

A New Form of Rubidium–7,7,8,8-Tetracyanoquinodimethane

BY BERT VAN BODEGOM, JAN L. DE BOER AND AAFJE VOS

Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

(Received 5 October 1976; accepted 22 October 1976)

Abstract. $\text{RbH}_4\text{C}_{12}\text{N}_4$, tetragonal, $a = b = 17.645$ (11), $c = 3.864$ (2) Å, $Z = 4$, $U = 1203.0$ Å³; $F(000) = 564$, $\mu(\text{Mo}) = 43.3$ cm⁻¹; systematic absences: $hk0$ with $h + k$ odd, $hh0$ with h odd; space group $P4/n$ with twinning according to (100) assumed. The final R is 0.065 for 275 observed reflexions.

Introduction. For the simple alkali metal–TCNQ radical salt RbTCNQ two types (I and II) were known which showed phase transitions at 374 and 231 K respectively (Vegter, Hibma & Kommandeur, 1969; Sakai, Shirotani & Minomura, 1972). The low-temperature structure of RbTCNQ-I (Hoekstra, Spoelder & Vos, 1972) and the high-temperature structure of RbTCNQ-II (Shirotani & Kobayashi, 1973) have been determined. Recently, we found among crystals of RbTCNQ-I, grown in the crystal-growth apparatus described by Pott & Kommandeur (1967), just one crystal with a different structure. The cell dimensions were determined from fifteen reflexions measured on a four-circle automatic Nonius diffractometer with Mo radiation [$\lambda(\text{Mo } K\alpha) = 0.71069$ Å]. Rotation and Weissenberg photographs showed the symmetry relations $I(hkl) = I(h\bar{k}l) = I(khl) = I(k\bar{h}l) = I(\bar{h}\bar{k}l)$. These relations and the geometry of the cell pointed to the space group $P4/nmm$.

The crystal, $0.070 \times 0.070 \times 0.384$ mm, was mounted on the top of a glass fibre and aligned along the tetragonal c axis. We collected intensities on a three-circle automatic Nonius diffractometer with the θ – 2θ method and Zr-filtered Mo radiation. All reflexions with h, k and $l \geq 0$, except the $hk0$ reflexions with $h + k$ odd, were measured up to $\theta = 30^\circ$ at room temperature. Deviations from linearity of the scintillation-counting equipment were kept below 1% by the use of attenuation filters; every 2 h a reference reflexion was measured three times; corrections were made for intensity changes in the primary beam, for Lorentz and polarization effects and for absorption. This latter correction was calculated with the Busing & Levy (1957) scheme: $8 \times 8 \times 10$ volume fragments and six accurately located planes were taken into account. 1874 reflexions were measured, 1517 having a net intensity greater than zero. Reflexions with a net negative intensity were given zero weight.

An approximate model of the structure was obtained by comparing the crystallographic data of RbTCNQ-III [referred to as (III)] with those of RbTCNQ-I (I). The $hk0$ reflexions of (III) and the $0kl$ reflexions of (I) are very similar, indicating that the (001) projection of (III) (Fig. 1) is approximately the same as the pseudo-tetragonal (100) projection of (I) (Hoekstra, Spoelder & Vos, 1972, Fig. 3). The dashed lines in Fig. 1 give the unit cell of (I) in this projection. The solid lines give the unit cell of (III) as deduced from zero and higher-layer Weissenberg photographs around c . The c axis of (III) is about half that of (I), so that in (III) each TCNQ column in the c direction contains only one TCNQ molecule per cell. The packing of the TCNQ units obtained in this way obeys the space group $P4/n$, but does not contain the m symmetry planes of $P4/nmm$. As in the latter space group no reasonable structure could be found, we have adopted the space group $P4/n$. In this space group the TCNQ groups lie at the inversion centres (at $z = \frac{1}{2}$); Rb ions lie on the fourfold axis (at $z = 0.56$) and at the inversion centre of the fourfold inversion axis (at $z = \frac{1}{2}$). The tilt of the TCNQ group was assumed to be approximately equal to that in (I). We have explained the symmetry relation $I(hkl) = I(khl)$ by assuming twinning according to (100) with the twin ratio 1. Fig. 1 shows that this is a reasonable assumption. Assumption of random disorder as an alternative explanation of the extra symmetry is not possible as this would reduce the cell dimensions.

