

The Structures of Some Charge-Transfer Complexes Containing TCNQ as Acceptor and Their Electrical Anisotropy

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Abstract

The crystal structures of four complexes formed by 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, C₁₂H₄N₄) and 1,2-di(2-thienyl)ethylene (DTE, C₁₀H₈S₂), stilbene (STB, C₁₄H₁₂), 2,2',5,5'-tetramethoxystilbene (TMS, C₁₈H₂₀O₄) and dithieno-[3,2-*b*:2',3'-*d*]thiophene (DTT, C₈H₄S₃) were determined by X-ray analysis. [Crystal data: DTE:TCNQ, *C*2/*m*, *a* = 13.105 (4), *b* = 12.016 (3), *c* = 7.187 (3) Å, β = 122.15 (2)°, *Z* = 2; STB:TCNQ, *C*2/*m*, *a* = 13.468 (4), *b* = 12.204 (3), *c* = 7.235 (3) Å, β = 122.95 (2)°, *Z* = 2; TMS:TCNQ, *P*1, *a* = 11.833 (6), *b* = 8.441 (4), *c* = 7.137 (3) Å, α = 95.10 (4), β = 88.58 (4), γ = 112.26 (6)°, *Z* = 1; DTT:TCNQ, *P*2₁/*a*, *a* = 32.334 (3), *b* = 7.570 (2), *c* = 7.229 (2) Å, β = 92.18 (1)°, *Z* = 4.] For structure solution Patterson, direct and vector-search methods were used. Full-matrix least-squares refinements led to *R* values of 4.4% for DTE:TCNQ, 3.9% for STB:TCNQ, 4.6% for TMS:TCNQ and 3.9% for DTT:TCNQ over 836, 881, 2456 and 2691 reflexions, respectively. All compounds form mixed stacks of nearly coplanar donor and acceptor molecules in 1:1 relation. The interplanar spacings correspond to the van der Waals separation. Disorder was found with respect to the DTE and STB molecules in these TCNQ complexes. Both molecules were treated by group refinement. Anisotropic electrical conductivities measured for all compounds are very low, corresponding to mixed-stack packing.

Introduction

All the title compounds were prepared as part of a program of synthesizing polyvinylene arylenes and polyvinylene heteroarylenes with conjugated π-electron systems as well as complexes with electron-acceptor molecules like the well known 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (Long, Sparks & Trueblood, 1965). The DTE, STB and TMS complexes of TCNQ were synthesized and chemically

characterized by Chatzitheodorou (1982), and DTT:TCNQ by Beimling (1982). The compounds were expected to belong to the same category of organic semiconductors. In view of the fairly low electrical conductivity they are expected to be built up in mixed-stack arrangements. A component thickness of approximately 3.5 Å compared to the 7 Å of the *c* axis of all complexes is also a possible indication of mixed-stack arrangements running largely parallel to this direction (Herbstein, 1971). This was confirmed by the results of the structure analyses for all the title compounds.

Experimental

The crystals of all the title compounds, obtained from acetonitrile solution, were black and needle shaped. The cell constants and possible space groups were obtained from oscillation and Weissenberg photographs; in all cases a centre of symmetry was indicated by the hypercentric distribution of the normalized structure factors. Accurate cell dimensions and intensities were obtained from diffractometer measurements (Siemens and Stoe) with Ni-filtered Cu *K*α radiation and θ range 3 to 65°.

The data for all compounds were corrected for Lorentz, polarization and absorption effects. For the final least-squares refinements the weighting scheme was $w = xy$, with $w = 0$ for $AF_o > |F_c|$ and $x = 1$ for $\sin \theta > B$, $x = \sin \theta / B$ for $\sin \theta \leq B$, $y = 1$ for $F_o < C$ and $y = C / F_o$ for $F_o > C$, where $A = 0.5$, $B = 0.6$, $C = 4.0$. Unobserved reflexions were weighted zero. The following numbers of independent reflexions were collected {unobserveds [$I < 2\sigma(I)$] are given in parentheses}: DTE:TCNQ 836 (93), STB:TCNQ 881 (155), TMS:TCNQ 2456 (552), DTT:TCNQ 2691 (277). For DTE:TCNQ, TMS:TCNQ and DTT:TCNQ one reflexion each and for STB:TCNQ four low-angle reflexions with high negative ΔF values were excluded from refinement since some of them probably suffered from extinction. An anomalous-dispersion correction (f' and f'') for S was taken from

Table 1. *Additional crystal data*

	DTE:TCNQ	STB:TCNQ	TMS:TCNQ	DTT:TCNQ
M_r	396.50	384.44	504.55	400.51
V (\AA^3)	958.15	997.88	660.14	1768.25
D_m (g cm^{-3})	1.32 (3)	1.25 (3)	1.23 (3)	1.45 (5)
D_x (g cm^{-3})	1.374	1.279	1.269	1.504
μ (Cu $K\alpha$) (cm^{-1})	24.75	6.21	7.10	37.84
Crystal size (mm)	0.21 \times 0.18 \times 0.29	0.13 \times 0.03 \times 0.72	0.28 \times 0.10 \times 0.73	0.50 \times 0.14 \times 0.06
Transmission factors (maximum/minimum)	0.68/0.61	0.98/0.94	0.93/0.82	0.80/0.50
Maximum shift/error ratio in final LS cycle	0.52	0.34	0.10	0.14

International Tables for X-ray Crystallography (1968). Atomic scattering factors for N, S and C were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). All computations were performed on a Cyber 175 computer using *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEPII* (Johnson, 1976). Crystal data are given in the *Abstract* and in Table 1.

