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The Crystal Structure of the 1:1 Radical Cation–Radical Anion Salt of 2,2′-Bis-1,3-dithiole (TTF) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ)*

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The salt of the radical cation of 2,2′-bis-1,3-dithiole (TTF) and the radical anion of 7,7,8,8-tetracyanoquinodimethane (TCNQ), $C_{18}H_8N_4S_4$, crystallizes in the monoclinic system, space group $P2_1/c$, with cell constants: $a=12{\cdot}298$ (6), $b=3{\cdot}819$ (2), $c=18{\cdot}468$ (8) Å, $\beta=104{\cdot}46$ (4)°, $Z=2$, $D_m=1{\cdot}62$ (1) and $D_c=1{\cdot}615$ g cm^{-3}. Intensities for 1373 independent reflections were collected on an automated diffractometer. The structure was solved by standard heavy-atom methods and has been refined by full-matrix least-squares calculations to an R value of 0·044. The TTF radical cations and the TCNQ radical anions form homologous columnar stacks with interplanar spacings of 3·47 and 3·17 Å, respectively. The dihedral angle between the least-squares planes of the cations and the anions is 58·5° and is approximately bisected by [010].

Introduction

Research in the field of high-conductivity organic salts has been extensive and intensively pursued in the last few years (Shchegolev, 1972). Stable radical anion salts derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been of considerable importance in these studies (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962). High conductivity for organic salts of TCNQ is usually on the order of 10^2 ohm^{-1} cm^{-1}. Recently, Ferraris, Cowan, Walatka & Perlstein (1973) reported that the newly synthesized complex of TTF (2,2′-bis-1,3-dithiole) and TCNQ had a maximum conductivity of 10^4 ohm^{-1} cm^{-1} at 66°K. Qualitatively, the data show a semiconductor to metal transition at the critical temperature. Further experiments by Coleman, Cohen, Sandman, Yamagishi, Garito & Heeger (1973) revealed that a few 'anomalous' crystals of TTF–TCNQ exhibited an even higher conductivity [$\sigma_{58^\circ K} > 10^6$ ohm^{-1} cm^{-1} with a slope ($d\sigma/dT$) which is apparently divergent]. They interpreted these data as arising from superconducting fluctuations (paraconductivity). Both groups suggested that the transition to an insulating state near 60°K was the result of crystal distortion or a structural change. Recent microwave experiments on TTF–TCNQ do not indicate paraconductivity (Bloch, Ferraris, Cowan & Poehler, 1973) as suggested by the earlier four-probe conductivity measurements (Coleman *et al.*, 1973). However, as Coleman *et al.* (1973) have stated, 'the data indicate that the divergent behavior is characteristic of only rare microscopically perfect crystals of (TTF) (TCNQ)'. Thomas (1973) has recently predicted that structural imperfections (dislocations, stacking faults, planar faults from homogeneous shear) can render superconductivity unattainable. In fact, most crystals of TTF–TCNQ (see below) may contain such crystalline imperfections, and this may account for the inability to reproducibly observe the 'fluctuating' superconductivity of Coleman *et al.* (1973).

We have determined the crystal structure of TTF–TCNQ in order to provide a sound basis for further, more quantitative, analysis of the relationship between the three-dimensional arrangement of the radical cations and radical anions and the high conductivity of this material. A preliminary report of the structure has appeared (Phillips, Kistenmacher, Ferraris & Cowan, 1973).

Experimental

Crystalline samples, obtained from saturated acetonitrile solution, were prepared by Mr John Ferraris of these laboratories. A single crystal suitable for X-ray examination was found with some difficulty, since many of the crystals showed twinning on optical or X-ray examination. Several of the specimens also exhibited steps and striations along the (001) face of the crystal. Finally, a crystal with dimensions 1·1 × 0·25 × 0·04 mm, along **b**, **a***, and **c**, respectively, was used for intensity-data collection. The single crystal appeared free of stepping and striation upon preliminary examination. However, deformation problems were apparently not completely absent even in this crystal (see below). Oscillation and Weissenberg photographs were consistent with the monoclinic space group $P2_1/c$. Unit-cell dimensions were obtained from the 2θ, ω, and χ values of 14 reflections on the diffractometer. The density was measured by flotation in a bromoform–chloroform mixture. The crystal data are summarized in Table 1.

