV-visible absorptions for non-minima (where the number of imaginary frequencies >1) are shown for comparison only. UV-visible data for all stable minimum complexes was calculated using TD-DFT (B3LYP, B3PW91 and BH&HLYP) with the 6-31G(d) basis set and is shown in Table 2.3.

	19	a		1	6b
	$\lambda_{max} nm$	f		$\lambda_{max} nm$	f
B3LYP	445.5	0.0027	B3LYP	616.69	0.0015
	300.7	0.0629		448.13	0.1730
	289.3	0.0066		268.85	0.0616
B3PW91	439.7	0.0025	B3PW91	605.04	0.0015
	297.9	0.0628		448.19	0.1734
	289.8	0.0065		269.17	0.0658
BH&HLYP	380.9	0.0029	BH&HLYP	436.47	0.1679
	275.0	0.0042		348.83	0.0922
	267.9	0.0739		259.04	0.0431
	1	9d			
	λ_{max} nm	f		λ _{max} nm	f
B3LYP	557.16	0.1824	B3LYP	436.2	0.0011
	326.00	0.0088		337.6	0.0063
	275.21	0.0427		300	0.0598
B3PW91	556.30	0.1846	B3PW91	432	0.0010
	331.41	0.0093		335.1	0.0059
	274.04	0.0415		297.4	0.0580
BH&HLYP	476.34	0.1415	BH&HLYP	377.4	0.0013
	393.12	0.0465		278	0.0047
	260.37	0.0120		275.7	0.0617
	19	e			
	λ_{max} nm	f			
B3LYP	243.21	0.0009			
	239.02	0.1071			
B3PW91	242.43	0.0008			
	235.20	0.1081			

Table 2.3. TD-DFT data calculated at 6-31G(d) for minimum energy geometries.

Specific data on individual complexes are presented in Tables 2.4-2.8 and Figures 2.3-2.7.

Fluorine atom-Benzene Complex

Of all the model complexes (I-IV) in Figure 2.1, only the σ geometry produced a stable minimum at 1.4Å on the potential surface scan (seen in Chart 2.1, Appendix 2). When the η_1 , η_2 and η_6 starting geometries were fully optimised, the same stationary point, **17a**, was obtained. Structure **19a** was obtained on fully constraining the geometry.



Figure 2.3. The optimised C_6H_6F complexes.

Structures 17a and 19a were calculated as a transition state and stable minimum, respectively. The benzene ring remains planar. However, some distortion was observed within the carbon-carbon bonds (seen in Table 2.3) compared to the typical C-C bond length in benzene (d = 1.40Å).

Table 2.4. Optimised geometries of structures 19a and 17a.

19a	C_3-C_2	C_2-C_1	C_1-C_6	C ₆ -F	H_1-C_6	al	a2
B3LYP	1.41	1.36	1.49	1.42	1.1	129	126
B3PW91	1.41	1.36	1.48	1.41	1.1	130	125
BH&HLYP	1.41	1.35	1.48	1.4	1.09	130	125
17a	C_4-C_3	C_3-C_2	C_2-C_1	C ₁ -F	H_2-C_1		
B3LYP	1.39	1.40	1.40	2.1	1.08		
B3PW91	1.39	1.40	1.40	2.0	1.08		
BH&HLYP	1.38	1.39	1.39	2.3	1.07		

Angles are expressed in degrees. Bond lengths are in Angstroms.

The wavefunctions were calculated to be stable with the specified DFT methodologies for both structures **17a** and **19a**. Significant spin contamination in **19a** was not observed $<S^2 = 0.79>$ when optimised with the B3LYP or B3PW91 methods. However, a total spin of $<S^2 = 0.86>$ was calculated with the BH&HLYP method, indicating that these results are heavily spin contaminated. No spin contamination was observed $<S^2 = 0.75>$ in **17a** for

any of the DFT methods. The dipole moments for **17a** and **19a** were determined 2.5 and 1.95 Debye, respectively.

Bromine atom-Benzene Complex

The potential surface scan for the η_1 , η_2 and σ geometries (Figure 2.1) produced minima at 2.9Å. The η_6 geometry produced a minimum at 3.3Å (Charts 2.3-5, Appendix 2). When the η_1 , η_2 and σ starting geometries were fully optimised a stationary point **16b** and transition state **17b** were obtained (Figure 2.2). Constrained optimisation of the η_6 geometry afforded structure **18b** when calculated with the three DFT methods (Figure 2.3). Vibrational frequency analyses for **18b** revealed a stable minimum, a transition state and a higher order saddle point for the B3LYP, B3PW91 and BH&HLYP methods, respectively.



Figure 2.4. C₆H₆Br complexes.

Structures **16b** and **17b** are both calculated to have stable wavefunctions when calculated with the three DFT methods. However, the wavefunction for **18b** is calculated to be unstable when calculated with the three of the DFT methods. The benzene ring remains planar within the optimised geometries, showing a negligible difference from the typical C-C bond lengths in benzene (d = 1.40Å). Spin contamination was not observed $\langle S^2 =$

0.75> in the optimised structures using any of the DFT methods. The dipole moments of structures **16b**, **17b** and **18b** were calculated at 3.3, 3.08 and 0.5 Debye, respectively.

16b	C_3-C_4	C_4-C_5	C_5-C_6	C ₆ -Br	H_1-C_6	a1	a2
B3LYP	1.39	1.38	1.40	2.7	1.08	104	173
B3PW91	1.40	1.38	1.40	2.6	1.08	105	172
BH&HLYP	1.39	1.37	1.39	2.7	1.07	104	172
17b	C_4-C_3	C_3-C_2	C_2-C_1	C ₁ -Br	H_2-C_1	al	
B3LYP	1.39	1.39	1.40	2.9	1.08	102	
B3PW91	1.38	1.39	1.40	2.8	1.08	95	
BH&HLYP	1.38	1.38	1.39	2.9	1.07	102	
18b	C_5-C_6	C_6-C_1	C_1-C_2	C-Br	H-C		
B3LYP	1.39	1.39	1.39	3.5	1.08		
B3PW91	1.39	1.39	1.39	3.3	1.08		
BH&HLYP	1.38	1.38	1.38	3.4	1.07		

Table 2.5. Optimised geometries of structures 16b-18b.

Angles are expressed in degrees. Bond lengths are in Angstroms.

Iodine atom-Benzene Complex

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The potential surface scan for the η_1 , η_2 and σ geometries produced minima at 3Å. The η_6 geometry produced a minimum at 3.7Å (Charts 2.6-8, Appendix 2). Structures **16c** and **17c** were calculated to be a stable minimum and transition state, respectively when optimised with the three DFT methods (Figure 2.3). Constrained optimisation of the η_6 geometry produced a higher order saddle point **18c** (in Figure 2.3) when calculated with the B3LYP and B3PW91 methods. No optimised geometry was obtained for structure **18c** when calculated with the BH&HLYP method. A single point BH&HLYP/6-31 G(d) energy calculation was therefore performed on a B3LYP/6-31 G(d) optimised geometry **18c**.



Figure 2.5. C₆H₆I' complexes.

Structures **16c** and **17c** were found to have stable wavefunctions. The wavefunction for structure **18c** was unstable. Spin contamination was not observed, with $\langle S^2 = 0.75 \rangle$ in structures **16c-18c**. The dipole moments of structures **16c**, **17c** and **18c** are calculated at 2.7, 2.3 and 2.5 Debye, respectively.

Table 2.6. Optimised geometries of structures 16c-18c.

16c	C_2-C_3	C_2-C_1	C_1-C_6	C ₆ -I	H_1-C_6	A1	a2
B3LYP	1.40	1.40	1.41	3.2	1.088	104	177
B3PW91	1.40	1.40	1.41	3.1	1.085	103	176
BH&HLYP	1.39	1.40	1.40	3.3	1.076	101	178
17c	C_4-C_3	C_3-C_2	C_2-C_1	C ₁ -I	H_2-C_1	A1	
B3LYP	1.41	1.41	1.40	3.3	1.085	110	
B3PW91	1.40	1.14	1.40	3.2	1.085	109	
BH&HLYP	1.40	1.40	1.40	3.4	1.083	108	
18c	C_5-C_6	C_6-C_1	C_1-C_2	C-I	H-C		
B3LYP	1.40	1.40	1.40	4.3	1.086		
B3PW91	1.40	1.40	1.40	4.3	1.085		
BH&HLYP			-	-			

Angles are expressed in degrees. Bond lengths are in Angstroms.

Hydroxy radical-Benzene Complex

Full optimisation of the η_1 , η_2 and η_6 starting geometries (Figure 2.1) resulted in the same minimum energy geometry, **19d**. The σ geometry produced a stable minimum at 1.45Å on the potential surface scan. (Chart 2.8, Appendix 2). The eclipse conformer, **19d**, is shown. The 'anti'-structure of **19d** was also optimised by rotation of the OH group and was included in order to establish whether the eclipsed structure of **19d** was the minimum energy rotomer, Table 2.1, page 75).



Both structures calculated with the three DFT methods were found to be stable minima with no imaginary frequencies. The benzene ring remains planar but distortion was observed within the carbon-carbon bonds, compared to the typical C-C bond length in benzene (d = 1.40Å) when optimised using the specified DFT methods. (Table 2.6)

Table 2.16. Optimised geometries of the eclipse and anti conformers of structure 19d.

Method	C_3-C_2	C_2-C_1	C_1-C_6	C_6-O	H_1-C_6	H ₇ -O	al	a2
B3LYP	1.42	1.34	1.45	1.45	1.1	0.96	105	125
B3PW91	1.42	1.33	1.44	1.45	1.1	0.96	106	125
BH&HLYP	1.42	1.32	1.44	1.43	1.1	1.95	106	125

Angles are expressed in degrees. Bond lengths are in Angstroms.

The wavefunctions for both the conformers of **19d** were calculated as stable using the specified DFT methodologies. Significant spin contamination was not observed with B3LYP or B3PW91, where $\langle S^2 = 0.79 \rangle$. However, the BH&HLYP results show a total spin of $\langle S^2 = 0.85 \rangle$ indicating that these results are spin contaminated. The dipole

moments of the eclipse-conformer and the anti-conformer are calculated as 1.56 and 1.63 Debye, respectively.

Methyl radical-Benzene Complex

Full optimisation of the η_1 , η_2 and η_6 starting geometries (Figure 2.1) resulted in the same minimum energy geometry, **19e**. The σ geometry produced a stable minimum at 1.5Å on the potential surface scan (Chart 2.9, Appendix 2).



19e anti-conformer **Figure 2.16.** The C₆H₆CH₃ complex **19e**.

All three DFT methods afforded structure **19e** to be a stable minimum with no imaginary frequencies. The benzene ring remains planar. A slight distortion in bond length is observed within the carbon-carbon bonds, compared to the typical C-C bond length in benzene (d = 1.40Å), when optimised using the specified DFT methods.

Table 2.17. Optimised geometries for 19d anti-conformer.

Method	C_3-C_2	C_2-C_1	C_1-C_6	C_6-C_7	H_1-C_6	a1	a2
B3LYP	1.41	1.36	1.50	1.55	1.1	129	125
B3PW91	1.41	1.36	1.50	1.54	1.1	129	125
BH&HLYP	1.40	1.35	1.49	1.53	1.1	129	125

Angles are expressed in degrees. Bond lengths are in Angstroms.

The wavefunction was calculated to be stable when using each the of the DFT methodologies. Significant spin contamination was not observed with $\langle S^2 = 0.79 \rangle$ when using the B3LYP and B3PW91 methods. However, a total spin of $\langle S^2 = 0.85 \rangle$ was calculated using BH&HLYP, indicating that these results were spin contaminated. The dipole moment of **19e** was calculated to be 0.32 Debye.

Discussion

After chlorine, the most used free-radical halogenations are probably those that incorporate bromine. The Br' atom is considerably less reactive and more selective in hydrogen abstraction reactions than the Cl'. The relative reactivities of tertiary, secondary and primary hydrogens toward Br' are 25000:7100:1 (27°C),¹⁵⁵ compared to 4.2:3.5:1.0 for Cl'(25°C). Because of this, the selectivities observed in free radical bromination reactions are generally independent of solvent, unlike chlorination reactions. Yet, the reactivities of bromine atoms in hydrogen abstraction reactions have been shown to decrease slightly in benzene and carbon disulfide solvents.^{155,156} It has been shown that aromatics act as regulators of bromine atom reactivity by controlling bromine atom concentration by complexation.¹⁵⁶ The C₆H₆Br' species has been characterised spectroscopically,^{48,155} and the evidence that this complex is present in solution suggests that it either has the same selectivity as the free Br', or that the complex is either sufficiently unreactive, or present in low concentrations, that it does not adequately influence the selectivity.¹⁵⁵

It can be seen from the results reproduced in Table 2.12 that the η_1 and η_2 complexes **16b** and **17b**, have comparable stability to that calculated for the C₆H₆Cl[•] complex **5**. These complexes are also significantly more stable at all levels of theory, than either the corresponding η_6 complex **18b** or σ complex. The single negative frequency of the structure **17b** indicates that this complex is a transition structure, and the vibrations are consistent with an intermediate between η_1 complexes.

$\Delta H^{\circ}_{298}/\text{kJ mol}^{-1}$	B3LYP	B3PW91	BH&HLYP
16b Br η_1	-32.75(0)	-53.73(0)	-108.59(0)
17b Br η_2	-31.52(1)	-51.68(1)	-106.83(1)
18b Br 76	4.30(0)	-26.14(1)	-91.74(2)
σ Br (not shown)	10.6	N/A	N/A

Table 2.12. Energy calculations for the Ar-Br' complexes from this work.

Inspection of Table 2.1 shows the calculated C-Br (16b) and Br above-bond (17b) distances to be approximately 2.7 and 2.9Å, for the minimum and transition state geometries, respectively. Identical observations were reported by Tsao *et al.*⁸² for the η_1

and η_2 geometries. The calculations performed by Tsao *et al.*⁸² employed the use of the BH&HLYP and B3LYP methods using the large 6-311++G(d,p) basis set. In this case, lower complexation energies were reported (-16.7 and -15.4 kJ mol⁻¹ for the Ar-Br' η_1 and η_2 geometry, respectively) than those achieved from this work from the 6-31G(d) basis set suggesting that the smaller basis set may overestimate the stability of the complex.

The reasonable calculated stability of these complexes correlates well with the observation that these adducts exist in solution.^{48,135,147,155-159} The low enhancement of selectivity in free radical brominations carried out in aromatic solvent may be attributed to the complex having little relative impact on an already endothermic reaction, where differentiation between substrates in the abstraction is already significant. This contrasts with the exothermic chlorination reaction, where the differentiation between substrates is small, so a relatively small change to the abstracting complex will have a much larger relative impact on the outcome of the reaction.

The results obtained for the Ar-Br' complex are also reflected in those obtained for the Ar-I' complex with the most stable representation also the minimum η_1 type geometry **16c**. The η_2 geometry, in both cases **17b** and **17c**, represents the transition state of migration of the halogen between two corresponding η_1 complexes. The transition states **17b** and **17c** are only 1-2 kJ mol⁻¹ less stable than the minimum η_1 geometries, indicating that of inter-conversion for the η_1 Ar-I' structures is a facile process. This has also been noted by Tsao *et al.*⁸² and implies that the iodine atom is effectively delocalised across the aromatic ring.

The energies obtained for the Ar-I' complexes, presented in Table 2.1, are in reasonably good agreement with those reported in the literature. Tsao *et al.*⁸² reported complexation energy between -3.7 and -7.9 kJ mol⁻¹ for the minimum η_1 geometry iodine complex. The transition state η_2 geometry was calculated by Tsao *et al.*⁸² to have an energy of

-2.7–6.9 kJ mol⁻¹. These results support the observations made for the calculated η_1 and η_2 geometries from this work.

Detailed studies of the potential energy surface of the iodine-benzene charge transfer complex have recently been published.⁵¹ MP2 calculations have suggested that the above-bond **17c** and the above-carbon **16c** conformations represent the most stable geometries of the iodine-benzene charge-transfer complex.⁵¹ Jarzeba *et al.*⁸⁷ have suggested that the above-bond geometry, described by their calculations for the Ar-Cl[•] complex, may also be applied to other Ar-halogen complexes, including the Ar-Br complex. Both of the above postulations from Jarzeba *et al.*⁸⁷ and Grozema *et al.*⁵¹ regarding the postulated structures for the Ar-I[•] and Ar-Br[•] complexes correlate with findings from this work.

The formation of benzene-halogen complexes (Ar-X₂) has been widely studied in the literature because of the charge transfer properties associated with these complexes.^{48,51,82,87,135,145,147,156,158,159,160-162} The solid state structures of Cl₂/C₆H₆, I₂/C₆H₆ and Br₂/C₆H₆ have a hexahapto, η_6 , geometry by X-ray analysis.^{49,50} On the basis of this spectroscopic analogy, it has been proposed that the halogen atoms typically form π structures of the same, η_6 geometry.¹³⁵

Consideration of the possible η_6 halogen complexes **18a**, **18b** and **18c**, shows that only the Br and I complexes **18b** and **18c**, respectively, had minima with an η_6 geometry. The Br ring distance was calculated to be ≈ 3.5 Å, and the calculated binding energy was around 30 kJ mol⁻¹ less than the corresponding η_1 and η_2 complexes **16b** and **17b**, respectively, with the B3LYP and B3PW91 functionals. This indicates a relatively weak interaction, and that these species should not be present in significant quantities in experimental systems. The calculated η_6 structures are consistent with the reported experimental data^{49,50,135} and the data recently published by Tsao *et al.*⁸² However, given the extremely low barrier to complex interconversion for the η_1 and η_2 complexes, and the subsequent apparent delocalisation of the halogen, the averaged structure that would result would be consistent with an observed η_6 complex. The B3LYP and B3PW91 stability calculations detected an internal instability within the wavefunction for the η_6 complex. This implies that the wavefunction does not correspond to the ground state η_6 complex. In the GAUSSIAN programme, re-running the stability calculation specifying the keywords stable = opt allows the SCF solution to be tested and the wavefunction to be re-optimised in order to find a lower energy solution, should any instability be found. In addition, the keywords guess = mix, were included. These keywords, allow the program to mix the HOMO and LUMO within the wavefunction in an effort to destroy α - β and spatial symmetries.⁵⁸ The re-calculated B3LYP energy for **18b** is of slightly lower energy (4.09 kJ mol⁻¹) than the previous calculation (Table 2.1) and the wavefunction was found to be stable, however, the positive sign indicates that, at the B3LYP level, this is not a stable complex.

