d'effets subsidiaires dus aux forces de van der Waals et surtout aux interactions dipole–dipole. Pour confirmer cette hypothèse, nous avons entrepris un calcul pour estimer la part qui revient à l'interaction quadrupolaire dans l'énergie de cohésion du cristal.

Références

ALEXANDRE, M. & RIGNY, P. (1972). *Mol. Cryst.* Sous presse.
BONHAM, R. A. & MOMANY, F. A. (1963). *J. Phys. Chem.* 67, 2474.

BUSING, W. R., MARTIN, K. Q. & LEVY, H. A. (1964). *ORFLS, a Fortran Crystallographic Least-squares Program.* UJAEC Report ORNL-TM-305.
HANSON, A. W. (1964). *Acta Cryst.* 17, 559.
HANSON, A. W. (1965). *Acta Cryst.* 19, 19.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
IWASAKI, F. & SAITO, Y. (1970). *Acta Cryst.* B26, 251.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
PASCARD, R. (1972). *Mol. Cryst.* Sous presse.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175.

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

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The crystals are monoclinic, space group Cm with cell dimensions: $a=9\cdot505$, $b=12\cdot748$, $c=7\cdot417$ Å, $\beta=92\cdot45°$ and $Z=2$. The structure was deduced from Patterson synthesis and refined by the full-matrix least-squares method from three-dimensional intensity data collected by the diffractometer method using Mo $K\alpha$ radiation. The final R value is $0\cdot051$ for the 646 observed reflexions. The component molecules are stacked alternately in infinite columns parallel to the c axis. The spacings between overlapping molecules are $3\cdot42$ and $3\cdot44$ Å. The charge transfer interaction seems to be weak. Bond lengths and angles in the component molecules agree reasonably well with values for other structures.

Introduction

The crystal structure of the 1:1 complex of anthracene with 1,2,4,5-tetracyanobenzene (TCNB) was determined as part of a series of investigations of the crystal structures of charge transfer complexes containing TCNB as an electron acceptor (Ohashi, Iwasaki & Saito, 1967; Kumakura, Iwasaki & Saito, 1967; Niimura, Ohashi & Saito, 1968). Our interest lies in the study of molecular interaction.

Experimental

Orange crystals of the 1:1 molecular complex with parallelepiped form were obtained on standing a solution of the component molecules in a mixture of dichloromethane and ethyl acetate at room temperature. The intensity data and unit-cell dimensions were measured with a Rigaku four-circle diffractometer.

The crystal data are:

$C_{14}H_{10} \cdot C_{10}H_2N_4$, F.W. 356·4, monoclinic, $a=9\cdot505\pm0\cdot001$, $b=12\cdot748\pm0\cdot002$, $c=7\cdot417\pm0\cdot002$ Å, $\beta=92\cdot45\pm0\cdot02°$, $U=897\cdot9$ Å^3, $D_m=1\cdot30$ g.cm^{-3} by flotation, $Z=2$, $D_x=1\cdot31$ g.cm^{-3}, μ(Mo $K\alpha$, $\lambda=0\cdot70926$ Å)$=0\cdot67$ cm^{-1}.

Space group: $C2/m$, Cm or $C2$ from the systematic absences, hkl absent when $h+k$ odd.

A specimen of dimensions $0\cdot15\times0\cdot20\times0\cdot29$ mm was mounted with the c axis parallel to the φ axis of the diffractometer. Mo $K\alpha$ radiation monochromated by graphite crystal was used. The ω-scan technique was employed at rate of 1° per minute. In total 1660 reflexions were measured up to $2\theta=70°$. However those reflexions of which $|F_o|$ was less than $3\cdot0$ were regarded as unobserved in view of the accuracy of measurement. The remaining 646 reflexions were adopted for the structure determination. They were corrected for
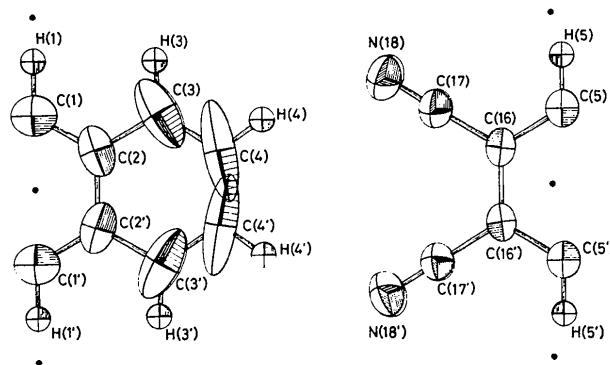