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Table 1. *Crystal data for* 2,2′-*bis*-1,3-*dithiole*–7,7,8,8-*tetracyanoquinodimethane*

	$C_{18}H_8N_4S_4$
$a = 12{\cdot}298\ (6)$ Å	M.W. 408·55
$b = 3{\cdot}819\ (2)$	Space group: $P2_1/c$
$c = 18{\cdot}468\ (8)$	$Z = 2$
$\beta = 104{\cdot}46\ (4)°$	$D_m = 1{\cdot}62\ (1)$ g cm^{-3}
$V = 839{\cdot}9$ Å^3	$D_c = 1{\cdot}615$

Intensity measurements were made on a Syntex $P\bar{1}$ computer-controlled diffractometer with a graphite monochromator. The prism axis (**b**) of the sample crystal was tilted relative to the φ axis. Intensity data were collected with Mo $K\alpha$ radiation by the θ–2θ scan technique. Individual scan speeds were determined by a rapid scan at each Bragg peak, and the rate of scanning varied from 1°/min to 24°/min. Three standard reflections were measured frequently during the time of the experiment, and their intensities showed no unusual fluctuations or decay with time. All reflections in the octants hkl and $hk\bar{l}$ out to $2\theta = 55°$ were collected; these totaled 1490 independent reflections of which 61 had net intensities less than zero. These 61 reflections were assigned F's and $\omega(F)$'s equal to zero. The remaining 1429 reflections were assigned observational variances on the basis of the following formula:

$$\sigma^2(I) = S + (B_1 + B_2)\ (T_S/2T_B)^2 + (0{\cdot}03I)^2,$$

where S, B_1, and B_2 are the scan and background counts in times T_S and T_B. Intensities and their standard deviations were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 5{\cdot}6$ cm^{-1}).

Solution and refinement of the structure

The two sulfur atoms in the asymmetric unit were located from an analysis of an unsharpened three-dimensional Patterson synthesis. Previous two-dimensional work on the structure by Daly, Wilson & Sanz (1973) had been communicated to us, and this information was useful in the interpretation of the three-dimensional map. A Fourier synthesis based on the signs derived from the location of the two sulfur atoms revealed the remaining heavy atoms in the asymmetric unit ($R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}18$). Five cycles of full-matrix least-squares refinement, the quantity minimized being $\sum\omega(|F_o| - |F_c|)^2$, lowered R to 0·13. A detailed scan of the individual $\omega(\Delta F)^2$'s at this stage showed that the $h0\bar{l}$ reflections (a total of 128 reflections) had excessively high values. The data-collection output indicated that these reflections were not centered in the counter during the data scan. We have attributed this to shear deformations in the crystal (the fit of F_o to F_c became increasingly better as h increased). These reflections were removed from the data set, and two subsequent cycles of isotropic least-squares lowered R to 0·086. At this point a difference Fourier map was calculated, and the four hydrogen atoms in the asymmetric unit were located and assigned isotropic temperature factors of the atom to which they were attached. Four further cycles of refinement, with anisotropic temperature components for the sulfur atoms refined, led to final R indices of 0·044 (excluding zeros) and 0·046 (including zeros). The final weighted R value $[(\sum\omega(F_o - F_c)^2/\sum\omega F_o^2)^{1/2}]$ and goodness-of-fit $[(\sum\omega(F_o - F_c)^2/(n-p))^{1/2}]$ for $n = 1306$ observations of non-zero weight and $p = 63$ are 0·052 and 2·1, respectively. The maximum shift over error for any parameter was 0·5. The quantity $\langle\omega(\Delta F)^2\rangle$ showed no unusual dependence on $|F_o|$ or $(\sin\theta)/\lambda$. The scattering factors for S, C, and N were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The scattering curve for H was that of Stewart, Davidson & Simpson (1965). Final atomic parameters are collected in Table 2.*