The results obtained for the η_6 geometry from this work show similarities with those obtained by Tsao *et al.*⁸² It was reported by Tsao *et al.*⁸² that calculations performed at B3LYP and BH&HLYP, using both the 6-31 G(d) and 6-311++G(d,p) basis sets afforded a Br-ring distance between 3.8 and 4.2Å. However, the B3LYP calculations performed by Tsao *et al.*⁸² afforded an internal stability in the wavefunction for this geometry. Their BH&HLYP calculations, on the other hand, predicted two imaginary frequencies. The DFT calculated complexation energy for the η_6 geometry was predicted by Tsao *et al.*⁸² to be approximately -4.1 kJ mol⁻¹. The differences between the calculated energies from this work and those presented by Tsao *et al.*⁸² can be attributed to the larger basis set, 6-31++G(d,p), used by Tsao *et al.*⁸²

Analogous with the Ar-Br' η_6 geometry, the Ar-I' η_6 optimised structure **18c** was found to show a weak interaction where the I'-ring distance was calculated at 4.1Å. All three of the DFT methods predicted that this was a higher order saddle point, with two negative frequencies. The complexation energy from this work was calculated between -0.5 and -2.4 kJ mol⁻¹. Similarly, Tsao *et al.*⁸² reported that the complexation energy of the Ar-I' η_6 geometry was -3.3 kJ mol⁻¹ at the BH&HLYP/SDD level of theory. They found that two degenerate imaginary frequencies were predicted from vibrational frequency analysis. Initial wavefunction stability calculations in this work for structure **18c** detected an internal instability. However, this was subsequently corrected by re-running the calculation using the keywords previously mentioned for the stability calculations for structure **18b**. Conversely, Tsao *et al.*⁸² reported no evidence of wavefunction instability. This difference may be attributable to the use of different basis sets adopted for the calculation of the iodine atom. In this work the LanL2DZ basis set was used, where Tsao *et al.*⁸² used the effective core potentials basis set by Stuttgart and Dredsen, (SDD),^{163,164} The SDD basis set is more recent and this may explain why Tsao *et al.*⁸² did not experience the wavefunction instability observed when LanL2DZ is used instead.

The calculated potential energy scan for **18c** (Chart 2.7, Appendix 2) is very flat, which can often cause problems with optimisation of structures. The same observation was made by Tsao *et al.*⁸² In contrast to the calculations presented here, Tsao *et al.*⁸² do not report that there was any evidence of spin contamination of the structures obtained with the BH&HLYP functional.

The calculations by Tsao *et al.*⁸² were performed at the BH&HLYP and B3LYP methods using the 6-311++G(d,p) basis set. Given that Tsao *et al.*⁸² have used this much larger basis set in their calculations than the ones presented in this work, and applied a different basis set, SDD, to the iodine atom, the deviations from the calculated energies of ca. $5 - 7 \text{ kJ mol}^{-1}$ illustrate that the much more economical B3LYP/6-31 G(d) method performs remarkably well.

On constraining the Ar-Br' σ geometry, an energy of $\Delta H^{\circ} = 10.6$ kJ mol⁻¹ was obtained for a stable minimum with a stable wavefunction using the B3LYP/6-31 G(d) basis set. No such structure was found upon using the B3PW91 and BH&HLYP methods. The positive enthalpy indicates that this complex will not form under standard conditions. Accordingly, Tsao *et al.*⁸² do not acknowledge a σ geometry for the Br' complex at any level of theory. The energy predicted indicates that a σ complex for the bromine atom is not likely to form. Indeed, this is confirmed by experimental and theoretical data presented by Berho *et al.*⁸³ in the study of stabilities of a series of cyclohexadienyl type structures. These observations would appear to reinforce the predicted preferred formation of η_1 and η_2 geometries for the Ar-Halogen complexes, rather than formation of a σ complex.

 π -Complex charge transfer structures have been proposed to exist as the precursors to electrophilic aromatic substitution.^{147,148,159,165,166} These complexes are transiently observed as critical intermediates in electrophilic aromatic bromination and nitration with dibromine (Br₂) and the nitronium cation (NO⁺), respectively. UV-visible spectra and X-ray crystallographic analyses of these transients reveal a highly-structured π character where the acceptor is located either above the centre or above a carbon atom within the aromatic ring.¹⁴⁷ It was further proposed that the π complexes are converted in a rate limiting transformation to the σ adduct.¹⁴⁷ However, it is worth noting that the highly unstable σ adduct is unlikely to be isolated owing to its facile proton loss. Indeed, one key question that comes to light is why the low energy π complex, X₂/arene, can take on a structure so close to the high-energy σ adduct structure.¹⁴⁷

In contrast to the situation for the Br and I' radical complexes, the results in Table 2.1 for the complexes of F', 'OH and 'CH₃ radicals predict the formation of a σ cyclohexadienyl structure. Due to the unstable nature of σ cyclohexadienyl radicals, few experimental data are available.^{83,109,110,167} The C-X' bond lengths are predicted as forming between 1.4 and 1.5Å for the σ cyclohexadienyl type geometries of all these radicals, structures **19a**, **19d** and **19e**, respectively. Inspection of the structures shows that they are a true cyclohexadienyl structure due to the change in hybridisation of the *ipso* carbon from sp² to sp³. The differences between the optimised geometries for these radicals **19a**, **19d** and **19e** is negligible, irrespective of the nature of the X. The unpaired electron is delocalised over the five atoms of the benzene ring. It appears that, in the minimum energy calculated structures for adducts **19a**, **19d** and **19e**, unlike those of the C₆H₆Br[•] (structures **16b-18b**), C₆H₆Cl[•] (**2** and **3**) and C₆H₆I[•] structures (**16c-18c**) the spin density for the σ type geometries is almost all transferred (approximately 97%) to the benzene ring, suggesting that there is little interaction between the radical and the π electron system. The spin densities are tabulated in Table 2.2 and are graphically represented in Figure 2.2.

For the C₆H₆F σ type radical, the estimated experimental formation energies are exothermic and calculated to be -82.84 kJ mol⁻¹.⁸² The calculated DFT energies derived here and those presented by Berho *et al.*⁸³ and Tsao *et al.*⁸² overestimate this value significantly, as seen in Table 2.13. However, the C₆H₆F[•] energies calculated from this work at the 6-31 G(d) basis set are in reasonable agreement with the other calculated energies obtained for this species within the literature.^{82,83} The calculated UV data for structure **19a** (Figure 2.7) shows intense absorption at 280-300nm. This absorption is typical of cyclohexadienyl type radicals.⁴²

Table 2.13. DFT predicted energies of the $C_6H_6F'\sigma$ -type radical.

$\Delta H^{\circ}_{298}/\text{kJ mol}^{-1}$								
Basis set	B3LYP	B3PW91	BH&HLYP					
6-31G(d)	-133	-155	-197	This work				
6-31G(d)	-150			Berho et al.83				
6-311++G(d,p)	-120-129	N/A	-130-138	Tsao et al ⁸²				

Given the improvement expected for these systems with larger basis sets, our lower-level models compare very well with the experimental value. The BAC-MP4 level of theory has also been used predicts the fluorocyclohexadienyl radical stabilisation to be - 138.9 kJ mol^{-1.83} The larger and more diffuse basis set 6-311++G(d,p) consumes more resources than the average size 6-31 G(d) basis set, for what appears to be very little improvement relative to the experimental value of -82.8 kJ mol⁻¹. However, comparisons of the energies obtained with the BH&HLYP method from this work (-197 kJ mol⁻¹) and those obtained by Tsao *et al.*⁸² (-120-129 kJ mol⁻¹) shows that a larger basis set does afford an improvement using this method. The use of coupled cluster methods, inclusive of triple terms (CCSD(T)) has been shown to give energies that are in much better agreement (-100 kJ mol⁻¹) with the estimated experimental value (-82 kJ mol⁻¹).⁸²

A higher-energy Ar-F[•] η_2 geometry was also obtained, with one imaginary frequency, indicating a transition state structure. An identical structure was obtained by Tsao *et al.*⁸²

whose energy for which was calculated between -80 and -100 kJ mol⁻¹. By following the normal mode corresponding to the imaginary frequency of the η_2 geometry, the σ structure is obtained. This indicates that the transition state allows for the fluorine atom to migrate around the periphery of the ring. The energy difference between the σ and the η_2 geometries is approximately 80 kJ mol⁻¹ and this corresponds to the barrier height for this process, which is much higher than for the other halogens.⁸² This is consistent with the σ -bond in the structure of the C₆H₆F[•] complex being more difficult to break than the non-covalent interactions of the other halogens with benzene.

Optimisation of a fully constrained η_6 geometry resulted in the geometry of the σ type structure. This differs to the report by Tsao *et al.*,⁸² whose optimisation of the η_6 geometry resulted in a higher order saddle point when calculated with the BH&HLYP level of theory but a minimum with the B3LYP method. However, Tsao *et al.*⁸² reported an internal instability within the wavefunctions using either DFT method. This indicates that the structure is more likely to be an electronic excited state. The calculated energy of formation at either DFT method was reported to be very small (*ca.* 5 kJ mol⁻¹),⁸² which would suggest that the η_6 structure is unlikely to form under standard conditions.

Evidence from ESR spectroscopy indicates that the assignment of a σ -based geometry is reasonable and further supports the assertion that the η_6 -geometry is not present in experimental systems to a significant degree. ESR of the C₆H₆F[•] radical within an argon matrix at 4K illustrated that the unpaired electron was delocalised within aromatic species, corresponding to a σ complex.⁹² A subsequent report⁵³ details the use of microwave discharge to give new infrared signals that identify the trapping of the C₆H₆F[•] radical in solid argon at 14K. The prominent 599cm⁻¹ absorption of the unsubstituted reaction product indicates that the F atom is localised to a single carbon atom. It was reported that no absorption for the C-F stretch was observed, however a weak coupling of the C-F stretching vibration in the 1000-1200cm⁻¹ spectral region was detected.⁵³ These observations are consistent with a weak C-F interaction. It was thus proposed that the C-F bond is perpendicular to that of the benzene ring in the C₆H₆F[•] complex.⁵³ The calculated IR spectra for the σ complex **19a** (Figure 2.12) and the η_2 geometry structure **17a** (Figure 2.13) can be compared with the experimental observations. Inspection of the calculated IR data (Figure 2.12) for structure **19a**, from this work, shows an intense absorption recorded at 1025 cm⁻¹, attributable to the C-F stretch. It can be seen from the calculated IR spectrum of **17a** that no absorption exists for the C-F stretch in the 1000-1500 cm⁻¹ region, thus correlating with the experimental spectra. Since the F[•] radical was proposed as being perpendicular to the benzene ring, this would suggest that the trapped complex is more likely to resemble the η_2 geometry of structure **17a** and does not resemble the σ complex **19a**.



Figure 2.12. Calculated B3LYP/6-31G(d) IR spectrum of the C₆H₆F' complex 19a.



Figure 2.13. Calculated B3LYP/6-31G(d) IR spectrum of the C_6H_6F complex 17a. The spectrum is shown for comparison, since the species 17a would not be spectroscopically observed under standard pressure and temperature.

The reactions of the hydroxyl radical with aromatic hydrocarbons are of fundamental interest as well as being of importance in biochemistry and atmospheric chemistry. For example, the oxidative degradation of tropospheric benzene is initiated almost exclusively by 'OH.¹⁰² Since benzene and several of its degradation products are carcinogenic, it is of particular importance that these reactions are well understood. The hydroxyl radical is implicated in DNA damage due to ionising radiation and such damage can lead to cell mutation and/or cell death.¹⁶⁸ OH is especially characterised as being electrophilic in its reaction with the bases of DNA, in particular the sugar moiety. However, other kinetic correlations with non-aromatic substrates suggest that 'OH may not always be electrophilic in its radical reactions.¹⁶⁸

The predicted energies of formation of the 'OHC₆H₆ complex are -30, -75 and -125 kJ mol⁻¹ using the B3LYP, B3PW91 and BH&HLYP methods, respectively, for the eclipse-conformer of **19d**. The anti isomer of **19d** gave corresponding values of -42, -87 and -136 kJ mol⁻¹, indicating that it is more stable. Early experimental evidence on the addition of 'OH to benzene, leading to the formation an adduct, or hydroxycylohexadienyl radical, has been well documented, ^{96,100,101,109,149,169,170} where heats of formation of the order -40 – -80 kJ mol⁻¹ have been obtained. ^{96,109,171} These are in good agreement with the calculated B3LYP and B3PW91 values from this work. The large energy obtained from calculation using the BH&HLYP method (Table 2.1) indicates the unsuitability of this method for the calculation of stabilisation energies, since these energies are not consistent within the range of the experimental values of -40 – -80 kJ mol⁻¹. ^{96,109,171} This value is lower than that for the highly electronegative fluorine radical, but still higher than for the corresponding halogen complexes, indicating a stronger complex, consistent with more σ -bonding character.

The reaction of 'OH with benzene is of particular importance because the atmospheric decomposition of benzene is primarily initiated through the addition of the 'OH radical to the aromatic ring.^{6,83,89,90,92-102} Due to the relative importance of this reaction, and the advances in computational chemistry, a number of theoretical studies have been conducted on the formation of this complex and its associated reaction pathways.⁹⁹ Berho *et al.*⁸³ estimated the enthalpy of formation for the hydroxycylcohexadienyl radical where values of -70.2 and -73.7 kJ mol⁻¹ were obtained using B3LYP/6-31G(d) and BAC-MP4 calculations, respectively. The DFT calculated energy reported by Berho *et al.*

*al.*⁸³ is markedly different from the B3LYP calculated energy obtained from this work. Berho *et al.*⁸³ do not mention the inclusion of ZPE corrections in their reported energies. The uncorrected energy B3LYP from this work (-67.9 kJ mol⁻¹) would appear to be in more consistent with the complexation energy of -70.2 kJ mol⁻¹ reported by Berho *et al.*⁸³ The zero-point energy is a correction to the electronic energy in order to account for the effects of molecular vibrations which persist even at 0K. The scaling factor is used to eliminate known systematic errors in calculated frequencies, thus the final predicted energy of a molecule must always include a scaled zero-point correction.⁵⁸

Recently, B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels of theory have been used to calculate molecular energy structures and vibrational energies of the hydroxycylcohexadienyl radical.^{102,171} The values for the enthalpy of formation obtained by Chen et al.^{102,171} were calculated between -41 and -45 kJ mol⁻¹, which is in fairly good agreement with the B3LYP values obtained from this work (Table 2.1) and with values obtained experimentally,¹⁰⁹ (-40 - -80 kJ mol⁻¹). From the energy of formation, the equilibrium constant for the reaction of 'OH with benzene is therefore estimated to be of the order 6.39×10^{-17} molecule s⁻¹, which indicates that the reaction is diffusion controlled. The structures obtained by Chen et al.^{102,171} have been used in energy calculations at higher levels of theory, including the complete basis set method (CBS) and G3 methodologies.

The dipole moments for the two different conformers, related to one another by internal rotation about the OH group, are shown in Table 2.14, along with the corresponding results obtained by Chen *et al.*^{102,171} The optimised geometry **19d** of the eclipse-conformer has a H_7 -O-C₆-H₁ torsion angle of 51°. The optimised structure of the anti-conformer of **19d** has a corresponding torsion angle of 180°.

Torsion	Dipole moment
H ₇ -O-C ₆ -H ₁	(Debye)
51.7°	1.54^{a}
51.7°	1.58^{b}
180°	1.65 ^a
178°	1.72^{b}

Table 2.14. Dipole moments of the eclipse- and anti-conformers at B3LYP/6-31G(d)

^{*a*}Chen *et al.* at B3LYP/6-31 G(d,p) level of theory. ^{*b*}This work at B3LYP/6-31 G(d) level of theory.



The larger dipole moment and increased stability observed in the anti-conformer is attributable to hyperconjugation of the lone pair of electrons on oxygen with the antibonding orbital of adjacent C-C bonds.¹⁷¹ The maximum value for the dipole also suggests that this conformer is withdrawing significantly more electrons from the benzene ring, relative to the eclipse-conformer.¹⁷¹ The lengths of the C₂-C₃ and C₃-C₅ bonds are slightly longer (1.42Å), and the C₁-C₆ C₆-C₅ bonds slightly shorter (1.38Å), than the C-C bond length in benzene in both conformers. This observation was also made by Chen *et al.*¹⁷¹ and is consistent with strong bonding of the electron-withdrawing OH moiety. This implies that this species is unlikely to rapidly react further without significant electronic reorganisation, and helps to explain why the hydroxyl radical is more prominent in its reaction directly with aromatic species than either chlorine, bromine or iodine. It also explains why little effect of different aromatic solvents is noted in the reactions of hydroxyl radical, as the contribution toward the abstraction process is likely to be insignificant, relative to free hydroxyl.

The methyl radical is of particular importance as a radical model, as carbon-based radicals appear in a number of different biological reactions, especially those initiated by coenzyme- B_{12} .^{172,173} The calculated complexation energies for structure **19e**, shown in Table 2.1 are quite low, relative to those noted for the other cyclohexadienyl-type species

19a and **19d**. These low values for the stabilisation energies obtained for structure **19e** with the B3LYP method correlate with the experimental observation that related complexes are highly unstable.¹⁷⁴ This is consistent with the very low rate constant of complex formation that has been measured within the range of 372-484K, indicating that the addition of the CH₃ radical to the benzene ring is inefficient.¹⁷⁴ The uncorrected B3LYP/6-31G(d) energy calculated from this work (-55.4 kJ mol⁻¹) compares with the stabilisation calculated by Berho *et al.*⁸³ of the methyl-benzene radical complex of - 41 kJ mol⁻¹ using the B3LYP/6-31G(d) and BAC-MP4 methods, and with that calculated at -68 kJ mol⁻¹ using the AM1 method. The differences in calculated energy from that presented in the literature, are probably attributable to the possible omission of ZPE corrections by Berho *et al.*⁸³

The BH&HLYP method does not seem to treat this radical appropriately since the value obtained from using this method shows an ambiguous increase relative to the proposed instability from such a species.^{83,174} The overestimation of the predicted energy is likely to be attributable to the spin contamination observed in the calculation using this method. Optimisation of the eclipse conformer did not afford a stable minimum of this geometry and the resultant structure was that of the anti-conformer.

