The Crystal Structure of the 1:1 Molecular Complex of Phenanthrene and 1,2,4,5-Tetracyanobenzene

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$C_{14}H_{10} \cdot C_{10}H_2N_4$ is monoclinic, space group $C2/m$, with $a = 9.413$ (1), $b = 13.104$ (2), $c = 7.260$ (1) Å, $\beta = 93.06$ (1)°, $Z = 2$. The structure was refined with constraints on molecular geometry to an R of 0.044 for 617 counter reflections. Alternate planar phenanthrene and tetracyanobenzene molecules, with dimensions in good agreement with those from independent determinations, form stacks along c. The mean separation of the molecular planes is 3.45 Å and the interplanar angle is 3.1°. Phenanthrene conforms to the site symmetry $2/m$ by random statistical occupation of two mirror-related sites in the disordered structure, and pulsed NMR studies show no evidence of motion between these sites up to 360 K. The structure is closely related to that of the anthracene/tetracyanobenzene complex, and the relative orientation of the two molecules is as predicted by analogy with the latter. This orientation does not maximize charge-transfer interactions, and appears to be determined by packing requirements.

Introduction

Wright, Ohta & Kuroda (1976) showed that anthracene and phenanthrene form a continuous series of mixed molecular complexes with the electron acceptor 1,2,4,5-tetracyanobenzene, of composition (anthracene)$_x$(phenanthrene)$_{1-x}$TCNB (with $0 \le x \le 1$). In order to understand better the relation between the crystal structures of this series of mixed complexes and those of the two parent complexes, we have determined the structure of the phenanthrene/TCNB complex. The crystal structure of the anthracene/TCNB complex has been reported (Tsuchiya, Marumo & Saito, 1972).

Experimental

Slow cooling of a hot concentrated solution of equimolar quantities of pure phenanthrene and TCNB in glacial acetic acid yielded yellow crystals of the complex, elongated along c. Weissenberg photographs revealed the same systematic absences (*hkl* absent when $h + k$ odd) as anthracene/TCNB (Tsuchiya, Marumo & Saito, 1972), with similar cell dimensions. Cell parameters and intensities were measured on a Rigaku four-circle diffractometer at room temperature with Mo $K\alpha$ radiation. 1522 reflections with $2\theta < 60°$ were examined. Those with $|F_o| < 3\sigma(F_o)$ were regarded as unobserved, and the remaining 617 reflections were used in the structure determination.

Lorentz and polarization corrections were applied, but none was made for absorption [μ(Mo $K\alpha$) = 0.66 cm^{-1}].

Crystal data

$C_{24}H_{12}N_4$, $M_r = 356.4$, monoclinic, $a = 9.413$ (1), $b = 13.104$ (2), $c = 7.260$ (1) Å, $\beta = 93.06$ (1)°, $U = 894.2$ Å^3, $D_m = 1.32$ (by flotation), $Z = 2$, $D_c = 1.32$ g cm^{-3}, space group $C2/m$, Cm or $C2$ (from systematic absences).

Structure solution and refinement

The crystal data suggest that the anthracene and phenanthrene complexes have closely related crystal structures. However, the molecular symmetries of anthracene and phenanthrene are different. A packing very similar to that of the anthracene complex is obtained if the space group is assumed to be $C2$, with the centres of mass of the phenanthrene molecules occupying special positions $2(a)$ $(0,y,0)$ and those of the TCNB molecules occupying positions $2(b)$ $(0,y,\frac{1}{2})$, with molecular and crystallographic twofold axes coincident. Examination of the Patterson synthesis confirmed this model and suggested that the molecules lay close to the (102) plane. A group-refinement procedure, with the known molecular geometries of phenanthrene (Kay, Okaya & Cox, 1971) and TCNB (Prout & Tickle, 1973), molecular centres (X_i, Y_i, Z_i)

