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# Structural Evolution of the One-Dimensional Organic Conductor Triethylammonium–7,7,8,8-Tetracyano-*p*-quinodimethane (1:2) [TEA–$(TCNQ)_2$] in the Temperature Range 40 to 345 K

BY ALAIN FILHOL AND MICHEL THOMAS

*Institut Laue–Langevin*, 156*X*, *F*-38042 *Grenoble CEDEX*, *France*

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## Abstract

The X-ray structure of TEA–$(TCNQ)_2$ has been measured at 110, 173, 234 and 345 K, which, in addition to data in the literature, enables a detailed description of the structural evolution of the compound with temperature. The charge transfer estimated from bond lengths indicates a partial localization (0·6 and 0·4 e) of the charges, on the two independent TCNQ molecules, in the temperature range considered. The unit-cell thermal expansion has been measured in the range 156 to 367 K. An anomaly at 200–220 K was found and the related structural changes are described. Since electrical-conductivity anomalies at 200–220 K have already been reported and sometimes attributed to a metal–insulator phase transition, an attempt is thus made to interpret the temperature dependence of the stacking distances in the TCNQ columns in terms of Peierls-like lattice distortions – namely dimerization and tetramerization.

## Introduction

Some years ago it was usually assumed that, in the crystalline state, TCNQ salts with a regular stacking of the TCNQ molecules were the only ones with one-dimensional (1D) metal-like properties. TCNQ salts with irregular stacking (tetrads, diads, *etc.*) were classified as semiconductors or insulators, depending on the quality of the molecular overlap in the columns. Another idea was that irregular stacking at high temperature could be the result of a 'virtual' Peierls transition, *i.e.* a Peierls transition that would have occurred above the melting point of the compound (*e.g.* Kommandeur, 1975).

In fact, this approach was too simple, and the study of 1D conductors with cationic conducting chains (cations of the TTF* family) has shown that strict regular stacking is not in itself necessary for metal-like behaviour. Similar observations have also been made for TCNQ salts [*e.g.* for MEM–$(TCNQ)_2$ by van Bodegom (1979) and for TMA–TCNQ–I by Filhol, Gallois, Laugier, Dupuis & Coulon (1982) and Gallois, Coulon, Pouget, Filhol & Dupuis (1983)]. It was thus of interest to reconsider the case of TEA–$(TCNQ)_2$, which is one of the best known TCNQ salts because large single crystals have been available for a long time.

TEA–$(TCNQ)_2$ is generally considered as a good 1D semiconductor ($\sigma_{\|300\,\mathrm{K}} \sim 5{\cdot}7\ \Omega^{-1}\ \mathrm{cm}^{-1}$) and in fact its structure (Kobayashi, Ohashi, Marumo & Saito, 1970; Jaud, Chasseau, Gaultier & Hauw, 1974; Potworowski, 1974; Filhol, Zeyen, Chenavas, Gaultier & Delhaes, 1980) shows typical irregular tetradic stacking of the TCNQ molecules (Fig. 1). However, the temperature dependence of the longitudinal conductivity of this compound shows an anomaly at 200–220 K (see *e.g.* Brau & Farges, 1974) which is in fact a jump of one order of magnitude if the samples are small, needle-shaped single crystals (Grassi, Brau & Farges 1979; Farges, 1979). Furthermore, some authors (*e.g.* Vlasova *et al.*, 1975) have postulated that this transition is of the *metal–insulator* type while others incline towards a *semiconductor–semiconductor* mechanism.

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* TTF–TCNQ: tetrathiafulvalene–TCNQ; TMA–TCNQ–I [$TMA^+.TCNQ^{2/3-}.(I_3^-)_{1/3}$]: trimethylammonium–TCNQ–iodine; MEM–$(TCNQ)_2$: ethyl(methyl)morpholinium–$(TCNQ)_2$.

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In spite of many studies on its physical properties and especially on its electronic transport properties, the mechanism of conduction in TEA–(TCNQ)$_2$ is not yet clearly understood. However, a detailed knowledge of the structural changes with temperature is certainly a key point in the interpretation of results. Although one may perhaps predict, from the room-temperature structure, the temperature dependence of the unique stacking distance and of the overlap mode in a regular TCNQ column, it is certainly not possible for irregular stacks which show several interplanar distances and several overlap modes.

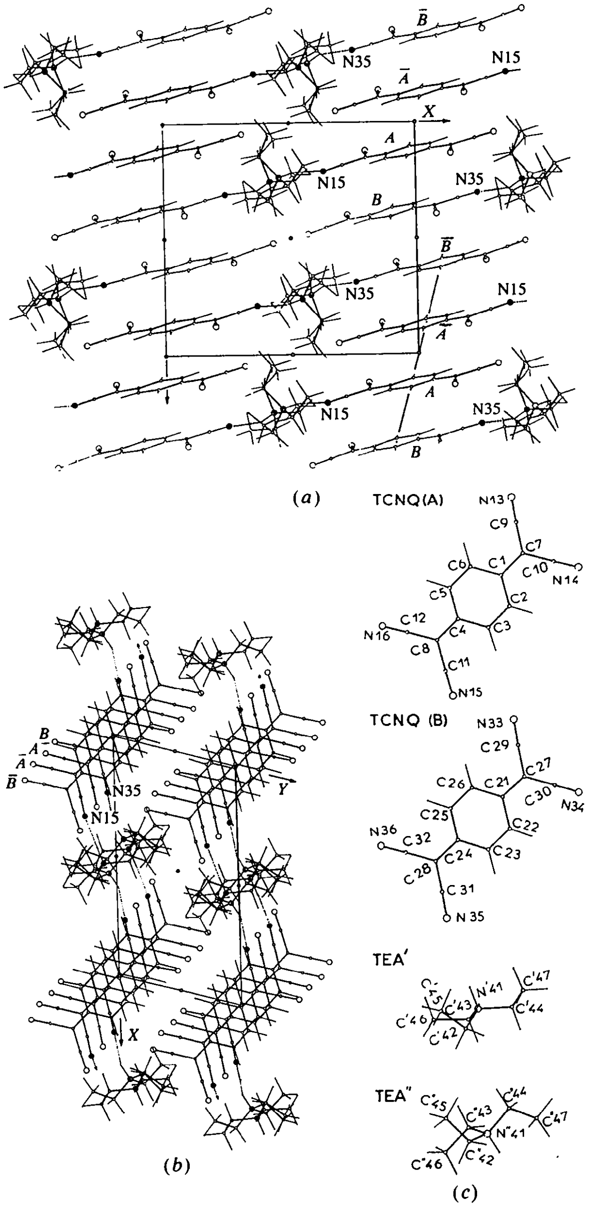

Fig. 1. The 40 K structure of TEA–(TCNQ)$_2$ (from Filhol *et al.*, 1980). Large open and filled circles: N. (*a*) Projection along the *b* axis on to the *ac* plane. (*b*) Projection along the *c* axis on to the *ab* plane. (*c*) Atom labelling scheme.

The present paper is thus intended to provide a detailed examination of the structure of TEA–(TCNQ)$_2$ in the temperature range 40 to 345 K. Preliminary results have already been published (Filhol, Chasseau, Gaultier & Hauw, 1977) but new developments in the study of the compound justify a more complete presentation and discussion.

### Thermal expansion

In the following, all data from the literature have been converted to apply to the cell axes defined by Jaud *et al.* (1974), since each laboratory has used its own set of cell axes (Fig. 2).

#### (i) *Experiment*

The cell dimensions of TEA–(TCNQ)$_2$ have been measured from powder and single-crystal samples in the total temperature range 15 to 367 K (Fig. 3).

The *single-crystal* measurements were made on the AED–Siemens X-ray four-circle diffractometer of the ILL at Grenoble, equipped with a cold nitrogen gas flow device. The temperature, measured using a thermocouple, was known to ±2 or ±3 K depending on the experimental constraints. At each temperature, the cell dimensions were refined from the Eulerian angles corresponding to ten strong accurately centred reflections.

*Powder* patterns of TEA–(TCNQ)$_2$ have been obtained at 200, 117, 98, 70, 40 and 15 K (±0·5 K) successively (Fig. 4) on the D1B neutron diffractometer [$\lambda = 2{\cdot}524(4)$ Å] at the ILL (Institut Laue–Langevin, 1981). This instrument was equipped with a linear position-sensitive detector with 400 cells, providing an angular resolution of 0·1° for the Bragg angle $\theta$. At each temperature two spectra were recorded with the detector shifted by one-half of a cell width thus providing a final resolution of 0·05°. Gaussian fits were used to locate Bragg peaks accur-

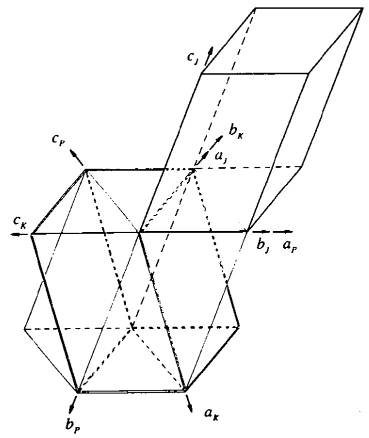

Fig. 2. The various TEA–(TCNQ)$_2$ unit cells reported in the literature. Heavy lines: Jaud *et al.* (1974). Light lines: Potworowski (1974). Double lines: Kobayashi *et al.* (1970).

ately, even when they partially overlapped. The indexing of reflections up to high $\theta$ angles was made possible by the knowledge of the 40 K neutron structure factors (Filhol *et al.*, 1980). No extra diffraction lines are observed in the low-temperature patterns with respect to the present description of the lattice of the compound. At each temperature, the cell parameters were refined from the observed scattering angles of 15 to 18 strong reflections ($\sin\theta/\lambda_{\max} < 0{\cdot}16$ Å$^{-1}$). No internal reference was used but the comparison between neutron powder and X-ray single-crystal data at 98, 117 and 200 K showed that the same small zero shift had to be applied to all the powder spectra.

### (ii) *Results*

The variation with temperature of the cell dimensions of TEA–(TCNQ)$_2$ (Fig. 3) shows a change in the slopes at about 200–220 K, especially for parameters $a$ and $\alpha$. This indicates that TEA–(TCNQ)$_2$ certainly undergoes a structural phase transition in the temperature range for which anomalies in its electronic properties have already been reported. Presumably no change in the lattice symmetry occurs at the transition since no superlattice or satellite reflections have ever been observed below 200 K, even by Potworowski (1974), who measured the structure at 108 K using film techniques. However, a small deviation from centrosymmetry cannot be excluded. To be complete we note here that, in a preliminary neutron experiment, Carneiro (1982) has observed at 210 K satellite reflections with wavevector $0{\cdot}045a^* + 0{\cdot}002b^* + 0{\cdot}0c^*$ but this result needs confirmation. Obviously, this point is of crucial importance for the understanding of the behaviour of the compound and, thus, further experiments are planned.

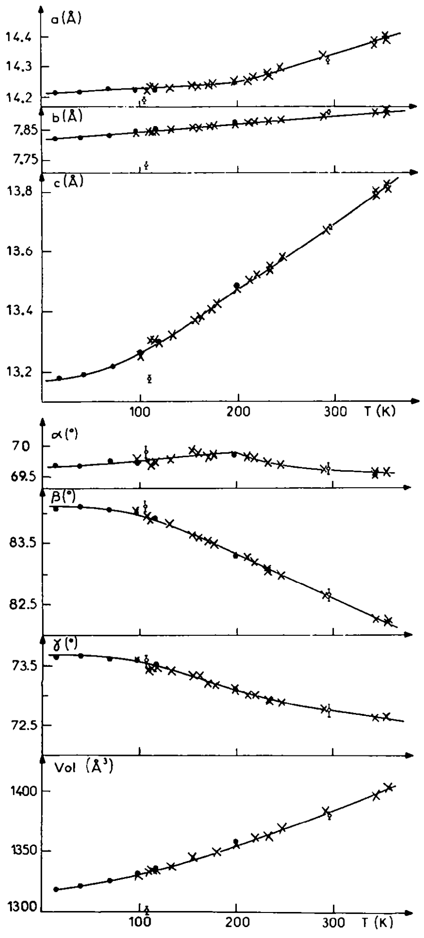

Fig. 3. Cell parameters of TEA–(TCNQ)$_2$ as a function of temperature. ●: Neutron powder data; ×: X-ray data (this work); ◇: Potworowski (1974). The lines are only guides to the eye.

From data in Fig. 3 a preliminary analysis of the thermal expansion of TEA–(TCNQ)$_2$ crystals is nevertheless possible, although the results must not be taken too literally because they are sensitive to the difficult choice of polynomials fitting scattered data. It is apparent, however, that the volumic thermal expansion $\alpha_v = (1/V)\,\partial V/\partial T$ increases quasi-linearly with $T$ but shows different slopes below and above 200–220 K. Above 200–220 K, the linear thermal expansions along all three cell axes are nearly constant ($\alpha_a \sim 0{\cdot}67\times10^{-4}$, $\alpha_b \sim 0{\cdot}29\times10^{-4}$, $\alpha_c \sim 1{\cdot}64\times10^{-4}$ K$^{-1}$ at 300 K) and their values are similar to that observed in other 1D TCNQ salts. Below 200–220 K, $\alpha_c$ decreases rapidly while $\alpha_a$ and $\alpha_b$ remain nearly constant, but with a value divided by more than six for $\alpha_a$. The magnitude and orthogonal directions of the principal linear thermal expansion ($\alpha_1, \alpha_2, \alpha_3$) have also been computed† since they reflect the

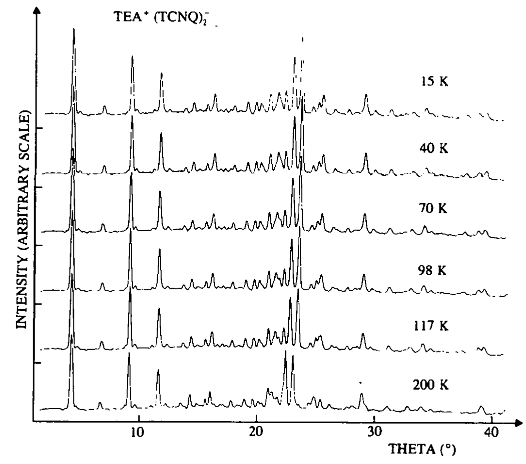

Fig. 4. Neutron powder spectra of TEA–(TCNQ)$_2$ as a function of temperature.