The structure of the methylcyclohexadienyl radical **19e** is typical of a σ -type complex, despite the low stability of this complex. The C-C bonds *ipso* to the CH₃ are 1.5Å, the C-CH₃ bond length is 1.5Å and the angle of the hydrogen atom is 125°, which suggests that the substituted carbon atom is sp³ hybridised. As with the other σ -bonded cyclohexadienyl radicals (**19a** and both conformers of **19d**) the majority of the spin density is located on the benzene ring (Table 2.9 and Figure 2.6, **19e**). The calculated UV spectrum (Figure 2.11) shows maxima between 280 and 320nm, which correlate with the typical absorptions at 280-300nm, observed experimentally for cyclohexadienyl radicals.^{42,149}

As has been established, the electronic redistribution required to achieve a cyclohexadienyl-type structure implies there should be little contribution of the

complexed methyl species **19e** in the reactions of carbon-based radicals. As such, a significant aromatic solvent effect would not be expected in such reactions.

In conclusion, the most stable geometries to best represent the benzene-bromine and the benzene-iodine structures are the π -type radical complexes. The formation of "loose" complexes is favoured when the nucleophilicity of the incoming radical is low. Such behaviour is expected where radical species are able to stabilise the incipient negative charge in addition to ionising the aromatic species.^{96,100,168,169}

The results obtained for the calculation of the relative stabilities yields the following order of stability from the most stable to the least,

$$FC_6H_6 > HOC_6H_6 > BrC_6H_6 \approx CH_3C_6H_6 > IC_6H_6$$

Qualitatively, these results are in reasonable agreement with experimental data, where available. The 'BrC₆H₆, 'CH₃C₆H₆ and 'IC₆H₆ radical complexes are so unstable that they are unlikely to be observed in the laboratory since the corresponding Br', I' and 'CH₃ radicals cannot add efficiently to the benzene ring.^{110,167} The weak binding implies that the complexes may easily dissociate. For the 'CH₃ + C₆H₆ reaction, a very low rate constant has been estimated by Holt *et al.*¹⁷⁴ in the range of 372-484K, indicating that the addition channel is inefficient and thus the complex is unlikely to form readily.⁸³ The C₆H₆OH radical complex has been isolated and its equilibrium constant¹⁰⁹ and UV spectrum¹⁴⁹ have been measured. The FC₆H₆ radical has also been isolated, and its spectra experimentally recorded,^{53,92} however the predominant reaction path for C₆H₆ + 'F, is unclear as both addition and abstraction pathways have been suggested.^{53,83}

The interactions of fluorine, hydroxyl, and methyl radicals with benzene are all best represented, using B3LYP/6-31G(d), as the σ -type cyclohexadienyl type complexes as the most stable geometries. The way the energy calculation is handled between the DFT methods clearly shows how these methods may differ and reinforces the need to trial more than one functional for different systems when trying to obtain reliable energy

calculations. In general, the BH&HLYP functional appears to poorly describe these systems.

Each of the σ -complexes show a broad shoulder absorption in the calculated UV spectra around 280-300nm, which is characteristic of the experimental data obtained for cyclohexadienyl σ -type geometries.⁴² The optimised geometry for the σ radicals is more or less the same irrespective of the nature of the radical, suggesting that there is little interaction between the radical and the π electron system. From the calculated stability of these σ -type radicals it seems that electronic effects do not have an important role in controlling their stability. An exception to this is the C₆H₆OH[•] complex, due to the potential for hyperconjugation of the lone pair of electrons on oxygen with the π electrons on the aromatic ring. The larger dipole moment seen in the anti-conformer corresponds to this effect. Chen *at al.*¹⁷¹ have detailed the comparison of the HOMO's from the two conformers and showed that more electrons are in the ring HOMO for the anti- than the eclipse-conformer. This would further confirm the hyperconjugation between the lone pair of electrons of the aromatic system.

The stabilisation energies in Table 2.1 are in reasonably good agreement with the available experimental and theoretical results already present in the literature. Thus, it is reasonable that the use of such calculations can be extended to other aromatic-radical systems of interest, such as those contributing to atmospheric and enzyme chemistry.

Chapter 3

An investigation into the aromatic solvent effect on the reactions involving the chlorine radical

Russell illustrated that there is a clear kinetic correlation between the nature of the aromatic solvent in which the chlorination reaction of 2,3-DMB was carried out and the degree of tertiary *versus* primary hydrogen abstraction.²⁷ More particularly, the effect of the aromatic on the increased selectivity was reduced when electron withdrawing substituents were present and augmented for aromatics with electron donating substituents. The solvent effect is found to correlate with the basicity of the solvent.^{29,30} To examine the thermodynamic aspects of the solvent effect, a range of substituted aromatics have been chosen for this investigation (Figure 3.1).

Figure 3.1. Aromatic complexes of chlorine with various substituents X.

Five of the substituted aromatics chosen to be modelled with the chlorine radical, compounds **20-24**, were used in experimental studies by Russell²⁹ and Walling.³⁰ Bromobenzene **25** was chosen to compare with the other halobenzenes described in the literature, aniline **26** was chosen for investigation because of its basic properties, and phenol **27** was chosen as a simpler and less computationally demanding analogue of

anisole, but also it has implications for many environmental systems where phenolic compounds are produced through the natural degradation of lignin, despite the fact that it participates in free radical reactions itself.

Results

Standard DFT (B3LYP, B3PW91 and BH&HLYP) calculations were performed with the 6-31G(d) basis set using the methodologies established in Chapter One. Complexation enthalpies (ΔH°) for formation of C₆H₅XCl[•] were calculated based on the reaction in Scheme 3.1:

$$C_6H_5X + Cl' \longrightarrow C_6H_5XCl'$$

Scheme 3.1. Reversible complexation of the chlorine radical to a substituted aromatic.

Optimisation afforded the Cl[•] radical at the *ipso*, *ortho* and *para* positions of the aromatic ring, denoted by suffixes **a**, **b** and **c** to the compound number, respectively, with the *meta* position denoted by suffix **d**. The data from these calculations is summarised in Table 3.1. Spin densities for all structures were also calculated and are summarised in Table 3.2.



6-31G(d)		ΔH° (kI mol ⁻	1)		dC-X (Å)
x	B3LYP	B3PW91	BH&HLYP	B3LYP	B3PW91	BH&HLYP
20a CH ₃ ipso	-42.92 (0)	-48.65 (0)	-23.83(0)	2.65	2.67	2.63
ZPE	0.1290	0.1293	0.1336			
20b CH ₃ ortho	-50.38 (0)	-49.22 (0)	-31.17 (0)	2.54	2.54	2.51
ZPE	0.1290	0.1292	0.1336			
20c CH ₃ para	-48.67 (0)	-40.64 (0)	-29.24 (0)	2.56	2.57	2.55
ZPE	0.1289	0.1293	0.1334			
21b OCH3 ortho	-60.60 (0)	-58.48 (0)	-36.30(0)	2.60	2.51	2.54
ZPE	0.1345	0.1349	0.1395			
21c OCH ₃ para	-58.95 (0)	-57.42 (0)	-36.16 (0)	2.57	2.48	2.53
ZPE	0.1345	0.1348	0.1395			
22a NO ₂ ipso	-16.18 (1)	-13.49 (1)	-4.15 (1)	2.68	2.66	2.67
ZPE	0.1037	0.1040	0.1081			
22d NO ₂ meta	-30.59 (0)	-28.99 (0)	-14.60 (0)	2.54	2.50	2.50
ZPE	0.1039	0.1043	0.1083			
23b Fortho	-40.11 (0)	-39.88 (0)	-20.90 (0)	2.56	2.49	2.59
ZPE	0.0932	0.0934	0.0966			
23c F para	-45.72 (0)	-44.40 (0)	-25.85 (0)	2.56	2.48	2.58
ZPE	0.0933	0.0967	0.0935			
24b Cl ortho	-36.54 (0)	-35.94 (0)	-18.55 (0)	2.58	2.56	2.63
ZPE	0.0918	0.0919	0.0951			
24c Cl para	-41.51 (0)	-40.83 (0)	-22.13 (0)	2.58	2.47	2.59
ZPE	0.0918	0.0920	0.0951			
25b Br ortho	-37.19 (0)	-35.80 (0)	-18.94 (0)	2.58	2.59	2.62
ZPE	0.0914	0.0915	0.0947			
25c Br para	-41.19 (0)	-39.64 (0)	-22.42 (0)	2.55	2.52	2.53
ZPE	0.0914	0.0916	0.0947			
26a NH ₂ ipso	-65.98 (1)	-64.71 (1)	-40.47 (1)	2.77	2.71	2.70
ZPE	0.1181	0.1185	0.1222			
26b NH ₂ ortho	-76.32 (0)	-76.76 (0)	-50.22 (0)	2.57	2.47	2.47
ZPE	0.1186	0.1190	0.1229			
26c NH ₂ para	-71.3 (0)	-71.89 (0)	-46.22 (0)	2.56	2.48	2.5
ZPE	0.1183	0.1186	0.1226			
27b OH ortho	-63.17 (0)	-61.93(0)	-38.73 (0)	2.55	2.44	2.43
ZPE	0.1058	0.1061	0.1096	100 (100 MZ	1000 - 700-000-0	
27c OH para	-57.25 (0)	-55.91 (0)	-34.89	2.56	2.47	2.53
ZPE	0.1058	0.1061	0.1097			

Table 3.1. Calculated energies of formation of the $C_6H_5XCl^{\circ}$ complexes 20-27. The numbers of imaginary frequencies are in parenthesis. All energies have been scaled.^{\dagger}

⁺ DFT Scale Factors at the 6-31G(d) basis set. B3LYP = 0.9084, B3PW91 = 0.9772, BH&HLYP = 0.99.
	B3LYP	B3PW91	BH&HLYP		B3LYP	B3PW91	BH&HLYP
26a ipso				21c para			
Ipso	4%	4%	2%	Ipso	14%	17%	16%
Ortho	17%	19%	17%	Meta	14%	14%	15%
Meta	21%	21%	18%	Para	9%	7%	2%
Nitrogen	7%	6%	4%	Oxygen	6%	6%	4%
Chlorine	51%	50%	59%	Chlorine	59%	56%%	64%
26b ortho				27b ortho			
Ipso	16%	15%	18%	Ipso	13%	15%	17%
Ortho	13%	9%	8%	Ortho	13%	12%	7%
Meta	11%	20%	12%	Meta	11%	13%	10%
Nitrogen	10%	10%	8%	Oxygen	6%	6%	4%
Chlorine	50%	46%	54%	Chlorine	56%	54%	62%
26c para				27c para			
Ipso	15%	15%	15%	Ipso	14%	16%	19%
Ortho	10%	13%	10%	Meta	12%	15%	14%
Para	11%	11%	6%	Para	8%	8%	3%
Nitrogen	11%	10%	9%	Oxygen	5%	5%	3%
Chlorine	53%	51%	60%	Chlorine	58%	56%	61%
20a ipso	×			23b ortho			
Ipso	15%	18%	11%	Ipso	11%	14%	9%
Ortho	7%	1%	8%	Ortho	6%	4%	2%
Meta	17%	23%	15%	Meta	12%	19%	10%
Chlorine	61%	58%	66%	Bromine	5%	2%	4%
				Chlorine	66%	61%	75%
20b ortho				23c para			
Ipso	15%	18%	11%	Ipso	16%	19%	18%
Meta	7%	1%	8%	Meta	12%	14%	12%
Para	17%	23%	15%	Para	5%	3%	2%
Chlorine	61%	58%	66%	Bromine	4%	3%	1%
				Chlorine	64%	61%	67%
20c para				24b ortho			
Ipso	18%	20%	19%	Ipso	10%	16%	11%
Meta	13%	16%	17%	Ortho	11%	7%	10%
Para	7%	4%	4%	Meta	14%	14%	9%
Chlorine	62%	60%	60%	Chlorine	70%	61%	69%
				Ring Cl	2%	2%	1%
21b ortho				24c para			
Ipso	15%	18%	12%	Ipso	15%	19%	12%
Ortho	125	10%	4%	Meta	12%	15%	9%
Meta	15%	8%	13%	Para	15%	2%	10%
Oxygen	5%	5%	4%	Chlorine	56%	62%	68%
Chlorine	58%	59%	58%	Ring Cl	2%	2%	1%

Table 3.2. Spin densities from the optimised C₆H₅XCl[•]complexes.

25b ortho				22a ipso			
Ipso	10%	16%	11%	Ipso	9%	8%	3%
Ortho	11%	7%	10%	Ortho	6%	6%	2%
Meta	14%	14%	9%	Para	8%	10%	3%
Chlorine	70%	61%	69%	Chlorine	77%	76%	92%
Ring Cl	2%	2%	1%				
25c para				22d meta			
Ipso	15%	19%	12%	Ortho	13%	16%	13%
Meta	12%	15%	9%	Meta	5%	2%	2%
Para	15%	2%	10%	Para	12%	15%	13%
Chlorine	56%	62%	68%	Chlorine	70%	67%	72%
Ring Cl	2%	2%	1%				

Table 3.2. Continued.

TD-DFT calculations at the three levels of DFT were performed at the 6-31G(d) basis set on all optimised minimum geometries (Table 3.3). The transition structures were omitted since as they are already of a higher energy than the ground state minimum and thus would not be spectroscopically visible. Stability calculations were performed at the three DFT methods with the 6-31G(d) basis set, in order to test the wavefunction stability.

B3LYP		LYP	B3P	W91	BH&HLYP	
Structure	nm	f	nm	f	nm	f
266	426.83	0.1399	426.29	0.1400	434.91	0.1614
200	309.72	0.0596	311.55	0.0573	340.82	0.0488
260	519.61	0.199	519.82	0.2016	518.45	0.2899
200	312.31	0.0763	316.19	0.0675	345.61	0.0448
20.0	459.55	0.1456	460.41	0.1461	489.01	0.1891
20a	310.89	0.0349	315.88	0.0352	343.66	0.0375
205	426.95	0.1587	426.94	0.1589	428.24	0.1961
200	304.56	0.0373	318.57	0.0379	335.37	0.0715
200	451.74	0.1903	451.99	0.1914	445.92	0.2385
200	307.03	0.0408	312.17	0.0409	341.41	0.0743
276	434.75	0.1675	434.36	0.1685	445.05	0.2060
270	307.17	0.0367	311.02	0.0354	337.69	0.0441
270	452.11	0.1617	451.18	0.1627	435.80	0.2341
270	307.12	0.0511	311.33	0.0478	337.34	0.0604
21h	429.61	0.1633	428.93	0.1640	437.66	0.1844
210	303.94	0.0227	305.50	0.0257	277.97	0.0385
216	492.34	0.1913	492.14	0.1899	480.68	0.2700
210	285.90	0.1132	285.86	0.1126	272.59	0.1149
25h	439.40	0.1603	439.33	0.1600	431.13	0.1581
250	316.79	0.0241	322.10	0.0260	352.88	0.0761
250	514.52	0.1768	513.09	0.1794	464.12	0.2108
230	328.67	0.0351	329.48	0.0255	345.66	0.0590
24b	435.82	0.1659	435.69	0.1658	427.54	0.1649
240	315.25	0.0434	321.23	0.0238	352.47	0.0819
240	484.28	0.1873	483.75	0.1892	457.57	0.1347
240	315.64	0.0308	320.81	0.0322	350.22	0.0839
23h	450.62	0.1823	450.41	0.1845	439.65	0.2256
250	270.59	0.1046	270.70	0.1053	260.37	0.0617
230	401.80	0.1367	401.43	0.1352	396.06	0.1460
250	275.98	0.0612	275.14	0.0978	263.89	0.0727
22d	516.51	0.0135	513.00	0.0147	441.95	0.0989
22d	478.70	0.1156	477.33	0.1149	382.66	0.0788

Table 3.3. TD-DFT absorption maxima from the optimised minimum C₆H₅XCl complexes.

Reaction

field

calculations were performed on structures 23 and 24 (see Chapter 1), 20a-c, 24b, 24c and 26a-c in the presence of the corresponding solvent using the polarisable continuum model (PCM) and the isodensity PCM (IPCM) model.^{120,175-178} For these calculations, single-point energy energies of the optimised complexes in the corresponding solvents were performed at the same theoretical level as for the gas phase calculations. The differences

in the energies of the gas-phase and solvated complexes are presented in Tables 3.4 and 3.5.

Structure		PCM			IPCM	
	B3LYP	B3PW91	BH&HLYP	B3LYP	B3PW91	BH&HLYP
14 C_6H_6/CI	-15.74	-15.81	-11.78	-30.58	-31.20	-25.24
15 C ₆ H ₆ /Cl [•]	-15.09	-15.27	-21.36	-29.70	-30.27	-22.47
26a NH ₂ ipso	-63.23	-65.07	-67.28^{a}	-77.32	-80.41	-86.62^{a}
26b NH ₂ ortho	-53.07	-54.30	-51.65	-55.80	-57.05	-56.62
26c NH ₂ para	-66.07	-67.56	-67.56	-72.07	-74.51	-74.51
20a CH ₃ ipso	-15.00	-16.22	-12.22	-34.69	-36.73	-32.36
20b CH ₃ ortho	-11.97	-12.87	-13.96	-28.82	-17.52	-30.77
20c CH ₃ para	-13.56	-20.54	-14.92	-32.39	-40.05	-33.17
24b Cl ortho	-27.61	-26.65	-22.31	-28.64	-28.16	-21.94
24c Cl para	-27.96	-27.03	-44.82	-25.31	-24.05	-18.81

Table 3.4. The difference in stabilisation energy between solution-state complexes and gas-phase complexes. Energy differences are in kJ mol⁻¹. Larger negative values represents solution-state complexes that are more stable than the corresponding gas-phase structures.

^{*a*}Spin contaminated, $\langle S^2 \rangle = 0.82$.

Table 3.5. The difference in stabilisation energy between the solution-state complexes of aniline and chlorobenzene with the gas-phase complexes. Energy differences are in kJ mol⁻¹. Larger negative values represents solution-state complexes that are more stable than the corresponding gas-phase structures.

