

Dithio-derivatives of *p*-Quinodimethanes Fused with 1,2,5-Thiadiazoles: a Novel Type of π -Donor–Acceptor System

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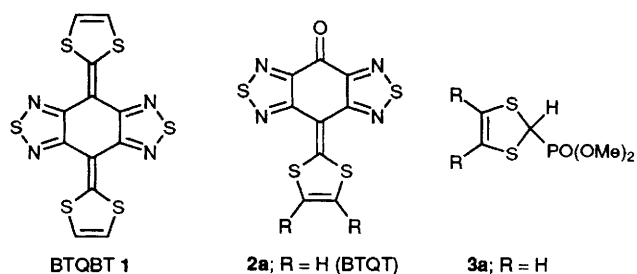
4*H*,8*H*-(1,3-Dithiol-2-ylidene)benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazol-4-one BTQT, which forms a novel three-dimensional crystal by interheteroatom contacts, shows a non-ohmic behaviour.

Molecules containing both donor and acceptor units are expected to exhibit unusual electrical properties owing to intramolecular charge transfer.¹ We have found that BTQBT **1**[†] containing 1,3-dithiole rings as donor units and thiadiazole rings as acceptor ones is a novel organic semiconductor which shows a fairly good electrical conductivity as a single component.² Another interesting feature of BTBQT is the crystal structure in which a sheet-like network is formed by intermolecular interactions between the S atoms of the 1,3-dithiole rings. We have now replaced one of the 1,3-dithiole groups by a carbonyl group to give BTQT **2a**,[†] which is expected to be more polarized than BTQBT. We report here the preparation, properties and structures of BTQT and its derivatives.

BTQBT was prepared by a Wittig–Horner reaction of the corresponding dione with two equivalents of a carbanion derived from phosphonate ester **3a**.² When one equivalent of **3a** was used in this reaction, BTQT **2a** (mp 424–426 °C) was obtained in 40% yield. The derivatives **2b–d** were similarly prepared by using phosphonate esters **3b–d**.³ BTQT **2a** and the benzo derivative **2d** were sublimed at 350 °C to give single crystals as dark-violet needles. The longest absorption maxi-

mum was observed at 620 nm (sh) in a KBr disk, which is red-shifted compared with that of BTQBT [542 nm (sh)]. The carbonyl stretching frequency was observed at 1645 cm⁻¹, indicating that **2a** is highly polarized.

The cyclic voltammograms (CV) of **2a**, **2b** and **2d** could not be measured owing to their low solubility in organic solvents. However, the CV of the bis(butylthio) derivative **2c** in benzonitrile showed both an oxidation peak ($E_{pa} + 1.25$ V vs. standard calomel electrode, SCE) and a reduction peak ($E_{pc} - 0.51$ V vs. SCE). These potentials are higher than those of the corresponding tetrakis(butylthio)-substituted BTQBT



[†] BTQBT **1**, 4*H*,8*H*-4,8-bis(1,3-dithiol-2-ylidene)benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole; BTQT **2a**, 4*H*,8*H*-8-(1,3-dithiol-2-ylidene)benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazol-4-one.

2a; R = H (BTQT)

2b; R = Me

2c; R = SBUⁿ

2d; R, R = benzo

3a; R = H

3b; R = Me

3c; R = SBUⁿ

3d; R, R = benzo

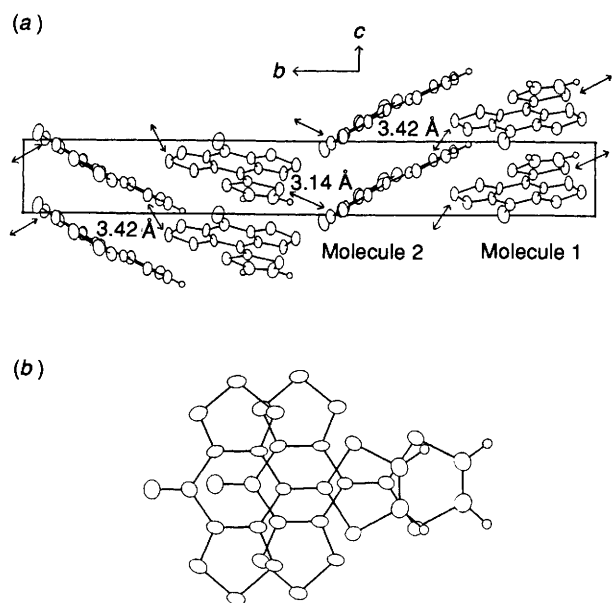


Fig. 1 Crystal structure of 2a. (a) Stacking along the *c* axis. (b) Overlap mode of the molecule 1.