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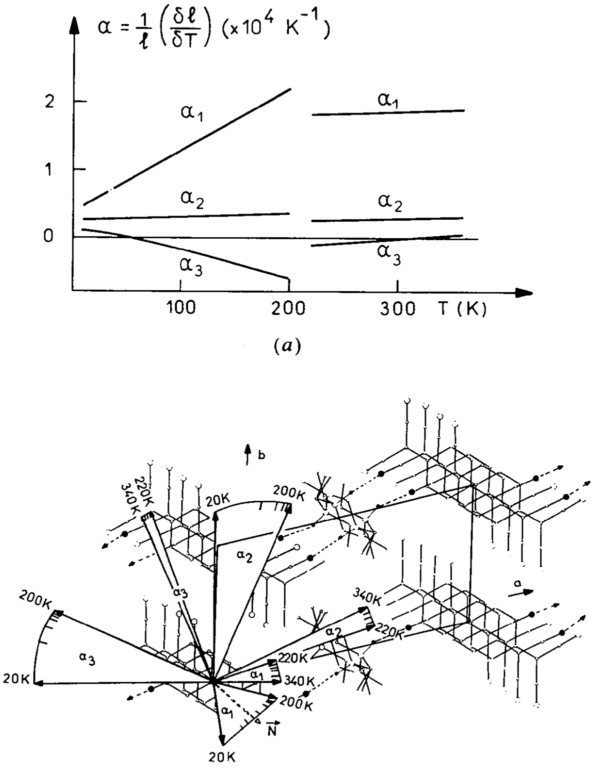
† A table of the magnitudes and directions of the principal thermal expansions at 12 temperatures and lists of structure factors and anisotropic thermal parameters obtained at 110, 173, 234, 295 and 345 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP38757 (127 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

anisotropy of the relative contributions of intra- and intermolecular forces to the crystal packing. As shown in Fig. 5 the largest expansion ($\alpha_1$) remains roughly directed along the normal to the mean TCNQ molecular plane while the intermediate ($\alpha_2$) and the smaller ($\alpha_3$) expansions take very different orientations with temperature. Below 200 K, $\alpha_2$ and $\alpha_3$ are roughly directed along the transverse and elongation axes, respectively, of the average molecular species corresponding to H-bonded TEA···TCNQ molecules. Above 200 K, $\alpha_2$ is roughly parallel, and $\alpha_3$ roughly perpendicular, to the mean axis of the H bonds. Furthermore, $\alpha_3$ is negative over a wide temperature range indicating that, in the corresponding direction, TEA–(TCNQ)$_2$ crystals exhibit a Poisson contraction below 200 K and a Poisson expansion above 220 K.

A more detailed examination of the thermal expansion of TEA–(TCNQ)$_2$ (Brau, Farges, Filhol & Grassi, 1983) led to the conclusion that the results may be understood in terms of static and dynamic disorder of the cation.



(a)

(b)

Fig. 5. Thermal expansion of TEA–(TCNQ)$_2$. (a) Magnitudes of the principal linear thermal expansions ($\alpha_1$, $\alpha_2$, $\alpha_3$). (b) Principal thermal-expansion directions displayed as vectors of 10 Å length on the c projection of the structure. The directions are given in steps of 30 K in both temperature ranges: 20 to 200 K and 220 to 340 K. N is the normal to the mean TCNQ molecular plane.

## Structures

### *Experimental*

The X-ray structure of TEA–(TCNQ)$_2$ has been measured at 110, 175, 234 and 345 K with the experimental conditions described in Table 1. The least-squares refinements were performed with the XRAY system (Stewart, 1976). Since the goal of this work was not the study of the disorder of the TEA molecule (Filhol *et al.*, 1980), no allowance was made for disorder, except when necessary to ensure satisfactory refinement as measured by the residual (*i.e.* for the most disordered atoms at the lowest temperatures). The final atomic coordinates are given in Table 2; the atomic thermal motions are displayed in Fig. 6.*

### *Results*

The room-temperature structure of TEA–(TCNQ)$_2$ was first described by Kobayashi *et al.* (1970) from photographic data and then remeasured on a four-circle diffractometer by Jaud *et al.* (1974) and Potworowski (1974). This latter author has also determined the X-ray structure at 108 K from Weissenberg data while Filhol *et al.* (1980) have published the neutron structure at 40 K. We present here the X-ray structures of TEA–(TCNQ)$_2$ at 110, 173, 234 and 345 K, as well as a reprocessing of the 295 K data from Jaud *et al.* (1974), thus making possible the description of the structural evolution of TEA–(TCNQ)$_2$ in the temperature range 40 to 345 K. The

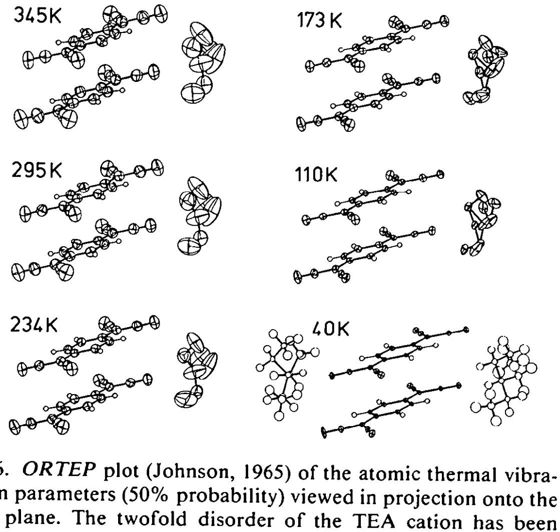


Fig. 6. *ORTEP* plot (Johnson, 1965) of the atomic thermal vibration parameters (50% probability) viewed in projection onto the *ac* plane. The twofold disorder of the TEA cation has been resolved partially for the 173 and 110 K structures and totally for the 40 K structure (Filhol *et al.*, 1980). For clarity, in this latter case, the TEA' cation is shown on site $x-1$, $y$, $z$ while TEA'' is shown on site $x$, $y$, $z$.

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* See deposition footnote.

Table 1. *Main experimental conditions for the nine structure determinations of TEA–(TCNQ)$_2$*

| Temperature | 40 ± 0·5 K(a) | 108 ± 5 K(b) | 110 ± 5 K | 173 ± 3 K | 234 ± 3 K | 295 ± 2 K(c) | 298 K(b) | RT(d) | 345 ± 3 K |
|---|---|---|---|---|---|---|---|---|---|
| Instrument | | | | | | | | | |
| Type | 4-circle diff. | Weissenberg | 4-circle diff. | 4-circle diff. | 4-circle diff. | 4-circle diff. | 4-circle diff. | Weissenberg | 4-circle diff. |
| Model | *D*10 | | Philips PW 1100 | Siemens AED | Siemens AED | Siemens AED | Picker FACS-I | | Siemens AED |
| Laboratory | ILL | Toronto | CNRS, Grenoble | ILL | ILL | Bordeaux | Toronto | Tokyo | ILL |
| Radiation | | | | | | | | | |
| Nature | Neutrons | X-rays | X-rays | X-rays | X-rays | X-rays | X-rays | X-rays | X-rays |
| Wavelength (Å) | 1·452; 1·439 | Mo *Kα* | Cu *Kα* | Cu *Kα* | Cu *Kα* | Cu *Kα* | ? | Cu *Kα* | Cu *Kα* |
| Monochromator | Cu(111); Cu(200) | Graphite | | | | | | | |
| Cryostat/furnace | Helium | $N_2$ gas flow | $N_2$ gas flow(f) | $N_2$ gas flow(e) | $N_2$ gas flow(e) | | | | $N_2$ gas flow(e) |
| Cell parameters used for the structure refinements | | | | | | | | | |
| $a$(Å) | 14·215 (4) | 14·187 (8)(g) | 14·226 | 14·237 | 14·268 | 14·328 | 14·313(g) | 14·440 (10)(g) | 14·375 |
| $b$(Å) | 7·826 (3) | 7·727 (9) | 7·843 | 7·857 | 7·871 | 7·886 | 7·882 | 7·885 (10) | 7·898 |
| $c$(Å) | 13·192 (3) | 13·179 (12) | 13·282 | 13·410 | 13·538 | 13·678 | 13·678 | 13·711 (20) | 13·790 |
| $\alpha$(°) | 69·67 (3) | 69·90 (10) | 69·77 | 69·90 | 69·71 | 69·59 | 69·60 | 69·61 (4) | 69·54 |
| $\beta$(°) | 84·11 (3) | 84·10 (9) | 83·93 | 83·50 | 83·05 | 82·62 | 82·64 | 82·33 (4) | 82·27 |
| $\gamma$(°) | 73·66 (3) | 73·57 (7) | 73·55 | 73·22 | 72·94 | 72·75 | 72·75 | 71·94 (7) | 72·64 |
| Volume (Å$^3$) | 1320·5 | 1301·13 | 1333·5 | 1348·5 | 1363·0 | 1382·8 | 1380·5 | 1390·3 | 1399·3 |
| Measured reflections | | | | | | | | | |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0·68 | 0·7045 | 0·7045 | 0·613 | 0·609 | 0·609 | | | 0·609 |
| No. of independent obs. reflections | 4054 | 2719 | 3953 | 3926 | 3660 | 2782 | 3869 | 2308 | 2806 |
| Sample dimensions (mm$^3$) | 8·5; 11·5 | | (0·2 × 0·2 × 0·2) | (0·2 × 0·2 × 0·2) | (0·2 × 0·2 × 0·2) | | | < (0·3 × 0·3 × 0·3) | (0·2 × 0·2 × 0·2) |
| Refinements | | | | | | | | | |
| Absorption correction | Yes | | | | | | | | |
| Extinction correction | Yes | Yes | | | | | | | |
| Analysis of disorder | Yes | Partial | Partial | Partial | No | No | No | No | No |
| $R = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum F_o^2]^{1/2}$ | 0·080 | 0·120 | 0·107 | 0·064 | 0·071 | 0·068 | 0·071 | 0·123 | 0·066 |

Notes: (*a*) Filhol *et al.* (1980). (*b*) Potworowski (1974). (*c*) Jaud *et al.* (1974), reprocessed data. (*d*) Room temperature. Kobayashi *et al.* (1970). (*e*) Renaud & Fourme (1971), assembly modified by us. [See also André, Fourme & Renaud (1967).] (*f*) Manufactured by Leybold–Heraeus. (*g*) The values given here are the published cell parameters converted to cell axes ($a_J$, $b_J$, $c_J$) defined in Fig. 2 and used throughout the present paper.

Table 2. *Fractional coordinates* (×10$^4$), *equivalent isotropic temperature factors and population parameters*

For each atom successive lines are relative to data at 345, 295 [reprocessed data of Jaud *et al.* (1974)], 234, 173 and 110 K. E.s.d.'s are given in parentheses. $B_{\mathrm{eq}}=\frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. For H atoms $B$ values are given.

| | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| TCNQ($A$) | | | | |
| C(1) | 651 (2) | −827 (4) | 1152 (2) | 2·29 (1) |
| | 644 (3) | −830 (5) | 1153 (3) | 1·86 (1) |
| | 633 (2) | −839 (3) | 1151 (2) | 1·47 (1) |
| | 617 (2) | −845 (3) | 1151 (2) | 1·10 (1) |
| | 594 (3) | −853 (6) | 1167 (4) | 0·76 (1) |
| C(2) | −257 (2) | −1276 (4) | 1460 (3) | 2·33 (1) |
| | −267 (3) | −1276 (5) | 1464 (3) | 2·01 (1) |
| | −281 (2) | −1298 (3) | 1461 (2) | 1·50 (1) |
| | −301 (2) | −1310 (3) | 1462 (2) | 1·11 (1) |
| | −322 (3) | −1320 (6) | 1467 (4) | 0·70 (1) |
| C(3) | −1079 (2) | 31 (4) | 1583 (2) | 2·29 (1) |
| | −1090 (3) | 19 (5) | 1588 (3) | 1·91 (1) |
| | −1108 (2) | 11 (3) | 1588 (2) | 1·45 (1) |
| | −1129 (2) | −1 (3) | 1582 (2) | 1·11 (1) |
| | −1146 (3) | −6 (6) | 1583 (3) | 0·76 (1) |
| C(4) | −1064 (2) | 1917 (4) | 1417 (2) | 2·13 (1) |
| | −1072 (3) | 1908 (5) | 1417 (3) | 1·83 (1) |
| | −1093 (2) | 1909 (3) | 1410 (2) | 1·42 (1) |
| | −1111 (2) | 1897 (3) | 1405 (2) | 1·05 (1) |
| | −1122 (3) | 1879 (6) | 1398 (4) | 0·72 (1) |
| C(5) | −155 (2) | 2355 (4) | 1108 (2) | 2·27 (1) |
| | −162 (3) | 2357 (5) | 1104 (3) | 1·95 (1) |
| | −175 (2) | 2361 (3) | 1097 (2) | 1·53 (1) |
| | −196 (2) | 2362 (3) | 1092 (2) | 1·13 (1) |
| | −202 (3) | 2360 (6) | 1084 (4) | 0·72 (1) |
| C(6) | 663 (2) | 1060 (5) | 975 (3) | 2·34 (1) |
| | 659 (3) | 1062 (5) | 969 (3) | 1·98 (1) |
| | 651 (2) | 1056 (3) | 969 (2) | 1·52 (1) |
| | 633 (2) | 1053 (3) | 965 (2) | 1·15 (1) |
| | 618 (3) | 1065 (6) | 953 (4) | 0·74 (1) |
| C(7) | 1492 (2) | −2185 (5) | 1015 (3) | 2·48 (1) |
| | 1484 (3) | −2184 (5) | 1020 (3) | 2·09 (1) |
| | 1481 (2) | −2194 (4) | 1014 (2) | 1·62 (1) |
| | 1468 (2) | −2199 (3) | 1017 (2) | 1·20 (1) |
| | 1451 (3) | −2219 (6) | 1027 (4) | 0·81 (1) |
| C(8) | −1905 (2) | 3277 (4) | 1556 (3) | 2·22 (1) |
| | −1912 (3) | 3266 (5) | 1553 (3) | 1·91 (1) |
| | −1936 (2) | 3264 (3) | 1553 (2) | 1·50 (1) |
| | −1957 (2) | 3256 (3) | 1545 (2) | 1·17 (1) |
| | −1971 (3) | 3236 (6) | 1542 (4) | 0·82 (1) |
| C(9) | 2404 (3) | −1787 (5) | 716 (3) | 3·12 (1) |
| | 2404 (3) | −1792 (6) | 718 (3) | 2·60 (1) |
| | 2404 (2) | −1798 (4) | 710 (2) | 1·95 (1) |
| | 2390 (2) | −1796 (3) | 713 (2) | 1·41 (1) |
| | 2373 (3) | −1784 (6) | 724 (4) | 0·91 (1) |
| C(10) | 1487 (3) | −4047 (5) | 1178 (3) | 2·89 (1) |
| | 1483 (3) | −4068 (6) | 1185 (3) | 2·47 (1) |
| | 1470 (2) | −4077 (4) | 1187 (2) | 1·86 (1) |
| | 1455 (2) | −4092 (3) | 1194 (2) | 1·34 (1) |
| | 1439 (3) | −4115 (6) | 1204 (4) | 0·89 (1) |
| C(11) | −2826 (3) | 2886 (5) | 1842 (3) | 2·82 (1) |
| | −2837 (3) | 2884 (5) | 1844 (3) | 2·36 (1) |
| | −2854 (2) | 2874 (4) | 1848 (2) | 1·83 (1) |
| | −2878 (2) | 2853 (3) | 1847 (2) | 1·35 (1) |
| | −2889 (3) | 2840 (6) | 1842 (4) | 0·87 (1) |
| C(12) | −1901 (3) | 5141 (5) | 1402 (3) | 2·71 (1) |
| | −1915 (3) | 5142 (5) | 1403 (3) | 2·33 (1) |
| | −1932 (2) | 5149 (4) | 1394 (2) | 1·77 (1) |
| | −1950 (2) | 5144 (3) | 1385 (2) | 1·35 (1) |
| | −1959 (3) | 5145 (6) | 1361 (4) | 1·01 (1) |
| N(13) | 3159 (3) | −1517 (6) | 469 (3) | 4·63 (1) |
| | 3160 (3) | −1523 (6) | 469 (3) | 3·87 (1) |
| | 3154 (2) | −1513 (4) | 465 (2) | 2·85 (1) |
| | 3145 (2) | −1509 (3) | 467 (2) | 2·03 (1) |
| | 3130 (3) | −1519 (6) | 474 (4) | 1·30 (1) |
| N(14) | 1478 (3) | −5558 (5) | 1301 (3) | 4·13 (1) |
| | 1476 (3) | −5577 (5) | 1307 (3) | 3·52 (1) |
| | 1466 (2) | −5597 (3) | 1312 (2) | 2·61 (1) |
| | 1448 (2) | −5616 (3) | 1329 (2) | 1·88 (1) |
| | 1426 (3) | −5635 (6) | 1347 (4) | 1·32 (1) |
| N(15) | −3576 (2) | 2635 (6) | 2071 (3) | 4·37 (1) |
| | −3589 (3) | 2623 (6) | 2078 (3) | 3·69 (1) |
| | −3612 (2) | 2612 (4) | 2089 (2) | 2·82 (1) |
| | −3634 (2) | 2580 (4) | 2094 (2) | 2·13 (1) |
| | −3640 (3) | 2542 (6) | 2097 (4) | 1·55 (1) |
| N(16) | −1924 (3) | 6652 (4) | 1298 (3) | 3·80 (1) |
| | −1929 (3) | 6656 (5) | 1299 (3) | 3·28 (1) |
| | −1949 (2) | 6667 (3) | 1288 (2) | 2·50 (1) |
| | −1970 (2) | 6669 (3) | 1275 (2) | 1·92 (1) |
| | −1988 (3) | 6693 (6) | 1241 (4) | 1·38 (1) |

| | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| TCNQ($A$) | | | | |
| H(17) | −273 (23) | −2537 (44) | 1551 (25) | 5·62 (82) |
| | −283 (23) | −2505 (44) | 1590 (25) | 3·81 (74) |
| | −306 (20) | −2577 (39) | 1584 (22) | 4·05 (65) |
| | −316 (18) | −2607 (35) | 1593 (19) | 2·11 (49) |
| | −322 (39) | −2677 (77) | 1645 (44) | 2·60 |
| H(18) | −1740 (23) | −189 (44) | 1704 (24) | 5·43 (79) |
| | −1694 (24) | −207 (46) | 1743 (26) | 4·27 (80) |
| | −1720 (19) | −237 (37) | 1766 (21) | 3·56 (60) |
| | −1759 (19) | −281 (35) | 1769 (20) | 2·33 (51) |
| | −1770 (40) | −351 (75) | 1808 (44) | 2·60 |
| H(19) | −184 (26) | 3531 (51) | 1014 (28) | 7·21 (95) |
| | −143 (24) | 3546 (46) | 1031 (26) | 4·14 (77) |
| | −142 (21) | 3620 (40) | 979 (23) | 4·31 (67) |
| | −180 (19) | 3671 (38) | 990 (20) | 2·64 (53) |
| | −209 (39) | 3662 (77) | 933 (44) | 2·60 |
| H(20) | 1275 (25) | 1380 (49) | 791 (28) | 6·74 (92) |
| | 1256 (22) | 1276 (44) | 788 (25) | 3·62 (73) |
| | 1259 (19) | 1317 (37) | 778 (21) | 3·46 (59) |
| | 1266 (21) | 1332 (38) | 794 (22) | 3·06 (59) |
| | 1262 (41) | 1272 (76) | 831 (44) | 2·60 |

| | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| TCNQ($B$) | | | | |
| C(21) | −1789 (2) | 2632 (4) | 4039 (2) | 2·24 (1) |
| | −1804 (3) | 2644 (5) | 4034 (3) | 1·98 (1) |
| | −1818 (2) | 2639 (3) | 4032 (2) | 1·48 (1) |
| | −1833 (2) | 2648 (3) | 4026 (2) | 1·13 (1) |
| | −1837 (3) | 2652 (6) | 4015 (3) | 0·73 (1) |
| C(22) | −893 (2) | 3139 (4) | 3725 (3) | 2·34 (1) |
| | −902 (3) | 3149 (5) | 3719 (3) | 1·95 (1) |
| | −918 (2) | 3154 (3) | 3711 (2) | 1·53 (1) |
| | −930 (2) | 3163 (3) | 3703 (2) | 1·11 (1) |
| | −947 (3) | 3180 (6) | 3690 (3) | 0·74 (1) |
| C(23) | −63 (2) | 1887 (4) | 3581 (2) | 2·22 (1) |
| | −72 (3) | 1889 (5) | 3575 (3) | 1·91 (1) |
| | −83 (2) | 1894 (3) | 3566 (2) | 1·46 (1) |
| | −93 (2) | 1899 (3) | 3561 (2) | 1·07 (1) |
| | −103 (3) | 1911 (6) | 3549 (4) | 0·76 (1) |
| C(24) | −54 (2) | −25 (4) | 3745 (2) | 2·15 (1) |
| | −56 (3) | −30 (5) | 3744 (3) | 1·80 (1) |
| | −70 (2) | −32 (3) | 3740 (2) | 1·36 (1) |
| | −85 (2) | −22 (3) | 3734 (2) | 1·01 (1) |
| | −93 (3) | −16 (6) | 3732 (3) | 0·73 (1) |
| C(25) | −944 (2) | −528 (4) | 4066 (3) | 2·35 (1) |
| | −957 (3) | −526 (5) | 4060 (3) | 1·97 (1) |
| | −973 (2) | −543 (3) | 4064 (2) | 1·51 (1) |
| | −990 (2) | −539 (3) | 4058 (2) | 1·08 (1) |
| | −994 (3) | −543 (6) | 4059 (4) | 0·77 (1) |
| C(26) | −1776 (2) | 745 (5) | 4200 (3) | 2·45 (1) |
| | −1785 (3) | 743 (5) | 4192 (3) | 2·07 (1) |
| | −1809 (2) | 735 (3) | 4195 (2) | 1·54 (1) |
| | −1823 (2) | 735 (3) | 4189 (2) | 1·11 (1) |
| | −1821 (3) | 732 (6) | 4183 (3) | 0·74 (1) |
| C(27) | −2646 (2) | 3920 (5) | 4204 (3) | 2·66 (1) |
| | −2660 (3) | 3925 (5) | 4204 (3) | 2·26 (1) |
| | −2676 (2) | 3923 (4) | 4205 (2) | 1·75 (1) |
| | −2688 (2) | 3929 (3) | 4202 (2) | 1·30 (1) |
| | −2691 (3) | 3934 (6) | 4198 (4) | 0·92 (1) |
| C(28) | 801 (2) | −1342 (5) | 3603 (3) | 2·27 (1) |
| | 796 (3) | −1340 (5) | 3603 (3) | 1·90 (1) |
| | 784 (2) | −1350 (3) | 3604 (2) | 1·42 (1) |
| | 767 (2) | −1344 (3) | 3603 (2) | 1·06 (1) |
| | 756 (3) | −1326 (5) | 3612 (3) | 0·66 (1) |
| C(29) | −3538 (3) | 3412 (6) | 4534 (3) | 3·50 (1) |
| | −3551 (3) | 3412 (6) | 4535 (4) | 2·97 (1) |
| | −3571 (2) | 3408 (4) | 4535 (3) | 2·27 (1) |
| | −3582 (2) | 3403 (4) | 4535 (2) | 1·75 (1) |
| | −3584 (3) | 3383 (7) | 4547 (4) | 1·31 (1) |
| C(30) | −2680 (3) | 5815 (6) | 4067 (3) | 3·31 (1) |
| | −2683 (3) | 5820 (6) | 4064 (3) | 2·75 (1) |
| | −2703 (2) | 5823 (4) | 4070 (2) | 2·11 (1) |
| | −2713 (2) | 5826 (3) | 4075 (2) | 1·51 (1) |
| | −2708 (3) | 5843 (6) | 4068 (4) | 0·91 (1) |
| C(31) | 1710 (2) | −883 (5) | 3297 (3) | 2·74 (1) |
| | 1704 (3) | −893 (5) | 3298 (3) | 2·33 (1) |
| | 1697 (2) | −907 (4) | 3300 (2) | 1·75 (1) |
| | 1688 (2) | −903 (3) | 3304 (2) | 1·23 (1) |
| | 1682 (3) | −898 (6) | 3308 (3) | 0·85 (1) |

Table 2 (*cont.*)

