'Organic Metals': Alkylthio Substitution Effects in Tetrathiafulvalene–Tetracyanoquinodimethane Charge-transfer Complexes

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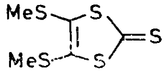
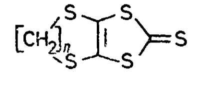
Summary The synthesis and diverse conductivity properties of the tetracyanoquinodimethane (TCNQ) complexes of several tetrakis-(alkylthio)-tetrathiafulvalenes are described, and compared with those of tetrathiafulvalene–TCNQ and related complexes.

It is well known that the replacement of TTF in the organic 'metal' TTF–TCNQ (tetrathiafulvalene–tetracyanoquinodimethane) by related π-donors alters the solid-state properties remarkably. Recent examples include TSeF–TCNQ where the principal metal–insulator transition is reduced to 29 K as compared to 54 K for TTF–TCNQ,[1] and bis-cyclopentenotetraselenafulvalene–TCNQ which remains metallic to very low temperatures.[2] Two desirable features in the design of related TTF π-donors for use in the preparation of conducting charge-transfer salts are an increased electronic polarizability and decreased band occupancy, both of which are favourable toward diminishing energetically costly electron–electron correlations which inhibit electrical transport.[3] We have attempted to incorporate these features into TTF by alkylthio substitution, and report here the synthesis and diverse conductivity properties of the TCNQ salts of the three tetrakis-(alkylthio)-tetrathiafulvalenes (**3**), (**4a**), and (**4b**).

Previous workers have failed to effect the direct phosphite coupling of the known dithiolethione (**1**) to the tetrathiafulvalene (**3**), which has been synthesized from (**1**) by an alternative multistep procedure.[4] We have found that (**1**) affords (**3**) directly in 56% yield when heated (30 min, 105–115 °C) with triethyl phosphite. Similarly, direct coupling of the thiones (**2a**)[5a] and (**2b**)[5b] gave, in 44—45% yield, the hitherto unknown condensed TTF derivatives (**4a**) and (**4b**) respectively. All three TTF derivatives (**3**), (**4a**), and (**4b**) afforded 1 : 1 black crystalline salts when heated in solution (acetonitrile, tetrahydrofuran, and chlorobenzene, respectively) with TCNQ.‡

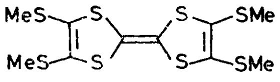


(1)

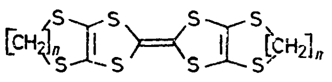


(2)

a; n = 2
b; n = 3



(3)



(4)

a; n = 2
b; n = 3

The π-donor abilities of (**3**), (**4a**), and (**4b**) are smaller than that of TTF as seen from comparing the $E_{\frac{1}{2}}$ values in the Table. This leads to smaller charge-transfer with

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‡ All new compounds have been characterized spectroscopically and analytically. M.p.s (**2b**) 140—141 °C; (**4a**) and (**4b** >250 °C (decomp.).

TABLE

	$E^1_{\frac{1}{2}}$[a]	$E^2_{\frac{1}{2}}$[a]	$\sigma(RT)/(\Omega\ \text{cm})^{-1}$
(3)	+0·496	+0·668	10^{-5}[c]
(4a)	+0·532	+0·773	50[b]
(4b)	+0·580	+0·861	80[b]
(TTF)	+0·342	+0·721	20[b]

[a] Reversible oxidations in MeCN with added Et_4NClO_4 (0·05M) *vs.* Ag/Ag$^+$ (0·1N in MeCN) with a glassy carbon electrode as the working electrode; the resulting values are given in V with respect to the saturated calomel electrode. [b] Four-probe measurements on compressed pellets (1 : 1 TCNQ salt) using silver-paint electrodes. [c] Same as footnote b except for single crystals (1 : 1 TCNQ salt).

TCNQ and hence should decrease the band occupancy in the crystalline state. Moreover the difference between E^1 and E^2 for these π-donors remains low which is important to allow desirable double-occupancy fluctuations in the conducting state.

The room temperature electrical conductivities measured on compressed pellets of the TCNQ salts of (**3**), (**4a**), and (**4b**) (see Table) when compared to the corresponding value of 20 $\Omega^{-1}\ \text{cm}^{-1}$ for TTF–TCNQ show a somewhat higher conductivity for the salts of (**4a**) and (**4b**) which within band theory may be associated with more favourable polarizability and band occupancy conditions caused by the π-donors (**4a**) and (**4b**). Clearly further detailed studies of the electronic and structural properties of the latter two TCNQ salts are required to confirm these conditions.

In contrast, single-crystal measurements on the TCNQ salt of (**3**) indicate relatively low conductivity. Since the first half-wave potential of (**3**) is lower than that of either (**4a**) or (**4b**), it is likely that the large difference in conductivity values results from special steric requirements of the rotating methylthio groups.[6]

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[2] A. N. Bloch, D. O. Cowan, K. Beckgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Letters*, 1975, **34**, 1561.

[3] A. F. Garito and A. J. Heeger, *Accounts Chem. Res.*, 1974, **7**, 232; See, for example, H. Shiba, *Phys. Rev.*, 1972, **B6**, 930.

[4] P. R. Moses and J. Q. Chambers, *J. Amer. Chem. Soc.*, 1974, **96**, 945.

[5] (a) M. Mizuno, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, 1976, **41**, 1484; (b) Electrochemical reduction of carbon disulphide followed by alkylation with 1,3-dibromopropane.

[6] Similar behaviour has been previously observed for 4,5,4′,5′-tetrapropyltetrathiafulvalene–TCNQ and 4,5,4′,5′-bis-(tetramethylene)-tetrathiafulvalene–TCNQ: L. B. Coleman, F. G. Yamagishi, A. F. Garito, A. J. Heeger, D. J. Dahm, M. G. Miles, and J. D. Wilson, *Phys. Letters*, 1975, **51**A, 412; H. K. Spencer, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, 1976, **41**, 730. Similar values have been obtained by Schumaker and Engler for the TCNQ salt of (**3**), R. R. Schumaker and E. M. Engler, to be published.