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Crystal Structure and Related Physical Properties of $[N,N,N,N',N',N'$-Hexamethylhexamethylenediammonium$]^{2+}$-[Tetracyanoquinodimethane$]_4^{2-}$: as a Two-dimensional Magnetic System

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The crystal structure, electrical conductivity and magnetic properties of (HMHDA)$(TCNQ)_4$ are studied. It appears that this ion-radical salt consists of planar arrays of $(TCNQ)_2^-$ dimers (diads) in weak interaction. The structure may thus be considered as quasi two-dimensional, the magnetic behavior being in line with two-dimensionality.

Organic radical-ion salts and charge transfer complexes, especially those based on tetracyanoquinodimethane (TCNQ), have received considerable attention in recent years.[1] As shown by crystallographic studies these compounds are often formed in linear chains of molecules. Physical properties such as electrical conductivity exhibit a high degree of anisotropy, makes these systems considered as quasi one-dimensional electronic substances.

Some questions have arisen as to the existence of a real electronic one-dimensionality.[2] There is always some interchain coupling whatever the mechanism is, and at 0 K the system must be three-dimensional. Many experimental and theoretical works deal with the cross-over from a one-dimensional behavior to a three-dimensional one, but at the present stage the situation is far from clear.

Our purpose was to investigate the dimensionality effects by synthesizing an homologous series of compounds, in which we would be able to vary the distance between the radical-ion chains. One way to accomplish this could be the use of cations such as polymethylene-diammoniums: $R_3N^+-(CH_2)_n-N^+R_3$. According to the length of the polymethylene chain we could expect a gradual variation of distances between TCNQ stacks. Thus the larger the number of CH_2 groups, the more rigorous should be the one-dimensionality of the electronic or magnetic system.

Hadek *et al.*[3] synthesized a series of TCNQ salts with N,N,N,N',N',N'-hexamethylpolymethylenediammonium cations model compounds for polymeric TCNQ salts. However, only the electrical conductivity was measured on powdered samples. This study incited us to prepare TCNQ salts of cations $(CH_3)_3N^+-(CH_2)_n-N^+(CH_3)_3$ and examine their crystal structure and physical properties on single crystals.

In this paper we will report a detailed study of the salt with $n=6$:

$$[(CH_3)_3N^+-(CH_2)_6-N^+(CH_3)_3](TCNQ)_4^{2-}$$

or (HMHDA)$(TCNQ)_4$. Contrary to our expectation TCNQ molecules in this salt do not crystallize in one-dimensional stacks. Actually the structure consists of diads with two-dimensional magnetic interactions.

Table 1. Crystal data for (HMHDA)$(TCNQ)_4$

$(C_{12}H_{30}N_2)(C_{12}H_4N_4)_4$—Molecular mass = 1016		
Triclinic—Space group $P\bar{1}$		
$a=14.172$ (8) Å	$\alpha=77.67$ (5)°	$V=1371.2$ Å^3
$b=13.487$ (8) Å	$\beta=99.20$ (5)°	$Z=1$
$c=7.785$ (4) Å	$\gamma=75.51$ (5)°	$D_c=1.304$ g·cm^{-3}
$F(000)=530$	Cu $K\alpha$($\lambda=1.5418$ Å)	$\mu=6.33$ cm^{-1}

Experimental

Preparation of (HMHDA)$(TCNQ)_4$. To a hot methanol solution (40 ml) of Li-TCNQ (420 mg) was added a hot methanol solution (20 ml) of N,N,N,N',N',N'-hexamethylhexamethylenediammonium diiodide (460 mg). The solution was allowed to cool slowly down to room temperature. The resulting complex (700 mg) was collected and washed with water, methanol and ether. A deep blue crystalline product of (HMHDA)$(TCNQ)_2$ was obtained.

To a hot acetonitrile solution (40 ml) of (HMHDA)$(TCNQ)_2$ obtained as above was added a solution (40 ml) of neutral TCNQ (408 mg) in acetonitrile heated at the same temperature. After being cooled down to room temperature the crystalline precipitate (600—700 mg) was filtered and washed successively with acetonitrile and ether.

The stoichiometry of the complexes was checked by electronic absorption spectroscopy with a Cary spectrophotometer, using acetonitrile as a solvent.

Crystal Data. The space group and unit cell dimensions were obtained initially from oscillation and Weissenberg photographs by using Cu $K\alpha$ radiation. The cell constants were subsequently refined on a Siemens computer-controlled three-circle diffractometer. Intensity data of 4763 independent reflexions were collected on this diffractometer from a crystal of dimensions $0.1\times0.22\times0.35$ mm with a $\theta/2\theta$ scan, a scintillation counter and Cu $K\alpha$ radiation; 2793 reflexions are significantly above zero. The c direction is the growth

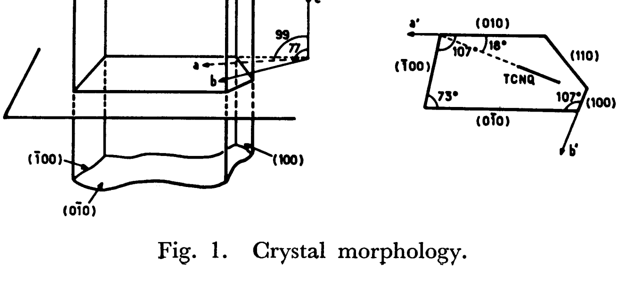
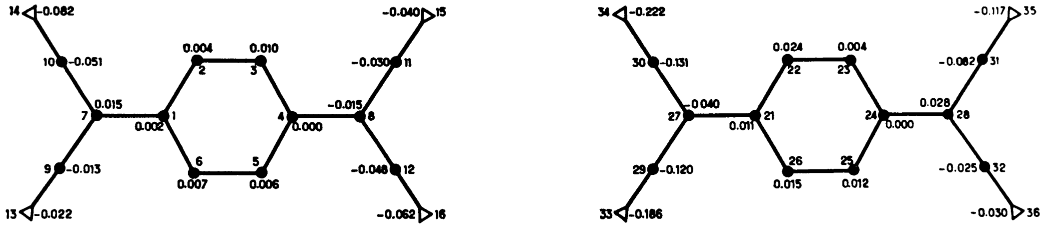


Fig. 1. Crystal morphology.



