The Structure of Dibenzo-1,4,5,8-tetrathiafulvalenium 2,5-Dichloro-7,7,8,8-tetracyano-*p*-quinodimethanide,* DBTTF–TCNQCl₂, at 295 and 115 K

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Abstract

$C_{14}H_8S_4^+.C_{12}H_2Cl_2N_4^-$, $M_r = 577.6$, triclinic, $P\bar{1}$, $Z = 1$; at 295 K, $a = 3.7564$ (7), $b = 7.867$ (1), $c = 20.085$ (2) Å, $\alpha = 91.13$ (1), $\beta = 93.28$ (1), $\gamma = 91.46$ (1)°, $V = 592.2$ Å³, $Z = 1$, $D_c = 1.619$, $D_m = 1.618$ (5) Mg m⁻³. A full-matrix least-squares refinement with 1891 observed reflections, $I > 2\sigma(I)$, terminated at $R = 0.041$. The DBTTF cations and the TCNQCl₂ anions form separated, homologous stacks with an interplanar spacing of 3.51 and 3.41 Å respectively. The molecular planes are tilted in opposite directions relative to the short a axis. The overlap of the DBTTF cations within the stack is the 'double bond over ring' type. The TCNQCl₂ anions overlap by a sidewards slide placing one quinone double bond over the adjacent quinone ring. The interstack S⋯N distance is 3.682 (4) Å. At 115 K the volume of the unit cell is reduced to 577.0 Å³, mainly due to a shortening of the a axis to 3.691 (1) Å. The refinement with 596 observed intensities terminated at $R = 0.066$. The only detectable structural effect of the cooling is a significant reduction of the intermolecular distances. The S⋯N distance is 3.63 (2) Å.

Introduction

DBTTF–TCNQCl₂, Fig. 1, belongs to the large group of charge-transfer compounds whose physical properties have been studied extensively in recent years. The conductivity of the present compound is ~4000 Ω⁻¹ m⁻¹ at room temperature and increases slowly upon cooling. Below 200 K the conductivity decreases rapidly. Anomalies in the thermopower as well as in the conductivity at $T = 180$ K separate conducting and non-conducting regimes. The magnetic susceptibility is 1.5×10^{-8} m³ kg⁻¹ at 300 K, and increases slowly on cooling. A drastic drop in the susceptibility and a change in the dielectric constant at 40 K have been

* The recommended IUPAC name is $\Delta^{2,2'}$-bi-2*H*-1,3-benzo-dithiolylidenium 2,5-dichloro-7,7,8,8-tetracyano-*p*-quinodimeth-anide.
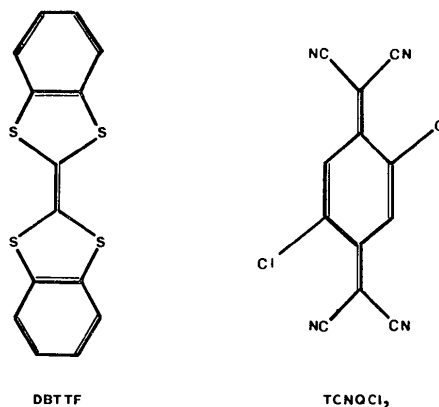
Fig. 1. Donor and acceptor molecules.

observed. A detailed discussion of these results has been published elsewhere (Jacobsen, Pedersen, Mortensen & Bechgaard, 1980). The present paper gives the results of a crystal-structure investigation of the compound at 295 and at 115 K. The crystals used have been prepared by Jacobsen *et al.*

Experimental

A single crystal 0.48 × 0.45 × 0.05 mm giving Weissenberg photographs of a satisfactory quality was selected for data collection. The unit-cell dimensions and reflection intensities were measured with a four-circle diffractometer (CAD-4). Graphite-mono-chromatized radiation was used [λ(Mo $K\alpha$) = 0.71073 Å]. All reflections in the interval 0.049 < (sin θ)/λ < 0.661 Å⁻¹ were scanned in the ω–2θ mode.

A set of 2844 intensities was calculated from the total set of 5804 observations by averaging symmetry-equivalent reflections. (The index of agreement among symmetry-equivalent reflections $R_{ic} = 0.04$.) 1891 averaged net intensities, having $I > 2\sigma(I)$ and corrected for Lp effects, were used in the structure analysis. No corrections were made for absorption ($\mu = 0.585$ mm⁻¹) or extinction. Corrections for anomalous dispersion were taken from Cromer & Liberman (1970).

Atomic scattering factors for the neutral non-H atoms were taken from Cromer & Mann (1968); for H those calculated for spherical H atoms by Stewart, Davidson & Simpson (1965) were used.

