Radical Ion Salts and Complexes, Part XVII.† TCNQ Salts of 1,4-Dimethylpyridine and 2,3-Bis(1-methyl-4-pyridinio)butane

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X-Ray structure determination of the complex salts $[MeNC_5H_4Me]^+[TCNQ_2]^-$ [1,4–dimethylpyridinium 2(7,7,8,8-tetracyanoquinodimethane) (1–); **I**] and $[Me(NC_5H_4)(Me)CH-CH(Me)(C_5H_4N)Me]^{2+}[TCNQ_4]^{2-}$ [*meso*-2,3-bis(*N*-methyl-4-pyridyl)butane(2+) 4(7,7,8,8-tetracyanoquinodimethane) (2–); **II**], where $TCNQ=(CN)_2C(C_6H_4)C(CN)_2$, shows that, although in both salts the TCNQ moieties are stacked in columns, lateral shifts break these columns into diads for **I** and tetrads for **II** causing their electrical conductivities to be only moderate ($\sigma = 2\text{–}4 \times 10^{-3}$ ohm^{-1} cm^{-1}).

The salts were prepared by refluxing solid 1,4-dimethylpyridinium iodide (for **I**) or 1-methyl-4-ethylpyridinium iodide (for **II**) with purified TCNQ in triply dried and distilled acetonitrile. Unexpectedly, the 1-methyl-4-ethylpyridinium cation dimerised in the course of the preparation. X-Ray data were measured for **I** with a Hilger and Watts Y290 four-circle diffractometer and for **II** with an Enraf-Nonius CAD4 diffractometer. Reflections used in the refinements, having $I > 3\sigma(I)$, numbered 1398 for **I** and 3236 for **II**. Both structures were solved with the aid of Patterson syntheses and refined by weighted least squares calculations–full-matrix for **I** and block-matrix for **II**. The molecular structures of **I** and **II** are shown in Fig. 1 and 2 respectively.

If the space group is $P\bar{1}$, the non-centrosymmetric cation in **I** must be randomly reversed in order that the single molecule in the cell can be located on a centre of symmetry. Since the aim of the structure determination was to study the packing, mainly of the TCNQ moieties, the resulting superposition of N and C was approximated as a single C atom. Attempts to refine the actual non-centrosymmetric molecule in *P*1 were unsuccessful. In both determinations, ring H atoms were visible in difference maps but were included in the refinement in calculated fixed positions. The diffuse electron density in the regions of methyl H atoms indicated no preferred orientations, so these H atoms and the other bridge H atom in **II** were omitted from the calculations. The random reversal of the cation in **I** and the omission of some H atoms in both structures contribute to the rather poor final *R* factors, 0.090 for **I** and 0.066 for **II**. Standard uncertainties of bond lengths and angles are rather high for the same reasons; bonds: 0.008–0.011 Å in **I** and 0.004–0.009 Å in **II**; angles: 0.5–0.7° in **I** and 0.3–0.4° **II**. The non-exact superposition of randomly reversed cations, coupled with a small degree of torsional motion of the $C(CN)_2$ groups of TCNQ about the C-ring bond, cause a number of atoms to have apparently high thermal factors.

As in all semiconducting TCNQ salts, the electron path in both **I** and **II** must be mainly along stacks of almost planar TCNQs. In **I**, the TCNQs are orientated with their planes parallel to (001) and they are stacked in centrosymmetrically related pairs (diads) with their centres shifted by roughly $a/3$ and $c/2$. This gives rise to the situation found in many semiconducting TCNQ salts in which the ring of one TCNQ lies over an exocyclic double bond of the next TCNQ in the stack. The perpendicular separation between quinonoid rings is 3.11 Å within the diad and 3.22 Å between adjacent diads along *c*. The row of diads formed by unit cell repetition along the *a* axis gives rise to layers of TCNQs in the (010) plane when these rows are repeated along *c*. However, the TCNQ of lower *z* coordinate in each diad of one row (*e.g.* molecule A of Fig. 3) is shifted about $a/2$ relative to each of the nearest TCNQs of higher *z* in the row below (*e.g.* molecule A″ of Fig. 3), thus interrupting the conductivity path perpendicular to the TCNQs. The fairly low powder compaction semiconductivity measured by us, $\sigma_{300} = 1.7 \times 10^4$ ohm^{-1} cm^{-1}, (*cf.* 4.2×10^{-4} ohm^{-1} cm^{-1} [5] and 3.54×10^{-4} ohm^{-1} cm^{-1} [6] measured elsewhere) is consistent with this interrupted nature of the TCNQ stacking.