$0.2115x+0.9458y-0.2463z=1.6033$
TCNQ A

$0.2061x+0.9486y-0.2402z=8.2296$
TCNQ B

Fig. 2. Details of molecular planes and equations to the planes.

Table 2. Final positional and thermal parameters for non-hydrogen atoms
(The figures in parentheses indicate standard deviations.)

	x	y	z	$B/\text{Å}^2$
C (1)	0.0736 (3)	0.1081 (3)	0.1639 (5)	3.7
C (2)	0.0693 (3)	0.1114 (3)	0.3453 (5)	4.0
C (3)	−0.0188 (3)	0.1327 (3)	0.3967 (5)	4.1
C (4)	−0.1117 (3)	0.1517 (3)	0.2708 (5)	3.6
C (5)	−0.1070 (3)	0.1489 (3)	0.0890 (5)	3.8
C (6)	−0.0189 (3)	0.1281 (3)	0.0385 (5)	3.7
C (7)	0.1651 (3)	0.0852 (3)	0.1129 (6)	4.2
C (8)	−0.2024 (3)	0.1720 (3)	0.3230 (5)	4.0
C (9)	0.1714 (3)	0.0815 (3)	−0.0667 (6)	4.1
C (10)	0.2559 (3)	0.0631 (4)	0.2406 (6)	4.6
C (11)	−0.2082 (3)	0.1745 (4)	0.5036 (6)	4.9
C (12)	−0.2940 (3)	0.1889 (4)	0.2016 (6)	4.9
N (13)	0.1754 (3)	0.0783 (4)	−0.2115 (6)	6.1
N (14)	0.3285 (3)	0.0455 (4)	0.3463 (6)	6.3
N (15)	−0.2132 (3)	0.1765 (4)	0.6485 (5)	6.3
N (16)	−0.3685 (3)	0.2034 (4)	0.1029 (6)	6.9
C (21)	0.1748 (3)	0.5907 (3)	−0.0094 (5)	3.8
C (22)	0.1740 (3)	0.5933 (3)	0.1728 (5)	4.0
C (23)	0.0875 (3)	0.6117 (3)	0.2287 (5)	4.1
C (24)	−0.0066 (3)	0.6313 (3)	0.1088 (5)	3.9
C (25)	−0.0058 (3)	0.6306 (3)	−0.0746 (5)	3.9
C (26)	0.0810 (3)	0.6111 (3)	−0.1310 (5)	3.8
C (27)	0.2647 (3)	0.5663 (3)	−0.0653 (6)	4.1
C (28)	−0.0952 (3)	0.6493 (3)	0.1692 (5)	4.1
C (29)	0.2683 (3)	0.5581 (4)	−0.2441 (6)	4.6
C (30)	0.3582 (3)	0.5394 (4)	0.0596 (6)	4.9
C (31)	−0.0964 (3)	0.6472 (4)	0.3528 (6)	5.2
C (32)	−0.1907 (3)	0.6701 (4)	0.0536 (6)	4.4
N (33)	0.2705 (4)	0.5513 (4)	−0.3860 (6)	6.4
N (34)	0.4325 (3)	0.5167 (4)	0.1620 (6)	6.7
N (35)	−0.0974 (3)	0.6458 (4)	0.4987 (6)	7.0
N (36)	−0.2681 (3)	0.6862 (4)	−0.0352 (6)	6.2
C (41)	0.5038 (6)	0.3337 (6)	−0.0403 (1)	8.6
C (42)	0.4876 (5)	0.2096 (6)	−0.5829 (8)	7.3
C (43)	0.3445 (4)	0.3098 (5)	−0.5133 (8)	6.7
C (44)	0.4775 (5)	0.1747 (6)	−0.0262 (1)	8.4
C (45)	0.4286 (6)	0.1028 (7)	−0.0233 (1)	9.3
C (46)	0.4492 (4)	0.0294 (6)	−0.0361 (8)	7.1
N (47)	0.4524 (3)	0.2561 (3)	−0.4413 (5)	5.0

Table 3. Final positional and thermal parameters for hydrogen atoms
(The figures in parentheses indicate standard deviations.)

