

The Crystal Structure of the 2 : 3 Complex of Rubidium and 7,7,8,8-Tetracyanoquinodimethane, Rb_2TCNQ_3 , at 113 K

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Abstract

Rb_2TCNQ_3 [$\text{Rb}_2(\text{C}_{12}\text{H}_4\text{N}_4)_3$, $\text{C}_{36}\text{H}_{12}\text{N}_{12}\text{Rb}_2$] is isostructural with Cs_2TCNQ_3 . The space group is $P2_1/c$ with $a = 7.269$ (2), $b = 10.264$ (3), $c = 21.328$ (6) Å, $\beta = 97.11$ (2)°, $U = 1579.2$ Å³ and $Z = 2$. The intensities were collected at 113 K with Mo radiation on an automatic Nonius CAD-3 diffractometer. Anisotropic least-squares refinement decreased the weighted residual R_F to 0.038 for 3631 observed reflexions. The TCNQ groups are stacked in columns along the b axis and lie either at inversion centers (groups c) or at general positions (groups nc) in the arrangement nc...c...nc...nc...c...nc... etc. Comparison with the room-temperature structure shows that decreasing the temperature from 300 to 110 K gives the same percentage reduction in the nc...c and nc...nc distances. Rb ions also lie in linear arrays along b and are surrounded by edge-sharing cubes of eight N atoms. The cubes show an elongation in the stacking direction which is much more pronounced for the Rb than for the Cs salt. Within the TCNQ stack the shifts 'parallel' to the TCNQ planes do not depend on the temperature but quite strongly on the atomic radii, whereas the reverse is the case for the distances between the planes.

Introduction

In crystals of TCNQ complexes the TCNQ groups, which bear a (partly) negative charge, are often stacked in columns. The way in which the groups are stacked and especially the separations between successive TCNQ moieties have been reported (Chasseau, Castagné, Gaultier, Hauw, Dupuis, Neel & Filhol, 1976; Castagné, 1975; Blessing & Coppens, 1974) to depend on the nature of the donor groups and on the temperature. The aim of the present paper is to study the effect of the atomic radii and of temperature on Cs_2TCNQ_3 -type structures. The structure of Cs_2TCNQ_3 has been determined at room temperature by Fritchie & Arthur (1966). In an earlier study of

Rb_2TCNQ_3 at room temperature the present authors have shown this compound to be isomorphous with Cs_2TCNQ_3 (van der Wal & van Bodegom, 1978). In the present paper the structure determination of Rb_2TCNQ_3 at 113 K is described and a comparison is made between the two Rb_2TCNQ_3 and the Cs_2TCNQ_3 structures.

Experimental

Dark-purple crystals were grown by mixing hot solutions of TCNQ and RbI in acetonitrile.

Low-temperature cell dimensions were obtained from the $\sin^2 \theta / \lambda^2$ values of 116 reflexions measured with Zr-filtered Mo radiation ($\lambda = 0.71069$ Å) on a three-circle Nonius diffractometer. The crystal was cooled down to 113 K by a stream of cold nitrogen gas (van Bolhuis, 1971). In Table 1 low-temperature cell dimensions are compared with the room-temperature values and the values for Cs_2TCNQ_3 .

Table 1. Crystal data of Rb_2TCNQ_3 at 294 and 113 K and of Cs_2TCNQ_3 at 294 K

Numbers in parentheses here and elsewhere in this paper are (unless stated otherwise) the estimated standard deviations in the last significant digits.