In **II**, the TCNQs are nearly parallel to (001) but are stacked in tetrads, the general direction of which is approximately along [$\bar{1}$02]. This has a similar effect to that described for the diads in **I**, causing the TCNQ of lowest *z* coordinate in one tetrad to be positioned about midway between the nearest TCNQs of highest *z* in the row of tetrads below (Fig. 4). The perpendicular separations between the planes of the rings of the TCNQs within the tetrad are A···B = 3.13 and A···A′ = 3.32 Å, and between tetrads B···B″ = 3.18 and B···B‴ = 3.19 Å. As in **I**, the $C(CN)_2$ groups are slightly bowed and twisted relative to the quinonoid rings.

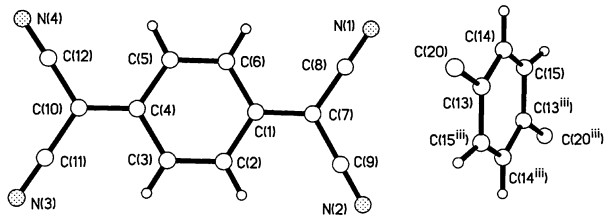

Fig. 1 The asymmetric unit of **I** and centrosymmetrically related atoms in the cation, showing the atom numbering scheme. i = 1 − *x*, 1 − *y*, 1 − *z*. C(13) represents $\frac{1}{2}C + \frac{1}{2}N$ in the randomly reversed cation.

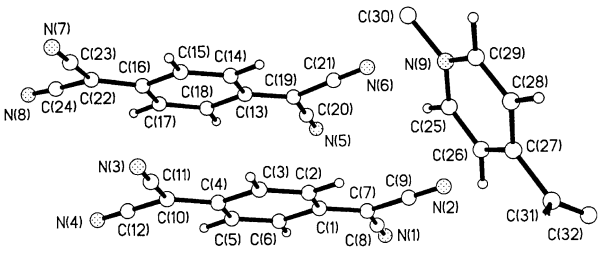

Fig. 2 The asymmetric unit of **II**, showing the atom numbering scheme. The half cation shown is joined to the centrosymmetrically related other half by a bond C(31)–C(31^i); i = 1 − *x*, 1 − *y*, −*z*.

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† Part XVI: W. Waclawek, S. C. Wallwork, G. J. Ashwell and E. J. Chaplain, *Acta Crystallogr., Sect. C*, 1983, **39**, 131.