	x	y	z	$B/\text{Å}^2$
H (17)	0.133 (3)	0.098 (3)	0.438 (5)	4.0
H (18)	−0.021 (3)	0.135 (3)	0.526 (5)	4.0
H (19)	−0.168 (3)	0.159 (3)	−0.002 (5)	4.0
H (20)	−0.019 (3)	0.128 (3)	−0.087 (5)	4.0
H (37)	0.239 (3)	0.580 (3)	0.259 (5)	4.0
H (38)	0.089 (3)	0.610 (3)	0.358 (5)	4.0
H (39)	−0.070 (3)	0.645 (3)	−0.162 (5)	4.0
H (40)	0.080 (3)	0.611 (3)	−0.256 (5)	4.0
H (54)	0.547 (4)	0.156 (4)	−0.214 (7)	8.5
H (64)	0.452 (4)	0.232 (4)	−0.165 (7)	8.5
H (55)	0.354 (4)	0.132 (4)	−0.266 (7)	9.0
H (65)	0.453 (4)	0.053 (4)	−0.300 (7)	9.0
H (56)	0.432 (4)	0.076 (4)	0.051 (7)	7.0
H (66)	0.407 (4)	−0.020 (4)	−0.028 (7)	7.0
H (71)	0.563 (4)	0.299 (4)	−0.428 (7)	8.6
H (81)	0.474 (4)	0.408 (4)	−0.483 (7)	8.6
H (91)	0.515 (4)	0.338 (4)	−0.272 (7)	8.6
H (73)	0.332 (4)	0.380 (4)	−0.612 (7)	6.7
H (83)	0.312 (4)	0.263 (4)	−0.574 (7)	6.7
H (93)	0.310 (4)	0.327 (4)	−0.418 (7)	6.7
H (72)	0.547 (4)	0.160 (4)	−0.514 (7)	7.5
H (82)	0.441 (4)	0.175 (4)	−0.640 (7)	7.5
H (92)	0.501 (4)	0.263 (4)	−0.682 (7)	7.5

direction of the crystals; the a and b directions, which belong respectively to the large and small lateral faces of the crystal, are tilted from the plane perpendicular to the c direction (Fig. 1).

Structure Determination. The structure was solved from a three dimensional Patterson synthesis and refined by block diagonal least squares. Refinement of the positional and isotropic thermal parameters of the 39 non-hydrogen atoms gave the residual $R=0.15$.

Positional parameters of the 23 hydrogen atoms were found on the difference Fourier synthesis. Further refinement of the non-hydrogen and hydrogen atoms with the aid of anisotropic and isotropic thermal parameters respectively gave a final value of 0.07 for R. The following weighting scheme was used

$$\sqrt{\omega} = 1 \qquad \text{if } |P_0| < P_1$$

$$\sqrt{\omega} = \frac{P_1}{P_0} \qquad \text{if } |P_0| > P_1$$

where $P_1=40$,

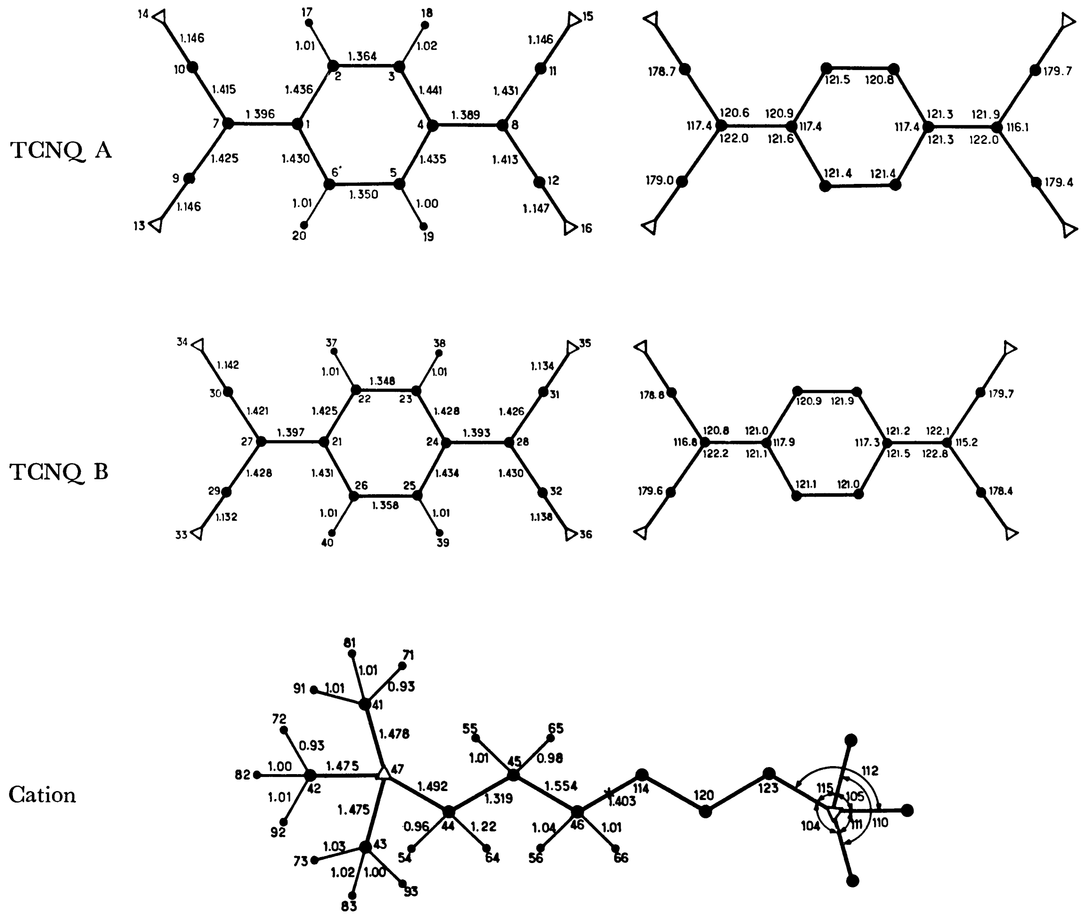


Fig. 3. Bond lengths (Å) and angles of TCNQ (A), TCNQ (B) and the cation.

The final positional and thermal parameters, together with their standard deviations, are listed in Tables 2 and 3.