Table 2. *Final heavy-atom parameters and hydrogen positional parameters*

(Heavy-atom positional parameters × 10^4; hydrogen × 10^3).

	x	y	z	B
S(1)	−935 (1)	−1835 (2)	791 (1)	*
S(2)	1473 (1)	−1811 (2)	850 (1)	*
N(1)	3857 (2)	5918 (6)	1898 (1)	3·57 (5)
N(2)	7482 (2)	6204 (6)	1902 (1)	3·44 (5)
C(1)	−12 (2)	−3415 (7)	1598 (2)	2·91 (5)
C(2)	1072 (2)	−3415 (7)	1622 (2)	2·82 (5)
C(3)	114 (2)	−766 (6)	346 (1)	2·31 (4)
C(4)	4593 (2)	5098 (7)	1657 (1)	2·25 (4)
C(5)	6574 (2)	5247 (7)	1656 (1)	2·29 (4)
C(6)	5469 (2)	4077 (6)	1319 (1)	2·07 (4)
C(7)	5241 (2)	2048 (6)	666 (1)	1·89 (4)
C(8)	4116 (2)	918 (6)	314 (1)	2·03 (4)
C(9)	6107 (2)	1029 (6)	320 (1)	2·01 (4)
H(1)	−39	−419	196	
H(2)	165	−412	208	
H(8)	356	150	58	
H(9)	685	169	65	

* Anisotropic thermal parameters (× 10^5) defined by the ellipsoid equation:

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right].$$

S(1)	314 (5)	4935 (55)	226 (2)	26 (11)	83 (2)	98 (8)
S(2)	279 (5)	4918 (55)	233 (2)	82 (11)	43 (2)	121 (8)

Discussion

Molecular geometry

Drawings of the TTF radical cation and the TCNQ radical anion are shown in Figs. 1 and 2, respectively; interatomic distances and angles are also given in these figures. Estimated standard deviations (e.s.d.'s) are in the range 0·003 Å (S–C), 0·003–0·004 Å (C–C, C–N) and 0·2–0·3° for the bond angles.

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* Observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30293 (11 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The molecular symmetry of the TTF cation (required to be at least $\bar{1}$) is nearly *m*, with S(1)–C(1) and S(2)–C(2) differing by about three e.s.d.'s. The TTF radical cation is not as planar as one might expect from its pseudo-aromatic character [Table 3, plane (*a*)]; conversely, it has assumed a molecular conformation nearly identical with that found in the neutral molecule (Cooper, Kenney, Edmonds, Nagel, Wudl & Coppens, 1971). The two halves of the fulvalene ring system are slightly distorted in anti-envelope conformations giving rise to an overall chair conformation for the molecular ion. The central plane of the molecule [defined by atoms S(1), S(2), C(3) and their centrosymmetric equivalents, plane (*b*), Table 3] is extremely planar with a maximum deviation of 0·0009 Å (0·007 Å in neutral TTF). The exterior plane [defined by S(1), S(2), C(1) and C(2), plane (*c*), Table 3] makes an angle of 2·2° (2·1° in neutral TTF) to the central plane. This exterior plane and its centrosymmetric mate lie some 0·118 Å (0·116 Å in neutral TTF) apart.

Table 4 gives a detailed comparison of the dimensions found here for the TTF radical cation and those of Cooper *et al.* (1971) for neutral TTF. The principal differences in these parameters are as follows: (i) the sulfur–carbon distances in the cation are nearly all equivalent, while in TTF itself the sulfur to bridging-carbon distances are significantly longer than the sulfur to exterior-carbon bond lengths; (ii) the bond lengths C(1)–C(2) and C(3)–C(3′) are both longer (0·01 and 0·02 Å, respectively) in the cation. There are essentially no significant differences in bond angles between the neutral and ionized species. Although we have not attempted a quantitative interpretation of these results, the trend observed in the transition from the neutral molecule to the 'delocalized' radical cation would seem qualitatively to be in the correct direction.