Monoclinic Space group $P2_1/c$			
	Rb_2TCNQ_3 at 294 K	Rb_2TCNQ_3 at 113 K	Cs_2TCNQ_3 at 294 K*
a	7.297 (1) Å	7.269 (2) Å	7.34 (1) Å
b	10.392 (1)	10.264 (3)	10.40 (2)
c	21.444 (2)	21.328 (6)	21.98 (4)
β	97.45 (1)°	97.11 (2)°	97.18 (5)°
U	1612.3 Å ³	1579.2 Å ³	1664.7 Å ³
$\text{Rb}_2(\text{C}_{12}\text{H}_4\text{N}_4)_3$			$\mu(\text{Mo } K\alpha) = 3.33 \text{ mm}^{-1}$
FW = 783.52			$d_c = 1.62 \text{ Mg m}^{-3}$ (294 K)
$F(000) = 772$			$d_m = 1.57$ (294 K; pycnometer)
$Z = 2$			

* Fritchie & Arthur (1966).

A crystal of dimensions $0.35 \times 0.35 \times 0.20$ mm was used for the intensity measurements. We collected the intensities with Zr-filtered Mo radiation, using the θ - 2θ method. All independent reflexions with $0 \leq l \leq 23$ were measured at 113 K up to $\theta = 35^\circ$. For 1259 reflexions a second measurement in the region $h = -1, +1$ to $+4$, $k < 0$ and $l \geq -1$ was carried out. In addition to the corrections for the intensity changes of the primary beam, we corrected for Lorentz and polarization effects, and for absorption. The last corrections were calculated according to the Busing & Levy (1957) scheme: $8 \times 6 \times 8$ volume elements and 10 accurately located bounding planes were taken into account. For the 1259 reflexions which were measured twice, the agreement factor

$$R_M = \frac{\sum_H \sum_{i=1}^2 |M_i(\mathbf{H}) - \langle M(\mathbf{H}) \rangle|}{\sum_H \sum_{i=1}^2 |M_i(\mathbf{H})|}$$

is 0.026 for $M = I$, 0.019 for $M = |F|^2$ and 0.010 for $M = |F|$. Reflexions with a negative net intensity were given zero weight. For the remaining reflexions the weight w_c was calculated from the relation $w_c = [\sigma_c(F_o)]^{-2}$, $\sigma_c(F_o)$ being the standard deviation in $|F_o|$ due to counting statistics and errors in the filter factors. For the structure determination 3803 independent reflexions with net intensities greater than zero were available.

Determination of the structure

As no phase transition was observed between room temperature and 113 K, we started the refinement with the room-temperature parameters (van der Wal & van Bodegom, 1978). The unit cell contains one independent Rb⁺ ion and two independent TCNQ units, a unit (c) at a center of symmetry and a non-centrosymmetric unit (nc) lying at a general position. Unless stated otherwise, the computations were made with the XRAY (1973) set of programs. For the non-hydrogen atoms the scattering curves were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). For Rb dispersion corrections ($f' = -0.9$, $f'' = 3.15$) as given by Dauben & Templeton (1955) were applied. H atoms were constrained at 1.08 Å relative to their respective C atoms; only their isotropic temperature parameters were refined. Least-squares refinement with anisotropic temperature parameters for the non-hydrogen atoms gave $R = 0.054$, and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.038$; 3631 observed reflexions with $|F_o| \geq 2\sigma(F_o)$ and weights $w = [w_c^{-1} + E|F_o|^2]^{-1}$ were used with $E = 1.5 \times 10^{-4}$. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} = 1.71$ with the number of observed reflexions $N_o = 3631$ and the number of variables $N_v = 233$. During the last cycle of the refine-

ment all shifts were smaller than 0.4σ . Final positional parameters are given in Table 2.*

Consideration of the thermal ellipsoids for the individual atoms shows that in the C-C_a≡N groups the thermal ellipsoids of C_a are elongated along the C-C_a≡N direction (Fig. 1). The same phenomenon has been observed by Blessing & Coppens (1974; Fig. 2) and has been ascribed to the deformations in the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34278 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final positional parameters for Rb₂TCNQ₃ at 113 K ($\times 10^5$)

H atoms were constrained to their respective C atoms. For numbering of atoms, see Fig. 5.