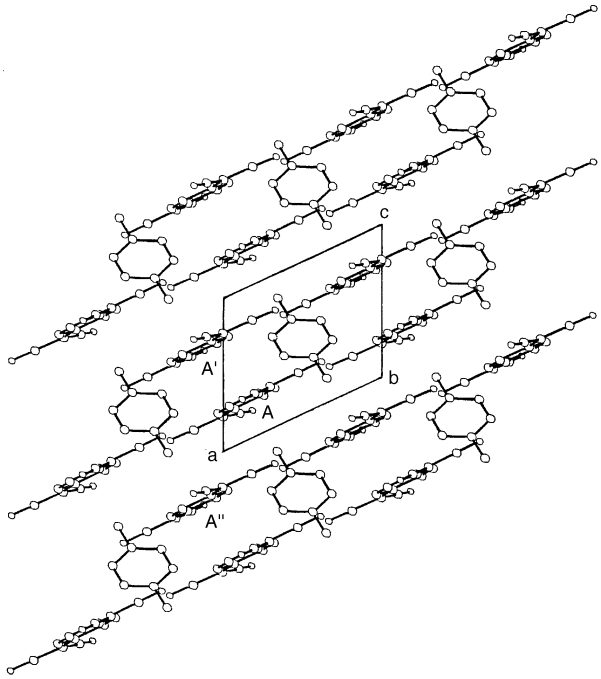

Fig. 3 Projection of the packing arrangement of **I** along the *y* axis

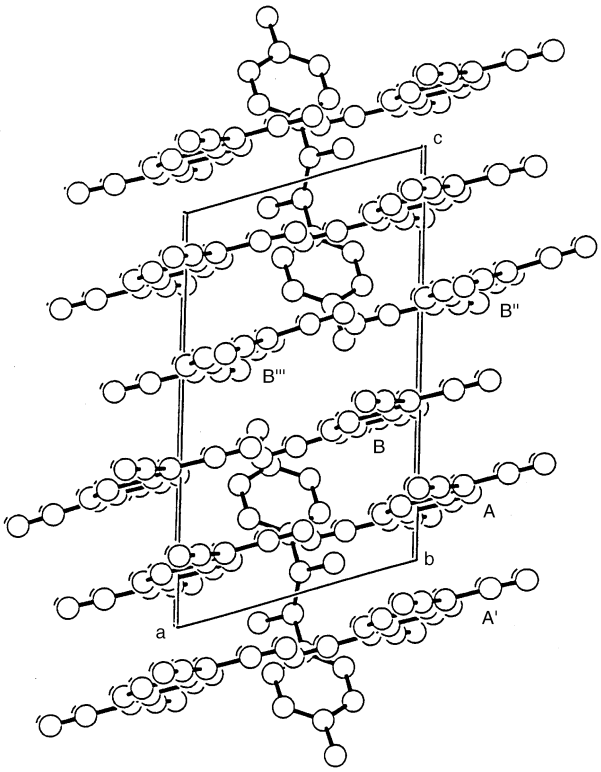

Fig. 4 Projection of the packing arrangement of **II** along the *y* axis

Like the diads in **I**, the tetrads occur as layers in the (010) plane, and again the interrupted stack arrangement of TCNQs is consistent with our measurements of the moderate semiconductivity of this salt and its anisotropy ($\sigma_{300}/10^{-4}$ ohm^{-1} cm^{-1} $\approx$ 9(2) along [100], 7(2) along [001] and 1.8(2) along [010]; *i.e.* lower conductivity across the planes of cations compared with the similar conductivities in the other two directions).

The packing of TCNQs and cations is very similar in the two structures—the doubling of the cation size from **I** to **II** basically doubles the *c* cell dimension and the number of TCNQs in the stacking unit (diad to tetrad). The tetrad in **II** is prevented from having a doubled cumulative shift parallel to the lengths of the TCNQs by having a shift from A to A′ opposite in direction to that from B to A. The bond lengths of the TCNQs give a rough indication of the charge distribution.[7,8] In **I** they indicate an average charge close to the expected 0.5 electrons. Molecule A in **II** is indicated as having a similar charge but molecule B dimensions correspond to *ca*. 0.3 electrons. This may not be significantly different from 0.5, in view of the approximate nature of the calculation but, if it is genuinely low, it could indicate some back donation from the cation.

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Crystal Data.—For **I** $C_7H_{10}N^+(C_{12}H_4N_4)_2^-$, $M = 516.5$, triclinic, $P\bar{1}$ (assumed), $a = 7.833(3)$, $b = 13.889(4)$, $c = 7.171(4)$ Å, $\alpha = 106.81(4)$, $\beta = 112.50(2)$, $\gamma = 95.36^o$ $U = 671.3(6)$ Å^3, $Z = 1$, $D_c = 1.278(1)$ g cm^{-3}, μ(Mo-Kα) = 0.88 cm^{-1}, $F(000) = 267$.

For **II** $C_{16}H_{22}N_2^{2+}(C_{12}H_4N_4)_4^{2-}$, $M = 1059.1$, triclinic, $P\bar{1}$ (assumed), $a = 7.798(4)$, $b = 14.249(2)$, $c = 13.690(5)$, $\alpha = 109.53(2)$, $\beta = 103.37(3)$, $\gamma = 95.42(2)^o$, $U = 1370.1(9)$ Å^3, $Z = 1$, $D_m = 1.27(1)$ g cm^{-3}, $D_c = 1.284(1)$ g cm^{-3}, μ (Cu-Kα) = 6.6 cm^{-1}, $F(000) = 548$.

References: 8

Tables: 8 (atomic coordinates, thermal parameters, bond lengths, bond angles, for each of **I** and **II**)

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