Acta Cryst. (1974). B**30**, 1294

The Crystal Structure of Sodium 7,7,8,8-Tetracyanoquinodimethanide

BY M. KONNO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 28 *December* 1973; *accepted* 18 *January* 1974)

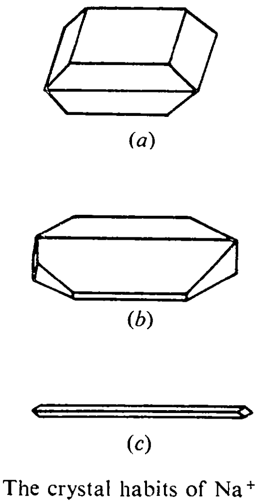
Crystals of Na^+TCNQ^- are triclinic with space group $C\bar{1}$ and lattice constants $a=6{\cdot}993$ (1), $b=23{\cdot}707$ (2), $c=12{\cdot}469$ (2) Å, $\alpha=90{\cdot}14$ (2), $\beta=98{\cdot}58$ (1), $\gamma=90{\cdot}76$ (1)° and $Z=8$. Reflexions with h and k both odd are very weak, while those with h and k even are generally strong. The average structure was deduced from Patterson maps based on strong even reflexions only. The atomic coordinates thus derived were adjusted with reference to the odd-reflexion Patterson function. Refinement by the block-diagonal least-squares method with the 1254 observed reflexions reduced the R value to 0·046. The TCNQ radical ions form a columnar structure along the a axis with alternating interplanar distances of 3·21 and 3·49 Å. Accordingly, TCNQ dimers are recognized in the structure. A sodium ion is surrounded octahedrally by six negatively charged nitrogen atoms of $TCNQ^-$ at 2·419–2·565 Å.

Introduction

Recent measurements of electrical conductivities, magnetic susceptibilities, heat capacities and other physical properties of the simple salts of alkali metals and TCNQ have revealed that phase transitions occur in all these salts except those of Li (Vegter, Himba & Kommandeur, 1969; Vegter, Kuindersma & Kommandeur, 1971; Sakai, Shirotani & Minomura, 1972). The structure analyses of high- and low-temperature modifications will certainly shed light on the mechanism of the phase transition and lead to a theoretical model to explain magnetic properties. Hoekstra, Spoelder & Vos (1972) determined the crystal structure of the low-temperature modification (reddish-purple) of Rb^+TCNQ^-. They observed that the crystal broke during the transition. Our X-ray work on Na^+TCNQ^- was initiated to obtain structural information concerning the phase change which occurs at 348°K. In the present paper the crystal structure of the low-temperature modification is reported.

Experimental

Crystals of Na^+TCNQ^- were kindly supplied by Dr Sakai of this Institute. Three different types of crystal could be identified by external morphology: they are illustrated in Fig. 1. Preliminary oscillation and Weissenberg photographs indicated that the crystals were all twinned and based on the same triclinic unit cell. In the type (*a*) crystal, two individuals are related to each other by 180° rotation around the common b^* axis. In the type (*b*) crystal, two type (*a*) crystals are further twinned by rotation around the c axis to form quadruplets. Type (*c*) crystals are similar to (*a*) in the mode of twinning, but features of intensity distribution are different. Fig. 2 illustrates the two types of twinning. After taking Weissenberg photographs of a number of type (*a*) crystals, two crystal specimens were selected of which one twin component was much larger than the other. One of these crystals with dimensions 0·4 × 0·25 × 0·08 mm was mounted with the c axis parallel to the φ axis of the goniostat in order to have two neighbouring reflexions from the two individuals on the equatorial plane. Using 14 strong reflexions which were separated by more than 0·7° in ω, the value $K=I(hkl)_{\rm I}/I(hkl)_{\rm II}$ was estimated to be 6·5, where I is the intensity and I and II stand for the twin components. All the accessible reflexions with 2θ less than 45° were measured using Mo $K\alpha$ radiation. The ω-scan technique was employed because of twinning. The reflexion distance g (de Boer & Vos, 1972) was calculated for each reflexion in order to judge whether neighbouring reflexions overlapped or not. For g greater than the scan range the reflexions were considered as being free. If the two neighbouring reflex-


(*a*)

(*b*)

(*c*)

Fig. 1. The crystal habits of Na^+TCNQ^-.

ions overlapped, the intensities of the two reflexions were measured at the same time and were separated later according to the value of K. Three standard reflexions were measured every three hours. The observed intensities were corrected for Lorentz and polarization effects but corrections for absorption and extinction were not made. In total, 1254 independent reflexions with $|F| \geq 3\sigma$ were collected.