Structure determination and refinement

DTE:TCNQ and *STB:TCNQ*

After repeated attempts had failed to solve the structure with *MULTAN* (Main *et al.*, 1977) we examined the three-dimensional, sharpened, origin-removed Patterson function of *DTE:TCNQ*, hoping to find the S—S vectors. We found some vectors belonging unambiguously to the TCNQ molecule, particularly the short C—N triple bond, but not the S—S vectors.

A Fourier synthesis phased on the five atoms of the asymmetric unit of TCNQ located the DTE molecule situated around $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ but perpendicular to the mirror plane and not parallel, as had been expected. This result implied that the DTE molecules are disordered. Refinements of all non-hydrogen atoms converged to R 7.6% with 'bad' geometry and high anisotropic temperature parameters for the thiophene system. We then introduced the thiophene ring together with C(5) as a fixed group with the known geometry taken from an earlier structure (Ruban & Zobel, 1975). Use of the *RIGBOD* program of *XRAY76* (Stewart *et al.*, 1976) to find the optimal fit, however, failed, because the model was shifted too close to the centre of the ellipsoid describing the electron density.

A graphical superposition of the DTE model (see Fig. 1a) on the electron density, however, gave a satisfactory fit.

A group refinement (isotropic temperature factors) with population parameter of 0.5 for S(1), C(1)–C(5) and H(1)–H(5) led to $R = 6.6\%$. The group restriction was then removed, the positional parameters of these atoms were fixed and the thermal

parameters for the non-hydrogen atoms were refined anisotropically, converging to reasonable values at an R value of 5.2%. Three final least-squares cycles with the positional parameters of the DTE molecule refined but with a damping factor of 0.3 reduced R to 4.4% and R_w to 5.8%. Table 2* contains final non-hydrogen-atom parameters showing fairly large e.s.d.'s for the DTE atoms, due to the disorder. Nevertheless this seems to be the best description of *DTE:TCNQ* under the present circumstances. Further refinements would have moved these atoms back to the 'odd' positions before introducing the group refinement. Fig. 2 shows the atom numbering, bond lengths and angles in the DTE molecule. The data for TCNQ are listed in Table 3.

In the case of *STB:TCNQ*, the peak configuration produced by *MULTAN* likewise did not lead to a solution of the structure. But by comparison with the known structure of *DTE:TCNQ* which was expected to be isotopic with *STB:TCNQ* (see Table 1), the TCNQ molecule could be recognized and was translated to the same origin as in *DTE:TCNQ*. A difference Fourier synthesis phased on the five atoms of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for all four structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38608 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

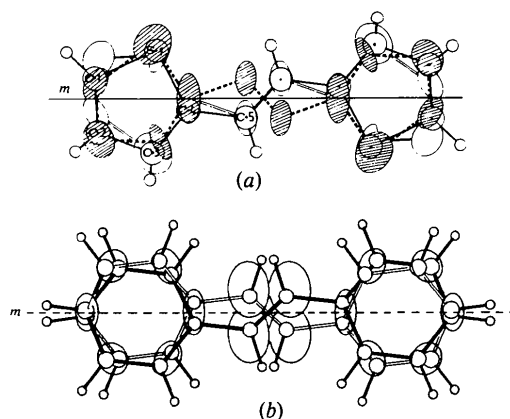


Fig. 1. Disorder model for (a) DTE and (b) STB (see text).

the asymmetric unit of TCNQ revealed the five highest peaks to be the C atoms of the asymmetric unit of the STB molecule, located around $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ as expected, and with the same disorder with respect to the central vinylene bridge. After including all non-H atoms and introducing anisotropic temperature parameters R converged to 15.3%. By superposition of this model containing strongly anisotropic temperature parameters with a 'correct' STB molecule taken from its pyromellitic dianhydride (Kodama & Kumakura, 1974), we obtained the atomic coordinates for the two separated molecules (Fig. 1b) in the same way as for DTE:TCNQ.

Table 2. DTE:TCNQ and STB:TCNQ: fractional coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)