and the angles between molecular and crystal axes $(\omega_i, \varphi_i, \psi_i)$, was used in the initial refinement of this model. For phenanthrene, X, Y and Z may be set to zero. Since rotation is allowed only about b, $\omega = \psi = 0$ and the adjustable parameters are φ and the isotropic temperature factor B. Similarly, for TCNB the adjustable parameters are Y, φ and B. This refinement converged with $R = 0.229$. Further refinement with anisotropic temperature factors reduced R to 0.173. Full-matrix refinement with the same space group, treating all atoms as independent and varying individual atomic coordinates and anisotropic temperature factors, converged with $R = 0.103$. However, the resulting molecular geometry of phenanthrene was unreasonably distorted, suggesting the possibility of disorder. A difference synthesis based on the results of group refinement with anisotropic temperature factors revealed a second orientation of the phenanthrene molecule, apparently related to the first by a mirror plane through the origin, perpendicular to b. Attempts to refine the positions of molecules in these two orientations independently with adjustable occupancy factors yielded unreasonable results. A mirror-image relation between the two orientations was therefore adopted and further isotropic group refinement was carried out with several different occupancy factors for the two sites, treated as a pair (Table 1). These results suggest that the two sites are occupied with equal probability, and this was assumed in subsequent refinement. Refinement of anisotropic temperature factors, with fixed atomic coordinates, further reduced R to 0.153 ($C2$) or 0.164 ($C2/m$). There is no clear distinction between these alternative space groups if the two sites are equally occupied, as the lower R for the former may simply be a consequence of the increased number of adjustable parameters. Further refinement of the anisotropic temperature factors of all atoms and atomic coordinates of TCNB, with fixed atomic coordinates for phenanthrene and space group $C2$, converged with $R = 0.140$. With space group $C2/m$, refinement varying all parameters reduced R to 0.093, but the molecular geometry of phenanthrene was again distorted, probably because of the close proximity of pairs of C atoms in the disordered model. These calculations used the Hitac 8700/8800 computer at the University of Tokyo Computer Centre, with the

Table 1. *Results of refinements with different occupancy factors for the phenanthrene molecule*

First site	Second site	R	Space group
		Weight	
0.9	0.1	0.227	
0.85	0.15	0.222	
0.8	0.2	0.191	$C2$
0.7	0.3	0.182	
0.5	0.5	0.177	
0.5	0.5	0.182	$C2/m$

UNICS programs (Crystallographic Society of Japan, 1967) and scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1962).

In view of the accuracy of the intensities, it was felt that the refinement was still unsatisfactory. Further refinement was therefore carried out with the Oxford *CRYSTALS* programs (Carruthers, 1975) on the Oxford University ICL 1906A computer, with scattering factors taken from *International Tables for X-ray Crystallography* (1974). Refinement was by least squares with a large-block approximation to the normal matrix, with the positional parameters of all atoms in one block and the scale factor and anisotropic temperature factors in a second. $C2/m$ was used, with constraints (Waser, 1963; Rollett, 1969) derived from the known molecular geometries of phenanthrene (Kay, Okaya & Cox, 1971) and TCNB (Prout & Tickle, 1973) on all bond lengths and angles. In addition, the difference in mean square displacements along the bond direction of the two atoms forming each bond was constrained to be zero with an e.s.d. of 0.005 Å^2, and the molecules were constrained to be planar within an e.s.d. of 0.01 Å. This refinement converged with $R = 0.079$. Fourier syntheses in the planes of phenanthrene and TCNB revealed electron density in the expected H atom positions. The H atoms were therefore placed geometrically, with $C-H$ 1.00 Å, to lie in the relevant molecular plane along the bisector of the appropriate $C-C-C$ angle, and assigned isotropic temperature factors of 0.05 Å^2. Further constrained refinement varying all positional parameters, anisotropic temperature factors (for C and N) and isotropic temperature factors (for H) converged with $R = 0.054$. The only constraints were those used previously for mean square displacements along the bonds, together with the planarity constraints on phenanthrene, with the $C-H$ lengths constrained to be 1.00 Å with an e.s.d. of 0.01 Å and the $C-C-H$ angles constrained to their common mean with an e.s.d. of $1°$. Each reflection was then assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r(X)$, where n is the number of coefficients, A_r, for a Chebyshev series, T_r is the polynomial function, and X is $F_o/F_o(\text{max.})$. Four coefficients, A_r, were used, with values 50.4, 66.1, 14.3 and -2.1 (Rollett, 1965). The final refinement converged with $R = 0.044$. The average and maximum parameter shifts in the final cycle of refinement were 0.12 and 1.00 e.s.d. respectively.

