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Graphical Abstract

Self Sensitized Photooxidation of Tetrathienyltetrathia-fulvalenes: Synthesis of Thienyl substituted 1,2,5,8-tetrathiecine-6,7-dione, a New Heterocyclic System

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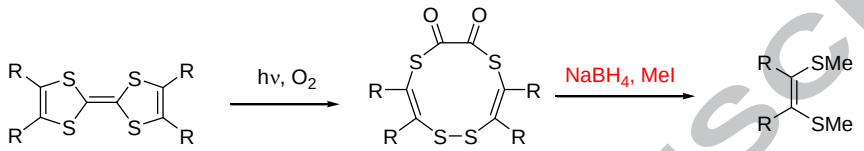

R = 2- or 3-thienyl

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Self Sensitized Photooxidation of Tetrathienyltetrathiafulvalenes : Synthesis of Thienyl substituted 1,2,5,8-tetrathiecine-6,7-dione, a New Heterocyclic System

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ARTICLE INFO

ABSTRACT

Irradiation of tetrathienyltetrathiafulvalenes in an oxygen saturated solution gives tetrathienylsubstituted 1,2,5,8-tetrathiecine-6,7-diones, *via* singlet oxygen generation followed by cycloaddition onto the TTF double bond and a final rearrangement process. The thermal and photochemical behaviour and reductive methylation of this new class of macro-heterocyclic system has also been investigated.

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Tetrathiafulvalene (TTF) derivatives have been extensively studied due to their usefulness as organic polymeric conducting and photo-switchable materials for applications such as transistors and solar cells.[1] We have previously prepared the tetrathienyl substituted systems **1a,b** and have studied their electrochemical properties and applications.[2] We were next interested in the preparation of the planar conjugated systems **A** (fig. 1) and we envisaged that these might be accessed *via* the known TTF derivatives **1a** and **1b**.

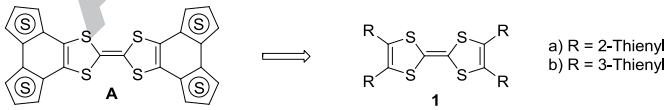
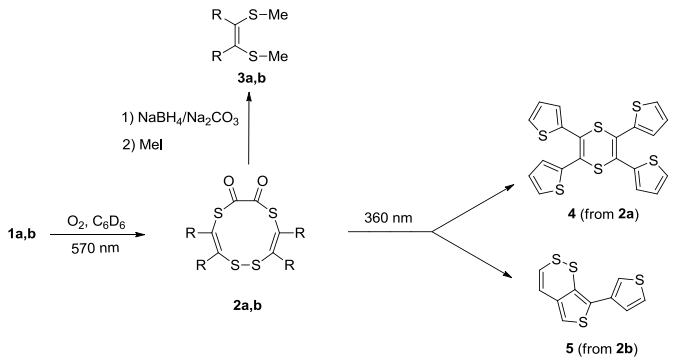


Figure 1 – Possible Synthetic Targets

Based on our previous work on the photooxidative cyclisation of thienyl substituted systems which afforded aromatic polycondensed heterocycles,[3] we considered the possibility of employing iodine as a photo-oxidant. Initial experiments on both **1a** and **1b** using this reagent were unsuccessful, as even in the absence of irradiation, the reaction of iodine with either compound led to the formation of insoluble tar material. Consequently we studied the irradiation of **1a** and **1b** in an oxygen saturated solution. However, under these conditions it was found that a completely different reaction pathway was observed and the thienyl substituted 1,2,5,8-tetrathiecine-6,7-diones **2a** and **2b** (scheme 1) were formed in near quantitative yields.[4] The structure of compound **2b** was confirmed by X-ray analysis (fig. 2).



Scheme 1- Photochemical synthesis and reactivity of 1,2,5,8-tetrathiecine-6,7-diones

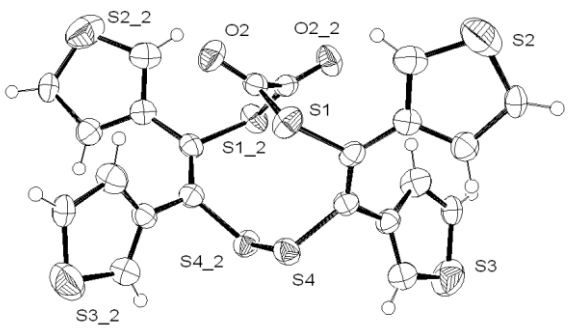


Figure 2- Crystal structure of the asymmetric unit of compound **2b** Ellipsoids enclose 30% probability.[5] C_6D_6 crystallization molecule was removed for clarity.