	x	y	z
Rb(1)	51175 (4)	24418 (3)	26316 (1)
N(2)	-38607 (34)	815 (25)	17223 (13)
N(3)	21857 (36)	729 (26)	24178 (14)
N(4)	46564 (36)	30356 (28)	-9645 (13)
N(5)	-11512 (35)	30111 (26)	-17689 (13)
N(6)	-43286 (34)	33382 (27)	12685 (12)
N(7)	15294 (35)	34841 (26)	20814 (12)
C(8)	-23344 (41)	2206 (27)	16347 (14)
C(9)	-4695 (36)	4211 (27)	15135 (13)
C(10)	9656 (41)	2252 (27)	20224 (15)
C(11)	-14431 (36)	10920 (26)	4011 (14)
C(12)	-513 (37)	9034 (26)	9245 (14)
C(13)	18202 (36)	12357 (25)	8373 (14)
C(14)	22414 (37)	17254 (26)	2765 (14)
C(15)	8328 (37)	19116 (27)	-2480 (14)
C(16)	-10359 (37)	15818 (27)	-1626 (14)
C(17)	31510 (39)	27602 (27)	-9023 (14)
C(18)	12887 (33)	24309 (31)	-8256 (12)
C(19)	-721 (36)	27266 (25)	-13492 (14)
C(20)	-28271 (39)	36312 (27)	12114 (13)
C(21)	-9531 (35)	39852 (27)	11361 (13)
C(22)	4194 (38)	37282 (27)	16639 (14)
C(23)	-18642 (36)	46579 (26)	335 (14)
C(24)	-4887 (36)	44955 (26)	5756 (13)
C(25)	14165 (37)	48546 (25)	5182 (15)
H(26)	-28605	8551	4470
H(27)	29074	11023	12243
H(28)	36538	19759	2301
H(29)	-21205	17251	-5495
H(30)	-32796	43995	705
H(31)	24791	47348	9140

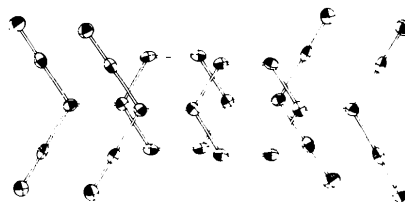


Fig. 1. Thermal motion (50% probability ellipsoids) in Rb₂TCNQ₃ at 113 K.

electron density distribution (in comparison with the model of non-bonded atoms used in the refinement) resulting from chemical bonding.

Description of the structure

Packing

Views of the structure along [100] and [010] are given in Figs. 2 and 3. Both the TCNQ groups and the Rb atoms are arranged in columns along the *b* axis.

Short intermolecular distances are given in Table 3. Each Rb⁺ ion is surrounded by a distorted cube of eight N atoms. The cation–nitrogen distances for Rb₂TCNQ₃ at 294 K and 113 K and for Cs₂TCNQ₃ at 294 K are listed in Table 4. Figs. 3 and 4 show that each N atom of the coordination cube belongs to a different TCNQ molecule. This is a general phenomenon for all TCNQ salts of Rb studied so far (Hoekstra, Spoelder & Vos, 1972; Shirovani & Kobayashi, 1973; van Bodegom, de Boer & Vos, 1977).

Individual TCNQ groups within a column

In Fig. 5 the bond lengths and angles of the two crystallographically non-equivalent TCNQ groups at

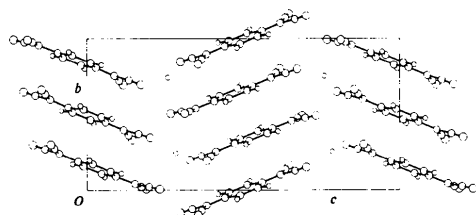


Fig. 2. View of the structure along [100].

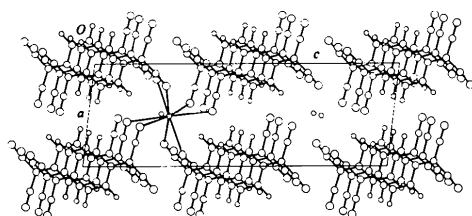


Fig. 3. View of the structure along [010].