For the reflexions $h0l$ and hhl the contribution of the two twin individuals is the same. This is also true for the $hk0$ reflexions if T is exactly a mirror plane for the [001] projection. During the refinement of the structure we constrained the parameters of the TCNQ units and the Rb ions in such a way that this was the case. The TCNQ units were given $2mm$ symmetry in projection with one mirror plane coinciding with a or b ; for the thermal parameters of the Rb ions the constraint $U_{11}[\text{Rb}(1)] = U_{11}[\text{Rb}(2)]$ was used. This implies the systematic extinction of the reflexions $hh0$ for h odd. We refined the structure by full-matrix least squares with the X-RAY system (1973) set of programs. Only non-hydrogen atoms were refined with anisotropic thermal parameters and the constraints mentioned above. Of the $hk0$, $h0l$ and hhl reflexions

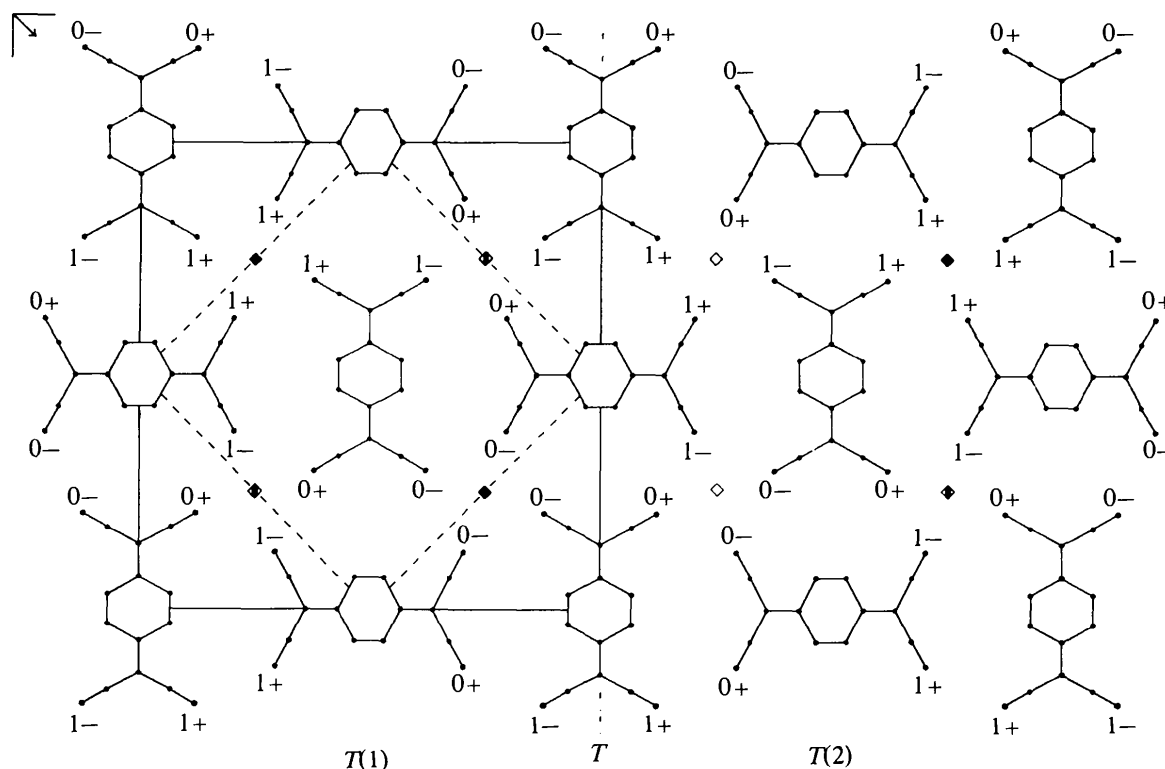


Fig. 1. Projection of the structure on (001). Dashed lines indicate the unit cell of RbTCNQ-I, solid lines indicate that of RbTCNQ-III. The z coordinate of the N atoms is marked with 1+, 1-, 0+, and 0- which correspond to $z = 1.06, 1.0, 0.0$ and -0.06 respectively. T = twinning plane, $T(1)$ = twin individual 1, $T(2)$ = twin individual 2. Note that the tilt of the molecules is changed at the twinning plane, but the N atoms remain at practically the same position as a result of their location close to $z = 0$ (and 1).

Table 1. Fractional atomic coordinates and temperature factors U_{ij} ($\times 10^2$)

Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the last significant digits. The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{13})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
N(1)	0.1220 (5)	0.2043 (6)	1.061 (11)	3.4 (5)	5.8 (6)	9.4 (16)	0.4 (5)	-1.2 (17)	-0.2 (29)
C(2)	0.0682 (6)	0.1744 (6)	0.999 (11)	3.4 (5)	3.5 (5)	5.0 (12)	0.1 (4)	-0.7 (17)	-3.9 (20)
C(3)	0.0000*	0.1386 (8)	0.883 (6)	2.1 (6)	2.9 (7)	3.8 (16)	0.0*	0.3 (12)	0.0*
C(4)	-0.0682*	0.1744*	0.978 (11)	3.4*	3.5*	5.0*	-0.1*	-0.7*	3.9*
N(5)	-0.1220*	0.2043*	1.005 (17)	3.4*	5.8*	9.4*	-0.4*	-1.2*	0.2*
C(6)	0.0000*	0.0691 (10)	0.684 (9)	3.2 (8)	4.6 (9)	2.8 (17)	0.0*	-1.1 (16)	0.0*
C(7)	0.0683 (5)	0.0323 (6)	0.570 (13)	2.0 (4)	4.4 (6)	7.1 (22)	0.0 (4)	-1.8 (14)	-0.7 (11)
C(8)	-0.0683*	0.0323*	0.596 (12)	2.0*	4.4*	7.1*	0.0*	-1.8*	0.7*
Rb(1)	$\frac{1}{2}\dagger$	$\frac{1}{2}\dagger$	0.565 (2)	3.63 (7)	3.63†	4.7 (4)	0.0†	0.0†	
Rb(2)	$\frac{1}{2}\dagger$	$\frac{1}{2}\dagger$	$\frac{1}{2}\dagger$	3.63*	3.63†	4.0 (3)	0.0†	0.0†	