Fig. 1. *ORTEP* plot of the thermal ellipsoids enclosing a probability of 50% (Johnson, 1965), viewed along the c^* axis.

Lorentz and polarization effects, but correction for absorption was not made in view of the small size of the specimen and low absorption coefficient.

Solution and refinement of the structure

The space group $C2/m$ was tentatively assumed, though Cm was proved to be the true space group at a later stage of the refinement. In the space group $C2/m$ the general positions are eightfold. There are only two pairs of component molecules in a unit cell; therefore, the centres of the molecules must lie on twofold special positions and the molecules are required to have a symmetry $2/m$. The component molecules must be centred at positions $2a$: 000, $\frac{1}{2}\frac{1}{2}0$; and $2c$: $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, in order to obtain the familiar mixed stacks of the component molecules. The orientations of the molecules were easily deduced from a study of the Patterson projection along the b axis as well as from packing considerations. The trial structure was refined by the full-matrix least-squares method assuming firstly isotropic and then anisotropic thermal motion. The R value ($\sum||F_o|-|F_c||/\sum|F_o|$) converged at 0.098. At this stage the geometry of both component molecules was normal. The electron density maps, however, showed broader and slightly lower peaks at the atomic positions of the anthracene molecule owing to a large thermal motion. In view of the accuracy of the intensity measurement, it was felt that the refinement was still unsatisfactory.

Closer examination of the observed and calculated structure amplitudes revealed that the agreement between F_o and F_c is slightly poor for those reflexions of which l is odd. This fact suggests that the true space group might be Cm rather than $C2/m$ or $C2$. Thus a trial structure based on the space group Cm was refined by the full-matrix least-squares method. In order to prevent strong parameter interaction, it was necessary to refine the atoms of TCNB in one cycle keeping those of the anthracene molecule fixed and to refine the atoms of anthracene in the next cycle keeping those of TCNB

fixed. After several cycles of the refinement the structure converged at $R=0.054$. However, the refinement lead to an absurd geometry of the component molecules, for example, a C–C bond distance in the anthracene molecule became as short as 1.27 Å. It was then decided to refine the structure keeping the molecular symmetry $2/m$ unchanged. In order to retain the molecular symmetry $2/m$, the following relations must hold, for example, between the positional parameters of the atoms C(1), C(2) and C(12): $x_2+x_{12}=2x_1$, $z_2+z_{12}=2z_1$, $y_2=y_{12}$. Positional parameters of C(12)
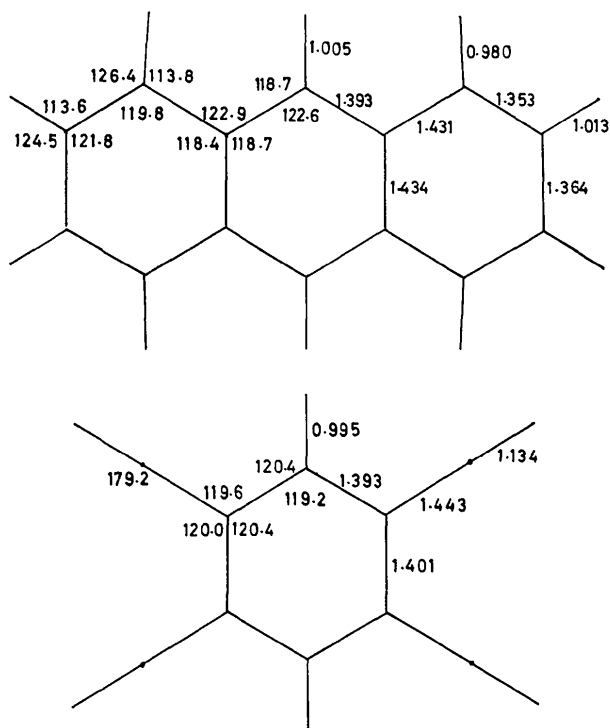

