# Novel Electron Acceptors derived from Isothianaphthene

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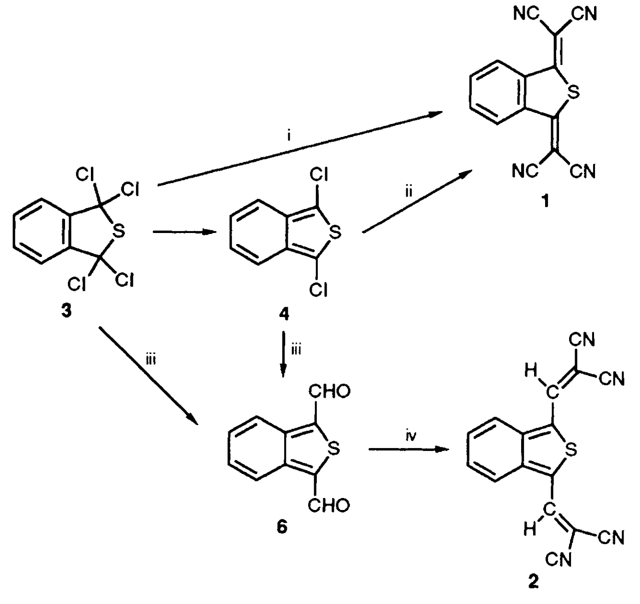
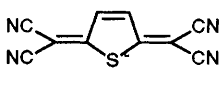
The synthesis and properties of 1,3-dihydro-1,3-bis(dicyanomethylene)isothianaphthene **1** and its higher homologue 1,3-bis(1,3-dicyanovinylene)isothianaphthene **2** are reported; these compounds, which are the first electron acceptors of the isothianaphthene series, show electrochemical behaviour that contrasts with that of their thiophene analogues; the molecular structure of **1** was determined by X-ray analysis.

In contrast to the extensively studied tetracyanoquinodimethane (TCNQ), only a few TCNQ analogues of thiophene or condensed thiophenes have been synthesized and examined as potential electron acceptors.[1] Our ongoing interest in the chemistry of isothianaphthene[2] has prompted us to investigate the synthesis and properties of the isothianaphthene analogue **1** of TCNQ, as well as its vinylogue **2**. These compounds represent the first electron acceptors of the isothianaphthene series.

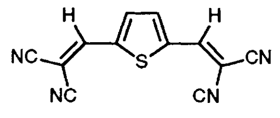
The synthesis of the tetracyano compounds **1** and **2** was



Scheme 1 *Reagents*: i, DBU, $CH_2(CN)_2$; ii, TCEO; iii, Bu$^t$Li, DMF; iv, $CH_2(CN)_2$; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TCEO = tetracyanoethylene oxide



**5**



**7**

achieved starting from either tetrachlorothiophthalene **3** or 1,3-dichloroisothianaphthene **4**, as outlined in Scheme 1. Thus, **1** was obtained in low yield (5%) by warming tetrachloride **3** with malononitrile in DMF (dimethylformamide) solution. A better result was obtained by an adaptation of the synthesis used to prepare the thiophenequinodimethane **5** from 2,5-dichlorothiophene.[3] In this reaction, **1** was produced in 25% yield by refluxing dichloride **4** with tetracyanoethylene oxide in 1,2-dibromoethane for two days, followed by silica chromatography.†

As previously noted, dialdehyde **6** could not be obtained by treatment of either **3** or **4** with n-butyllithium followed by DMF, since only a monolithiated isothianaphthene intermediate is formed by the base.[2] We have now found that 1,3-dilithioisothianaphthene can be generated under forcing conditions. Thus, reaction of either **3** or **4** with an excess of *tert*-butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMDA) in hexane at 0 °C, followed by warming to room temperature (45 min) and reaction with DMF gave, after hydrolysis, dialdehyde **6**. Condensation of **6** with malononitrile gave tetranitrile **2**.

Table 1 Half-wave redox potentials of acceptors (**1**, **2**, **5** and **7**)[a]

| Acceptor | $E_1^{1/2}$/V | $E_1^{1/2}$/V | $\Delta E$/V |
|---|---|---|---|
| Benzothiophene **1** | −0.31 | −0.78 | 0.47 |
| Benzothiophene vinylogue **2** | −0.25 | −0.62 | 0.37 |
| Thiophene **5**[4] | 0.07 | −0.54 | 0.61 |
| Thiophene vinylogue **7**[5] | −0.42 | −0.83 | 0.41 |

[a] Experimental conditions: electrolyte $Bu_4NPF_6$ 0.1 mol dm$^{-3}$ in dry dichloromethane, under argon, room temp., *vs.* Ag/AgCl, Pt electrode, scan rate 100 mV s$^{-1}$.

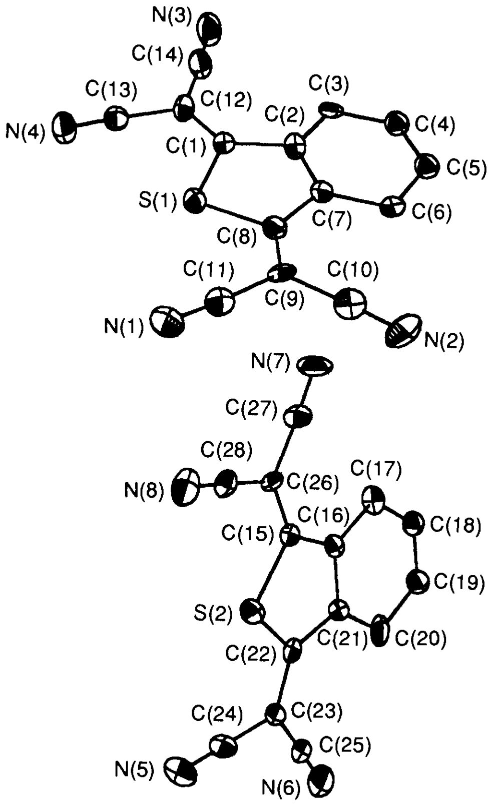


Fig. 1 Single crystal X-ray structure of benzothiophene-TCNQ **1**

We compared the cyclic voltammetric data of the benzothiophene–TCNQ **1** and vinylogue **2** with thiophene–TCNQ **5** and its vinylogue **7**. The data are summarized in Table 1.

