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# Neutron Structure at 40 K of an Organic Semiconductor, the Ion Radical Salt of Triethylammonium with 7,7,8,8-Tetracyano-p-quinodimethane: TEA+.(TCNQ)2-

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## Abstract

The TEA+.(TCNQ)2- structure at 40 K has been determined from neutron diffraction measurements on single crystals. The cell is triclinic, space group $P\bar{1}$, with $a = 14 \cdot 215$ (6), $b = 7 \cdot 826$ (3), $c = 13 \cdot 192$ (3) Å, $\alpha = 69 \cdot 67$ (3), $\beta = 84 \cdot 11$ (3), $\gamma = 73 \cdot 66$ (3)°, $Z = 2$. The refinement gave a final $R$ of 0·08 for 4054 observed reflections. The 40 K structure is not very different from the 300 K structure, but at the low temperature the twofold disorder of the cation could be resolved: the TEA cation is disordered over two equi-populated positions and each of these counter ions shares a hydrogen bond with either TCNQ($A$) or TCNQ($B$). Interplanar distances between TCNQ are: $AA' = 3 \cdot 13$, $BB' = 3 \cdot 26$, $AB = 3 \cdot 11$ Å. The charge transfer, estimated from the bond lengths, is about 0·5 e for both TCNQ anions.

## Introduction

Several of the best one-dimensional organic metals known belong to the large family of tetracyanoquinodimethane (TCNQ) salts and charge-transfer complexes, which are therefore of considerable interest.

Although the more conductive salts have been the most extensively investigated, the ion radical salt of triethylammonium (TEA) and TCNQ with stoichiometry TEA+.(TCNQ)2-, which is a good semiconductor ($\sigma_{300\,K} = 570\ \Omega^{-1}\ m^{-1}$), has also been the subject of detailed studies. A reason for this is that large single crystals of TEA+.(TCNQ)2- may be grown rather easily, which is not often the case for metallic salts.

Physical properties, measured over a wide temperature range on powder samples of TEA+.(TCNQ)2-, have been reported: electric con-

ductivity (Siemons, Bierstedt & Kepler, 1963; Néel & Dupuis, 1972), magnetic susceptibility (Kepler, 1963; Flandrois, Dupuis, Delhaes, Amiell & Néel, 1972), and specific heat (Delhaes, Keryer, Flandrois & Manceau, 1977).

More detailed experiments on single crystals have been reported: electrical conductivity at 300 K (Néel & Dupuis, 1972), and in the range 77 to 335 K (Farges, Brau & Gutmann, 1972; Brau & Farges, 1972), Hall effect in the range 293 to 353 K (Farges, Brau, Vasilescu, Dupuis & Néel, 1970), evidence from EPR spectroscopy of a triplet exciton between 40 and 90 K (Flandrois, Amiell, Carmona & Delhaes, 1975).

The room-temperature structure of $TEA^+ . (TCNQ)_2^-$ was first described by Kobayashi, Ohashi, Marumo & Saito (1970) and redetermined by Jaud, Chasseau, Gaultier & Hauw (1974).* No structural data at other temperatures were available until now† to enable better understanding of the temperature dependence of the electron transport properties of $TEA^+ . (TCNQ)_2^-$. In fact, the transfer integrals are directly related to the TCNQ interplanar spacing and overlap, the temperature dependence of which is not directly predictable. The cation–anion and the inter-chain coupling may also exhibit substantial changes with temperature.

The work reported here is the first part of a study of the structure of $TEA^+ . (TCNQ)_2^-$ in the range 40 to 360 K by X-ray and neutron diffraction. Preliminary results have been reported (Filhol, Chasseau, Gaultier & Hauw, 1977).

## Experimental

Large single crystals of $TEA^+ . (TCNQ)_2^-$ were grown by cooling a saturated solution in acetonitrile. The crystals obtained were 1 mm thick platelets which were then cut to suitable size.

Neutron diffraction measurements were carried out on the D10 four-circle diffractometer located at a thermal neutron guide tube of the high-flux reactor of the Institut Laue–Langevin at Grenoble.‡ Low temperatures were obtained by a continuous-flow liquid-helium cryostat (Claudet, Tippe & Yelon, 1976) which had a temperature stability of better than 0·5 K.

Intensities were recorded by means of $\omega$ scans of 41 steps.

In a first experiment a sample of volume 8·5 mm³ was used to collect data within the range $0 < \sin \theta/\lambda < 0·53$ Å⁻¹. The neutron beam had a wavelength of 1·452 Å [flat Cu(111) monochromator in reflection] with a flux at the sample of about $10^{10}$ n m⁻² s⁻¹ and negligible $\lambda/2$ component. The crystal showed natural faces $(100)(\bar{1}00)(100)(\bar{1}00)(\bar{1}0\bar{1})(\bar{1}0\bar{1})$, and the cut face was approximately (120). The crystal was broken during heating to room temperature at the end of the experiment.

