Table 2. *Selected bond distances (Å) and bond angles (°) and their e.s.d.'s*

C(1)—C(2)	1·486 (8)	S(10)—O(11)	1·484 (5)
C(1)—N(3)	1·282 (6)	S(10)—C(12)	1·787 (5)
C(1)—C(4)	1·484 (7)	C(15)—C(18)	1·504 (7)
N(3)—S(10)	1·714 (4)		

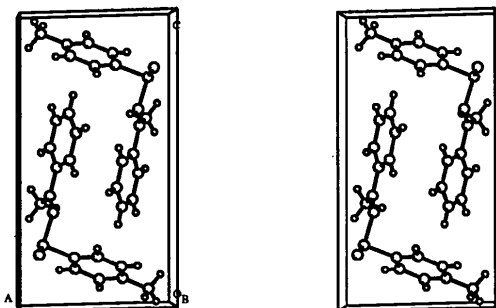|			
C(2)—C(1)—N(3)	124·3 (5)	N(3)—S(10)—C(12)	97·1 (2)
C(2)—C(1)—C(4)	118·9 (5)	O(11)—S(10)—C(12)	107·6 (2)
N(3)—C(1)—C(4)	116·8 (4)	S(10)—C(12)—C(13)	118·6 (4)
C(1)—N(3)—S(10)	119·6 (4)	S(10)—C(12)—C(17)	121·1 (4)
C(1)—C(4)—C(5)	120·2 (5)	C(14)—C(15)—C(18)	120·2 (6)
C(1)—C(4)—C(9)	121·2 (5)	C(16)—C(15)—C(18)	121·7 (6)
N(3)—S(10)—O(11)	103·4 (2)		

Fig. 2. Stereoscopic illustration of the molecular packing.

The bond angle N(3)—C(1)—C(4) of 116·8 (4)° is smaller than the 122·0° value for the imine (Bernstein & Schmidt, 1972), while C(2)—C(1)—N(3) of 124·3 (5)° is larger (Table 2). This wider angle at C(2)—C(1)—N(3) is presumably derived from avoiding steric interaction of the C(2) methyl and S(10) sulfinyl groups. According to Bürgi & Dunitz (1971), an electron-withdrawing group should lead to lengthening of the C=N bond. Indeed, the bond length C(1)—N(3) of 1·282 (6) Å is longer than the normal 1·262 Å of the imine (Bernstein & Schmidt, 1972). Least-squares-plane calculations show that all

three groups (phenyl ring, methyl and sulfinyl) are distorted from the central plane defined by C(4)—C(1)—N(3). The dihedral angles, with respect to the central plane, are 9·97° for the phenyl ring [C(4) to C(9)], 1·72° for the methyl group [C(2)—C(1)—C(4)] and 5·25° for the sulfinyl group [C(1)—N(3)—S(10)]. This non-planar conformation further relieves the repulsive interaction of the above three groups around C=N. The bond angle N(3)—S(10)—C(12) and bond lengths S(10)—C(12) and S(10)—O(11) are normal (Hua, Badejo, McCann & Takusagawa, 1987). The configuration at C=N is *trans* (the sulfinyl and phenyl groups are *trans*). The molecular packing is shown in Fig. 2.

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Structure of a Charge-Transfer Complex, Dithieno[3,4-b:3',4'-d]thiophene–Tetracyanoquinodimethane (DTT1–TCNQ)

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Abstract. Dithieno[3,4-b:3',4'-d]thiophene–tetracyanoquinodimethane, $C_8H_4S_3.C_{12}H_4N_4$, $M_r = 400·51$, monoclinic, $P2_1/c$, $a = 7·272$ (3), $b = 7·674$ (3), $c = 32·613$ (9) Å, $\beta = 93·6$ (2)°, $V = 1816$ (1) Å³, $Z = 4$, $D_x = 1·464$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·54184$ Å, $\mu = 18·16$ cm^{-1}, $F(000) = 816$, $T = 293$ K, $R = 0·085$ based on 1843 reflections ($F_o > 4\sigma$). The low accuracy of this structural determination is due to the fact that only needle-shaped single crystals shorter than 70 μm were obtainable by

either solvent or melt crystallization. The structure consists of the facing of discrete dimers (DTT1–TCNQ). No short contacts are observed in the crystal packing. The geometric features are very close to those found in an isomorphous charge-transfer complex (DTT–TCNQ). The low degree of charge transfer is also confirmed in this alternated stack structure.