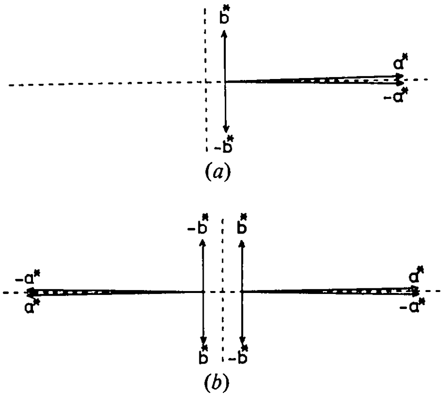


Fig. 2. Mutual orientation of components in twinning crystals. (a) Mutual orientations of two components for crystals of type (a). (b) Mutual orientations of four components for crystals of type (b).

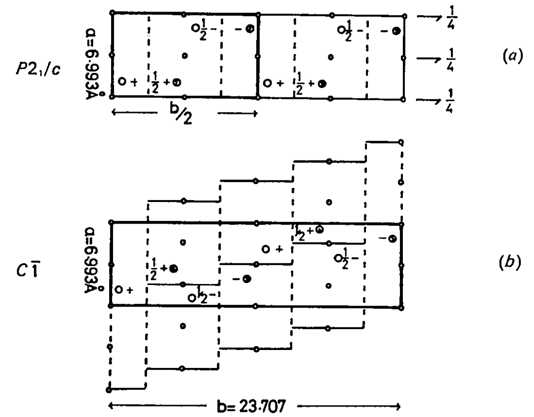


Fig. 3. Derivation of a polysynthetic structure. (a) Two unit cells based on the space group $P2_1/c$. (b) A polysynthetic twinning derived from (a). The space group is triclinic $C\bar{1}$.

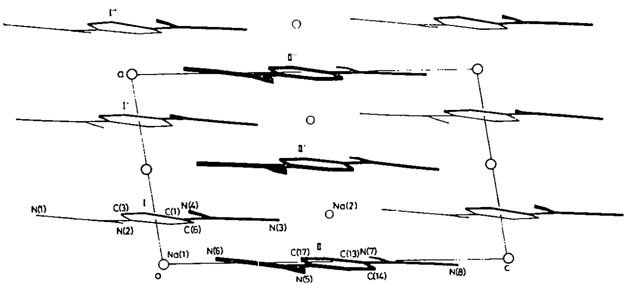


Fig. 4. The structure viewed along the b axis. A set of TCNQ's related to those in the figure by a shift of $\mathbf{a}/2+\mathbf{b}/2$ is not drawn.

The crystal is triclinic and extra extinction rules not explained by the space group were observed. The extra extinctions and the characteristic features of the intensity distribution can be most conveniently interpreted on the basis of a non-primitive lattice C with the cell dimensions listed in Table 1. The space group is $C\bar{1}$ or $C1$. $C\bar{1}$ was tentatively assumed and this was verified at a later stage by calculation of the structure factors.

In addition to the usual systematic absence hkl for $h+k$ odd, the following characteristic features of the intensity distribution were recognized. When h and k are even, hkl and $h\bar{k}l$ are very nearly equal in intensity and they are generally strong (hereafter referred to as an 'even reflexion'), whereas they are unequal and weak if h and k are odd (hereafter referred to as an 'uneven reflexion'). $h0l$ is absent or very weak if $h/2+l$ is odd. $0k0$ appeared for only $k=4n$, where n is an integer.