Fig. 2. Bond lengths (Å) and angles (°).

Table 1. *The final atomic parameters and their estimated standard deviations*

The anisotropic temperature factors are of the form:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right].$$

	x $\times 10^4$	y $\times 10^4$	z $\times 10^4$	B_{11} $\times 10^4$	B_{22} $\times 10^4$	B_{33} $\times 10^4$	B_{12} $\times 10^4$	B_{13} $\times 10^4$	B_{23} $\times 10^4$
C(1)	0	1076 (4)	0	170 (6)	71 (3)	179 (9)	0	−7 (6)	0
C(2)	1179 (6)	557 (2)	−549 (13)	106 (3)	112 (2)	131 (4)	−26 (2)	−3 (3)	11 (3)
C(3)	2398 (8)	1089 (5)	−1141 (14)	192 (6)	210 (6)	191 (8)	−110 (10)	−16 (11)	31 (11)
C(4)	3519 (6)	533 (5)	−1646 (13)	107 (4)	454 (16)	196 (7)	−101 (6)	4 (4)	39 (7)
C(12)	−1179	557	549	106	112	131	26	−3	−11
C(13)	−2398	1089	1141	192	210	191	110	−16	−31
C(14)	−3519	533	1646	107	454	196	101	4	−39
C(5)	−37 (5)	1100 (3)	5000 (12)	90 (3)	60 (2)	169 (7)	0	7 (4)	0
C(6)	1145 (5)	549 (2)	4501 (13)	71 (2)	64 (2)	144 (4)	−4 (2)	5 (2)	2 (2)
C(7)	2377 (5)	1114 (2)	3985 (13)	91 (3)	65 (2)	203 (6)	−3 (2)	21 (3)	−2 (2)
N(8)	3337 (5)	1569 (2)	3580 (13)	116 (3)	90 (2)	307 (6)	−19 (2)	53 (3)	0 (3)
C(16)	−1220	549	5498	71	64	144	4	5	−2
C(17)	−2451	1114	6014	91	65	203	3	21	2
N(18)	−3411	1569	6419	116	90	307	19	53	0

Table 1 (cont.)

	x $\times 10^3$	y $\times 10^3$	z $\times 10^3$	B
H(1)	0	186 (4)	0	4·6 (1·0)
H(3)	231 (5)	186 (4)	−114 (6)	8·3 (1·3)
H(4)	432 (3)	98 (4)	−207 (4)	7·9 (0·9)
H(13)	−231	186	114	8·3
H(14)	−432	98	207	7·9
H(5)	−4	188 (3)	500	2·0 (0·8)

are no longer independent: they are functions of x_1, z_1, x_2, z_2 and y_2. Thus the number of independent parameters is reduced. Similar relations must hold for all other atoms in an asymmetric unit and also for thermal parameters. Four cycles of the least-squares refinement under the restrictions given above decreased the R value to 0·051 for the 646 observed reflexions. The shape and size of the molecules arc quite plausible in this case. In the least-squares refinement unit weight was given to all the reflexions. Atomic scattering factors for all the atoms were taken from *International Tables for X-ray Crystallography* (1962). Final atomic parameters are listed in Table 1. Observed and calculated structure factors are compared in Table 2.