Results and discussion

The final atomic coordinates are given in Table 2.*
Projections of the structure are shown in Figs. 1 and 2.

The crystal is built up of stacks along c of alternating donor and acceptor molecules characteristic of $\pi-\pi^*$ electron donor–acceptor complexes. Bond distances and angles are given in Table 3. These are in good agreement with those in phenanthrene (Kay, Okaya &

Table 2. *Final atomic coordinates* $(\times 10^4)$, *with standard deviations in parentheses*

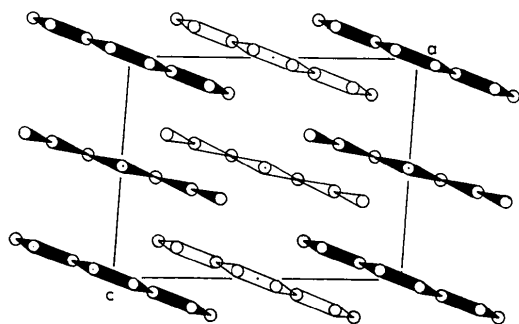|	x	y	z
C(1)	−744 (3)	−283 (2)	−349 (3)
C(2)	−1495 (5)	−1180 (3)	−749 (4)
C(3)	−2896 (5)	−1146 (4)	−1417 (5)
C(4)	−3573 (3)	−223 (4)	−1737 (4)
C(5)	−2871 (5)	673 (4)	−1395 (5)
C(6)	−1435 (4)	656 (3)	−696 (4)
C(7)	−690 (4)	1588 (3)	−336 (4)
C(8)	0	1067 (2)	5000
C(9)	1232 (1)	534 (1)	5510 (2)
C(10)	2510 (2)	1092 (1)	6032 (2)
N(1)	3510 (2)	1547 (1)	6444 (2)
H(1)	−1030 (13)	−1855 (8)	−506 (14)
H(2)	−3418 (13)	−1798 (9)	−1666 (14)
H(3)	−4585 (11)	−213 (10)	−2226 (13)
H(4)	−3361 (13)	1339 (9)	−1637 (14)
H(5)	−1191 (12)	2247 (8)	−586 (13)
H(6)	0	1830 (7)	5000

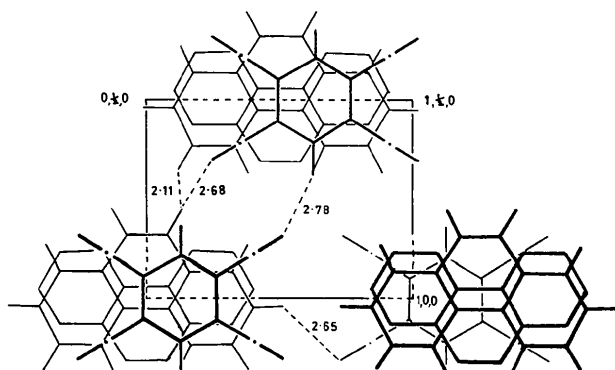Fig. 1. Projection of the structure along **b**.

Fig. 2. Projection of the structure on the plane of the phenanthrene molecule at the origin. The transformation matrix from the fractional atomic coordinates of the monoclinic unit cell to the orthogonal (Å) best-plane coordinates X, Y and Z (with Z perpendicular to the molecular plane) is:

$$\begin{pmatrix} 8.7961 & 0.0000 & 2.2192 \\ 0.0000 & 13.1040 & 0.0000 \\ -3.3516 & 0.0000 & 6.9125 \end{pmatrix}.$$