6-31G(d)	B3LYP	BH&HLYP	B3WP91
Aniline in chlorobenzene solvent		PCM	
26a	-58.81	-61.65	-60.48
26b	-49.51	-47.53	-50.61
26c	-61.62	-58.52	-62.96
		IPCM	
26a	-77.32	-86.62	-80.41
26b	-55.80	-56.62	-57.05
26c	-72.07	-71.99	-74.51
6-31G(d)	B3LYP	BH&HLYP	B3WP91
Chlorobenzene in aniline solvent		PCM	
24b	-29.51	-24.08	-28.61
254c	-27.96	-22.53	-27.03
		IPCM	
24b	-28.64	-21.94	-27.93
254c	-25.31	-18.81	-24.05

Toluene-chlorine complexes

The structures of the three isomers **20a-c** were optimised and vibrational frequency analyses confirmed that all three structures obtained were stable minima (Figure 3.2). The geometric parameters for each isomer are presented in Table 3.5, Appendix 3.



Figure 3.2. Optimised C₆H₅CH₃Cl[•] complexes 20a-c.

No spin contamination was found in any of the calculations for the isomers $20a-c < S^2 = 0.75>$. Stability calculations found the wavefunction to be stable for all isomers 20a-c at all three levels of theory. The dipole moments were calculated to be 4.0, 4.1 and 4.7 Debye for 20a, 20b and 20c, respectively.

Anisole-Chlorine Complexes

The structures of the two isomers **21b** and **21c** were optimised and vibrational frequency calculations confirmed both structures to be stable minimum geometries (Figure 3.3). Optimisation from the starting *ipso* geometry **21a** resulted in structure **21b**. The geometric parameters for each isomer are presented in Table 3.6, Appendix 3.



Figure 3.3. Optimised C₆H₅OCH₃Cl[•] complexes 21b and 21c.

No spin contamination was found in any of the calculations for structures **21b** and **21c** $\langle S^2 = 0.75 \rangle$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moments for **21b** and **21c** were calculated to be 4.1 and 5.8 Debye, respectively.

Nitrobenzene complexes

The structures of the two isomers 22a and 13d were optimised with vibrational frequency analyses indicating a transition state geometry and a stable minimum for structures 22a and 22d, respectively (Figure 3.4). Optimisation from the starting *ortho* geometry 22b resulted in structure 22a. The geometric parameters for each isomer are presented in Table 3.7, Appendix 3.



Figure 3.4. Optimised structures of the C₆H₅NO₂Cl complexes 22a and 22d.

No spin contamination was found in any of the calculations for structures 22a and $22d < S^2 = 0.75$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moment was calculated to be 4.9 and 4.6 Debye for 22a and 22d, respectively.

Fluorobenzene-chlorine complexes

The two structures isomers 23b and 23c were optimised and vibrational frequency analysis confirmed both structures to be stable minima (Figure 3.5). Optimisation from the starting *ipso* geometry 23a resulted in structure 23b. The geometric parameters for each isomer are presented in Table 3.8.



Figure 3.5. Optimised structures of the C6H5FCl complexes 23b and 23c.

No spin contamination was found in any of the calculations for structures 23b and 23c $<S^2 = 0.75>$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moment was calculated to be 3.69 and 4.44 Debye for 23b and 23c, respectively.

Chlorobenzene-chlorine complexes

The structures of the two isomers **24b** and **24c** were optimised and vibrational frequency analysis confirmed both structures to be stable minima (Figure 3.6). Optimisation from the starting *ipso* geometry **24a** resulted in structure **24b**. The geometric parameters for each isomer are presented in Table 3.9, Appendix 3.



Figure 3.6. Optimised structures for C₆H₅ClCl^c complexes 24b and 24c.

No spin contamination was found in any of the calculations for structures **24b** and **24c** $<S^2 = 0.75>$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moment was calculated to be 4.29 and 3.47 Debye for **24b** and **24c**, respectively.

Bromobenzene-Chlorine Complexes

The two structures of isomers **25b** and **25c** were optimised and vibrational frequency calculations confirmed both structures to be stable minima (Figure 3.7). Optimisation from the starting *ipso* geometry **25a** resulted in structure **25b**. The geometric parameters for each isomer are presented in Table 3.10, Appendix 3.



Figure 3.7. Optimised structures of C6H5BrCl complexes 25b and 25c.

No spin contamination was found in any of the calculations for structures 25b and 25c $<S^2 = 0.75>$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moments were calculated to be 3.4 and 3.5 Debye for 25b and 25c, respectively.

Aniline-Chlorine Complexes

Three structures **26a-c**, shown in Figure 3.8, were optimised where the chlorine radical is positioned at the ipso (**26a**), *ortho* (**26b**) and para positions (**26c**), respectively. Vibrational frequency analysis calculated stable minima for the *ortho* and para isomers, **26b** and **26c**, and a transition structure for the ipso isomer **26a**. The geometric parameters for each isomer are presented in Table 3.11, Appendix 3.



Figure 3.8. Optimised structures of C6H5NH2Cl' complexes 26a-c.

Spin contamination was not observed, $\langle S^2 = 0.75 \rangle$. The wavefunction was calculated to be stable for all structures **26a-c** at the three levels of theory. The dipole moments for the complexes **26a-c** were calculated to be 4.3, 4.2 and 5.9 Debye, respectively.

Phenol-Chlorine complexes

The structures of the two isomers **27b** and **27c** were optimised and vibrational frequency calculations confirmed both structures to be stable minimum geometries (Figure 3.9). Optimisation from the starting ipso geometry **27a** resulted in structure **27b**, which is not unexpected since both structures are near the same global minimum on the potential surface. The geometric parameters for each isomer are presented in Table 3.12.



Figure 3.9. Optimised structures of C₆H₅OHCl complexes 27b and 27c.

No spin contamination was found in any of the calculations for structures 27b and 27c $\langle S^2 = 0.75 \rangle$. Stability calculations found the wavefunction to be stable for both isomers at all three levels of theory. The dipole moments for 27b and 27c were calculated to be 3.9 and 5.2 Debye, respectively.

Discussion

The solvent effect in free radical chlorinations is experimentally well documented.^{11,17,26-38} It has been noted that the basicity of the aromatic solvent donor is the most important correlate in determining relative rates of hydrogen abstraction.²⁷ This, in turn should directly relate to the strength of complexation. Thus, there should be a relationship between the computationally determined binding constant between chlorine and the aromatic solvent and the experimental relative rate of hydrogen abstraction determined in that solvent.

From Table 3.1 it can be seen that the stabilities of the chlorine-aromatic radical complexes follow a general trend, with more electron-donating substituents resulting in more stable complexes, and less electron-donating substituents affording less stable complexes in the series:

$$C_{6}H_{5}NH_{2}-Cl^{\bullet} > C_{6}H_{5}OCH_{3}-Cl^{\bullet} > C_{6}H_{5}OH-Cl^{\bullet} > C_{6}H_{5}CH_{3}-Cl^{\bullet} > C_{6}H_{5}F-Cl^{\bullet} > C_{6}H_{5}Cl-Cl^{\bullet}$$

$$\approx C_{6}H_{5}Br-Cl^{\bullet} > C_{6}H_{5}NO_{2}-Cl^{\bullet}$$

This trend is consistent with improved stability of the complex afforded by the increased supply of electron density from the lone pairs of nitrogen, oxygen and the halogens, which are able to conjugate with the aromatic system. The strongly inductive electron-withdrawing properties of halogen substituents mean, however, that very little overall stabilisation is observed for complexes 23-25, relative to the unsubstituted C_6H_5Cl complex.

The results in table 3.1 indicate that all three DFT methods are consistent in terms of trend, with the B3LYP and B3PW91 giving comparative stabilisation energies across all species **20-27**. The BH&HLYP method appears to underestimate the stabilisation energy of all complexes by around 20 kJ mol⁻¹, but otherwise the relative energies within the series are consistent with the other two methods. It is assumed that this underestimation

of energies relates to the poor description of the chlorine-aromatic complex in general, as noted in previous chapters.

The calculated UV-Visible spectra for the aromatic complexes **20-27** predict an intense charge transfer band around 440-490 nm (shown in Table 3.3) arising from the substantial spin density of approximately 60-70% at the chlorine atom (Table 3.2). These predicted UV charge transfer bands around 440-490nm from the TD-DFT calculations (Table 3.3) are in good agreement with the experimentally observed bands for complexes **20**, **22** and **24**, which have been recorded at 490nm and are consistent with the bands observed for the benzene-Cl⁺ complex **14** from experiment.^{42,179,180} The aromatic-chlorine complexes may be characterised, similarly to the aromatic-radical complexes in Chapters 1 and 2, as charge transfer complexes, by their large dipole moments, where values between 3.7 and 4.7 Debye are calculated for the complexes with halogens.^{48,135,145-148} Weaker absorptions (seen in Table 3.13) are also predicted from the TD-DFT calculations at around 300-320nm, and are characteristic of cyclohexadienyl type radicals.^{42,94,149,180,181} This is consistent with the mixed σ - π geometry observed, as has been noted in previous chapters.

For the aromatic complexes with electron-donating, non-halogen substituents, 20, 21, 26 and 27, the *ortho* species was the most stable structure obtained. This improved stability correlates with shorter C-Cl bond lengths seen in the calculated *ortho* structures 20b, 26b and 27b than for the either the *para* structures 20c, 26c and 27c or the *ipso* structures 20a and 26a. This correlation does not hold for the anisole complex 21, however, the differences in distance of the C-Cl bond between *ortho* and *para* in this case are slight and may not be significant. In general, it is expected that a stronger interaction results in shorter bond distances, especially in complexes of this type.¹⁸² The preference for the *ortho* structure over the *para* structure indicates that electronic effects are more significant in contributing to stability than steric effects in these cases, and that this electronic effect is not fully transmitted through conjugative effects to the *para* position. This contrasts with the situation for the unsubstituted complex 14, which shows an almost equal distribution of spin-density, and thus electronic requirement, at both the *ortho* and *para* positions (Table 1.9, Chapter one). One possible explanation could be that there is an additional proximal stabilising interaction directly between the chlorine radical and the substituent.

Table 3.1 shows an energy difference of approximately 2 kJ mol⁻¹ between the *ortho* and *para* isomers of the C₆H₅CH₃Cl[•] complex, **20b** and **20c**. Uc *et al.*⁸⁶ have reported an energy difference of 3 kJ mol⁻¹ between the *ortho* and *para* isomers of the C₆H₅CH₃Cl[•] complex when calculated with the BH&HLYP/6-31G(d,p) level of theory.⁸⁶ This estimate is in good agreement with values obtained for structures **20b** and **20c** from this work.

The small energy difference between the *ortho and para* substituted complexes mean that, realistically, the *para* isomers are more likely to be the abstracting species. This is because *ortho* substitution would hinder the hydrogen abstraction reaction of hydrocarbons, relative to the corresponding *para* complex, due to the bulky substitution at the *ortho* position with concomitant steric hindrance at the site of hydrogen abstraction.

The halobenzenes, 23-25, differ from the electron-donating substituents in that the *para* isomers are relatively more stable than the *ortho* isomers by approximately 5 kJ mol⁻¹. This difference can be attributed to steric hindrance, particularly for the largest atoms (Cl and Br). In addition, the repulsive interaction between the two electronegative halogen atoms, when they are in close proximity to one another, also disfavours addition at the *ortho* position. An alternative explanation relies on the short-range transmission of inductive effects.¹⁸⁹ Inductive electron withdrawal through the σ -bond framework will be expected to have the greatest destabilising effect at the closest range, *ie.* at the *ortho* position, whereas these effects will be minimised at the more remote *para* position.¹⁸⁹

Ipso geometries were obtained for toluene **20a**, nitrobenzene **22a** and aniline **26a**. It is becoming increasingly acknowledged that *ipso* complexes should be considered in the radical reactions of nitrobenzene, toluene and aniline, in addition to complexes at the

meta, *ortho* and *para* positions.^{85,86,109} It can be seen from Table 3.1 that the *ipso* isomers **20a**, **22a** and **26a** are less stable than the corresponding *ortho* and *para* isomers by approximately 12 kJ mol⁻¹. Consistent with this observation, Uc *et al.*⁸⁶ have predicted that the *ipso* isomer of the C₆H₅CH₃Cl[•]complex **20a** is approximately 10 kJ mol⁻¹ less stable than the corresponding *ortho* and *para* isomers when calculated at the BH&HLYP/6-31G(d,p) level of theory. This estimate agrees well with the difference in energies calculated for the C₆H₅CH₃Cl[•]complex isomers, **20a-20c** in Table 3.1.

The Cl-aromatic distances for the *ipso* isomers **22a**, **20a** and **26a** (\approx 2.7Å, shown in Table 3.1) are slightly longer than those of the *ortho* and *para* isomers, by approximately 0.2Å. A Cl-aromatic distance of 2.7Å was reported in a theoretical study of the reaction of chlorine atoms with nitrobenzene.⁸⁵ Uc *et al.*⁸⁶ reported the Cl-aromatic bond length in the *ipso* C₆H₅CH₃Cl^{*}isomer to be 2.65Å when calculated with B3LYP/6-31G(d,p). These values are in good agreement with Cl-aromatic distances (\approx 2.7Å) for the *ipso* isomers **20a**, **22a** and **26a** presented in Table 3.1. The slight increased distance in the Cl-aromatic interaction observed in the *ipso* isomers, relative to the *ortho* and *para* isomers, is due to the steric hindrance effects between the substituents on the aromatic ring and the incoming chlorine radical. Due to these repulsive effects, the *ipso* isomers **20a**, **22a** and **26a** are naturally less stable than the alternate isomers, **20b**, **20c**, **22d**, **26b** and **26c**. This is exemplified by the fact that a transition state geometry was obtained for the *ipso* isomers **22a**.

In contrast with the steric effects for chlorine destabilising formation of the *ipso* complex, a recent theoretical study⁸⁶ of the addition of atomic radicals to toluene found that addition of fluorine radical to afford *ipso* isomer was favoured. This result agreed with the previous experimental data obtained by the same authors.¹⁰⁵ Uc *et al.*⁸⁶ have also postulated that the addition of $O(^{3}P)$ to the *ipso* position of toluene may explain the formation of phenol in experimental systems.

Experimentally,^{85,86,105,112} it has been found that as Cl^{*} approaches the favoured site of addition to the aromatic ring, a significant amount of spin polarisation is transferred to the substituted carbon.^{85,105,112} The calculated spin densities for the *ortho* and *para* substituted structures **20b**, **20c**, **26b** and **26c** (Table 3.2) correlate with this observation, since the highest degree of spin polarisation can be seen at the *ipso* site of the substituted carbon.

Nitro substitution leads to the *meta*-substituted complex being energetically preferred. Due to the strongly de-activating nature of the NO₂ substituent, there is a decrease in the overall electron density of the aromatic ring, consistent with a weaker interaction, reflected in the calculated energies (Table 3.1). Hence, the low exothermic energies for both the calculated structures **22a** and **22d** are consistent with a weakly bound structure. This implies that the chlorine atom-nitrobenzene complex should be short lived, which can account for the low experimental relative reactivities of tertiary *versus* primary hydrogen abstraction of 2,3-DMB when conducted in nitrobenzene solvent.²⁷

The log of the relative rates of complex formation for the *para* complexes **20c**, **21c** and **23c-27c** and *meta* complex **22d**, as obtained by assuming that the differences in the activation barrier of complex formation are negligible, have been plotted against the Brown-Okamoto σ^+ values (Figure 3.10).¹⁸³⁻¹⁸⁵ These σ constants were devised for electron donating groups that can interact with a developing positive charge in the transition state. This plot gives a good correlation coefficient, (R² = 0.973) with a negative ρ value of -2.69. The ρ value obtained is suggestive of the reaction complex satisfying electron demand to a reasonably electron-deficient intermediate. Thus, the electron donating substituents help to stabilise the electron-deficient radical as it becomes proximal to the aromatic ring.



Figure 3.10. Plot of the log of the calculated relative rates of complexation against σ^+ . $\rho = -2.69$, indicating stabilisation of an electron-deficient transition state or intermediate.

Interestingly, this correlation is much worse when the data for the unsubstituted complex **14** is included. In this case, the predicted complexation rate is lower than would be predicted by the Hammett correlation. This suggests a systematic variation in the calculation when a substituent is present. One possibility is that the complexation energy for the $C_6H_6Cl^{\circ}$ complex **14** is underestimated at -35.12 kJ mol⁻¹ and should be around 44 kJ mol⁻¹ when calculated with the B3LYP/6-31G(d) method. This could be due to the inadequacies of the B3LYP method with only a small basis set. Re-optimisation of the $C_6H_6Cl^{\circ}$ complex **14** using the B3LYP/6-311+G(d,p) method, affords a stabilisation energy of -39.39 kJ mol⁻¹. This indicates that the complex is underestimated with the B3LYP/6-31G(d), in relation to the correlation with the substituted complexes presented in Figure 3.10.

The selectivity observed for complexation of chlorine with substituted aromatics, discussed above, closely resembles that seen in the reactions of aromatic with cations,

and it is likely that the underlying processes that dictate *ipso*, *ortho*, *meta* and *para* substitution closely parallel those already examined in electrophilic substitution reactions. This is reinforced by the good correlation of the stabilisation energies with σ^+ , which was a scale originally developed for electrophilic substitution reactions.

Electrophilic attack on benzene derivatives is one of the most widely studied aromatic processes in the literature and involves highly electron deficient cation intermediates.^{147,148} The substituents CH₃, NH₂, OCH₃ and OH are known to donate electron density to the aromatic- π system and therefore activate and enhance the reactivity of benzene towards electrophilic attack at the ortho and para positions of the ring.8 The ortho and para carbocation reaction intermediates generated by electrophilic attack, afford more stable carbocations than those generated by attack at either the ipso or meta positions, due to resonance contributors that locate the carbocation adjacent to the electron-donating moiety (Figure 3.11). As a result, these ortho and para intermediates, and hence the transition states which lead to them, are more stable than the alternatives. In the case of attack on toluene, the resultant carbocations, in Figure 3.11, are also slightly stabilised by the C_{methyl}-C_{ring} dipole.⁸



Figure 3.11. Reaction of Cl' at the ortho and para positions of toluene.