Introduction. In the field of electro- and superconducting materials charge transfer systems have achieved major consideration because of their stability and processability and also in view of their relatively easy preparation by chemical or electrochemical synthesis. Moreover, due to their high crystallinity and purity they have been studied since the earliest development of electronic organic materials science. Recently, charge-transfer complexes based on thiophene oligomers have been prepared and studied (Hotta & Waragai 1989). The net charge transfer and DC conductivity are low. We have prepared, characterized (Catellani, Destri & Porzio, 1988) and polymerized (Bolognesi, Catellani, Destri, Zamboni & Taliani, 1987) dithieno[3,4-b:3',4'-d]thiophene, obtaining films exhibiting interesting optical and electronic properties. Aiming to prepare charge-transfer complexes with strong interaction between constituents, we have synthesized and studied dithieno[3,4-b:3',4'-d]thiophene–tetracyanoquinodimethane (DDT1–TCNQ); we report here the structure of this charge-transfer complex with particular reference to the isomorphous complex based on dithieno[2,3-b:2',3'-d]thiophene (DTT) (Bettinelli *et al.*, 1984).

Experimental. The synthesis of dithieno[3,4-b:3',4'-d]thiophene was carried out according to the literature (De Jong & Janssen 1971). DTT1–TCNQ charge-transfer complex was synthesized as follows: 50 mg (0·255 mmol) of DTT1 and 52·1 mg (0·255 mmol) of TCNQ in 10 ml of dry acetonitrile were refluxed for 30 min under nitrogen atmosphere. After cooling, dark green crystals precipitated (m.p. 479·5–481 K dec.). The elemental analysis is satisfactory. C = 59·80 (calc. 60%), H = 2·00 (calc. 2%), S = 23·55 (calc. 24%), N = 13·91 (calc. 14%).

Recrystallization of the needle-shaped material was attempted from a variety of solvents, always obtaining twinned or multiple crystals. No encouraging results were obtained by melt crystallization. Very small single crystals (no longer than 70 μm) were crystallized by slow evaporation of an acetonitrile solution (*ca* 1 month at 273 K). In Table 1 are summarized the experimental details and the crystal data. Intensity data were collected on a Philips PW-1100 computer-controlled diffractometer with a crystal positioned at a random orientation. The data

Table 1. *Working conditions*

Scan mode	θ–2θ
Scan speed (° min^{-1})	1·8
Scan width (°)	1·5
θ range (°), d_{min} (Å)	3–65, 0·85
Measured reflections	h $-31/38$, k 0/9, l 0/8
Number of collected reflections	3075
Number of observed reflections (with $I > 4\cdot0\sigma$)*	1843
Standard reflections (measured every 60 reflections)	$\bar{1}$12, $\bar{1}\bar{1}$2, 11$\bar{2}$
Wavelength (Å) (Cu $K\alpha$ graphite monochromated radiation)	1·54184
μ (cm^{-1})	18·42
Temperature	293 K
Approximate crystal size (mm)	0·07 × 0·025 × 0·015
Power used (kV × mA)	40 × 35

The variation in transmittance was estimated as +30% and an absorption correction was applied (see text).

* $\sigma^2(I)$ = peak counts + total background counts.