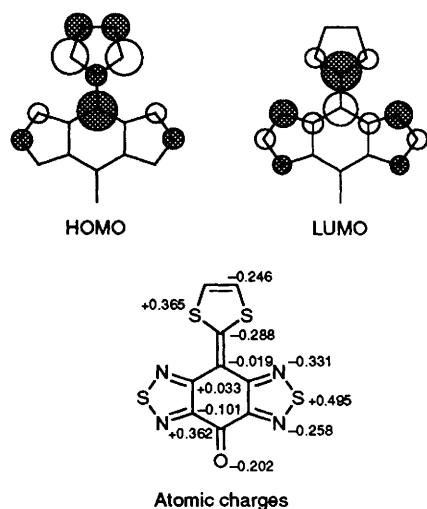


Fig. 2 HOMO, LUMO and net atomic charges of 2a calculated by the MNDO method

($E_{pa} + 0.83$ V, $E_{pc} - 0.83$ V), reflecting the electron-withdrawing property of the carbonyl group.

In order to determine the molecular structure of BTQT as well as study intermolecular interactions, an X-ray structural analysis was carried out.† There exist two crystallographically independent molecules (1 and 2) in the crystal of 2a. The molecules are planar and the intramolecular distances between the S of the dithiole and the N of the thiadiazole (2.80 and 2.82 Å for molecule 1, and 2.77 and 2.83 Å for molecule 2) are shorter than the sum of the van der Waals distances (3.35 Å). Similar short S...N contacts are observed in BTQBT² and related molecules.⁴ Molecules 1 and 2 are both uniformly

† Crystal data for 2a: $C_9H_2N_4OS_4$, $M = 310.41$, monoclinic, space group $P2_1$, $Z = 4$, $a = 9.311(2)$, $b = 30.089(4)$, $c = 3.868(1)$ Å, $\beta = 101.09(1)^\circ$, $V = 1063(1)$ Å³, $D_c = 1.94$ g cm⁻³. The final R value is 4.61% for 1961 reflections with $|F_o| > 3\sigma|F_o|$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

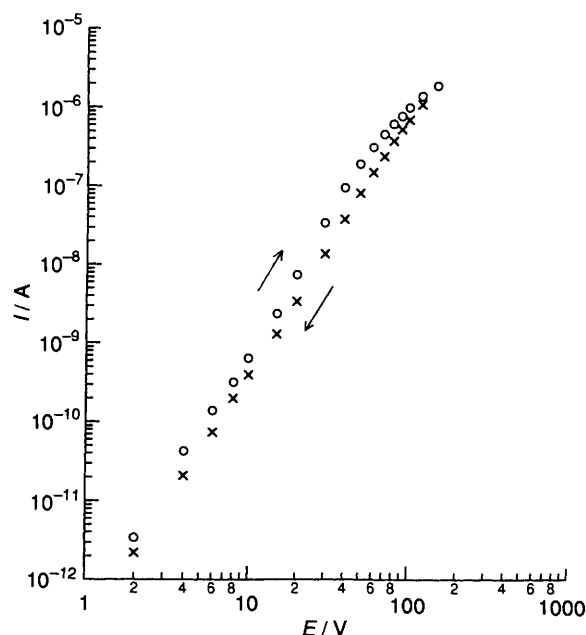


Fig. 3 Relationship between current (I) and voltage (E) for a single crystal of 2a at room temperature