Table 1. *Crystallographic data*

$Na(C_{12}H_4N_4)$, F.W. 227·2
Space group: triclinic $C\bar{1}$
$a=6{\cdot}993\ (1)$, $b=23{\cdot}707\ (2)$, $c=12{\cdot}469\ (2)$ Å
$\alpha=90{\cdot}14\ (2)$, $\beta=98{\cdot}58\ (1)$, $\gamma=90{\cdot}76\ (1)°$
$U=2044$ Å^3
$D_m=1{\cdot}48\ \mathrm{g\ cm^{-3}}$, $Z=8$, $D_x=1{\cdot}48\ \mathrm{g\ cm^{-3}}$
$\mu(\mathrm{Mo}\ K\alpha,\ \lambda=0{\cdot}7107\ \text{Å})=1{\cdot}56\ \mathrm{cm^{-1}}$

Structure determination

Initially the average structure was deduced on the basis of even reflexions only. It was assumed that (i) $I(hkl)=I(h\bar{k}l)$, (ii) $h0l$ is absent when $h/2+l$ is odd, and (iii) $\alpha=\gamma=90°$.

These conditions, combined with the extra extinction rule $0k0$ for $k\neq 4n$, indicate that the average structure is based on the space group $P2_1/n$ and the lattice vectors are $\mathbf{a}/2$, $\mathbf{b}/2$ and $\mathbf{c}$, where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the lattice vectors of the original triclinic unit cell. The general position of the space group $P2_1/n$ is fourfold. The TCNQ molecules are thus required to lie on a set of twofold positions, since there are only two formula units in the new unit cell. The average structure was deduced from the three-dimensional Patterson function based on 'even reflexions' only. The orientation of the TCNQ molecules could be fixed by the peaks around the origin. Initial positional parameters of the TCNQ molecules thus deduced gave a conventional R value of 0·53. Three-dimensional electron density maps phased on the basis of the TCNQ molecules clearly showed the positions of the Na atoms. The R value then reduced to 0·29.

The relationship between the average structure and the real structure based on the triclinic space group $C\overline{1}$ can easily be derived in terms of the following polysynthetic twinning (Ito, 1950). Fig. 3 illustrates the relationship. In Fig. 3(*a*) two consecutive unit cells are drawn with the lattice vectors **a**, **b**/2 and **c**. Arrangement of the equivalent points conforms to the space group $P2_1/c$. If the structural units between the adjacent *c* glide planes are shifted by **a**/4 'en echelon' a polysynthetic structure shown in Fig. 3(*b*) is generated. Addition of a set of eight equivalent points related to the first by translation **a**/2 gives the average structure mentioned above. The structure shown in Fig. 3(*b*) is based on the triclinic space group $C\overline{1}$.

Close examination of the odd Patterson function on the basis of 'uneven reflexions' (Sakurai, 1958) revealed unequivocally the deviations of the actual structure from the averaged structure. The trial coordinates of all the atoms could easily be deduced. Several cycles of least-squares refinement were carried out with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms. The *R* value converged to 0·046 for the 1254 observed reflexions. At the final stage of the refinement all the parameter shifts were less than half of the corresponding standard deviations. Unit weight was given to all reflexions. The atomic scattering factors for C, H, N and Na^+ were those listed in *International Tables for X-ray Crystallography* (1962). The calculated and

Table 3. *Atomic parameters of non-hydrogen atoms* (× 10^4)