Table 2. *Atomic fractional coordinates* ($\times 10^4$) *of the DTT1–TCNQ complex and* U_{eq} (Å^2 $\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
S1	8258 (3)	-4636 (2)	478 (1)	78 (1)
S2	10137 (2)	536 (2)	742 (0)	59 (1)
S3	11222 (2)	130 (3)	2037 (1)	70 (1)
N1	7597 (9)	4203 (7)	1968 (2)	75 (4)
N2	6957 (9)	2762 (8)	-360 (2)	78 (4)
N3	3545 (9)	-1585 (9)	-46 (2)	84 (4)
N4	3112 (8)	-6097 (8)	743 (2)	77 (4)
C1	8803 (9)	-4298 (9)	976 (3)	68 (5)
C2	9403 (7)	-2566 (8)	1048 (2)	51 (4)
C3	9354 (7)	-1629 (9)	680 (2)	54 (4)
C4	8760 (9)	-2531 (9)	342 (2)	73 (5)
C5	11179 (8)	1192 (10)	1584 (2)	60 (4)
C6	10533 (7)	189 (8)	1261 (2)	51 (4)
C7	10082 (7)	-1558 (8)	1401 (2)	50 (4)
C8	10368 (7)	-1732 (9)	1808 (2)	58 (4)
C9	7179 (8)	2788 (8)	2006 (2)	57 (4)
C10	6631 (7)	989 (8)	2038 (2)	48 (3)
C11	6823 (8)	229 (8)	2443 (2)	59 (4)
C12	5996 (7)	54 (7)	1701 (2)	45 (3)
C13	5804 (7)	805 (7)	1298 (2)	48 (3)
C14	5171 (7)	-122 (7)	968 (2)	47 (3)
C15	4652 (7)	-1910 (7)	1014 (2)	45 (3)
C16	4865 (7)	-2694 (8)	1415 (2)	52 (3)
C17	5523 (7)	-1766 (7)	1749 (2)	50 (3)
C18	3759 (7)	-2133 (7)	275 (2)	58 (4)
C19	3987 (7)	-2871 (7)	676 (2)	50 (3)
C20	3492 (8)	-4678 (8)	722 (2)	58 (3)

* U_{eq} is defined as $(U_{11} \times U_{22} \times U_{33})^{0\cdot33}$.

were corrected for Lp effects and for absorption (North, Phillips & Mathews, 1968; correction factors range from 0·45 to 1·00). No correction for decay (less than 3% during the data collection) was applied. Unit-cell parameters were determined by least-squares refinement of the setting angles of 25 strong reflections (θ range 8–14°). The structure was solved by *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) using the solution with the highest figure of merit out of 64 different sets (2500 relationships, E_{min} 1·5). A subsequent Fourier map revealed the positions of all non-H atoms,

Table 3. *Selected interatomic distances (Å) and angles (°) in the molecule, with e.s.d.'s in parentheses*

DTT1		TCNQ	
S1—C1	1·667 (8)	N1—C9	1·136 (8)
S1—C4	1·721 (7)	N2—C11	1·134 (8)
S2—C3	1·764 (8)	N3—C18	1·128 (8)
S2—C6	1·721 (7)	N4—C20	1·127 (8)
S3—C5	1·686 (8)	C9—C10	1·443 (8)
S3—C8	1·710 (7)	C10—C11	1·442 (8)
C1—C2	1·413 (9)	C10—C12	1·369 (8)
C2—C3	1·397 (9)	C12—C13	1·433 (8)
C3—C4	1·349 (9)	C13—C14	1·348 (8)
C2—C7	1·448 (8)	C14—C15	1·433 (8)
C5—C6	1·365 (9)	C15—C16	1·440 (8)
C6—C7	1·460 (9)	C16—C17	1·363 (8)
C7—C8	1·339 (8)	C12—C17	1·449 (8)
		C18—C19	1·427 (8)
		C19—C20	1·443 (8)
C1—S1—C4	93·7 (3)	C9—C10—C11	116·3 (5)
C3—S2—C6	90·0 (3)	C9—C10—C12	121·5 (5)
C5—S3—C8	92·0 (3)	C11—C10—C12	122·2 (5)
S1—C1—C2	111·1 (5)	C12—C13—C14	122·0 (5)
S1—C4—C3	109·4 (5)	C13—C14—C15	120·0 (5)
S2—C3—C2	113·3 (5)	C14—C15—C16	118·8 (5)
S2—C6—C7	115·0 (5)	C15—C16—C17	121·4 (5)
S3—C5—C6	113·0 (6)	C16—C17—C12	119·4 (5)
S3—C8—C7	112·3 (5)	C17—C12—C13	118·5 (5)
C1—C2—C3	110·5 (6)	C15—C19—C18	122·1 (5)
C2—C3—C4	115·3 (6)	C15—C19—C20	120·4 (5)
C3—C2—C7	113·4 (5)	C18—C19—C20	117·4 (5)
C2—C7—C6	108·3 (5)		
C5—C6—C7	113·2 (2)		
C6—C7—C8	112·0 (2)		

