

2,2'-(Cyclopenten-3,5-diylidene)bis(1,3-dithiole)s: Novel Electron Donors undergoing Deprotonation by Oxidation

Yoshiro Yamashita,* Shoji Tanaka and Masaaki Tomura

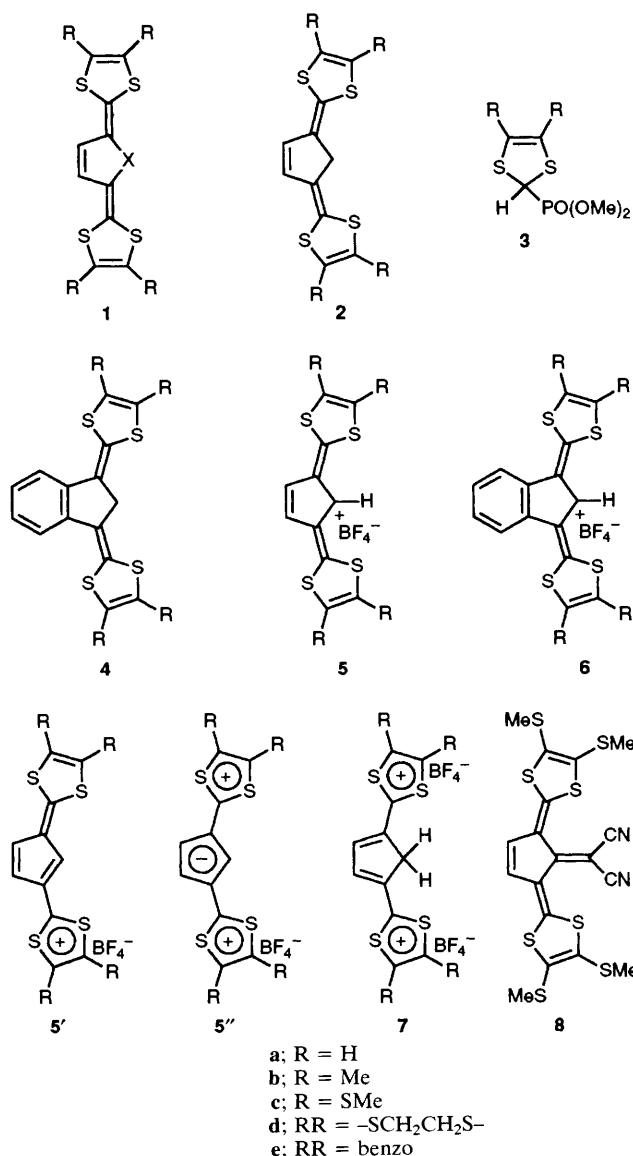
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

The title bis(1,3-dithiole) donors containing a dimethylenecyclopentene skeleton afford a novel type of deeply coloured cation by deprotonation from the dication states.

Tetrathiafulvalene (TTF) analogues **1** with extended π -conjugation have attracted much attention as electron donors giving organic conductors owing to decreased Coulombic repulsion.¹ Cation radical salts of some derivatives show a metallic temperature dependence of conductivity.² We have now

prepared the title compounds **2** containing a 3,5-dimethylenecyclopentene skeleton as new bis(1,3-dithiole) donors and found that they undergo novel deprotonation by oxidation to give interesting cations.

New donors **2b–d** (**2b**, m.p. 233–235 °C; **2c**, 152–153 °C; **2d**,



243–245 °C; **2e**, 272–277 °C) were prepared by a Wittig-Horner reaction of the corresponding carbanions derived from phosphonate esters **3** with cyclopent-4-ene-1,3-dione in **8**, **46**, **36** and **31**% yields, respectively;† the parent compound **2a** could not be isolated as stable crystals. The benzo derivatives **4d**, **e** (**4d**, m.p. 249–252 °C; **4e**, 290–295 °C) were also prepared by the similar reaction from indane-1,3-dione in **7** and **8**% yields, respectively. The successful formation of **2** and **4** is rather surprising since 1,3-diketones usually undergo deprotonation upon treatment with strong bases.

The cyclic voltammograms (CV) of the donors **2b–e** and **4d**, **4e** in benzonitrile showed irreversible waves (Fig. 1). The E_{pa} and E_{pc} values are summarized in Table 1. The E_{pa} values of **2b–e** are lower than that of TTF, indicating that they are stronger electron donors than TTF. The high electron-donating ability is attributed to the extended π -conjugation system.⁴ It should be noted that the cathodic peaks were observed at very low potentials, indicating that during the CV measurements some reaction occurred to give products which have reduction potentials at the E_{pc} values.