* Constrained.

† Special position.

used, only reflexions with $|F|$ greater than $2\sigma(F)$ were taken into account. The weight for these reflexions was $w = [\sigma^2(F) + EF^2]^{-1}$, $\sigma(F)$ being the standard deviation in F due to counting statistics and errors in the filter factors; the constant $E = 0.0004$ was chosen so as to make $\langle w(F_o - F_c)^2 \rangle$ as similar as possible for dif-

ferent values of $|F|$ and $(\sin \theta)/\lambda$. X-ray scattering factors according to Cromer & Mann (1968) were used. The weighted residual $R = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ was 0.065 for the 275 reflexions considered. For all independent reflexions hkl (h, k and $l \geq 0$; $h \geq k$; $hk0$ for $h + k$ even; 639 reflexions) with $|F| \geq 2\sigma(F)$, the

weighted residual R , with $F_{c(\text{twin})}(hkl) = [\frac{1}{2}F_c^2(hkl) + \frac{1}{2}F_c^2(khl)]^{1/2}$, is 0.099. In Table 1 the final fractional coordinates and temperature parameters are given.*

Discussion. The TCNQ molecules are stacked in a plane-to-plane manner along c and form columns of monads. The perpendicular distance between the successive TCNQ molecules is 3.33 Å. In RbTCNQ-I there are columns with alternating perpendicular distances of 3.159 and 3.484 Å; in the columns of

RbTCNQ-II the TCNQ molecules are at equal distances of 3.43 Å from each other. Fig. 2 illustrates the projection of two successive TCNQ molecules along the normal of their best planes. This normal makes an angle of 30.7° with c . The type of overlapping of the TCNQ molecules in the stacks is the same as in RbTCNQ-II (Shirota & Kobayashi, 1973, Fig. 2) while the arrangement of the stacks is the same as in RbTCNQ-I. Bond angles and lengths in the TCNQ molecule of RbTCNQ-III are, within twice their standard deviations of 1.0–5.2° and 0.02–0.04 Å respectively, equal to those found in RbTCNQ-I. Within the standard deviation, the Rb ions are surrounded by a cube of N atoms with Rb–N distances of 3.08 (4) Å.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32233 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

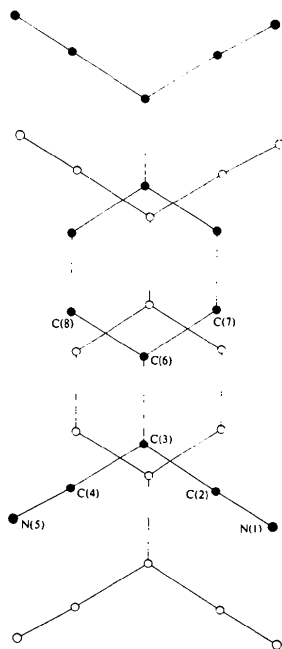


Fig. 2. Nearest-neighbour overlap of TCNQ.

The authors are grateful to Mr A. B. Verweij for growing the crystal. Part of the research has been supported by the Dutch Organization for the Advancement of Pure Research (ZWO). The computations were carried out at the Computing Centre of the University of Groningen.

References

- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 HOEKSTRA, A., SPOELDER, T. & VOS, A. (1972). *Acta Cryst.* **B28**, 14–25.
 POTT, G. T. & KOMMANDEUR, J. (1967). *Mol. Phys.* **13**, 373–390.
 SAKAI, N., SHIROTANI, I. & MINOMURA, S. (1972). *Bull. Chem. Soc. Japan*, **46**, 3321–3328.
 SHIROTANI, I. & KOBAYASHI, H. (1973). *Bull. Chem. Soc. Japan*, **46**, 2595–2596.
 VEGTER, J. G., HIBMA, T. & KOMMANDEUR, J. (1969). *Chem. Phys. Lett.* **3**, 427–429.
 X-RAY system (1973). Dutch version of the X-RAY 72 system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.