2-(Thiopyran-4′-yliden)-1,3-dithioles fused with Thiophene Units: Intramolecular S···S Interaction affecting the Redox Properties and Molecular Geometries

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The title molecules (**1**) are strong electron donors like tetrathiafulvalene (TTF) but possess non-planar geometries with short intramolecular contacts between S atoms (av. 3.06 Å in **1b**, X-ray); by contrast, their cation radicals are endowed with molecular planarity, and the shorter S···S contacts (av. 2.87 Å in $\mathbf{1b}^{\cdot+}$, X-ray) result in the enhanced attractive interaction as well as much smaller Coulombic repulsion in $\mathbf{1}^{2+}$ than in TTF^{2+}.

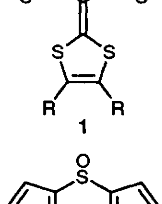
Intermolecular interaction through short S···S contacts has been known to play a significant role in determining the solid-state properties of organic molecular crystals. Noteworthy examples include the superconducting behaviour in the cation radical salts of tetrathiafulvalene (TTF) derivatives[1] as well as the electrical conduction of certain sulfur heterocycles as a single component.[2] On the other hand, only a few studies have so far been done on the effects of intramolecular S···S contacts on the redox properties of organic π-electron systems.[3] As suggested by the transannular two-centre–three-electron bonding in the cation radicals of alicyclic dithioethers,[4] repulsive or attractive interaction through the intramolecular S···S contacts may affect the electronic structures and stabilities in the oxidised and/or reduced forms of π-electron systems. We report here the intriguing redox behaviour accompanied by the drastic structural change in the title electron donors **1** exhibiting short S···S contacts.

Dithienothiopyrone **4**[5] was oxidised with peracetic acid giving the corresponding sulfoxide **3** [mp 230–232 °C (decomp.)] in 32% yield. The Wittig–Horner reactions of **3** with 2-methoxyphosphinyl-1,3-dithiole[6] or -1,3-benzodithiole[7] afforded **2a** [mp 198–200 °C (decomp.)] and **2b** [mp 238–240 °C (decomp.)], respectively, in 77 and 85% yields. Reductive deoxygenations of **2a** and **2b** with NaI in the presence of $\mathrm{Me_3SiCl}$ gave **1a** and **1b** in 41 and 71% yields, respectively.†

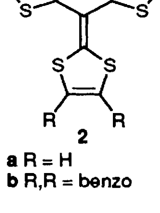
Cyclic voltammograms of **1a** and **1b** showed two pairs of reversible waves corresponding to the two-stage one-electron oxidations. The first oxidation potential (E_1^{ox} *vs.* SCE in MeCN) of **1a** (+0.32 V) is very close to that of TTF (+0.31 V), and that of **1b** (+0.45 V) is lower than that of dibenzo-TTF (+0.57 V), indicating the strong electron donating properties of **1a** and **1b**. It is noteworthy that the second oxidation potentials (E_2^{ox}) of **1a** (+0.45 V) and **1b** (+0.52 V) are much lower than those of TTF (+0.68 V) and dibenzo-TTF (+0.89 V). Quite small differences between E_1^{ox} and E_2^{ox} (0.13 V in **1a** and 0.07 V in **1b**) correspond to the facile oxidation of $\mathbf{1}^{\cdot+}$ to $\mathbf{1}^{2+}$, showing the reduced Coulombic repulsion on the molecular skeleton of **1** compared with those of TTF derivatives.

The conventional explanation for the redox properties of **1** can be considered based on the repulsive steric interaction between S atoms of the thiophene rings and those of 1,3-dithiole moiety in $\mathbf{1}^{\cdot+}$. That is, one-electron oxidation causes a decrease in π-bond order of the central C=C bond, allowing the easy rotation of the two molecular halves around the central bond in the cation radical species.[6,8] However, this is not the case for **1** as shown by X-ray structural analyses‡ of both neutral **1b** and cation radical salt $\mathbf{1b}^{\cdot+}\cdot\mathrm{ClO_4}^{-}\cdot\mathrm{CH_2Cl_2}$ obtained by the electrochemical oxidation of **1b** in $\mathrm{CH_2Cl_2}$.

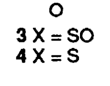
Neutral **1b** possesses a non-planar structure with a dihedral angle of *ca.* 30° between the two thiophene rings [Fig. 1(*a*)]. Although there exist two crystallographically independent molecules in the crystal, their geometries are identical within the experimental errors. Thus, the molecular deformation is not due to the crystal packing force but due to the inherent nature of **1b**. The interatomic distances for S···S (3.03–3.09 Å)



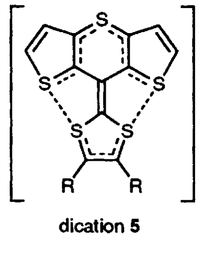
1



2
a R = H
b R,R = benzo



3 X = SO
4 X = S



dication **5**

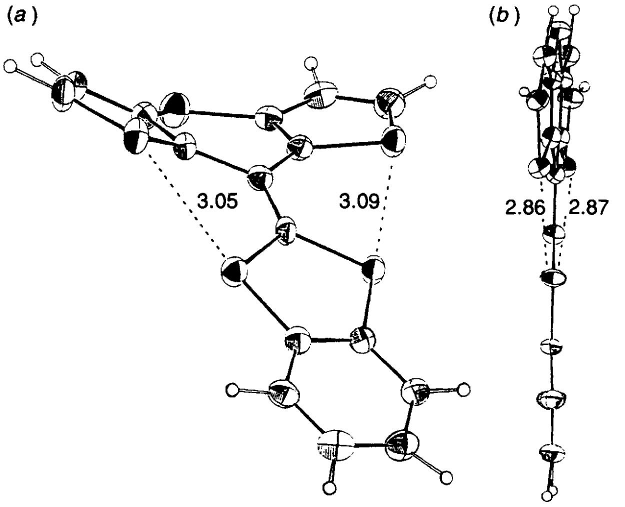


Fig. 1 ORTEP drawings of the butterfly-shaped neutral **1b** (*a*) and the side view of planar $\mathbf{1b}^{\cdot+}$ (*b*). Intramolecular S···S contacts are shown by broken lines.