Cox, 1971) and TCNB (Prout & Tickle, 1973) or its complexes (see, for example, Tsuchiya, Marumo & Saito, 1972). The TCNB molecule is planar, the maximum deviation from the least-squares best plane through the molecule being only 0·002 Å. With the exception of C(2) and C(3), the mean deviation of the C atoms of phenanthrene from the best plane through the central ring of the molecule is only 0·001 Å, which is much smaller than the e.s.d. of 0·01 Å used in the planarity constraint. C(2) and C(3) show larger deviations from this plane (0·017 and 0·009 Å respectively), as found by Kay, Okaya & Cox (1971), which probably result from repulsions between H(1) and the corresponding atom related by the twofold symmetry axis of the molecule. The distance between these two H atoms (2·04 Å), although shorter than the normal van der Waals contact distance (2·34 Å, Kitaigorodsky, 1961), is not as short as H—H distances in more overcrowded aromatic hydrocarbons {*e.g.* 1·82 and 1·87 Å in tetrabenzo[*a,cd,j,lm*]perylene (Kohno, Konno, Saito & Inokuchi, 1975)}. The angle between the best planes through phenanthrene and TCNB is 3·1°: it is commonly found that donor and acceptor molecules are not exactly parallel if the acceptor does not lie symmetrically above the donor, as in this case (Prout & Wright, 1964). The mean interplanar spacing between phenanthrene and TCNB (3·45) is close to that in the anthracene (3·42), naphthalene (3·43), tetramethyl-*p*-phenylenediamine (3·40) and pyrene (3·50 Å) complexes of tetracyanobenzene. There is no correlation

Table 3. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

Atoms designated with single and double primes respectively are related by the twofold axis and mirror plane to the corresponding unprimed atoms.

C(1)—C(2)	1·392 (5)	C(2)—H(1)	0·999 (9)
C(2)—C(3)	1·381 (7)	C(3)—H(2)	0·997 (9)
C(3)—C(4)	1·381 (7)	C(4)—H(3)	0·999 (9)
C(4)—C(5)	1·364 (7)	C(5)—H(4)	0·998 (9)
C(5)—C(6)	1·418 (6)	C(7)—H(5)	0·996 (9)
C(1)—C(6)	1·407 (5)	C(8)—C(9)	1·387 (2)
C(6)—C(7)	1·426 (5)	C(9)—C(9')	1·398 (3)
C(1)—C(1')	1·469 (6)	C(9)—C(10)	1·442 (2)
C(7)—C(7')	1·363 (8)	C(10)—N(1)	1·141 (2)
		C(8)—H(6)	1·000 (9)
C(6)—C(1)—C(2)	118·5 (3)	C(4)—C(3)—H(2)	120·1 (7)
C(6)—C(1)—C(1')	119·0 (2)	C(3)—C(4)—H(3)	119·6 (7)
C(1')—C(1)—C(2)	122·5 (2)	C(5)—C(4)—H(3)	119·8 (7)
C(1)—C(2)—C(3)	120·6 (4)	C(4)—C(5)—H(4)	120·4 (7)
C(2)—C(3)—C(4)	120·7 (4)	C(6)—C(5)—H(4)	120·0 (7)
C(3)—C(4)—C(5)	120·6 (3)	C(6)—C(7)—H(5)	119·1 (7)
C(4)—C(5)—C(6)	119·6 (4)	C(7')—C(7)—H(5)	119·9 (7)
C(5)—C(6)—C(1)	120·0 (3)	C(9')—C(8)—C(9)	119·4 (2)
C(5)—C(6)—C(7)	120·1 (4)	C(9")—C(9)—C(8)	120·3 (1)
C(1)—C(6)—C(7)	119·9 (3)	C(9")—C(9)—C(10)	120·5 (1)
C(6)—C(7)—C(7')	121·0 (2)	C(9)—C(10)—N(1)	178·9 (2)
C(1)—C(2)—H(1)	119·9 (7)	C(8)—C(9)—C(10)	119·2 (1)
C(3)—C(2)—H(1)	119·5 (7)	C(9)—C(8)—H(6)	120·3 (1)
C(2)—C(3)—H(2)	119·2 (7)	C(9')—C(8)—H(6)	120·3 (1)