The U_{eq} 's here, and in Tables 4 and 5, are calculated after Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
DTE:TCNQ				
N(1)	0.3681 (1)	0.1780 (1)	0.2056 (3)	8.3 (1)
C(11)	0.3098 (1)	0.0999 (1)	0.1709 (3)	5.9 (1)
C(12)	0.2424 (2)	0.0000	0.1319 (3)	5.1 (1)
C(13)	0.1232 (2)	0.0000	0.0655 (3)	4.8 (1)
C(14)	0.0579 (1)	0.1025 (1)	0.0301 (3)	5.4 (1)
S(1)	0.2592 (3)	0.6013 (3)	0.3761 (5)	13.8 (2)
C(1)	0.1321 (3)	0.5297 (4)	0.3101 (7)	7.9 (3)
C(2)	0.1467 (4)	0.4193 (5)	0.3249 (7)	8.3 (2)
C(3)	0.2706 (3)	0.3861 (4)	0.3951 (7)	4.6 (1)
C(4)	0.3388 (2)	0.4776 (2)	0.4214 (5)	5.4 (1)
C(5)	0.4603 (3)	0.4605 (3)	0.4811 (5)	5.9 (1)
STB:TCNQ				
N(1)	0.3591 (1)	0.1756 (1)	0.5248 (2)	7.2 (1)
C(11)	0.3030 (1)	0.0989 (1)	0.4451 (2)	5.2 (1)
C(12)	0.2369 (2)	0.0000	0.3509 (3)	4.8 (1)
C(13)	0.1198 (2)	0.0000	0.1798 (3)	4.6 (1)
C(14)	0.0565 (1)	0.1013 (1)	0.0859 (2)	5.1 (1)
C(1)	0.3387 (2)	0.5218 (2)	0.2575 (4)	5.0 (3)
C(2)	0.2656 (3)	0.6118 (3)	0.1420 (6)	6.8 (4)
C(3)	0.1489 (3)	0.5964 (5)	-0.0333 (6)	7.6 (6)
C(4)	0.1034 (2)	0.4915 (8)	-0.0939 (5)	8.0 (1)
C(5)	0.1723 (3)	0.4022 (5)	0.0147 (6)	7.5 (7)
C(6)	0.2881 (3)	0.4176 (3)	0.1889 (5)	6.0 (5)
C(7)	0.4604 (2)	0.5376 (3)	0.4388 (4)	6.3 (1)

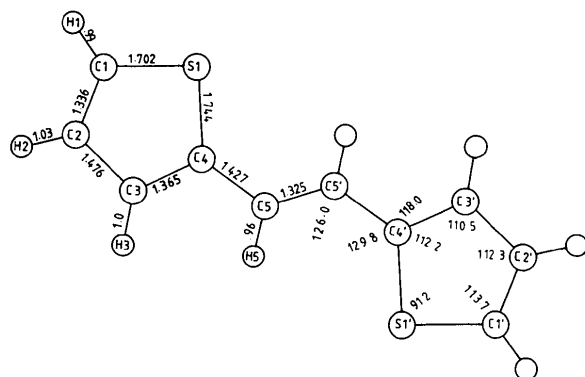


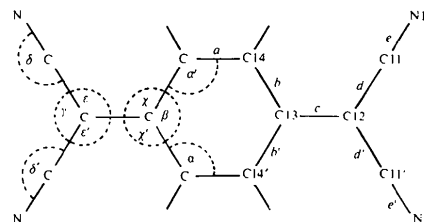
Fig. 2. Bond lengths (\AA) and angles ($^\circ$) of DTE (average e.s.d.'s in bond lengths: 0.006 \AA for C-S and C-C, 0.07 \AA for C-H; for C-S-C, C-C-C angles: 0.3 $^\circ$).

Group refinements were carried out in the same way as described above with individual isotropic temperature parameters, followed by refinements with fixed atom coordinates and anisotropic temperature parameters, always with the population parameter 0.5 for the STB atoms. The final R values (damping factors of 0.3) were $R = 3.9\%$, and $R_w = 5.5\%$. Table 2* contains the final non-hydrogen-atom positional parameters. Fig. 3 shows the atom numbering, bond lengths and angles; the TCNQ data are listed in Table 3. In both DTE:TCNQ and STB:TCNQ the final difference electron density map showed maxima only $< 0.2 e \text{\AA}^{-3}$.

The disorder of DTE and STB was a little surprising since there was nothing in the photographs that suggested a possible disorder, not even after abnormally long exposure times, taken after the disorder became known. Refinements were tried in space groups $C2$ or Cm instead of $C2/m$, but with much less success. Disorder has, however, been frequently observed in crystals containing thiophene or stilbene (Brown, 1966; Bernstein, 1975; Zobel, 1977; Bar & Bernstein, 1978; Zobel & Ruban, 1981).

* See deposition footnote.

Table 3. Bond distances (\AA) and angles ($^\circ$) in the TCNQ molecules



A prime denotes the corresponding quantities which are not related by crystallographic symmetry.

	DTE	STB	TMS	DTT
<i>a</i>	1.338 (3)	1.343 (2)	1.343 (3)	1.345 (3)*
<i>b</i>	1.443 (2)	1.445 (2)	1.442 (3)	1.438 (3)*
<i>b'</i>			1.439 (3)	1.444 (3)*
<i>c</i>	1.370 (3)	1.377 (3)	1.372 (3)	1.376 (3)*
<i>d</i>	1.428 (2)	1.432 (2)	1.432 (3)	1.432 (3)*
<i>d'</i>			1.429 (3)	1.433 (3)*
<i>e</i>	1.150 (2)	1.143 (2)	1.140 (3)	1.140 (3)*
<i>e'</i>			1.146 (3)	1.143 (3)*
α	121.4 (2)	121.1 (1)	121.0 (1)	120.0 (2)*
α'			121.1 (2)	121.1 (2)*
β	117.2 (2)	117.7 (1)	117.8 (2)	117.9 (2)*
γ	114.6 (2)	114.8 (1)	116.0 (2)	116.2 (2)*
δ	177.3 (2)	177.6 (1)	178.7 (3)	179.2 (2)*
δ'			179.5 (2)	179.0 (2)/ 177.1 (2)
<i>e</i>	122.7 (1)	122.6 (1)	122.2 (2)	122.1 (2)*
<i>e'</i>			121.8 (1)	121.3 (2)
χ	121.4 (1)	121.2 (1)	121.5 (1)	121.3 (2)
χ'			120.7 (2)	120.9 (2)

* Arithmetic-mean value, if values lie within 3σ (see Fig. 5 for details).