A platelet sample of volume 11·5 mm³ was used in a second experiment to collect data within the range $0·53 < \sin \theta/\lambda < 0·65$ Å⁻¹. This crystal showed natural faces $(100)(\bar{1}00)(010)(0\bar{1}0)(110)(001)$ and the cut face was approximately $(00\bar{1})$. The neutron beam had a slightly shorter wavelength ($\lambda = 1·439$ Å) than for the first experiment because of technical constraints in the setting of the new monochromator installed on the D10 facility. The latter was a vertically focusing Cu(200) monochromator (Zeyen, Freund & Hustache, 1980) which increased the observed intensity for $TEA^+ . (TCNQ)_2^-$ by a factor of six.

Lattice parameters at 40 K (Table 1) were calculated from neutron powder patterns obtained on the multicounter D1B diffractometer* of the ILL ($\lambda = 2·253$ Å). Single-crystal measurements gave similar values, though they are less accurate because of the shape and size of the crystal and because perfect centring of the crystal could not be achieved.

The integrated intensities were obtained with the program COLL5N of the ILL which employs the minimal $\sigma(I)/(I)$ criterion (Lehmann & Larsen, 1974) to define the peak–background separation. Data were corrected for the Lorentz factor and for the dead time

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\* See last footnote in preceding column.

### Table 1. Crystal and refinement data

$TEA^+ . (TCNQ)_2, C_6H_{16}N^+ . (C_{12}H_4N_4)_2^-, M_r = 510·6$
Triclinic, space group $P\bar{1}, Z = 4$
Cell dimensions at 40 K
  $a = 14·215$ (6), $b = 7·826$ (3), $c = 13·192$ (3) Å,
  $\alpha = 69·67$ (3), $\beta = 84·11$ (3), $\gamma = 73·66$ (3)°, $V = 1320·5$ Å³
$\rho_c = 1·284$ Mg m⁻³
$\mu_o = 0·211$ (6) mm⁻¹

$\sin \theta/\lambda$ (max.) = 0·68 Å⁻¹
Total number of independent reflections: 5234
Number of reflections with $F_o > 2\sigma(F_o)$: 4054
Isotropic extinction coefficient: $g \simeq 2 \times 10^{24}$ m⁻²
Number of variables: 472

| Statistics | Crystal First | Second | Average |
|---|---|---|---|
| $R = [\sum (\|F_o\| - \|F_c\|)^2/\sum F_o^2]^{1/2}$ | 0·068 | 0·099 | 0·080 |
| $R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$ | 0·060 | 0·084 | 0·068 |
| $R(F^2) = (\sum \|F_o^2 - F_c^2\|/\sum F_o^2)^{1/2}$ | | | 0·094 |

Scattering lengths (fm): $b_N = 9·38, b_C = 6·65, b_H = -3·74$.

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\* The cell (I) used by Kobayashi et al. (1970) and the cell (II) used by Jaud et al. (1974) and in the present paper are different. The axis transformation from (I) to (II) leads to the following values: $a = 14·440, b = 7·885, c = 13·711$ Å, $\alpha = 69·61, \beta = 82·33, \gamma = 71·93°$ for $TEA^+ . (TCNQ)_2^-$ at 300 K.

† Note added in proof: We have since learned that the X-ray structure of $TEA^+ . (TCNQ)_2^-$ at 108 K has been determined by J. A. Potworowski (1974, Thesis, University of Toronto, Canada).

‡ Information on neutron beam facilities at the HFR available for users is obtainable from B. Maier, Institut Laue–Langevin, 156X, 38042 Grenoble CEDEX, France.

of the detector ($\tau = 7 \times 10^{-6}$ s). The vacuum and thermal shields of the D10 cryostat are aluminium spheres and no absorption correction is required. The absorption by the sample, however, was corrected in both data sets. The value of the absorption coefficient for $\text{TEA}^+.(\text{TCNQ})_2^-$ was measured on four samples $|\mu = 0.211$ (6) mm$^{-1}|$ with a neutron wavelength of $\lambda = 1.439$ Å. The averaging of symmetry-related reflections led to 5234 independent observations. Inspection of the profiles showed that diffuse lines due to the aluminium shielding of the cryostat do not alter the intensities significantly except for some of the weak reflections. Reflections with $F_o < 2\sigma(F_o)$ were thus rejected and the remaining 4054 reflections included in the refinement.

A summary of crystallographic information for $\text{TEA}^+.(\text{TCNQ})_2^-$ is given in Table 1.

## Structure determination

The results of previous X-ray work at room temperature (Kobayashi et al., 1970; Jaud et al., 1974) led to a surprising conformation of the TEA ion. In fact, the N atom of TEA is shown with $sp^2$-like geometry instead of the expected $sp^3$ hybridization. The C—C—N angles of the methylene groups have values close to 120° and the thermal ellipsoids of the TEA atoms are very large and all elongated in roughly the same direction. These observations suggest that the TEA ion is disordered at room temperature. Disorder also exists at 40 K but, as shown below, it could be resolved at this temperature because of the considerable sharpening of the peaks on the Fourier maps and because H atoms appear as negative peaks which cannot be confused with peaks of partially populated C or N atoms.

