Table 6. *Least-squares planes and interplanar angles for* (1) *and* (2) *and the results of molecular-mechanics calculations*

Plane	(1a) r.m.s.d. (Å)	(1b) r.m.s.d. (Å)	(2) r.m.s.d. (Å)
A = C(1)C(2)C(3)C(4)C(5)C(6)	0·012	0·016	0.000
B = C(1)C(6)C(7)C(8)C(9)C(10)	0·009	0·010	–
C = C(1)C(10)C(11)C(19)C(2)	0·022	0·025	0·002
D = C(11)C(12)C(19)C(20)C(27)C(28)	0·022	0·017	0·000
E = C(13)C(14)C(15)C(16)C(17)C(18)	0·005	0·006	–
F = C(21)C(22)C(23)C(24)C(25)C(26)	0·005	0·004	0·009

Angle	(1a) (°)*	(1b) (°)	MM (°)	(2) (°)	MM (°)
A,B	1·9	2·2	1·2	0·0	3·5
A,C	3·6	3·3	3·5	0·2	1·5
B,C	2·4	4·3	–	–	1·9
C,D	4·8	4·9	4·8	1·4	8·0
D,E	57·6	48·3	60	–	39†
D,F	52·9	58·0	–	77·3	39
E,F	70·1	74·9	60	0·0	0

* Standard deviations in angles 0·5–0·8°.

† The angle is 90° if the π system is forced to be planar.

The shortest intramolecular contacts involving the substituent phenyl rings are H(3)···C(26) = 2·70 (4) and 2·72 (4) Å and H(9)···C(14) = 2·68 (4) and

2·66 (4) Å for (1a) and (1b) and H(3)···C(22) = 2·76 (4) Å for (2).

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Structure of Di(*S*-methylthiouronium)–Tri(7,7,8,8-tetracyano-*p*-quinodimethane) Dihydrate, (MT)₂(TCNQ)₃.2H₂O*

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Abstract. $(C_2H_7N_2S)_2(C_{12}H_4N_4)_3.2H_2O$, $M_r = 831\cdot0$, triclinic, $P\bar{1}$, $a = 8\cdot033$ (2), $b = 13\cdot002$ (3), $c = 9\cdot895$ (3) Å, $\alpha = 94\cdot32$ (2), $\beta = 108\cdot12$ (2), $\gamma = 88\cdot90$ (3)°, $V = 979\cdot4$ (6) Å³, $Z = 1$, $D_x = 1\cdot141$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot0$ cm⁻¹, $F(000) = 430$, room temperature, $R = 0\cdot039$ for 1928 observed reflections. The structure contains stacks of planar TCNQ radical anions located as trimers with a distance of 3·17 Å between molecules in trimers and 3·33 Å between neighbouring trimers. The central molecule of a trimer is centrosymmetric and has a charge of about −0·9 e; the charge of the non-centrosymmetric molecules is about −0·4 e. Hydrogen bonds connect cations, water molecules and anions and have an unusual effect on the anion

packing. Among the known trimerized TCNQ salts (MT)₂(TCNQ)₃.2H₂O has the highest electrical conductivity.

Introduction. As part of our continuing study of conducting organic materials, a new TCNQ salt of *S*-methylthiouronium was grown. The simple MT–TCNQ salt, prepared and studied earlier, exhibits low electrical conductivity due to the presence of isolated TCNQ radical anion pairs. The structure and some physical properties of the new conducting salt, (MT)₂(TCNQ)₃.2H₂O, are reported below.

Experimental. Black plate-like crystals of (MT)₂(TCNQ)₃.2H₂O were grown from a mixture of 5 cm³ ethanolic thiouronium iodide solution (1·1 mmol) and 20 cm³ boiling solution of TCNQ in acetonitrile (1 mmol). This mixture was left exposed

* TCNQ = 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropane-dinitrile.

to air for a few days. The same proportion between ethanolic and acetonitrile was conserved at recrystallization. The composition of crystals was controlled by spectral analysis, the cation/anion ratio being 2/3. The water molecule was revealed in the successive Fourier syntheses during analysis of the crystal structure. The presence of H_2O molecules was confirmed by the infrared reflection spectrum of the crystal. For both polarizations the weak peak at about 3580 cm^{-1} was observed. The same peak was found in the infrared spectrum of $(DEPE)_4^{2+}.(TCNQ)_2^{2-}.H_2O$ (Ashwell, 1978).