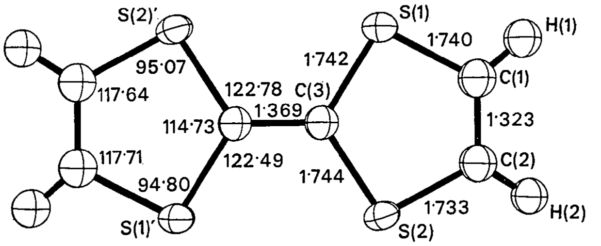


Fig. 1. Interatomic distances and angles in the TTF cation. Thermal ellipsoids are drawn at the 50% probability level (*ORTEP*, Johnson, 1965). Only the sulfur atoms have been refined anisotropically.

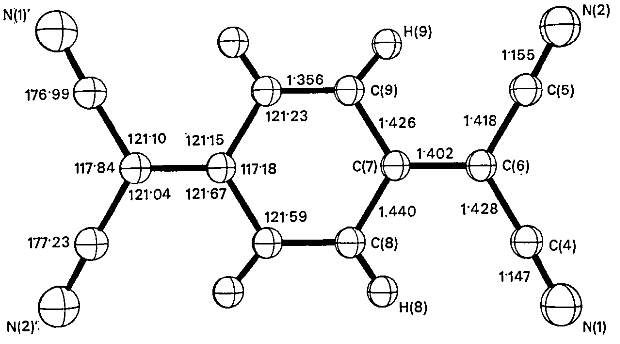


Fig. 2. Interatomic distances and angles in the TCNQ anion. Thermal ellipsoids are drawn at the 50% probability level (*ORTEP*, Johnson, 1965). All atoms are isotropic.

Table 3. *Some least-squares planes and deviations* (Å)

In each of the equations of the planes, *X*, *Y* and *Z* are coordinates (Å) referred to the orthogonal axes *a*, *b* and *c**. The atoms used to define the plane have been equally weighted.†

(*a*) TTF molecular plane $(0{\cdot}0171X-0{\cdot}9093Y-0{\cdot}4157Z=0{\cdot}0)$

S(1), S(1)′	+, −0·023	C(1), C(1)′	−, +0·015
S(2), S(2)′	+, −0·021	C(2), C(2)′	−, +0·010
C(3), C(3)′	+, −0·008		

(*b*) TTF central plane $(0{\cdot}0182X-0{\cdot}9036Y-0{\cdot}4280Z=0{\cdot}0)$

S(1), S(1)′	+, −0·0002	C(3), C(3)′	−, +0·0009
S(2), S(2)′	+, −0·0002		

(*c*) TTF exterior phane $(0{\cdot}0164X-0{\cdot}9185Y-0{\cdot}3950Z=0{\cdot}0591)$

S(1)	0·001	C(1)	−0·002
S(2)	−0·001	C(2)	0·002

(*d*) TCNQ quininoid ring $(-0{\cdot}0121X+0{\cdot}8348Y-0{\cdot}5504Z=-0{\cdot}0741)$

C(6), C(6)′	+, −0·002	C(8), C(8)′	−, +0·002
C(7), C(7)′	−, +0·002	C(9), C(9)′	−, +0·002

Other atoms

N(1)	0·046	N(2)	0·080
C(4)	0·010	C(5)	0·029

(*e*) TCNQ molecular plane $(-0{\cdot}0181X+0{\cdot}8295Y-0{\cdot}5582Z=-0{\cdot}1112)$

N(1), N(1)′	+, −0·022	N(2), N(2)′	+, −0·028
C(4), C(4)′	−, +0·016	C(5), C(5)′	−, +0·012
C(6), C(6)′	−, +0·024	C(7), C(7)′	−, +0·016
C(8), C(8)′	−, +0·000	C(9), C(9)′	−, +0·015

† Estimated positional uncertainties: S, 0·0007; N, 0·0025; C, 0·0030 Å.