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| TCNQ(*B*) | | | | |
| C(32) | 833 (2) | −3245 (5) | 3775 (3) | 2·69 (1) |
| | 821 (3) | −3247 (5) | 3776 (3) | 2·25 (1) |
| | 809 (2) | −3262 (4) | 3783 (2) | 1·71 (1) |
| | 792 (2) | −3261 (3) | 3786 (2) | 1·19 (1) |
| | 781 (3) | −3246 (6) | 3792 (3) | 0·77 (1) |
| N(33) | −4247 (3) | 2992 (6) | 4791 (4) | 5·13 (1) |
| | −4262 (3) | 2983 (7) | 4791 (4) | 4·50 (1) |
| | −4282 (2) | 2982 (5) | 4791 (3) | 3·53 (1) |
| | −4295 (2) | 2971 (4) | 4799 (3) | 2·79 (1) |
| | −4293 (3) | 2949 (8) | 4811 (5) | 2·25 (1) |
| N(34) | −2696 (3) | 7358 (5) | 3949 (4) | 4·78 (1) |
| | −2714 (3) | 7347 (5) | 3951 (4) | 4·05 (1) |
| | −2725 (2) | 7355 (4) | 3965 (3) | 3·02 (1) |
| | −2731 (2) | 7347 (3) | 3978 (2) | 2·19 (1) |
| | −2725 (3) | 7347 (6) | 3974 (4) | 1·40 (1) |
| N(35) | 2440 (2) | −550 (5) | 3053 (3) | 3·89 (1) |
| | 2442 (3) | −578 (6) | 3059 (3) | 3·37 (1) |
| | 2445 (2) | −595 (4) | 3064 (2) | 2·55 (1) |
| | 2440 (2) | −611 (3) | 3075 (2) | 1·79 (1) |
| | 2433 (3) | −591 (6) | 3078 (3) | 1·24 (1) |
| N(36) | 859 (3) | −4761 (4) | 3905 (3) | 3·85 (1) |
| | 855 (3) | −4782 (5) | 3911 (3) | 3·20 (1) |
| | 843 (2) | −4798 (3) | 3919 (2) | 2·39 (1) |
| | 830 (2) | −4806 (3) | 3927 (2) | 1·71 (1) |
| | 818 (3) | −4814 (6) | 3947 (3) | 1·19 (1) |
| H(37) | −892 (23) | 4417 (44) | 3655 (24) | 5·52 (81) |
| | −906 (24) | 4453 (46) | 3610 (26) | 4·28 (79) |
| | −912 (20) | 4467 (39) | 3594 (22) | 4·12 (65) |
| | −915 (18) | 4470 (35) | 3593 (20) | 2·47 (52) |
| | −962 (39) | 4510 (74) | 3550 (43) | 2·60 |
| H(38) | 542 (22) | 2265 (42) | 3429 (24) | 4·87 (76) |
| | 526 (24) | 2214 (46) | 3358 (26) | 4·34 (79) |
| | 484 (19) | 2262 (36) | 3352 (20) | 3·23 (58) |
| | 525 (17) | 2236 (33) | 3354 (19) | 2·13 (48) |
| | 540 (39) | 2185 (75) | 3318 (43) | 2·60 |
| H(39) | −928 (22) | −1737 (42) | 4168 (24) | 4·85 (77) |
| | −934 (23) | −1774 (44) | 4144 (25) | 3·54 (71) |
| | −981 (19) | −1832 (37) | 4151 (21) | 3·44 (59) |
| | −1002 (17) | −1762 (35) | 4150 (19) | 1·99 (48) |
| | −973 (39) | −1822 (75) | 4165 (43) | 2·60 |
| H(40) | −2388 (24) | 393 (46) | 4388 (26) | 6·06 (86) |
| | −2339 (21) | 420 (40) | 4356 (22) | 2·75 (64) |
| | −2413 (20) | 386 (38) | 4368 (21) | 3·59 (61) |
| | −2427 (18) | 424 (33) | 4380 (19) | 1·89 (46) |
| | −2426 (40) | 418 (75) | 4374 (44) | 2·60 |

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) | p.p. |
|---|---|---|---|---|---|
| TEA (or TEA′ and TEA″) | | | | | |
| N(41) | 4394 (4) | 887 (7) | 2357 (4) | 7·11 (2) | 1 |
| | 4396 (5) | 873 (8) | 2365 (4) | 6·62 (2) | 1 |
| | 4404 (4) | 870 (5) | 2384 (3) | 5·80 (1) | 1 |
| | 4653 (5) | 1063 (9) | 2293 (6) | 2·66 (1) | ½ |
| | 4232 (4) | 663 (9) | 2496 (5) | 1·98 (1) | ½ |
| | 4582 (10) | 1044 (14) | 2368 (10) | 2·03 (2) | ½ |
| | 4215 (6) | 610 (13) | 2521 (8) | 0·96 (2) | ½ |
| C(42) | 3925 (5) | 1868 (12) | 1428 (6) | 8·08 (3) | 1 |
| | 3891 (5) | 1820 (10) | 1427 (6) | 6·02 (2) | 1 |
| | 3859 (3) | 1773 (6) | 1443 (3) | 3·71 (1) | 1 |
| | 3843 (2) | 1774 (4) | 1433 (3) | 2·15 (1) | 1 |
| | 3826 (3) | 1782 (7) | 1426 (4) | 1·27 (1) | 1 |
| C(43) | 4336 (5) | 1478 (13) | 3239 (6) | 7·68 (3) | 1 |
| | 4326 (5) | 1524 (13) | 3237 (6) | 6·56 (3) | 1 |
| | 4289 (4) | 1573 (9) | 3249 (4) | 5·10 (2) | 1 |
| | 4235 (3) | 1688 (7) | 3271 (3) | 3·60 (1) | 1 |
| | 4224 (4) | 1726 (9) | 3281 (5) | 1·88 (1) | 1 |
| C(44) | 5240 (6) | −745 (10) | 2397 (9) | 10·31 (3) | 1 |
| | 5236 (7) | −755 (10) | 2374 (9) | 9·16 (3) | 1 |
| | 5235 (5) | −779 (7) | 2402 (7) | 7·89 (2) | 1 |
| | 5149 (4) | −829 (6) | 2532 (6) | 5·47 (1) | 1 |
| | 5108 (6) | −894 (10) | 2606 (7) | 3·36 (2) | 1 |
| C(45) | 4233 (6) | 3108 (12) | 541 (7) | 9·62 (3) | 1 |
| | 4248 (6) | 3096 (12) | 564 (7) | 8·35 (3) | 1 |
| | 4247 (4) | 3157 (8) | 574 (5) | 6·05 (2) | 1 |
| | 4257 (3) | 3223 (6) | 596 (4) | 3·85 (1) | 1 |
| | 4141 (13) | 3391 (35) | 505 (14) | 1·94 (4) | ½ |
| | 4432 (17) | 3172 (34) | 660 (17) | 2·00 (3) | ½ |
| C(46) | 3592 (8) | 2899 (18) | 3398 (9) | 11·34 (5) | 1 |
| | 3565 (8) | 2990 (17) | 3374 (9) | 9·80 (5) | 1 |
| | 3543 (6) | 3176 (15) | 3292 (7) | 9·35 (4) | 1 |
| | 3754 (10) | 3762 (18) | 3083 (10) | 4·59 (3) | ½ |
| | 3344 (8) | 3100 (17) | 3300 (10) | 3·67 (3) | ½ |
| | 3773 (13) | 3733 (25) | 3128 (16) | 3·17 (4) | ½ |
| | 3307 (10) | 3230 (19) | 3245 (11) | 1·81 (3) | ½ |
| C(47) | 5147 (6) | −2335 (11) | 2327 (7) | 8·38 (3) | 1 |
| | 5132 (6) | −2355 (11) | 2299 (7) | 7·27 (3) | 1 |
| | 5155 (5) | −2376 (8) | 2272 (6) | 6·41 (2) | 1 |
| | 5512 (8) | −1721 (24) | 1911 (8) | 5·53 (4) | ½ |
| | 5088 (5) | −2446 (9) | 2320 (7) | 2·26 (1) | ½ |
| | 5506 (11) | −1786 (30) | 1903 (13) | 3·23 (5) | ½ |
| | 5081 (10) | −2443 (18) | 2251 (13) | 1·89 (3) | ½ |

discussion below does not consider the least accurate data, *i.e.* Kobayashi *et al.* (1970) and the 108 K structure from Potworowski (1974) which has been refined using cell parameters of poor accuracy and in bad agreement with ours.

To help the reader, we briefly recall here the major features of the structure of TEA–(TCNQ)$_2$ (Fig. 1). The crystal is triclinic, $P\bar{1}$, with $Z=2$ and a TEA cation and one [TCNQ(*A*), TCNQ(*B*)] anion in the asymmetric unit. The planar TCNQ molecules (*A* and *B*) are stacked face to face with the repeat sequence *BAAB* leading to three independent spacing distances ($d_{AA}$, $d_{BB}$, $d_{AB}$) and three independent overlapping modes. The packing may thus be described as a set of TCNQ columns (in effect, a stack of tetrads) parallel to **c** and spaced in the **a** direction by chains of TEA cations. The TEA molecules exhibit a twofold disorder and the corresponding species (TEA′ and TEA″) are not symmetrical. Two half-populated hydrogen bonds [N(15)···H–N(41)′ and N(35)···H–N(41)″] link molecules TCNQ(*A*) to TEA′ and TCNQ(*B*) to TEA″ respectively. No major modification of this arrangement with temperature has been reported up to now. However, the evolution with temperature deserves a more detailed discussion.

### (i) *TCNQ molecules*

The bond lengths and angles at each temperature are listed in Tables 3 and 4 while the corresponding values averaged over chemically equivalent species are indicated in Table 5. X-ray data show no apparent shortening of bond lengths due to the thermal motion (riding model) even for the C≡N bonds. On the contrary, the mean length of the C≡N bonds is found to be 0·015 Å shorter from X-ray than from neutron data. This is clearly due to the non-coincidence of the atomic nucleus and charge centroid. Becker, Coppens & Ross (1973) have observed a slightly smaller shift (0·0085 Å) for the C≡N bonds of the neutral tetracyanoethylene, a value which is attributed mainly to the charge displacement of the C atom towards the N atom. In the case of TEA–(TCNQ)$_2$, each TCNQ anion bears on average half an electron which is perhaps responsible for the largest shift of the charge centroid observed for this compound.

Table 3. *Bond lengths* (Å)

For the TEA molecule, if disorder is not taken into account, the observed bond lengths are mean values of little significance. Thus we give only the distances between corresponding atoms of the TEA′ and TEA″ species, when available. The e.s.d.'s are given in parentheses.

| | 345 ± 3 K | 298 K[(a)] | 295 ± 2 K[(b)] | 234 ± 3 K | 173 ± 3 K | 110 ± 5 K | 40 ± 0·5 K[(c)] |
|---|---|---|---|---|---|---|---|
| TCNQ(*A*) | | | | | | | |
| C(1)–C(2) | 1·425 (6) | 1·410 (4) | 1·425 (6) | 1·431 (4) | 1·437 (4) | 1·432 (7) | 1·433 (3) |
| C(2)–C(3) | 1·354 (6) | 1·355 (4) | 1·348 (6) | 1·357 (3) | 1·358 (3) | 1·359 (6) | 1·375 (2) |
| C(3)–C(4) | 1·433 (6) | 1·428 (4) | 1·432 (6) | 1·435 (4) | 1·434 (4) | 1·423 (7) | 1·440 (3) |
| C(4)–C(5) | 1·423 (6) | 1·420 (3) | 1·425 (6) | 1·433 (4) | 1·432 (4) | 1·444 (7) | 1·440 (3) |
| C(5)–C(6) | 1·349 (6) | 1·349 (4) | 1·350 (6) | 1·356 (3) | 1·361 (3) | 1·353 (6) | 1·371 (3) |
| C(6)–C(1) | 1·430 (6) | 1·433 (4) | 1·430 (6) | 1·433 (4) | 1·431 (4) | 1·441 (7) | 1·435 (3) |
| C(1)–C(7) | 1·398 (6) | 1·399 (4) | 1·392 (6) | 1·401 (3) | 1·402 (3) | 1·420 (6) | 1·404 (3) |
| C(4)–C(8) | 1·399 (6) | 1·400 (3) | 1·395 (6) | 1·398 (3) | 1·404 (3) | 1·411 (6) | 1·401 (3) |
| C(7)–C(9) | 1·414 (7) | 1·420 (4) | 1·420 (7) | 1·423 (4) | 1·422 (4) | 1·430 (7) | 1·423 (3) |
| C(7)–C(10) | 1·411 (6) | 1·425 (4) | 1·422 (7) | 1·423 (4) | 1·429 (4) | 1·427 (7) | 1·422 (3) |
| C(8)–C(11) | 1·422 (6) | 1·422 (4) | 1·421 (7) | 1·413 (4) | 1·420 (4) | 1·412 (7) | 1·420 (3) |
| C(8)–C(12) | 1·415 (6) | 1·422 (4) | 1·419 (7) | 1·425 (4) | 1·426 (4) | 1·437 (7) | 1·422 (3) |
| C(9)–N(13) | 1·153 (7) | 1·151 (4) | 1·150 (8) | 1·143 (4) | 1·149 (4) | 1·148 (7) | 1·170 (2) |
| C(10)–N(14) | 1·149 (7) | 1·142 (4) | 1·146 (7) | 1·150 (4) | 1·150 (4) | 1·146 (7) | 1·170 (2) |
| C(11)–N(15) | 1·138 (7) | 1·146 (4) | 1·141 (7) | 1·147 (4) | 1·148 (4) | 1·149 (7) | 1·167 (3) |
| C(12)–N(16) | 1·142 (6) | 1·144 (4) | 1·146 (7) | 1·147 (4) | 1·148 (4) | 1·149 (7) | 1·164 (3) |
| C(2)–H(17) | 0·97 (4) | | 0·93 (4) | 0·97 (3) | 0·98 (3) | 1·01 (6) | 1·084 (5) |
| C(3)–H(18) | 1·00 (4) | | 0·92 (4) | 0·94 (3) | 0·97 (3) | 0·99 (5) | 1·093 (5) |
| C(5)–H(19) | 0·88 (5) | | 0·92 (4) | 0·96 (3) | 1·00 (3) | 0·97 (6) | 1·102 (5) |
| C(6)–H(20) | 0·96 (5) | | 0·91 (4) | 0·94 (3) | 0·97 (3) | 0·96 (6) | 1·092 (5) |
| TCNQ(*B*) | | | | | | | |
| C(21)–C(22) | 1·429 (6) | 1·428 (4) | 1·433 (6) | 1·432 (4) | 1·435 (4) | 1·422 (7) | 1·440 (3) |
| C(22)–C(23) | 1·346 (6) | 1·353 (4) | 1·347 (6) | 1·351 (3) | 1·356 (3) | 1·368 (6) | 1·364 (3) |
| C(23)–C(24) | 1·444 (6) | 1·419 (3) | 1·442 (6) | 1·446 (4) | 1·442 (4) | 1·442 (7) | 1·441 (3) |
| C(24)–C(25) | 1·421 (6) | 1·436 (3) | 1·430 (6) | 1·435 (4) | 1·438 (3) | 1·436 (7) | 1·442 (3) |
| C(25)–C(26) | 1·353 (6) | 1·349 (4) | 1·344 (7) | 1·354 (3) | 1·353 (3) | 1·348 (6) | 1·365 (2) |
| C(26)–C(21) | 1·424 (6) | 1·430 (4) | 1·430 (7) | 1·434 (4) | 1·438 (4) | 1·438 (7) | 1·438 (3) |
| C(21)–C(27) | 1·394 (6) | 1·397 (4) | 1·391 (7) | 1·395 (3) | 1·393 (3) | 1·400 (6) | 1·406 (3) |
| C(24)–C(28) | 1·396 (6) | 1·394 (3) | 1·387 (6) | 1·390 (3) | 1·390 (3) | 1·382 (6) | 1·391 (2) |
| C(27)–C(29) | 1·427 (7) | 1·418 (4) | 1·423 (8) | 1·426 (4) | 1·428 (4) | 1·437 (7) | 1·420 (3) |
| C(27)–C(30) | 1·429 (7) | 1·428 (5) | 1·429 (7) | 1·432 (5) | 1·430 (4) | 1·440 (7) | 1·424 (3) |
| C(28)–C(31) | 1·430 (6) | 1·419 (4) | 1·421 (7) | 1·423 (4) | 1·432 (4) | 1·433 (7) | 1·421 (3) |
| C(28)–C(32) | 1·425 (6) | 1·418 (4) | 1·428 (8) | 1·430 (4) | 1·431 (4) | 1·431 (7) | 1·433 (3) |
| C(29)–N(33) | 1·140 (8) | 1·140 (4) | 1·142 (8) | 1·138 (5) | 1·144 (4) | 1·137 (8) | 1·168 (3) |
| C(30)–N(34) | 1·166 (7) | 1·145 (5) | 1·147 (8) | 1·156 (5) | 1·150 (4) | 1·136 (7) | 1·163 (3) |
| C(31)–N(35) | 1·138 (7) | 1·143 (4) | 1·138 (7) | 1·147 (4) | 1·146 (4) | 1·148 (6) | 1·169 (2) |
| C(32)–N(36) | 1·138 (6) | 1·145 (4) | 1·145 (7) | 1·145 (4) | 1·148 (4) | 1·162 (7) | 1·165 (2) |
| C(22)–H(37) | 0·98 (4) | | 0·98 (4) | 0·99 (3) | 0·99 (3) | 0·99 (6) | 1·083 (5) |
| C(23)–H(38) | 0·98 (4) | | 0·95 (4) | 0·92 (3) | 0·97 (3) | 0·99 (6) | 1·086 (5) |
| C(25)–H(39) | 0·91 (4) | | 0·94 (4) | 0·98 (3) | 0·93 (3) | 0·96 (6) | 1·088 (5) |
| C(26)–H(40) | 0·98 (4) | | 0·88 (4) | 0·96 (3) | 0·95 (3) | 0·95 (6) | 1·088 (5) |
| TEA′ and TEA″ | | | | | | | |
| N(41)′–N(41)″ | | | | | 0·74 (1) | 0·68 (2) | 0·64 |
| C(42)′–C(42)″ | | | | | | | 0·11 |
| C(43)′–C(43)″ | | | | | | | 0·28 |
| C(44)′–C(44)″ | | | | | | | 0·53 |
| C(45)′–C(45)″ | | | | | | | 0·40 |
| C(46)′–C(46)″ | | | | | 0·85 (2) | 0·83 (3) | 0·91 |
| C(47)′–C(47)″ | | | | | 0·95 (2) | 0·89 (2) | 0·93 |