Least squares planes were calculated through each quinonoid ring of the TCNQ molecules;** the distances of the atoms from these planes are shown in Fig. 2.

Electrical and Magnetic Measurements. The d.c. conductivities of single crystals (typical dimensions: $2 \times 0.2 \times 0.05$ mm) were determined by using a classical four-electrode technique. The electrical contacts were made with silver wires and silver paint.

Magnetic susceptibilities were obtained on microcrystalline samples by using Faraday's method in the temperature range 2.5—362 K. The core diamagnetism (-5.7×10^{-4} emu/mol) was calculated from Pascal's constants and from the value measured for TCNQ molecule.[4)]

EPR measurements were carried out on single crystals with a Varian X-band spectrometer equipped with thermal variation accessories.

Results

Molecular and Crystal Structure. The dimensions of the two crystallographically independent types of TCNQ moiety are shown in Fig. 3. The average bond lengths of molecules A and B are nearly equal within experimental error, the differences between the averaged lengths of chemically equivalent bonds not exceeding 0.01 Å. The electronic charge of each TCNQ, calculated by the method developed by Flandrois and Chasseau,[5)] is 0.46 electron and 0.50 electron for A and B, respectively. The negative charge is thus delocalized, leaving a half negative charge on each TCNQ molecule.

TCNQ A: The carbon atoms of the quinonoid ring are nearly in the same plane, the C–(CN)$_2$ groups being out of this plane and on the same side (Fig. 2). The dihedral angles between the plane of the quinonoid ring and the planes of the C(7)–(CN)$_2$ and C(8)–(CN)$_2$ groups are respectively 1.8° and 1.6°. The twist angles of the cyanomethylene groups around the C(1)–C(7) and C(4)–C(8) bonds are respectively 0.8° and 0.3°.

TCNQ B: The carbon atoms of the quinonoid ring are in the same plane : the C–(CN)$_2$ groups are clearly out of this plane, particularly the C(27)–(CN)$_2$ group, and on the same side. The dihedral angles between the plane of the quinonoid ring and the planes of the C(27)–(CN)$_2$ and C(28)–(CN)$_2$ groups are respectively 7.1° and 2.2°. The twist angles of the cyanomethylene groups around the C(21)–C(27) and C(24)–C(28) bonds are respectively 0.5° and 1.2°.

In each TCNQ, both –C(CN)$_2$ groups lie entirely on the same side of the quinonoid skeleton of the TCNQ molecule, so that the molecule has the shape of a shallow boat. In TCNQ B, the stronger deformation may be explained by a very short intermolecular distance

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** XYZ are orthogonal atomic coordinates in Å where X is along a, Y in the (ab) plane orthogonal to a and Z orthogonal to the (XY) plane.

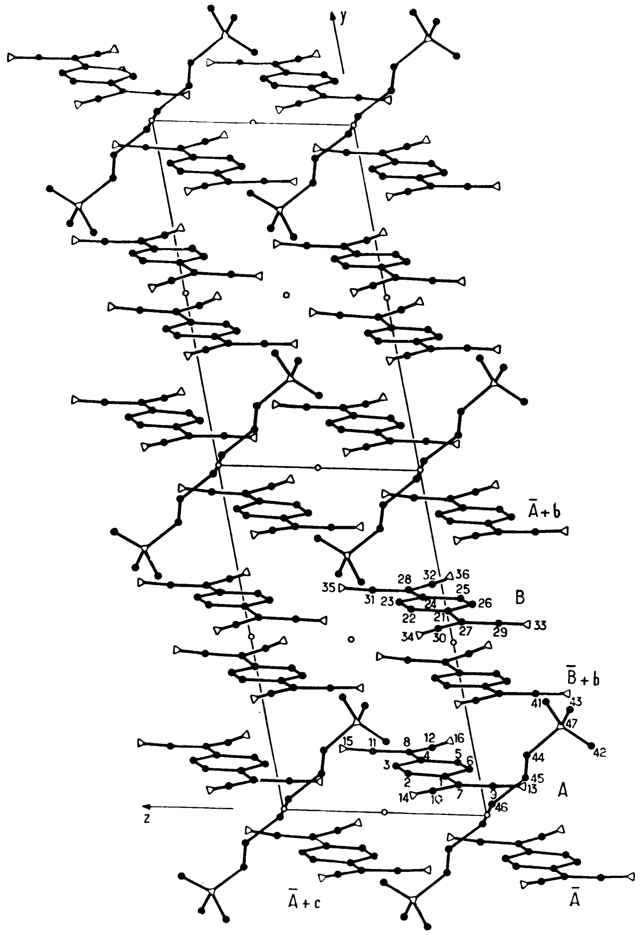

Fig. 4a. Projection of the crystal structure along the a axis.

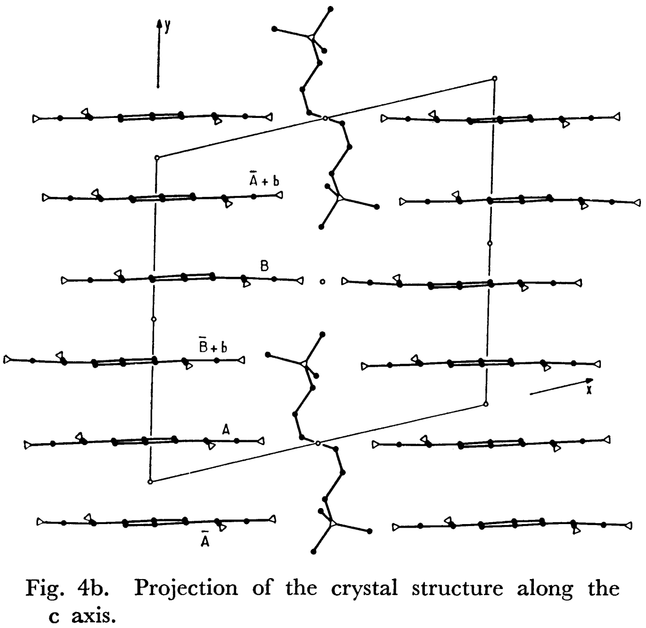

Fig. 4b. Projection of the crystal structure along the c axis.