The least-squares refinement (XRAY 70; Stewart, Kundell & Baldwin, 1970) was started with the positional parameters from the room-temperature X-ray study of Jaud et al. (1974). These authors did not locate the 24 H atoms of the asymmetric unit. Thus, repeated calculations were performed consisting of (i) examination of a Fourier or difference map for new peaks, (ii) introduction of positive peaks as C or N atoms and negative ones as H atoms, (iii) refinement of the corresponding coordinates and population parameters.

Three strong and unforeseen positive peaks located close to N(41), C(46) and C(47) (Fig. 1) were observed and labelled N(41)′, C(46)′ and C(47)′ respectively. The population parameters (p.p.) of these six atoms were observed to be roughly 0.5. Then 21 H atoms with p.p. either 0.5 or 1 were located. The latter were all bonded to TEA atoms within 0.9 to 1.2 Å. Finally, C(43) and C(44) were split into pairs labelled C(43), C(43)′ and C(44), C(44)′, respectively, while C(42) and C(45) remained unsplit.

At this stage the twofold disorder of the TEA ion was evident, though only partially resolved, and the H atoms with p.p. $= 1$ could be assigned as pairs of very close half-populated H atoms.

It was thus more appropriate to use rigid-body constraints to complete the refinement. This was done by means of the ORION program (André, Fourme & Renaud, 1971). The three methyl and the three methylene groups of each of the two disordered TEA ions were taken as individual rigid-body groups with C—H $= 1.09$ Å, H—C—H $= 109.5°$ and p.p. $= 0.5$. The atoms of the TCNQ molecules and the remaining N and H atoms of the TEA ions were refined as individual atoms.

Two methylene groups could then be located near the initial position of C(45) while the C(42)H$_2$ and C(42)′H$_2$ methylene groups were resolved on the basis of geometrical considerations. The refinement gave $R = 0.083$, with the isotropic temperature factors of H atoms within a given methyl or methylene group constrained to be equal.
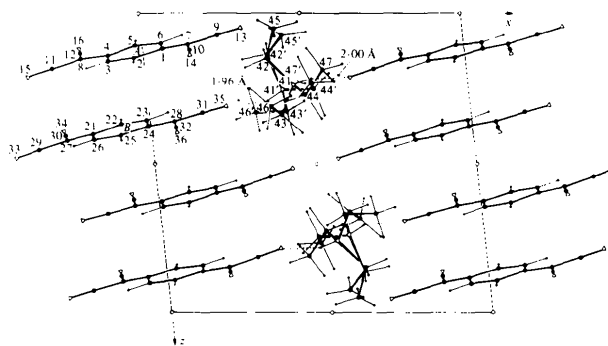


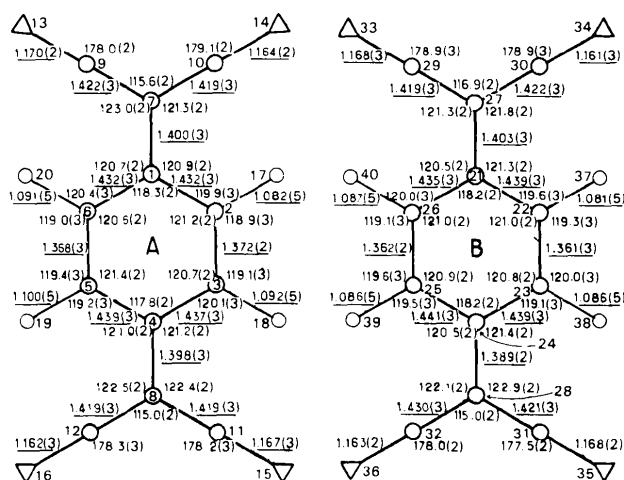Fig. 1. Projection of the structure along the $b$ axis on to the $ac$ plane.



Fig. 2. Bond lengths (Å) (underlined) and angles (°) of molecules TCNQ($A$) and ($B$). E.s.d.'s are given in parentheses.

Table 2. *Fractional coordinates* ($\times 10^4$) *of atoms, isotropic thermal parameters B or equivalent isotropic parameters* $B_{eq}$

For individual atoms, e.s.d.'s are given in parentheses. For atoms introduced in rigid groups, the refinement program provides e.s.d.'s only on the Euler angles $(\theta_1,\theta_2,\theta_3)$ and on the coordinates $(x_0,y_0,z_0)$ of the origin of each group. Typical values for these e.s.d.'s are 0·8 (°) for $\theta_1,\theta_2,\theta_3$; 0·0015 for $x_0$; 0·010 for $y_0$; 0·008 for $z_0$.