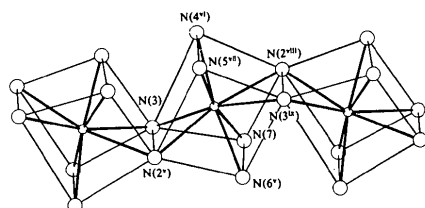


Fig. 4. Surroundings of the metal cations in Rb₂TCNQ₃ and Cs₂TCNQ₃.

Table 3. Short intermolecular distances (Å)

All distances smaller than the sum of the relevant van der Waals radii [$r_C = 1.7$, $r_N = 1.5$, and $r_H = 1.2$ Å; (Pauling, 1960)] plus 0.2 Å are given.

Symmetry code

(i)	$-x, -y + 1, -z$	(iv)	$-x, y - \frac{1}{2}, -z + \frac{1}{2}$
(ii)	$-x, -y, -z$	(v)	$x + 1, y, z$
(iii)	$x - 1, y, z$		

(a) Molecule c to molecule nc distances

N(7)–C(10)	3.371 (4)	C(24)–C(14)	3.570 (4)
C(21)–C(12)	3.273 (4)	C(25)–C(15)	3.436 (4)
C(22)–C(12)	3.298 (4)	C(23 ^b)–C(17)	3.436 (4)
C(23)–C(16)	3.251 (4)	C(24 ^b)–C(19)	3.294 (4)
C(24)–C(15)	3.385 (4)	C(25 ^b)–C(18)	3.518 (4)
C(25)–C(14)	3.319 (4)	C(20)–C(12)	3.548 (4)
C(22 ^a)–N(5)	3.392 (4)	C(21)–C(13)	3.571 (4)
C(24 ^a)–C(18)	3.264 (4)	C(22)–C(9)	3.463 (4)
C(25 ^a)–C(19)	3.269 (4)	C(24)–C(16)	3.380 (4)
C(20)–C(11)	3.350 (4)	C(24)–C(11)	3.572 (4)
C(21)–C(11)	3.356 (4)	C(21 ^b)–C(19)	3.474 (4)
C(22)–C(13)	3.337 (4)	C(23 ^b)–C(18)	3.433 (4)
C(23)–C(15)	3.527 (4)	C(24 ^b)–C(17)	3.535 (4)

(b) Molecule nc to molecule nc' distances

N(5)–C(10 ^h)	3.371 (4)	C(11)–C(16 ^h)	3.356 (4)
C(8)–C(19 ^h)	3.584 (4)	C(12)–C(15 ^h)	3.248 (4)
C(9)–C(15 ^h)	3.593 (4)	C(14)–C(16 ^h)	3.507 (4)
C(11)–C(14 ^h)	3.253 (4)	C(8)–C(17 ^h)	3.453 (4)
C(12)–C(16 ^h)	3.177 (4)	C(9)–C(18 ^h)	3.296 (4)
C(13)–C(16 ^h)	3.249 (4)	C(11)–C(15 ^h)	3.138 (4)
C(8)–C(18 ^h)	3.360 (4)	C(11)–C(13 ^h)	3.547 (4)
C(9)–C(19 ^h)	3.279 (4)	C(12)–C(18 ^h)	3.538 (4)
C(10)–C(19 ^h)	3.381 (4)		

(c) Interchain distances

N(2)–H(27 ^h)	2.670 (3)	N(4)–H(30 ^v)	2.875 (3)
N(4)–H(29 ^v)	2.751 (3)	C(8)–N(7 ^h)	3.259 (4)
N(6)–H(28 ^h)	2.865 (3)	N(3)–C(20 ^v)	3.258 (4)
C(10)–C(22 ^h)	3.453 (5)	N(6)–H(31 ^h)	2.753 (3)
N(3)–C(22 ^v)	3.201 (4)	C(10)–N(7 ^h)	3.316 (4)

Table 4. Cation–nitrogen contact distances (Å) in Rb₂TCNQ₃ (at 294 and 113 K) and Cs₂TCNQ₃ (294 K)

Distances to N atoms involved in two adjacent cubes (Fig. 3) are given in the lower block.

