Synthesis of $\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (DTTTF) and Some of its Charge-transfer Salts

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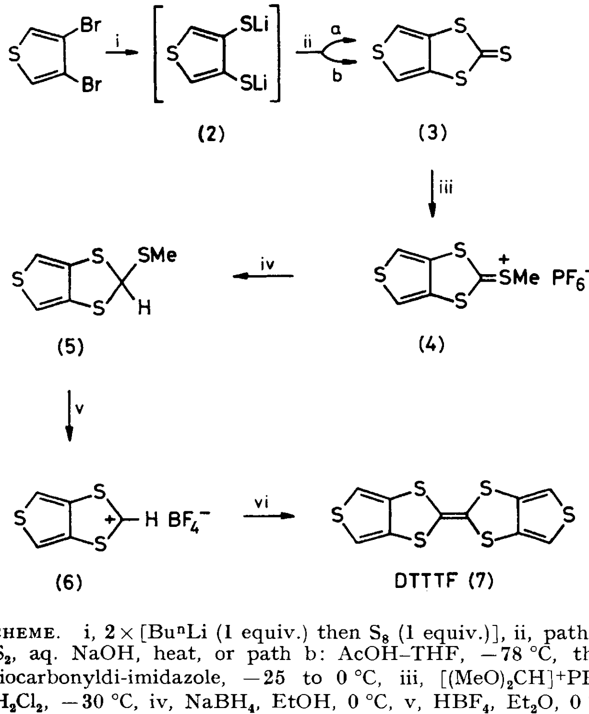
Summary The title compound (DTTTF) was prepared by the coupling of the corresponding thieno-1,3-dithiolium salt, obtained from thieno-1,3-dithiolane-2-thione synthesized from 3,4-dibromothiophen.

IN our systematic study of highly conducting TTF–TCNQ-type[1] organic charge-transfer salts (TTF = tetrathiafulvalene, TCNQ = tetracyanoquinodimethane), one aspect of our recent work concerns the chemical control of the Peierls transition through variations in interchain coupling.[2] We report here the synthesis of a new TTF-type donor, namely $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole or di[thieno(3,4-*d*)]-1,4,5,8-tetrathiafulvalene, DTTTF (**1**). The oxidation potential for DTTTF, *vide infra*, is much higher than that of TTF and, in fact, even higher than that of the donor dibenzotetrathiafulvalene (DBTTF). Thus, DTTTF may be more likely to form partially charged complexes with strong acceptors, such as $\mathrm{TCNQF_4}$, for which available donors yield only completely charged, Mott–Hubbard insulators.[3,4] We anticipate that salts of DTTTF with TCNQ-like acceptors could have interchain couplings and phonon instabilities different from TTF–TCNQ and, hence, distinctive low-temperature characteristics.



SCHEME. i, 2 × [$\mathrm{Bu^nLi}$ (1 equiv.) then $\mathrm{S_8}$ (1 equiv.)], ii, path a: $\mathrm{CS_2}$, aq. NaOH, heat, or path b: AcOH–THF, −78 °C, then thiocarbonyldi-imidazole, −25 to 0 °C, iii, $\mathrm{[(MeO)_2CH]^+PF_6^-}$, $\mathrm{CH_2Cl_2}$, −30 °C, iv, $\mathrm{NaBH_4}$, EtOH, 0 °C, v, $\mathrm{HBF_4}$, $\mathrm{Et_2O}$, 0 °C, vi, $\mathrm{Pr^i_2NEt}$, MeCN, −30 °C.

As shown in the Scheme, (**3**)[5] was prepared by a convenient one-flask reaction, in which 3,4-dibromothiophen (**1**)[6] was twice treated with $\mathrm{Bu^nLi}$ followed by elemental sulphur in either diethyl ether or tetrahydrofuran (THF) at −78 °C to provide lithium 3,4-dimercaptothiophen (**2**). After the solvent was evaporated, a large excess of $\mathrm{CS_2}$ and 2N NaOH was added and the mixture was heated to refluxing temperature for 3 h (path a). The product was separated by filtration and recrystallized from $\mathrm{CH_2Cl_2}$–hexane to yield (**3**) (33%). Alternatively, the dilithio-intermediate (**2**) could be protonated with glacial acetic acid (3 equiv.) in THF at −78 °C. The resulting dithiole was then allowed to react with an excess of thiocarbonyldi-imidazole (*ca.* 1·8 equiv.) in a dilute solution in THF at −25 °C to 0 °C to afford a 39% yield of (**3**) (path b).