Table 4. *A comparison of the bond lengths and angles in TTF and TTF–TCNQ*

	TTF–TCNQ*	TTF†
S(1)–C(1)	1·740 (3) Å	1·723 (2) Å
S(1)–C(3)	1·742 (3)	1·756 (2)
S(2)–C(2)	1·733 (3)	1·729 (2)
S(2)–C(3)	1·744 (3)	1·758 (2)
C(1)–C(2)	1·323 (4)	1·314 (3)
C(3)–C(3)′	1·369 (4)	1·349 (3)
C(1)–S(1)–C(3)	94·8 (2)°	94·5 (2)°
C(2)–S(2)–C(3)	95·1 (3)	94·3 (2)
S(1)–C(1)–C(2)	117·1 (2)	118·0 (2)
S(2)–C(2)–C(1)	117·6 (2)	118·6 (2)
S(1)–C(3)–S(2)	114·7 (3)	114·5 (2)
S(1)–C(3)–C(3)′	122·5 (3)	122·7 (2)
S(2)–C(3)–C(3)′	122·8 (3)	122·8 (2)

* This study.
† Cooper *et al.* (1971).

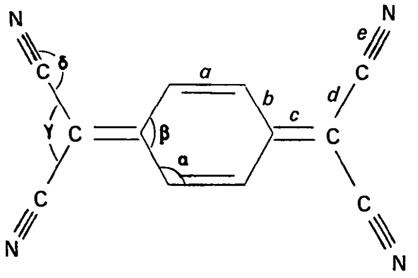
The dimensions of the TCNQ radical anion (Fig. 2) are, in general, in good agreement with the results of other structure analyses (Herbstein, 1971; Hoekstra, Spoelder & Vos, 1972). Table 5 gives a comparison of our averaged molecular dimensions, *mmm* molecular symmetry, with those compiled by Herbstein (1971) for $TCNQ^{-0\cdot5}$ and $TCNQ^{-1}$; the agreement between our values and those for $TCNQ^{-1}$ is good. Assignment of about −1 charge to the TCNQ residue (and concurrently about +1 charge to the TTF cation) is consistent with the observed molecular dimensions, the crystal packing to be discussed later, and spectroscopic data from these laboratories (Ferraris *et al.*, 1973).

Typically, the TCNQ anion is nearly planar, especially the quininoid nucleus, plane (*d*), Table 3. The cyano groups lie somewhat out of this plane, but this is not unusual (Herbstein, 1971). The overall planarity of the TCNQ ion can be ascertained from plane (*e*), Table 3.

Crystal packing and molecular stacking

The crystal structure is dominated by homologous stacks of cations and anions parallel to the short *b* axis. Packing views down [010] and [100] are given in Figs. 3 and 4. The normal to the TTF molecular plane is tilted 24·5° with respect to the *b* axis. The interplanar

Table 5. *A comparison of the bond lengths and angles in* $TCNQ^{-0\cdot5}$, $TCNQ^{-1}$, *and TTF–TCNQ (averaged values, mmm molecular symmetry)*



	$TCNQ^{0\cdot5-}$	TTF–TCNQ	$TCNQ^{-1}$
a	1·354 (2) Å*	1·356 (3) Å†	1·356 (10) Å*
b	1·434 (2)	1·433 (3)	1·425 (7)
c	1·396 (2)	1·402 (3)	1·401 (8)
d	1·428 (3)	1·423 (3)	1·417 (4)
e	1·17 (1)	1·151 (4)	1·15 (1)
α	121·1 (2)°	121·4 (2)°	121·2 (6)°
β	117·9 (2)	117·2 (2)	117·4 (4)
γ	115·9 (2)	117·8 (2)	115·2 (4)
δ	178·5 (2)	177·1 (2)	178·6 (6)

* Herbstein (1971).
† This study.

