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New electron acceptors containing thieno[3,4-*b*]pyrazine units

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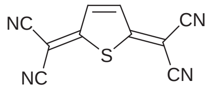
Tetracyano-*p*-quinodimethane (TCNQ) analogues containing the title heterocyclic units were synthesized, and the interesting crystal structures of the neutral compounds and the charge-transfer complexes with TTF were revealed by X-ray analysis.

Electron acceptors containing sulfur atoms are of interest as components for organic conductors since the intermolecular interactions leading to multi-dimensionality can be expected to result from interheteroatom contacts.[1] With this in mind, the TCNQ analogue **1** containing a thiophene unit was prepared.[2] Furthermore, π-extended compounds **2**[3] and **3**[4] were prepared to decrease on-site Coulombic repulsion. Benzothiophene–TCNQ **2** is a weak acceptor due to the fused benzene ring.[3] In order to overcome this disadvantage, we have now replaced the benzene ring by electron-withdrawing pyrazine rings to give **4**. We have also prepared new acceptors **5** which are pyrazine fused derivatives of π-extended acceptor **3**. The new acceptors **4** and **5** are expected to be planar molecules due to the absence of *peri*-hydrogen atoms, and the nitrogen atoms of the pyrazines may be involved in the interheteroatom contacts.

The acceptors **4** and **5** were prepared from 5,7-dibromothieno[3,4-*b*]pyrazines **6** which were obtained by bromination with NBS of the corresponding thieno[3,4-*b*]pyrazines.[5] Reaction of **6a** with tetracyanoethylene oxide (TCNEO) in refluxing 1,2-dibromoethane afforded **4a** and **5a** in 6 and 5% yields, respectively. The reaction in the presence of Cu powder gave **4a** in 15% yield along with a trace amount of **5a**. Reaction of **6b** with TCNEO without Cu gave **5b** in 30% yield along with a trace amount of **4b**. The reaction in the presence of Cu gave **4b** and **5b** in 24 and 6% yields, respectively. Such a reaction of TCNEO with dibromo compounds was used in the synthesis of **1–3**. In these cases, the yields were higher than those of **4a**,**b**, but no dimerization products such as **5** were obtained. The low yields of **4** may be attributed to the lability of the pyrazine ring to TCNEO.[6] The mechanism of formation of **5** is still unclear.

The absorption maxima of **5** are red-shifted compared to those of **4** as shown in Table 1. The PM3 calculations[7] show the smaller HOMO–LUMO gap of **5a** compared to those of **4a** and TCNQ, where the LUMO energies of TCNQ, **4a** and **5a** are −3.06, −2.85 and −2.84 respectively, and the HOMO energies of TCNQ, **4a** and **5a** are −9.58, −9.72 and −9.01 eV, respectively. It is noteworthy here that the LUMO level becomes a little higher with increasing π-extension. Actually the first reduction potentials of **5** are lower than those of **4** as shown in Table 1, indicating that compounds **5** are weaker electron acceptors than **4**. The same trend is observed in the system of **1** and **3**.[3] The differences between the first and second reduction potentials (ΔE) decrease in **5** compared to **4**, indicating the decrease in on-site Coulombic repulsion in **5** due to the extended π-conjugation.



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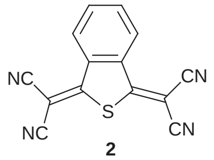

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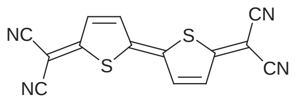

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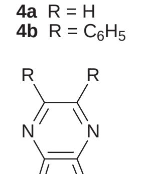
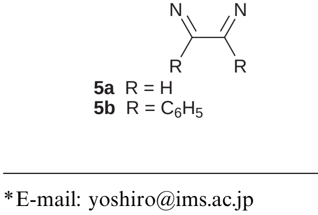
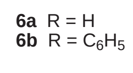