| | $x$ | $y$ | $z$ | $B_{eq}$ | | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| TCNQ($A$) | | | | | TEA: population parameter = 0·5 | | | | |
| C(1) | 596 (1) | −858 (2) | 1158 (2) | 0·55 | N(41) | 4568 (3) | 1040 (4) | 2366 (3) | 1·11 (6) |
| C(2) | −316 (1) | −1340 (2) | 1464 (2) | 0·65 | C(42) | 3823 | 1796 | 1465 | 0·9 (4) |
| C(3) | −1152 (1) | −22 (2) | 1580 (2) | 0·63 | C(43) | 4142 | 1650 | 3364 | 1·6 (2) |
| C(4) | −1135 (1) | 1892 (3) | 1389 (2) | 0·68 | C(44) | 4931 | −1074 | 2739 | 1·17 (9) |
| C(5) | −216 (1) | 2369 (2) | 1073 (2) | 0·53 | C(45) | 4170 | 3335 | 507 | 1·1 (1) |
| C(6) | 615 (1) | 1051 (2) | 958 (2) | 0·67 | C(46) | 3820 | 3790 | 3061 | 2·0 (1) |
| C(7) | 1444 (1) | −2206 (2) | 1030 (2) | 0·64 | C(47) | 5544 | −1749 | 1867 | 1·7 (1) |
| C(8) | −1975 (1) | 3238 (2) | 1529 (2) | 0·75 | H(48) | 5166 (6) | 1584 (10) | 2149 (9) | 1·7 (2) |
| C(9) | 2368 (1) | −1798 (2) | 730 (2) | 0·76 | H(49) | 3765 | 658 | 1201 | 2·0 (3) |
| C(10) | 1435 (1) | −4100 (2) | 1220 (2) | 0·86 | H(50) | 3118 | 2387 | 1784 | 2·0 (3) |
| C(11) | −2892 (1) | 2817 (3) | 1841 (2) | 1·01 | H(51) | 4715 | 968 | 3972 | 2·4 (2) |
| C(12) | −1979 (1) | 5136 (2) | 1352 (2) | 0·83 | H(52) | 3520 | 1046 | 3635 | 2·4 (2) |
| N(13) | 3138 (1) | −1516 (2) | 483 (2) | 1·18 | H(53) | 4277 | −1596 | 2925 | 2·7 (2) |
| N(14) | 1422 (1) | −5647 (2) | 1364 (2) | 1·12 | H(54) | 5355 | −1533 | 3472 | 2·7 (2) |
| N(15) | −3653 (1) | 2508 (2) | 2109 (2) | 1·52 | H(55) | 3669 | 3781 | −163 | 2·9 (2) |
| N(16) | −1994 (1) | 6685 (2) | 1232 (2) | 1·27 | H(56) | 4913 | 2784 | 256 | 2·9 (2) |
| H(17) | −357 (3) | −2763 (5) | 1600 (5) | 1·81 | H(57) | 4142 | 4537 | 754 | 2·9 (2) |
| H(18) | −1838 (3) | −434 (6) | 1800 (5) | 2·03 | H(58) | 4437 | 4373 | 2709 | 3·1 (2) |
| H(19) | 184 (3) | 3823 (5) | 925 (5) | 1·80 | H(59) | 3597 | 4083 | 3809 | 3·1 (2) |
| H(20) | 1296 (3) | 1473 (6) | 719 (5) | 1·78 | H(60) | 3210 | 4433 | 2498 | 3·1 (2) |
| | | | | | H(61) | 6166 | −1132 | 1654 | 2·8 (2) |
| TCNQ($B$) | | | | | H(62) | 5112 | −1368 | 1148 | 2·8 (2) |
| C(21) | −1842 (1) | 2661 (2) | 4009 (2) | 0·56 | H(63) | 5809 | −3278 | 2204 | 2·8 (2) |
| C(22) | −940 (1) | 3199 (2) | 3681 (2) | 0·62 | | | | | |
| C(23) | −104 (1) | 1927 (2) | 3543 (2) | 0·54 | TEA': population parameter = 0·5 | | | | |
| C(24) | −96 (1) | −2 (2) | 3735 (2) | 0·59 | N(41)' | 4221 (3) | 634 (4) | 2536 (3) | 1·09 (6) |
| C(25) | −1000 (1) | −539 (2) | 4061 (2) | 0·57 | C(42)' | 3834 | 1788 | 1382 | 1·1 (4) |
| C(26) | −1838 (1) | 744 (2) | 4184 (2) | 0·51 | C(43)' | 4265 | 1810 | 3205 | 1·1 (1) |
| C(27) | −2696 (1) | 3949 (2) | 4190 (2) | 0·66 | C(44)' | 5200 | −731 | 2523 | 1·7 (1) |
| C(28) | 752 (1) | −1317 (2) | 3606 (2) | 0·50 | C(45)' | 4370 | 3201 | 728 | 1·5 (1) |
| C(29) | −3581 (1) | 3410 (2) | 4534 (3) | 1·16 | C(46)' | 3303 | 3265 | 3271 | 1·8 (1) |
| C(30) | −2712 (1) | 5837 (2) | 4062 (2) | 0·84 | C(47)' | 5113 | −2441 | 2246 | 1·8 (1) |
| C(31) | 1667 (1) | −877 (2) | 3306 (2) | 0·64 | H(48)' | 3731 (18) | −100 (11) | 2908 (10) | 2·0 (2) |
| C(32) | 774 (1) | −3243 (2) | 3798 (2) | 0·55 | H(49)' | 3876 | 721 | 1015 | 1·8 (2) |
| N(33) | −4302 (1) | 2938 (2) | 4813 (3) | 2·66 | H(50)' | 3069 | 2433 | 1517 | 1·8 (2) |
| N(34) | −2735 (1) | 7378 (2) | 3972 (2) | 1·35 | H(51)' | 4865 | 2469 | 2898 | 2·6 (2) |
| N(35) | 2436 (1) | −585 (2) | 3078 (2) | 1·02 | H(52)' | 4438 | 810 | 4016 | 2·6 (2) |
| N(36) | 821 (1) | −4821 (2) | 3952 (2) | 0·96 | H(53)' | 5450 | −1210 | 3352 | 3·4 (2) |
| H(37) | −920 (3) | 4628 (5) | 3558 (5) | 1·59 | H(54)' | 5691 | 36 | 1988 | 3·4 (2) |
| H(38) | 570 (3) | 2353 (5) | 3304 (5) | 1·67 | H(55)' | 3999 | 3917 | −46 | 3·3 (2) |
| H(39) | −1010 (3) | −1990 (5) | 4217 (5) | 1·62 | H(56)' | 5122 | 2463 | 605 | 3·3 (2) |
| H(40) | −2510 (3) | 299 (5) | 4420 (5) | 1·86 | H(57)' | 4374 | 4235 | 1103 | 3·3 (2) |
| | | | | | H(58)' | 2699 | 2600 | 3487 | 3·7 (2) |
| | | | | | H(59)' | 3151 | 4397 | 2496 | 3·7 (2) |
| | | | | | H(60)' | 3382 | 3843 | 3887 | 3·7 (2) |
| | | | | | H(61)' | 4650 | −3188 | 2843 | 4·6 (2) |
| | | | | | H(62)' | 5841 | −3387 | 2254 | 4·6 (2) |
| | | | | | H(63)' | 4792 | −1958 | 1449 | 4·6 (2) |

