New π-Electron Donors containing Two Tetrathiafulvalene Units Fused to 1,4-Dithiine and a Conducting Charge-transfer Complex with Tetracyanoquinodimethane

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The synthesis of new electron donors containing two TTF units fused to 1,4-dithiin and a crystal structure of a conducting charge-transfer complex is described.

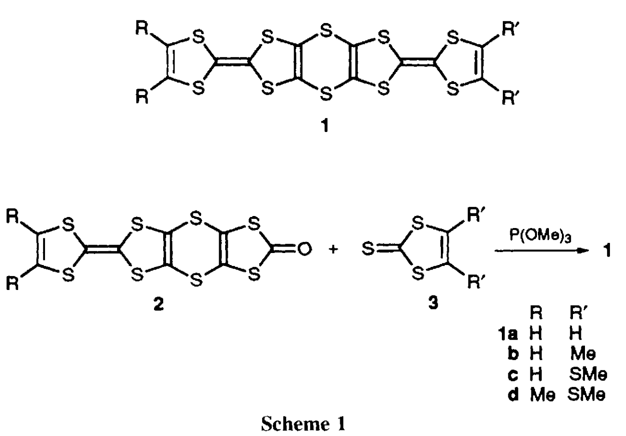
Molecular systems involving two tetrathiafulvalene (TTF) donor units linked by heteroatoms have attracted considerable interest as components for organic metals.[1] Recently we have reported the syntheses and crystal structures of derivatives in which two TTF moieties are linked with one (TTF–Te–TTF)[2] or two (TTF–Te–Te–TTF)[3] tellurium atoms. Analogous derivatives involving sulfur and selenium (TTF–S–TTF and TTF–Se–TTF)[4] have also been reported. It was found that derivatives of this type tend to exhibit a two-dimensional network of sulfur···sulfur and sulfur···heteroatom intermolecular interactions, which is considered to be one of the most important features of conducting and superconducting organic materials. Indeed, they give rise to highly conducting ion-radical salts and charge-transfer complexes.[5] Our further efforts have been directed to the synthesis of rigid (to render steric hindrance) molecular systems of this type which would involve two doubly bridged TTF moieties linked by two heteroatoms.

In this communication we report the synthesis and properties of a new donor system involving two TTF units fused to a dithiine ring **1**, analogous to the previously reported ditellurine derivatives,[6] and the unique solid-state properties of a charge-transfer complex of its dimethylthio derivative with TCNQ.

The synthesis of derivatives of type **1** has been achieved by refluxing a mixture of 1 equiv. of the corresponding 1,3-dithiole-2-one derivative **2**[7] with 2.5–3 equiv. of the corresponding substituted 1,3-dithiole-2-thione **3**, in toluene, in the presence of 8–10 fold excess of trimethylphosphite for 1 h, as shown in Scheme 1. In all cases, the precipitate formed was filtered, extracted with carbon disulfide, and the product isolated by column chromatography, to afford derivatives **1** in 50–58% yield.[†] The remaining insoluble solid which was not extracted with carbon disulfide, and was totally insoluble in other common organic solvents, presumably contains the symmetrical product of dimerization of **2**.

The electrochemical oxidation potentials of derivatives **1**, compared with of that of TTF and other related TTF derivatives are presented in Table 1. Although compounds of type **1** possess higher oxidation potentials than TTF, but similar to those of $(TTF)_2S$, they are advantageous because of their ability to delocalize charge more efficiently [smaller coulombic repulsion, (ΔE)]. It is noteworthy that whereas derivatives containing two TTF moieties and connected by one heteroatom [$(TTF)_2Te$[1] and $(TTF)_2S$[3]] exhibit two reversible one-electron oxidation waves and one irreversible two-electron oxidation wave, respectively, compounds of type **1** undergo three fully reversible oxidation waves, in a 1 : 1 : 2 ratio.

Attempts to obtain conducting charge-transfer (CT) complexes and ion-radical salts of **1** by both chemical and electrochemical oxidation are under way. Thus, **1c** (R=H, R′ = SMe) forms shiny black crystals of a CT complex with TCNQ. An X-ray structure determination[‡] shows that the asymmetric unit of the complex consists of two crystallographically independent donor molecules and a TCNQ molecule, *i.e.* 1 TCNQ per 4 TTF units (Fig. 1). The donor molecules consist of two practically planar TTF moieties (maximum deviation 0.06 Å). The donor stacks are distinguished by a very large number of intermolecular S···S contacts less than or approximately twice the van der Waals radius of sulfur (3.65 Å). The 'fir-tree'-like stacking arrangement in Figs. 2 and 3, with a high density of intra- and inter-stack S···S contacts, is unique even compared to the arrangement of donor stacks in BEDT–TTF salts. The analogy is reinforced by the presence of intervening sheets of acceptors, but in this case, as opposed to BEDT–TTF salts, the acceptors are partially charged and suitably stacked planar TCNQ molecules, rather than fully charged nearly spherical anions. Furthermore, it is noteworthy that the V-shaped molecules, which form a two-dimensional network of S···S contacts, afford a better overlap within the stack because they are nested one into another.