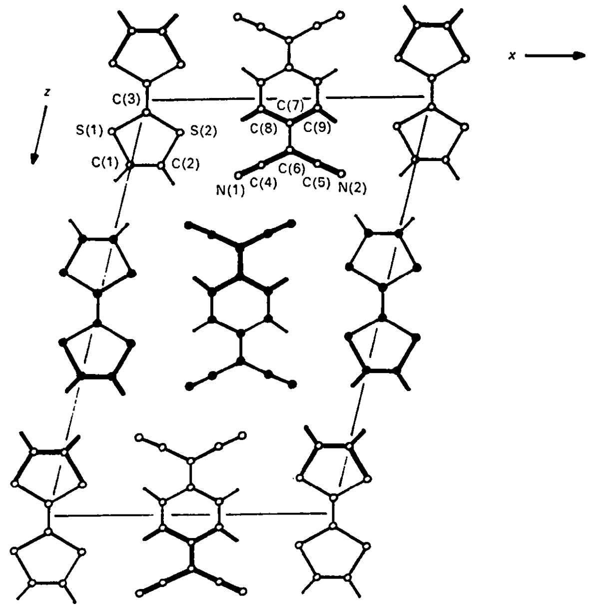


Fig. 3. A view normal to the *ac* plane of the crystal packing in TTF–TCNQ. The shaded molecules have their centroids at $y=\frac{1}{2}$.

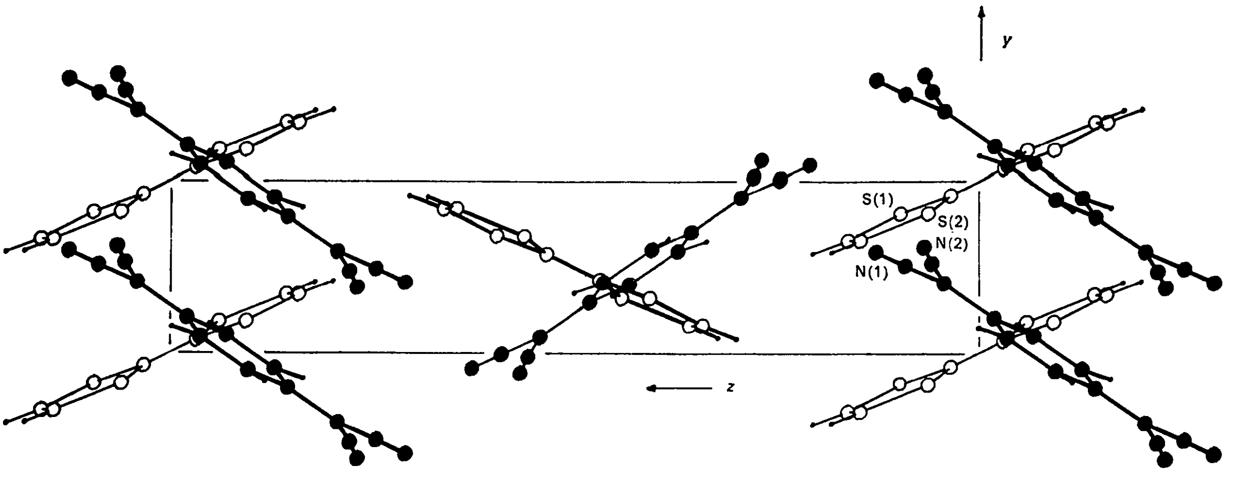


Fig. 4. A view down [100] of the crystal packing in TTF–TCNQ. The shaded molecules have their centroids at $x=\frac{1}{2}$.

stacking distance is 3·47 Å [compared to 3·62 Å for neutral TTF with a similar, but less symmetric molecular overlap (Phillips *et al.*, 1973)]. The tilt of the TCNQ molecular plane with respect to the *b* axis is 34·0°, and opposite in direction to the tilt of the TTF cation, see Fig. 4. The TCNQ interplanar stacking distance is 3·17 Å which represents the shortest reported distance for columnar stacking of TCNQ anions. The 'ring-double bond' overlap of molecular planes is characteristic of both the cation and anion stacking (Figs. 5 and 6). This mode of stacking of the TCNQ anion is relatively common (Herbstein, 1971). There are no unusually short interatomic contacts in the structure (Table 6).

