square antiprism with vertices defined by 4 Ag(2) at 3·21 Å and 4 Ca at 3·54 Å; next nearest neighbours are 4 Ag(1) at 3·47 Å and 4 Ag(2) at 3·52 Å. Similarly the Ag(2) atoms lie inside an irregular square prism defined by 2 Ag(1) at 2·80 Å, 4 Ag(2) at 2·85 Å and 2 Ca at 3·21 Å with next nearest neighbours 2 Ag(2) at 3·00 Å and 2 Ca at 3·52 Å. Thus the total coordination numbers are 12 each for Ag(1) and Ag(2) and 16 for Ca.

This structure can be regarded as showing some formal resemblances to the $D8_{1-3}$ structures and also to that of U_2F_9. For example it can be derived from the $D8_2$ structure (γ-Cu_5Zn_8) by omitting Cu(1) in 8(*c*) and making appropriate changes in the parameters of the other atoms.

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Structural data on electrically conductive caesium tetracyanoquinodimethanide, $Cs_2[(NC)_2CC_6H_4C(CN)_2]_3$.

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Electronic conductivity remarkably high for organic solids is observed in a series of salts formed from 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Acker, Harder, Hertler, Mahler, Melby, Benson & Mochel, 1960). Theoretical and experimental aspects of electronic conduction and interaction in these compounds have been studied by several researches (Kepler, Bierstedt & Merrifield, 1960; Chesnut, Foster & Phillips, 1961; Chesnut & Phillips, 1961; Chesnut & Arthur, 1962; Jones & Chesnut, 1963). This communication reports a limited X-ray investigation of the molecular arrangements in one of these conducting crystals.

The 7,7,8,8-tetracyanoquinodimethane anion–radical salt with caesium,

$$Cs_2^+[(CN)_2C:C_6H_4:C(CN)_2]_2^{\dot{-}}[(CN)_2C:C_6H_4:C(CN)_2]\,,$$

prepared from CsCl and TCNQ (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962) crystallizes in the monoclinic system in the space group $P2_1/c$ (C_{2h}^5) with

$$a=7\cdot32\pm0\cdot03,\ b=10\cdot43\pm0\cdot03,\ c=21\cdot96\pm0\cdot04\ \text{Å};$$
$$\beta=97\cdot0°\pm0\cdot1,\ \text{cell volume}=1664\pm15\ \text{Å}^3,\ Z=2\,,$$
$$\text{formula}=Cs_2(C_{12}H_4N_4)_3\,,$$

observed density $1\cdot753\pm0\cdot005$ g.cm^{-3}, X-ray density 1·759 g.cm^{-3}, 31 atoms per asymmetric unit, 124 atoms per unit cell.

The [100], [010] and [001] Patterson projections were used to determine the approximate position of the heavy caesium atom. Calculation of structure factors using only the caesium atom contribution produced trial signs for use with the observed structure factors. The signed factors were used to compute electron density distribution projections which were interpreted with the aid of a model planar TCNQ unit consistent with chemical and bond-distance information. The preliminary lighter atom positions were then used in conjunction with the caesium atom positions to recalculate structure factor signs for use with the observed values.

The atomic positions of Table 1 and Fig. 1 resulted from adjustment of the caesium and TCNQ model positions according to successive $\varrho(x,z)$, $\varrho(y,z)$, and $\varrho(x,y)$ maps until the discrepancy value R was reduced to 0·18 for the $F(h0l)$, 0·28 for the $F(0kl)$, and 0·29 for the $F(hk0)$ values without corrections for absorption,

Table 1. *Atomic parameters for* $Cs_2/(TCNQ)_2^{\dot{-}}/(TCNQ)$

Atom	*x*	*y*	*z*
N(1)	0·618	0·960	0·150
C(1)	0·768	0·995	0·147
C(2)	0·956	0·039	0·143
C(3)	0·089	0·028	0·197
N(2)	0·198	0·019	0·240
C(4)	0·001	0·087	0·091
C(5)	0·239	0·160	0·033
C(6)	0·863	0·126	0·037
C(7)	0·195	0·108	0·083
N(3)	0·567	0·317	0·115
C(8)	0·717	0·352	0·112
C(9)	0·905	0·396	0·108
C(10)	0·038	0·385	0·162
N(4)	0·147	0·376	0·205
C(11)	0·950	0·444	0·056
C(12)	0·812	0·483	0·002
C(13)	0·144	0·465	0·048
N(5)	0·516	0·674	0·080
C(14)	0·666	0·709	0·077
C(15)	0·854	0·753	0·073
C(16)	0·987	0·742	0·127
N(6)	0·096	0·733	0·170
C(17)	0·899	0·801	0·021
C(18)	0·093	0·822	0·013
Cs	0·514	0·2275	0·2645

The six hydrogen positions are not included since they were not involved in the calculations.

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* Contribution No. 898.