Electrical conductivity was measured on a single crystal in the temperature range 77–300 K. The temperature dependence of the conductivity has a semiconductor character. The activation energy is isotropic and has the value 0·19 (1) eV. Anisotropic conductivities were measured at room temperature along the c axis by the four-probe method and by the two-probe method in the plane normal to the c axis. The measurements in this plane were made in two perpendicular directions [**a'**] and [**b'**], where [**b'**] is normal to the well developed (010) face of crystal. The observed values of electrical conductivity are: $\sigma_c = 0·180$, $\sigma_{a'} = 0·011$, $\sigma_{b'} = 0·007 \ \Omega^{-1} \text{cm}^{-1}$.

X-ray measurements on Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan technique, $2\theta_{\max} = 50°$, total intensity data were collected up to $\sin\theta/\lambda = 0·595 \text{ Å}^{-1}$. Crystal size $0·1 \times 0·1 \times 0·3$ mm. Unit-cell dimensions were obtained from oscillation photographs and refined by least-squares method using diffractomemeter setting angles of 22 strong reflections with $20 < 2\theta < 30°$. The space group $P\bar{1}$ was chosen on the basis of intensity statistics in the range of indices: $0 \le h \le 10$, $-12 \le k \le 12$, $-10 \le l \le 16$. 2284 reflections measured, 2084 unique, 1928 with $I > 2\sigma(I)$. Three reflections monitored every 50 reflections showed no significant intensity drift. Lorentz–polarization correction, no absorption correction. Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV).

The initial S atomic coordinates were determined from the Patterson maps; C, N and O atoms were located from the successive Fourier syntheses. The positions of H atoms were deduced from the difference Fourier syntheses. Full-matrix least-squares refinement (on F) with anisotropic thermal parameters for non-H atoms and isotropic for H atoms gave $R = 0·039$, $wR = 0·040$, $S = 2·10$, $(\Delta/\sigma)_{\max} = 0·2$. The weighted difference $\sum w(|F_o| - |F_c|)^2$ was minimized, $w = 1/\sigma^2(F_o)$. A final difference map showed no peak or hole more than $0·3 \text{ e Å}^{-3}$. 271 parameters for 45 atoms were refined. All calculations were performed with the XTL program (Usov, Kuzmin, Rozhdestvenskaya & Fundamenskii, 1980).

Table 1. *Final atomic positional and isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$$