Symmetry code

(v)	$x + 1, y, z$	(viii)	$-x, y + \frac{1}{2}, -z + \frac{1}{2}$
(vi)	$x, -y + \frac{1}{2}, z + \frac{1}{2}$	(ix)	$-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$
(vii)	$x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$		

	N...Rb Rb ₂ TCNQ ₃ , 294 K	N...Rb Rb ₂ TCNQ ₃ , 113 K	N...Cs Cs ₂ TCNQ ₃ , 294 K
N(5 ^h)	2.892 (6)	2.890 (3)	3.071 (5)
N(7)	2.941 (6)	2.927 (3)	3.132 (5)
N(4 ^h)	3.118 (6)	3.093 (3)	3.297 (7)
N(6 ^v)	3.179 (6)	3.123 (3)	3.360 (7)
Mean value	3.033	3.008	3.215
N(2 ^h)	3.286 (7)	3.223 (3)	3.402 (6)
N(3)	3.263 (7)	3.228 (3)	3.331 (6)
N(2 ^v)	3.291 (7)	3.246 (3)	3.383 (6)
N(3 ^h)	3.401 (7)	3.346 (3)	3.487 (6)
Mean value	3.310	3.261	3.401

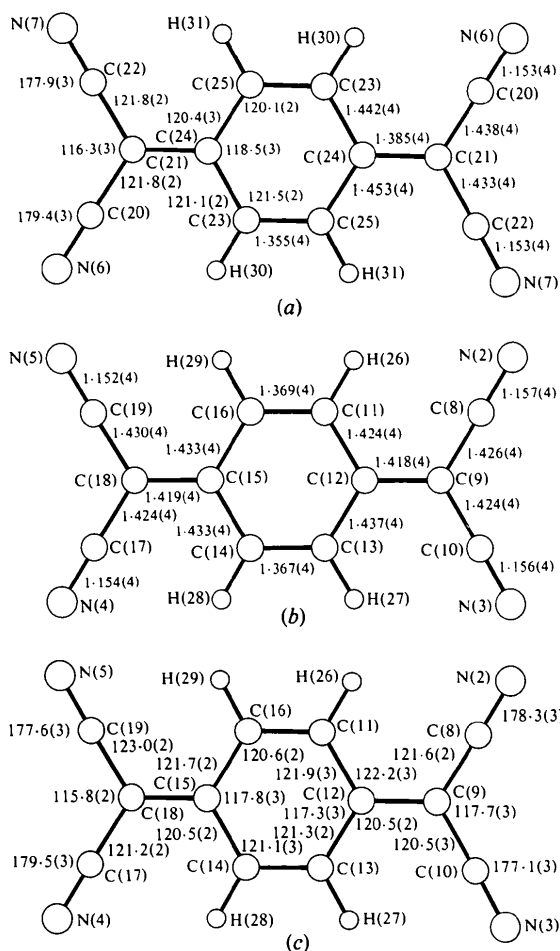


Fig. 5. Molecular geometries (Å and deg) of the TCNQ units in Rb_2TCNQ_3 at 113 K, (a) molecule c, (b), (c) molecule nc. Values for bond lengths are not corrected for libration effects.

113 K are shown. As far as bond lengths and angles are concerned both molecules have approximate *mmm* symmetry; average values for corresponding bond lengths are given in Table 5.

From Table 6, which gives the equations of the best planes through the quinodimethane groups in Rb_2TCNQ_3 and the deviations of the atoms from the

Table 6. Least-squares planes for the quinodimethane group of the TCNQ units in Rb_2TCNQ_3 at 294 and 113 K, deviations of atoms from these planes and interplanar angles

x, y, z are relative coordinates in the axial system *a, b* and *c*. The atoms used to define the planes are equally weighted.