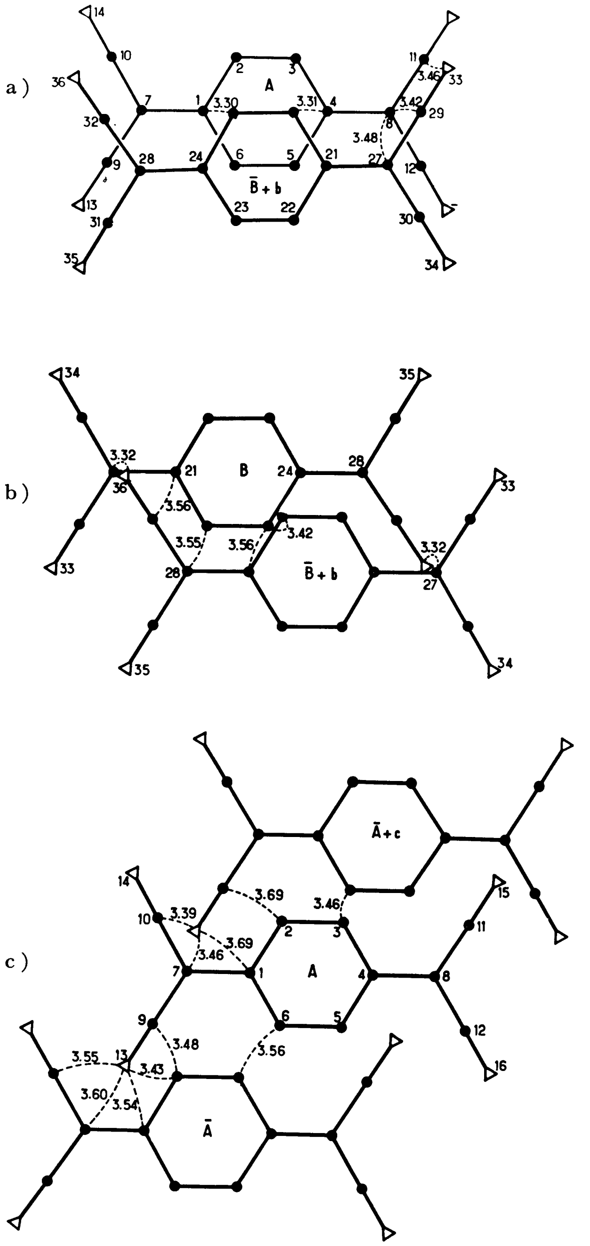

Fig. 5. Projection along the normal to the quinonoid ring of TCNQ molecules: a) B̄+b on A; b) B̄+b on B; c) Ā and Ā+c on A. Some short distances between atoms of neighboring molecules are given.

between the N(34) atom and the C(41) atom of a cation methyl group (C–N=3.21 Å).

These results also confirm the general correlation found between the rotation of the $C(CN)_2$ groups and the length of the C–C bond adjacent to the quinonoid ring:[5] if this bond is shorter than 1.41 Å as in the present case the rotation is sligth, always less than 2°.

In the methylene chain, we found unusual and anomalous bond lengths (Fig. 3); the very short distance (1.32 Å) between the C(44) and C(45) atoms does not characterize a localized double bond; in the same way, the distance 1.40 Å of C(46)–C(46), cannot be a conjugated bond. Disorder, suggested by the high values of the temperature factors, may be a good explanation of these anomalous results. For the sake of comparison, the C–C bond lengths are 1.48, 1.56, and 1.48 Å in *N,N,N,N′,N′,N′*-hexamethylhexamethylenediammonium dibromide[6] and 1.53, 1.55, and 1.50 Å in *N,N,N,N′,N′,N′*-hexamethylhexamethylenediammonium dichloride dihydrate.[7)]

Figures 4a and 4b show a general view of the crystal structure projected respectively along the a and c axes. The unit cell contains one cation and four roughly parallel TCNQ molecules, A, $\overline{B}$, B, $\overline{A}$,*** with two crystallographically independent molecules; the dihedral angle between the planes of the molecules A and B is 0.6°.

Cations, centered at 1/2, 0, 0 alternate in the a direction with the TCNQ groups; these groups make an angle of 56° with the best plane through the hexamethylene chain and an angle of 38° with the N(47)–$\overline{N}$(47) direction.

A good insight of the molecular arrangement is given by the projection of TCNQ moieties along the normal to the quinonoid ring (Fig. 5). This figure gives evidence for the pairing in (A, $\overline{B}$+b) diads. Within the (A, $\overline{B}$+b) dimer, the mode of overlap looks like those found, for example, in morpholinium–TCNQ salts:[8,9)] the double bond of the quinonoid ring of one molecule is placed above the ring of the second one. The interplanar distance is 3.22 Å.