In the case of anisole and phenol, the cation located adjacent to the substituent is further stabilised as it forms an oxonium ion, even though there may be some de-stabilisation from the electrostatic interaction with the C-O dipole. In the case of aniline, where NH_2 is strongly activating, the corresponding situation results in an imonium ion, as shown in

Figure 3.12. Neither the formation oxonium nor imonium ion can be achieved from attack at the *meta* position.



Figure 3.12. The structures of the imonium ions

Conversely, halogen substituents, although known to be the *ortho* and *para* directing towards electrophilic species, are overall weakly de-activating substituents.⁸ The electronegativity of the halogen results in the electron density of the aromatic being less available for donation to an electrophilic agent than in the case of benzene. Additionally, reactions at the *ortho* and *para* positions involve carbocation intermediate structures (shown centred, Figure 3.12) that are strongly destabilised by the carbon-halogen dipole.



Figure 3.12. Reaction of Cl' at the ortho and para positions of a halobenzene.

The centrally positioned structures (in Figure 3.12) are known as α -halocarbocations. In these structures, interaction with a halogen lone pair is possible to give an halonium ion structure (Figure 3.13), which is stabilising. This resonance structure cannot be achieved by attack at the *meta* position.



Figure 3.13. The structures of halocarbocations.

The electron-withdrawing NO_2 is a substituent that is recognised as being powerfully deactivating.⁸ The effect of this substituent makes the aromatic ring much less reactive. However the effect of de-activation in the *meta* addition is less than the effect of de-activation in the *ortho* and *para* reactions. All of the structural intermediates for nitrobenzene involve the electrostatic repulsion of the carbocation charge from the strong dipole of the nitro group. Hence, all positions in nitrobenzene are de-activated relative to benzene. Reaction at the *meta* position is de-activated less than the reaction at *ortho* and *para* reactions. The *meta* reaction only involves structures in which the positive charges are separated. Therefore this reaction, although of higher energy than the reaction of benzene, is still of lower energy than for the *ortho* and *para*



Figure 3.14. Carbocation intermediates of the meta reaction in nitrobenzene.

However, the electronegative nature of the halogen substituents decrease any additional stabilisation provided from hyperconjugation of the lone pair electrons with the aromatic ring. Hence, the lower stabilities of the halobenzenes and nitrobenzene are to be expected with the electron attracting influence of these substituents, which in turn de-activates the aromatic centre. It is clear from the complex stabilisation energies in Table 3.1 that the inductive properties of the substituents, as well as resonance, can also influence the stabilities of the aromatic-chlorine complexes.

The effects described above have particular influence on the experimentally observed selectivities of hydrogen abstraction reactions in a variety of aromatic solvents.

Specifically, Russell reported a correlation between basicity of the solvent, as represented by σ_{meta} , and the relative rates of hydrogen abstraction from the 1° and 3° sites of DMB.²⁷ Plotting Russell's data against σ_{meta} gives an R² value of 0.84. The complexation energies calculated for **14**, **20c**, **21c**, **22d** and **23c-27c** do not show a correlation with this Hammett parameter. However, when complexes **14** and **20c** are ignored, a correlation of (R² = 0.958) is obtained. When the all of complexes are re-optimised at B3LYP/6-311G(d,p) a correlation of (R² = 0.983) is obtained, however complexes **14** and **20c** are again omitted (Figure 3.15). This could potentially relate to the remaining complex's ability to form imonium ion resonance contributors and may indicate that the carbocation resonance contributors of **20c** are currently not well described with the choice of basis set. This correlation shows that the increase in the stability of the chlorine-solvent complex parallels the basicity of the solvent and thus is consistent with the experimental solvent effect.²⁷



Figure 3.15. The correlation of the estimated relative rate of complexation vs σ_{meta} .

Examining the B3LYP/6-311G(d,p) calculated complexation energies relative to the experimental relative reactivity data³⁷, a similar correlation coefficient ($R^2 = 0.95$) is

observed (Figure 3.16) which further suggests that the calculated energies are reliable. This correlation confirms the important role of the complex in determining hydrogen selectivity.



Figure 3.16. The correlation of the estimated relative rate of complexation vs the experimental 3°:1° rates of abstraction.

Whilst these complexes clearly show a reasonable correlation with experimental rates of hydrogen abstraction, solvation will play an important role in modulating complex stability. Solvation effects were examined using two different SCRF (Self consistent reaction field) methods to model the Ar-Cl[•] complexes, namely the PCM (Polarised continuum model) and the IPCM (Isodensity PCM) model. The PCM and IPCM methods differ in how the cavity and reaction field are defined. The PCM model defines the solvent cavity as the union of a series of interlocking spheres. The IPCM model defines the cavity as an isodensity surface of the molecule and is regarded as a more natural representation for the cavity since is corresponds to the reactive shape of the molecule, rather than the pre-defined shape as a set of overlapping spheres. Both of these methods model the solvent as a continuum of uniform dielectric constant, which is known as the reaction field. In each method the solute is placed into a cavity within the solvent.

The solvation effects in Table 3.12 are compared to the gas-phase energies at the same theoretical level. The stabilisation energies of complexes **5** and **6** are calculated to be approximately 15 kJ mol⁻¹ and 30 kJ mol⁻¹ more stable than the corresponding gas-phase structures, using the PCM and the IPCM models, respectively. Thus solvation by benzene affords significantly more stable complexes relative to those in the gas-phase model complex. This observation is in agreement with the PCM calculations performed by Tsao *et al.*⁸² on the solvation effects of benzene on a series of C₆H₆X[•] complexes.

In general, solvation effects calculated with both PCM and IPCM models show an increase in the stabilities relative to the calculated gas-phase complexes.⁸²

Four of the solvents studied by Russell³⁷, aniline, benzene, toluene and chlorobenzene, have already been parameterised in the Gaussian 03^{186} program and should reflect the solvent continuum well. These also represent a reasonable range of dielectric constants (ϵ), from 2.2 for benzene to 6.9 for aniline. Other solvents can, in principle, be accessed by specifying the dielectric constant, however, this is only one of many internal parameters used to define solvents and changing this parameter may not adequately define the new solvent properly. Thus this study was restricted to the solvent models that are considered the most reliable, moreover this has not been previously explored in the literature.

Both models afford very similar levels of stabilisation no matter which functional they are calculated with as shown in Tables 3.4 and 3.5. The largest increase in complex stability is seen when using both PCM and IPCM models for structures **26a-c** run in aniline as solvent, and which contain the strongly activating NH_2 substituent (Table 3.5). The majority of this stabilisation can be attributed to solvation, as when the aniline complexes are run with other solvents of lower dielectric constants, *eg* chlorobenzene, a relatively small decrease in stabilisation is observed. For the PCM model, the lowest degree of stabilisation is observed with solvents with small dielectric constants, such as benzene and toluene. These solvents better approximate the situation in the gas phase, so the stabilities of the complexes in these solvents are more similar to the gas phase values.

The IPCM model provides a similar degree of stabilisation for all solvents, *ca* 28-30 kJ mol⁻¹, regardless of solvent, except in the case of aniline. Table 3.4. In this case, the electron-donating capacity of the aromatic is perhaps better modelled, as the improvement in stabilities better reflects those expected from correlation with σ^+ . This continuum model is therefore the most likely to provide appropriate results for more extended studies.

Whilst the aromatic complexes 20-27 as a whole appear to reflect what is seen is Russell's chlorination experiments, other workers have examined the chemistry of some of the individual complexes, particularly in the context of atmospheric chemistry. It is useful to examine the details of our calculated complexes in the context of the wider literature.

Uc *et al.*⁸⁶ have studied the isomeric adduct stability in the addition of the atomic radicals, H, O(³P), F and Cl, to toluene using the B3LYP and BH&HLYP methods with the 6-31G(d,p) basis set. They reported that the B3LYP method affords "loose" structures when calculating the structures of the chlorine-toluene isomers. The C-Cl distances were recorded at 2.65, 2.59, 2.54 and 2.56Å for the *ipso, ortho, meta* and *para* isomers, respectively. In a similar study by Berho *et al.*⁸³ "loose" geometries consistent with these structures were obtained and described as erroneous since the C-Cl distance was not of a length expected for such a bond. It can be argued that the "loose" structure is the correct geometry and is not necessarily erroneous due to the pre-conceived value for a C-Cl bond length. In light of results from this work, experimental evidence from ESR spectroscopy⁵⁴ and *ab initio* calculations of other benzene-radical systems,^{82,85,87} the formation of such "loose" complexes appears to be expected within the mainstream literature. Moreover, the formation of such intermediates is often assigned in other radical reactions with aromatic compounds.^{38,94,95,109,110,159,179}

Comparison of the BH&HLYP calculated complexation energies, presented in Table 3.6, from this work with those obtained at BH&HLYP/6-31G(d,p) by Uc *et al.*⁸⁶ shows a

good correlation. Uc *et al.*⁸⁶ did not publish the values obtained from the B3LYP calculations due to the calculation of the longer C-Cl bond length of 2.5Å.

	ipso	ortho	meta	para	
BH&HLYP	-19.7	-28.4	-23.1	-25.1	Uc et al.86
BH&HLYP	-23.8	-31.2	~~	-29.2	This work
B3LYP	-42.9	-50.4	(7	-48.7	This work
B3PW91	-40.7	-49.2		-40.6	This work

Table 3.6. Energy of formation of the C₆H₅CH₃Cl[•] complex.

Energies in kJ mol⁻¹.

The perturbation of the aromatic ring upon complexation is reflected by a variation in carbon-carbon bond distances, as shown in the table in Figure 3.15. These changes are similar to those reported by Uc *et al.*, shown in Figure 3.15, despite their report that the carbon at the site of addition was sp^3 hybridised, and the C-Cl bond length was of the order of 1.93Å. No such carbon hybridisation was observed in this work, and the Cl-C-H/C angle was 80° with the Cl-C bond lengths >2.5Å. This suggests that there is minimal structural rearrangement once the Cl atom is complexed, and could have implications for interconversion of these complexes.



	20a			
BH&HLYP/6-31G(d,p)	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₁ -C ₇
Uc <i>et al.</i> ⁸⁶	1.49	1.34	1.42	1.51
This work	1.40	1.37	1.38	1.50

Figure 3.17. Calculated C-C bond distances for complex 20a.

It can be seen from structure **20b** (Figure 3.2) that the methyl group has rotated through approximately 90°. This is attributable the interaction between the methyl hydrogen, H_8 , with the chlorine atom. Optimisation of the anti-*ortho* **20b** (anti) isomer (Figure 3.18) using the three DFT methods with the 6-31G(d) basis set, affords the energies shown in Table 3.7.

 Table 3.7. Comparison of the energies of formation for the two toluene-Cl complex rotomers 20b and

 20b(anti) All energies are corrected and scaled. The numbers of imaginary frequencies are in parenthesis.

CH _{3 ortho}	B3LYP	B3PW91	BH&HLYP
20b eclipse	-50.4 (0)	-49.2 (0)	-31.2 (0)
20b anti rotomer	-49.5 (1)	-47.7 (1)	-29.2 (1)



46 M

Figure 3.18. Anti-ortho isomer.

Vibrational frequency analyses for **20b** (anti) predicted a transition structure, when using all three DFT methods. Comparison of the energies in Table 3.15 clearly shows that the eclipse rotomer is the most stable, but only by $1-2 \text{ kJ mol}^{-1}$

The reaction of nitrobenzene with chlorine atoms has been recently investigated.^{85,179} The displacement mechanism of the reaction is proposed to occur *via* a short lived $C_6H_5NO_2$ -Cl complex which decomposes to form C_6H_5Cl and NO_2 .¹⁷⁹ This proposal was based on a similar mechanism in the reaction of OH radicals with nitrobenzene¹⁰⁹ and a series of chlorinated aromatics.¹⁰⁰ It can be seen from Figure 3.7 that the *ipso* and *meta* isomers, **22a** and **22d** were afforded from geometry optimisation calculations. For both isomers, the C-Cl distance was calculated to be >2.5Å. The complexation energy of the *meta*

isomer complex was calculated to be -30, -28 and -14 kJ mol⁻¹ using the B3LYP, B3PW91 and BH&HLYP DFT methods, respectively.

B3LYP and MP2 methods have been used by Praña *et al.*⁸⁵ to examine the formation of the C₆H₅NO₂-Cl complex, in order to complement experimental data obtained by Frosig *et al.*¹⁷⁹ A *meta* C₆H₅NO₂-Cl intermediate was obtained along the potential energy surface of the Cl + C₆H₅NO₂ reaction, which is consistent with complex **22d** from this work. Prana *et al.*⁸⁵ reported a Cl-C_{*meta*} distance of 2.56Å, which strongly agrees with the DFT geometries obtained for structure **22d** in this work (Table 3.1).

QCISD(T) single point calculations were performed on the *meta* complex by Praña⁸⁵ on B3LYP optimised geometries, the energies of which are presented in Table 3.8. The energies obtained by Praña *et al.*⁸⁵ are extremely consistent with the B3LYP and B3PW91 energies obtained in this work for the *meta* isomer **22d** with the 6-31G(d) basis set, of -30.6 and -29.0 kJ mol⁻¹, respectively.

Level	C ₆ H ₅ NO ₂ -Cl
B3LYP/6-31G(d,p)	21.20
[QCSID(T)//B3LYP]	-31.38
B3LYP/cc-pVDZ	27.61
[QCSID(T)//B3LYP]	-27.61
B3LYP/aug-cc-pVDZ	20.12
[QCSID(T)//B3LYP]	-30.12
B3LYP/cc-pVTZ	-26.35

Table 3.8. Energies for the transition state as calculated by Praña et al.⁸⁵

Vibrational frequency analyses from this work afforded stable minima for the *meta* isomers using DFT methods. In contrast, Praña *et al.*⁸⁵ obtained one negative imaginary frequency at the B3LYP/6-31G(d,p) level of theory. The *meta* geometry reported by Praña *et al.*⁸⁵ has C₁ symmetry, where the chlorine is situated directly over the *meta* ring carbon. The geometry in this thesis is entirely consistent.

The kinetics and mechanism of the reaction of both chlorine atoms and OH radicals with a number of halobenzenes have been extensively reviewed.^{94,95,97,108,109,113} All the studies in the literature conclude that for the reaction of monohalogenated aromatics with chlorine atoms, the reaction proceeds *via* a displacement mechanism in which the incoming Cl displaces the halogen. It is also speculated that the reaction mechanism proceeds *via* the formation of an intermediate complex.^{94,95,108,109,113} The kinetics and mechanism for the reaction of Cl atoms with C₆H₅F, C₆H₆ and C₆H₅Cl are similar (seen in Table 3.16, below) for the reactions outlined as follows.⁹⁴

$$Cl' + C_6H_5X \rightarrow C_6H_4X' + HCl$$
(3a)

$$Cl' + C_6H_5X \longrightarrow C_6H_5X-Cl'$$
 (3b)

$$C_6H_5X-Cl' \rightarrow C_6H_5X+Cl'$$
 (-3b)

$$C_6H_5X-Cl'+Cl' \rightarrow \text{products}$$
 (3c)

Such reactions proceed slowly with effective rate constants of the order 10^{-16} cm³ molecule⁻¹ s⁻¹ *via* hydrogen abstraction and complex formation in which the complex undergoes rapid decomposition to reform the reactants.

The approach of the chlorine radical towards the monohalogenated aromatic in structures **23-25** produces the *ortho* and *para* isomers, as expected for electrophilic attack. The calculated geometries of the complexes **23-25** show very little difference from one another and this is also reflected in their calculated energies of formation, which can be compared in Table 3.1. Therefore, very little difference is observed in the estimated rates of complex formation. This clearly shows that reaction at the aromatic, within a solvent medium, is uncompetitive with the alternative of hydrogen abstraction reactions at the substrate.

The estimated experimental enthalpy of formation of the Cl-C₆H₅F complex is -35.9 \pm 10 kJ mol⁻¹.⁹⁴ This is in good agreement with the calculated energies for **23b** and **23c** at the three DFT methods (seen Table 3.1). A study conducted by Bunce *et al.*¹¹¹ investigating the effects of fluorinated benzenes on the hydrogen selectivities of 2,3-

DMB found that the solvent effect was diminished with increasingly fluorinated benzenes. The effect of the aromatic compound on the selectivity diminished in the order $C_6H_6 > C_6H_5F > C_6H_4F_2 > C_6H_3F_3$ and had disappeared completely in the case of C_6F_6 . These effects were attributed to the electron attracting nature of fluorine. The electronwithdrawing power of the halogen destabilises the developing positive charge within the aromatic ring, despite stabilisation by imonium-like resonance structure. Multiple fluorine substitutions will diminish the stabilising effects further.

Table 3.9. Kinetic data for the gas phase reaction of Cl atoms with aromatic compounds.94

Aromatic	k_{3a}^{a}	$k_{3b}k_{3c}/k_{-3b}^{b}$	$K_{3b} = (k_{3b})/k_{-3b}^{c}$	k_{-3c}^{d}
C_6H_6	1.3 ± 1.0	4.5 ± 1.1	3.2 ± 2.4	3 x 10 ⁷
C_6H_5F	0.11 ± 0.01	1.71 ± 0.14	1.1 ± 0.8	9 x 10 ⁷
C ₆ H ₅ Cl	<2.5	5.3 ± 0.6	3.4 ± 2.5	3 x 10 ⁷

^{*a*}Units of 10⁻¹⁶ cm³ molecule⁻¹. ^{*b*}Units of 10⁻²⁸ cm⁶ molecule⁻² s⁻¹. ^{*c*}Units of 10⁻¹⁸ cm³ molecule⁻¹, estimated assuming $k_{3c} = (1-5) \times 10^{10}$ cm³ molecule⁻¹ s⁻¹. ^{*d*}Units of s⁻¹, estimated assuming $k_{3b} = 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

In contrast, the reactions of Cl atoms with C_6H_5Br and C_6H_5I are rapid at $1.3 \pm 0.2 \times 10^{-11}$ and $3.3 \pm 0.7 \times 10^{-11}$ cm³ molecule ⁻¹ s⁻¹, respectively, to produce a C_6H_5Cl in yield close to 100% by halogen substitution.^{95,113} This can be attributed to bromine and iodine being better leaving groups than Cl. The displacement reactions of the monohalogenated aromatics display differences in thermochemistry:

$Cl + C_6H_5F \rightarrow C_6H_5Cl + F$	$\Delta H = 128 \text{ kJ mol}^{-1}$
$\mathrm{Cl} + \mathrm{C}_6\mathrm{H}_5\mathrm{Cl}^* \to \mathrm{C}_6\mathrm{H}_5\mathrm{Cl} + \mathrm{Cl}^*$	$\Delta H = 0 \text{ kJ mol}^{-1}$
$\mathrm{Cl} + \mathrm{C}_6\mathrm{H}_5\mathrm{Br} \to \mathrm{C}_6\mathrm{H}_5\mathrm{Cl} + \mathrm{Br}$	$\Delta H = -59 \text{ kJ mol}^{-1}$
$Cl + C_6H_5I \rightarrow C_6H_5Cl + I$	$\Delta H = -125 \text{ kJ mol}^{-1}$

Displacement of bromine from bromobenzene and iodine from iodobenzene are exothermic processes and are therefore spontaneous. These reactions have been observed experimentally.^{95,113} Previous studies^{95,113} have postulated that the bromo- and

iodobenzene complex decomposes to $C_6H_5Cl + X^{\cdot}$, for which a general reaction scheme (Figure 3.19) has been put forward.