Notes: (*a*) Potworowski (1974). (*b*) Jaud *et al.* (1974), reprocessed data. (*c*) Filhol *et al.* (1980).

The conformation of TCNQ(*A* and *B*) molecules is found to be slightly temperature dependent (Fig. 7). At all temperatures the TCNQ(*A*) molecules are close to planar except for a torsional angle* of the C(4)–(C≡N)$_2$ group around the C(4)–C(8) bond, the magnitude of which increases with *T* [0·3(1)° at 40 K, 1·2(1)° at 345 K]. The quinonoid ring of TCNQ(*B*) molecules shows a boat-like conformation which is especially visible at low temperatures. The C(21)–(C≡N)$_2$ group has the larger out-of-plane deviation [1·2(1)° at 40 K, 3·3(1)° at 345 K].

### (ii) *TEA molecules*

Because of the atomic thermal motion, the twofold disorder of the TEA cations is increasingly difficult to resolve at high temperatures. Thus, the detailed behaviour with temperature of the TEA′ and TEA″ species is not described here. The disorder at the TEA

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* For a given TCNQ molecule, the angle between the least-squares mean planes of the quinonoid ring and of a cyanomethylene group has been split into its torsional and inclination (out-of-plane) components.

Table 4. *Bond angles (°) for the TCNQ molecules only*

E.s.d.'s are given in parentheses.

| | 345 K | 298 K$^{(a)}$ | 295 K$^{(b)}$ | 234 K | 173 K | 110 K | 40 K$^{(c)}$ |
|---|---|---|---|---|---|---|---|
| TCNQ(*A*) | | | | | | | |
| C(6)–C(1)–C(2) | 117·5 (4) | 117·8 (2) | 117·6 (4) | 118·0 (2) | 117·8 (2) | 118·6 (4) | 118·3 (2) |
| C(3)–C(4)–C(5) | 117·2 (4) | 117·8 (2) | 117·6 (4) | 117·5 (2) | 117·9 (2) | 118·3 (4) | 117·8 (2) |
| C(1)–C(2)–C(3) | 121·4 (4) | 121·6 (2) | 121·9 (4) | 121·3 (3) | 121·4 (2) | 121·1 (5) | 121·2 (2) |
| C(2)–C(3)–C(4) | 121·0 (4) | 120·7 (2) | 120·5 (4) | 120·9 (2) | 120·8 (2) | 120·7 (4) | 120·7 (2) |
| C(4)–C(5)–C(6) | 121·9 (4) | 121·4 (2) | 121·8 (4) | 121·7 (3) | 121·4 (2) | 121·3 (5) | 121·4 (2) |
| C(5)–C(6)–C(1) | 120·9 (4) | 120·8 (2) | 120·6 (4) | 120·6 (3) | 120·8 (2) | 120·0 (4) | 120·6 (2) |
| C(6)–C(1)–C(7) | 121·6 (4) | 120·8 (2) | 121·4 (4) | 121·1 (2) | 121·1 (2) | 120·4 (4) | 120·7 (2) |
| C(2)–C(1)–C(7) | 120·8 (4) | 121·4 (2) | 121·1 (4) | 121·0 (3) | 121·1 (2) | 121·0 (5) | 120·9 (2) |
| C(3)–C(4)–C(8) | 121·6 (4) | 121·3 (2) | 121·4(4) | 121·5 (2) | 121·4 (2) | 120·9 (4) | 121·2 (2) |
| C(5)–C(4)–C(8) | 121·1 (4) | 120·9 (2) | 121·0 (4) | 121·0 (2) | 120·8 (2) | 120·8 (4) | 121·0 (2) |
| C(1)–C(7)–C(9) | 122·2 (4) | 123·1 (3) | 122·6 (4) | 122·7 (3) | 122·8 (2) | 122·1 (5) | 123·0 (2) |
| C(1)–C(7)–C(10) | 122·1 (4) | 121·4 (3) | 122·3 (4) | 121·5 (2) | 121·3 (2) | 121·7 (4) | 121·3 (2) |
| C(4)–C(8)–C(11) | 122·2 (4) | 122·4 (2) | 122·7 (4) | 122·6 (3) | 122·4 (2) | 123·0 (5) | 122·4 (2) |
| C(4)–C(8)–C(12) | 122·4 (4) | 122·6 (2) | 122·7 (4) | 122·3 (2) | 122·2 (2) | 121·6 (4) | 122·5 (2) |
| C(9)–C(7)–C(10) | 115·7 (4) | 115·5 (3) | 115·1 (4) | 115·7 (2) | 115·9 (2) | 116·3 (4) | 115·6 (2) |
| C(11)–C(8)–C(12) | 115·4 (4) | 114·9 (2) | 114·6 (4) | 115·2 (2) | 115·4 (2) | 115·5 (4) | 115·0 (2) |
| C(7)–C(9)–N(13) | 117·8 (6) | 178·8 (3) | 178·1 (6) | 178·7 (3) | 178·5 (3) | 176·7 (5) | 178·0 (2) |
| C(7)–C(10)–N(14) | 179·3 (5) | 179·2 (3) | 179·2 (6) | 179·0 (3) | 179·5 (3) | 179·5 (5) | 179·1 (2) |
| C(8)–C(11)–N(15) | 177·6 (5) | 177·9 (3) | 178·2 (6) | 177·9 (3) | 177·9 (3) | 178·7 (6) | 178·2 (3) |
| C(8)–C(12)–N(16) | 177·8 (5) | 178·9 (3) | 178·6 (6) | 178·1 (3) | 177·9 (3) | 176·9 (5) | 178·3 (3) |
| C(1)–C(2)–H(17) | 118 (2) | | 118 (3) | 119 (2) | 118 (1) | 118 (2) | 119·9 (3) |
| C(4)–C(3)–H(18) | 115 (2) | | 116 (3) | 116 (2) | 117 (2) | 118 (3) | 120·1 (3) |
| C(4)–C(5)–H(19) | 114 (3) | | 118 (3) | 119 (2) | 118 (1) | 116 (3) | 119·2 (3) |
| C(1)–C(6)–H(20) | 119 (3) | | 115 (3) | 116 (2) | 117 (2) | 115 (3) | 120·4 (3) |
| C(3)–C(2)–H(17) | 121 (2) | | 120 (3) | 120 (2) | 120 (1) | 120 (2) | 118·9 (3) |
| C(2)–C(3)–H(18) | 123 (2) | | 124 (3) | 123 (2) | 122 (2) | 121 (3) | 119·1 (3) |
| C(6)–C(5)–H(19) | 124 (3) | | 121 (3) | 119 (2) | 121 (1) | 122 (3) | 119·4 (3) |
| C(5)–C(6)–H(20) | 120 (3) | | 125 (3) | 123 (2) | 122 (2) | 124 (3) | 119·0 (3) |
| TCNQ(*B*) | | | | | | | |
| C(26)–C(21)–C(22) | 117·7 (4) | 117·6 (2) | 117·2 (4) | 117·9 (2) | 117·6 (2) | 117·4 (4) | 118·2 (2) |
| C(23)–C(24)–C(25) | 117·8 (4) | 117·7 (2) | 117·1 (4) | 117·6 (2) | 117·9 (2) | 117·9 (4) | 118·2 (2) |
| C(21)–C(22)–C(23) | 121·6 (4) | 121·3 (2) | 121·5 (4) | 121·4 (3) | 121·5 (2) | 121·5 (4) | 121·0 (2) |
| C(22)–C(23)–C(24) | 120·4 (4) | 121·2 (2) | 121·1 (4) | 120·8 (2) | 120·7 (2) | 120·5 (4) | 120·8 (2) |
| C(24)–C(25)–C(26) | 121·3 (4) | 121·3 (2) | 121·4 (4) | 121·2 (3) | 121·1 (2) | 120·8 (4) | 120·9 (2) |
| C(25)–C(26)–C(21) | 121·2 (4) | 121·0 (2) | 121·7 (4) | 121·1 (3) | 121·3 (2) | 122·0 (4) | 121·0 (2) |
| C(26)–C(21)–C(27) | 120·7 (4) | 120·9 (2) | 120·9 (4) | 120·4 (3) | 120·7 (2) | 121·2 (4) | 120·5 (2) |
| C(22)–C(21)–C(27) | 121·6 (4) | 121·5 (2) | 121·9 (4) | 121·7 (3) | 121·7 (2) | 121·4 (4) | 121·3 (2) |
| C(23)–C(24)–C(28) | 122·2 (4) | 121·9 (2) | 121·6 (4) | 121·5 (2) | 121·5 (2) | 121·3 (4) | 121·4 (2) |
| C(25)–C(24)–C(28) | 122·4 (4) | 120·5 (2) | 121·3 (4) | 120·9 (2) | 120·6 (2) | 120·8 (4) | 120·5 (2) |
| C(21)–C(27)–C(29) | 121·8 (4) | 121·0 (3) | 121·9 (5) | 121·8 (3) | 121·5 (2) | 121·0 (5) | 121·3 (2) |
| C(21)–C(27)–C(30) | 122·1 (4) | 121·8 (3) | 121·4 (5) | 121·7 (3) | 122·0 (2) | 121·6 (4) | 121·8 (2) |
| C(24)–C(28)–C(31) | 122·2 (4) | 122·2 (2) | 122·6 (4) | 122·6 (3) | 122·6 (2) | 123·5 (4) | 122·9 (2) |
| C(24)–C(28)–C(32) | 122·4 (4) | 122·5 (2) | 121·9 (4) | 122·1 (2) | 122·3 (2) | 122·2 (4) | 122·1 (2) |
| C(29)–C(27)–C(30) | 116·1 (4) | 117·2 (3) | 116·8 (5) | 116·5 (2) | 116·5 (2) | 117·4 (4) | 116·9 (2) |
| C(31)–C(28)–C(32) | 115·5 (4) | 115·3 (2) | 115·5 (4) | 115·3 (2) | 115·1 (2) | 114·4 (3) | 115·0 (2) |
| C(27)–C(29)–N(33) | 179·2 (6) | 179·7 (4) | 178·9 (6) | 179·1 (4) | 179·5 (4) | 179·2 (6) | 178·9 (3) |
| C(27)–C(30)–N(34) | 179·1 (6) | 179·2 (4) | 179·2 (6) | 179·7 (3) | 179·6 (3) | 179·4 (5) | 178·9 (3) |
| C(28)–C(31)–N(35) | 178·7 (5) | 178·8 (4) | 178·4 (6) | 178·4 (3) | 177·8 (2) | 178·6 (4) | 177·5 (2) |
| C(28)–C(32)–N(36) | 179·6 (5) | 178·6 (3) | 179·0 (6) | 178·9 (3) | 178·7 (2) | 178·6 (5) | 178·0 (2) |
| C(21)–C(22)–H(37) | 118 (1) | | 118 (3) | 119 (2) | 119 (1) | 117 (3) | 119·6 (3) |
| C(24)–C(23)–H(38) | 121 (2) | | 117 (3) | 119 (2) | 118 (1) | 114 (3) | 119·1 (3) |
| C(24)–C(25)–H(39) | 117 (3) | | 116 (3) | 118 (2) | 119 (1) | 118 (2) | 119·5 (3) |
| C(21)–C(26)–H(40) | 119 (3) | | 118 (2) | 119 (2) | 117 (1) | 116 (2) | 120·0 (3) |
| C(23)–C(22)–H(37) | 121 (2) | | 121 (3) | 120 (2) | 119 (1) | 122 (3) | 119·3 (3) |
| C(22)–C(23)–H(38) | 119 (2) | | 122 (3) | 120 (2) | 122 (1) | 125 (3) | 120·0 (3) |
| C(26)–C(25)–H(39) | 122 (3) | | 123 (3) | 120 (2) | 120 (1) | 122 (2) | 119·6 (3) |
| C(25)–C(26)–H(40) | 120 (3) | | 120 (2) | 120 (2) | 122 (2) | 122 (3) | 119·1 (3) |