Scheme 1

Table 1 Cyclic voltammetry data for **1** compared to TTF and selected TTF derivatives [glassy-carbon working electrode, *vs.* Ag/AgCl, in benzonitrile–NBu_4ClO_4 (0.1 mol dm^{-3})]

Compound	E_1^{ox}	E_2^{ox}	E_3^{ox}	$\Delta E = E_2^{ox} - E_1^{ox}$
TTF	0.36	0.82	—	0.46
2,3-Me_2TTF	0.27	0.72	—	0.45
$(TTF)_2S$[a]	0.49	0.61	0.86	0.12
$(TTF)_2Te$[b]	0.38	0.72	0.80	0.34
1a	0.47	0.67	0.89	0.20
1b	0.43	0.64	0.88	0.21
1c	0.49	0.75	0.89	0.26
1d	0.47	0.76	0.87	0.29

[a] Ref. 3, in CH_2Cl_2, E_3^{ox} irreversible. [b] Ref. 1, in MeCN–THF, E_3^{ox} irreversible.

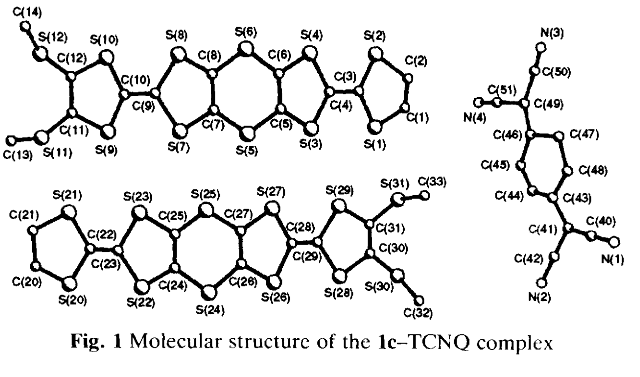


Fig. 1 Molecular structure of the **1c**–TCNQ complex

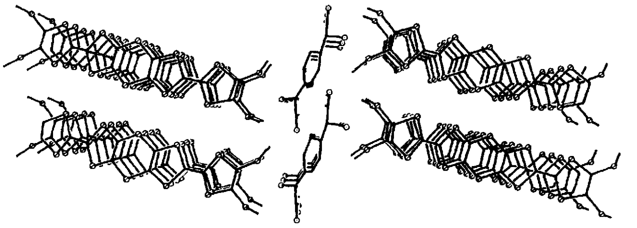


Fig. 2 Packing diagram of the **1c**–TCNQ complex, as viewed down the *b*-axis

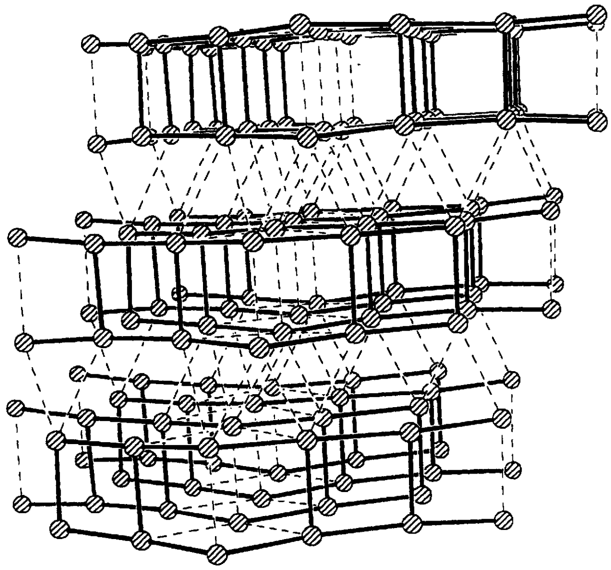


Fig. 3 Schematic representation of the crystal structure of the **1c**–TCNQ complex. Only S atoms are shown. Dotted lines represent S···S intermolecular distances (Å) shorter than the doubled sum of van der Waals radius of S (0.65 Å): S(1)···S(26^{I}) 3.75, S(1)···S(29) 3.68, S(1)···S(31) 3.60, S(2)···S(28^{II}) 3.62, S(3)···S(24^{I}) 3.59, S(3)···S(27) 3.63, S(4)···S(24^{II}) 3.52, S(4)···S(25^{I}) 3.65, S(5)···S(22^{I}) 3.57, S(5)···S(25) 3.44, S(5)···S(27) 3.57, S(6)···S(22^{II}) 3.54, S(6)···S(23^{I}) 3.59, S(6)···S(24^{II}) 3.45, S(6)···S(27^{I}) 3.62, S(7)···S(24^{I}) 3.65, S(7)···S(25) 3.57, S(8)···S(22^{II}) 3.63, S(8)···S(25^{I}) 3.60, S(10)···S(20^{II}) 3.66, S(11)···S(21) 3.50. Symmetry operations I $-$ 1/2 + *x*, 1/2 + *y*, *z*; II *x*, *y* $-$ 1, *z*.