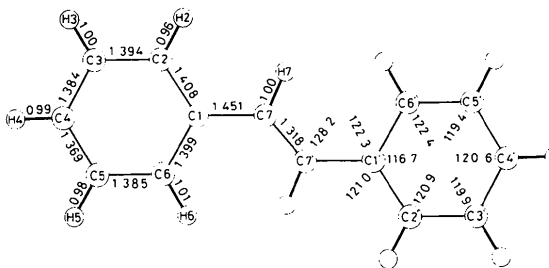


Fig. 3. Bond lengths (Å) and angles (°) of STB (average e.s.d.'s in bond lengths: 0.006 Å for C—C, 0.05 Å for C—H; for C—C—C angles: 0.3°).

TMS:TCNQ

The structure of TMS:TCNQ could not be determined by direct methods. The *E* map obtained from *MULTAN* (Main *et al.*, 1977) showed a planar net of interleaved six-membered rings. The structure was solved with the vector-search method of Nordman (1966) and Schilling (1969).

The TMS molecule was readily found in an orientation search, using the STB molecule (Kodama & Kumakura, 1974). The orientation search for TCNQ, using a search group taken from the above-mentioned structures, was more difficult. The highest orientation peaks were wrong and the correct structure was found only after the less prominent peaks were considered. With a suitable line-up of the two molecules one can demonstrate that most of the intramolecular vectors of TCNQ occur with double weight in the vector set of TMS. This similarity was responsible for the failure of the first TCNQ orientation searches. A subsequent location search confirmed the relative positions of the two molecules as 0,0,0 and 0,0, $\frac{1}{2}$, which were also obtained from packing considerations. A difference Fourier calculation supplied the two missing methyl C atoms. The *R* value before refinement was 38%. The

Table 4. *TMS:TCNQ*: fractional coordinates and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(1)	0.4058 (2)	0.1347 (3)	-0.1885 (3)	9.3 (1)
C(11)	0.32131 (2)	0.0369 (3)	-0.1520 (3)	7.4 (1)
C(12)	0.1979 (2)	-0.0881 (2)	-0.1038 (2)	6.6 (1)
C(13)	0.1008 (2)	-0.0440 (2)	-0.0523 (2)	6.1 (1)
C(14)	0.1094 (2)	0.1315 (2)	-0.0452 (2)	6.3 (1)
N(101)	0.1829 (2)	-0.4009 (3)	-0.1176 (3)	10.0 (1)
C(111)	0.1898 (2)	-0.2614 (3)	-0.1121 (3)	7.7 (1)
C(114)	-0.0134 (2)	-0.1727 (2)	-0.0037 (2)	6.4 (1)
C(1)	0.1538 (1)	-0.0101 (2)	0.4219 (2)	5.6 (1)
C(2)	0.2027 (2)	-0.1390 (2)	0.3947 (2)	6.3 (1)
C(3)	0.3215 (2)	-0.0978 (2)	0.3409 (3)	7.2 (1)
C(4)	0.3948 (2)	0.0685 (3)	0.3096 (3)	7.5 (1)
C(5)	0.3482 (2)	0.1967 (2)	0.3324 (3)	7.0 (1)
C(6)	0.2299 (2)	0.1564 (2)	0.3891 (3)	6.4 (1)
C(7)	0.0275 (1)	-0.0544 (2)	0.4787 (2)	5.9 (1)
C(8)	0.1629 (2)	-0.4397 (2)	0.3907 (3)	9.0 (1)
C(9)	0.5346 (2)	0.4151 (3)	0.2492 (5)	11.2 (1)
O(1)	0.1233 (1)	-0.3014 (2)	0.4260 (2)	8.6 (1)
O(2)	0.4102 (1)	0.3656 (2)	0.2999 (3)	9.9 (1)

refinement was straightforward and converged (with isotropic H atoms, all other atoms anisotropic) to a final *R* = 4.6%, and *R*_w = 5.3%. Table 4* contains the positional parameters of the TMS:TCNQ complex. Atom numbering, bond lengths and bond angles for the TMS molecule are shown in Fig. 4; TCNQ dimensions are in Table 3.

DTT:TCNQ

The structure was easily solved with *MULTAN* (Main *et al.*, 1977) using the known TCNQ molecule as input for renormalizing the structure factors. All non-hydrogen atoms of the asymmetric unit were

* See deposition footnote.