Figure 3.19. The general scheme for the reaction of Cl atoms with monosubstituted aromatic compounds. Only one product isomer is shown for simplicity.⁹⁴

The similar energies of complexation of chlorine to both bromobenzene and iodobenzene indicate that the rate of the displacement reaction is controlled by the leaving step, as rates of initial complexation should be extremely similar. The differential stability of fluorine radical, bromine radical and iodine radical therefore account for the major differences in thermochemistry for these displacements.

Available literature on the reaction of chlorine atoms with either aniline, to form complex **26**, or anisole to form complex **21**, is limited. Complexation with phenol to afford complex **27** is complicated by the fact that this species is itself highly reactive towards hydrogen abstraction reactions. However, inspection of structures **21b**, **21c**, **26b**, **26c**, **27b** and **27c** demonstrate many similarities with other aromatic-chlorine radical complexes that have been studied in the literature. DFT calculations from this work predict that structures **21b**, **21c**, **26b**, **26c**, **27b** and **27c** are the most stable of all of the complexes studied. This is not surprising, since the OMe, NH₂ and OH groups are known to be strongly activating. This enhanced electron density within the aromatic system further stabilises the unpaired electron of the chlorine atom and this effect is reflected in the stabilisation energies. Moreover, inspection of the spin densities (in Table 3.10) for

structures **21b**, **21c**, **26b**, **26c**, **27b** and **27c** shows that a greater proportion of the spin density on Cl' is transferred to the aromatic system, compared with the other complexes.

The reaction of aniline has recently been investigated with 'OH radicals in the temperature region of 239 to 358K.¹⁰⁹ The decay rates recorded for 'OH radicals in the presence of aniline revealed the formation of an aromatic-radical adduct that subsequently decomposes.¹⁰⁹ This implies that the complex with 'OH with aniline is stable enough for observation.

Formation of a phenol complex with molecular chlorine has been reported in a study on the kinetics and mechanism of the reaction between chlorine and phenol in acidic aqueous solutions.¹⁸⁷ In aqueous solutions below pH 2, the reaction between chlorine, Cl₂, and phenol proceeds *via* a series of reactions. The first reaction corresponds to the second order formation of a [Cl₂-C₆H₅OH] intermediate, with an observed rate constant of $2.3 \pm 0.5 \times 10^4 \text{ M}^{-1}$ at 5.0°C . The second reaction is a first order decomposition of the intermediate, which occurs *via* three parallel pathways, namely, a hydrogen ion and chloride ion dependent path, a hydrogen ion dependent path, and a hydrogen ion and chloride ion independent path. The formation of the Cl₂-C₆H₅OH intermediate (and its physical properties) was proposed to be very similar to the reported X₂C₆H₆ charge transfer complexes of halogens^{135,146,188} in particular to the benzene-chlorine complex, where the halogen lies along the axis perpendicular to the benzene ring.¹⁸⁷ The work in this thesis suggests that the same differences that exist between the Cl₂-C₆H₆ complex and the C₆H₆Cl⁺ complex **14** are likely to exist between the phenol-Cl₂ complex and the phenol-Cl⁺ complex **27**.

In summary, it is clear that the calculated complexes of chlorine with substituted aromatics are similar in overall structure to the C_6H_6/Cl^2 complex 14. The stabilisation of the electron-deficient chlorine radical is well reflected both in the *ortho*, *meta* and *para* selectivity shown by the most stable complexes, and in the excellent correlation of the stabilisation energies with σ +. It is apparent though that there are deficiencies when using the B3LYP/6-31G(d) method that can to be corrected by using a larger basis set,

however re-optimisation may further improve the energies. The stability of the *para* complexes **20c**, **21c**, **23c-27c** and the *meta* complex **22d** correlate with the observed relative selectivities of $3^{\circ}:1^{\circ}$ hydrogen abstraction in DMB. This suggests a clear, but perhaps indirect, relation of the complex stability, a thermodynamic parameter, to the kinetics of the reaction. The interaction of benzene with the transition state of hydrogen abstraction will thus be further explored in Chapter Four.

Chapter 4

A Theoretical Examination of the Solvation of Transition States in Hydrogen Abstraction Reactions.

The relative stabilities of radical intermediates are usually considered significant in determining the relative rates of hydrogen abstraction, since formation of these intermediates tends to be both rate determining and highly endothermic. Thus, Hammond's postulate indicates the structure of the transition state for reaction should be best reflected by that of the radical intermediate.¹⁶ To properly identify kinetic effects, especially those that impact on selectivity, it is necessary to consider the nature of this transition state, which is possible using theoretical methods.

Hydrogen abstraction reactions may become polarised in the transition state, affording an avenue for interaction with the solvent (Figure 4.1).¹ The effect of solvent polarity has been noted for a number of reactions.¹⁹⁰ Whilst it has primarily been the aromatic effect that has been noted for chlorinations,²⁷⁻²⁹ the aromatic group is also able to stabilise an incipient positive charge¹⁹¹⁻¹⁹² which may provide either alternative or additional contributing factors to the changes in selectivity observed in radical reactions. This chapter aims to examine the nature of the transition state for hydrogen abstraction from a selection of alkanes to provide and improved description of the aromatic solvent effect.

$$R-CH_2H + Cl^{-} \longrightarrow [R-CH_2 - -H_{--}Cl]^{\ddagger} \longrightarrow R-CH_2 + HCl$$

Figure 4.1. Polarisation in the transition state of the hydrogen abstraction reaction of an alkane with chlorine atom.

Results

The reactions of both the C_6H_6/Cl^{-} complex (14), page 45 and the un-complexed chlorine radical with the alkanes methane, ethane, propane and butane were examined as examples of methyl, primary, secondary and tertiary hydrogen abstraction reactions, respectively. The enthalpies of the reactions and the transition states structures from reactions 4.1-4.8 were calculated:

$Cl^{\cdot} + CH_4 \rightarrow TS^{\dagger} \rightarrow \cdot CH_3 + HCl$	(reaction 4.1)
$C_6H_6 + Cl^{\cdot} + CH_4 \rightarrow C_6H_6/Cl^{\cdot} + CH_4 \rightarrow TS^{\dagger} \rightarrow C_6H_6 + HCl + {}^{\cdot}CH_3$	(reaction 4.2)
$Cl^{\cdot} + C_2H_6 \rightarrow TS^{\dagger} \rightarrow C_2H_5 + HCl$	(reaction 4.3)
$C_6H_6 + Cl^{\cdot} + C_2H_6 \rightarrow C_6H_6/Cl^{\cdot} + C_2H_6 \rightarrow TS^{\dagger} \rightarrow C_6H_6 + HCl + {}^{\cdot}C_2H_5$	(reaction 4.4)
$Cl' + C_3H_8 \rightarrow TS^{\dagger} \rightarrow C_3H_7 + HCl$	(reaction 4.5)
$C_6H_6 + Cl^{\cdot} + C_3H_8 \rightarrow C_6H_6/Cl^{\cdot} + C_3H_8 \rightarrow TS^{\dagger} \rightarrow C_6H_6 + HCl + {}^{\cdot}C_3H_7$	(reaction 4.6)
$Cl^{\cdot} + C_4H_{10} \rightarrow TS^{\dagger} \rightarrow {}^{\cdot}C_4H_9 + HCl$	(reaction 4.7)
$C_6H_6 + Cl^{\cdot} + C_4H_{10} \rightarrow C_6H_6/Cl^{\cdot} + C_4H_{10} \rightarrow TS^{\dagger} \rightarrow C_6H_6 + HCl + C_4H_9$	(reaction 4.8)

For those reactions incorporating the single molecule of benzene as solvent, the interaction of benzene and the chlorine radical to form the charge transfer complex 14 was assumed, as established and discussed at length in Chapter 1. TS^{\dagger} represents the transition state for each reaction. The relative energies for the transition states are obtained by calculating the calculated energy difference from the un-complexed starting materials.

The geometries of all components and complexes were optimised using GAUSSIAN 03.¹⁸⁶ B3LYP, B3PW91 and BH&HLYP methods were used to obtain minimum energy structures and carry out vibrational frequency analyses. The BH&HLYP/6-31G(d) method was used to obtain transition state geometries for the complexes, however, transition state structures were unable to be identified using either the B3LYP or B3PW91 methods using the 6-31G(d) basis set. This is consistent with previous observations of Jursic¹⁹³ who was also unable to identify transition states for hydrogen atom abstraction by chlorine with these functionals and the 6-31G(d) basis set. For these cases, vibrational analyses indicated that lower than expected vibrational modes along the

abstraction pathway were likely to interfere with the optimisation. The 6-31G(2df,p) basis was tried with the B3LYP functional and also failed to optimise to an appropriate transition state structure. To counter this problem and afford a better description of the more highly-conjugated transition state structure, the 6-311+G(d,p) basis set was used to obtain transition state geometries with the B3LYP and B3PW91 functionals. In this case, transition state structures were obtained for all except the butyl derivatives at the B3PW91/6-311+G(d,p), for which the vibrational modes along the abstraction path were still extremely low, preventing optimisation with both GAUSSIAN 03^{186} and the SPARTAN¹³² molecular modelling packages. For this reason, only profiles for the BH&HLYP and B3LYP calculations are presented in their entirety (Figures 4.4-4.7).

Vibrational frequency analyses and IRC calculations for all levels of theory were used to confirm that the transition state corresponded to the hydrogen abstraction reaction. The vibrational modes of the negative frequencies were animated to verify the correct transition structure visually. No spin contamination was observed for the optimised structures with the value for $\langle S^2 \rangle$ calculated at 0.75 in each case.

The transition state structures for hydrogen abstraction from methane, ethane, propane and *t*-butane both in the absence and presence of benzene are depicted below in Figures 4.2 and 4.3.


Figure 4.2. Optimised transition state geometries for the hydrogen abstraction reaction of chlorine with methane 28, ethane 29, propane 30 and *t*-butane 31.



Figure 4.3. Optimised transition state geometries for the hydrogen abstraction reaction of chlorine in the presence of benzene with methane 32, ethane 33, propane 34 and *t*-butane 35.

Table 4.1. Effect of the presence of the aromatic on the energy of the transition state. The relative energy is determined as the difference between the complexed transition state (32-35) and sum of the corresponding non-complexed transition state (28-31) and benzene. ZPE is not included.

Loval of theory	Stabi	lisation en	nergy (kJ	mol ⁻¹)
Level of meory	32	33	34	35
BH&HLYP/6-31G(d)	-8.9	-9.3	-9.2	-9.3
B3LYP/6-311+G(d,p)	-4.7	-4.4	-4.5	-4.1
B3PW91/6-311+G(d,p)	-3.9	-3.6	-3.7	n/c

Table 4.2. Calculated H-Cl and H-C bond distances and for structures 28-31.

Level of theory	H	-Cl dista	nce (d1, Å	(<i>)</i>]	H-C dista	nce (d2, Å	Á)
Level of theory	28	29	30	31	28	29	30	31
BH&HLYP/6-31G(d)	1.410	1.425	1.439	1.457	1.499	1.477	1.455	1.429
B3LYP/6-311+G(d,p)	1.396	1.417	1.440	1.480	1.568	1.531	1.490	1.423
B3PW91/6-311+G(d,p)	1.387	1.409	1.444	n/c	1.572	1.530	1.460	n/c

Table 4.3. Calculated H-Cl and H-C bond distances and for structures 32-35.

Level of theory	H	-Cl dista	nce (d1, A	Á)	I	H-C dista	nce (d2, Å	Á)
Level of meory	32	33	34	35	32	33	34	35
BH&HLYP/6-31G(d)	1.413	1.427	1.440	1.458	1.498	1.480	1.462	1.436
B3LYP/6-311+G(d,p)	1.396	1.414	1.435	1.474	1.576	1.547	1.509	1.440
B3PW91/6-311+G(d,p)	1.384	1.402	1.435	n/c	1.590	1.554	1.486	n/c

Table 4.4. Calculated Cl-Ph bond distances and for structures 32-35, taken as the distance to the nearest carbon of the aromatic ring.

Level of theory	Cl	-Ph dista	nce (d3, <i>À</i>	(<i>Ì</i>
Level of theory	32	33	34	35
BH&HLYP/6-31G(d)	3.940	3.952	3.908	3.933
B3LYP/6-311+G(d,p)	4.222	4.156	4.124	4.102
B3PW91/6-311+G(d,p)	4.834	4.480	4.276	n/c

Table 4.5. Calculated spin densities for structures 28-35 at the BH&HLYP/6-31G(d) level of theory.

Atom		Uncomp	lexed TS			Compl	exed TS	
Atom	28	29	30	31	32	33	34	35
C1	20%	20%	25%	31%	20%	20%	25%	30%
C (abstraction)	80%	80%	75%	69%	80%	80%	75%	70%
H (abstracted)	-5%	-8%	-8%	-7%	-12%	-7%	-7%	-6%

Table 4.6. Vibrational frequencies for structures 28-35 corresponding to the transition state trajectory.

Level of theory		Uncomp	lexed TS			Complexed TS				
Level of meory	28	29	30	31	32	33	34	35		
BH&HLYP/6-31G(d)	-846	-793	-729	-692	-800	-721	-652	-611		
B3LYP/6-311+G(d,p)	-367	-379	-374	-401	-327	-310	-314	-349		
B3PW91/6-311+G(d,p)	-288	-281	-286	n/c	-242	-212	-224	n/c		

Table 4.7. Calculated dipole moments for structures 28-35 at the BH&HLYP/6-31G(d) level of theory.

		Uncomple	exed TS			Comple	exed TS	
	28	29	30	31	32	33	34	35
Dipole moment (debye)	3.14	3.60	3.85	4.00	3.06	3.46	3.67	3.77

Reaction of CI radical with alkanes



Figure 4.4. Reaction profiles of methane, ethane, propane and *t*-butane with chlorine atom at the BH&HLYP/6-31G(d) level of theory.



Reaction of CI radical with Alkanes (B3LYP/6-311+G(d,p))

Figure 4.5. Reaction profiles of methane, ethane, propane and *t*-butane with chlorine atom at the B3LYP/6-311+G(d,p) level of theory.



Reaction of CI-Ph complex with alkanes





Reaction of Cl complex with Alkanes (B3LYP/6-311+G(d,p))

Figure 4.7. Reaction profiles of methane, ethane, propane and *t*-butane with chlorine in the presence of benzene at the B3LYP/6-311+G(d,p) level of theory.

Discussion

The effect of a number of different solvents in the influence of selectivity has been widely studied experimentally,^{17,27-29,30,33-36,38,39,87,118,126-128155,190} with polar and aromatic solvents showing the greatest increase in selectivity of abstraction from tertiary DMB hydrogens over primary.^{27,28,30,41,42,88} The stabilities of the radical intermediates are generally reflected in the associated BDE's of the C-H bonds. The presence of the solvent clearly assists the hydrogen abstraction reaction with the stabilisation of the solvent–Cl complex thought to be responsible for the increased selectivity. However, this process is not well understood.

Direct theoretical modelling of the hydrogen abstraction reactions of DMB in benzene solvent is currently impractical due to the large number of degrees of freedom. For this reason, model abstraction reactions with methane, ethane, propane and *t*-butane were examined both with free chlorine and the C_6H_6/Cl^{-} complex, 14. Wang *et al.*^{195,197} have indicated that, in the case of the related hydrogen abstraction by the CS₂.Cl complex, density functional methods are entirely appropriate to obtain a semi-quantitative description of the reaction profile with a lower computational cost relative to correlated methods for such large systems makes these methods particularly attractive.

Hydrogen abstraction by chlorine has attracted much attention in the literature because of its perceived importance in atmospheric processes and there are a number of studies that have examined this reaction. ^{1,2,6,25,53,83,92,110}, In this study, the DFT methods afford transition states for abstraction that have the C-H-Cl atoms involved in the abstraction collinear (Figure 4.2). The bond distances in the transition state of abstraction for both the H-Cl and C-H bonds are reported in Table 4.2. These indicate a clear trend with increasing H-Cl bond lengths in the transition state when progressing from less substituted (methane) to more substituted (*t*-butane) substrates. Concomitantly, the C-H bond length in the transition state decreases with increasing alkane substitution. This trend is consistent with each of the DFT methods used, even though the absolute values vary from method to method.

By consideration of the Hammond postulate these bond-length changes suggest that as the substrates for hydrogen abstraction become more substituted, the transition states develop earlier, as reflected in the closer resemblance to the starting material structures. This earlier transition state affords a more exothermic reaction for more substituted alkanes. The greater ease of reaction is confirmed when the energies of the transition states are examined (Figure 4.4). In this case, the transition state energy, relative to the starting materials at infinite separation, decreases from 57 kJmol⁻¹ for abstraction from methane, to 35 kJmol⁻¹ from ethane, to 17 kJmol⁻¹ to form the 2° radical of propane and finally 2.9 kJmol⁻¹ to form the 3° radical from *t*-butane, at the BH&HLYP/6-31G(d) level of theory. This trend is entirely consistent with that expected from the BDEs of the respective alkanes⁸ and is followed when the other DFT functionals, B3LYP and B3PW91, are employed (see, for example Figure 4.5). With these latter functionals, the barrier is consistently calculated as being lower than that obtained with the BH&HLYP/ functional, by around 30-40 kJmol⁻¹. This indicates a systematic difference between the different functionals for which the greatest contributing factor seems to be weak complex formation.