The values of β_{ij} refer to the expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Here and elsewhere in this paper the estimated standard deviations in the last figure are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	−1 (4)	2523 (1)	24 (2)	176 (7)	9 (1)	43 (2)	3 (2)	24 (3)	2 (1)
Na(2)	2501 (4)	7 (1)	5052 (2)	178 (7)	10 (1)	40 (2)	1 (2)	29 (3)	−1 (1)
C(1)	2387 (8)	476 (2)	828 (4)	91 (11)	10 (1)	34 (4)	−2 (3)	11 (6)	0 (2)
C(2)	2688 (8)	580 (2)	−247 (5)	124 (13)	9 (1)	43 (4)	−0 (3)	11 (6)	4 (2)
C(3)	2667 (8)	156 (2)	−988 (4)	121 (13)	10 (1)	41 (4)	−4 (4)	19 (7)	1 (2)
C(4)	2366 (8)	−419 (2)	−699 (4)	117 (12)	10 (1)	35 (4)	−10 (3)	9 (6)	−0 (2)
C(5)	2121 (8)	−528 (2)	382 (4)	122 (13)	8 (1)	38 (4)	0 (3)	6 (6)	4 (2)
C(6)	2153 (8)	−102 (2)	1129 (4)	136 (13)	8 (1)	33 (4)	5 (3)	8 (6)	5 (2)
C(7)	2408 (8)	913 (2)	1600 (4)	117 (12)	7 (1)	37 (4)	0 (3)	5 (6)	1 (2)
C(8)	2348 (8)	−863 (2)	−1472 (4)	141 (14)	7 (1)	39 (4)	4 (3)	20 (7)	5 (2)
C(9)	2537 (8)	−747 (2)	−2564 (5)	126 (13)	7 (1)	41 (4)	8 (3)	12 (7)	2 (2)
C(10)	2268 (8)	−1438 (2)	−1166 (4)	115 (12)	10 (1)	40 (4)	0 (3)	17 (6)	1 (2)
C(11)	2317 (8)	802 (2)	2710 (5)	138 (13)	7 (1)	43 (4)	−2 (4)	10 (7)	−2 (2)
C(12)	2598 (8)	1485 (2)	1289 (4)	116 (12)	9 (1)	36 (4)	−1 (3)	16 (6)	−2 (2)
C(13)	−65 (8)	2047 (2)	5810 (4)	106 (12)	8 (1)	42 (4)	−1 (3)	10 (6)	−1 (2)
C(14)	−393 (8)	2622 (2)	6116 (5)	136 (13)	9 (1)	43 (4)	2 (4)	25 (7)	−3 (2)
C(15)	−395 (8)	3036 (2)	5386 (5)	146 (13)	8 (1)	43 (4)	−0 (3)	17 (7)	−3 (2)
C(16)	−165 (8)	2936 (2)	4284 (4)	116 (12)	9 (1)	35 (4)	3 (3)	19 (6)	−3 (2)
C(17)	193 (8)	2358 (2)	4001 (4)	166 (15)	10 (1)	34 (4)	−1 (4)	27 (7)	−2 (2)
C(18)	181 (8)	1939 (2)	4727 (4)	129 (12)	8 (1)	38 (4)	3 (3)	21 (6)	−2 (2)
C(19)	−79 (8)	1610 (2)	6584 (4)	142 (13)	10 (1)	35 (4)	−4 (4)	11 (7)	−3 (2)
C(20)	−194 (8)	3377 (2)	3510 (5)	127 (13)	9 (1)	39 (4)	−1 (3)	5 (7)	1 (2)
C(21)	−361 (7)	3951 (2)	3824 (4)	86 (11)	10 (1)	27 (4)	2 (3)	8 (6)	2 (2)
C(22)	50 (8)	3265 (2)	2433 (4)	151 (13)	7 (1)	42 (4)	−6 (4)	19 (6)	−4 (2)
C(23)	167 (8)	1033 (2)	6288 (4)	115 (12)	9 (1)	25 (4)	7 (3)	−1 (6)	6 (2)
C(24)	−190 (8)	1722 (2)	7690 (5)	147 (13)	7 (1)	44 (4)	−7 (3)	15 (7)	−0 (2)
N(1)	2708 (8)	−648 (2)	−3442 (4)	254 (16)	14 (1)	51 (4)	4 (4)	40 (7)	2 (2)
N(2)	2207 (8)	−1901 (2)	−915 (4)	197 (13)	9 (1)	50 (4)	9 (3)	27 (6)	3 (2)
N(3)	2219 (8)	693 (2)	3590 (4)	233 (15)	14 (1)	44 (4)	2 (4)	20 (7)	2 (2)
N(4)	2742 (8)	1938 (2)	1003 (4)	194 (13)	9 (1)	47 (4)	0 (3)	19 (6)	3 (2)
N(5)	−422 (7)	4409 (2)	4084 (4)	176 (12)	9 (1)	51 (4)	−2 (3)	18 (6)	−4 (2)
N(6)	221 (8)	3174 (2)	1549 (4)	232 (15)	15 (1)	45 (4)	−3 (4)	27 (7)	−5 (2)
N(7)	279 (7)	581 (2)	5992 (4)	193 (13)	10 (1)	47 (4)	2 (3)	25 (6)	−3 (2)
N(8)	−274 (8)	1835 (2)	8572 (4)	238 (15)	12 (1)	38 (4)	−6 (4)	18 (6)	−3 (2)