(a) Equations of the planes

Centrosymmetric: C(21), C(23), C(24) and C(25)

Non-centrosymmetric: C(9), C(11), C(12), C(13), C(14), C(15), C(16) and C(18)

Rb_2TCNQ_3 (294 K)

TCNQ-c: $-1.569x + 9.644y + 7.061z - 4.822$

TCNQ-nc: $-1.353x + 9.685y + 7.135z = 1.561$

R.m.s. deviation from the plane (Å)

0.008

0.009

Rb_2TCNQ_3 (113 K)

TCNQ-c: $-1.617x + 9.497y + 7.090z = 4.749$

TCNQ-nc: $-1.380x + 9.544y + 7.175z = 1.537$

0.005

0.009

(b) Deviations of the atoms from the respective plane ($\text{Å} \times 10^3$) at 294 K and at 113 K (in parentheses) for TCNQ-c (above) and TCNQ-nc (below)

N(6)	2 (2)	N(7)	-20 (-21)	C(20)	1 (2)	C(21)	-1 (0)
C(22)	-9 (-10)	C(23)	0 (0)	C(24)	1 (1)	C(25)	0 (0)
N(2)	30 (31)	N(3)	-3 (-3)	N(4)	3 (3)	N(5)	21 (23)
C(8)	18 (17)	C(9)	2 (2)	C(10)	0 (0)	C(11)	-1 (-1)
C(12)	-1 (0)	C(13)	-1 (-1)	C(14)	0 (0)	C(15)	-1 (-1)
C(16)	0 (0)	C(17)	3 (2)	C(18)	1 (1)	C(19)	12 (11)

(c) Interplanar angles ($^\circ$) between planes c and nc*

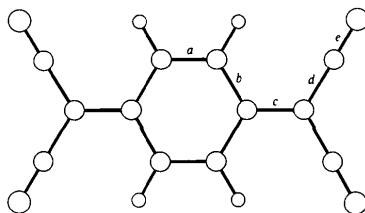
294 K	1.76	113 K	1.94
	2.28 [†]		2.47 [†]

* Standard deviations are estimated to be equal to or smaller than 1 in the last digit given.

[†] For planes defined by all heavy atoms of the TCNQ groups.

Table 5. Mean bond lengths (Å) for the TCNQ groups in Rb_2TCNQ_3 at 294 and 113 K and in Cs_2TCNQ_3 at 294 K

The numbering system is illustrated below. Figures in parentheses are standard deviations of the mean. No libration corrections have been applied.



Molecule c	a	b	c	d	e
Rb_2TCNQ_3 , 294 K	1.340 (9)	1.447 (6)	1.376 (9)	1.439 (9)	1.135 (6)
Rb_2TCNQ_3 , 113 K	1.355 (4)	1.447 (3)	1.385 (4)	1.436 (3)	1.153 (3)
Cs_2TCNQ_3 , 294 K	1.341 (5)	1.444 (4)	1.371 (5)	1.428 (4)	1.140 (4)
Molecule nc	a	b	c	d	e
Rb_2TCNQ_3 , 294 K	1.368 (6)	1.430 (4)	1.410 (6)	1.425 (4)	1.142 (4)
Rb_2TCNQ_3 , 113 K	1.368 (3)	1.432 (2)	1.418 (3)	1.426 (2)	1.155 (2)
Cs_2TCNQ_3 , 294 K	1.355 (4)	1.427 (3)	1.410 (4)	1.419 (3)	1.152 (3)

respective planes, we can see that the TCNQ groups are not planar. The $C\equiv N$ groups especially are bent out of the planes, as has been observed in many other TCNQ compounds. It should be noted that the planes for the *c* and the *nc* groups are not exactly parallel to each other (Table 6).

The TCNQ columns

From Fig. 2 we can see that the centrosymmetric (*c*) and non-centrosymmetric (*nc*) TCNQ groups form the arrangement $nc\dots nc\dots c\dots nc\dots nc\dots c$ etc. along *b*.