The majority of the spin density (ca. 69-80%, Table 4.5) is located on the carbon to which the abstracted hydrogen is bonded. The spin density on the abstracted H is low and negative (ca. 7-8%). These properties are characteristic of proton shared bonding^{123,124} which may also account for low stretching frequencies corresponding to the transitions state for the B3LYP and B3PW91 methods (Table 4.6). Due to the shared nature of the bond, the BH&HLYP method would be expected to perform better.¹⁴¹ The calculated spin densities also support the bond-length data with a greater spin density on the chlorine atom and lesser on the putative radical carbon in reactions with propane and butane than for those with methane and ethane. However, the calculated changes here are marginal and are too small to be considered reliable, despite constituting a consistent trend.

IRC calculations of the transition structure for each of the alkanes confirmed the existence of pre- and post-complexes on the potential surface where the chlorine atom interacts favourably with the alkane and the alkyl radical interacts favourably with the departing hydrogen chloride, respectively. In the case of the pre-complex the stabilisation afforded is small at the BH&HLYP/6-31G(d) level but increases slightly for more substituted positions on the alkyl chains, in all cases. The post-reaction complex is

around 7 kJmol⁻¹ less stable than the transition state in each case. This results in a highly endothermic process for the methyl radical with BH&HLYP with progressively less endothermic reaction profiles as the substitution of the alkyl radical increases. This is consistent with the experimentally observed trends in reactivity.¹⁵⁹

Pre- and post-complexes were also identified for hydrogen abstraction by chlorine from DMB in the calculations by Wang *et al.*,¹⁹⁵⁻¹⁹⁷ however, the magnitude of stabilisation was more significant using B3LYP/6-311G(d), being reported as 3.5 kcalmol⁻¹ and 8.5 kcalmol⁻¹ for the primary and tertiary pre-complexes, respectively. In contrast, these authors calculated pre-complex stabilisations more consistent with those presented in this work when using UMP2 theory. The B3LYP/6-311+G(d,p) pre-complex energies calculated in this work are consistent with those presented by Wang *et al.*¹⁹⁵ for the smaller basis set, with the stabilisation for the methane-chlorine pre-reaction complex being 2.4 kJmol⁻¹, that for ethane (comparable to the 1° radical of DMB), 12.5 kJmol⁻¹, for propane 23.7 kJmol⁻¹ and for t-butane (comparable to the 3° radical of DMB) 34.3 kJmol⁻¹. In a similar frontier orbital interaction to the charge transfer complex **14**, the electrophilic chlorine radical interacts with the alkane to accept an electron from the C-H bond, thus forming the transition state, where the HOMO-SOMO interaction predominates. A net stabilisation is achieved in the system by the dipole of the chlorine inducing a dipole in the system to form a donor-acceptor type intermediate.

The overall process becomes more exothermic for each alkane when the B3LYP and B3PW91 functionals are employed (Figure 4.5), this results in an endothermic abstraction from methane and ethane overall, whereas abstraction from propane and *t*-butane become exothermic. This is consistent with the observation that the tertiary and secondary sites are the most reactive.⁸ The overall trend throughout the series remains the same for each of the density functional methods.

Wang *et al.*¹⁹⁵ justified the use of the B3LYP functional by calculating single point energies at UCCSD(T)/6-31G(d)//B3LYP/6-311G(d), which corresponded well in trend with the energies obtained for B3LYP/6-311G(d)//B3LYP/6-311G(d). This could be further confirmed by using other high-accuracy methods developed for free radical thermochemistry, such as the G3X-RAD method developed by Radom *et al.*¹⁹⁶

The direct effect of benzene solvent can be examined by calculating the transition state complexes and reaction profiles in the presence of benzene. Table 4.1 lists the difference between the transition state energies of the uncomplexed systems, with benzene at infinity and the corresponding complexed systems. Interestingly, benzene does effect some stabilisation on the transition state, however this does not appear to vary with the degree of substitution at the radical centre. The magnitude is also relatively small, being at most 9 kJmol⁻¹ at the BH&HLYP level of theory and less if zero point correction is added or if one of the other functionals is employed. This small contribution to transition state stabilisation is unsurprising since presence of the chlorine atom (located >3.9 Å from the aromatic ring at all levels of theory) in the transition state structures is a major contributor to the stabilisation (Table 4.4). The lesser contribution of the chlorine is also reflected in the slightly lower values for the dipole moment (Table 4.7) which could indicate less charge transfer.

The small changes in transition state stability are reflected by the changes in the bond lengths (Table 4.3). Whilst some lengthening at the C-H bonds in the transition state complexes with benzene and a corresponding shortening of the H-Cl bond is observed (relative to the corresponding uncomplexed transition states) these variations are small. They are consistent with transition states moving towards a structure which is marginally more product-like in the presence of benzene and thus, overall a slightly more endothermic reaction once the initial complexation with benzene is achieved.

Table 4.6 shows the calculated negative vibrational frequencies that correspond to hydrogen abstraction. It may be seen from that the stretching frequencies decrease for the complexed Cl⁻ reactions. This would support the assertion that the benzene moiety perturbs the chlorine atom to form a transition state that is more thermodynamically "product-like" for tertiary and secondary hydrogen abstraction. However, a transition state that is more kinetically controlled and "reactant-like" is predicted for primary hydrogen abstraction. This is consistent with the experimental observation that greater tertiary selectivity is observed in the chlorination reaction of DMB when conducted in an aromatic solvent.^{17,27,28}

If the energies of the transition states for hydrogen abstraction are considered, relative to the energy for the abstracting species (Cl' or Ph-Cl'), the increased activation barrier is consistent with the observed changes in structure. In addition, the activation barriers calculated by Wang et al.^{195,197} at the B3LYP/6-311G(d,p) level of theory for the CS₂ complex reaction with DMB are entirely consistent with those presented here for the aromatic complex with 1° and 3° hydrogens and are of very similar magnitude. This is unsurprising since the two species behave in a similar fashion in reactions with DMB. On this basis, a very similar argument can be presented to that of Wang et al.^{195,197} that indicates the major contribution to the differences in observed selectivity is due to the increased stabilisation of the abstracting species. Namely, that the reaction of less substituted alkanes with the chlorine-benzene complex becomes relatively more difficult since the primary driving force of a strong H-Cl interaction is diminished by the already strong Ph-Cl interaction. While the abstraction by the reactive species, Ph-Cl to form the tertiary centre can still proceed with relative ease (the reaction is nearly isothermic when the zero point energies are included) the reaction to form a primary radical is endothermic by around 28 kJmol⁻¹ with the zero point correction included.

Figure 4.6 includes two additional points for the abstraction reaction from butane and propane at -12.6 kJmol⁻¹ and -7.2 kJmol⁻¹, respectively. These represent stable minima identified from the IRC calculation. The points at -29.0 and -28.8 kJmol⁻¹ are also stable minima and must therefore represent a 'pre-precomplex', whereby the alkane forms a preliminary complex before properly interacting with the chlorine. This is consistent with the C-H bond distance, which is not stretched in these complexes. The interactions in these cases appear to be due to weak C-H interactions^{198,199} and persist throughout the reaction. It is likely however, that if these represent a favourable interaction, some energy must be expended with these bulkier alkanes to obtain an appropriate orientation for the reaction to take place. This is consistent with the higher energy pre-complex structures identified by the IRC.

No such 'pre-precomplex' structures were specifically identified at the B3LYP/6-311+G(d,p) level of theory, however this avenue was not thoroughly investigated. This is partly due to the difficulty in obtaining structures with so many weakly bound components. This is a specific limitation of many current theoretical methods and the

development of functionals specifically optimised for weak complexes is of great interest.²⁰⁰⁻²⁰⁰² The major problem with these complexes lies in eradicating the very low, negative vibrational frequencies that arise. Typically tighter convergence criteria are used however this increases the computing time substantially, especially where a large number of atoms are being calculated. Consequently, complete convergence on the maximum displacement (*i.e.* the maximum structural change of one coordinate as well as the average root mean square change over all structural parameters) can often be slow for larger systems. In practice it is sometimes practical to stop the convergence criteria when the maximum force on the atoms in the system has been achieved.

The difficulty in calculating these structures is particularly highlighted when trying to obtain structures for the hydrogen abstraction from t-butane at the B3PW91/6-311+G(d,p) level. Repeated optimisations afforded transition structures whereby the negative vibrational mode of -171 cm^{-1} corresponded to methyl group. The values presented in Table 4.6 would suggest that the frequency corresponding to the tertiary hydrogen abstraction of t-butyl would be approximately 100 cm⁻¹ when calculated with B3PW91. The problems thus encountered trying to optimise to the correct transition geometry can therefore be attributed to the closeness in magnitude of these two frequencies.

It was shown in Chapter 3 that application of a solvent continuum model assisted in the stabilisation of the Cl-aromatic complex. Given that the greatest tertiary selectivity is seen experimentally when the chlorination reaction is conducted in aromatic and polar solvents, it is unlikely that there is a high preponderance of "free chlorine" atoms.^{11,17,26-30,118,127,128}

The calculations presented in this chapter suggest that the predominant role of the aromatic moiety is to achieve selectivity by initially lowering the reactivity of the chlorine atom by complex formation, rather than directly stabilising the transition state.¹¹ This effect acts progressively on going from abstraction from methane to abstraction from the tertiary centre of *t*-butane, resulting in an improvement in selectivity. These results are thus consistent with the observed experimental effects for DMB observed by Russell^{17,27,28} and others,^{30,41,42,88} to provide a platform through which other reactions of this type can be reliably explored.

The aim of this project was to identify a suitable model to predict accurately the properties of non-covalent aromatic radical systems using theoretical methods. The key methodologies were identified as DFT (B3LYP, BH&HLYP and B3PW91) using the 6-31G(d) basis set following an extensive trial. These theoretical methods proved viable since they afforded qualitative results without a great compromise on accuracy and speed which could be applied to other related systems.

The model system was developed through a series of geometries, η_1 , η_2 and η_6 . Releasing any geometry constraints of these models afforded structure **14** (page 45) this was calculated to be the minimum energy geometry whose thermochemical and geometric parameter correlated with the experimental and theoretical data available in the literature.^{54,43,88,82,83,110}

The structure of the C₆H₆/Cl[·] radical complex had remained a topic of debate for some time. 41,42,43,44,54,88 Russell²⁶⁻²⁹ originally proposed a π -type structure, which became the structure favoured by Ingold *et al.*^{115,116,,126} Skell *et al.*^{41,42} however, favoured the σ -complex as that adopted by the C₆H₆/Cl[·] radical complex.

With the advent of new methodologies and improved computer systems, such compounds can be modelled readily. Experimental work had identified that enhanced selectivity of tertiary hydrogen abstraction was observed when abstraction reactions were conducted in aromatic solvents, particularly within those aromatics containing an electron donating substituent.²⁶⁻²⁹

The primary objective of this project was to develop the model and to allow for modifications to related Ar-radical systems using the established theoretical methods.

With our model base secured, we exchanged the Cl[•] for a series of other radicals, namely, F[•], Br[•], I[•], [•]OH and [•]CH₃. The following order of stability from the most stable to the least was predicted as follows:

 $FC_6H_6 > HOC_6H_6 > BrC_6H_6 \approx CH_3C_6H_6 > IC_6H_6$

The relative energies for the σ - π complexes for the Br', I' and σ -complex 'CH₃ structures were calculated at -32, -13 and -29 kJ mol⁻¹ at B3LYP\6-31G(d), respectively. These weak binding energies indicate that the complexes would easily dissociate and are so unstable that it would be unlikely that they would be observed under laboratory conditions, since the corresponding radical can not effectively add to the aromatic ring.^{110,167} The most stable geometry for the fluorine and hydroxyl complexes was the sp³ hybridised σ geometry. The C-X' bond lengths are predicted as forming between 1.4 and 1.5Å for the σ cyclohexadienyl type geometries of these radicals. Unlike the σ - π complexes, the unpaired electron is evenly delocalised over five carbons of benzene and the spin density is approximately all (97%) transferred to the ring, suggestive of little interaction between the radical and the aromatic π system. The stability of the Cl' radical complex was analysed when subjected to increases and decreases of electron density by using a series of substituted aromatic compounds commonly used as solvents.

It is well known that the effects of resonance by either electron-donating or electronwithdrawing groups can also influence radical stability.⁸ Substituents which are electrondonating enhanced the radical stability, where electron-withdrawing substituents afford little radical stabilisation. The following general trend was predicted,

$$C_{6}H_{5}NH_{2}-Cl' > C_{6}H_{5}OCH_{3}-Cl' > C_{6}H_{5}OH-Cl' > C_{6}H_{5}CH_{3}-Cl' > C_{6}H_{5}F-Cl' > C_{6}H_{5}Br-Cl' \approx$$

$$\approx$$

$$C_{6}H_{5}Br-Cl' > C_{6}H_{5}NO_{2}-Cl'$$

Generally, the calculated complexes of chlorine with substituted aromatics mirror the structure to the C₆H₆/Cl[•] complex 14 (page 45). Throughout Chapters 1, 2 and 3, the B3LYP\6-31G(d) level of theory appeared to be the most consistent with the literature, where applicable. However as the size of the molecular system became larger, deficiencies in the correlation relationship were becoming apparent. The use of the triple- ζ basis set, 6-311+G(d,p) showed an improvement in the calculated energies, however the correlation with the toluene-Cl[•] complex failed to show any improvement.

The influence of the C₆H₆/Cl^{\cdot} radical complex in the hydrogen abstraction reaction was examined Chapter 4. It soon became apparent that analysis of the transition structures with the double- ζ basis set, 6-31G(d) was inadequate. Moreover, the BH&HLYP methods proved, overall to produce more consistent results in terms of optimised geometries and calculated stabilization energies. The results show quite clearly that presence of the aromatic is to provide initial stabilisation to the chlorine radical by complex formation however this complex does not constitute the transition state in any of the reactions with alkanes. The results obtained are consistent with experimental observations, whereby an increased stability is observed from the progression of abstraction of the 1°, 2° and 3° hydrogen. ^{17,27,28,30,41,42,88}

The calculation of a full set of data for the transition structures proved to be particularly challenging and further work to explore these in detail would be useful. However, many new avenues have been explored from the completion of this study in addition to obtaining many of the reliable calculated complex energies.

Future work

Although DFT has shown the viability of relatively inexpensive methods to study radical systems, a number of challenges still remain. In particular, the successful modelling radical transition states and reaction profiles.

It is possible that re-optimising these geometries at the higher level of theory may solve any discrepancies. In particular using compound methods such as G3-RADX could initially provide an improvement on the calculated BH&HLYP energies *via* single point calculations. Additional IRC calculations would also give a detailed picture of the reaction profile, where each point would be fully optimised on both the forward and reverse reaction however this inevitably places a much increased demand on resources. One of the key steps is of great importance is the ability to model reactions where there is clearly a solvent effect either on rate or on selectivities. For example the effect on aromatic complexation in ionic liquids is of particular importance. Ionic solvents have been recognised as an environmentally greener alternative than organic counterparts.²⁰³ In addition, it has been demonstrated that they can improve the rates and the selectivities

in a number of reactions.^{204,205} Of particular interest is the increased solubility of benzene within an ionic media, relative to similar sized aliphatic compounds.^{206,207} The presence of the π electrons enable a stronger electrostatic field, this coupled with increased polarisability lead to addition stabilisation of the benzene within the ionic medium.²⁰³ By modifying the Ar-Cl' system with an ionic liquid models such as imidizole would provide an interesting area of research. Similarly, the study could also be extended to other electron deficient systems such as cations. The cation- π interaction is generally dominated by electrostatic and cation-induced polarisation.²⁰⁸ DFT and *ab initio* methods have been used in comparative studies of cation- and anion- π interactions.²⁰⁹ A particular feature was found that for a number of complexes (Benzene complexed with the following, H⁺/Li⁺/Na^{+/}F⁻/Cl⁻/Br⁻) the binding energies were large and negative indicating that formation is favorable. Cation- π distances were typically found to be 1.1-2.4Å and have the more negative energies, presumably because the shorter distances allow for more effective polarisation of the π cloud in relation to anion- π distances calculated ca. 3.5Å.²⁰⁹ The DFT (B3LYP) approach was found to overestimate the interaction in cation- π complexes and underestimate the interaction in anion- π complexes. The interaction of ionic and electron deficient moieties in aromatic systems have a profound effect in many reactions and a theoretical approach to these may lead to a greater understanding and insight into the structure-reactivity/selectivity relationship of non-covalent aromatic stabilisation.

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		<u>ŋ</u>	<u>1-complex</u>			<u>n</u> 2	complex		<u>n₆ complex</u>
	Basis Set				Basis Set				Basis Set
	6-31G*	6-31G**	6-311G**	6-311+G**	6-31G*	6-31G**	6-311G**	6-311+G**	6-31G**
<u>Bond (Å)</u> <u>C1-C2</u>	1.392	1.391	1.389	1.389	1.410	1.410	1.408	1.407	1.405
<u>C2-C3</u>	1.406	1.406	1.403	1.404	1.399	1.399	1.396	1.397	1.393
<u>C3-C4</u>	1.404	1.404	1.401	1.402	1.389	1.389	1.386	1.386	1.395
<u>C4-C5</u>	1.388	1.387	1.385	1.385	1.409	1.409	1.407	1.408	1.405
<u>C5-C6</u>	1.406	1.405	1.403	1.403	1.409	1.409	1.407	1.408	1.405
<u>C6-C1</u>	1.408	1.408	1.405	1.406	1.403	1.403	1.401	1.401	1.396
<u>H1-C6</u>	1.085	1.084	1.082	1.083	1.085	1.085	1.083	1.083	1.086
<u>H2-C1</u>	1.085	1.085	1.083	1.084	1.085	1.085	1.083	1.083	1.086
<u>H3-C2</u>	1.086	1.086	1.084	1.085	1.085	1.085	1.083	1.083	1.086
<u>H4-C3</u>	1.086	1.086	1.084	1.085	1.086	1.085	1.083	1.083	1.086
<u>H5-C4</u>	1.086	1.085	1.083	1.085	1.086	1.086	1.084	1.084	1.086
<u>H6-C5</u>	1.088	1.085	1.083	1.084	1.086	1.086	1.084	1.084	1.086
<u></u>	2.716	2.718	2.721	2.720	2.763	2.765	2.769	2.769	3.265

Table A1.1 Variation of geometries of the unconstrained ROB3LYP models with basis set.