Table 6. *Short interatomic contacts*

$S(1)\cdots H(9^d)$	2·99 Å	$C(5)\cdots N(1^l)$	3·29 Å
$S(1)\cdots N(2^e)$	3·25	$C(5)\cdots C(7^c)$	3·36
$S(2)\cdots H(8^a)$	3·02	$C(6)\cdots C(7^c)$	3·26^s
$S(2)\cdots N(1^b)$	3·20	$C(6)\cdots C(8^c)$	3·39^s
$S(2)\cdots C(2^c)$	3·59^s	$C(6)\cdots N(1^k)$	3·41
$C(1)\cdots H(1^i)$	3·04	$C(6)\cdots C(9^c)$	3·42^s
$C(1)\cdots N(2^e)$	3·27	$C(7)\cdots C(7^h)$	3·28
$C(2)\cdots N(1^b)$	3·34	$C(7)\cdots C(9^h)$	3·40
$C(2)\cdots N(2^k)$	3·36	$C(7)\cdots C(8^h)$	3·44
$C(3)\cdots C(3^g)$	3·46^s	$C(8)\cdots C(9^h)$	3·28
$C(4)\cdots C(8^c)$	3·27^s	$N(1)\cdots H(2^c)$	2·81
$C(4)\cdots N(1^k)$	3·28	$N(2)\cdots H(1^f)$	2·59
$C(4)\cdots C(7^c)$	3·43^s	$N(2)\cdots H(2^l)$	2·62
$C(5)\cdots C(9^c)$	3·25^s	$N(2)\cdots H(2^j)$	2·80

(*a*) x,y,z; (*b*) $x,-1+y,z$; (*c*) $x,1+y,z$; (*d*) $-1+x,y,z$; (*e*) $-1+x,-1+y,z$; (*f*) $1+x,1+y,z$; (*g*) $-x,-1-y,-z$; (*h*) $1-x,1-y,-z$; (i) $-x,\frac{1}{2}+y,\frac{1}{2}-z$; (*j*) $1-x,\frac{1}{2}+y,\ \frac{1}{2}-z$; (*k*) $1-x,-\frac{1}{2}+y,\frac{1}{2}-z$; (*l*) $1-x,\frac{3}{2}+y,\frac{1}{2}-z$; (*s*) contacts involved in the stacking of TTF or TCNQ molecular ions.

In order to illustrate the uniqueness of the TTF–TCNQ structure, we compare it to the following previously determined structures: *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD)–TCNQ (Hanson, 1965); *N*-methylphenazinium (NMP)–TCNQ (Fritchie, 1966); *N,N′*-dimethylbenzidazolium (NNDB)–TCNQ (Chasseau, Gaultier & Hauw, 1972); *N,N′*-dimethyldihydrophenazinium (DMPH)–TCNQ (Goldberg & Shmueli, 1973). In selecting the above four structures to compare to TTF–TCNQ, we have employed the following criteria: (i) the salt must have a 1:1 cation-to-anion ratio, (ii) the donor molecule is completely organic and nominally flat, (iii) there is some evidence that the ground state, *i.e.* the crystalline state at room temperature, is at least partially ionic in character. The dominant features of the above four structures are summarized in Table 7.

Consideration of the results presented in Table 7 suggests three important ways in which TTF–TCNQ differs from the 'normal' cation–TCNQ salt: (1) the interplanar spacing in the homologous TCNQ columns is nearly 0·10 Å less than that in NMP–TCNQ. The effect of this interplanar shrinkage on the band energy gap should be significant (Anderson, Lee & Saitoh, 1973); (2) TTF–TCNQ is the only system in which the cations are capable of electrical conductivity in the ground state; the similarity in the columnar stacking of the TTF cations and the TCNQ anions suggests that the TTF columns play an integral part in the observed macroscopic conductivity; (3) the TTF–TCNQ structure is the only one in which the

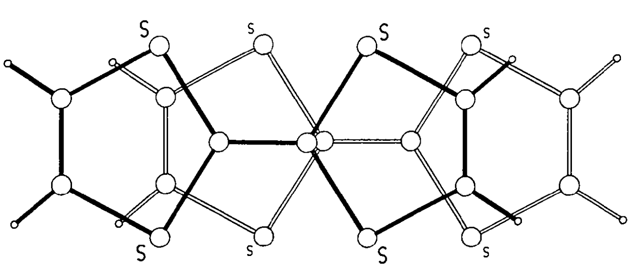


Fig. 5. Molecular overlap in the columnar stacking of TTF cations. The view direction is normal to the least-squares molecular plane.