Positional parameters of hydrogen atoms (× 10^3)

H(2)	287 (8)	97 (2)	−47 (5)
H(3)	285 (9)	21 (3)	−170 (5)
H(5)	199 (9)	−91 (3)	66 (5)
H(6)	196 (8)	−19 (3)	188 (5)
H(14)	−51 (8)	274 (3)	699 (5)
H(15)	−51 (9)	341 (3)	563 (5)
H(17)	32 (9)	231 (3)	323 (5)
H(18)	38 (9)	159 (3)	451 (5)

Mean isotropic temperature factor of hydrogen atom is 1·5 Å^2.

observed structure factors are compared in Table 2.* The atomic parameters and their estimated standard deviations are listed in Table 3.

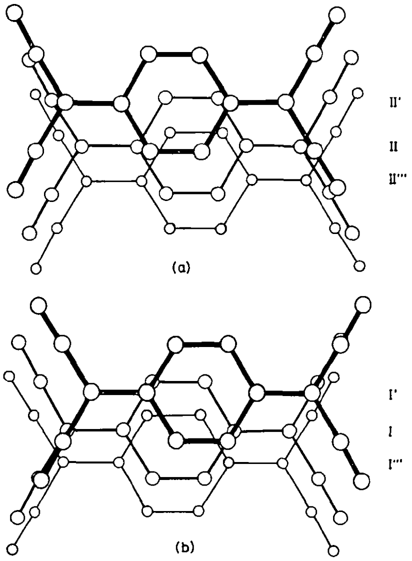


Fig. 5. Nearest-neighbour overlap. (*a*) Within a column of TCNQ I. (*b*) Within a column of TCNQ II.

Description of the structure and discussion

Fig. 4 shows a projection of the structure along the *b* axis. Two crystallographically independent molecules (I and II) exist. TCNQ radical ions form dimers and these are stacked along the *a* axis in a plane-to-plane manner to form columns. The planes of two TCNQ ions are inclined at an average angle of 74° to the *a* axis. One column consists of TCNQ I ions with alternating interplanar distances of 3·223 and 3·505 Å, and the other, consisting of TCNQ II, has interplanar separations of 3·200 and 3·480 Å. The short contacts within a column are given in Table 4. Short interplanar spacings in a dimer indicate strong charge-transfer interactions. Sodium ions are arranged among the columns of TCNQ ions.

The overlapping of adjacent TCNQ units is illustrated in Fig. 5. The overlapping within a dimer is a modified ring–ring overlap with a shift of the molecular centre along its short axis. The same overlapping mode was observed in crystals of reddish-purple Rb$^+$TCNQ$^-$, Cs$_2$TCNQ$_3$ and morpholinium$_2$-TCNQ$_3$. The interplanar distances range from 3·16 to 3·26 Å (Hoekstra, Spoelder & Vos, 1972; Fritchie & Arthur, 1966; Sundaresan & Wallwork, 1972*a*). In ditoluenechromium–TCNQ the same overlapping mode was observed with a much longer interplanar spacing of 3·42 Å (Shibaeva, Atovmyan & Rozenberg, 1969). The overlapping of adjacent dimers is a modified ring–ring overlap with a diagonal shift of the molecular centre. This mode of overlap is similar to that in *N*-

Table 4. *Relevant intermolecular distances* (Å)

The C···C and C···N distances shorter than 3·5 Å are listed.