Between dimers there is only very weak overlap. The centrosymmetric pair of molecules B and $\overline{B}$+b has an interplanar separation of 3.38 Å. Only two short intermolecular contacts exist:

$$C_{25}(B) - C_{25}(\overline{B}+b) = 3.42\ \text{Å}$$

$$N_{36}(B) - C_{27}(\overline{B}+b) = 3.32\ \text{Å}$$

Between molecules A and $\overline{A}$, related by the symmetry operation −x, −y, −z, there is no real overlap, but the interplanar spacing is short (3.22 Å). Two short intermolecular contacts of 3.48 Å and 3.56 Å exist between C(9, A)–C(2, $\overline{A}$) and C(6, A)–C(3, $\overline{A}$) respectively. Similarly the $\overline{A}$+c molecule, related to A by the symmetry operation −x, −y, −z+1, has a short contact of 3.46 Å between the C(6, $\overline{A}$+c) and C(3, A) atoms, the interplanar spacing A—$\overline{A}$+c being 3.38 Å.

Thus the lattice appears to be constituted of diads in weak interaction in a plane parallel to the (b c) plane. Each diad D_1=(A, $\overline{B}$+b) is surrounded by five other diads in this plane: D_2=($\overline{A}$, B−b), D_3=($\overline{A}$+c, B−b+c), D_4=($\overline{A}$+b, B), D_5=(A+c, $\overline{B}$+b+c) and D_6=(A−c, $\overline{B}$+b−c),†† the distances between the centres of gravity of these diads being respectively D_1–D_2=7.44 Å, D_1–D_3=7.95 Å, D_1–D_4=7.17 Å, D_1–D_5=7.78 Å=D_1–D_6.

The planes containing these arrays of diads are separated by sheets of *N,N,N,N′,N′,N′*-hexamethylhexamethylenediammonium cations, giving rise to a quasi two-dimensional molecular lattice.

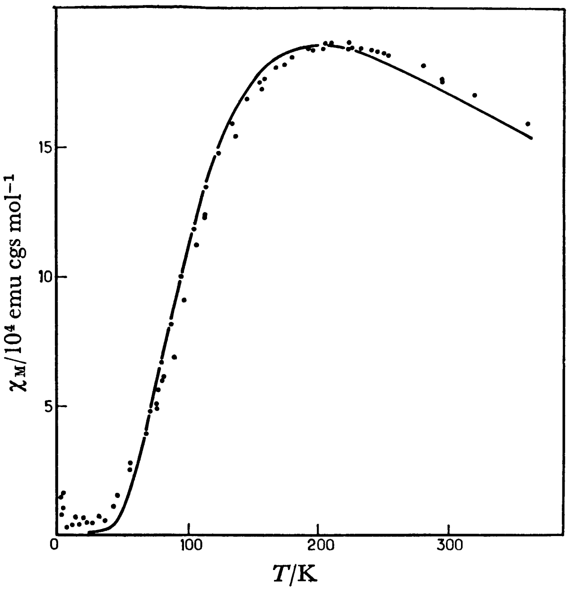

Fig. 6. Temperature dependence of paramagnetic susceptibility. The continuous line is a singlet-triplet fitting with J=0.028 eV.

In this way, (HMHDA) (TCNQ)$_4$ differs from most other radical anion salts in which the TCNQ molecules occur in continuous columns within which there is closer molecular contact than between adjacent columns. Nevertheless a structure exhibiting similar features has already been observed in some other 1:4 TCNQ salts such as *N,N′*-Diethyl-4,4′-bipyridinium–(TCNQ)$_4$.[10)]

Electrical Conductivity. The conductivity at 300 K along the long crystal axis (c axis, Fig. 1) is *ca.* 4× 10^{-3} (Ω cm)$^{-1}$. The radical-anion salt behaves as a typical semiconductor in the range 150—330 K, with an exponential dependence of conductivity on temperature obeying the equation: $\sigma=\sigma_0 \exp(-E_a/kT)$, with a continuous dependence of E on temperature from 0.15 eV at *ca.* 150 K to 0.30 eV near room temperature.

Magnetic Properties. The temperature dependence of paramagnetic susceptibility is shown in Fig. 6 after substracting the diamagnetic part from the measured susceptibility. The curve exhibits a maximum at *ca.* 210 K. Below this temperature the susceptibility decreases to zero, although a slight increase appears at very low temperatures (T>10 K). The behavior is typical for semiconducting TCNQ salts [10)] and may be interpreted in terms of an excited triplet state lying above the singlet diamagnetic ground state. The χ upright at low temperatures is probably due to impurities or lattice defects and corresponds to *ca.* 0.1% of the spins giving a slight Curie contribution.

For a compound with two electrons per mole, the susceptibility due to an excited triplet state is given by

$$\chi_M = 2Ng^2\mu_B^2/[kT(3+\exp(J/kT))] \qquad (1)$$

where J is the energetic singlet-triplet separation, μ_B the Bohr magneton, g the g-factor, N the Avogadro number and k the Boltzmann constant.

The paramagnetic susceptibility of (HMHDA)-(TCNQ)$_4$ can be fitted by this expression within a

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*** $\overline{A}$ and $\overline{B}$ are related to A and B respectively by the symmetry operation −x, −y, −z.