The products **5b–e** and **6d**, **e** of oxidation with NOBF₄ in tetrahydrofuran could be isolated in 66, 84, 95, 82, 85 and 87%

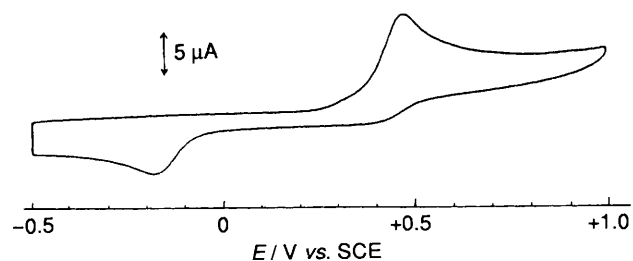


Fig. 1 Cyclic voltammogram of donor **2e** in PhCN measured under the conditions in Table 1

Table 1 Oxidation potentials^a of donors **2** and **4**

Donor	E_{pa}/V	E_{pc}/V
2b	+0.23	-0.45
2c	+0.40	-0.22
2d	+0.38	-0.22
2e	+0.46	-0.18
4d	+0.62	-0.15
4e	+0.67	-0.12
TTF	+0.49	+0.43

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

Table 2 Melting points and absorption maxima of cations **5** and **6**

Cation	M.p. (decomp.), t/°C	λ_{max}/nm (log ϵ) ^a
5b	252–254	595 (4.80)
5c	200–202	633 (4.92)
5d	210–215	668 (4.73)
5e	247–250	591 (5.02)
6d	262–267	718 (4.86)
6e	257–260	644 (4.96)

^a In MeCN.

yields, respectively. They were also obtained by electrochemical oxidation in dichloromethane using Bu₄NBF₄ as electrolyte. The reduction peak potentials of the cations **5** and **6** are in complete agreement with those of the corresponding **2** and **4**. The formation of the cations **5** and **6** can be explained by deprotonation from the dications **7** whose acidity becomes high owing to the presence of the electron-withdrawing 1,3-dithiolium and the stability of the cyclopentadienyl anion formed by deprotonation.

The cations **5** are very stable in contrast to the instability of the 3,5-bis(diphenylmethylene)cyclopentenyl cation which was recently reported.⁵ They are considered to exist in resonance forms **5'** and/or **5''**. The NMR spectra of **5c**‡ showing three kinds of proton signals and six kinds of carbon signals suggest a dipolar structure. They have intense absorptions in the long wavelength region due to intramolecular charge transfer. The absorption maxima are summarized in Table 2. The alkylthio groups cause a marked red shift of the absorptions. The absorptions of the benzo-fused derivatives **6d**, **e** are at ca. 50 nm longer wavelength than those of the corresponding **5**. The spectrum of **6d** is shown in Fig. 2. These cations are of interest as dyes because of their intense absorptions.⁶ The tetramethyl **5b** and dibenzo derivatives **5e** and **6e** showed fluorescence emission, whereas no fluorescence was observed for the alkylthio derivatives **5c**, **d** and **6d**

† Satisfactory elemental analyses were obtained for all new compounds.

‡ ¹H NMR of **5c**, δ (CD₃CN) 2.63 (s, 12H), 6.57 (2H, d, J 2.0 Hz) and 7.34 (1H, t, J 2.0 Hz); ¹³C NMR of **5c**, δ (CD₃CN) 19.37, 121.77, 122.09, 129.10, 139.97 and 181.10.

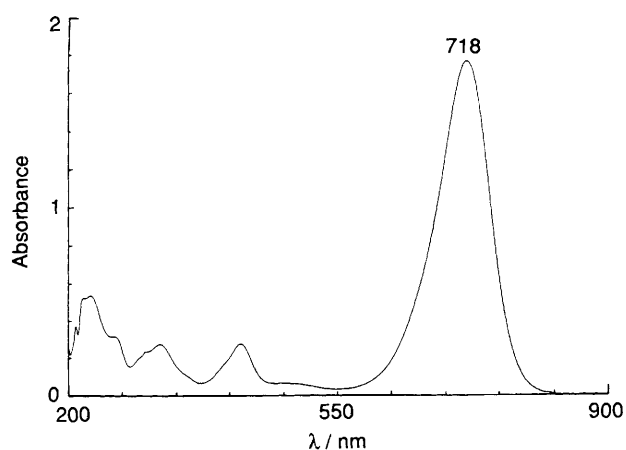


Fig. 2 Absorption spectrum of cation **6d** in CH_2Cl_2

probably owing to heavy atom effects. The observation of fluorescence suggests a planar structure for the cations. The cation **5c** reacted with malonotrile in the presence of triethylamine to give another interesting coloured compound **8** [λ_{max} (CH_2Cl_2) 534 nm].

The donors **2c** and **2e** gave charge-transfer complexes with tetracyanoquinodimethane (molar ratio 1 : 1) whose electrical conductivities as compressed pellets were 2.2×10^{-4} and $3.1 \times 10^{-5} \text{ S cm}^{-1}$, respectively. Both complexes showed nitrile stretching frequencies at 2178 cm^{-1} , indicating that complete

charge transfer occurs.⁷ The conductivities of the cations **5e** and **6e** as compressed pellets were 1.6×10^{-7} and $1.7 \times 10^{-6} \text{ S cm}^{-1}$, respectively. The better conductivity of the benzo-fused derivative is attributed to decrease of on-site Coulombic repulsion.

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