An attempt to refine the population parameters of all methyl and methylene groups gave mean values of p.p. = 0·5 for both TEA⁺ ions so that p.p. was assumed to be exactly 0·5 in subsequent cycles of refinement. The Zachariasen formula, $I_c/I_o = k(1 + gI_c)$, was used to correct the data for extinction ($g = 1·02 \times 10^{-4}$, $k =$

0·95). Nevertheless, the 27 strongest reflections were not included in the refinement because extinction is probably anisotropic. A difference map at this stage showed no significant peaks. The weights for the refinements were based on counting statistics and were adjusted slightly after an initial refinement to obtain
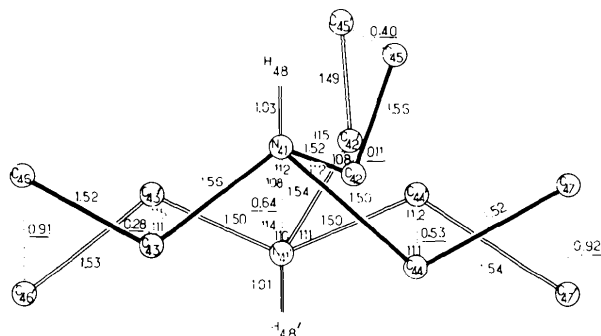
Fig. 3. Bond lengths (Å), angles (°) and distances (Å) (underlined) between resolved pairs of disordered atoms of TEA ions. For clarity the H atoms are not shown. E.s.d.'s were not calculated from values given in Table 2, but the observed discrepancy between chemically equivalent bond lengths and angles leads to observed e.s.d.'s of respectively 0·03 Å and 3°, which are reasonable for such a disordered molecule.
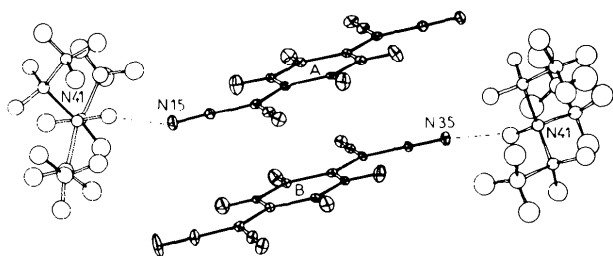


Fig. 4. *ORTEP* plot (Johnson, 1965) of the atomic thermal vibration parameters (probability 50%) viewed in projection on to the *ac* plane. For clarity the TEA cation is shown on site *x* − 1, *y*, *z* while TEA' is shown on site *x*,*y*,*z*.

$\langle w|F_o - F_c|^2 \rangle$ independent of $F_o$. Final $R$ values are listed in Table 1,* coordinates of atoms in Table 2. A projection of the structure is shown in Fig. 1. Bond lengths and angles are given on Figs. 2 and 3. Fig. 4 is an *ORTEP* (Johnson, 1965) plot of the structure.