Confirmation of the structure of compound **2a**, which did not give suitable crystals for X-ray analysis, was obtained by comparison of IR, ^{1}H- and ^{13}C data with that for **2b,** which supported the assignment. Further to this, reductive ring opening/methylation of the heteromacrocyclic system gave the corresponding dithioethenes **3a,b**, whose structures were confirmed by X-ray analysis (fig. 3 and 4).

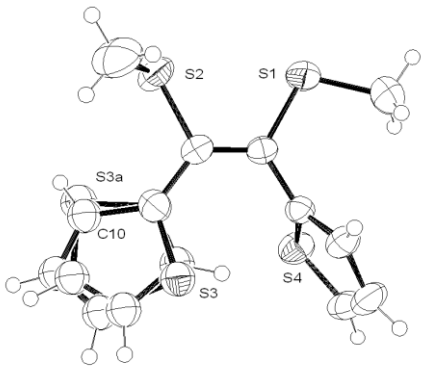


Figure 3- Crystal structure of compound **3a**. Ellipsoids enclose 50% probability.[6]

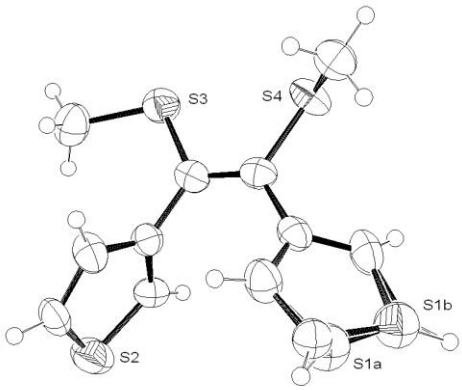
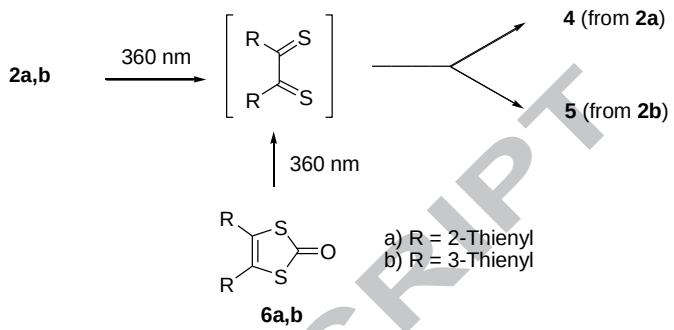


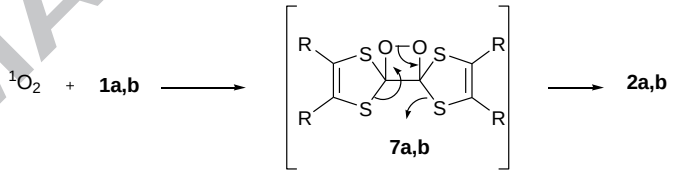
Figure 4- Crystal structure of compound **3b**. Ellipsoids enclose 50% probability.[7]

It was also determined that compounds **2a,b** are also stable to further irradiation at 570 nm, however at shorter wavelengths (360 nm) both decompose to give tetrathienyl-1,4-dithiine **4**[8b] and 1,2-dithiine **5**[8a], respectively (scheme 2).We previously reported[8a-c] the same behavior during the photorearrangement of the corresponding thienyl-1,3-dithiolones **6a,b,** where the formation of a dithioketone intermediate explains this outcome in both cases (scheme 2).[8d]



Scheme 2 – Photofragmentation of 1,2,5,8-tetrathiecine-6,7-diones

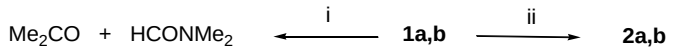
A mechanistic rationale for the formation of **2a,b** is that photochemically excited **1a,b** both act as sensitizers of singlet oxygen, which undergoes cycloaddition to the double bond of **1a,b** to give the unstable dioxetanes **7a,b**. These intermediates then undergo rearrangement to the tetrathiecines **2a,b** which represents a previously unreported heterocyclic system. (Scheme 3)



Scheme 3 – Mechanism for the formation of compounds **2a,b**

An analogous singlet oxygen cycloaddition-rearrangement sequence was previously reported for some tetrathioethenes however in this case, the presence of an independent sensitizer was required,[9] whereas **1a,b** undergo self-sensitized photooxidation.

