Synthesis of a New Organic π-Donor: 2-(Thiopyran-4-ylidene)-1,3-dithiole and its Conducting Salts with 7,7,8,8-Tetracyanoquinodimethane

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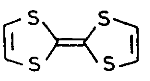
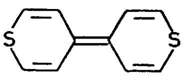
Summary The new organic π-donor, 2-(thiopyran-4-ylidene)-1,3-dithiole (**3**), iso-π-electronic to both tetrathiafulvalene (**1**) and $\Delta^{4,4'}$-bithiopyran (**2**) and obtained by a three-step synthesis in 15% overall yield, reacts with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give two semiconducting salts.

THE considerable current interest in organic charge-transfer salts was stimulated by the finding that the donor tetrathiafulvalene (TTF) (**1**) reacts with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give a salt which exhibits the electrical properties of a quasi-one-dimensional metal.[1,2]



(1)



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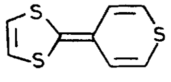
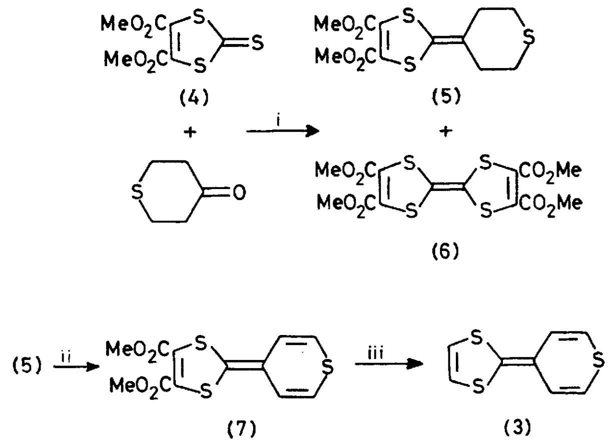


(3)

We have recently reported[3] the characterization of a new class of highly conducting salts of TCNQ and the cation derived from $\Delta^{4,4'}$-bithiopyran (BTP) (**2**), a donor which is iso-π-electronic with the widely studied (**1**). We now describe the synthesis of the new organosulphur donor 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT) (**3**), a molecule with structural 'fragments' of both (**1**) and (**2**), but with reduced molecular symmetry [C_{2v} compared to D_{2h} for (**1**) and (**2**)].



SCHEME. i, $(RO)_3P$ (R = Me or Et); ii, chloranil; iii, LiBr, HMPA.

The synthetic route to (**3**) is summarized in the Scheme. The thione[4] (**4**) reacts with a ten-fold molar excess of thiacyclohexan-4-one in the presence of either trimethyl or triethyl phosphite in refluxing benzene to give (**5**),† an orange solid, m.p. 124 °C, in 30% yield, λ_{max} (MeCN) 407 (log ϵ 3·30), 327 (3·98), and 262 (4·08) nm. Compound (**6**), the methoxycarbonyl derivative of (**2**),[5,6] is also formed in this reaction, and (**5**) is isolated by elution of the crude reaction product on a silica gel column with hexane–benzene. Dehydrogenation of (**5**) is accomplished with chloranil in refluxing xylene to give the purple diester (**7**) in 80% yield, m.p. 147—147·5 °C, λ_{max} (MeCN) 482 (log ϵ 3·0), 376sh (3·91), 352 (4·56), 337 (4·44) 323sh (4·21), and 251sh (3·84) nm. Decarboxylation of (**7**) with lithium bromide in hexamethylphosphoric triamide[7] (HMPA) at 150—160 °C gives (**3**) in 60% yield [15% overall yield from (**4**)] which is isolated by crystallization from benzene–hexane as an ochre solid and is further purified by gradient sublimation, m.p. 127 °C, λ_{max} (MeCN) 359 (log ϵ 4·5), 348sh (4·4), and

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† All new compounds gave satisfactory analyses for all elements and had spectral (i.r., ^{1}H n.m.r., and mass) properties in accord with the assigned structures.

252 (3·6) nm. The absorption spectrum of (**3**) suggests that it is intermediate in polarizability between (**1**) and (**2**).[3] The presence of a medium-intensity low-energy transition in (**7**), which is absent in (**3**), is reminiscent of the spectra of (**1**) and (**6**).[5] In MeCN solution containing 0·1M tetraethylammonium perchlorate, (**3**) undergoes two reversible one-electron oxidations at a platinum electrode, $E_1 = 0{\cdot}28$, $E_2 = 0{\cdot}64$ V *vs.* S.C.E. Our value of E_1 for (**3**) may be compared to those reported for (**1**) and (**2**) (0·20[8] and 0·33 V,[9] respectively).

The cation radical of (**3**) may be generated[8] by the addition of perchloric acid and triethylamine to a solution of (**3**) in MeCN. In this experiment, the spectrum of neutral (**3**) is lost and new absorption appears at lower energy, λ_{max} 622 (log ϵ 3·7), 525 (3·6), and 457 (4·5) nm. The last peak is also prominent in the spectra, in MeCN solution, of the TCNQ salts of (**3**) (see below). Again, these results suggest that the cation of (**3**) is intermediate in polarizability between those of (**1**) and (**2**).

TCNQ reacts with (**3**) in either MeCN or ethyl acetate solution to give salts of both 1:1 and 2:3 stoicheiometry; these salts have distinct *X*-ray powder diffraction patterns. While it is apparent that (**3**) is comparable to (**1**) and (**2**) in size, polarizability, and ease of oxidation in solution, the conductivity of its TCNQ salts is lower than that of the TCNQ salts of (**1**) and (**2**). For the present, the data suggest that these new TCNQ salts of (**3**) contain energy gaps, either structural or electronic in origin. It is further apparent that crystal packing considerations, especially localised intermolecular contacts, are at least as important as desirable molecular properties in determining the physical properties of TCNQ salts of (**1**), (**2**), and (**3**).

TABLE. Conductivities[a] of TCNQ salts of (**1**), (**2**), and (**3**).

Salt	Conductivity /Ω^{-1} cm^{-1}
(**1**)-TCNQ	10
(**2**)-TCNQ	1
(**2**)-2TCNQ	8
(**3**)-TCNQ	10^{-2}
2(**3**)-3TCNQ	10^{-1}

[a] Measured on compressed pellets at room temperature.

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