††

A, B	x,	y,	z	$\overline{B}$+b	−x,	−y+1,	−z
$\overline{A}$, $\overline{B}$	−x,	−y,	−z	$\overline{A}$+c	−x,	−y,	−z+1
A+c	x,	y,	z−1	B−b+c	x,	−y+1,	−z
A−c	x,	y,	z−1	B−b+c	x,	y−1,	z+1
B−b	x,	y−1,	z	$\overline{B}$+b−c	−x,	−y+1,	−z−1

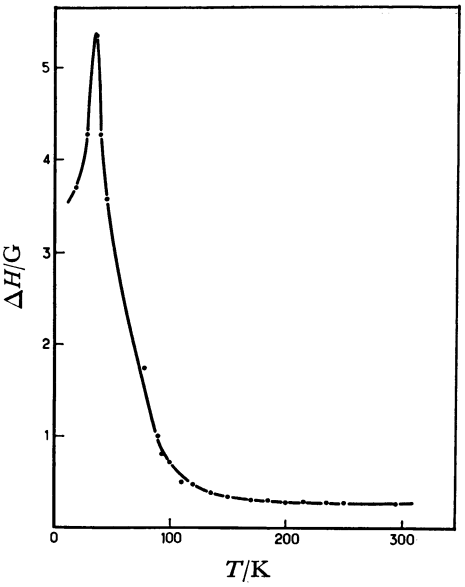

Fig. 7. Temperature dependence of EPR linewidth for the orientation of single crystal giving the largest variation with temperature.

good approximation (Fig. 6); the continuous line corresponds to a J-value of 0.028 eV.

The triplet character of the paramagnetic excitation is generally evidenced by a splitting of EPR spectra, caused by the dipole-dipole interaction of the electrons in the triplet state: [11] at high temperatures EPR spectra show an exchange-narrowed single line, but as the temperature is lowered the line broadens until finally it splits into a doublet. Actually no fine structure splitting could be detected in (HMHDA)(TCNQ)$_4$. The spectra showed a single line at all temperatures, although a rapid increase of linewidth was observed for some crystal orientations, when the temperature was lowered below 100 K (Fig. 7). The sharp maximum between 30 and 40 K reflects the disappearance of the activated part of the susceptibility and the prominence of the Curie contribution.

The linewidth exhibited a temperature dependent anisotropy. The variations shown in Fig. 8 correspond to rotations of the crystal around the c axis. When $\theta=0$ the magnetic field is along b′ axis (Fig. 1). Similar results were obtained at Q-band with a Varian spectrometer: the linewidth behavior is thus field independent. Figure 8 shows that the results can be fitted with the empirical expression:

$$\Delta H = a + b(3\cos^2\theta - 1) + c(3\cos^2\theta - 1)^2 \tag{2}$$

where a, b, and c are temperature-dependent parameters.

Discussion

Electrical Conductivity and Structure. Since the structure is two-dimensional the electrical conductivity should be isotropic in the corresponding plane. However, because of the smallness of crystals it was impossible to measure the conductivity along the b′-direction (Fig. 1).

The value of σ at room temperature along the c axis is very close to that of TCNQ salts of 1:4 stoichiometry with similar crystal structures.[10] This value is surprisingly high in comparison with other diadic compounds having a very weak overlap between the diads.

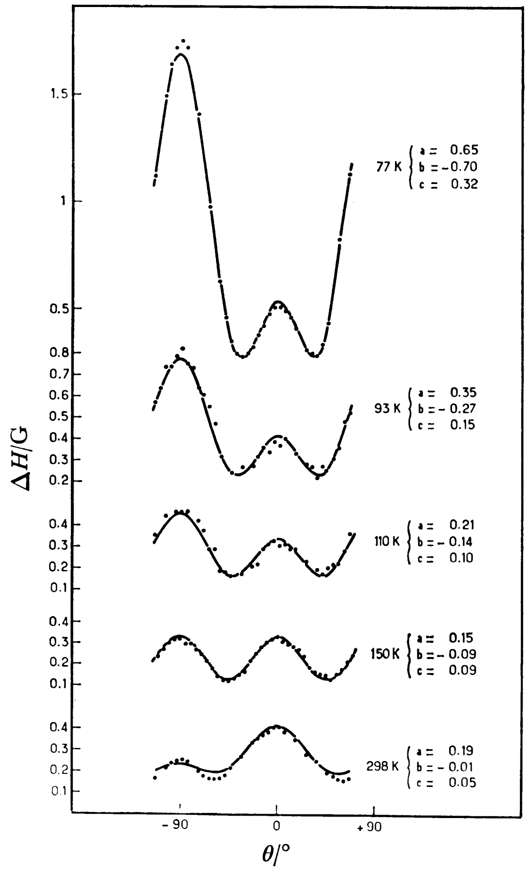

Fig. 8. Angular variation of the EPR linewidth at different temperatures for a single crystal. The rotation axis is the c axis. The parameters a, b, and c are in: $\Delta H = a + b(3\cos^2\theta - 1) + c(3\cos^2\theta - 1)^2$.

From a systematic examination of conductivities and structural data[12] it appears that the electrical conductivity depends on the plane-to-plane distances of TCNQ molecules, their types of overlap and the electronic charge distribution between TCNQ molecules (for a number of electrons smaller than the number of TCNQ molecules). A non-uniform distribution indicates that some charge localization occurs, leading to a smaller conductivity. In (HMHDA)(TCNQ)$_4$ the charge seems to be distributed uniformly, each TCNQ bearing a half electronic charge. The apparent delocalization compensates for the poor molecular overlaps and some rather large distances (3.38 Å) (Fig. 4), giving rise to a conductivity value better than expected.

Magnetic Properties and Structure. *Thermal Variation of* χ_p: A singlet-triplet behavior of χ_p is generally found for TCNQ salts in which each spin interacts strongly with only one adjacent spin. This occurs when TCNQ molecules form alternating stacks, composed of diads, triads or tetrads. The triplet character of the magnetic excitations is well understood[11] and clearly indicated experimentally by the dipolar splitting observed in EPR spectra at low excitation concentration.