Та	ble	A1	.2.	Variat	tion	of	Geometry	effects	on	the	η_2	comp	le	x.
_											-			

METHOD								
	<u>R</u>	OB3LYP	U	B3LYP	<u>R(</u>	<u>DB3PW91</u>	U	B3PW91
BASIS SET	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
<u>Bond (A)</u> <u>C1-C2</u>	1.405	1.405	1.405	1.405	1.403	1.404	1.402	1.404
<u>C2-C3</u>	1.412	1.412	1.412	1.412	1.409	1.410	1.410	1.410
<u>C3-C4</u>	1.40	1.401	1.400	1.401	1.398	1.399	1.398	1.399
<u>C4-C5</u>	1.390	1.391	1.390	1.391	1.388	1.389	1.388	1.388
<u>C5-C6</u>	1.411	1.412	1.411	1.412	1.409	1.410	1.408	1.401
<u>C6-C1</u>	1.393	1.394	1.393	1.387	1.391	1.392	1.391	1.392
<u>H1-C6</u>	1.087	1.091	1.087	1.091	1.087	1.091	1.087	1.091
<u>H2-C1</u>	1.086	1.089	1.086	1.089	1.086	1.090	1.086	1.090
<u>H3-C2</u>	1.086	1.089	1.086	1.089	1.086	1.090	1.086	1.090
<u>H4-C3</u>	1.086	1.089	1.086	1.090	1.086	1.090	1.086	1.090
<u>H5-C4</u>	1.086	1.090	1.086	1.090	1.087	1.090	1.086	1.090
<u>H6-C5</u>	1.086	1.090	1.086	1.091	1.087	1.090	1.087	1.090
<u>d1</u>	2.774	2.748	2.775	2.750	2.709	2.680	2.712	2.681

Table A1.2. Cor	Table A1.2. Continued										
NETHOD		$\underline{\eta}^2 \underline{\text{complex}}$									
METHOD	ROBH&HL	YP	UBH&HL	YP							
BASIS SET	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ							
<u>Bond (Å)</u> <u>C1-C2</u>	1.394	1.395	1.394	1.395							
<u>C2-C3</u>	1.396	1.397	1.396	1.397							
<u>C3-C4</u>	1.391	1.392	1.391	1.392							
<u>C4-C5</u>	1.382	1.382	1.382	1.382							
<u>C5-C6</u>	1.397	1.398	1.397	1.399							
<u>C6-C1</u>	1.384	1.385	1.384	1.384							
<u>H1-C6</u>	1.078	1.082	1.078	1.082							
<u>H2-C1</u>	1.078	1.082	1.077	1.082							
<u>H3-C2</u>	1.077	1.082	1.077	1.082							
<u>H4-C3</u>	1.078	1.082	1.077	1.082							
<u>H5-C4</u>	1.078	1.082	1.078	1.082							
<u>H6-C5</u>	1.078	1.082	1.078	1.082							
<u>d1</u>	2.825	2.795	2.817	2.786							

<u>METHOD</u> BASIS SET	ROB3LYP	<u>UB3LYP</u> 6-31+G*	<u>ROB3PW91</u> 6-31+G*	<u>UB3PW91</u> 6-31+G*	ROBH&HLYP	UBH&HLYP 6-31+G*
<u>Bond (Å)</u> <u>C1-C2</u>	1.410	1.410	1.408	1.408	1.396	1.397
<u>C2-C3</u>	1.393	1.393	1.391	1.391	1.385	1.385
<u>C3-C4</u>	1.407	1.408	1.405	1.405	1.394	1.395
<u>C4-C5</u>	1.406	1.406	1.403	1.403	1.393	1.394
<u>C5-C6</u>	1.389	1.389	1.387	1.387	1.382	1.382
<u>C6-C1</u>	1.407	1.408	1.405	1.405	1.394	1.395
<u>H1-C6</u>	1.086	1.086	1.086	1.086	1.078	1.078
<u>H2-C1</u>	1.085	1.085	1.086	1.086	1.077	1.077
<u>H3-C2</u>	1.086	1.086	1.086	1.086	1.078	1.077
<u>H4-C3</u>	1.086	1.086	1.086	1.086	1.078	1.078
<u>H5-C4</u>	1.087	1.087	1.087	1.087	1.078	1.078
<u>H6-C5</u>	1.086	1.086	1.087	1.087	1.078	1.078
<u>d1</u>	2.730	2.720	2.666	2.659	2.774	2.742

Table A1.3. Variation of geometry effects on the η 1 complex with theoretical method.

Table AT.4. variation of geometry encets on the o-complex with theoretical method.						
<u>σ-complex</u>						
METHOD	ROB3LYP	<u>UB3LYP</u>	<u>ROB3PW91</u>	<u>UB3PW91</u>	ROBH&HLYP	UBH&HLYP
BASIS SET	6-31+G*	6-31+G*	6-31+G*	6-31+G*	6-31+G*	6-31+G*
<u>Bond (Å)</u> <u>C1-C2</u>	1.415	1.416	1.414	1.416	1.471	1.473
<u>C2-C3</u>	1.389	1.389	1.387	1.386	1.357	1.362
<u>C3-C4</u>	1.403	1.403	1.400	1.401	1.409	1.409
<u>C4-C5</u>	1.403	1.404	1.400	1.401	1.409	1.409
<u>C5-C6</u>	1.389	1.389	1.387	1.386	1.357	1.362
<u>C6-C1</u>	1.415	1.416	1.414	1.416	1.470	1.473
<u>H1-C6</u>	1.086	1.086	1.086	1.086	1.077	1.077
<u>H2-C1</u>	1.084	1.084	1.085	1.085	1.083	1.083
<u>H3-C2</u>	1.086	1.086	1.086	1.086	1.077	1.077
<u>H4-C3</u>	1.086	1.086	1.087	1.087	1.078	1.078
<u>H5-C4</u>	1.087	1.087	1.087	1.087	1.077	1.077
<u>H6-C5</u>	1.086	1.086	1.087	1.087	1.078	1.078
<u>d1</u>	2.606	2.585	2.530	2.493	1.923	1.916

Table A1.4. Variation of geometry effects on the σ -complex with theoretical method.

Potential energy curves calculated at B3LYP/6-31G(d). ZPE corrections have not been included.



Chart A2.1. Structure 4.















Chart A2.7. Structure 11.









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UV/Visible



Figure A2.1. Calculated UV/Visible spectra for the C_6H_6F σ -complex 4.


Figure A2.2. Calculated UV/Visible spectra data for the C_6H_6Br complex.



Figure A2.3. Calculated UV/Visible spectra data for the C_6H_6I complex.





Figure A2.5. Calculated UV/Visible spectra data for the C₆H₆CH₃ complex 14.

Table A3.1. Geometric parameters for toluene-chlorine ipso isomer. Structure, 20a

Methods	C_1 - C_6	C_1-C_2	C ₂ -C ₃	C_3-C_4	C ₄ -C ₅	C5-C6	C ₇ -C ₁	d1	al	a2
B3LYP/6-31G*	1.421	1.421	1.387	1.400	1.400	1.387	1.507	2.653	95.3	170.1
B3PW91/6-31G*	1.420	1.420	1.385	1.399	1.398	1.385	1.503	2.570	95.8	169.0
BH&HLYP/6-31G*	1.408	1.408	1.379	1.390	1.389	1.379	1.501	2.632	94.5	171.1

Table A3.2. Geometric parameters for toluene-chlorine ortho isomer. Structure, 20b

Methods	C_1 - C_6	C_1 - C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_7-C_1	d1	a1	a2
B3LYP/6-31G*	1.392	1.425	1.416	1.386	1.402	1.400	1.504	2.541	105.1	171.5
B3PW91/6-31G*	1.390	1.426	1.399	1.383	1.400	1.417	1.498	2.444	105.8	169.1
BH&HLYP/6-31G*	1.383	1.413	1.405	1.377	1.391	1.391	1.497	2.517	103.8	171.9

Table A3.3. Geometric parameters for toluene-chlorine para isomer. Structure, 20a

Methods	C_1-C_6	C_1-C_2	C_2-C_3	C ₃ -C ₄	C_4-C_5	C5-C6	C ₇ -C ₁	d1	a1	a2
B3LYP/6-31G*	1.408	1.408	1.385	1.415	1.415	1.385	1.507	2.568	105.2	172.3
B3PW91/6-31G*	1.407	1.407	1.382	1.415	1.415	1.382	1.502	2.511	104.1	170.4
BH&HLYP/6-31G*	1.397	1.397	1.377	1.403	1.403	1.377	1.500	2.551	103.8	173.0

Table A3.4. Geometric parameters for anisole-chlorine ortho isomer. Structure, 21b.

Methods	C_1-C_6	C_1 - C_2	C_2-C_3	C ₃ -C ₄	C_4-C_5	C_5-C_6	C_2-O_1	d1	a1	a2
B3LYP/6-31G*	1.414	1.424	1.408	1.382	1.414	1.379	1.341	2.601	104.6	172.3
B3PW91/6-31G*	1.410	1.422	1.408	1.384	1.414	1.377	1.341	2.544	103.4	170
BH&HLYP/6-31G*	1.409	1.410	1.396	1.374	1.404	1.367	1.331	2.544	103.4	170

Table A3.5. Geometric parameters for anisole-chlorine para isomer. Structure, 21c

Methods	C_1 - C_6	C_1 - C_2	C_2-C_3	C ₃ -C ₄	C ₄ -C ₅	C5-C6	C_4-O_1	d1	a1	a2
B3LYP/6-31G*	1.414	1.417	1.378	1.414	1.408	1.386	1.350	2.570	105.7	172.2
B3PW91/6-31G*	1.412	1.411	1.378	1.423	1.410	1.381	1.352	2.480	104.7	173.7
BH&HLYP/6-31G*	1.402	1.408	1.368	1.402	1.396	1.378	1.338	2.530	104.5	172.1

 Table A3.6. Geometric parameters for nitrobenzene-chlorine ipso isomer. Structure, 22a

Methods	C_1-C_6	C_1-C_2	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	C5-C6	C ₂ -N	d1	a1	a2
B3LYP/6-31G*	1.389	1.405	1.405	1.389	1.400	1.400	1.482	2.749	95.0	173.3
B3PW91/6-31G*	1.386	1.404	1.404	1.386	1.398	1.398	1.478	2.673	95.1	172.6
BH&HLYP/6-31G*	1.382	1.388	1.388	1.382	1.388	1.388	1.461	2.624	91.7	177.1

Table A3.7. Geometric parameters for nitrobenzene-chlorine meta isomer. Structure, 22d

Methods	C_1 - C_6	$C_1 - C_2$	C ₂ -C ₃	C ₃ -C ₄	C_4-C_5	C ₅ -C ₆	C ₂ -N	d1	a1	a2
B3LYP/6-31G*	1.410	1.386	1.397	1.398	1.390	1.413	1.475	2.597	102.4	174.0
B3PW91/6-31G*	1.411	1.383	1.395	1.396	1.388	1.413	1.470	2.508	102.7	172.4
BH&HLYP/6-31G*	1.395	1.379	1.386	1.386	1.383	1.398	1.458	2.671	100.4	179.5

Table A3.8. Geometric parameters for fluorine-chlorine ortho isomer. Structure, 23b

Methods	C_1 - C_6	C_1 - C_2	C ₂ -C ₃	C_3-C_4	C_4-C_5	C5-C6	Cl-C ₆	d1	a1	a2
B3LYP/6-31G*	1.389	1.405	1.405	1.389	1.400	1.400	1.482	2.582	95.0	173.3
B3PW91/6-31G*	1.386	1.404	1.404	1.386	1.398	1.398	1.478	2.673	95.1	172.6
BH&HLYP/6-31G*	1.382	1.388	1.388	1.382	1.388	1.388	1.461	2.593	91.7	177.1

Table A3.9. Geometric parameters for fluorone-chlorine para isomer. Structure, 23c.

Methods	C_1 - C_6	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C5-C6	Cl-C ₆	d1	a1	a2
B3LYP/6-31G*	1.410	1.386	1.397	1.398	1.390	1.413	1.475	2.581	102.4	174.0
B3PW91/6-31G*	1.411	1.383	1.395	1.396	1.388	1.413	1.470	2.472	102.7	172.4
BH&HLYP/6-31G*	1.395	1.379	1.386	1.386	1.383	1.398	1.458	2.583	100.4	179.5

Table A3.10. Geometric parameters for chlorobenzene-chlorine ortho isomer. Structure, 24b

Methods	C_1-C_6	C_1-C_2	C_2-C_3	C ₃ -C ₄	C ₄ -C ₅	C5-C6	Cl-C ₆	d1	al	a2
B3LYP/6-31G*	1.406	1.413	1.392	1.407	1.402	1.383	1.743	2.585	103.4	173.0
B3PW91/6-31G*	1.416	1.416	1.384	1.400	1.397	1.387	1.729	2.464	103.5	173.1
BH&HLYP/6-31G*	1.394	1.399	1.385	1.392	1.391	1.375	1.731	2.632	101.5	174.8

Table A3.11. Geometric parameters for chlorobenzene-chlorine para isomer. Structure, 24c

Methods	C_1-C_6	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C5-C6	Cl-C ₅	d1	a1	a2
B3LYP/6-31G*	1.408	1.411	1.388	1.408	1.405	1.382	1.740	2.583	105.4	172.6
B3PW91/6-31G*	1.415	1.415	1.383	1.401	1.401	1.383	1.733	2.474	105.5	172.7
BH&HLYP/6-31G*	1.395	1.399	1.381	1.395	1.393	1.375	1.728	2.599	103.5	173.9

Table A3.12. Geometric parameters for bromobenzene-chlorine ortho isomer. Structure, 25b

Methods	C_1 - C_6	C_1-C_2	C_2-C_3	C ₃ -C ₄	C ₄ -C ₅	C5-C6	C ₃ -Br	d1	al	a2
B3LYP/6-31G*	1.406	1.413	1.392	1.407	1.401	1.383	1.895	2.585	103.6	173.1
B3PW91/6-31G*	1.405	1.412	1.389	1.407	1.400	1.381	1.879	2.501	104.3	171.3
BH&HLYP/6-31G*	1.394	1.399	1.384	1.393	1.391	1.375	1.881	2.621	101.5	174.9

Table A3.13. Geometric parameters for bromobenzene-chlorine para isomer. Structure, 25c										
Methods	C_1-C_6	$C_1 - C_2$	C_2-C_3	C ₃ -C ₄	C ₄ -C ₅	C ₅ -C ₆	C ₅ -Br	d1	a1	a2
B3LYP/6-31G*	1.407	1.389	1.407	1.405	1.383	1.411	1.892	2.589	105.5	172.7
B3PW91/6-31G*	1.407	1.386	1.407	1.404	1.380	1.411	1.878	2.507	105.9	171.0
BH&HLYP/6-31G*	1.401	1.379	1.388	1.390	1.378	1.401	1.885	2.591	103.0	174.0

Table A3.14. Geometric parameters for aniline-chlorine ipso isomer. Structure 26a

Methods	C_1-C_6	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_2-N_1	d1	al	a2
B3LYP/6-31G*	1.384	1.425	1.425	1.384	1.401	1.401	1.369	2.779	92.3	170.9
B3PW91/6-31G*	1.382	1.425	1.425	1.382	1.399	1.399	1.364	2.713	92.1	170
BH&HLYP/6-31G*	1.409	1.424	1.400	1.376	1.405	1.363	1.363	2.771	88.3	172.2

 Table A3.15. Geometric parameters for aniline-chlorine ortho isomer. Structure 26b

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Methods	C_1 - C_6	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_2-N_1	d1	a1	a2
B3LYP/6-31G*	1.411	1.432	1.412	1.382	1.414	1.380	1.367	2.571	110.6	169.1
B3PW91/6-31G*	1.382	1.432	1.408	1.382	1.412	1.377	1.363	2.472	110.1	166.4
BH&HLYP/6-31G*	1.408	1.420	1.400	1.374	1.405	1.367	1.362	2.475	105.8	170.2

Table A3.16. Geometric parameters for aniline-chlorine para isomer. Structure,26c

Mathe	CC	00	CC	CC	CC	CC	CN	41	-1	<u></u>
Methods	$C_1 - C_6$	$C_1 - C_2$	$C_2 - C_3$	C3-C4	$C_4 - C_5$	C5-C6	$C_2 - N_1$	ar	al	az
B3LYP/6-31G*	1.378	1.417	1.417	1.378	1.416	1.416	1.370	2.569	106.5	171.9
B3PW91/6-31G*	1.375	1.415	1.415	1.375	1.416	1.416	1.365	2.486	106.8	170
BH&HLYP/6-31G*	1.368	1.406	1.406	1.368	1.408	1.408	1.364	2.503	105.5	170.8

Table A3.17. Geometric parameters for phenol-chlorine ortho isomer. Structure, 24b

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Methods	C_1-C_6	C_1-C_2	C_2-C_3	C ₃ -C ₄	C_4-C_5	C5-C6	C ₅ -O	d1	al	a2
B3LYP/6-31G*	1.413	1.380	1.415	1.387	1.401	1.427	1.344	2.552	114.5	166.7
B3PW91/6-31G*	1.415	1.377	1.412	1.386	1.397	1.428	1.339	2.445	115.1	163.3
BH&HLYP/6-31G*	1.408	1.369	1.403	1.379	1.388	1.414	1.336	2.470	111.1	166.5

Table A3.18. Geometric parameters for phenol-chlorine para isomer. Structure, 24c

Methods	C_1-C_6	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C5-C6	C5-O	d1	a1	a2
B3LYP/6-31G*	1.383	1.415	1.416	1.380	1.409	1.409	1.353	2.566	105.7	172.0
B3PW91/6-31G*	1.380	1.416	1.417	1.378	1.407	1.406	1.348	2.479	106.0	170.1
BH&HLYP/6-31G*	1.375	1.404	1.407	1.371	1.397	1.395	1.342	2.530	104.4	172.1

UV-vis spectra





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