The voltammetry of compounds **1** and **2** shows two reversible redox waves corresponding to two one-electron reductions. Both first half waves for **1** and **2** are at much lower potentials than those found for the thiophene TCNQ **5**. Another feature is that it is easier to reduce dicyano vinyl **2** than **1**. In fact, each time the aromaticity is broken to form the dianionic species, the reduction potential of the first wave is lowered. On the other hand, the second wave (**1**: −0.78, **2**: −0.62) decreases with the extended conjugation. This indicates an effective reduction of the on-site coulombic repulsion in the dianionic states of the vinylogues as expected.

The single crystal X-ray structure of compound **1** has been determined and is presented in Fig. 1 and 2.‡ The compound

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† Compound **1**, 25% yield, m.p. 254 °C, orange–red crystals (from acetonitrile) $\lambda_{max}$/nm ($CH_2Cl_2$) 408 (4.90) $^1$H NMR ($CDCl_3$) δ 8.79 (dd, 2H, *J* 5.9, *J* 3.1 Hz), 7.95 (dd, 2H, *J* 6.1, *J* 3.1 Hz). IR ν(CN)/cm$^{-1}$ 2220.

Compound **2**, 85% yield, m.p. 305 °C (decomp.), $\lambda_{max}$ 540 (4.57). $^1$H NMR ($CDCl_3$), 8.43 (s, 2H), 7.92 (dd, 2H, *J* 6,6, *J* 3.2 Hz), 7.66 (dd, 2H, *J* 6,2, *J* 3.2 Hz). IR ν(CN)/cm$^{-1}$ 2200. HRMS Calcd. for $C_{16}H_6N_4S$, 286.0313. Found 286.0310.

Compound **6**, yellow–brown crystal (from hexane–chloroform) yield from **3** = 63%; from **4** = 90%. m.p. 161–163 °C. $\lambda_{max}$/nm ($CH_2Cl_2$) 409 (3.87). $^1$H NMR ($CDCl_3$), δ 76.43 (2H, s), 8.43 (2H, dd, *J* 6.7, *J* 3.1 Hz), 7.58 (2H, dd, *J* 6,7, *J* 31 Hz). IR ν(CO)/cm$^{-1}$ 1640.

Compound **7**, 95% yield from malononitrile and thiophene-2,5-dicarboxaldehyde, m.p. 210 °C, IR ν(CN)/cm$^{-1}$ 2210, $\lambda_{max}$/nm ($CHCl_3$) 416.

‡ *Crystal data* for **1**, $C_{14}H_4N_4S$, triclinic space group $P\bar{1}$, $a$ = 7.540(3), $b$ = 10.788(7), $c$ = 16.084(4) Å, α = 103.09(4), β = 90.02(4), γ = 110.46(6)°, $U$ = 1189 Å$^3$, $Z$ = 4, $F$(000) = 528, Mo-Kα radiation (graphite monochromator), μ = 2.49 cm$^{-1}$. The structure was solved using direct methods (SHELX86)[6] and refined by least-squares analysis[7] giving values of $R$ = 0.033, $R_w$ = 0.036 for 832 observed ($F_o > 3\sigma F_o$) reflections from 1170 unique data, which were collected using a ω/2θ scan mode on a CAD4 diffractometer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

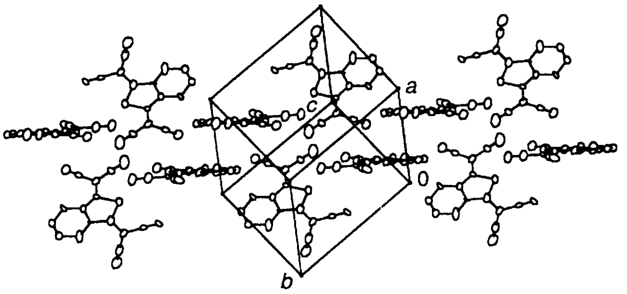

**Fig. 2** Unit-cell packing of benzothiophene-TCNQ **1**

crystallizes with two molecules in the asymmetric unit. The molecule is essentially planar with slight puckering of the cyanide groups at the methylene bridge. The closest intermolecular distance is 3.05 Å between N(3) $(1 - x, 2 - y, 2 - z)$ and N(7) $(x, y, z)$. Compound **1** represents the first benzothiophene-related acceptor to be characterized by X-ray analysis.

It is particularly interesting to note several key bond lengths of this compound. The S(1)–C(1), C(1)–C(2) and C(1)–C(12) lengths are 1.74, 1.49 and 1.33 Å, respectively. These values are in keeping with a benzenoid structure for **1** (as shown in Scheme 1) rather than one which is highly dipolar in nature. It is also noteworthy that **1** is planar, in contrast to its boat-shaped benzenoid analogue benzo-TCNQ.[8]

In view of their electron-acceptor properties, both **1** and **2** are of interest in the organic metals field since they would be expected to form conducting salts with appropriate organic donors.[9] The preparation of such salts has not yet been investigated, but will provide an interesting area for further study.

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