Table 2. *Observed and calculated structure factors*

Description of the structure and discussion

The thermal motion ellipsoids are illustrated by an *ORTEP* plot in Fig. 1 (Johnson, 1965). The motion of the TCNB molecule appears to consist chiefly of a rigid body libration about the centre of gravity. The anthracene molecule seems to librate with much greater amplitude. The molecular motion has been analysed in terms of the rigid body vibrations using the approach described by Cruickshank (1956a). The translation (T) and the libration (ω) tensors are listed in

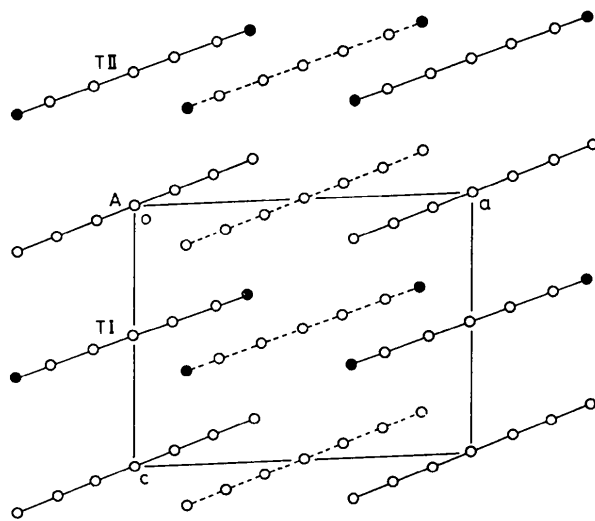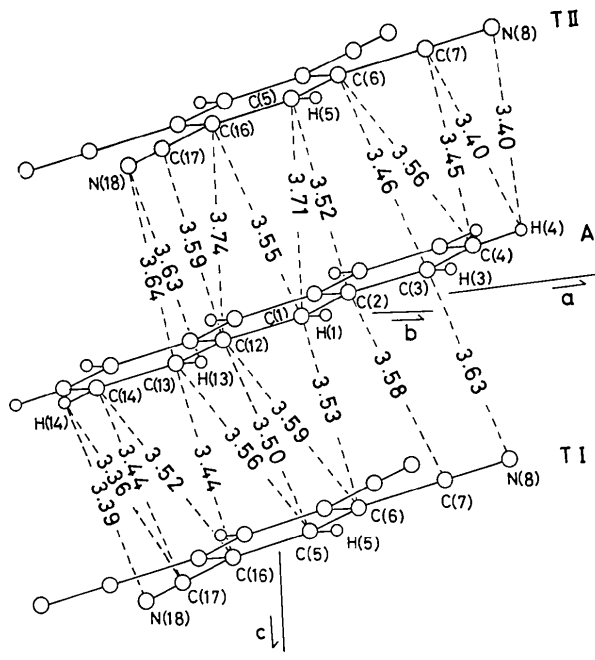Fig. 3. Projection of the structure along the b axis.

Fig. 4. Intermolecular distances between the overlapping molecules. The average interplaner spacings are 3·42 Å between A and T I and 3·44 Å between A and T II.

Table 3. These results show that the libration of an anthracene molecule about the axis perpendicular to the molecular plane is as large as 8·6°. This apparently large libration may be interpreted as an orientational disorder similar to that observed in the crystal of the 1:1 complex of naphthalene and TCNB (Kumakura, Iwasaki & Saito, 1967). This point will be discussed later.

The bond lengths were corrected for the effect of thermal vibration (Cruickshank, 1956a, 1961). The bond lengths and angles are given in Table 4 and Fig. 2. The bond lengths of anthracene, C(1)–C(2), C(2)–C(2') and C(2)–C(3) are nearly equal to those obtained for anthracene alone (Cruickshank, 1956b; Ahmed &

Cruickshank, 1952; Sinclair, Mathieson & Robertson, 1950) and are consistent with those observed in the anthracene–s-trinitrobenzene complex (Brown, Wallwork & Wilson, 1964). The bond lengths, C(3)–C(4) and C(4)–C(4') are appreciably shorter than those of anthracene alone because of large libration or disorder. The position of the carbon atom C(4) was not confirmed in the anthracene–TCNQ complex (Williams & Wallwork, 1968) for the same reason. The TCNB molecule has the same shape and size as those in other crystals. Fig. 3 shows a projection of the structure along the b axis.

