5,8-Bis(1,3-dithiol-2-ylidene)-5,8-dihydroquinoxalines: Novel Electron Donors with Low Oxidation Potentials

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The synthesis and properties of the title electron donors which are tetrathiafulvalene (TTF) or bis(ethylenedithio)TTF (BEDT–TTF) analogues with a quinoid structure are described; the crystal structure of a derivative is also presented.

Bis(1,3-dithiole) donors with extended π-conjugation are of interest as components of organic conductors due to their highly donating properties as well as the decreased Coulombic repulsion.[1] Typical examples are of *p*-quinodimethane analogues **1**[2] and vinylogous ones **2** of tetrathiafulvalene (TTF).[3,4] Compound **2b** was very recently synthesized by Bryce *et al.*[4] as a highly electron-donating derivative of bis(ethylenedithio)TTF which is the most important donor for organic superconductors. Although compounds **1** are stronger electron donors than **2** due to the quinoid structure, they were found to be unstable and rapidly decomposed in solution.[2] In contrast, pyrazine-fused derivatives **3** are expected to be stable due to the electron-withdrawing heterocycle, and in fact, the dibenzo derivative **3d** was prepared as a stable solid.[5] The donors **3** seem to have characteristics such as interheteroatom interactions, delocalization of electrons, and large polarization, which are considered to be favourable for affording highly conducting materials.[6] We have now prepared the parent compound **3a**, and its derivatives **3b** and **3c**, and found that they are very strong electron donors. We report here their properties and the crystal structure of **3d**.

New compounds **3a–c** (**3a**, m.p. 279–280 °C; **3b**, decomp. 320 °C, **3c**, decomp. 265–267 °C) were quantitatively prepared by a retro-Diels–Alder reaction of cyclopentadiene adducts **4a–c** which were synthesized by a Wittig–Horner reaction of the corresponding phosphorus reagents **5a–c**[2,7] with dione **6**[5] in 8, 41 and 50% yields, respectively. They are stable in the solid state under air. The absorption maxima are observed at longer wavelengths compared with those of TTF and BEDT–TTF as shown in Table 1, suggesting that **3** are polarized by charge transfer from the 1,3-dithiole ring to the pyrazine ring. The existence of the polarization is supported by the fact that the absorptions of the derivatives **3b** and **3c** having electron donating substituents are red-shifted compared with that of the parent compound **3a**.

The oxidation potentials of the donors (Table 1) were measured by cyclic voltammetry. The values for **3a–d** are lower than those for TTF. It is noteworthy that BEDT–TTF analogue **3c** is a stronger donor than TTF, while **2b** is a weaker donor than TTF.[4] The high electron donating ability of **3** is attributed to the quinoid structure which can generate a new aromatic sextet upon oxidation. Another interesting feature is that the differences (Δ*E*) between the first and second oxidation potentials are smaller than those for TTF and BEDT–TTF. This fact indicates that the on-site Coulomb repulsion in **3** is decreased due to the extended π-conjugation as is well documented for related systems.[1,2]

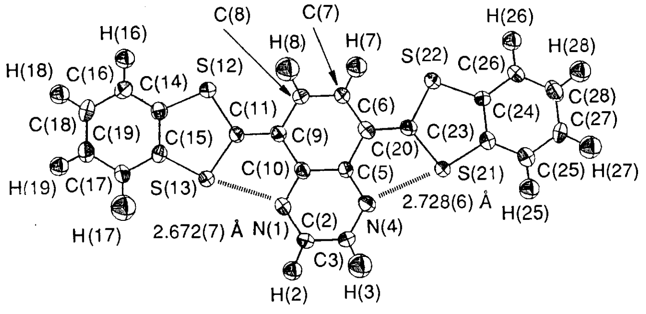
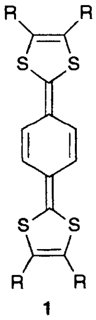


Fig. 1 Molecular structure of **3d** (ORTEP); selected bond lengths (Å): N(1)–C(2) 1.335(11), C(2)–C(3) 1.367(11), C(3)–N(4) 1.335(10), N(4)–C(5) 1.324(10), C(5)–C(6) 1.472(10), C(6)–C(7) 1.420(12), C(7)–C(8) 1.361(11), C(8)–C(9) 1.449(10), C(9)–C(10) 1.445(11), C(10)–N(1) 1.346(10), C(10)–C(5) 1.430(10), C(6)–C(20) 1.373(10), C(20)–S(21) 1.757(8), S(21)–C(23) 1.751(7), C(23)–C(24) 1.405(11), C(24)–S(22) 1.740(8), S(22)–C(20) 1.753(7), C(9)–C(11) 1.377(10), C(11)–S(12) 1.757(8), S(12)–C(14) 1.748(7), C(14)–C(15) 1.424(11), C(15)–S(13) 1.743(8), S(13)–C(11) 1.755(7)