This property does not apply for planar molecules like most of the known TTF derivatives, which can form several modes of slipped stacks.[8] The partial but different degree of charge transfer in both donor and acceptor moieties stacked along the same direction increases the possibilities for conductivity along that direction.

Due to the stoichiometry and to the above unique structural features, derivatives of type **2** represent a most promising new family of donors which could afford new conducting and superconducting complexes and salts. Indeed, although the estimated degree of charge transfer in the complex (from IR)[9] is 0.6 for TCNQ, which amounts to 0.15 per TTF unit, compared to 0.59 in the TTF–TCNQ complex, the complex **1c**–TCNQ exhibits a conductivity of 6 S cm^{-1} at 20 °C (four-probe measurement, pressed pellet). The conductivity of the complex diminishes on decreasing the temperature indicating semiconducting properties which have also been confirmed by variable-temperature magnetic succeptibility measurements down to 5 K. A similar room temp. conductivity has been found also for the salt obtained from **1c** and iodine. Attempts to obtain single crystals of complexes and ion-radical salts based on **1** are currently under way.

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Footnotes

† *Selected data*: **2a**, 51% yield, mp 245–246 °C; ^{1}H NMR (CDCl$_3$), δ 6.2 (4H, s); MS, *m/z* 468 (M$^+$). **2b**, 55% yield, mp 247–248 °C; ^{1}H NMR (CDCl$_3$), δ 6.06 (2H, s), 1.73 (6H, s); MS, *m/z* 496 (M$^+$). **2c** 54% yield, mp 240–241 °C; ^{1}H NMR (CDCl$_3$), δ 6.30 (2H, s), 2.38 (6H, s). **2d**, 50% yield, mp 233–234 °C; ^{1}H NMR, δ 2.53 (6H, s), 1.95 (6H, s); MS, *m/z* 588 (M$^+$).

‡ A shiny black thin plate (0.57 × 0.32 × 0.11 mm) has been used for X-ray structure analysis: monoclinic, space group *Cc*, at 153 K, a = 12.900(3), b = 7.740(2), c = 49.85(1) Å, β = 90.65(3)°, V = 1326 Å, $F(000)$ = 2688. 4570 reflections were collected with a Syntex P-1 diffractometer [λ(Mo-Kα) = 0.710 69 Å], graphite monochromator, ω–2θ scan, $2\theta < 48°$. 2931 reflections with $F_o > 4\sigma(F_o)$ were observed from 2942 independent reflections. The structure was solved by direct methods and refined by least squares using the block-diagonal approximation with isotropic temperature factors for carbon and nitrogen, and anisotropic temperature factors for sulfur atoms. 393 parameters, R = 5.76, R_w = 6.77, GOF = 2.10. DIFABS was applied for absorption correction. SHELX PLUS programs were used for all calculations and drawings. 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.

References

1 K. Bechgaard, K. Lerstrup, M. Jorgensen, I. Johannsen and J. Christiansen, in ISSP-ISOS Proceedings, *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer, Berlin, 1990, p. 349; M. Adam and K. Mullen, *Adv. Mater.*, 1994, **6**, 439.

2 J. Y. Becker, J. Bernstein, S. Bittner, J. A. R. P. Sarma and L. Shahal, *Tetrahedron Lett.*, 1988, 6177.

3 J. Y. Becker, J. Bernstein, M. Dayan and L. Shahal, *J. Chem. Soc., Chem. Commun.*, 1992, 1048.

4 M. R. Bryce, G. Cooke, A. S. Dhindsa, D. J. Undo and M. B. Hursthouse, *Tetrahedron Lett.*, 1992, 1783.

5 J. Y. Becker, J. Bernstein, A. Ellern, M. Dayan and L. Shahal, *Adv. Mater.*, 1994, **6**, 758.

6 C.-S. Wang, A. Ellern, V. Khodorkovsky, J. Y. Becker and J. Bernstein, *J. Chem. Soc., Chem. Commun.*, 1994, 2115.

7 V. Khodorkovsky, J. Y. Becker and J. Bernstein, *Synthesis*, 1992, 1071.

8 See, *e.g.* J. Stevens, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, p. 347.

9 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.