The structure is composed of infinite columns in which the component molecules are stacked alternately

Table 3. *Rigid-body thermal parameters*

Anthracene   TCNB

Principal axes of the molecule in the form: $L\mathbf{a} + M\mathbf{b} + N\mathbf{c}$.

Moment of inertia (Atomic weight × Å²)	L	M	N	Moment of inertia (Atomic weight × Å²)	L	M	N
224·1	0·0974	0·0	−0·0459	402·8	0·0987	0·0	−0·0415
1088·8	0·0	−0·0784	0·0	1010·0	0·0	−0·0784	0·0
1312·8	0·0400	0·0	0·1269	1412·8	0·4367	0·0	0·1284

Molecular vibrational tensors

$$\mathbf{T} \times 10^4 \begin{pmatrix} 361\,(46) & 0 & 10\,(50) \\ & 600\,(65) & 0 \\ & & 291\,(96) \end{pmatrix} \text{Å}^2 \qquad \mathbf{T} \times 10^4 \begin{pmatrix} 355\,(14) & 0 & -16\,(15) \\ & 485\,(18) & 0 \\ & & 312\,(25) \end{pmatrix} \text{Å}^2$$

$$\boldsymbol{\omega} \times 10 \begin{pmatrix} 307\,(142) & 0 & -96\,(54) \\ & 47\,(29) & 0 \\ & & 728\,(25) \end{pmatrix} \text{deg}^2 \qquad \boldsymbol{\omega} \times 10 \begin{pmatrix} 221\,(55) & 0 & -19\,(10) \\ & 89\,(17) & 0 \\ & & 60\,(7) \end{pmatrix} \text{deg}^2$$

Principal axes of the T and ω tensors relative to the molecular axes.

R.m.s. amplitude	Direction cosines			R.m.s. amplitude	Direction cosines		
0·170 Å	0·134	0·0	0·991	0·175 Å	0·310	0·0	0·951
0·190	−0·991	0·0	0·134	0·190	−0·951	0·0	0·310
0·245	0·0	1·0	0·0	0·220	0·0	1·0	0·0
2·17°	0·0	1·0	0·0	2·41°	0·114	0·0	0·993
5·35	−0·977	0·0	0·212	2·98	0·0	−1·0	0·0
8·65	−0·212	0·0	0·977	4·73	0·993	0·0	−0·114

Table 4. *Bond lengths and angles with their estimated standard deviations*

Anthracene	Uncorrected	Corrected	TCNB	Uncorrected	Corrected
C(1)–C(2)	1·378 (8) Å	1·393 Å	C(5)–C(6)	1·389 (7) Å	1·393 Å
C(2)–C(2')	1·420 (4)	1·434	C(6)–C(6')	1·398 (3)	1·401
C(2)–C(3)	1·428 (10)	1·431	C(6)–C(7)	1·440 (7)	1·443
C(3)–C(4)	1·346 (10)	1·353	C(7)–N(8)	1·132 (7)	1·134
C(4)–C(4')	1·358 (9)	1·364	C(5)–H(5)	1·00 (4)	
C(1)–H(1)	1·00 (5)				
C(3)–H(3)	0·98 (5)				
C(4)–H(4)	1·01 (4)				