between these distances and the strength of the charge-transfer interaction. The shortest contact between atoms of different molecules in the stack is C(3)—C(12) (3·39 Å). The relative orientation of the molecules (Fig. 2) is very close to that predicted (Wright, Ohta & Kuroda, 1976) by analogy with the anthracene/TCNB structure, with the phenanthrene placed so as to occupy a space as similar as possible to that of the anthracene. This suggests that packing factors play an important role in determining the orientation. To investigate whether this orientation is also close to one maximizing the charge-transfer interaction between an isolated phenanthrene/TCNB pair, self-consistent-field molecular-orbital calculations were carried out (Ohta, Kuroda & Kunii, 1970) for a variety of orientations. The orientation maximizing the electronic stabilization is one in which the TCNB molecule is symmetrically placed with respect to two of the aromatic rings of phenanthrene (corresponding approximately to a 30° in-plane rotation of the TCNB molecule from its observed orientation). The observed orientation provides 80% of the maximum stabilization. Thus, the relatively weak attractive forces between phenanthrene

and TCNB appear to be less important than packing effects in determining the relative orientation of the molecules, although the observed orientation does not grossly disfavour the attractive interactions.

The shortest contacts between molecules in different stacks are shown in Fig. 2. The N—H contacts of 2·65 and 2·68 Å are only slightly shorter than the van der Waals contact distance (2·70 Å). However, the contact of 2·11 Å between H(2) and H(5) at $|-(1 + x), y - 1, -z|$ is significantly shorter than the normal van der Waals contact distance of 2·34 Å. If the phenanthrene molecule is rotated in-plane by 4°, this contact becomes normal (2·36 Å). Examination of the thermal ellipsoid plot for phenanthrene (Fig. 3) reveals a fairly large in-plane motion of the whole molecule. Analysis (Schomaker & Trueblood, 1968) of the anisotropic temperature factors (Table 4) shows that both molecules are moving as rigid bodies to a good approximation. For phenanthrene, the principal axes of the libration tensor (L) lie within 5° of the molecular axes, and the root mean square amplitude of libration about the axis perpendicular to the molecular plane is 6·7°, which is sufficient to relax the intermolecular H—H contact to its normal value. However, the possibility that each of the phenanthrene molecules is in fact a slightly disordered pair, related by in-plane rotation of approximately ±4° from the present orientation, cannot be excluded on the basis of these data alone. The in-plane motion for TCNB is significantly smaller than for phenanthrene, and this may be due to dipole–dipole interactions between cyano groups of neighbouring TCNB molecules.

The disorder at the donor site in this complex is of interest in view of the NMR studies of molecular motion in related complexes by Fyfe (1974) and Fyfe, Harold-Smith & Ripmeester (1976). For several complexes shown by diffraction studies to contain a disordered pair of naphthalene or pyrene molecules,
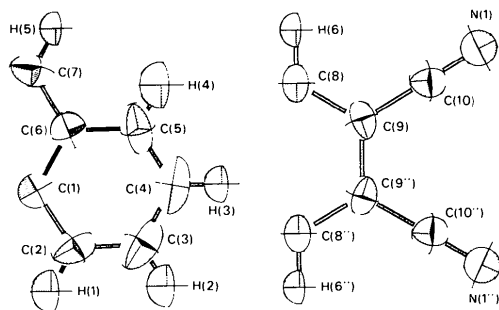

Fig. 3. Thermal ellipsoids for phenanthrene and tetracyanobenzene, at the 50% probability level, projected on the molecular planes (Johnson, 1965).

Table 4. *Analysis of rigid-body motion*

	L(deg²)			T(Å²)			S(deg Å)		
(a) Tensors with respect to orthogonal crystal axes									
Phenanthrene									
12·073	0·000	15·198	0·054	0·000	0·000	−0·048	0·000	0·029
0·000	7·103	0·000	0·000	0·046	0·000	0·000	−0·040	0·000
15·198	0·000	38·107	0·010	0·000	0·037	0·099	0·000	0·088
Tetracyanobenzene									
78·364	0·000	15·848	0·045	0·000	0·003	0·129	0·000	−0·990
0·000	3·739	0·000	0·000	0·049	0·000	0·000	0·076	0·000
15·848	0·000	13·312	0·003	0·000	0·053	0·094	0·000	−0·205
(b) Final reduced tensors									
Phenanthrene									
5·079	0	0	0·043	0	−0·012	−0·073	0	0
0	7·103	0	0	0·046	0	0	−0·040	0
0	0	45·101	−0·012	0	0·047	0	0	0·113
Tetracyanobenzene									
3·739	0	0	0·049	0	0	0·076	0	0
0	9·656	0	0	0·039	−0·003	0	0·009	0
0	0	82·019	0	−0·003	0·046	0	0	−0·084