Table 7. Shifts (Å) of *nc'* and *c* relative to *nc* as seen along the normal of the quinodimethane least-squares planes of *nc* or *c* and distances of types $nc\dots nc$ and $nc\dots c$ calculated according to (*D1*) and (*D2*) (in parentheses)

$S(\perp)$ shift perpendicular to longest molecular axis, $S(\parallel)$ shift along this axis. For definition of (*D1*) and (*D2*) see text. Standard deviations are estimated to be equal to or smaller than 1 in the last digit given.

	Rb ₂ TCNQ ₃ , 294 K	Rb ₂ TCNQ ₃ , 113 K	Cs ₂ TCNQ ₃ , 294 K
$S(\perp)$			
<i>nc'</i>	1.05	1.09	1.15
<i>c*</i>	0.23	0.23	0.35
	0.17	0.17	0.17
$S(\parallel)$			
<i>nc'</i>	0.06	0.06	0.09
<i>c*</i>	1.89	1.90	1.95
	1.90	1.91	1.95
(<i>D1</i>)(<i>D2</i>)			
$nc\dots nc$	3.12 (3.24)	3.07 (3.09)	3.12 (3.25)
$nc\dots c^*$	3.28 (3.21)	3.23 (3.17)	3.27 (3.21)
	3.28 (3.18)	3.23 (3.14)	3.29 (3.23)

* Upper value along the normal of *nc*, lower value along the normal of *c*.

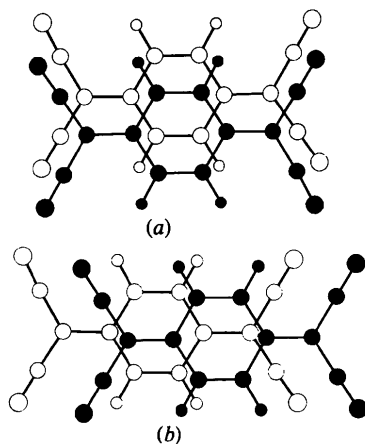


Fig. 6. (a) Projection of molecule *nc'* on the least-squares plane of the quinoid group of *nc*. (b) Projection of molecule *c* on the least-squares plane of the quinoid group of *nc*.

An important feature of such a column is the separation between adjacent TCNQ groups. As planes through adjacent TCNQ units of different types are not parallel, we have defined the separation between adjacent planes as the dot product $\mathbf{u} \cdot \mathbf{v}$ of \mathbf{u} connecting the centers of two molecules and the unit vector \mathbf{v} normal to the plane of one of the molecules. In Table 7 two series of TCNQ separations are listed, (*D1*) distances between adjacent least-squares planes defined by the quinodimethane groups only (see Table 6), and analogous (*D2*) distances, but calculated on the basis of least-squares planes through all non-hydrogen atoms of the TCNQ groups. The table shows that there are appreciable differences between corresponding distances in the two series because the orientations of the least-squares planes calculated for (*D1*) and (*D2*) are not the same. Strict definitions of TCNQ separations are thus required to make values reported for structure determinations of different compounds comparable.

Fig. 6 shows the projections of *nc'* (at $y = -0.14$) and of *c* (at $y = 0.50$) on *nc* ($y = 0.14$). Different shifts are observed for *nc'* and *c* relative to *nc*. Numerical values for the shifts are given in Table 7. As the planes of *nc* and *c* are not parallel, the shifts of the molecular centers relative to each other as seen in projection depend on whether one projects along the normal to *c* or to *nc*. Both sets of values are given in the table.

Discussion

The TCNQ units and the TCNQ stack

Comparison of the molecular geometries of corresponding TCNQ units in Table 5 does not reveal any significant changes resulting from either the variation in temperature or the variation in ion radius.

