Synthesis of a New Class of Highly Conducting Organic Ion–Radical Salts

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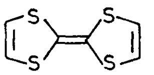
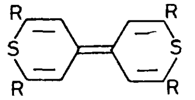
Summary The organosulphur donors $\Delta^{4,4'}$-bithiopyran and 2,2′,6,6′-tetramethyl-$\Delta^{4,4'}$-bithiopyran react with 7,7,8,8-tetracyanoquinodimethane to give a new class of ion-radical salts whose conductivities, measured on compressed pellets at room temperature, are comparable to those of the highest conducting classes of organic solids.

THE organic π-donor tetrathiafulvalene (**1**) reacts with the acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give an ion–radical salt which has the physical properties of a quasi-one-dimensional metal.[1] This finding has stimulated considerable interest in the systematic study of the ion-radical salts.[2] Indeed, alkyl derivatives of (**1**) and the selenium analogue of (**1**) and its alkyl derivatives, react with TCNQ in solution to give 1 : 1 salts.[3] $\Delta^{4,4'}$-Bithiopyran[4] (**2a**) is of interest in this connection since it also has D_{2h} symmetry, reversibly forms a dication in solution, and is iso-π-electronic to (**1**). We have synthesized ion–radical salts of both 1 : 1 and 1 : 2 stoicheiometry by reactions of (**2a**) and its 2,2′,6,6′-tetramethyl derivative[5] (**2b**) with TCNQ and compare our findings with earlier studies.

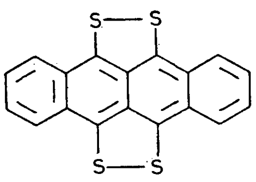


(1)



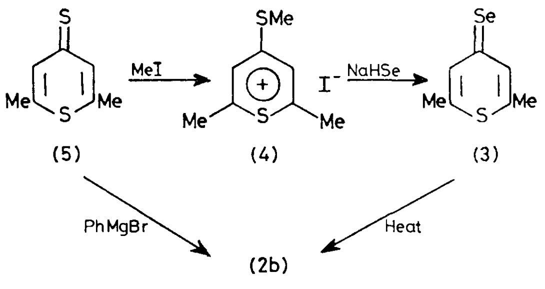
(2)

a; R = H
b; R = Me



(6)

Gradient sublimation[6] of crude (**2a**),[4] a yellow-brown solid, m.p. 180—185 °C (decomp.), gave a red-orange solid, m.p. 213—214 °C (decomp.) [lit.[4] m.p. 150 °C (slow decomp.)], *m/e* 192, λ_{max} (MeCN) 386 (log ε 4·81), 367(4·63), and 346sh(4·25) nm, with an i.r. spectrum in agreement with the previous report.†[4] The methodology used to synthesize (**2b**) is summarized in the Scheme. The route *via* 2,6-dimethylthiopyran-4-selone (**3**) is originally due to Traverso.[5] Our samples of the thiapyrylium salt (**4**) melt at a temperature higher [m.p. 157—159 °C (decomp.)] than that reported (lit.[7] m.p. 130—132 °C) earlier. Compound (**3**) exhibits m.p. 112 °C, which is higher than two previous reports (108—109 °C[5] and 100—102 °C[8]). We have also found that (**2b**) may be isolated in 5—10% yield from thiophilic[9] addition of PhMgBr to 2,6-dimethylthiopyran-4-thione (**5**) in ether. We prefer the route *via* (**3**) which gives (**2b**) in 20% yield, based on (**5**), for the ease of isolation and purification it affords. Our samples of (**2b**) exhibit m.p. 222·5 °C [lit. m.p. 218 °C (decomp.)[5] and 223 °C[8]], *m/e* 248, and λ_{max} (MeCN) 394 (log ε 4·81), 374(4·67), and 356sh (4·34) nm. Both (**2a**) and (**2b**) absorb with greater intensity than (**1**) at all wavelengths between 350 and 650 nm, suggesting that these donors are more polarizable than (**1**).



SCHEME

When (**2a**) or (**2b**) is mixed with TCNQ in the appropriate molar ratio in MeCN solution, salts with cation to anion ratios of both 1 : 1 and 1 : 2 are formed. This result contrasts with the behaviour of (**1**), its alkyl derivatives, and their selenium analogues which are reported to form

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† Both (**2a**) and (**2b**), as well as their salts with TCNQ gave satisfactory analyses for all elements present.

only 1 : 1 salts with TCNQ.[3] The naphthacenobisdithiole (**6**) is another organosulphur donor which forms highly conducting 1 : 1[10] and 1 : 2[11] salts with TCNQ.

TABLE. Room temperature conductivity data for some TCNQ salts.

Entry	Salt	Conductivity/ ohm^{-1} cm^{-1}
1	(**2a**)–TCNQ	1[a]; 30[b]
2	(**2a**)–2TCNQ	8[a]
3	(**2b**)–TCNQ	10^{-4} [a]; 10^{-3} [b]
4	(**2b**)–2TCNQ	0·5[a]
5	(**1**)–TCNQ	10[a] (ref. 12)
6	(**6**)–TCNQ	0·6[a] (ref. 12)
7	NMP–TCNQ	2[a] (ref. 14)

[a] Measured on compressed pellets. [b] Measured on single crystals by four-probe method.

The Table summarizes our room temperature conductivity data for the salts. The 1 : 1 salt of (**2b**) and TCNQ has been prepared previously[8] in dimethylformamide (DMF) solution, and we have found that the salt prepared in MeCN has an *X*-ray powder diffraction pattern identical to that prepared in DMF.‡ It is apparent from the Table that the new salts (entries 1, 2, and 4) have conductivities, measured on compressed pellets, comparable to analogous data reported for (**1**)–TCNQ,[10] (**6**)–TCNQ,[10] and *N*-methylphenazinium (NMP)–TCNQ[12] (entries 5—7), representatives of the best known classes of highly conducting organic solids.

Compound (**2a**) clearly has a larger molecular volume than (**1**);[13] a correlation between the molecular volume of (**1**) and its alkyl derivatives and the physical properties of their salts with TCNQ was discussed earlier.[14] On this basis, it is to be anticipated that the details of the differences between the physical properties of the new class of salts described herein, to be reported elsewhere, and salts, cited above, studied earlier, will strongly depend on the topographical arrays of their crystal structures.

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‡ The unit cell data, collected using Mo-K_{α} radiation, for the salt (**2b**)–TCNQ indicate an alternating cation–anion stacking arrangement, consistent with its semiconducting behaviour. The crystal is triclinic, space group $P\bar{1}$, $a = 7.190(4)$, $b = 8.401(2)$, $c = 10.135(3)$ Å, $\alpha = 107.22(3)°$, $\beta = 97.30(3)$, $\gamma = 102·71(3)°$.

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