

Preparation and Properties of Bis[5-(6-methyl-1,4-dithiafulven-6-yl)-2-thienyl]methanes affording Near-infrared Absorbing Cations by Oxidation

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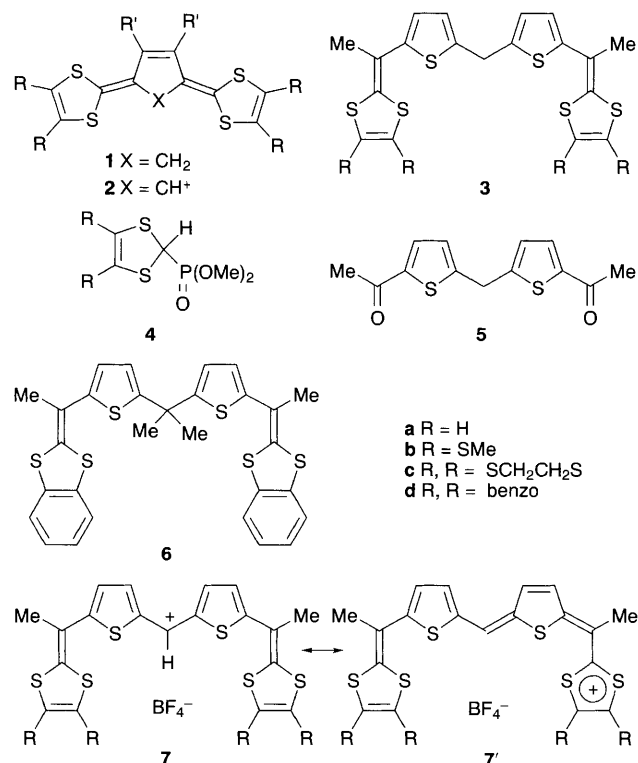
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The title bis(1,3-dithiole) compounds undergo deprotonation by oxidation to give stable cations with absorption maxima at 900–980 nm.

We reported recently that bis(1,3-dithiole) donors **1** undergo deprotonation from the dication states by oxidation to give novel deeply-coloured cations **2**.¹ Molecules possessing a methylene group adjacent to electron-donating moieties seem to undergo similar reactions to give the corresponding methyl cations. In order to show the generality of this type of reaction and to prepare interesting cations, we have now designed the title bis(1,3-dithiole) compounds **3** containing a dithienyl-methane skeleton. The resulting cations **7** are expected to be stabilized by electron-donating groups and to show interesting properties owing to their extended π -conjugation. We report here the preparation and physical properties of the compounds **3** and near-infrared (NIR) absorbing cations **7** derived from **3**.

The new compounds **3a–d** (**3a**, mp 74–75 °C; **3b**, 90–91 °C; **3c**, 167–168 °C; **3d**, 159–160 °C) were prepared by Wittig–Horner reaction of the corresponding carbanions derived from phosphonate esters **4a–d**² with ketone **5**³ in 47, 70, 93 and 86% yields, respectively.† The dimethyl derivative **6** (mp 140–142 °C) was prepared by a similar method from the corresponding ketone³ and **4d** in 33% yield.

The X-ray molecular structure of the ethylenedithio derivative **3c** is shown in Fig. 1.‡ The two thiophene rings are orthogonal, while the thienyldithiafulvenyl subunits are nearly planar with the largest deviations of 0.39 and 0.63 Å from the mean planes. The interatomic distances between the sulfur atoms of the thiophene and the dithiole (3.01 and 3.02 Å) are shorter than the sum of the van der Waals radii (3.70 Å), indicating that attractive interactions exist between them.⁴



The cyclic voltammograms of **3** showed irreversible oxidation waves (E_{pa}), but in the reverse scan new reduction peaks due to the oxidation products were observed at lower potentials (E_{pc}), as shown in Fig. 2(a). The redox potentials are summarized in Table 1. On the other hand, the dimethyl derivative **6** did not exhibit such electrochemical behaviour. These results suggest that the reduction peaks observed in the voltammograms of **3** correspond to the reduction of the cations **7** which arose from deprotonation subsequent to electrochemical oxidation of **3**.

The cations **7a–d** were actually obtained by chemical oxidation of **3a–d** with nitrosyl tetrafluoroborate in dichloromethane in 42, 32, 38 and 48% yields, respectively. They could also be obtained by hydride abstraction with triphenyl-carbenium tetrafluoroborate in dichloromethane in good yields. These cations are fairly stable, both in the solid and solution states. The ¹H NMR spectrum of **7b**§ in CD₃CN did not change