whose positional and thermal parameters were refined by full-matrix least squares minimizing $w(F_o - KF_o)^2$, $w = 3·04/[\sigma^2(F_o) + 0·003F_o^2]$. After a difference Fourier map, which allowed the localization of all H atoms (ρ max. and min. 0·3 e Å^{-3}), six more anisotropic least-squares cycles were carried out refining the thermal (isotropic) parameters of H atoms, whose positions were constrained to ride on the bonded C atom. $R = 0·085$, $wR = 0·088$, $\Delta/\sigma < 0·15$, $S = 3·00$. Both real and imaginary components of the anomalous dispersion were included in the atomic-scattering-factor calculations (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 99, 149). All the computer programs used are part of *SHELX/SHELXS* package (Sheldrick, 1976, 1986). Atomic coordinates and equivalent thermal parameters are given in Table 2.*

Discussion. A schematic drawing of the molecule is shown in Fig. 1, while interatomic distances and angles are reported in Table 3. The compound presents a mixed-stack crystal structure, constituted by DTT1 and TCNQ molecules alternating along the *a* axis (see Figs. 2 and 3). The geometric features are

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53313 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

compared to those of the DTT1 molecule (Catellani, Destri & Porzio, 1988) and those of the isomorphous charge-transfer complex (Bettinelli *et al.*, 1984). DTT1–TCNQ molecules are nearly parallel, the dihedral angle between their best planes being 2·0 (2)° [3·2 (1)° in the DTT complex]. Each thiophene ring in the DTT1 molecule is planar, the maximum atomic displacement being 0·006 Å, moreover the dihedral angles between the central ring (S2) and terminal rings are 1·0 (2) (S1) and 1·6 (1)° (S3) [1·2 (1) and 2·4 (2)°, respectively, in DTT]. Distances and angles of the DTT1 residue are close to the ones observed in the DTT1 molecule, differences being within 4σ. An analogous situation is found when comparing the DTT molecule and the DTT charge-
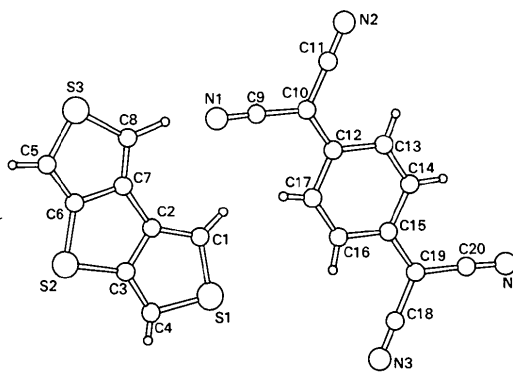

Fig. 1. Schematic drawing of the molecule with the atom-numbering scheme for DTT1 (left) and TCNQ (right).
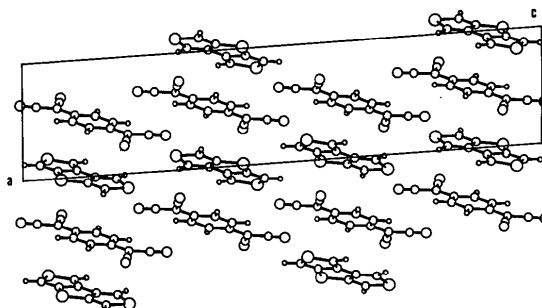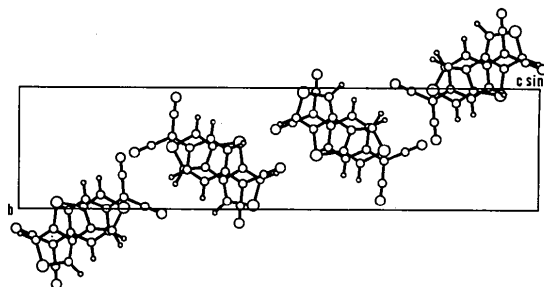

Fig. 2. Projection of the structure along [010].