Methylation of (**3**) with dimethoxycarbenium hexafluorophosphate at −30 °C in $\mathrm{CH_2Cl_2}$ gave (**4**) in 80% yield. Sodium borohydride reduction of (**4**) was carried out in ethanol at 0 °C to yield (**5**) nearly quantitatively. Treatment of (**5**) with fluoroboric acid in ether with a trace amount of acetic anhydride at 0 °C gave a quantitative yield of (**6**) as an unstable, bright yellow solid, which was used immediately in the preparation of (**7**). The coupling reaction of (**6**) to form DTTTF was effected by adding di-isopropylethylamine to a saturated solution of (**6**) in acetonitrile at −30 °C. After recrystallization from $\mathrm{CH_2Cl_2}$–hexane, DTTTF was isolated in 31% yield from (**4**) as bright yellow crystals, m.p. 259—260 °C (decomp.); ^{1}H n.m.r.: δ ($\mathrm{CDCl_3}$) 6·9 (s); $\nu_{\max}$ (KBr) 3100(vw), 1386(w), 1322(w), 836(w), 770(w), 750(m), and 707(w) $\mathrm{cm^{-1}}$; *m/e* (rel. intensity) 316 (M^+, 100), 158 (30), and 82 (15). The mass spectrum of DTTTF is like those of other TTF derivatives, with the molecular ion as the base peak, indicating the stability of the $\mathrm{DTTTF^+}$ cation. The fine structure of a group of peaks centred at m/e = 158 suggests the formation of the dication of (**7**). This is a common observation for other derivatives of TTF. The oxidation potential for (**7**) as determined from cyclic voltammetry is 0·430 V as compared with 0·075 for TTF and 0·320 V for DBTTF[7] ($\mathrm{Ag/AgNO_3}$ reference electrode).

Charge-transfer complexes of (**7**) with $\mathrm{TCNQF_4}$ and TCNQ were prepared by standard H-tube methods using acetonitrile as the solvent. The complex containing the acceptor TCNQ formed as red, plate-like crystals, while, surprisingly, two forms of the $\mathrm{TCNQF_4}$ salt were found: (α), thin dark-coloured needles, and (β), blue platelets. Preliminary crystal data [monoclinic, space group $C2/c$, a = 10·115(4), b = 12·402(6), c = 9·602(3) Å, β = 109·16(3)°, U = 1074 Å^3, Z = 2, D_m = 1·60(1) g cm^{-3}, D_c = 1·62 g cm^{-3}] indicate that the TCNQ salt may possess a mixed-stack arrangement as observed in other TCNQ salts of similar colour and cell dimensions.[8] The α-form of the $\mathrm{TCNQF_4}$ salt crystallizes in space group $C2/m$ with crystal data: monoclinic, $a = 21{\cdot}867(13)$, $b = 12{\cdot}794(8)$, $c = 3{\cdot}891(1)$ Å, $\beta = 91{\cdot}48(4)°$, $U = 1088$ Å^3, $Z = 2$, $d_m = 1{\cdot}81(1)$ g cm^{-3}, $d_c = 1{\cdot}82$ g cm^{-3}. This form is isostructural with TCNQ[2] and TCNQF$_4$[9] salts of HMTSF. Additionally, the α-form of DTTTF–TCNQF$_4$ has semiconducting properties ($\sigma_{RT} = 7 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) similar to HMTSF–TCNQF$_4$.[3] The unexpected second form (β) of DTTTF–TCNQF$_4$ crystallizes in space group $P2_1/a$: monoclinic, $a = 13{\cdot}059(6)$, $b = 24{\cdot}213(10)$, $c = 7{\cdot}135(2)$ Å, $\beta = 103{\cdot}38(3)°$, $U = 2195$ Å^3, $Z = 4$, $D_m = 1{\cdot}82(1)$ g cm^{-3}, $D_c = 1{\cdot}80$ g cm^{-3}. The crystal structure of this second form of DTTTF–TCNQF$_4$ may prove to be unusual and is currently under investigation. The hexafluorophosphate salt of DTTTF has been grown electrochemically and is a semiconductor with $\sigma_{RT} = 10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and has a gap for the conductivity of *ca.* 0·07 eV.

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