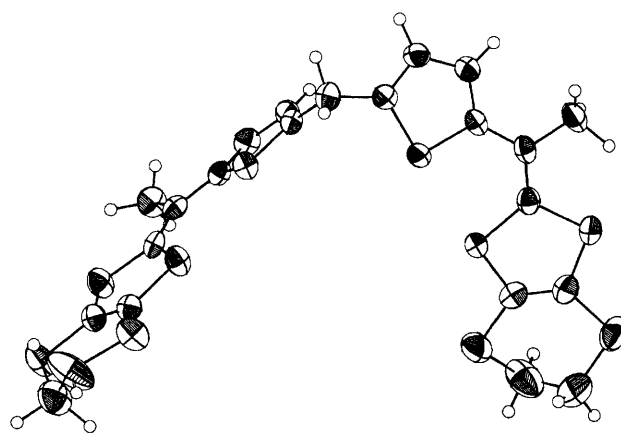


Fig. 1 Molecular structure of **3c**

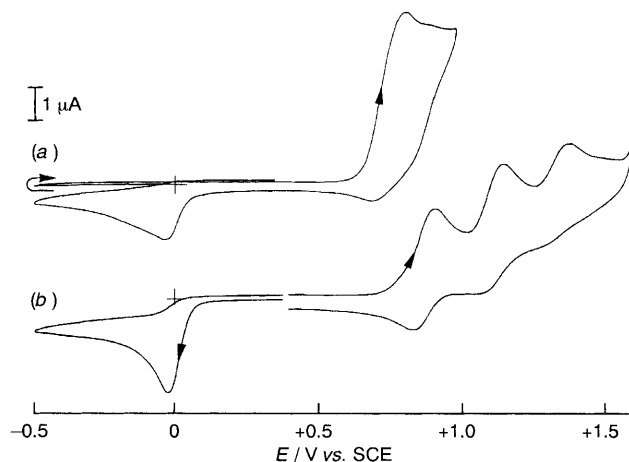


Fig. 2 Cyclic voltammograms of (a) **3b** and (b) **7b** in PhCN measured under the same conditions as given in Table 1

after storage at room temperature under air for several months. In this spectrum, the signal corresponding to the four *S*-methyl groups appeared as a broad singlet at 25 °C. Upon heating, this signal became sharp and the others shifted slightly downfield (ca. 0.15 ppm), suggesting that a conformational change occurs. The cyclic voltammograms of the cations **7a–c** in benzonitrile[¶] showed both reduction and oxidation waves, and the reduction peak potentials are in complete agreement with E_{pc} for **3a–c** [Fig. 2(b)]. For **7b**, three-stage one-electron oxidation waves corresponding to the formation of the dication radical, trication

and tetracation radical were observed at the peak potentials of 0.91, 1.15 and 1.39 V, respectively.

The cations **7** show intense absorptions in the NIR region (900–980 nm in acetonitrile) due to their polymethinecyanine type structure **7'**. The spectrum of **7b** is shown in Fig. 3 and the longest absorption maxima are summarized in Table 2. These values are considerably longer than that of some di(2-thienyl)methyl cation derivatives⁵ and 1,3-dithiolium dyes,⁶ owing to the expansion of π -conjugation. The electron-donating alkylthio groups on the 1,3-dithiole rings cause the absorptions to be greatly red-shifted. The absorption maxima observed in solution are over the absorption region for the Ga–As laser diode (780–840 nm). However, the absorptions are blue-shifted in thin films and **7b** exhibited a maximum at 824 nm as a thin film (Fig. 3). This finding indicates that they are interesting as NIR absorbing dyes.⁷ The cation **7b** reacted with sodium borohydride in acetonitrile to regenerate **3b** in 92% yield.

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Table 1 Redox potentials^a of compounds **3**

Compound	E_{pa}/V	E_{pc}/V
3a	+0.82	−0.13
3b	+0.82	−0.04
3c	+0.82	−0.05
3d	+0.93	−0.08

^a Bu₄NBF₄ (0.1 mol dm^{−3}) in PhCN, Pt electrode, scan rate 100 mV s^{−1}, E/V vs. saturated calomel electrode (SCE).

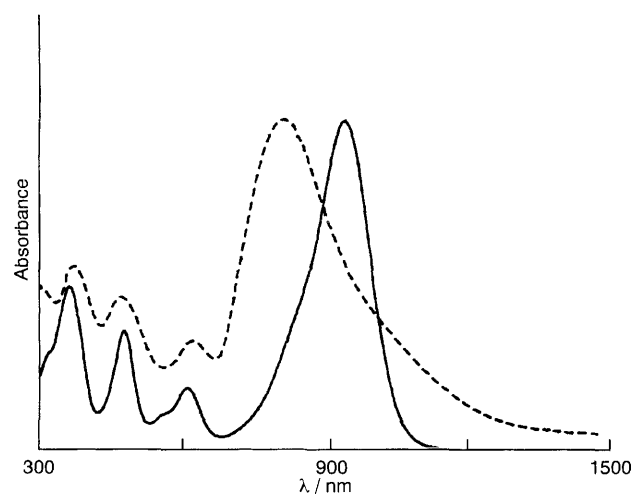


Fig. 3 Absorption spectra of **7b** in MeCN (—) and as a thin film (---)

Table 2 Melting points and absorption maxima of cations **7**

Cation	Mp (decomp.)/°C	λ_{max}/nm (log ϵ) ^a
7a	ca. 250	921 (4.85)
7b	177–179	950 (4.69)
7c	> 300	976 (4.38)
7d	281–283	906 (4.56)

^a In MeCN.

Footnotes

† Satisfactory spectral data were obtained for all new compounds.

‡ Crystal data for **3c**: C₂₃H₂₀S₁₀, $M = 617.09$, monoclinic, space group $P2_1/a$, $Z = 4$, $a = 10.551(2)$, $b = 24.797(3)$, $c = 9.907(2)$ Å, $\beta = 94.30(1)^\circ$, $V = 2584.8(8)$ Å³, $D_c = 1.59$ g cm^{−3}. The final R value is 0.0728 for 3944 reflections with $|F_o| > 3\sigma|F_o|$. The large thermal parameters for the C and H atoms of the ethylenedithio groups suggest that there exist some disorder in these regions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ ¹H NMR of **7b**, δ (CD₃CN, 25 °C) 2.04 (6H, s), 2.53 (12H, br s), 6.91 (2H, d, J 4.9 Hz), 7.27 (2H, d, J 4.9 Hz), 7.50 (1H, s).

¶ The E_{pc} value for **7d** could not be measured because of its low solubility.

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