Another class of radical-anion salts and charge transfer complexes is known to crystallize in regular stacks with equal exchange interaction between neighbors along a given stack. In some of them an activated paramagnetic susceptibility $\chi_p \alpha T^{-1} \exp(-\Delta E_p/kT)$ has been found. To our knowledge only charge transfer complexes with mixed stacks (···AD AD···) are concerned, such as TMPD–chloranil,[13] PD–chloranil[14] or TMPD–TCNQ.[15] No satisfactory explanation has been given concerning the origin of ΔE_p, but experimental results are interpreted by assuming a Wannier spin exciton model[16] where spin excitations are spatially uncorrelated.

At first view (HMHDA)(TCNQ)$_4$ seems to belong to none of the above classes. The lattice appears to be constituted of diads in weak interaction inside a plane. Moreover each diad bears an $S=1/2$ spin which is equally distributed on the two TCNQ molecules. So the spins appear to be delocalized on diads, the closest contacts of which are nearly van der Waals distances (3.42 Å to 3.51 Å). However, careful examination of the structure for C–C distances shows that there are more numerous close contacts between B molecules of two successive diads than between A molecules. So a slight tendency to the formation of tetrads AB BA is observed. If we calculate the zero-field parameter D for this arrangement from the approximately known spin-density distribution,[17] we get a value of several gauss. The value is small, but a splitting should be observed on the EPR spectra, which is not realized and thus seems to confirm the magnetic two-dimensionality of this system.

Angular Dependence of EPR Linewidth: The angular dependence of EPR linewidth shown in Fig. 8 is unusual. However, several similar features have been found for some TCNQ salts[18,19] and for charge transfer complexes of TMPD with TCNQ[15] and chloranil.[20] Two explanations have been proposed.

It has been shown that the angular variation, $\Delta H(\theta)$, of EPR linewidth in two-dimensional magnetic systems such as K_2MnF_4[21] or $(C_2H_{10}N_2)$ $(MnCl_4)$[22] is approximately described by an expression of the form $\Delta H(\theta)=A+B(3\cos^2\theta-1)^2$, where θ is the angle between the applied magnetic field and the normal to the plane of the two-dimensional magnetic systems. For several TCNQ salts Takagi and Kawabe[18,19] fitted their results with the empirical relation:

$$\Delta H(\theta) = \alpha(3\cos^2\theta-1)^2 + \beta\sin^4\theta \qquad (3)$$

In spite of the lack of detailed structural information they inferred that the TCNQ salts studied are two-dimensional.

On the other hand, Soos and coworkers[20] showed that the linewidth anisotropy of TMPD–chloranil for which the one-dimensionality is firmly established was accurately reproduced by the secular part of the electron dipolar interaction. The angular dependence could be expected for spatially uncorrelated spin excitations.

Both explanations could be convenient for (HMHDA)(TCNQ)$_4$. From the crystal stucture data it looks like a nearly two-dimensional magnetic system. However, it is quite certain that the angular dependence of linewidth could be fitted by the angular dependence in the second moment of the secular part of the electron dipolar interaction, if the spin-densities distributions were accurately known, which is not the case.[20] The thermal variation of the angular dependence of linewidth could reflect either a change of spin distribution with temperature or a continuous thermal modification of the lattice, or, more probably, both together.

Contrary to the recent assertion of Takagi and Kawabe,[23] the temperature dependence of the linewidth does not seem to be related to the structural symmetry of the cation. From the study of several TCNQ salts with cyanine dyes as cations they deduced that for symmetrical cations the linewidth decreases when the temperature is lowered, while it increases for salts with unsymmetrical cations. Actually HMHDA is structurally symmetrical and the linewidth increases sharply with decreasing temperature (Fig. 7). Thus the behavior of ESR linewidths is not well understood, for both semiconducting salts as well as conducting ones.[24]

g*-Tensor Anisotropy**: Since two-dimensionality could not be evidenced by electrical measurements for experimental reasons, we thought that it could be reflected by the ***g-tensor anisotropy. Actually the results show that the principal axis directions correspond to the molecular symmetry axes and not to the crystal axes.

The *g*-value perpendicular to the TCNQ molecular plane is found to be $g_{zz}=2.0021\pm0.0003$, the *g*-value along the in-plane molecular long axis is $g_{yy}=2.0028\pm0.0003$ and the third value $g_{xx}=2.0033\pm0.0003$. The average of this tensor: $\bar{g}\simeq 1/3\ (g_{xx}+g_{yy}+g_{zz})=2.0027\pm0.0003$ corresponds closely to the isotropic *g*-value of TCNQ anions in solution: 2.00263 ± 0.00005.[25]

Conclusion

From structural data it appears that (HMHDA)(TCNQ)$_4$ consists of planar arrays of $(TCNQ)_2^-$ dimers (diads) in weak interaction. Thus the structure may be considered as quasi two-dimensional, unlike most other TCNQ compounds for which a quasi one-dimensionality is generally assumed and sometimes established. The magnetic properties are in line with the two-dimensionality, although the linewidth behavior could be interpreted differently.

The study of this compound is interesting from another point of view. We recently obtained [26] a TCNQ salt with a parent cation: *N*,*N*,*N'*,*N'*-tetramethylhexamethylenediammonium (TMHDA). The salt, the stoichiometric formula of which is: (TMHDA)(TCNQ)$_2$(I)$_2$, has a metallic behavior above 120 K and contains iodine chains, although the method of preparation is the same. The reason why iodine is retained in the structure is not clear. The only difference with HMHDA is the substitution of two CH_3 groups by hydrogen atoms. A structural comparison between these compounds will be very useful. The study is in process.

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