4a R = H
4b $R = C_6H_5$



5a R = H
5b $R = C_6H_5$



6a R = H
6b $R = C_6H_5$

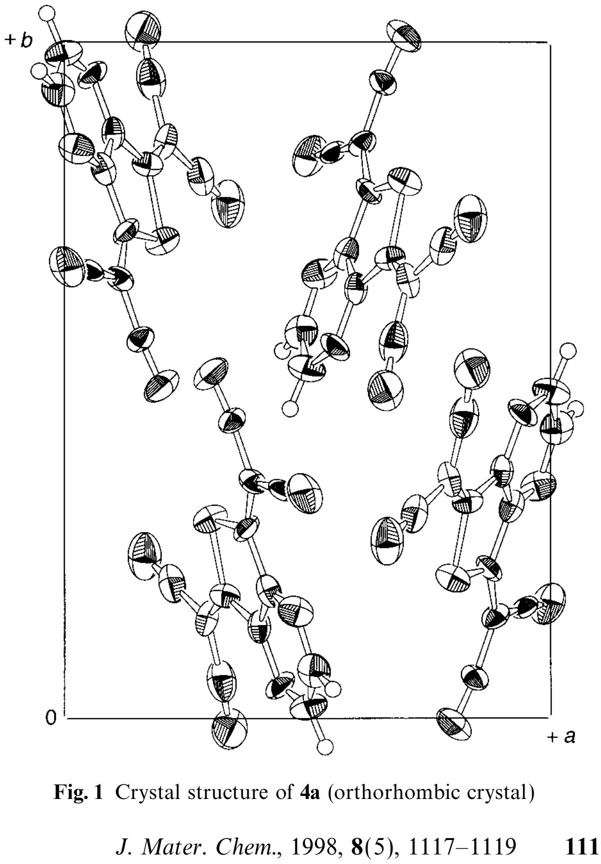


Fig. 1 Crystal structure of **4a** (orthorhombic crystal)

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Table 1 The absorption maxima and reduction potentials of acceptors

acceptor	λ_{max}/nm[a]	E_{red}/V[b]	ΔE/V
4a	403	−0.04, −0.56	0.52
4b	402	−0.10, −0.59	0.49
5a	512	−0.22, −0.47	0.25
5b	531	−0.28, −0.52	0.24
TCNQ	401	+0.22, −0.35	0.57

[a] In CH_2Cl_2. [b] 0.1 mol dm^{-3} Bu_4NClO_4 in CH_2Cl_2, Pt electrode, scan rate 100 mV S^{-1}, V *vs.* saturated calomel electrode (SCE).

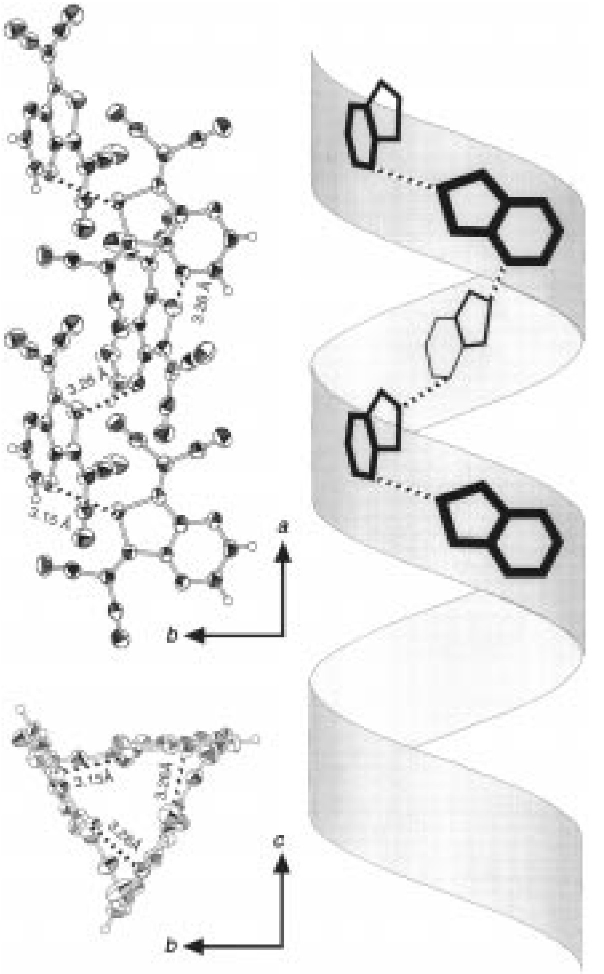

Fig. 2 Crystal structure of **4a** (monoclinic crystal)

The single crystals of **4a** were obtained as two crystal forms, *i.e.* orthorhombic (yellow cubes) and monoclinic forms (yellow needles).† In the orthorhombic crystal (Fig. 1) no short interheteroatom contact was observed. On the other hand, in the monoclinic crystal there exist three crystallographically independent molecules and three kinds of short S···N contacts (3.15, 3.26 and 3.28 Å) between the S atoms of the thiophene rings and the N atoms of the pyrazine ones, which are shorter than the sum of the van der Waals distance (3.35 Å). The net atomic charges of **4a** calculated by the PM3 method show that the sulfur and nitrogen atoms are positively and negatively charged, respectively, suggesting an electrostatic interaction leading to the S···N contacts. These interactions result in an interesting molecular network as shown in Fig. 2, where a helical structure is constructed.