Notes: (*a*) Potworowski (1974). (*b*) Jaud *et al.* (1974), reprocessed data. (*c*) Filhol *et al.* (1980).

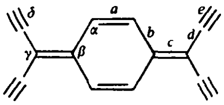
site is assumed to be random as no evidence of diffuse scattering corresponding to a degree of ordering of the species has ever been reported. Furthermore, we may recall here that crystallographic data alone do not allow us to choose between a static and a dynamic model of disorder.

### (iii) *Atomic thermal motion*

The atomic thermal motion ellipsoids of TEA–(TCNQ)$_2$ are displayed in Fig. 6. In spite of measurements made under a variety of experimental conditions (Table 1), the observed thermal ellipsoids for

Table 5. *Mean values for chemically equivalent bond lengths* (Å) *and angles* (°) *and values* ($\rho$) *for the estimated charge transfer*

$\rho_t$ is the total value of the charge transfer estimated from bond length (Flandrois & Chasseau 1977). $\rho_A$ and $\rho_B$ are the charge transfer values normalized to $\rho_t = 1$ for the TCNQ(*A*) and TCNQ(*B*) molecules. E.s.d.'s are given in parentheses.



| | 345 K | 298 K$^{(a)}$ | 295 K$^{(b)}$ | 234 K | 173 K | 110 K | 108 K$^{(a)}$ | 40 K$^{(c)}$ |
|---|---|---|---|---|---|---|---|---|
| TCNQ(*A*) | | | | | | | | |
| *a* | 1·351$_5$ (4) | 1·352 (3) | 1·349 (4) | 1·356$_5$ (2) | 1·359$_5$ (2) | 1·356 (4) | 1·358$_5$ (7) | 1·373 (2) |
| *b* | 1·427$_8$ (3) | 1·422$_5$ (2) | 1·428 (3) | 1·433 (2) | 1·433$_5$ (2) | 1·435 (4) | 1·415$_8$ (5) | 1·437 (2) |
| *c* | 1·398$_5$ (4) | 1·399$_5$ (3) | 1·393$_5$ (3) | 1·399$_5$ (2) | 1·403 (2) | 1·415$_5$ (4) | 1·392$_5$ (7) | 1·402$_5$ (2) |
| *d* | 1·415$_5$ (3) | 1·422$_3$ (2) | 1·420$_5$ (4) | 1·421 (2) | 1·424$_3$ (2) | 1·426$_5$ (4) | 1·410 (5) | 1·421$_8$ (2) |
| *e* | 1·145$_5$ (4) | 1·145$_8$ (2) | 1·145$_8$ (4) | 1·146$_8$ (2) | 1·148$_8$ (2) | 1·148 (4) | 1·147$_5$ (5) | 1·167$_8$ (2) |
| α | 121·1 (2) | 121·1 (1) | 121·2 (2) | 121·1 (2) | 121·1 (1) | 120·8 (2) | 120·8 (3) | 121·0 (1) |
| β | 117·4 (3) | 117·8 (2) | 117·6 (3) | 117·8 (1) | 117·9 (1) | 118·5 (3) | 118·5 (4) | 118·0 (1) |
| γ | 115·6 (3) | 115·2 (2) | 114·9 (2) | 114·9 (1) | 115·7 (1) | 115·9 (2) | 114·9 (5) | 115·3 (1) |
| δ | 178·1 (3) | 178·7 (2) | 178·5 (3) | 178·5 (2) | 178·5 (2) | 178·0 (3) | 178·6 (5) | 178·4 (1) |
| TCNQ(*B*) | | | | | | | | |
| *a* | 1·349$_5$ (4) | 1·351 (3) | 1·345$_5$ (4) | 1·352$_5$ (2) | 1·354$_5$ (2) | 1·358 (4) | 1·348$_5$ (6) | 1·364$_5$ (2) |
| *b* | 1·429$_5$ (3) | 1·428$_3$ (2) | 1·433$_8$ (3) | 1·436$_8$ (2) | 1·438$_3$ (2) | 1·434$_5$ (4) | 1·431$_5$ (5) | 1·440$_3$ (2) |
| *c* | 1·395 (4) | 1·395$_5$ (3) | 1·389 (4) | 1·392$_5$ (2) | 1·391$_5$ (2) | 1·391 (4) | 1·382$_5$ (7) | 1·398$_5$ (2) |
| *d* | 1·427$_8$ (4) | 1·420$_8$ (2) | 1·425$_3$ (4) | 1·427$_8$ (2) | 1·430$_3$ (2) | 1·435$_3$ (4) | 1·410$_8$ (5) | 1·424$_5$ (2) |
| *e* | 1·145$_5$ (4) | 1·143$_3$ (2) | 1·143 (4) | 1·146$_5$ (2) | 1·147 (2) | 1·145$_8$ (4) | 1·143$_3$ (5) | 1·166$_3$ (2) |
| α | 121·1 (2) | 121·2 (1) | 121·4 (2) | 121·1 (1) | 121·1 (1) | 121·2 (2) | 121·5 (3) | 121·0 (1) |
| β | 117·8 (3) | 117·6 (2) | 117·2 (3) | 117·8 (1) | 117·8 (1) | 117·7 (3) | 117·0 (4) | 118·2 (1) |
| γ | 115·8 (3) | 116·3 (2) | 116·2 (3) | 115·9 (1) | 115·9 (1) | 115·9 (3) | 116·4 (5) | 116·0 (1) |
| δ | 179·2 (3) | 179·1 (2) | 178·9 (3) | 179·0 (2) | 178·9 (1) | 179·0 (3) | 178·3 (5) | 178·3 (1) |
| Charge transfer (e) | | | | | | | | |
| $\rho_t$ | 1·14 | 1·21 | 0·92 | 0·98 | 0·96 | 1·14 | 1·08 | 0·94 |
| $\rho_A$ | 0·57 (5) | 0·54 (4) | 0·58 (5) | 0·60 (3) | 0·64 (3) | 0·72 (6) | 0·61 (7) | 0·56 (3) |
| $\rho_B$ | 0·43 (5) | 0·46 (4) | 0·42 (5) | 0·40 (3) | 0·36 (3) | 0·28 (6) | 0·39 (7) | 0·44 (3) |

Corresponding mean values: $\bar{\rho}_A = 0{\cdot}60\,(2)$; $\bar{\rho}_B = 0{\cdot}40\,(2)$.

Notes: (*a*) Potworowski (1974). (*b*) Jaud *et al.* (1974). (*c*) Filhol *et al.* (1980).

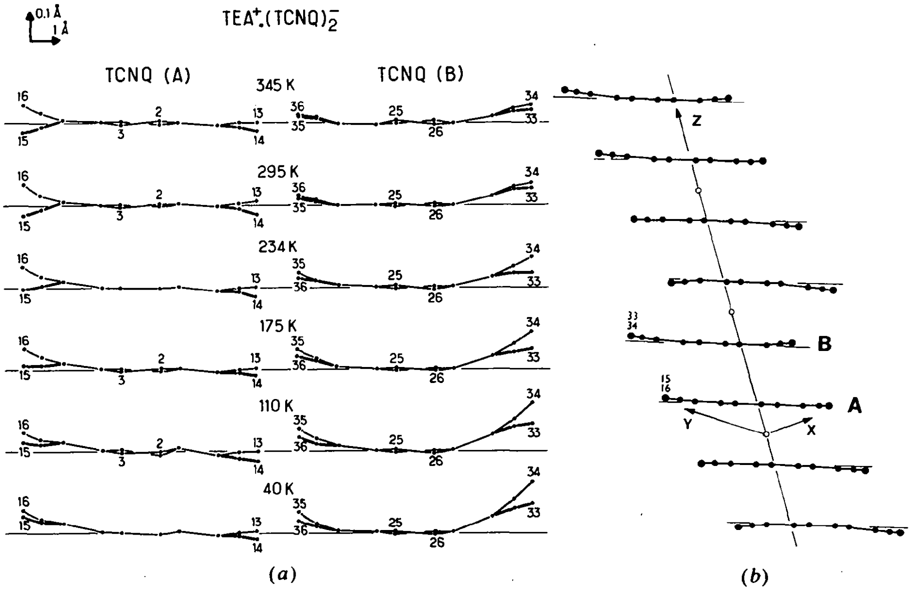


Fig. 7. Out-of-plane deviations of atoms of the TCNQ molecules in TEA–(TCNQ)$_2$. (*a*) Temperature dependence. Note that the vertical scale is 10 times the horizontal scale. (*b*) Side view of a TCNQ column at 40 K. The out-of-plane distance of atoms has been magnified by a factor of two.

all atoms in the structure, at six different temperatures, are in excellent agreement in shape and orientation. The size of the ellipsoids of the TCNQ molecules strongly increases with temperature as expected for ordered species. By contrast, the TEA cation has a twofold disorder, and if only the mean atomic positions are refined, the corresponding thermal ellipsoids are found to be strongly elongated in the direction of the disorder.

### (iv) *The charge transfer*

TEA–(TCNQ)$_2$ is a radical-ion salt and thus the total charge transfer between cation and anion is expected to be exactly $\rho_t = 1$ e except perhaps for a hypothetical back-transfer of the electrons (Farges, 1982). Therefore, one electron is shared, in an unknown ratio, by two TCNQ molecules.

From the data in Tables 3 and 5 the charge transfer may be estimated by the method suggested by Flandrois & Chasseau (1977) for X-ray data and adapted to neutron data by Filhol, Bravic, Gaultier, Chasseau & Vettier (1981). The observed values of $\rho_t$ are actually close to 1 (Table 5) with, however, deviations of the order of 10% (but within the error bars). The observed raw values ($\rho_A$ and $\rho_B$) of the charge transfer on molecules TCNQ($A$) and TCNQ($B$), respectively, were thus rescaled to $\rho_A + \rho_B = 1$ e. The final values (Table 5) show that the observed difference between $\rho_A$ and $\rho_B$ is not very significant for each structure taken individually, while the corresponding mean values clearly show a significant difference [$\bar{\rho}_A = 0{\cdot}60(2)$ e and $\bar{\rho}_B = 0{\cdot}40(2)$ e].

Our observation of a partial localization of the carriers along the TCNQ columns may be compared to that of Belousov, Vainrub & Vlasova (1976) who attributed the doublet structure of vibrational bands in the TEA–(TCNQ)$_2$ spectrum at 100 K to single modes from both TCNQ$^-$ and TCNQ$^0$ species. This doublet structure is not apparent at 300 K probably as a consequence of a line broadening and/or of a change with temperature of the charge localization. This latter effect is not evident from our data in Table 7 but these latter are relatively inaccurate.

### (v) *Crystal packing*

The major characteristics of the crystal packing of TEA–(TCNQ)$_2$ in the temperature range 40 to 345 K are summarized in Table 6.

*Stacking distances.* Because the TCNQ molecules are not strictly planar (Fig. 7), the stacking distances have been calculated with respect to the mean benzyl-ring plane of the molecules. The results (Fig. 8) show that the various interplanar spacings decrease with temperature, each to a different extent. The data extrapolated down to 0 K indicate that, at this temperature, each column is a pile of $BAAB$ tetrads which have an internal regular spacing ($d_{BB} > d_{AA} = d_{AB}$). At about 330 K we have $d_{AA} = d_{BB} > d_{AB}$ and a column is made of $AB$ diads, while at about 220 K all three spacing distances are more unequal. Finally, our data extrapolated to higher temperatures show that above 300 K the stacks tend towards $ABBA$ tetrads ($d_{AA} > d_{BB} = d_{AB}$). These hypothetical tetrads, which never occur because the temperature required (~500 K), is well above the decomposition temperature of the compound, would have a 'zigzag' arrangement of TCNQ molecules.