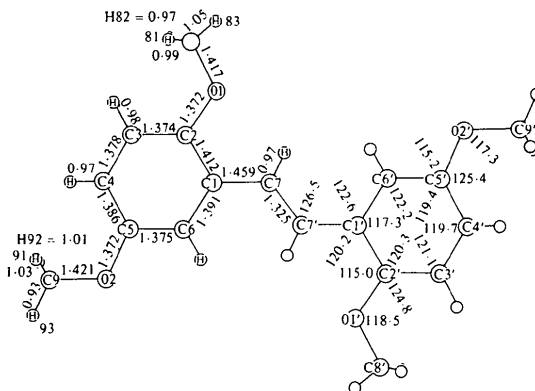


Fig. 4. Bond lengths (Å) and angles (°) of TMS (average e.s.d.'s in bond lengths: 0.003 Å for C—C and C—O, 0.03 Å for C—H; for C—C—C angles: 0.2°).

Table 5. *DTT:TCNQ*: fractional coordinates and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	0.80606 (1)	-0.18258 (7)	0.46699 (7)	4.00 (3)
S(2)	0.92439 (1)	0.03975 (7)	0.49643 (7)	4.04 (3)
S(3)	0.89892 (2)	-0.48197 (7)	0.64187 (8)	4.63 (3)
C(1)	0.80216 (7)	0.0338 (3)	0.3916 (3)	4.3 (1)
C(2)	0.83898 (7)	0.1205 (3)	0.3938 (3)	4.0 (1)
C(3)	0.87162 (6)	0.0094 (3)	0.4597 (3)	3.5 (1)
C(4)	0.85860 (6)	-0.1598 (3)	0.5051 (3)	3.3 (1)
C(5)	0.89210 (6)	-0.2668 (3)	0.5691 (3)	3.4 (1)
C(6)	0.92941 (6)	-0.1773 (3)	0.5729 (3)	3.8 (1)
C(7)	0.96371 (7)	-0.2822 (3)	0.6339 (3)	4.9 (1)
C(8)	0.95115 (8)	-0.4481 (4)	0.5646 (4)	5.5 (1)
N(1)	0.92618 (8)	-0.6107 (3)	0.1871 (4)	6.6 (1)
N(2)	1.00338 (7)	-0.1500 (3)	0.1532 (4)	6.7 (1)
N(3)	0.79651 (7)	0.4247 (3)	-0.2627 (3)	5.7 (1)
N(4)	0.72127 (6)	-0.0506 (3)	-0.1902 (3)	5.5 (1)
C(10)	0.89651 (6)	-0.1859 (3)	0.0414 (3)	3.2 (1)
C(11)	0.90011 (6)	-0.0022 (3)	-0.0107 (3)	3.5 (1)
C(12)	0.86697 (6)	0.0896 (3)	-0.0742 (3)	3.4 (1)
C(13)	0.82681 (6)	0.0085 (3)	-0.0927 (3)	3.2 (1)
C(14)	0.82321 (6)	-0.1742 (3)	-0.0394 (3)	3.5 (1)
C(15)	0.85633 (6)	-0.2666 (3)	0.0242 (3)	3.4 (1)
C(16)	0.93044 (6)	-0.2812 (3)	0.1042 (3)	3.7 (1)
C(17)	0.92769 (7)	-0.4645 (3)	0.1507 (3)	4.3 (1)
C(18)	0.97072 (6)	-0.2049 (3)	0.1289 (3)	4.4 (1)
C(19)	0.79276 (6)	0.0999 (3)	-0.1605 (3)	3.4 (1)
C(20)	0.75288 (6)	0.0172 (3)	-0.1781 (3)	3.9 (1)
C(21)	0.79500 (6)	0.2807 (3)	-0.2172 (3)	4.0 (1)

located in an electron density map. The refinement (H atoms isotropic, others anisotropic) converged to a final $R = 3.9\%$ and $R_w = 5.3\%$ with residual electron density within $\pm 0.4 \text{ e \AA}^{-3}$ in a final ΔF map. The positional parameters and equivalent U 's are listed in Table 5,* and Fig. 5 shows the molecular dimensions.

* See deposition footnote.

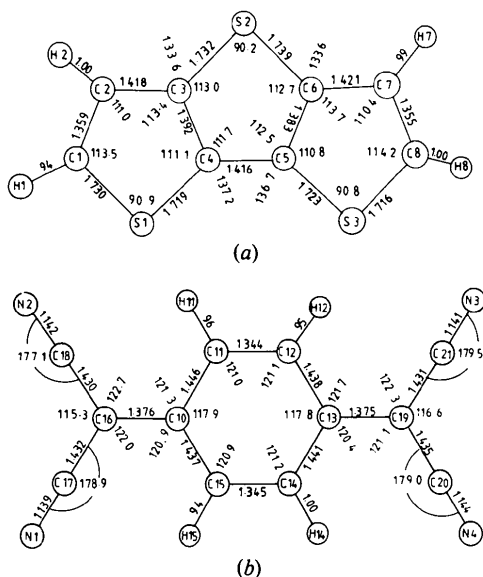


Fig. 5. Bond lengths (Å) and angles ($^{\circ}$) of DTT:TCNQ complex (average e.s.d.'s in bond lengths: 0.003 Å for C–C and C–S, 0.03 Å for C–H; for C–C–C and C–S–C angles 0.2 $^{\circ}$).