|	x	y	z	B_{eq}/B_{iso} (Å²)
MT				
S(1)	0·5929 (1)	0·6309 (1)	0·6049 (1)	4·39 (6)
N(2)	0·8247 (4)	0·5017 (2)	0·7359 (4)	3·9 (2)
N(3)	0·5944 (4)	0·5227 (2)	0·8252 (3)	3·7 (3)
C(4)	0·6739 (5)	0·5445 (3)	0·7342 (4)	2·8 (2)
C(5)	0·3807 (5)	0·6636 (3)	0·6166 (4)	3·7 (2)
H(6)	0·3876 (40)	0·6999 (23)	0·7093 (33)	6·0 (25)
H(7)	0·3407 (39)	0·7071 (23)	0·5511 (33)	8·1 (31)
H(8)	0·2978 (40)	0·6035 (24)	0·6069 (32)	6·6 (26)
H(9)	0·8763 (40)	0·5113 (23)	0·6705 (33)	7·8 (29)
H(10)	0·8874 (39)	0·4583 (23)	0·7992 (32)	9·1 (33)
H(11)	0·6428 (40)	0·4776 (23)	0·8957 (32)	4·9 (23)
H(12)	0·4927 (40)	0·5555 (23)	0·8299 (32)	5·3 (24)
TCNQ(A)				
N(13)	0·0333 (5)	0·3577 (3)	−0·0522 (4)	3·9 (2)
N(14)	0·5186 (5)	0·1877 (3)	0·0444 (4)	4·1 (2)
C(15)	0·0933 (5)	0·0916 (3)	0·0003 (3)	2·3 (2)
C(16)	0·1815 (4)	−0·0044 (3)	0·0275 (4)	2·3 (2)
C(17)	0·0917 (4)	−0·0924 (3)	0·0274 (4)	2·4 (2)
C(18)	0·1861 (5)	0·1828 (3)	−0·0018 (4)	2·4 (2)
C(19)	0·1010 (5)	0·2794 (3)	−0·0291 (4)	2·7 (2)
C(20)	0·3702 (6)	0·1845 (3)	0·0248 (4)	2·9 (2)
H(21)	0·1512 (39)	−0·1568 (23)	0·0415 (32)	2·1 (16)
H(22)	0·3042 (40)	−0·0082 (23)	0·0416 (32)	2·5 (17)
TCNQ(B)				
N(23)	0·6183 (5)	0·2604 (3)	0·7232 (4)	4·0 (2)
N(24)	0·1399 (5)	0·4394 (3)	0·6421 (4)	4·6 (2)
N(25)	−0·4405 (5)	−0·0956 (3)	0·6169 (4)	3·9 (2)
N(26)	0·0341 (4)	−0·2765 (2)	0·7144 (4)	3·7 (2)
C(27)	0·1880 (4)	0·1727 (2)	0·6790 (3)	2·2 (1)
C(28)	0·2718 (4)	0·0737 (3)	0·7024 (4)	2·4 (2)
C(29)	0·1780 (5)	−0·0123 (3)	0·6990 (4)	2·4 (2)
C(30)	−0·0082 (4)	−0·0088 (3)	0·6723 (4)	2·1 (2)
C(31)	−0·0918 (4)	0·0900 (3)	0·6472 (3)	2·3 (2)
C(32)	0·0026 (4)	0·1763 (2)	0·6517 (4)	2·2 (2)
C(33)	0·2844 (5)	0·2616 (3)	0·6807 (4)	2·5 (2)
C(34)	0·4697 (5)	0·2598 (3)	0·7054 (4)	2·8 (2)
C(35)	0·2035 (5)	0·3600 (3)	0·6591 (4)	3·3 (2)
C(36)	−0·0265 (5)	−0·1966 (3)	0·6941 (4)	2·6 (2)
C(37)	−0·2919 (5)	−0·0954 (3)	0·6398 (4)	2·6 (2)
C(38)	−0·1053 (4)	−0·0967 (3)	0·6693 (4)	2·3 (2)
H(39)	0·3967 (40)	0·0694 (23)	0·7174 (32)	1·8 (16)
H(40)	0·2385 (40)	−0·0778 (23)	0·7149 (32)	3·1 (18)
H(41)	−0·2164 (40)	0·0936 (23)	0·6336 (32)	1·1 (14)
H(42)	−0·0543 (40)	0·2464 (23)	0·6416 (32)	3·5 (19)
H₂O				
O(43)	0·3076 (4)	0·6030 (2)	0·9338 (3)	4·5 (2)
H(44)	0·3532 (41)	0·6724 (23)	0·9497 (32)	9·2 (33)
H(45)	0·2129 (40)	0·6142 (23)	0·8722 (32)	12·5 (40)
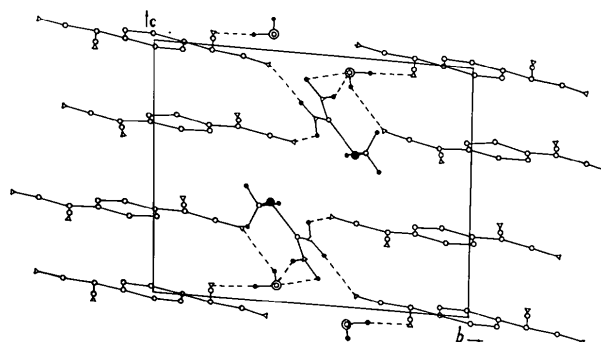
Fig. 1. Projection of the structure onto the (100) plane. The hydrogen bonds are represented by broken lines. Large filled circles: sulfur; double circles: oxygen; open triangles: nitrogen; open circles: carbon; small filled circles: hydrogen.
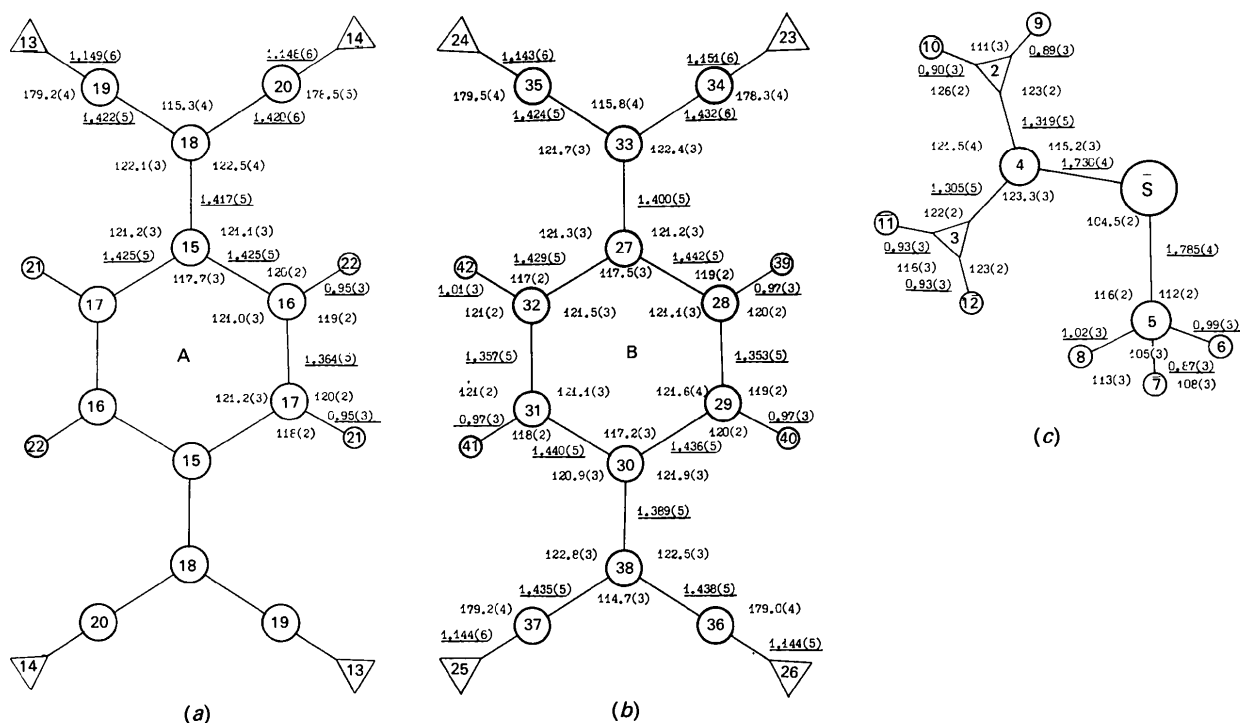
Fig. 2. Bond lengths (Å) and angles (°) in TCNQ(A), TCNQ(B) and the MT cation with e.s.d.'s in parentheses.