The lattice constants were determined by a least-squares refinement of 12 selected Friedel pairs in the interval $20 < \theta < 22°$. The space group $P\bar{1}$ rather than $P1$ was indicated by the E statistics and confirmed by the refinement of the structure.

Solution and refinement

The positions of all non-H atoms were obtained by standard direct methods. H atoms were introduced at geometrically reasonable positions with a fixed C—H bond length of 1·08 (1) Å and assigned an invariant isotropic temperature factor equal to that of the carrying C atom. The analysis was completed by six cycles of refinement with anisotropic temperature factors for O, S, Cl and C. The maximum shift/error in the last cycle was 0·02 and $R = 0·041$. Only random peaks and holes smaller than 0·4 e Å^{-3} were found in the corresponding difference electron density map. All least-squares calculations were of the full-matrix type minimizing $\sum (\Delta F)^2$; $|\Delta F| = ||F_o| - |F_c||$ and $R = \sum |\Delta F|/\sum |F_o|$.

The computer programs used were: locally written programs to convert the diffractometer data to relative structure factors; *SHELX* (Sheldrick, 1976) for solution and refinement of the structure; the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall,

Table 2. DBTTF–TCNQCl₂; *fractional coordinates* ($\times 10^3$) *for the* H *atoms at* 295 K, *with e.s.d.'s in parentheses*

$U = U_{eq}$ of carrying C atom (Table 1).

	x	y	z
H(4)	402 (10)	−567 (3)	87 (2)
H(5)	610 (10)	−593 (2)	200 (2)
H(6)	701 (9)	−328 (5)	275 (1)
H(7)	519 (10)	−59 (3)	237 (2)
H(12)	252 (8)	−281 (2)	482 (2)

The H(n) to C(n) distance has been fixed at 1·08 (1) Å.

1972) for least-squares planes analysis; *PLUTO* (Motherwell, 1978) for drawings.

Fractional atomic coordinates are listed in Tables 1 and 2.*

Results and discussion

The bond lengths and angles of the approximately planar DBTTF and TCNQCl₂ units are given in Fig. 2, and the packing of these units is illustrated in Figs. 3 and 4.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36086 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
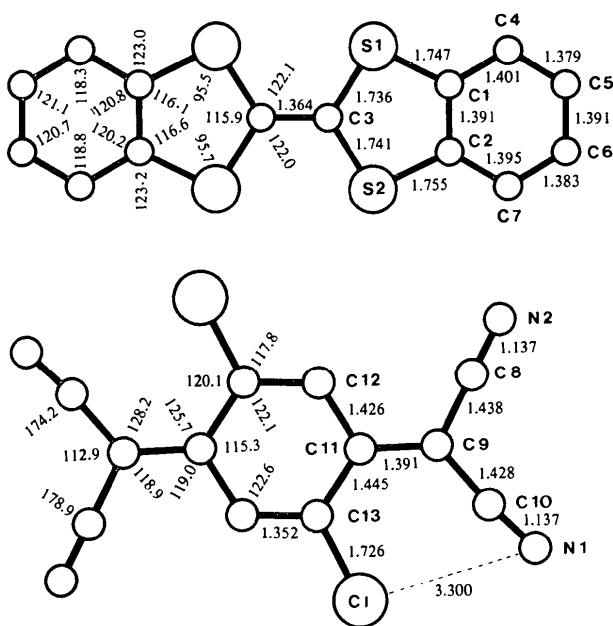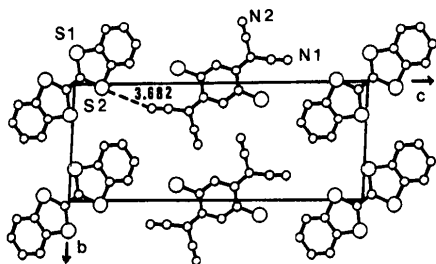
Table 1. DBTTF–TCNQCl₂; *fractional coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^4$) *for the* non-H *atoms at* 295 K, *with e.s.d.'s in parentheses*

U_{eq} is equivalent to the anisotropic parameters actually refined (Hamilton, 1959).