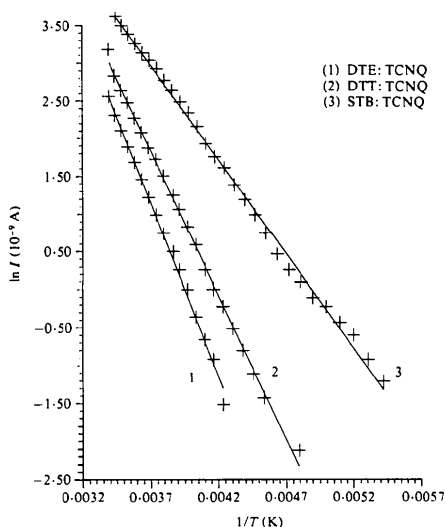


Fig. 6. Temperature dependence of electrical conductivity of three of the TCNQ complexes (see text).

Conductivity measurements

Electrical-conductivity measurements were carried out with powder samples and single crystals. In the latter case nearly parallelepiped-shaped crystals were used for voltage (U) and resistance (R) measurements. With very thin 'whisker' crystals ($\sim 0.05 \times 0.05 \times 5 \text{ mm}$) the four-point method (Irvin, 1962; van der Pauw, 1961), slightly modified, was used. Particularly good whiskers were obtained for DTE:TCNQ by recrystallizing from dichloroethane in an electrostatic field of about 5000 V cm^{-1} ; for the others the electrostatic field showed no influence. The resistances of the complexes were found to be Ohmic ($I \sim U$) in the voltage range used (0–50 V) and no transition to a space-charge-controlled effect with $I \sim U^2$ was found, so that no carrier injection from the electrodes occurred (at least no detectable one).

The temperature dependence of the conductivity was measured for DTE:TCNQ, STB:TCNQ and DTT:TCNQ using a liquid- N_2 thermostat as described earlier (Zobel, 1977). Since conductivity (σ) is inversely proportional to resistance, and by Ohm's Law directly proportional to the current flowing (I) at constant voltage, a plot of $\ln(I)$ versus $1/T$ at constant voltage should, according to the relation $\sigma = \sigma_0 \exp(\Delta E'/2kT)$ (Meier, 1974), be a straight line, with σ_0 the conductivity at $T = 0 \text{ K}$, $\Delta E'$ the thermal activation energy and k the Boltzmann constant. From the slopes of the lines (Fig. 6) $\Delta E'$ was derived and compared to the activation energy E_a obtained from optical absorption spectra (Chatzitheodorou, 1982) (Table 6). The agreement is very good for DTE:TCNQ, but not so for the rest. According to the

Table 6. Electrical-conductivity values σ ($\Omega^{-1} \text{ cm}^{-1}$) at room temperature

The estimated error of the single-measurement value might be roughly 10%, but much larger deviations occurred between different samples of the same compound, presumably due to lattice defects and to impurities, particularly at the surface. Values of Chatzitheodorou (1982) and Beimpling (1982) were measured at 1500 kg cm^{-2} ($\sim 1.47 \times 10^8 \text{ Pa}$).

	DTE: TCNQ	STB: TCNQ	TMS: TCNQ	DTT: TCNQ
Powder samples	$2.1 \times 10^{-9*}$	$7.6 \times 10^{-11*}$	$1.2 \times 10^{-11*}$	$1.0 \times 10^{-9\dagger}$
Single crystals <i>a</i>	4×10^{-11}	8×10^{-12}	3×10^{-12}	1×10^{-11}
in direction <i>b</i>	4×10^{-11}	3×10^{-12}	1×10^{-12}	2×10^{-9}
of axis <i>c</i>	5×10^{-9}	2×10^{-10}	4×10^{-11}	1×10^{-8}
Four-point method (whiskers)	2×10^{-8}	2×10^{-10}	1×10^{-9}	1×10^{-6}
E_a (eV)‡	0.77*	0.66*	0.87*	0.77†
$\Delta E'$ (eV)	0.75	0.52	Not measured	0.63

* Chatzitheodorou (1982).

† Beimpling (1982).

‡ 1 eV = $1.6 \times 10^{-19} \text{ J}$.

band model of an intrinsic semiconductor we can identify the thermal activation energy $\Delta E'$ derived from the temperature dependence of the electrical conductivity with the band separation ΔE . Therefore, the agreement should be better, but probably extrinsic effects due to impurity and/or surface effects play a more or less important role, since $\Delta E'$ was derived from conductivity measurements along the *c* direction of the single crystals, whereas E_a was obtained from powder samples.

The fast and monotonic decrease of conductivity with decreasing temperature shows the character of a regular semiconductor needing thermal activation energy for the electrons and holes. The conductivity is small at low temperatures caused by lack of carriers. This monotonic decrease is also a strong hint that no phase transition occurs, at least between room temperature and ~ 200 K.

Discussion

(a) Molecular geometry

A comparison between *trans*-1,2-di(2-thienyl)ethylene (I) (Ruban & Zobel, 1975) and the same molecule in the DTE:TCNQ complex (II) shows only a few differences. The S(1)–C(1) bond length is the same, whereas S(1)–C(4) is 1.744 (5) Å, significantly greater than the 1.701 (6) Å in (I), but close to the values of 1.733 (3) Å found for *trans*-1,4-di(2-thienyl)-1,3-butadiene and 1.731 (3) Å for 1,6-di(2-thienyl)-1,3,5-hexatriene (Buschmann, 1980) which can be regarded as values for a shortened single bond. The average C=C double and C–C single bonds of (I) and (II) show no significant differences, probably indicating only a very small amount of charge transfer.