Fig. 3. Projection of the structure along [100].

transfer complex. In particular, the C—S distances in the DTT1 complex are slightly longer in the inner thiophene ring [1·74 (1) Å average] than in the outer rings [1·70 (1) Å average] as observed to a similar extent for DTT [averaged values 1·756 (1) and 1·704 (1) Å respectively]. The π delocalization of the C—S bond is presumably smaller in the central ring. Further similarities between DTT1 in the complex and as a free molecule are detected by comparing the C—C distances: the difference between average 'double' and 'single' bonds is smaller in the central ring than in the outer rings.

The relatively low overall accuracy of the present crystal structure determination, due mainly to crystal quality, does not allow the discussion of finer details.

The TCNQ residue is planar, in fact the two dicyanomethylene-group best planes are bent only 0·6 (2) and 1·3 (2)° out of the quinonoid ring plane. The corresponding values found in the DTT–TCNQ complex are 1·2 (1) and 2·3 (1)° respectively. The C—C—N groups are all strictly linear and the C—C double bond connecting the cyano group and the quinonoid ring is 1·38 (1) Å (average), compared with 1·383 Å found in the DTT charge-transfer complex. The dimensions of the TCNQ molecule closely resemble those observed in the DTT complex (Bettinelli *et al.*, 1984, and references therein).

As both donor and acceptor molecules lie at a general position in the crystal (space group $P2_1/c$), the contacts between a molecule and two adjacent ones in the stack are not equivalent. In fact, the distances of TCNQ atoms at x, y, z and at $1 + x, y, z$ to the least-squares plane of DTT1 range from 3·28 to 3·56 Å (av. 3·38 Å) and from 3·31 to 3·58 Å (av. 3·49 Å), respectively. The partial dimerization

observed in the DTT–TCNQ complex is also detected in this case, although to a lesser extent. The shorter contact in the stack is 3·40 Å from S3 to C10. The molecular packing is governed by the short contacts involving adjacent molecules of TCNQ [N3···N3^i ($-x, -y, 1-z$) 3·235 (8) Å], or of DTT1 and TCNQ [S2···N4^{ii} ($x, 1 + y, 1 + z$) 3·370 (5) Å].

In conclusion, we remark that all the structural evidence strongly indicates that DTT1–TCNQ is a low-ionicity charge-transfer complex, as expected from comparison with the analogous DTT–TCNQ and oligothiophene-containing charge-transfer complexes (Hotta & Waragai, 1989). The DC conductivity measured on a 'single' crystal ($\sigma_{239K} = 2 \times 10^{-10}$ Ω^{-1} cm^{-1}) confirmed the above conclusions.

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Azoles. 29.* Structure of the Molecular Complex of 3,5-Dinitroindazole with Piperazine and Water (2/1/2)

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Abstract. $C_4H_{12}N_2^{2+} \cdot 2C_7H_3N_4O_4^- \cdot 2H_2O$, $M_r = 538\cdot43$, monoclinic, $P2_1/c$, $a = 12\cdot818$ (3), $b = 13\cdot769$ (4), $c = 6\cdot701$ (1) Å, $\beta = 104\cdot60$ (2)°, $V = 1144\cdot5$ (5) Å^3, $Z = 2$, $D_m = 1\cdot56$ (1), $D_x = 1\cdot56$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 1·005 mm^{-1}, $F(000) = 560$, room temperature, final $R = 0\cdot035$ for 1209 observed reflections. The piperazine ring lies on the centre of symmetry. Piperazine forms a double $H_2N^+<$ ammonium cation as a

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* Part 28: Gzella & Wrzeciono (1990).

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