Discussion. Atomic positional and isotropic or equivalent thermal parameters are listed in Table 1.* Structure projections onto the (100) plane, interatomic distances and angles for the centrosymmetric TCNQ(A) and non-centrosymmetric TCNQ(B) molecules and MT cation are shown in Figs. 1 and 2. The TCNQ molecules are grouped in trimers in B–A–B succession. The mean interplanar distance between A and B molecules in the trimer is 3·17 Å, the distance between B molecules of two neighbouring trimers is 3·33 Å. The two types of overlapping for neighbouring molecules are shown in Fig. 3. Trimers form infinite stacks along the c axis.

The A molecule is more planar than the B molecule. The largest deviation from the least-squares plane through all non-H atoms is 0·012 (3) for C(15) of A and 0·052 (4) Å for N(23) of B. The MT cation (without H atoms) is not planar, the largest deviation 0·105 (4) Å is observed for the C(5) atom. The dihedral angle between the mean planes through the TCNQ anion and the MT cation is 48·1 for A and 49·4° for B. A comparison with the MT–TCNQ structure (Abashev, Vlasova, Kartenko, Kuzmin, Rozhdestvenskaya, Semkin, Usov & Russkikh, 1987)
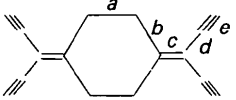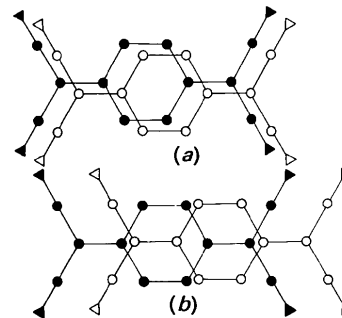
Fig. 3. TCNQ molecular overlap: (a) TCNQ(A)–TCNQ(B) and (b) TCNQ(B)–TCNQ(B).

shows that the new salt exhibits more anion planarity and more turn of the mean cation plane relative to the TCNQ molecule plane.

The bond lengths of molecules A and B are given in Table 2. The evaluation of the charge transfer was based on the correlation between bond distances and ionicity in the TCNQ anion (Flandrois & Chasseau, 1977; Kistenmacher, Emge, Bloch & Cowan, 1982). The calculated charge of the A molecule is $-0·9$ e and that of the B molecule is $-0·4$ e and thus the trimer has a charge $-1·7$ e. Further analysis of the B molecule bond lengths suggests that the charge is distributed asymmetrically and located on the part of TCNQ(B) near the cation. These considerations are supported by spectroscopic data: in the regions that