## Discussion

### (i) *TCNQ molecules*

Equivalent bond lengths and angles (Fig. 2) in TCNQ molecules *A* and *B* are in close agreement. Their means (Fig. 5) at 40 K compared with those at 300 K (Jaud *et al.*, 1974)† agree well except for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35347 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Bond lengths and angles published by these authors are slightly incorrect because of a mistake in the cell parameter $\gamma$ ($\gamma = 74\cdot30$ instead of 72·76°). The 300 K results quoted in the present paper were therefore recalculated.

C=C bonds of the ring, which are elongated by 0·019 (6) Å at low temperature, and the C≡N bonds, also elongated by 0·021 (6) Å.

This increase of the C≡N length, already observed in some other TCNQ salts, has been discussed by Filhol & Gaultier (1980). It does not seem to be explicable by the conjunction of the shift of the charge centroid from the nucleus position (0·008 Å in tetracyanoethylene; Little, Pautler & Coppens, 1971; Becker, Coppens & Ross, 1973) or by the temperature effect (riding model).

The magnitude of the charge transfer between cation and anions may by estimated by comparison of the C—C and C=C bond lengths in TCNQ (Flandrois & Chasseau, 1977). With the uncorrected bond lengths, the observed charge transfers for TCNQ molecules *A* and *B* are 0·57 (5) e and 0·47 (7) e at 40 K and 0·57 (5) e and 0·46 (7) e at 300 K. This excellent agreement between the two sets of values must not hide the fact that the method needs to be adapted to the case of neutron data (Filhol, Bravic, Gaultier, Chasseau & Vettier, 1980). The 300 and 40 K charge transfers thus obtained are consistent with the fact that TEA⁺.(TCNQ)₂⁻ is a radical ion salt for which the total charge transfer (molecule *A* plus molecule *B*) is expected to be unity and therefore cannot be temperature dependent. It follows that the true formula for this compound is closer to TEA⁺.TCNQ^{1/2−}. TCNQ^{1/2−} than to TEA⁺.TCNQ⁰.TCNQ⁻ as proposed by Kobayashi *et al.* (1970).

The main results of a TLS analysis (Schomaker & Trueblood, 1968) of the rigid-body molecular thermal motions are given in Table 3. They show that the molecular translational vibrations have quasi-isotropic amplitudes at 40 as well as at 300 K. These results are in agreement with the low-temperature specific heat which shows the existence of 3D phonons (Delhaes *et al.*, 1977). However, the molecular librations are anisotropic. This anisotropy is higher at 300 than at 40 K because the largest main amplitude of libration, the direction of which is closely parallel to the elongation axis of the molecule, is more temperature dependent than the other main amplitudes.
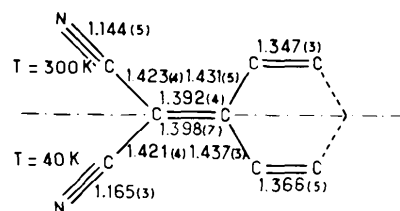


Fig. 5. Mean bond lengths (Å) of TCNQ molecules in TEA⁺.(TCNQ)₂ at 300 and 40 K. The values shown here are uncorrected for the riding model and the shift of the electron-cloud centroid. The observed e.s.d.'s are given in parentheses.

Table 3. *Selected results from a* **TLS** *rigid-body analysis of the molecular thermal motion*

Eigenvectors of tensors **T** and **L** are referred to the inertia axes of the corresponding TCNQ molecule. These axes are defined in Table 4. Results relative to the tensor **S** are not given.

| Temperatures | T Principal r.m.s. amplitudes (Å) | Eigenvectors | | | L Principal r.m.s. amplitudes (°) | Eigenvectors | | |
|---|---|---|---|---|---|---|---|---|
| 300 K* (X-rays) | | | | | | | | |
| TCNQ(*A*) | 0·22 (3) | 0·045 | 0·087 | −0·995 | 4·9 (1·6) | 0·042 | −0·052 | −0·998 |
| | 0·19 (3) | −0·838 | −0·540 | −0·085 | 2·2 (1·0) | 0·679 | 0·734 | −0·010 |
| | 0·19 (4) | −0·544 | 0·838 | 0·048 | 1·7 (0·7) | 0·733 | −0·677 | 0·066 |
| TCNQ(*B*) | 0·22 (3) | −0·117 | − 0·159 | 0·980 | 4·8 (1·6) | 0·062 | −0·077 | −0·995 |
| | 0·19 (3) | 0·273 | 0·944 | −0·186 | 2·2 (0·8) | 0·619 | 0·785 | −0·022 |
| | 0·17 (4) | 0·955 | −0·289 | −0·067 | 2·0 (0·7) | 0·783 | −0·614 | 0·096 |
| 40 K (neutrons) | | | | | | | | |
| TCNQ(*A*) | 0·09 (3) | 0·023 | 0·861 | −0·508 | 1·7 (1) | 0·321 | 0·039 | −0·946 |
| | 0·09 (3) | 0·932 | −0·202 | ·-0·301 | 1·2 (0·8) | 0·914 | 0·247 | 0·321 |
| | 0·07 (2) | −0·362 | −0·467 | −0·807 | 0·8 (0·5) | 0·246 | −0·968 | 0·044 |
| TCNQ(*B*) | 0·09 (2) | 0·470 | 0·430 | −0·771 | 2·3 (1·0) | −0·236 | −0·374 | −0·897 |
| | 0·07 (3) | −0·843 | 0·477 | −0·248 | 1·1 (0·9) | 0·385 | 0·812 | −0·440 |
| | 0·07 (2) | 0·262 | 0·767 | 0·586 | 0·6 (0·5) | 0·892 | −0·449 | −0·047 |

* Calculated from results of Jaud *et al.* (1974).