To confirm this role of tetrathiafulvalenes, we observed that during the irradiation of an oxygen saturated solution of **1a,b** in the presence of an excess of the singlet oxygen trapping agent *N,N*-dimethyl-2-propenamine, the formation of compounds **2a,b** was not observed. The only products observed were those arising from reaction of the enamine with singlet oxygen (propanone and dimethylformamide) as evidenced by GC-MS analysis. Similarly an experiment with an oxygen saturated solution of **1a,b** in the presence of methylene blue (a singlet oxygen sensitizer), with irradiation at 670 nm, which is a photochemically inert region for the tetrathiafulvalenes, gave compounds **2a,b** in quantitative yield (scheme 4).



i) 570 nm, O_2, benzene, *N,N*-dimethyl-2-propenamine
ii) 670 nm, O_2, chloroform, methylene blue

Scheme 4 – Singlet oxygen trapping and sensitization experiments

In summary, the first synthesis of a 1,2,5,8-tetrathiecine-6,7-dione, a new macroheterocylic structure, is reported from tetrathiafulvalenes and singlet oxygen. In addition, the observation that tetrathiafulvalenes act as singlet oxygen sensitizers and substrates might be of importance, especially as these compounds are used in photoswitchable devices and solar cells.

Acknowledgments

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4. Melting points were measured with a Kofler apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded at 200MHz and 50MHz, respectively on a Bruker AC 200F spectrometer or at 400 MHz and 100 MHz, respectively, on a Bruker Advance DPX400 instrument. Chemical shifts are reported relative to tetramethylsilane at 0.00 ppm. ESI- MS spectra were recorded with a LCQ-DECA Thermo Finnigan instrument. GC–MS experiments were carried out with a Saturn 2000 ion trap (EI, 70 eV) coupled with a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA, USA) equipped with a J&W DB5-MS column (30 m_0.25 mm ID, 0.25 µm film thickness). Photochemical experiments were carried out with a Photoirradiation system equipped with a 900 W Xenon source and a high radiance monochromator. Elemental analyses were performed on a Perkin Elmer PE 2004 Elemental Analyzer.

   Photochemistry of TTF: general procedure. A solution of tetrathiafulvalenes **1a** [λmax (logε) 337sh (4.19), 407 (3.67), 475 (2.95) (C_6H_6)]or, **1b** [λmax, logε) 340 (3.29), 406 (2.73) 480sh (2.02) (C_6H_6)]] (5.6 mg, 0.01 mmol) in C_6D_6 (0.5 mL) in a 5 mm nmr tube was saturated with oxygen by bubbling for 30 min. Light at the suitable wavelength, obtained from the above reported irradiation system, was focused on the solution. The progress of the reaction was monitored by ^{1}H-nmr analysis over 4 h.

   *(3Z,9Z)-3,4,9,10-tetra(thiophen-2-yl)-1,2,5,8-tetrathiecine-6,7-dione (**2a**):* The solvent was removed to give a waxy material (quantitative yield) which was characterized without further purification. Attempted crystallization was unsuccessful. Ir (KBr) 3100, 2925, 1665, 1408, 1216, 790 cm^{-1}; *m/z* (ESI): 587 (M+Na); ^{1}H-NMR (200MHz, $CDCl_3$) δ: 6.89 (apparent t, *J* = 4.5 Hz, 1 H), 6.98 (apparent t, *J* = 4.5 Hz, 1 H), 7.25 (d, *J* = 4.5 Hz, 1 H), 7.28 (d, *J* = 4.5 Hz, 1 H), 7.31 (d, *J* = 4.5 Hz, 1 H), 7.48 (d, *J* = 4.5 Hz, 1 H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 127.1, 128.1, 129.9, 130.1, 130.6, 131.7, 132.6, 142.7, 143.0, 190.9. Anal. $C_{22}H_{12}O_2S_8$: Expected C 46.78; H 2.14; Found: C 46.52; H 2.34.

   *(3Z,9Z)-3,4,9,10-tetra(thiophen-3-yl)-1,2,5,8-tetrathiecine-6,7-dione (**2b**)*: The reaction mixture was transferred to a small vial and slow evaporation at 5°C gave crystals of **2b**, suitable for X-ray analysis. m.p. 115-117°C (decomp.), yield 75%, Ir (KBr) 3099, 2922, 1660, 1410, 1078, 783 cm^{-1}; *m/z* (ESI): 587 (M+Na); ^{1}H-NMR (400 MHz, C_6D_6) δ: 6.59 (m, 1 H), 6.70 (m, 2 H), 7.02 (dd, *J* = 4.5, 1.0 Hz, 1 H), 7.39 (m, 2 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 125.0, 127.4, 128.6, 128.7, 128.9, 129.7, 132.6, 140.5, 140.8, 145.9, 191.7. Anal. $C_{22}H_{12}O_2S_8$: Expected C 46.78; H 2.14; Found: C 46.63; H 2.29.