	x	y	z	U_{eq}
S(1)	1397 (3)	−2641 (1)	139 (1)	358 (5)
S(2)	2042 (3)	383 (1)	1032 (1)	365 (5)
Cl	−2066 (3)	1292 (1)	6398 (1)	412 (6)
C(1)	3079 (9)	−2967 (5)	954 (2)	332 (19)
C(2)	3437 (9)	−1541 (4)	1375 (2)	310 (18)
C(3)	743 (9)	−479 (4)	248 (2)	299 (18)
C(4)	4095 (10)	−4561 (5)	1186 (2)	414 (22)
C(5)	5412 (11)	−4686 (5)	1838 (2)	471 (25)
C(6)	5817 (10)	−3250 (6)	2253 (2)	465 (27)
C(7)	4839 (10)	−1667 (5)	2030 (2)	408 (24)
C(8)	2314 (10)	−3938 (5)	5906 (2)	403 (22)
C(9)	899 (10)	−2305 (4)	6060 (2)	348 (20)
C(10)	113 (11)	−2113 (5)	6744 (2)	449 (25)
C(11)	439 (9)	−1138 (4)	5553 (2)	303 (17)
C(12)	1335 (9)	−1607 (4)	4895 (2)	319 (19)
C(13)	−930 (9)	552 (4)	5626 (2)	302 (18)
N(1)	−387 (13)	−2090 (5)	7297 (2)	696 (35)
N(2)	3487 (11)	−5220 (4)	5787 (2)	604 (27)

Fig. 2. Bond lengths (Å) and angles (°) of DBTTF and TCNQCl₂. The e.s.d.'s of bonds involving S or Cl are 0·003 Å, the other bond e.s.d.'s are 0·005 Å. The e.s.d.'s of the angles are 0·2–0·3°.
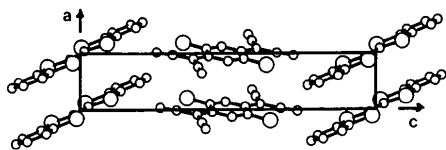
Fig. 3. DBTTF–TCNQCl$_2$ in the unit cell viewed along **b**.

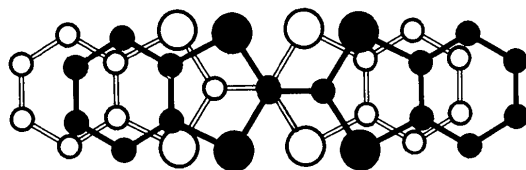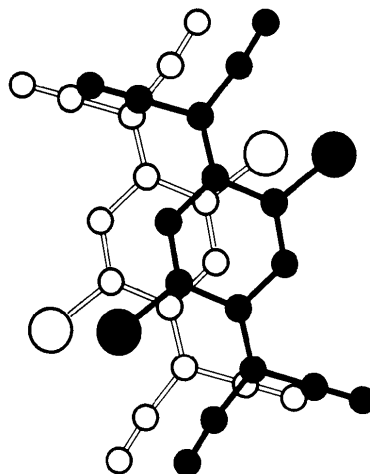Fig. 4. DBTTF–TCNQCl$_2$ in the unit cell viewed along **a**.

Fig. 5. The DBTTF overlap viewed along the normal to the plane defined by C(3), S(1), S(2) and their centrosymmetric mates.

Fig. 6. The TCNQCl$_2$ overlap viewed along the normal to the plane defined by C(11), C(12), C(13) and their centrosymmetric mates.

DBTTF is centrosymmetric, the centroid being at the origin of the cell. The lengths of the bonds from C(3) differ by 1–2 e.s.d.'s from those found in TTF–TCNQ (Kistenmacher, Phillips & Cowan, 1974). The fusion of the thiafulvalene ring with the benzene ring, however, causes significant changes in both rings, Fig. 2. DBTTF has the shape of a flat chair. The dihedral angle between the benzene ring and the 'central plane' defined by the atoms C(3), S(1), S(2) and their centro-symmetric mates is 2·3°. The root mean square deviation (r.m.s.d.) of the relevant atoms from these planes is 0·006 and 0·003 Å respectively.

TCNQCl$_2$ is centrosymmetric with the centroid at 0,0,½. Within 1–3 e.s.d.'s the bond lengths of TCNQCl$_2$, Fig. 2, agree with those found in TTF–TCNQ (Kistenmacher et al., 1974). The bond angles are significantly changed by introduction of the Cl atoms. The approximate *mmm* (D_{2h}) symmetry of the ring is, however, preserved.

A common feature of 2,5 substituted TCNQ's is a change of the angles around C(9), C(10) and C(11). The intramolecular Cl···N(1) distance, 3·300 (4) Å, is equal to the sum of the van der Waals radii (Bondi, 1964).

The DBTTF cations and the TCNQCl$_2$ anions form separated, homologous stacks as shown in Figs. 3 and 4. No short cation to anion distances exist. On the contrary, the 3·682 Å S···N distance is one of the longest observed in any compound of the TTF–TCNQ type.