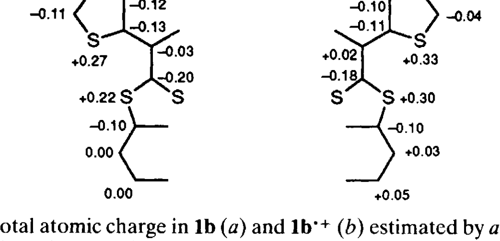


Fig. 2 Total atomic charge in **1b** (*a*) and $\mathbf{1b}^{\cdot+}$ (*b*) estimated by *ab initio* calculations (STO-3G). Those of hydrogen atoms are summed into the connected carbon atoms.

are shorter than the sum of van der Waals radii (3.70 Å), showing the presence of attractive interaction between them. The molecules of **1b** deform into a butterfly shape so as to prevent the repulsive interaction between sp^2 lone pairs of S atoms. On the other hand, the molecular geometry of **1b**$^{\cdot+}$ is planar despite the much shorter distances for S···S (2.86 and 2.87 Å) than those in neutral **1b** [Fig. 1(*b*)]. The largest deviation of atoms from the molecular plane is only 0.15 Å, and the rotation around the central bond is negligible (4.6°). These structural features indicate that the contraction of sp^2 lone pairs upon one-electron oxidation allowed the closer contacts of S atoms, and the increased overlap of 3p π orbitals of S resulted in the enhanced interaction in **1b**$^{\cdot+}$.

Ab initio calculations§ on **1b** and **1b**$^{\cdot+}$ indicate the considerable increase in atomic charge on thiophene S atoms in **1b**$^{\cdot+}$ (Fig. 2) in spite of the very small MO coefficient in HOMO of neutral **1b**. This finding suggests that the positive charge in **1b**$^{\cdot+}$ is redistributed over the planar π-electron system through the short S···S contacts. Such charge delocalization would reduce Coulombic repulsion in **1**$^{2+}$, and the easy oxidation of **1**$^{\cdot+}$ to **1**$^{2+}$ can be also accounted for by a contribution of the aromatic dication **5** with the delocalisation of 14 π electrons.

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Footnotes

† All new compounds gave satisfactory analytical values. Selected spectral data are as follows. **1a**: mp 105–107 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.37 (2H, d, *J* 5.4 Hz), 6.89 (2H, d, *J* 5.4 Hz), 6.49 (2H, s); UV–VIS (CH_2Cl_2) λ_{max} 402 nm (ε 16200 dm^3 mol^{-1} cm^{-1}) and 254 (15200). **1b**: mp 166–167 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d, *J* 5.4 Hz), 7.39–7.29 (2H, AA′BB′), 7.16–7.11 (2H, AA′BB′), 6.90 (2H, d, *J* 5.4 Hz); UV–VIS (CH_2Cl_2) λ_{max} 394 nm (ε 19600 dm^3 mol^{-1} cm^{-1}) and 256 (19100). **1b**$^{\cdot+}$·ClO_4·CH_2Cl_2: mp 234–235 °C (decomp.); UV–VIS (CH_2Cl_2) λ_{max} 564 nm (ε 15200 dm^3 mol^{-1} cm^{-1}), 500(sh) (10700), 338 (3700), 280 (17000) and 266 (16500).

‡ *Crystal data* **1b**: $C_{16}H_8S_5$, M = 360.52, monoclinic, space group $P2_1/a$, a = 12.539(1), b = 30.824(2), c = 7.717(1) Å, β = 90.67(1)°, V = 2982.3(4) Å^3, Z = 8, D_c = 1.607 g cm^{-3}. The final *R* value was 0.0606 for 2681 reflections with $|F_o| > 3\sigma\,|F_o|$. **1b**$^{\cdot+}$·ClO_4^-·CH_2Cl_2: $C_{17}H_{10}Cl_3O_4S_5$, M = 544.90, triclinic, space group $P\bar{1}$, a = 9.213(1), b = 14.487(2), c = 7.902(2) Å, α = 92.58(1), β = 93.42(1), γ = 106.09(1)°, V = 1009.5(3) Å^3, Z = 2, D_c = 1.793 g cm^{-3}. The final *R* value was 0.0984 for 3238 non-zero reflections. 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. The difference in the electronic structures between **1b** and **1b**$^{\cdot+}$ could not be discussed by comparisons of bond lengths because the estimated standard deviations are too large (0.009–0.015 Å for non-hydrogen atoms in both crystals).

§ All the calculations were carried out by using GAUSSIAN 86 program (ref. 9) at STO-3G level. Observed geometries in the crystal were used without optimisation. We thank the Computer Center, Institute for Molecular Science for use of the HITAC S-820/80 computer. Selected MO coefficients in HOMO of **1b** are as follows: S of thiopyran, −0.46; S of 1,3-dithiole, +0.38; S of thiophene, −0.09.

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