Table 2. *Comparison of the mean bond lengths* (Å) *in the TCNQ anion, TCNQ⁰ and TCNQ⁻*

	a	b	c	d	$b-c$	$c-d$	α^*	$f\dagger$	k^*
TCNQ (A)	1·364 (4)	1·425 (5)	1·417 (5)	1·421 (5)	0·008	−0·004	0·486	0·4	0·4
TCNQ (B)	1·355 (5)	1·437 (5)	1·395 (5)	1·432 (5)	0·042	−0·037	0·498	0·9	0·9
TCNQ⁰‡	1·344 (3)	1·442 (4)	1·373 (3)	1·435 (4)	0·069	−0·062	0·476	0·0	0·0
TCNQ⁻§	1·363 (5)	1·422 (3)	1·420 (3)	1·417 (3)	0·002	0·003	0·500	1·0	1·0

* Kistenmacher, Emge, Bloch & Cowan (1982).
† Flandrois & Chasseau (1977).
‡ Long, Sparks & Trueblood (1965).
§ Ashwell & Wallwork (1979).

are sensitive to the charge state of the TCNQ molecule (about 2200 and 1382 cm⁻¹) a weak multipletstructure has been observed (Semkin, Vlasova, Kartenko, Priev, Usov, Yartsev, Agroskin, Petrov, Abashev & Russkikh, 1989).

In the MT–TCNQ salt hydrogen bonds join every H atom of cation NH₂ groups with the N atom of anion cyanomethylene groups. In the (MT)₂-(TCNQ)₃.2H₂O salt two H atoms of the cation take part in a hydrogen bond with the O atom of the water molecule. In the centrosymmetric A molecule all N atoms are involved in hydrogen bonds; N(13) with the cation and N(14) with the water molecule (see Table 3). In the non-centrosymmetric B molecule hydrogen bonds are found only for N(24) and N(26) atoms lying on one diagonal of the TCNQ molecule, atom N(26) being connected with an H atom of the water molecule, atom N(24) with an H atom of the cation. The crystallographic arrangement and the interaction between anion, cation and the water molecule, strongly suggest an important role for water molecules in the packing of TCNQ molecules, the water molecule being distorted: the HOH angle is 98 (3)°, two hydrogen bonds are

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

X—H⋯Y	X—H	X—Y	H⋯Y	∠X—H⋯Y	$r_H + r_Y - 0.2^*$
N(2)—H(9)⋯N(24)	0·89 (3)	3·033 (5)	2·39 (3)	151 (3)	2·55
N(2)—H(10)⋯N(13)	0·90 (3)	2·999 (5)	2·10 (3)	180 (3)	2·55
O(43)—H(44)⋯N(14)	0·96 (3)	3·045 (5)	2·10 (3)	168 (3)	2·55
O(43)—H(45)⋯N(26)	0·83 (3)	3·067 (4)	2·32 (3)	150 (3)	2·55
N(3)—H(11)⋯O(43)	0·93 (3)	2·889 (4)	1·98 (3)	164 (3)	2·50
N(3)—H(12)⋯O(43)	0·93 (3)	2·889 (4)	2·11 (3)	153 (3)	2·50

* Hamilton & Ibers (1968) criterion. Van der Waals radii: $r_H = 1·20$, $r_N = 1·55$, $r_O = 1·50$ Å.

0·96 (3) for O(43)—H(44) and 0·83 (3) Å for O(43)—H(45).

Specific distribution of charge in the TCNQ molecules may reduce electron correlations (Semkin, Vlasova, Kartenko, Priev, Usov, Yartsev, Agroskin, Petrov, Abashev & Russkikh, 1989) and this contributes to the high electrical conductivity of the salt. The observation of crystal water molecules in a 2/3 TCNQ salt and the unusual effects on structure and physical properties seems to be unique.

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Structures of 3-Amino-4-nitro-1,2-dihydro-5-pyrazolone and its Acidic Ammonium Salt

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Abstract. $C_3H_4N_4O_3$ (1), $M_r = 144\cdot09$, monoclinic, $P2_1/n$, $a = 5\cdot277$ (1), $b = 8\cdot110$ (2), $c = 12\cdot335$ (1) Å, $\beta = 98\cdot526$ (8)°, $V = 522\cdot1$ (4) Å³, $Z = 4$, $D_m = 1\cdot83$ (1), $D_x = 1\cdot833$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot135$ mm⁻¹, $F(000) = 296$, $T = 295$ K, $R = 0\cdot038$ for 942 unique observed reflections. Acidic ammonium salt of (1): $NH_4^+ .C_3H_3N_4O_3^-$ (2), $M_r = 305\cdot21$, triclinic, $P\bar{1}$, $a = 6\cdot998$ (2), $b = 7\cdot203$ (1), $c = 12\cdot116$ (1) Å, $\alpha = 77\cdot899$ (7), $\beta = 84\cdot05$ (1), $\gamma = 85\cdot75$ (1)°, $V = 593\cdot1$ (6) Å³, $Z = 2$, D_m