In spite of the disorder, no particular distortion was found for the STB molecule. The average bond length of 1.380 (3) Å in the benzene ring is the same (within the limits of error) as the average of 1.385 (7) Å from values given by Bernstein (1975) and Finder, Newton & Allinger (1974) for 'molecule 1' of *trans*-stilbene,* which possessed an unusually shortened central double bond that is in excellent agreement with the 1.318 (4) Å found in this work. In both cases this might be somehow related to the disorder.

In the DTT molecule the S(2)–C(3) and S(2)–C(6) bond lengths of 1.732 (2) and 1.739 (2) Å indicate the same shortened single bonds as those found by Schaffrin & Trotter (1970) in dibenzothiophene; the other S–C bonds show no significant differences, but

there is a tendency for shortening in the double-bond direction. Only the C(4)–C(5) distance in the central thiophene ring, 1.416 (3) Å, is significantly shorter than in dibenzothiophene.

The bond distances and angles of all TCNQ molecules in the present work (Table 3) seem to be close to the values expected for a non-ionic TCNQ molecule.

The planarity of the ring systems can be judged by the values given in Table 7. The torsion angle of 3.74 (7)° between the five-membered ring of DTE and the ethylene bridge is in good agreement with that in (I). For STB the corresponding torsion angle is 1.59 (5)°, much less than the values of 11.5° for stilbene in the pyromellitic dianhydride complex (Kodama & Kumakura, 1974) and 11.9° in the stilbene–trinitrobenzene complex (Bar & Bernstein, 1978). For TMS a value of 3.5 (1)° was found.

(b) Crystal packing

All compounds are 1:1 complexes. The crystal structures of DTE:TCNQ, STB:TCNQ and TMS:TCNQ are dominated by homologous and parallel columns of alternating acceptor (*A*) and donor (*D*) molecules (Figs. 7 and 8) running approximately parallel to *c*. For DTT:TCNQ the mixed-stack columns are also nearly parallel to the *c* direction, but they are tilted in pairs to each other with an angle of 34.3 (1)° (Fig. 9). The overlap of the TCNQ acceptor with the different donor molecules is illustrated in Fig. 10. The stacking interaction is in all present cases between pairs of donor and acceptor molecules, but is nominally of the 'ring–double-bond' type (Herbstein, 1971) for three of the structures. This arrangement – which was not found for TMS:TCNQ with the lowest

Table 7. *Least-squares planes*

	DTE	STB	TMS	DTT*
(a) Average deviations of (Å) of ring atoms defining least-squares planes				
Donor (<i>D</i>)	0.012 (6)	0.003 (1)	0.005 (2)	I 0.0013 (12) II 0.0020 (13) III 0.0012 (8)
Acceptor (<i>A</i>)	0.002 (1)	0.0015 (5)	0.005 (3)	0.0022 (9)
(b) Interplane angle (<i>D</i> – <i>A</i>) (°)				
	2.7 (6)	2.2 (1)	2.3 (2)	I 2.72 (9) II 2.52 (10) III 2.75 (8)
(c) Plane distance (Å)†				
	3.32 (2)	3.36 (2)	3.342 (7)	3.343 (3)

* I, II, III refer to the thiophene rings containing S(1), S(2) and S(3), respectively.

† Shortest distances occurring between non-hydrogen atoms of a donor and the plane of the corresponding acceptor molecule for each CT complex.

* The crystal structure of *trans*-stilbene contains two independent centrosymmetric molecules in the asymmetric unit. Both molecules appear to be affected by disorder, but 'molecule 1' less so than 'molecule 2'.

electrical conductivity in this series – represents the case of maximum orbital overlap with a minimum of nuclear repulsion. This energetically favourable arrangement is predominant in charge-transfer complexes with segregated stacks (*e.g.* Kistenmacher, Phillips & Cowan, 1974; Kistenmacher, Phillips, Cowan, Ferraris, Bloch & Poehler, 1976). The mixed columns are packed more loosely in comparison to certain tetrathiafulvalene(TTF):TCNQ complexes. Thus, for DTE:TCNQ and DTT:TCNQ the S...N contacts are 3.532 (7) and 3.480 (2) Å; these values are much larger than the 3.20 Å in TTF:TCNQ (Kistenmacher *et al.*, 1974) and the 3.306 Å in 4,4',5,5'-tetramethyl- $\Delta^{2,2'}$ -bis-1,3-dithiole (TMTTF)_{1,3}:

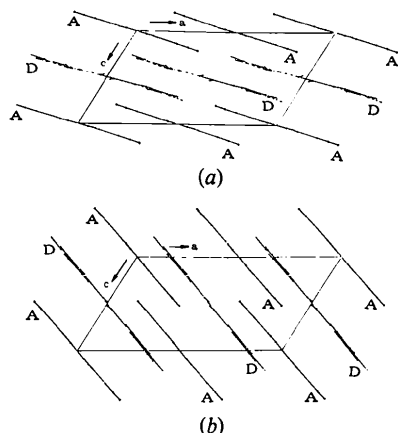


Fig. 7. View of the crystal packing of (a) DTE:TCNQ and (b) STB:TCNQ projected onto the *ac* plane. (A: acceptor, D: donor.)