For all three structures corresponding bond lengths for the *n* and *nc* groups show significant differences. According to the literature (Hoekstra, Spoelder & Vos, 1972; Jonkman & Kommandeur, 1972) there is a relation between the bond lengths in a TCNQ group and its charge. By use of the method of Flandrois & Chasseau (1977) charges of $-0.8 e$ and $0.0 e$ are calculated for *nc* and *c* respectively.

As for the packing in the stack, it can be seen from Table 7 that for all three structures the separations $nc\dots c$ are larger than the separations $nc\dots nc$ if distances of type (*D1*) are chosen. This leads to the tempting picture of a TCNQ stack being composed of TCNQ dimers, consisting of two *nc* ion radicals weakly linked together, separated by a neutral TCNQ unit. This picture has to be checked, however, by quantum-chemical calculations, as values of charge-transfer integrals (Pincus, 1972) rather than geometrical parameters are needed to obtain a correct description of the interaction between the TCNQ units.

Influence of temperature and ion radii

Consideration of the distances in Tables 4 and 7 shows that the influence of the atomic radii ($r_{\text{Rb}^+} = 1.48$, $r_{\text{Cs}^+} = 1.69$ Å; Pauling, 1960) on the atomic distances is larger than that of the temperature. For both the distances in the TCNQ stack and the $\text{Rb}\cdots\text{N}$ distances the largest changes due to the decrease in temperature are about 0.06 Å. It is noteworthy that within the TCNQ stack the shifts 'parallel' to the TCNQ planes (Table 7) do not depend on the temperature but quite strongly on the atomic radii, whereas the reverse is the case for the distances between the planes. Both for $\text{nc}\cdots\text{nc}$ and $\text{nc}\cdots\text{c}$ a contraction of 0.05 Å is observed due to the decrease in temperature.

Regarding the packing between the TCNQ stacks, we see from Figs. 3 and 4 that the distorted cubes around the Rb^+ ions are arranged in a row along b by sharing edges. Table 4 shows that in the Rb salt the cubes are elongated in the stacking direction. At room temperature all $\text{Rb}\cdots\text{N}$ (edge) distances are more than 0.3 Å longer than the sum of the van der Waals radii whereas the remaining $\text{Rb}\cdots\text{N}$ distances are only 0.05 Å longer than this sum on average. By lowering the temperature the two $\text{Rb}\cdots\text{N}$ distances shorter than $r_{\text{Rb}^+} + r_{\text{N}}$ remain practically the same, whereas for the remaining $\text{Rb}\cdots\text{N}$ distances shortenings varying from 0.03 to 0.06 Å are observed. Consideration of the $\text{Cs}\cdots\text{N}$ distances reveals that for the Cs salt the elongation of the cubes in the b direction is less pronounced than for the Rb salt at room temperature. For the non-edge N atoms the $\text{Cs}\cdots\text{N}$ distances are, as in Rb_2TCNQ_3 , not much larger (0.03 Å on average) than the sum of the van der Waals radii, whereas the $\text{Cs}\cdots\text{N}$ (edge) distances are smaller in comparison with this sum than for Rb_2TCNQ_3 .

A tentative explanation of the above phenomena can be given in terms of the incapability of the TCNQ molecules to decrease the distances along the stacking axis, as long as the temperature does not decrease. This rigidity of the TCNQ stacks can be ascribed to the distances being shorter than the van der Waals distances (Table 7 and Fig. 2). The decrease in atomic radius from Cs^+ to Rb^+ can therefore be accounted for only by changing the distance between the TCNQ stacks and by small shifts 'parallel' to the TCNQ planes in the stacks (see above). For the Rb^+ salt, especially, this gives an unfavorable packing with 'too long' $\text{metal}\cdots\text{N}$ (edge) distances. This unfavorable packing may be expected to be much pronounced for

the hypothetical isostructural K salt containing a still smaller positive ion [$r_{\text{K}^+} = 1.33$ Å (Pauling, 1960)] and may well be the reason why attempts to isolate this salt have failed so far.

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