*Overlap modes.* The three independent overlap modes of adjacent TCNQ molecules in a column are of the 'ring–external-bond' type with, however, some deviations from the ideal position. This latter may be characterized by a longitudinal ($\delta_z$) and a transverse ($\delta_y$) relative shift of the TCNQ centroids which, from data in Table 5, may be taken as $\delta_y = 0$ Å and $\delta_z = \pm 2{\cdot}115$ Å. The observed values of the shifts (Fig. 9) show that the $AB$ overlap is excellent and is independent of the temperature. On the other hand, both the $AA$ and $BB$ overlaps show a large $\delta_y$ transverse shift. However, they behave differently with temperature: the $AA$ overlap shows a pronounced decrease of its transverse shift $\delta_y$ at low temperatures and thus moves towards an $AB$-like overlap while the $BB$ overlap remains the worst at any temperature.

*Interchain coupling.* For 1D organic conductors the interchain coupling is generally believed to be an important parameter in the understanding of their electronic transport properties. In fact, not only the transverse conductivity but also both the longitudinal conductivity and the stabilization of the metallic state down to low temperatures are largely dependent on the strength of these interactions. However, the detailed discussion of structural results in terms of electronic coupling is not straightforward and, for

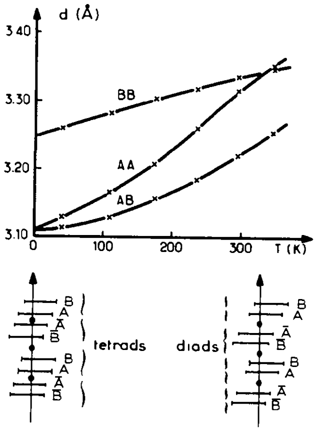


Fig. 8. Temperature dependence of the interplanar spacing between adjacent TCNQ molecules in the columns.

Table 6. *Main geometric parameters defining the crystal packing in TEA–(TCNQ)$_2$ at several temperatures*

| | |
|---|---|
| $\mathbf{N}_A$ and $\mathbf{N}_B$: | Normals to the planes respectively defined by atoms [C(1),C(2),C(3),C(4),C(5),C(6),C(7),C(8)] and [C(21),C(22),C(23),C(24),C(25),C(26),C(27),C(28)]. |
| $\mathbf{L}_A$ and $\mathbf{L}_B$: | Elongation axes of the above atom groups. |
| **N**, **L**: | Mean directions of respectively $\mathbf{N}_A$, $\mathbf{N}_B$ and $\mathbf{L}_A$, $\mathbf{L}_B$. |
| $\mathbf{N}_1$, $\mathbf{N}_2$, $\mathbf{N}_3$, $\mathbf{N}_4$: | Normals to the mean planes of the following groups of atoms: [C(7),C(9),C(10),N(13),N(14)], [C(8),C(11),C(12),N(15),N(16)], [C(27),C(29),C(30),N(33),N(34)], [C(28),C(31),C(32),N(35),N(36)]. |
| $\mathbf{T}_A$ and $\mathbf{T}_B$: | Axes of pairs of TCNQ molecules *AA* and *BB* within a *BAAB* tetrad. |
| **T**: | Stacking axis of a tetrad *BAAB*. |
| *d*: | Interplanar distances of TCNQ molecules within a column. They are defined as being the distance, in the direction **N**, of the centre of mass of quinonoid rings of adjacent TCNQ molecules. |
| $\delta_y$, $\delta_z$: | Relative shifts in directions *y* and *z* of the centre of mass of quinonoid rings of adjacent TCNQ molecules (with $\mathbf{z}\|\mathbf{L}$, $\mathbf{y} \wedge \mathbf{z}\|\mathbf{N}$). |

E.s.d.'s are given in parentheses. Some of the e.s.d.'s have been calculated with the algorithm proposed by Waser, Marsh & Cordes (1973).

| | 345 K | 295 K | 234 K | 173 K | 110 K | 40 K$^{(a)}$ |
|---|---|---|---|---|---|---|
| ($\mathbf{N}_A$, $\mathbf{N}_B$) | 0·41 (10)° | 0·42 (11)° | 0·46 (7)° | 0·60 (4)° | 0·62 (13)° | 0·79 (4)° |
| ($\mathbf{L}_A$, $\mathbf{L}_B$) | 1·82 | 1·71 | 1·61 | 1·50 | 1·38 | 1·54 |
| ($\mathbf{T}_A$, $\mathbf{T}_B$) | 5·47 (4) | 5·27 (4) | 4·86 (3) | 4·22 (3) | 3·54 (5) | 3·30 (3) |
| (**N**, **c**) | 17·00 (5) | 17·10 (5) | 17·24 (4) | 17·25 (3) | 17·33 (6) | 17·34 (3) |
| (**N**, **T**) | 30·48 (5) | 30·78 (5) | 31·22 (4) | 31·61 (3) | 32·00 (7) | 32·20 (3) |
| (**T**, **c**) | 13·65 (1) | 13·85 (1) | 14·15 (1) | 14·54 (1) | 14·84 (2) | 15·04 (1) |
| (**T**, **L**) | 120·18 (1) | 120·52 (1) | 121·04 (1) | 121·47 (1) | 121·92 (2) | 122·12 (1) |
| ($\mathbf{N}_1$, $\mathbf{N}_A$) | 0·4 (1) | 1·4 (1) | 1·11 (9) | 0·3 (1) | 0·5 (1) | 0·53 (9) |
| ($\mathbf{N}_2$, $\mathbf{N}_A$) | 1·3 (1) | 1·3 (1) | 1·20 (8) | 1·0 (1) | 0·6 (2) | 1·2 (1) |
| ($\mathbf{N}_3$, $\mathbf{N}_B$) | 1·3 (2) | 1·2 (2) | 1·7 (2) | 2·5 (1) | 3·0 (3) | 3·5 (1) |
| ($\mathbf{N}_4$, $\mathbf{N}_B$) | 1·1 (2) | 1·4 (2) | 1·8 (1) | 2·3 (1) | 2·2 (2) | 2·7 (1) |
| $d_{AA}$ | 3·349 Å | 3·315 Å | 3·260 Å | 3·207 Å | 3·165 Å | 3·124 Å |
| $d_{AB}$ | 3·252 | 3·218 | 3·185 | 3·157 | 3·127 | 3·107 |
| $d_{BB}$ | 3·346 | 3·335 | 3·315 | 3·303 | 3·281 | 3·253 |
| *AA* $\delta_y$ | 0·521 | 0·488 | 0·430 | 0·367 | 0·302 | 0·290 |
| *AA* $\delta_z$ | −1·847 | −1·857 | −1·876 | −1·896 | −1·918 | −1·916 |
| *AB* $\delta_y$ | −0·002 | −0·011 | −0·028 | −0·029 | −0·027 | −0·017 |
| *AB* $\delta_z$ | −1·997 | −2·000 | −2·004 | −2·000 | −1·999 | −1·999 |
| *BB* $\delta_y$ | 0·416 | 0·412 | 0·425 | 0·428 | 0·415 | 0·408 |
| *BB* $\delta_z$ | 1·918 | 1·933 | 1·952 | 1·989 | 2·015 | 2·039 |

Note: (*a*) The slight differences between our figures and those of Filhol *et al.* (1980) are only due to the use of a new definition of the **N** and **L** axes.

example, Grant (1982) has shown, for organic superconductors of the bis(tetramethyltetraselenafulvalene)–*X* [(TMTSF)$_2$–*X*] family, that the value of the interchain transfer integrals strongly depends on the geometry of the interaction and may be large even for interatomic distances larger than the van der Waals contact. Nevertheless a discussion restricted to interatomic distances often suffices.

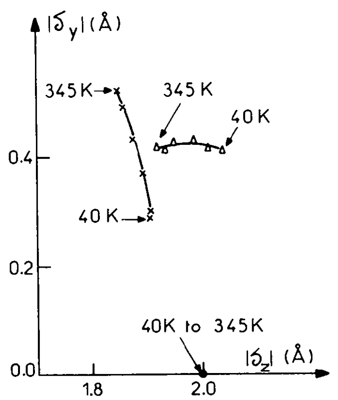


Fig. 9. Temperature dependence of the overlap modes of adjacent TCNQ molecules in the columns. $\delta_y$ and $\delta_z$: relative shift of the TCNQ centroids in the molecular elongation and transverse directions respectively. ×, △, ●: *AA*, *BB*, *AB* overlap modes respectively. The lines are only guides to the eye.

In the case of TEA–(TCNQ)$_2$ Brau & Farges (1974) have given a detailed study of the electrical-conductivity anisotropy (at 300 K: $\sigma_c/\sigma_{a^*} = 1850$, $\sigma_c/\sigma_b = 164$) over a wide temperature range. The conductivity anomaly at 200–220 K is observed for the three directions of measurement. The interchain coupling (*i.e.* the interatomic coupling) is not of the same kind in the **a** and **b** directions since the structure (Fig. 1) may be regarded as a packing along **a** of segregated *bc* layers of, alternately, TEA or TCNQ molecules.

*The* **a** *direction.* The TCNQ columns are separated by TEA columns and thus the shortest direct link (Table 7) between TCNQ chains of the closest TCNQ *bc* layers is an N(33)···N(33) (3·42–3·45 Å) interatomic distance, directed along the [1$\bar{1}$0] cell axis and substantially larger than the sum of the van der Waals radii (3·16 Å). Thus a coupling between the TCNQ chains in the **a** direction would be, at least partially, through the half-populated H bonds (Fig. 1). In fact, the H bonds cannot link neighbouring TCNQ chains

Table 7. *Shortest intermolecular interactions* (Å) *between TCNQ columns*

The given distances correspond to the shortest (up to 3·6 Å) interactions between N atoms of TCNQ molecules on site $x, y, z$ and C and N atoms of TCNQ molecules on the crystallographic site indicated in the table. At 300 K the sums of the atomic van der Waals radii are 3·38 and 3·16 Å for C···N and N···N contacts respectively. Typical values for the e.s.d.'s are: 0·006, 0·006, 0·004, 0·004, 0·008, 0·003 Å for the distances at 345, 293, 234, 173, 110 and 40 K respectively.

| | Sites | 345 K | 293 K$^{(a)}$ | 234 K | 173 K | 110 K | 40 K$^{(b)}$ |
|---|---|---|---|---|---|---|---|
| TCNQ(*A*)···TCNQ(*A*) | | | | | | | |
| N(14)···C(5) | $x, y-1, z$ | 3·329 | 3·315 | 3·293 | 3·281 | 3·251 | 3·258 |
| N(14)···C(6) | $x, y-1, z$ | 3·399 | 3·381 | 3·359 | 3·346 | 3·323 | 3·320 |
| N(16)···C(2) | $x, 1+y, z$ | 3·349 | 3·329 | 3·303 | 3·289 | 3·273 | 3·274 |
| N(16)···C(3) | $x, 1+y, z$ | 3·399 | 3·374 | 3·353 | 3·334 | 3·320 | 3·309 |
| N(16)···C(6) | $-x, 1-y, -z$ | 3·584 | 3·574 | 3·572 | 3·582 | 3·545 | 3·545 |
| TCNQ(*B*)···TCNQ(*B*) | | | | | | | |
| N(33)···N(33) | $-1-x, 1-y, 1-z$ | 3·454 | 3·448 | 3·430 | 3·424 | 3·445 | 3·448 |
| N(36)···N(36) | $-x, -1-y, 1-z$ | — | 3·592 | 3·542 | 3·498 | 3·431 | 3·417 |
| N(34)···C(25) | $x, 1+y, z$ | 3·459 | 3·457 | 3·415 | 3·387 | 3·363 | 3·348 |
| N(34)···C(26) | $x, 1+y, z$ | 3·450 | 3·449 | 3·405 | 3·380 | 3·360 | 3·335 |
| N(36)···C(22) | $x, y-1, z$ | 3·480 | 3·461 | 3·441 | 3·423 | 3·417 | 3·398 |
| N(36)···C(23) | $x, y-1, z$ | 3·470 | 3·454 | 3·433 | 3·414 | 3·402 | 3·389 |
| TCNQ(*A*)···TCNQ(*B*) | | | | | | | |
| No distance <3·6 Å | | | | | | | |

Notes: (*a*) Jaud *et al.* (1974). (*b*) Filhol *et al.* (1980).

directly because each TEA site is randomly occupied by either a TEA′ or a TEA″ which, in turn, is bonded to the chain either to its left or to its right but not to both at the same time. However, the TEA disorder being dynamic above 200–220 K [inversion motion of the cation with exchange of the H(41) atoms between the H(41)′ and H(41)″ positions] as discussed below, this may introduce a certain amount of coupling between adjacent TCNQ chains in the **a** direction. As already noted elsewhere, the TEA columns act as insulators in the **a** direction which is in fact the less conducting one. The interesting new feature concerning the electronic coupling is that the nature of the disorder (static or dynamic) modifies the external potential associated with the TEA chains.