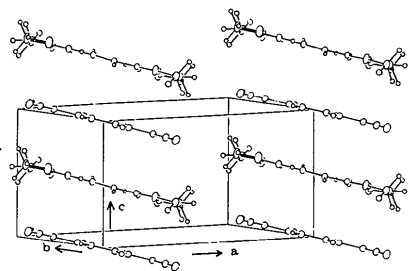


Fig. 8. View of the crystal packing of TMS:TCNQ parallel to the molecular planes.

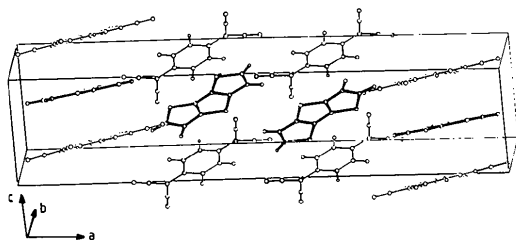


Fig. 9. View of the crystal packing of DTT:TCNQ.

TCNQ₂ (Kistenmacher *et al.*, 1976) but come close to the value of 3.45 Å found in TMTTF₁:TCNQ₁ (Phillips, Kistenmacher, Bloch, Ferraris & Cowan, 1977). In particular, the S...S contact of 3.605 (1) Å found in 1,4-bis(2-thienylvinyl)benzene (Zobel, 1976), shorter than the van der Waals distance of 3.70 Å (Pauling, 1969), was not repeated. The corresponding lengths are 4.058 (4) Å for DTE and 3.868 (1) Å for DTT. A certain amount of intrastack interaction can be assumed as judged by the plane distance (Table 7), which is 3.32 (2) Å for DTE:TCNQ; the same value was found in trithia(5)heterohelicene:TCNQ (Kono, Saito, Yamada & Kawazura, 1980), much shorter than the shortest distances of 3.57 to 3.91 Å in uncomplexed (but herring-bone-arranged) planar thiophene (Zobel, 1977; Buschmann, 1980). For STB:TCNQ the plane distance, 3.36 (2) Å, is also below the typical range for aromatic hydrocarbons such as pyrene (3.53 Å) (Camerman & Trotter, 1965), coronene (3.40 Å) (Robertson & White, 1945) or TCNQ itself (3.45 Å) (Long *et al.*, 1965) but is the same as in graphite (3.35 Å).

The intrastack plane distance of 3.342 (7) Å for TMS:TCNQ is shorter than the shortest interstack distance of 3.656 (4) Å between C(9) and N(1) and about the same as that in graphite (3.35 Å). No intermolecular distances significantly shorter than the sums of the usual van der Waals radii occur in DTT:TCNQ. The shortest intrastack atom contacts of 3.479 (2) and 3.533 (2) Å are S(1)...C(19) and S(3)...C(15) respectively. Interstack atom contacts are 3.174 (4) for N(2)...N(2), 2.62 (4) for

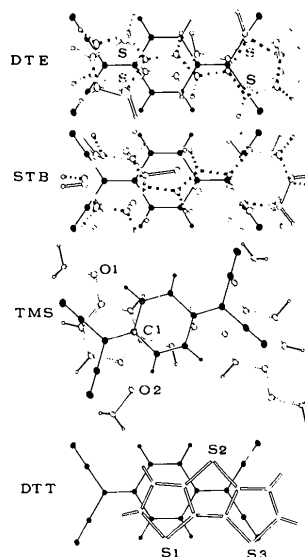


Fig. 10. Donor-acceptor overlap: parallel projections normal to the molecular planes (thermal ellipsoids are at 6% probability for clarity).

N(2)···H(8), 2.78 (3) for N(4)···H(2), 3.467 (3) for S(2)···N(1) and 3.568 (2) Å for S(1)···C(20). In conclusion, one can say that the average contact in the closest area is about the same between the planes as between the stacks.

The low conductivity is characterized by the mixed-stack arrangement and by a relatively low charge-transfer (CT) interaction, indicated by the absence of bond-length compensation in the TCNQ molecule and therefore a reduced delocalization of π electrons, and by lack of the characteristic CT maxima in the UV spectra (Chatzitheodorou, 1982; Beimling, 1982). The anisotropy of conductivity can be assumed to be the consequence of an interaction of π orbitals of neighbouring molecules in the stack direction, which lowers the potential barriers hindering the intermolecular electron transfer, and leads to the formation of narrow energy bands (Meier, 1974).

Summary

No trend of lengthening or shortening of the C=C double bonds of the acceptors (listed in Table 3) or of the donors was found in this series of CT complexes. Since molecular dimensions are rather insensitive to change of molecular charge (at least at this stage of accuracy) one should not emphasize these results too much. No contact distance significantly shorter than the sum of the usual van der Waals radii occurs. The intrastack spacings are shorter than for comparable single-compound structures and nearly the same for all the title compounds. The measured anisotropic conductivity is very low, of the order of 10^{-6} – 10^{-10} Ω^{-1} cm^{-1} , in agreement with the mixed-stack arrangements.

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