## (ii) *TEA ions*

In most of the reported TEA-containing structures, this ion is more or less disordered and observed bond lengths and angles are far from the expected values. The disorder is small or zero in (TEA)$_2$CuCl$_4$ (Lamotte-Brasseur, Dupont & Dideberg, 1973) and TEA–cyclic uridine-3',5'-phosphate (Coulter, 1969); it exists and has been fully described in (TEA)$_2$B$_{20}$H$_{18}$ and (TEA)$_3$B$_{20}$H$_{18}$NO (Schwalbe & Lipscomb, 1971*a,b*). In these four cases, bond lengths and angles are of the same order as those found for TEA$^+$.(TCNQ)$_2^-$.

Another point of interest is the conformation of the TEA ions. Both TEA ions in (TEA)$_2$B$_{20}$H$_{18}$ and one disordered TEA ion in (TEA)$_3$B$_{20}$H$_{18}$NO nearly have $C_3$ symmetry. Two TEA ions in (TEA)$_3$B$_{20}$H$_{18}$NO differ from $C_3$ symmetry by rotation of one of the ethyl groups about the corresponding C—N bond. Finally, in (TEA)$_2$CuCl$_4$ and in TEA–uridine phosphate, one TEA ion has this latter conformation, while the other has nearly $C_s$ symmetry. In TEA$^+$.(TCNQ)$_2^-$ both TEA ions have nearly $C_s$ symmetry but differ mainly in that the ethyl group, which is in the quasi-symmetry plane, points in the direction of the N—H bond for one TEA and in the opposite direction for the other.

The thermal parameters of the atoms of the TEA ions are larger than those for TCNQ. This suggests that the twofold disorder is too simple to completely describe the atom distributions.

## (iii) *Crystal packing*

The crystal packing at 40 K is not very different from that at 300 K. It is characterized by the existence of independent linear chains of planar TCNQ ions stacked face to face. The stacking sequence is *ABBA* leading to three different interplanar distances and two overlapping modes (tetrads). The TEA ions are arranged in the spaces between the columns. They are disordered over two equi-populated positions and each of these counter ions participates in a N—H···N hydrogen bond either with TCNQ(*A*) or with TCNQ(*B*) (Fig. 3). These bonds are not very strong N(15)—N(41) = 3·003 (5), N(35)—N(41)' = 2·894 (5), N(15)—H(48) = 2·00 (1), N(35)—H(48)' = 1·96 (3) Å, N(41)—H(48)···N(15) = 166·2 (0·8), N(41)'—H(48)'···N(35) = 153·4 (1·3)°.

The major difference between the 40 K and 300 K structures is in the TCNQ stacking. In fact, the three independent interplanar spacings decrease with temperature, each to a different extent. From values listed in Table 4, it is clear that TCNQ stacking is nearly *AB* diadic at 300 K (while intrinsically tetradic) and purely *BAAB* tetradic at 40 K. On the other hand, the overlapping of adjacent TCNQ molecules (Table 4) does not change very much with temperature except for the mutual shift $\delta y$ of the centre of mass of pairs of adjacent TCNQ(*A*) molecules. The angle ($\Omega$) between the mean planes of TCNQ molecules *A* and *B* increases slightly when temperature decreases, while the angles

Table 4. *Characteristics of the overlap of* TCNQ *molecules in* TEA$^+$.(TCNQ)$_2^-$

$d$ is the interplanar spacing; $\delta y$ and $\delta z$ are the shifts of the centre of mass in directions $y$ and $z$. Angles given are $\Omega$, between the planes of the rings of the molecules TCNQ($A$) and TCNQ($B$), and those between the following characteristic directions: cell axis **c**, mean normal **N** to planes of the TCNQ molecules, axis **T** of a tetrad *BAAB* of TCNQ molecules. Results are given for the 300 K (first line) and the 40 K (second line) structures. E.s.d.'s are given in parentheses.
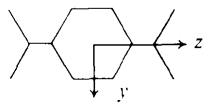
| Overlapping molecules | $d$ (Å) | $\delta y$ (Å) | $\delta z$ (Å) |
|---|---|---|---|
| TCNQ($A$),($A'$) | 3·313 (7) | 0·48 (2) | 1·85 (1) |
|  | 3·131 (5) | 0·28 (2) | 1·89 (1) |
| TCNQ($B$),($B'$) | 3·329 (7) | 0·40 (2) | 1·95 (1) |
|  | 3·257 (5) | 0·41 (2) | 2·06 (1) |
| TCNQ($A$),($B$) | 3·223 (7) | 0·01 (2) | 1·98 (1) |
|  | 3·115 (5) | 0·01 (2) | 1·98 (1) |