Reaction of the acceptor **4a** with an equal amount of TTF in acetonitrile afforded two kinds of charge-transfer complexes with TTF [a 1:2 complex (green plates) and a 3:2 complex (green needles)] in the same batch, which could be separated on the basis of the difference in the crystal form. The bond lengths of the TTF and acceptor molecules in the complexes are comparable to those of neutral ones.[8] The nitrile stretching frequencies for the 1:2 and 3:2 complexes were observed at 2225.4 and 2224.0 cm^{-1}, respectively, which are almost the same as that for the neutral **4a** (2224.2 cm^{-1}). These facts

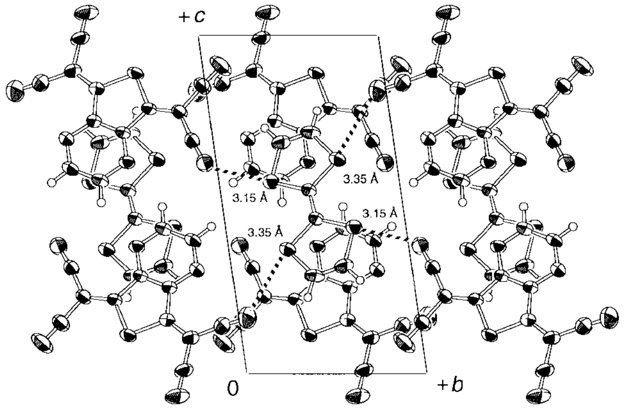

Fig. 3 Crystal structure of (TTF)·(**4a**)$_2$

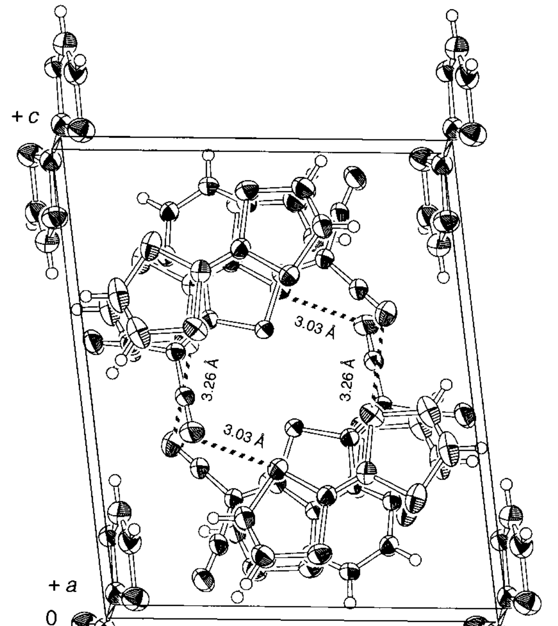

Fig. 4 Crystal structure of (TTF)·(**4a**)$_2$

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† *Crystal data* for **4a**: $C_{12}H_2N_6S$, $M=262.25$, orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=10.517(5)$, $b=14.683(5)$, $c=7.628(5)$ Å, $V=1177(1)$ Å^3, $D_c=1.479$ g cm^{-3}. The final R value was 0.037 for 405 reflections with $I>3\sigma(I)$. **4a:** $C_{12}H_2N_6S$, $M=262.25$, monoclinic, space group $P2_1/c$, $Z=12$, $a=12.636(2)$, $b=15.086(3)$, $c=18.350(5)$ Å, $\beta=93.57(1)°$, $V=3491(1)$ Å^3, $D_c=1.497$ g cm^{-3}. The final R value was 0.048 for 2508 reflections with $I>3\sigma(I)$. (TTF)·(**4a**)$_2$: $C_{30}H_8N_{12}S_6$, $M=728.83$, triclinic, space group $P\bar{1}$, $Z=1$, $a=7.3720(6)$, $b=7.5992(5)$, $c=14.3903(7)$ Å, $\alpha=96.607(5)$, $\beta=98.741(5)$, $\gamma=99.304(6)°$, $V=778.22(10$ Å^3, $D_c=1.555$ g cm^{-3}. The final R value was 0.053 for 2313 reflections with $I>3\sigma(I)$. (TTF)·(**4a**)$_2$: $C_{42}H_{16}N_{12}S_{14}$, $M=1137.51$, triclinic, space group $P\bar{1}$, $Z=1$, $a=7.4174(3)$, $b=11.6811(5)$, $c=13.9003(8)$ Å, $\alpha=95.824(4)$, $\beta=93.879(4)$, $\gamma=98.471(4)°$, $V=1180.90(10)$ Å^3, $D_c=1.599$ g cm^{-3}. The final R value was 0.056 for 4246 reflections with $I>3\sigma(I)$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Author, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/90.

suggest that the component molecules are almost non-ionic. Therefore, the conductivities are low [1 : 2 complex; 5×10^{-9} S cm^{-1} as a compressed pellet, 3 : 2 complex; 5×10^{-4} S cm^{-1} as a single crystal ($Ea = 0.11$ eV)]. However, the crystal structures are interesting as shown in Fig. 3 and 4.† In the 1 : 2 complex the TTF molecule bridges two acceptor molecules. To the best of our knowledge, this type of molecular overlapping has not been observed in the charge-transfer complexes. In the crystal there are short S···N contacts (3.15 and 3.35 Å) between the S atoms of the TTF and the N atoms of the CN group, which may result in the unique crystal structure. In the 3 : 2 complex a mixed stacking is formed and the S···N contacts (3.03 and 3.26 Å) are observed between the columns as shown in Fig. 4. Another TTF molecule is located at the position orthogonal to the column. These results suggest that TCNQ analogues containing polarizable heterocycles are promising electron acceptors to give organic conductors with multi-dimensional structures by the interheteroatom contacts.

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