C(2)–C(1)–C(12)	122·6 (4)°		C(6)–C(5)–C(16)	119·2 (3)°	
C(1)–C(2)–C(2')	118·7 (5)		C(5)–C(6)–C(6')	120·4 (4)	
C(1)–C(2)–C(3)	122·9 (4)		C(5)–C(6)–C(7)	119·6 (3)	
C(3)–C(2)–C(2')	118·4 (5)		C(7)–C(6)–C(6')	120·0 (4)	
C(2)–C(3)–C(4)	119·8 (4)		C(6)–C(7)–N(8)	179·2 (6)	
C(3)–C(4)–C(4')	121·8 (5)		C(6)–C(5)–H(5)	120 (1)	
C(2)–C(1)–H(1)	119 (1)				
C(2)–C(3)–H(3)	114 (1)				
C(4)–C(3)–H(3)	126 (1)				
C(3)–C(4)–H(4)	114 (1)				
C(4')–C(4)–H(4)	125 (1)				

along the c axis plane to plane. This is very similar to the 1:1 complex of naphthalene and TCNB. The whole structure conforms very closely to the space group $C2/m$, however, the centre of the TCNB molecule is shifted by about 0·04 Å along the a axis and the true space group is Cm. The TCNB molecule is planar within the experimental error. The anthracene is also planar with the maximum deviation of 0·01 Å for carbon atoms and 0·03 Å for hydrogen atoms. The planes of the anthracene and TCNB molecules make angles of 67·7° and 69·6° with the c axis respectively. The equations of the planes are given by

anthracene: $\quad 0\cdot3393X + 0\cdot9407Z = 0\cdot0$
TCNB: $\qquad 0\cdot3077X + 0\cdot9515Z = 3\cdot467$,

where X and Z are the coordinates in Å referred to the orthogonal crystal axes a and c^*. Both of the component molecules lie on the plane (102). The average interplanar spacing between the anthracene (A in Fig. 3) and TCNB I (T I in Fig. 3) is 3·42 Å and that between the anthracene (A in Fig. 3) and TCNB II (T II in Fig. 3) is 3·44 Å.

Fig. 4 shows some intermolecular distances between overlapping molecules. There is no atomic distance which is shorter than the usual van der Waals contacts. This feature seems to indicate that the charge transfer

interaction is weak: in fact the crystal is orange in colour. The shortest intermolecular atomic distances between non-overlapping molecules are listed in Table 5. Fig. 5 represents a projection of the structure upon the plane (102). Closest intermolecular contacts in the (102) layer occur between H(4) and N(18), the distance being 2·56 Å. The value is unusually shorter than the van der Waals distance between a hydrogen atom and a nitrogen atom (2·70 Å). In crystals of the 1:1 complex of naphthalene and TCNB the corresponding

Table 5. *Intermolecular distances between non-overlapping molecules less than* 3·6 Å

1	$x,$	$y,$	z	4	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	$-1+z$
2	$1+x,$	$y,$	z	5	$1+x,$	$y,$	$-1+z$
3	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	z				