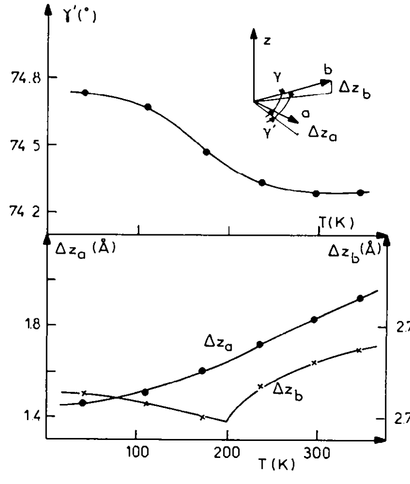


Fig. 10. Relative slip of TCNQ columns in TEA–(TCNQ)$_2$ as a function of temperature. Given a TCNQ column, we may characterize the slip in the **a** or **b** direction as the distance ($\Delta_a$ or $\Delta_b$) from a plane normal to the chain axis at the centroid of a given TCNQ molecule to the homologous TCNQ molecule in the neighbouring TCNQ chain. $\gamma'$ is the dihedral angle between sheets of TCNQ chains in the **b** direction and sheets of TCNQ and TEA chains in the **a** direction.

*The* **b** *direction.* Adjacent TCNQ chains have their molecules directly stacked side by side with short interatomic distances between TCNQ(*A*) molecules only (Table 7). In fact, adjacent TCNQ(*A*) molecules in the **b** direction exhibit, at any temperature, two C···N distances shorter than the sum of the van der Waals radii (3·38 Å) and two additional ones below 300 K. For adjacent TCNQ(*B*) molecules, distances shorter than 3·38 Å are observed only below 160 K.

Another way of looking at the temperature effect on the transverse coupling between chains is to consider separately the relative ionic re-orientations (Table 6) and the global effect of the cell expansion. This latter effect is both a change in the column spacing and a relative longitudinal slip of neighbouring chains. The observed values of the slip along **c** (Fig. 10) show that it is large in the **b** direction while it is small in the **a** direction. The 200–220 K anomaly is mainly visible for the latter direction, this being due to the behaviour of cell parameter $\alpha$.

## Discussion

This analysis of the structural evolution of TEA–(TCNQ)$_2$ with temperature may be compared to similar studies on two other TCNQ salts with 1:2 stoichiometry and irregular stacking, namely MEM–(TCNQ)$_2$ and Me-1,N-Et-Bz–(TCNQ)$_2$.* A striking

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* Me-1,N-Et-Bz–(TCNQ)$_2$: 1-methyl-3-ethylbenzimidazolium–(TCNQ)$_2$.

fact is that the three compounds behave quite differently with temperature. For example, the stacking of TEA–$(TCNQ)_2$ is highly tetradic at low temperature and highly diadic at room temperature while the reverse is observed in Me-1,N-Et-Bz–$(TCNQ)_2$ (Jaud, 1973). For MEM–$(TCNQ)_2$ (van Bodegom, 1979) one finds a high-temperature phase ($T > 335$ K) with high cation disorder and quasi-regular spacing of the TCNQ anions in the columns, an intermediate phase with strongly dimerized stacks and a low-temperature phase ($T < 19$ K) with tetramerized columns. The two transitions of this latter compound have been recognized to be electronic and spin-Peierls transitions respectively (Huizinga, 1980). We may then conclude that a variety of structural evolutions with temperature may be observed in the case of TCNQ salts of intermediate stoichiometry. The corresponding crystallographic data are thus of crucial importance (if not indispensable) to the interpretation of their transport and magnetic properties.

Our observation of a thermal-expansion anomaly (Fig. 3) indicates that TEA–$(TCNQ)_2$ undergoes a structural phase transition at 200–220 K and this is worth further discussion.

Marechal & McConnell (1965) attributed the increase in intensity of certain Bragg reflections in TEA–$(TCNQ)_2$ with rising temperature (*i.e.* Debye inversion) to the increase in concentration of thermally excited triplet excitons and to 'distortions' associated with exciton–photon interactions. However, Potworowski (1974) pointed out that the S-shaped intensity change may be due to a change in the atomic positions in the cell rather than to a Debye inversion. This interpretation is strongly supported by our thermal-expansion results.

Since the thermal-expansion anomaly is mainly visible in the cell parameters $a$ and $\alpha$, one may postulate that the corresponding structural modifications mainly concern the transverse interaction between chains in the **a** direction and thus that the TEA cation disorder is certainly a key point of the TEA–$(TCNQ)_2$ behaviour. In fact, Travers (1983) has demonstrated that the TEA disorder is static below 200–220 K and dynamic with increasing molecular motion, above.

We may also recall that Vlasova *et al.* (1975) have attributed the 200–220 K anomaly in the electrical conductivity of TEA–$(TCNQ)_2$ to a metal–insulator phase transition. Carneiro, Almeida & Alcacer (1982) have observed a Kohn anomaly in the phonon spectrum at $2k_F$ (but could not measure the phonon branches at $4k_F$) and have thus proposed a tentative interpretation of their results in terms of a Peierls-like phase transition. Steigmeier, Auderset, Baeriswyl, Almeida & Carneiro (1983) make the same assumption to interpret the temperature dependence (4 to 300 K) of the Raman spectra of the compound. It is therefore tempting to postulate that the thermal-expansion anomaly at 200–220 K is due to a Peierls-like lattice distortion, keeping in mind that effects such as cation disorder or large fluctuations may somewhat perturb the transition from its theoretical behaviour.

To this effect, one may try to interpret the temperature change of the stacking distances in the TCNQ columns (Fig. 8) in terms of the relative contributions of two successive distortions (namely a dimerization and a tetramerization) of an equivalent regular stacking (Carneiro, 1982). If the overlap modes are neglected and only the interplanar distances are considered, the stacking may be defined using the following three parameters: $D0$, the spacing distance in the equivalent regular stacks; $D2$, the dimerization parameter; $D4$, the tetramerization parameter. The position of the $n$th TCNQ molecule in the chain is now:

$$Xn = D0 \,.\, n + D2 \cos(4k_F \,.\, n \,.\, D0 + \varphi_2) + D4 \cos(2k_F \,.\, n \,.\, D0 + \varphi_4),$$

with $\varphi_2$ and $\varphi_4$ the phases of the distortions. Then, assuming centrosymmetric tetrads, Farges (1982) gave the following relations:

$$D0 = \frac{1}{2}\left(\frac{d_{AA} + d_{BB}}{2} + d_{AB}\right)$$

$$D2 = \frac{1}{4}\left(\frac{d_{AA} + d_{BB}}{2} - d_{AB}\right)$$

$$D4 = \frac{1}{2\sqrt{2}}(d_{BB} - d_{AA}).$$

The values of $D0$, $D2$ and $D4$ estimated from our data on TEA–$(TCNQ)_2$ (Fig. 8) are displayed in Fig. 11. They show that $D0$ smoothly increases with $T$ over the whole temperature range while $D2$ remains nearly constant. The $D4$ curve exhibits a point of inflection at 200–220 K and reaches the zero base line at ~340 K; however, this latter parameter imperfectly

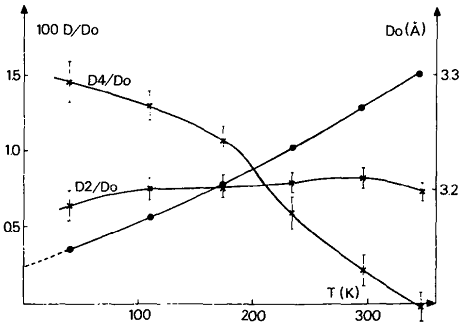

Fig. 11. Tentative interpretation of the temperature dependence of the stacking distances in the TCNQ columns in terms of both a dimerization ($D2$) and a tetramerization ($D4$) of an equivalent regular column ($D0$). This figure is from Farges (1982). Parameters $D0$, $D2$ and $D4$ are defined in the text. The lines are only guides to the eye.

describes the tetrads which formally exist at all temperatures (zigzag stacking).

Because of the 1:2 stoichiometry of TEA–$(TCNQ)_2$, dimerization and tetramerization distortions correspond to $4k_F$ and $2k_F$ Fermi wavevectors respectively. The behaviour of TEA–$(TCNQ)_2$ (magnitude of the $2k_F$ gap strongly temperature dependent; $4k_F$ gap nearly constant) leads to several assumptions for the mechanism of the 200–220 K phase transition: (1) the tetramerization could be an intermolecular component of a classical $2k_F$ Peierls lattice distortion with the dimerization an intrinsic feature of the TEA–$(TCNQ)_2$ structure due to the stoichiometry, as indicated by the invariance of $D2$ with $T$; (2) it may be a spin-Peierls transition while the dimerization comes from a $4k_F$ Peierls distortion which would be the consequence of strong electron–electron interactions (on-site Coulomb repulsion $U$ large) in the compound as already observed in some other salts, *e.g.* MEM–$(TCNQ)_2$ (Huizinga, 1980); (3) there is an order–disorder phase transition induced by molecular motion.

No clearly unambiguous description is yet possible but this study clearly shows the importance of a better understanding of the role of the cation disorder and points out the need for more information on a hypothetical superstructure below the transition which, for example, could be associated with a long-range ordering of the cations.

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*Note added in proof*: Our data in Table 6 have been used by Janssen, Visser, Jonkman, de Boer & Kommandeur (1983) to compute the transfer integrals in TEA–$(TCNQ)_2$ as a function of $T$. From the whole data set in Table 7 we concluded (see *Results*, § iv) that there is no very significant change, with temperature, of the charge transfer onto $TCNQ_A$ and $TCNQ_B$ species. However, Farges (1983*a*) recently noted that according to our own structure refinements a change, linear with $T$, of the charge distribution is apparent with characteristic values 0·5 and 0·5 e at $T$ ∞, and 0 and 1 e at $T \sim 48$ K. Finally we wish to note here that, based on our present results, Farges (1983*b*) gave a complementary analysis of the TCNQ chain behaviour, and for example noted that the structure change with $T$ is mainly a transverse shift of dimers which are the stable part of the stacks.

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# X-ray Structure and Crystal Packing Analysis of Triphenylbromomethane,* $C_{19}H_{15}Br$

BY A. DUNAND AND R. GERDIL†

*Département de Chimie Organique et Laboratoire de Radiocristallographie,*
*Université de Genève,* 30 *quai Ernest Ansermet, CH*-1211 *Genève* 4, *Switzerland*

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## Abstract

$M_r = 323{\cdot}2$, trigonal, $P\bar{3}$, $a = 13{\cdot}933(3)$, $c = 13{\cdot}438(4)$ Å, $V = 2266{\cdot}7$ Å$^3$, $Z = 6$, $D_m = 1{\cdot}42$, $D_x = 1{\cdot}421$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}866$ mm$^{-1}$, $F(000) = 984$, room temperature, final $R = 0{\cdot}049$ for 976 observed reflections. The molecules lie in special positions on the crystallographic threefold axes. They are associated in pairs and form two distinct $Ph_3C$–Br $\cdots$ Br–$CPh_3$ head-to-head arrangements characterized by long C–Br bonds and short Br $\cdots$ Br contacts. The shortest Br $\cdots$ Br distance (3·203 Å) is about 0·5 Å smaller than the sum of the van der Waals radii. The lattice energy was computed using two different sets of published Buckingham potential functions. These calculations account satisfactorily for all the salient features of the crystal packing. Analysis of the thermal motion showed that the rigid-body approximation holds reasonably well for the triphenylbromomethane molecule.

## Introduction

The present study is a natural extension to our recent investigation of the crystal structure and crystal packing of triphenylchloromethane (Dunand & Gerdil, 1982). Triphenylchloromethane (TPCM) and triphenylbromomethane (TPBM) crystallize in isomorphous systems and both structures display linear head-to-head C–$X \cdots X$–C arrangements with long C–$X$ bonds and unusually short $X \cdots X$ contacts. Previous studies by Landais (1953) and Stora & Poyer (1966) had already revealed the occurrence of short Br $\cdots$ Br intermolecular contacts in TPBM crystals.

## Experimental

Colourless hexagonal prisms of TPBM (Merck) grown from dry petroleum ether, m.p. 421–422 K, $D_m$ measured by flotation, hygroscopic crystal sealed under argon in Lindemann capillary, $0{\cdot}22 \times 0{\cdot}30 \times 0{\cdot}32$ mm; atomatic four-circle Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$; 38 reflections within range $10 \leq 2\theta \leq 30°$ used for measuring lattice parameters; 2585 independent reflections scanned in the $\omega$–$2\theta$ mode, scan width 1·0°, scan speed $0{\cdot}02°\ \text{s}^{-1}$, $6{\cdot}0 \leq 2\theta \leq 50°$, range of $hkl$: $-14 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 16$; three standard reflections monitored at 60 min intervals showed insignificant intensity variations: $2\bar{1}\bar{3}$, 241 and $\bar{5}43$ had average count rates and e.s.d.'s of 27423(217), 65720(523) and 55068(365); absorption corrections according to *CAMEL JOCKEY* method (Flack, 1975), minimum and maximum corrections 0·935 and 1·065 applied on $F_o$; 976 reflections considered observed at the $2\sigma(I)$ level and used in the structure analysis; no systematic absences; structure solved by heavy-atom method, H atoms located from difference synthesis; full-matrix least-squares refinement on $F$; calculations carried out with anisotropic temperature factors for non-H atoms and isotropic factors for H; final $R = 0{\cdot}049$, $wR = 0{\cdot}032$, $S = 1{\cdot}7$, $w = 1/\sigma^2(F_o)$; ratio of maximum least-squares shift-to-error = 0·4, average ratio = 0·1; no extinction correction; atomic scattering factors for C and Br from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion correction for Br from Cromer (1965); programs of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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* (Bromo)triphenylmethane.

† To whom correspondence should be addressed.

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