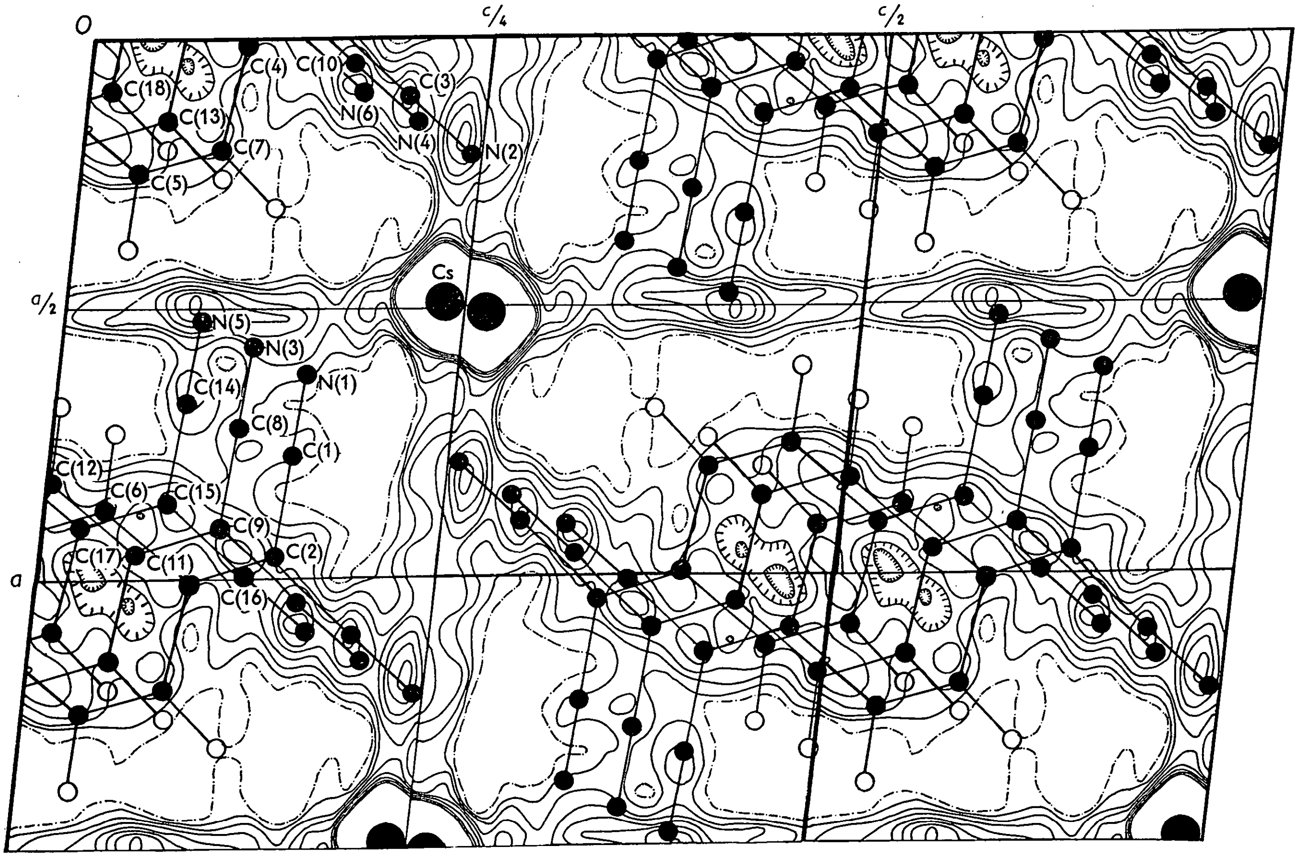

Fig. 1. Electron-density projection on (010) with equal interval contours of $\sim 2{\cdot}6$ e.Å^{-2} omitting contours close to the caesium atoms (shown as large circles). The carbon and nitrogen positions of the model are shown as small solid circles and the hydrogen positions as open circles.

extinction, or hydrogen atom contributions. This was done with the assumption of an isotropic temperature factor constant, B, of 3, and zero contribution for unobserved reflections. The TCNQ atom positions were confirmed by subtracting the caesium contribution and comparing the ϱ maps so obtained. This confirmation, together with the R values and prior chemical information, was accepted as evidence for the essential planarity of the TCNQ units.

Study of the atomic positions of Table 1 showed that the planar TCNQ units were stacked face-to-face in the crystal. In addition, the normal directions of the planar TCNQ units are tilted away slightly from the b axis. Rows of these stacks, all having the highly conductive crystalline b axis direction as the stack axis, are separated by the large caesium ions which are positioned almost in planes parallel to the c face ($z = 0{\cdot}25 \pm 0{\cdot}0145$, $0{\cdot}75 \pm 0{\cdot}0145$). The large size of the caesium ions in these positions is consistent with the occurrence of TCNQ units in the crystals in excess of those necessary for electrical neutrality. One-third of the TCNQ units have their centers coinciding with inversion centers of the unit cell. The TCNQ unit separations in the stack, measured perpendicularly to the planar units, is only $3{\cdot}21 \pm 0{\cdot}01$ Å between those units on the inversion centers and their contiguous units while it is $3{\cdot}44 \pm 0{\cdot}01$ Å between contiguous units not on inversion centers.

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