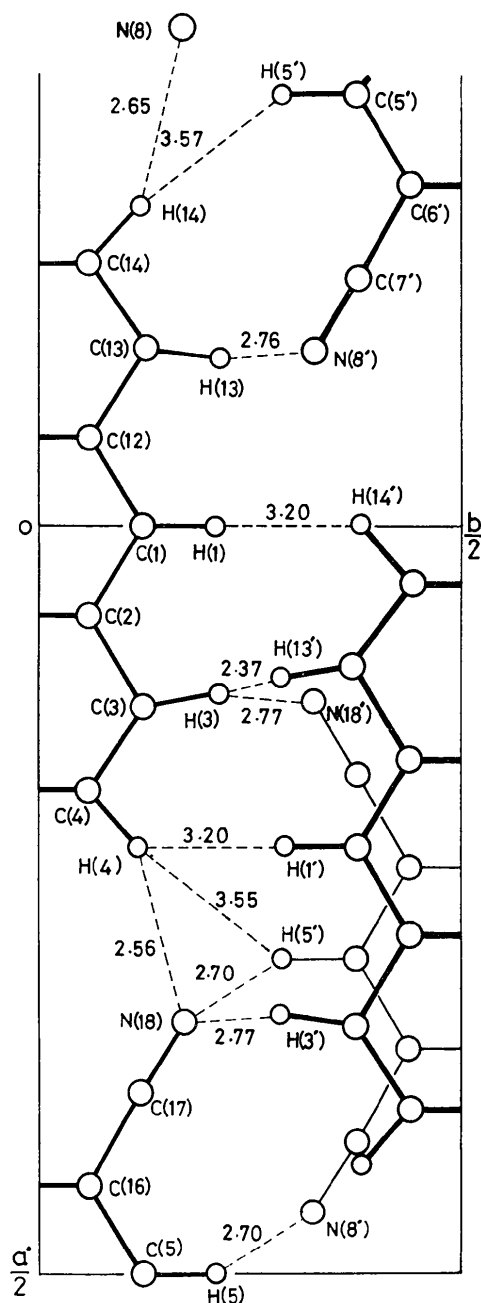| Atom (in unit 1)	to atom	in unit	d
C(4)	H(14)	2	3·42 (3) Å
C(7)	H(14)	2	3·51 (3)
N(8)	H(14)	2	2·65 (3)
H(4)	C(14)	2	3·42 (3)
H(9)	H(14)	2	3·28 (5)
C(3)	H(13)	3	3·13 (5)
C(5)	N(18')	3	3·49 (1)
C(7)	N(18')	3	3·56 (1)
C(7)	H(13')	3	3·37 (5)
C(7)	H(5')	3	3·60 (3)
N(8)	C(13')	3	3·55 (1)
N(8)	C(5')	3	3·49 (1)
N(8)	C(17')	3	3·56 (1)
N(8)	H(13')	3	2·76 (5)
N(8)	H(5')	3	2·70 (3)
H(1)	H(13')	3	3·12 (6)
H(1)	H(14')	3	3·20 (6)
H(3)	C(13')	3	3·13 (5)
H(3)	H(1')	3	3·12 (6)
H(3)	H(13')	3	2·37 (7)
H(4)	H(1')	3	3·20 (6)
H(5)	N(18')	3	2·70 (3)
H(5)	H(14')	3	3·57 (5)
C(3)	N(18')	4	3·56 (1)
H(3)	C(17')	4	3·36 (5)
H(3)	N(18')	4	2·77 (5)
H(4)	H(1')	4	3·55 (5)
C(4)	N(18)	5	3·58 (1)
H(4)	C(17)	5	3·44 (3)
H(4)	N(18)	5	2·56 (3)

Fig. 5. The molecular arrangement and the shortest intermolecular distances, viewed perpendicular to the plane (102).

distance is 2·73 Å. If the anthracene molecule is rotated in the plane (102) by 8·6°, which is the same magnitude as the amplitude of libration deduced from anisotropic thermal parameters, the H(4)–N(18) distance increases to 2·70 Å. Thus it is very likely that the anthracene molecules are disordered, taking one of the two alternative orientations in the same way as was observed in crystals of the naphthalene–TCNB complex. A structure factor calculation was undertaken assuming that the anthracene molecules take one of two disordered orientations rotated ±8·6° from the original