Angles (°)

|  |  |  |  |
|---|---|---|---|
| $\Omega$ | 0·2 (3) | (**c**,**N**) | − 16·9 (2) |
| $\Omega$ | 0·7 (3) |  | 17·0 (2) |
| (**c**,**T**) | 13·5 (2) | (**N**,**T**) | − 30·3 (3) |
|  | 13·9 (2) |  | 30·8 (3) |

between the cell axis **c**, the mean vector **N** normal to the TCNQ planes and the axis **T** of a tetrad *BAAB* of TCNQ molecules are insensitive to temperature.

Another aspect of the stacking of TCNQ molecules in the chains is that the cyanomethylene groups do not contribute equally to the overlap. In fact (Fig. 6), the cyanomethylene groups N(33) and N(34) of the TCNQ($B$) molecules are not involved in the overlap, while both sides of the groups of the other end [N(35) and N(36)] of those molecules do contribute. It is therefore striking to observe (Fig. 6) that the largest out-of-plane deviations for atoms of a TCNQ molecule are for N(33) and N(34) at 40 K (1·1 and 1·8 Å) as well as at 300 K (0·6 and 0·8 Å).

Comparison of the TEA$^+$.(TCNQ)$_2^-$ structures at 300 and 40 K shows that the differences are relatively small. In fact, for this temperature range, no phase transitions have been reported and thus the structure evolves monotonically (Filhol *et al.*, 1977). However, one has to keep in mind that anomalies in the electric conductivity have been observed on certain samples at temperatures between 196 and 268 K (Grassi, Brau & Farges, 1979; Farges, 1979).
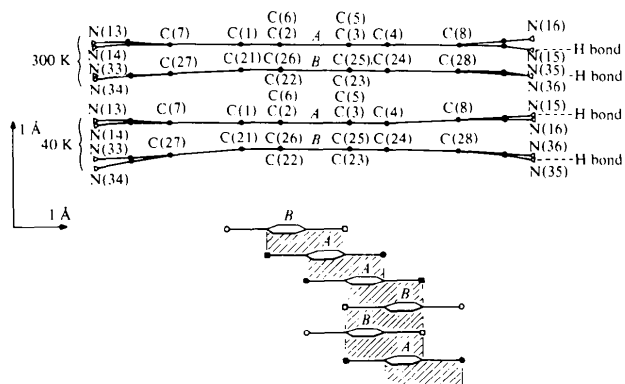
Fig. 6. Out-of-plane deviations of atoms of the TCNQ molecules in TEA$^+$.(TCNQ)$_2$ at 300 and 40 K (note that the scale along $y$ is twice that along $x$) in relation to the overlapping mode in the TCNQ stacks: ■: N(13)—N(14); ●: N(15)—N(16), overlap on one side; □: N(33)—N(34), overlap on both sides; ○: N(35)—N(36), no overlap.

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# Structure of 2,2,2-Trichloroethyl 2-(2-Benzyl-4-methoxycarbonyl-1-imidazolyl)-3-methylisocrotonate

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## Abstract

$C_{19}H_{19}Cl_3N_2O_4$ crystallizes in space group $P2_1/c$ with $a = 9.542$ (6), $b = 21.331$ (10), $c = 11.728$ (7) Å, $\beta = 117.94$ (3)°, $Z = 4$. The structure was refined to $R = 0.064$ for 2735 observed reflexions $[I > 2\sigma(I)]$. The interatomic distances and angles are in agreement with the given atom type and hybridization with the exception of N(1)–C(2) [1.377 (7) Å] in the imidazole moiety. The relative orientation of the imidazole ring to the benzyl group is defined by a torsion angle of −68.4 (6)°. The trichloroethyl acetate group is in a *trans* orientation to the benzyl group [−78.5 (5)°] whereas the α-isopropylidene group is *cis*. Molecular packing is realized through close contacts involving two Cl atoms and C atoms belonging to the methyl groups of the 4-methoxycarbonyl [C···Cl 3.476 (9) Å] and α-isopropylidene substituent [C···Cl 3.597 (6) Å]. The shortest intermolecular contact is 3.191 (8) Å between the methyl group (in the α-isopropylidene) and a carbonyl O atom.

## Introduction

During the study of the reaction of PCl$_5$ with a trichloroester of benzylpenicillin (I) at 333 K in non-aqueous medium, a corresponding benzylpenillate was formed; elimination of H$_2$S resulted in a final product identified by $^1$H NMR, $^{13}$C and IR methods (Kovačević, Herak & Gašpert, private communication). On the basis of chemical reaction and spectroscopic data two different structural formulae (II, III) were proposed. An X-ray structure determination establishes (II) as the correct one.