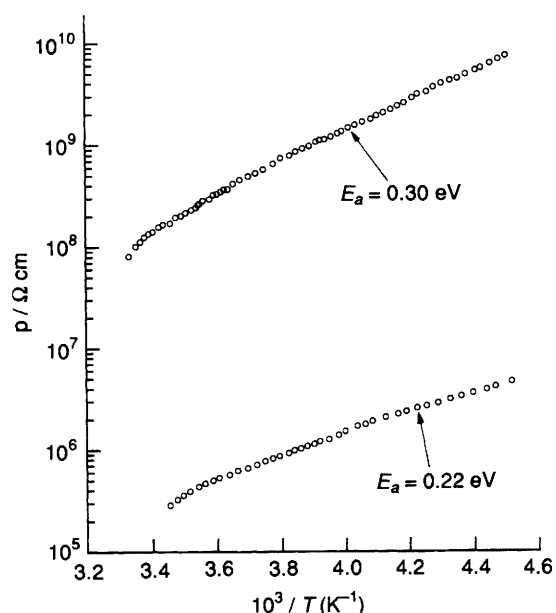


Fig. 4 Temperature dependence of the resistivity under different applied electric fields. This sample is different from that used in Fig. 3.

stacked with intermolecular distances of 3.36 and 3.40 Å, respectively. The overlap mode of molecule 1 is shown in Fig. 1(b), and that of molecule 2 is similar. This overlap is in accord with an effective interaction between the HOMO and LUMO shown in Fig. 2,⁵ suggesting that an intermolecular charge-transfer interaction is possible in the crystal.

Short interheteroatom contacts between molecules 1 and 2 are also observed as shown in Fig. 1(a). Thus, the S...S contact distance between the thiadiazole rings is 3.42 Å, and the distance between the S of the 1,3-dithiole and the N of the thiadiazole is 3.14 Å. The S of the thiadiazole in molecule 1 is also in contact with the O in molecule 2 (3.03 Å). These heteroatom contacts are in sharp contrast with those in BTQBT where the heteroatoms of the thiadiazole rings are not involved in the intermolecular interactions. The net

atomic charges of BTQT calculated by the MNDO method (Fig. 2) show that the molecule is highly polarized, with N and O negatively charged and S positively charged. Therefore, the S...N and S...O contacts observed may be attributed to electrostatic effects.

BTQT showed unusual behaviour on measurement of the resistivity of single crystals prepared by sublimation. The correlation of the current (i) with voltage (E) fails to obey Ohm's law as shown in Fig. 3. The electric field was applied between gold electrodes at a distance of *ca.* 0.5 mm. The current increases approximately in proportion to E^3 . This behaviour was independent of the polarity of the applied field and was reproducible for several runs in several crystals with different dimensions. On the other hand, sublimed crystals of the benzo derivative **2d** showed insulating properties ($\sigma < 10^{-10}$ S cm $^{-1}$) and did not show this unusual behaviour. In view of the fact that the E^3 behaviour extends to low applied voltages and is not strongly dependent on crystal thickness, then space-charge-limited behaviour is unlikely. We suppose that the nonlinear correlation observed in the BTQT crystal may be caused by increases of carrier number (n) and carrier mobility (μ) resulting from a subtle change of the intermolecular overlap of the highly polarized BTQT molecule induced by the electric field. In order to investigate this point, we measured the temperature dependence of resistivity under different applied electric fields; resistivities at room temperature of *ca.* 10^8 Ω cm (state I) and 3×10^5 Ω cm (state II) were

measured. The activation energies were determined to be 0.30 and 0.22 eV, respectively, as shown in Fig. 4. Since the carrier number n depends on the Boltzmann factor $\exp(-Eg/2kT)$, the ratio of n at room temperature between state I and state II can be calculated to be *ca.* 1/20. This value is not large enough to explain the *ca.* 300 times lower resistivity for state II. Further studies are now in progress to investigate the unusual properties of BTQT.

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- 5 MNDO calculations (MOPAC program: J. J. P. Stewart, *QCPE Bull.*, 1983, **3**, 439) were performed using the geometry determined from the X-ray analysis. These calculations were carried out at the Computer Centre of the Institute for Molecular Science.