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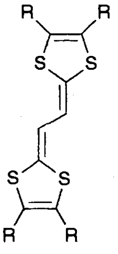
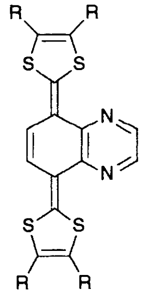
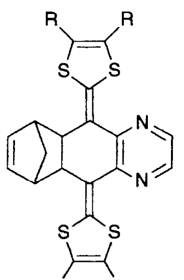


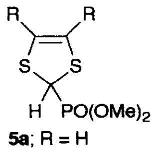
2a; R = H
2b; R, R = SCH$_2$CH$_2$S



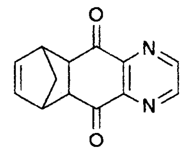
3a; R = H
3b; R = Me
3c; R, R = SCH$_2$CH$_2$S
3d; R, R = benzo



4a; R = H
4b; R = Me
4c; R, R = SCH$_2$CH$_2$S



5a; R = H
5b; R = Me
5c; R, R = SCH$_2$CH$_2$S



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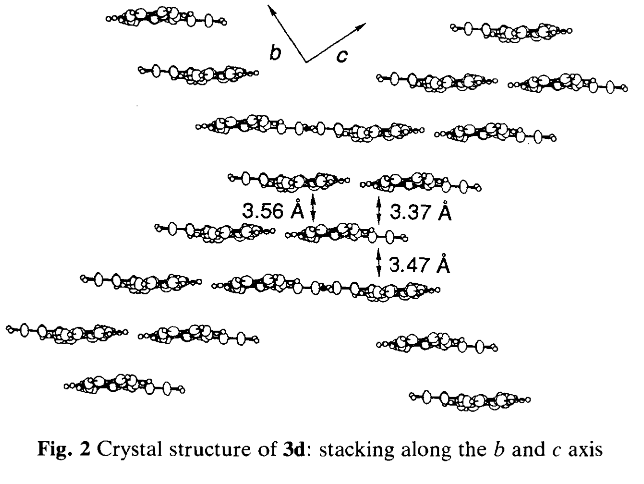

Fig. 2 Crystal structure of **3d**: stacking along the *b* and *c* axis

Table 1 Oxidation potentials[a] and absorption maxima of donors

Donor	E_1/V	E_2/V	ΔE	λ_{max}/nm (log ε)[b]
3a	+0.23	+0.43	0.17	504(4.80), 475(4.65)
3b	+0.17	+0.35	0.18	518(4.81), 489(4.65)
3c	+0.33	+0.49	0.16	522(4.71), 490(4.54)
3d	+0.44	+0.60	0.16	492(4.52), 462(4.38)
TTF	+0.46	+0.87	0.41	319(4.11), 309(4.12)
BEDT–TTF	+0.61	+0.94	0.33	347(4.04), 322(4.16)

[a] 0.1 mol dm^{-3} Bu_4NClO_4 in C_6H_5CN, Pt electrode, scan rate 100 mV s^{-1}, V *vs.* standard calomel electrode (SCE). [b] In CH_2Cl_2.

In order to investigate the structure of **3**, an X-ray structural analysis of **3d**, whose single crystal was obtained by sublimation, was carried out.† The molecule is almost planar. Selected bond lengths are given in Fig. 1. Interestingly, the distances between the S of the dithioles and the N of the pyrazines (2.67 and 2.73 Å) are significantly shorter than the sum of the van der Waals distance (3.35 Å). The short contacts may be useful for making the molecule planar as well as for the delocalization of electrons through the S ··· N contacts. The molecules of **3d** are stacked along the *b* and *c* axes as shown in Fig. 2. There are three types of overlapping with the distances between the molecular planes of 3.37, 3.47 and 3.56 Å. The novel crystal structure results in an electrical conductivity of 2.5 × 10^{-7} S cm^{-1} at room temperature as a single component. The temperature dependence of the conductivity shows a semiconducting behaviour with E_a of 0.31 eV. The value for the conductivity is low, but noteworthy since most organic compounds are insulators as single components.[8]

The donor **3b** gave a highly conducting TCNQ complex [σ = 0.5 S cm^{-1} (compaction pellet), D : A ratio = 3 : 2]. In addition, a perchlorate salt of **3b** [σ = 0.2 S cm^{-1} (single crystal), D : A = 3 : 2] was obtained by electrochemical oxidation. The formation of other charge transfer complexes and ion radical salts is now in progress.

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† *Crystal data* for **3d**: $C_{22}H_{12}N_2S_4$, M = 432.58, monoclinic, space group $P2_1/a$, a = 31.822(6), b = 9.688(3), c = 5.914(1) Å, β = 92.98(2)°, V = 1820.8(6) Å^3, Z = 4, D_c = 1.58 g cm^{-3}. The final R value is 6.68% for 2622 reflections with $|F_0| > 3\sigma|F_0|$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallography Data Centre. See Notice to Authors, Issue No. 1.