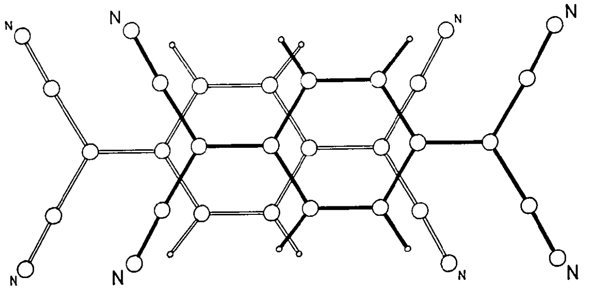


Fig. 6. Molecular overlap in the columnar stacking of TCNQ anions. The view direction is normal to the least-squares molecular plane.

Table 7. *Structural characteristics of several organic cation–TCNQ structures*

Compound	Structural motif	Stacking (distance)
TMPD–TCNQ	Parallel sheets of cations and anions	Mixed stacks of cations and anions (3·27 Å)
NMP–TCNQ	Parallel sheets of cations and anions	Segregated stacks of cations (3·36 Å) and anions (3·26 Å)
NNDB–TCNQ	Parallel sheets of cations and anions	Discrete dimers: cations (3·50 Å), anions (3·07 Å)
DMPH–TCNQ	Parallel sheets of cations and anions	Mixed stacks of cations and anions (~3·3 Å)
TTF–TCNQ	Interleaving herringbone packing of cations and anions	Segregated stacks of cations (3·47 Å) and anions (3·17 Å)

cations and anions are not arranged in approximately parallel sheets.

The structure factor and Fourier calculations were performed with the X-RAY 67 system of programs of Stewart (1967). The least-squares calculations were computed with a modified version of the *ORFLS* program of Busing, Martin & Levy (1962). All the remaining computations were done with locally written programs.

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Structure Cristalline de $K_5(UO_2)_2F_9$

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$K_5(UO_2)_2F_9$ crystallizes in the monoclinic system in space group $C2/c$: $a = 19{\cdot}860$ (1), $b = 6{\cdot}110$ (1), $c = 11{\cdot}706$ (4) Å, $\beta = 102{\cdot}58$ (4)°. The structure is composed of K^+ ions and $(UO_2)_2F_9^{5-}$ dimers. The latter can be considered as condensed ions formed by two $UO_2F_5^{3-}$ pentagonal bipyramids sharing one common fluorine atom. The U–O and U–F distances, respectively equal to 1·79 (8) and 2·29 (6) Å, are the same as in the original ion. However the condensation causes a torsion between the two planes formed by the fluorine atoms. The angle between these two planes is 120°. The U–U distance inside a dimer is 4·34 (1) Å. The next greatest distance between two uranium atoms is 6·10 (1) Å. $(UO_2)_2F_9^{5-}$ dimers are surrounded by 20 potassium atoms which form a hexagonal prism with two trigonal pyramids at each end.

Introduction

L'étude structurale du complexe $K_5(UO_2)_2F_9$ fait partie d'un projet d'études menées au laboratoire dans le but de mettre en évidence de nouveaux types d'ions complexes formés par l'ion uranyle avec des ions halogénures. Ce complexe est un des composés définis du système ternaire KF–UO_2F_2–H_2O (Sergienko & Davidovich, 1968). Nous nous proposons de décrire ici sa structure.

Techniques et méthodes expérimentales

L'appareillage utilisé se compose d'un générateur de rayons X Philips PW 1010 muni d'une anticathode de molybdène, d'un goniomètre de Weissenberg et d'une chambre de précession de Buerger. Les cristaux que nous avons obtenus sont maclés pour la plupart et ont des dimensions très faibles, de l'ordre de 0,1 mm. C'est pourquoi, il nous a été difficile de leur donner la forme sphérique souhaitable pour une correction rigoureuse