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On the Photoreactivity of 4,5-Dithiophen-3-yl-[1,3]dithiol-2-one. The First Preparation of a Thieno[3,4-*c*]dithiine

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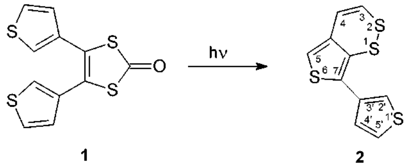
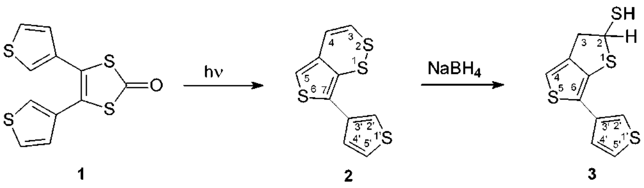
ABSTRACT



Irradiation of 4,5-dithiophen-3-yl-[1,3]dithiol-2-one 1 at λ > 330 nm gave the thieno[3,4-*c*]dithiine 2, the first example of this heterocyclic system

4,5-Dithiophen-3-yl-[1,3]dithiol-2-one **1** has proven to be a versatile precursor for the synthesis of TTFs[1−3] and metal dithiolenes[4] and for the preparation of polymer films for chemical modification.[5] With the ultimate goal of preparing the analogue of **1** in which the two thienyl rings are fused at the 2/2′ positions we attempted a photocyclization of **1** by irradiation at $\lambda > 330$ nm.[6] We found however that this failed to effect this transformation and obtained instead the thieno[3,4-*c*]dithiine **2**, which represents, to our knowledge, the first example of this heterocyclic system. (Scheme 1)

Scheme 1



The structure of this product was assigned on the basis of spectral evidence; for example, the mass spectrum gave a M^+ ion at $m/z = 254$ indicating the $C_{10}H_6S_4$ molecular formula and suggesting the loss of CO during the photoreaction. A further ion at $m/z = 190$ suggested the loss of S_2 (M-64), which was confirmed by neutral loss mass spectroscopy and indicated the presence of a −S−S− moiety in the molecule. ^1H and ^{13}C spectra, in particular 600 MHz heterocorrelated 2D experiments, were in good agreement with the proposed structure, and a NOE effect was observed between the protons at 6.92 and 7.09 ppm. (Figure 1)

Further to this, treatment of **2** with sodium borohydride led to a facile reductive cleavage of the S−S bond to give an intermediate thiol-thioaldehyde, which directly cyclized

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(1) (a) Charlton, A.; Underhill, A. E.; Kalaji, M.; Murphy, P. J.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2423.

(2) (b) Charlton, A.; Underhill, A. E.; Williams, G.; Kalaji, M.; Murphy, P. J.; Abdul Malik, K. M.; Hursthouse, M. B. *J. Org. Chem.*, **1997**, *62*, 3098.

(3) Charlton, A.; Salmaso, S.; Williams, G. O.; Kalaji, M.; Underhill, A. E.; Murphy, P. J.; Malik, K. M. A.; Hursthouse, M. B. *Synth. Met.* **1998**, *92*, 75.

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(5) Roberts-Bleming, S. J.; Kalaji, M.; Murphy, P. J. Unpublished work.

(6) Brooks, P.; Donati, D.; Pelter, A.; Ponticelli, F. *Synthesis* **1999**, 1303.

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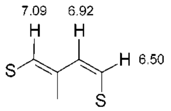
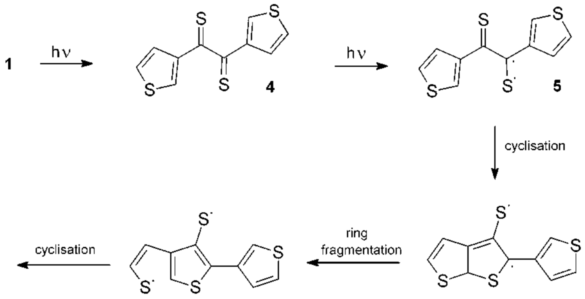


Figure 1.

to give the hemi-thioacetal derivative **3**, which gave crystals suitable for X-ray crystallographic analysis[10] confirming its structure (see Supporting Information for Ortep drawing of hemi-thioacetal **3** showing the two conformations of the thiophen-3-yl moiety).

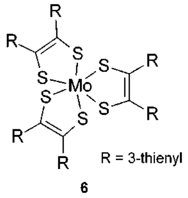
Previous reports on the photoreactivity of diarylvinylene dithiocarbonates[7,8] have reported that the loss of carbon monoxide is highly facile and should lead to the highly reactive dithione **4**. The mechanism of the reaction thus can be visualized as involving the intermediate diradical **5**, which undergoes cyclization, ring fragmentation, and a further cyclization to give **2**. (Scheme 2)

Scheme 2



It should be noted that when the photoreaction is carried out in the presence of $Mo(CO)_6$ (1 mol), the formation of **2** was completely inhibited and a deep-blue solid melting at 245−47° (decomp), with an absorption maximum at 565 nm, was obtained. On the basis of previous findings[7] we assigned the structure **6** to this compound, i.e., the formation of a metal complex between molybdenum and three molecules of the intermediate dithione **4**. (Scheme 3)

Scheme 3



In conclusion, we report the first synthesis of the thieno-[3,4-*c*]dithiine heterocyclic nucleus via a novel thiophene fragmentation process. We are currently investigating other reactions of this type and will report our findings in due course.

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Supporting Information Available: Experimental details and spectral/analytical data for synthetic intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Hartke, K.; Kissel, T.; Quante, J.; Matusch, R. *Chem. Ber.* **1980**, *113*, 1898.

(9) Sheldrick, G. *SHELX-97*, Relat. 97-2, Program for X-ray data diffraction; Göttingen University: Göttingen, 1997.

(10) **Crystal data for 3:** $C_{10}H_8S_4$, MW = 256.4, Monoclinic, $a = 38.697(6)$, $b = 4.937(2)$, $c = 11.157(2)$ Å, = 91.5(1)°, $V = 2130.8(10)$ Å^3 (by least-squares refinement of 50 randomly selected and automatically centered reflections), space group $C2/c$ (No. 15), $Z = 8$, F(000) = 1052, D_c=1.595 g cm^{-3}, μ (Mo Kα) 0.844 mm^{-1}. The data were collected on a Siemens P4 four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) in the range $-46 \leq h \leq 46$, $-1 \leq k \leq 5$, $-13 \leq l \leq 13$, ω scan mode for $3.2 \leq \theta \leq 25.0°$ scan range, scan width 1.1°, constant scan speed 3.0° min^{-1}. Three standard reflections measured every 97 reflections showed no variations; 4596 total reflections ($R_{\mathrm{int}} = 0.09$) were collected at 22 °C. Absorption correction was not applied. The structure was solved by direct methods implemented in SHELX-97.[9] The refinement was carried out by full-matrix anisotropic least-squares on F^2 for all reflections for all non-H atoms by using SHELX-97.[9] The hydrogen atoms were localized in the Fourier map and included in the structure-factor calculations. Final refinement of 166 parameters gave $R_1 = 0.050$ and $wR_2 = 0.109$ for $I > 2\sigma(I)$. Weighting scheme was $w = 1/[\sigma^2(F_o)^2 + 0.0561P^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Minimum and maximum height in last map were −0.34 and 0.34 e Å^{-3}, respectively. Atomic scattering factors, including f' and f'' were taken from ref 9. List of the fractional coordinates, bond lengths and angles, and thermal parameters have been deposited at the Crystallography Data Centre, U.K.