related by a rotation angle $\theta°$ about an axis normal to the molecular plane, there is evidence for dynamic disorder involving rotation about the small angle, $\theta°$, with a low energy barrier, and the larger angle, $(180 - \theta)°$, with a higher energy barrier. Since both naphthalene and pyrene have twofold symmetry axes perpendicular to the molecular plane, these reorientations are indistinguishable in diffraction studies. Phenanthrene has no twofold axis perpendicular to the molecular plane, and the observation of a mirror-related disordered pair, with equal occupancy of the two sites, could represent the first structural evidence for large angle in-plane rotation of the type proposed by Fyfe (1974). In order to investigate this possibility, we have carried out a preliminary study of the spin-lattice relaxation times (T_1) in this complex as a function of temperature, from 150–360 K, by pulsed NMR techniques similar to those described by Fyfe *et al.* (1976). T_1 was found to be very long (70–140 s) over the entire temperature range. There was no significant change in T_1 over the range 260–360 K, and a plot of $\log(T_1)$ *vs* $1/T$ showed only a shallow minimum around 215 K corresponding to a low energy barrier (approximately 5 kJ mol^{-1}). Examination of the packing (Fig. 2) suggests that large-angle in-plane reorientation of the phenanthrene molecules is unlikely to occur with such a low energy barrier. We therefore conclude that the major disorder in the complex is static with a random statistical distribution of phenanthrene molecules between the two mirror-related sites and no significant large-angle in-plane reorientation. The shallow minimum in T_1 at low temperatures suggests that the phenanthrene molecules on individual sites are better regarded as executing anisotropic thermal motion in a flat-bottomed potential well rather than as a further very slightly disordered pair.

The crystal structure is very similar to that of the anthracene/TCNB complex, and this is an important factor in allowing the formation of the mixed complexes referred to above. This similarity, together with that of the powder diffraction patterns of the mixed complexes, suggests that the latter also have the same lattice arrangement, with gradual substitution of phenanthrene in anthracene sites as the phenanthrene content is increased. The crystal spectra and other properties of the mixed complexes are consistent with this conclusion (Wright, Ohta & Kuroda, 1976).

References

CARRUTHERS, J. R. (1975). In *CRYSTALS User Manual*. Oxford Univ. Computing Laboratory.

CRYSTALLOGRAPHIC SOCIETY OF JAPAN (1967). 5020 *UNICS, The Universal Crystallographic Computation Program System*.

FYFE, C. A. (1974). *J. Chem. Soc. Faraday Trans.* 2, **70**, 1633–1641, 1642–1649.

FYFE, C. A., HAROLD-SMITH, D. & RIPMEESTER, J. (1976). *J. Chem. Soc. Faraday Trans.* 2, **72**, 2269–2282.

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

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* B**27**, 26–33.

KITAIGORODSKY, A. I. (1961). *Organic Chemical Crystallography*, p. 7. New York: Consultants Bureau.

KOHNO, Y., KONNO, M., SAITO, Y. & INOKUCHI, H. (1975). *Acta Cryst.* B**31**, 2076–2080.

OHTA, T., KURODA, H. & KUNII, T. L. (1972). *Theor. Chim. Acta*, **19**, 167–178.

PROUT, C. K. & TICKLE, I. J. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 520–523.

PROUT, C. K. & WRIGHT, J. D. (1964). *Angew. Chem.* **7**, 659–667.

ROLLETT, J. S. (1965). Editor, *Computing Methods in Crystallography*, p. 40. Oxford: Pergamon Press.

ROLLETT, J. S. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 169–172. Copenhagen: Munksgaard.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

TSUCHIYA, H., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* B**28**, 1935–1941.

WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

WRIGHT, J. D., OHTA, T. & KURODA, H. (1976). *Bull. Chem. Soc. Jpn*, **49**, 2961–2966.