Key to symmetry operations

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

Distances between TCNQ I′ and TCNQ I″ within a TCNQ diad

C(1)····C(4^{i})	3·305 (8)	C(1)····C(5^{i})	3·289 (7)
C(2)····C(5^{i})	3·342 (8)	C(3)····C(6^{i})	3·349 (8)
C(4)····C(6^{i})	3·377 (8)	C(7)····C(8^{i})	3·306 (8)
C(7)····C(10^{i})	3·481 (8)	C(8)····C(11^{i})	3·400 (8)
C(9)····C(11^{i})	3·373 (8)	C(9)····N(3^{i})	3·385 (8)
C(10)···C(12^{i})	3·384 (8)	C(12)···N(2^{i})	3·479 (8)
N(1)····N(3^{i})	3·423 (8)	N(2)····N(4^{i})	3·446 (8)

Distance between TCNQ I and TCNQ I′ of the two adjacent diads

C(12)···N(1^{ii})	3·487 (8)

Distances between TCNQ II and TCNQ II″ within a TCNQ diad

C(13)···C(15^{iii})	3·303 (8)	C(13)···C(16^{iii})	3·321 (8)
C(14)···C(16^{iii})	3·327 (8)	C(14)···C(17^{iii})	3·339 (8)
C(15)···C(18^{iii})	3·330 (8)	C(19)···C(20^{iii})	3·290 (8)
C(19)···C(21^{iii})	3·405 (8)	C(20)···C(24^{iii})	3·354 (8)
C(21)···C(23^{iii})	3·344 (8)	C(22)···C(24^{iii})	3·379 (8)
C(22)···N(8^{iii})	3·392 (8)	C(23)···N(5^{iii})	3·431 (7)
N(5)····N(7^{iii})	3·431 (7)	N(6)····N(8^{iii})	3·440 (8)

Distance between TCNQ II and TCNQ II′ of the two adjacent diads

C(24)···N(6^{iv})	3·467 (8)

---

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30352 (11pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

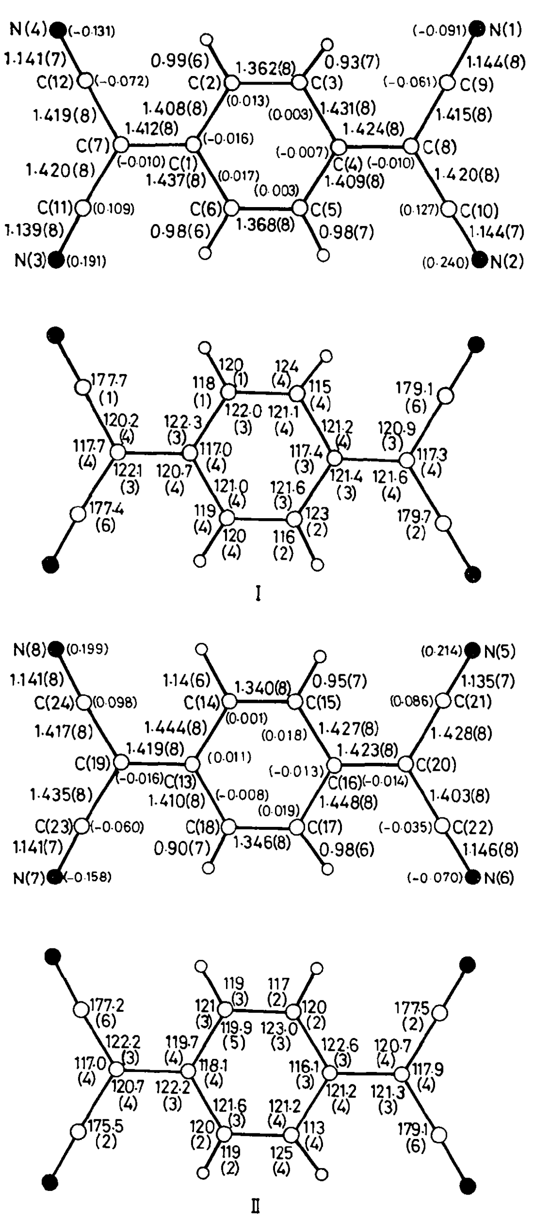


Fig. 6. Bond distances (Å) and bond angles (°) in TCNQ I and II with their standard deviations. The numbers in parentheses represent the atomic deviations from the least-squares planes through the quinodimethane skeletons.