The spacing between the DBTTF planes, defined by all non-H atoms (r.m.s.d. = 0·02 Å), is 3·51 Å. The tilt of the plane relative to the *a* axis is 22·9°. The overlap, shown in Fig. 5, is the well-known 'double bond over ring' type (Chasseau, Gaultier, Hauw, Fabre, Giral & Toreilles, 1978, and references therein). The spacing between the TCNQCl$_2$ planes, defined by all C atoms (r.m.s.d. = 0·009 Å), is 3·41 Å, and the tilt relative to

the *a* axis is 21·6°. The overlap, shown in Fig. 6, is unusual for 1:1 TCNQ compounds; it may be characterized by the term 'ring–internal-double-bond overlap'. The same type of overlap and the same interplanar distances have been found in ditoluene-chromium–TCNQ (Shibaeva, Atovmyan & Rozenberg, 1969). The type of overlap commonly found in TCNQ compounds may be called 'ring–external-double-bond overlap', i.e. the double bond of the > C=(CN)$_2$ group projects on the quinone ring in a more or less symmetrical way. Jacobsen et al. (1980) take the 'internal' type of overlap found in the present compound as evidence for a substantial interaction of Cl with the lowest unoccupied molecular orbital of the TCNQ framework. This point of view is supported by the fact that the 'external' type of TNCQ overlap is found in the 2,5-dialkyl substituted compounds TMTSF–DMTCNQ (Andersen, Bechgaard, Jacobsen, Rindorf, Soling & Thorup, 1978) and TTF–DETCNQ (Schultz, Stucky, Craven, Schaffman & Salamon, 1976). The 'internal' and the 'external' types of TCNQ overlap appear together in some compounds with a donor:acceptor ratio <1, e.g. (morpholinium)$_2$-(TCNQ)$_3$ (Sundaresan & Wallwork, 1972).

Structure investigation at 115 K

At 115 K the space group of DBTTF–TCNQCl$_2$ is $P\bar{1}$ with $a = 3·691$ (1), $b = 7·823$ (3), $c = 20·030$ (7) Å,

$\alpha = 91\cdot21$ (3), $\beta = 93\cdot09$ (8), $\gamma = 91\cdot89$ (3)°, $V = 577\cdot0$ Å^3, $Z = 1$. The 2·6% decrease in the cell volume is mainly due to the decrease in the length of the a axis. A data collection on the four-circle diffractometer was initiated. Unfortunately, the cooling system broke down half-way, leaving a scanty data set, $0kl$, $1kl$, $2kl$, $0\cdot049 < (\sin\theta)/\lambda < 0\cdot48$ Å^{-1}, for the analysis. 1086 scanned reflections were reduced and averaged ($R_{ic} = 0\cdot04$) to a set of 596 observed intensities. The full-matrix least-squares refinement of the coordinates and temperature factors, with S and Cl anisotropic, terminated at $R = 0\cdot066$. The e.s.d.'s of the bond lengths were 0·02–0·03 Å, and those of the angles were 1–2°. In view of the limitation of the low-temperature data set a detailed comparison with the results obtained from the room-temperature data is not warranted. No noteworthy discrepancies have been found. The interstack S···N distance is 3·63 (2) Å. It is concluded that the only detectable effect of the cooling is a closer packing in the unit cell. Lists of fractional atomic coordinates, thermal parameters, calculated and observed structure factors, as well as bond lengths and angles are available.*

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* See previous footnote.

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The Structure of Oxythiamin Chloride Dihydrate, a Potent Antagonist of Vitamin B₁

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Abstract

$C_{12}H_{16}N_3O_2S\cdot Cl\cdot 2H_2O$, $M_r = 337\cdot83$, m.p. 357–359 K (uncalibrated Thermolyne melting-point apparatus), crystallizes in the space group $P\bar{1}$ with $a = 7\cdot008$ (1), $b = 7\cdot968$ (1), $c = 15\cdot150$ (2) Å, $\alpha = 75\cdot45$ (1), $\beta = 104\cdot02$ (1), $\gamma = 91\cdot93$ (1)°, $V = 794\cdot1$ Å^3, $d_m = 1\cdot408$ (flotation in CCl_4–xylene), $d_c = 1\cdot412$ Mg m^{-3}, $Z = 2$, μ(Cu $K\alpha$) = 3·47 mm^{-1} and $F(000) = 358$ at 298 K (reduced cell parameters: $a = 7\cdot008$, $b = 7\cdot968$, $c = 15\cdot073$ Å, $\alpha = 103\cdot70$, $\beta = 102\cdot79$, $\gamma = 91\cdot93°$, $V = 794\cdot1$ Å^3). The structure was solved by direct methods and refined by full-matrix least squares to $R = 0\cdot034$ for all 2628 reflections and $R = 0\cdot031$ for the 2560 observed reflections. A comparison of the parameters from this structure of the free base of oxythiamin with those from thiamin indicates that there are significant changes throughout the pyrimidine ring when an oxo group replaces the 4'-amino. These changes are manifested by a change in preferred conformation and a change in the relative basicity of the two ring N atoms.

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