   *(Z)-1,2-bis(methylthio)-1,2-di(thiophen-2-yl)ethene (**3a**)*: To a stirred solution of **2a** (0.0056 g, 0.01 mmol) in ethanol (2 ml) were added of sodium borohydride (0.002 g, 0.03 mmol) and sodium carbonate (0.003 g, 0.03 mmol) dissolved in the minimum amount of water. After 2 h the solvent was removed and the residue was treated with water (3 ml) with containing dilute hydrochloric acid (0.03 mmol. Extraction with dichloromethane, drying ($MgSO_4$) and evaporation gave a oily residue which was purified by preparative layer chromatography eluting with ethyl acetate/light petroleum (1:3 v/v) to give compound **3a**, yield 82%, m.p. 68-70°C (cyclohexane); *m/z* (GC-MS): 284 (M^{+}), 222, 190; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.11 (s, 6 H), 6.84-6.89 (m, 4 H), 7.18-7.22 (m, 2 H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 16.5, 126.5, 126.6, 128.5, 132.3, 139.9. Anal. $C_{12}H_{12}S_4$ Expected 50.66; H, 4.25; Found: C, 50.48; H, 4.36.

   *(Z)-1,2-bis(methylthio)-1,2-di(thiophen-3-yl)ethene (**3b**:* Using the method described for **3a**, **3b** was obtained as a solid in 87% yield, m.p. 73-75°C (cyclohexane); *m/z* (GC-MS): 284 (M^{+}), 222, 190, 177; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.01 (s, 6 H), 6.78 (d, *J* = 4.8, 2 H), 6.89 (d, *J* = 1.9, 2 H), 7.12 (dd, *J* = 4.8, 1.9, 2 H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 16.2, 124.4, 124.9, 128.8, 130.6, 138.3. Anal. $C_{12}H_{12}S_4$ Expected 50.66; H 4.25; Found: C 50.74; H 4.31.

5. *Crystal data for **2b*** $C_{22}H_{12}O_2S_8$. C_6D_6 (CCDC 905430): M_W= 648.94, monoclinic, space group C 2/c, a = 25.434(1)Å, b = 8.2192(3) Å, c = 14.5227(8) Å, α = 90, β = 109.892(6), γ = 90 °, V = 2854.7(3) Å^3, Z = 4, D_c = 1.51 mg/mm^3, F (000) = 1320, crystal dimension 0.25 _ 0.15 _ 0.10 mm, radiation, MoK$_\alpha$ (λ = 0.71073 Å), 3274 intensity data were collected at 293(2) K, employing ω/2θ scanning technique, in the range of -13h32,-10k10, -19l19; the structure was solved by a direct method, all non-hydrogen were refined anisotropically from 2105 observed reflections by a full-matrix least-squares technique. R = 0.0702 [I > 2σ(I)] and wR$_2$(all data) = 0.2576

6. *Crystal data for **3a***: $C_{12}H_{12}S_4$ (CCDC 905432): M_W= 284.46, monoclinic, space group P n, a = 5.7939(3)Å, b = 7.6703(3) Å, c = 15.4023(6) Å, α = 90, β = 95.351(4), γ = 90 °, V = 681.50(5) Å^3, Z = 2, D_c = 1.386 mg/m3, F (000) = 296, crystal dimension 0.3 _ 0.1 _ 0.1 mm, radiation, MoKα (λ = 0.71073 Å), 4790 intensity data were collected at 293(2) K, employing ω/2θ scanning technique, in the range of -7h7,-10k10, -19l18; the structure was solved by a direct method, all non-hydrogen atoms but those disordered of the thienyl moiety were refined anisotropically from 2207 observed reflections by a full-matrix least-squares technique. R = 0.0386 [I > 2σ(I)] and wR$_2$(all data) = 0.0929

7. *Crystal data for **3b***: $C_{12}H_{12}S_4$ (CCDC 905431): M_W= 284.46, orthorombic, space group P 21 21 21, a = 6.9680(4)Å, b = 10.9233(9) Å, c = 7.2725(15) Å, α = 90, β = 90, γ = 90 °, V = 1314.7(2) Å^3, Z = 42, D_c = 1.437 mg/mm^3, F (000) = 592, crystal dimension 0.25 _ 0.12 _ 0.1 mm, radiation, MoKα (λ = 0.71073 Å), 4790 intensity data were collected at 293(2) K, employing ω/2θ scanning technique, in the range of -4h9,-14k9, -23l18; the structure was solved by a direct method, all non-hydrogen atoms but those disordered of the thienyl moiety were refined anisotropically from 2504 observed reflections by a full-matrix \least-squares technique. R = 0.0446 [I > 2σ(I)] and wR$_2$(all data) = 0.1016

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