(n-propyl)quinolinium–TCNQ and methyltriphenylphosphonium–TCNQ$_2$ above the transition temperature (Sundaresan & Wallwork, 1972*b*; Konno & Saito, 1973). The molecular geometry is summarized in Fig. 6. Differences between chemically equivalent bonds are not significant, and no meaningful difference is recognized between TCNQ I and II. Their average bond distances are longer for double bonds and shorter for single bonds than those observed in crystals of TCNQ (Long, Sparks & Trueblood, 1965). The deviations of atoms from the least-squares plane through the quinodimethane skeleton indicate that TCNQ moieties are not quite planar and the tails of C–(CN)$_2$ are twisted slightly around the C=C bonds, the average twist angle being 5°. The structure viewed along the *a* axis is presented in Fig. 7. A sodium cation is surrounded octahedrally by the six negatively charged nitrogen atoms of different TCNQ ions. The distances between them are in the range 2·419 to 2·565 Å. They agree with the sum of the ionic radius of Na$^+$ (1·0 Å) and the van der Waals radius of the nitrogen atom (1·5 Å).

The distances between nitrogen atoms surrounding a sodium cation ranges from 3·384 to 3·686 Å, which are longer than the sum of the van der Waals radii owing to the electrostatic repulsive force. In crystalline reddish-purple Rb$^+$TCNQ$^-$ and K$^+$TCNQ$^-$, cations are surrounded by eight nitrogen atoms which occupy the corners of a cube (Anderson & Fritchie, 1963). The structure of K$^+$TCNQ$^-$ is closely related to that of Na$^+$TCNQ$^-$. If Na(1) and TCNQ II are shifted by **a**/4, the structure of K$^+$TCNQ$^-$ is obtained. In Na, K and reddish-purple Rb salts of TCNQ, the structural features of the columns formed by the TCNQ units are very similar, with modified ring–ring overlap, whereas in the case of dark-purple Rb$^+$TCNQ$^-$ the interplanar spacing in the dimer is much wider than in the others, the overlapping mode being of the ring–external bond type (Shirotani & Kobayashi, 1974). The former group of simple salts undergoes the phase transition above room temperature and the latter at 231 °K, suggesting that the mode of overlapping and the interplanar spacings might affect the transition temperature.

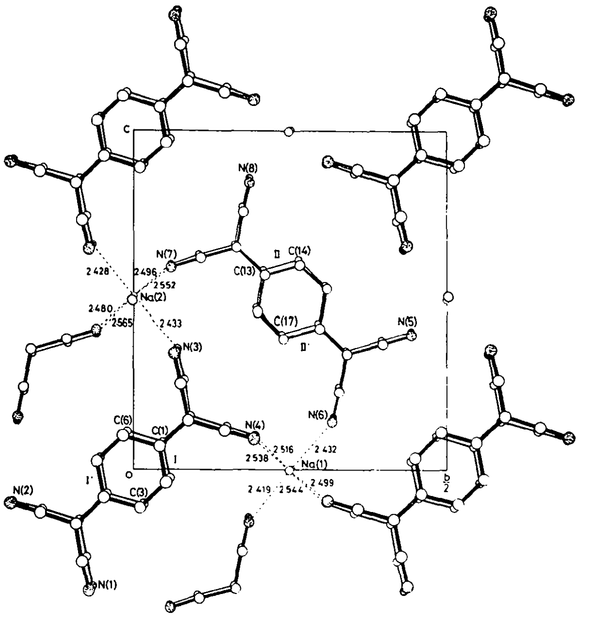


Fig. 7. The structure viewed along the *a* axis.

All the calculations were carried out on the FACOM 270-30 at this Institute with a local version of the Universal Crystallographic Computation Program System, UNICS (1967, Crystallographic Society of Japan). Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

References

ANDERSON, G. R. & FRITCHIE, C. J. (1963). Second National Meeting, Society for Applied Spectroscopy, San Diego, October 14–18, paper 111.

BOER, J. L. DE & VOS, A. (1972). *Acta Cryst.* B**28**, 839–848.

FRITCHIE, C. J. & ARTHUR, P. (1966). *Acta Cryst.* **21**, 139–145.

HOEKSTRA, A., SPOELDER, T. & VOS, A. (1972). *Acta Cryst.* B**28**, 14–25.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

ITO, T. (1950). *X-ray Studies on Polymorphism.* Tokyo: Maruzen.

KONNO, M. & SAITO, Y. (1973). *Acta Cryst.* B**29**, 2815–2824.

LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932–939.

SAKAI, N., SHIROTANI, I. & MINOMURA, S. (1972). *Bull. Chem. Soc. Japan*, **45**, 3321–3328.

SAKURAI, K. (1958). *Acta Cryst.* **11**, 840–842.

SHIBAEVA, R. P., ATOVMYAN, L. O. & ROZENBERG, L. P. (1969). *Chem. Commun.* pp. 649–650.

SHIROTANI, I. & KOBAYASHI, H. (1974). *Bull. Chem. Soc. Japan.* In the press.

SUNDARESAN, T. & WALLWORK, S. C. (1972*a*). *Acta Cryst.* B**28**, 491–497.

SUNDARESAN, T. & WALLWORK, S. C. (1972*b*). *Acta Cryst.* B**28**, 1163–1169.

VEGTER, J. G., HIMBA, T. & KOMMANDEUR, J. (1969). *Chem. Phys. Lett.* **3**, 427–429.

VEGTER, J. G., KUINDERSMA, P. I. & KOMMANDEUR, J. (1971). *Conduction in Low-Mobility Materials*, edited by KLEIN, N., TANNHAUSER, D. S. & POLLAK, M., pp. 363–373. London: Taylor and Francis.

Acta Cryst. (1974). B**30**, 1299

The Crystal Structure of the Triclinic 1:2 Complex of Hexamethylphosphoramide with 5,5-Diethylbarbituric Acid (Barbital)

BY I-NAN HSU* AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *U.S.A.*

(*Received* 26 *December* 1973; *accepted* 4 *February* 1974)

Hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, (M.W. 179·2) and barbital, $C_8H_{12}N_2O_3$, (M.W. 184·2) form a 1:2 triclinic complex, m.p. 124°C, space group $P\bar{1}$, with $a=6\cdot889\ (1)$, $b=12\cdot568\ (1)$, and $c=17\cdot944\ (2)$ Å, $\alpha=75\cdot76\ (1)$, $\beta=87\cdot85\ (1)$, and $\gamma=76\cdot31\ (1)^\circ$, $d_{meas}=1\cdot246$ g cm^{-3}, $Z=2[(CH_3)_2N]_3+4C_8H_{12}N_2O_3$, and a monoclinic complex of undetermined composition, m.p. 67°C, space group Cc or $C2/c$ with $a=45\cdot64$, $b=20\cdot29$, and $c=13\cdot91$ Å, $\beta=106\cdot4^\circ$, $d_{meas}=1\cdot172$ g cm^{-3}, $Z=48$ molecules. The crystal structure of the triclinic complex has been determined by the heavy-atom method, from 6020 integrated X-ray intensities measured on a computer-controlled four-circle diffractometer, using graphite-monochromated Cu $K\alpha$ radiation. Refinement by a block-diagonal least-squares procedure gave a final R value of 0·062 for all reflections. The hydrogen bonding is of interest as a model for possible barbiturate–phospholipid interactions. There are two rather strong NH···O=P hydrogen bonds (N···O distances 2·81, 2·84 Å) formed at the phosphoryl oxygen atom. There are also two NH···O=C hydrogen bonds which both form at the same barbital oxygen atom (N···O distances 2·92, 2·93 Å).

Introduction

The drug-active barbiturates, such as 5,5-diethylbarbituric acid or barbital (Fig. 1), form crystal complexes with a variety of molecules which are of biological interest, such as adenine derivatives (Kyogoku, Lord & Rich, 1968; Kim & Rich, 1968; Voet, 1972), amides (Gartland & Craven, 1974; Hsu & Craven, 1974*a*), and imidazole (Hsu & Craven, 1974*b*). The most important molecular interactions in these crystal structures are the hydrogen bonds. Those hydrogen bonds in which the barbiturate NH groups are donors tend to be short, whereas those in which barbiturate oxygen atoms are acceptors tend to be long (Gartland & Craven, 1974; Hsu & Craven, 1974*b*). This suggests that barbiturates are better hydrogen-bonding donors than acceptors and that the preferred barbiturate binding sites in bio-

---

* Present address: Department of Chemistry, University of Toronto, Ontario, Canada M5S 1A1.