position. A half weight was assigned for each disordered anthracene and the anisotropic temperature factors of the same order as the TCNB molecule were tentatively assigned. This model resulted in an R value of 0·14. A difference Fourier synthesis showed residual peaks at the original atomic positions of anthracene. No attempt has been made to refine such a disordered model, since strong parameter interaction prevented further refinement. However, the possibility of orientational disorder of the anthracene molecule can by no means be excluded. Thus it is doubtful whether the
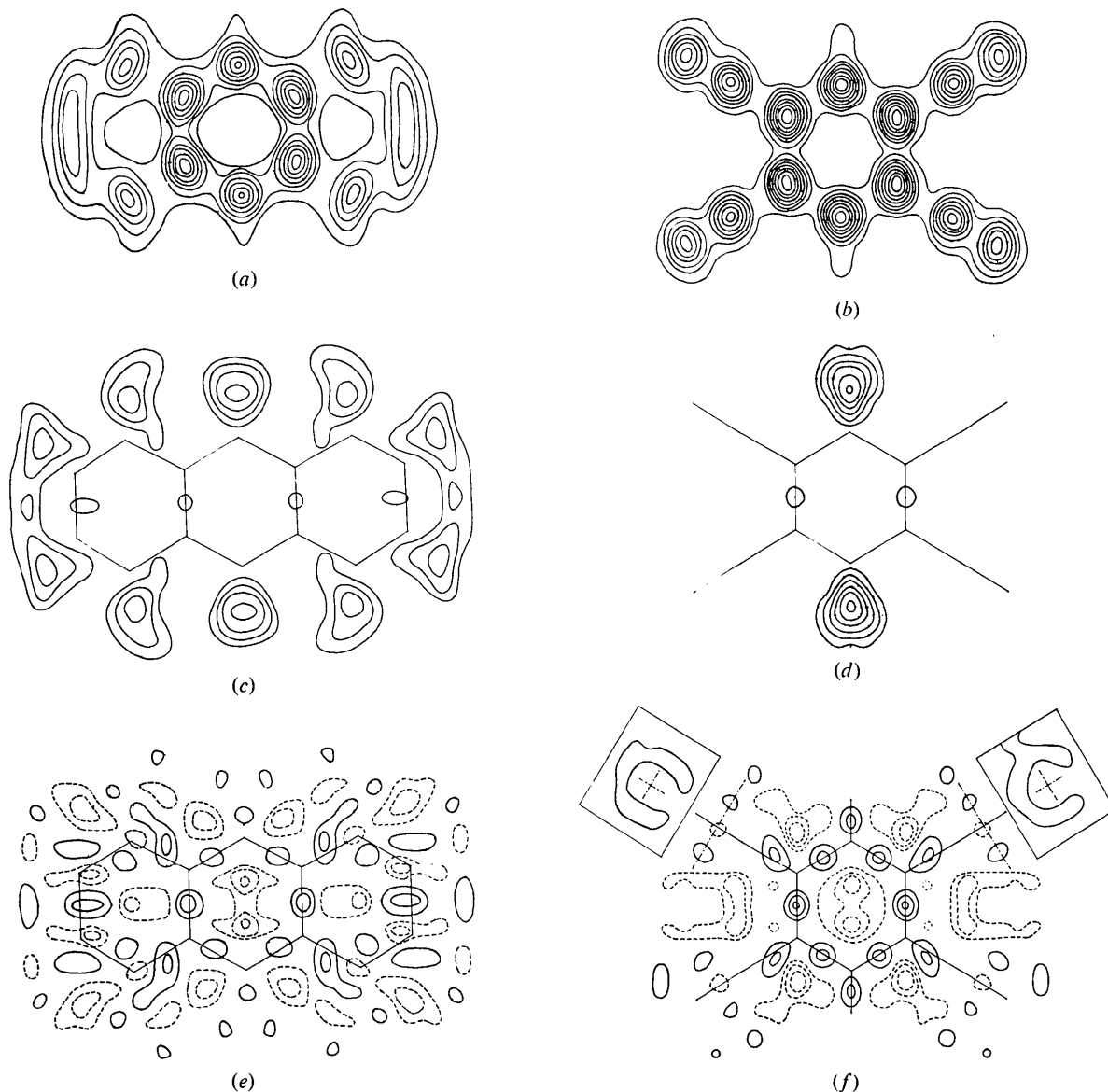

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 6. Sections of Fourier syntheses through the plane (102). (a), (b) Fourier syntheses of electron density. The contours are at intervals of 1·0 e.Å⁻³, starting with 1·0 e.Å⁻³. (c), (d) Difference Fourier syntheses. The carbon and nitrogen atoms were included in the calculation of F_c. The contours are at intervals of 0·1 e.Å⁻³, starting with 0·1 e.Å⁻³. (e), (f) Difference Fourier syntheses. All the atoms were included in the calculation of F_c. The solid contours are at intervals of 0·05 e.Å⁻³, starting with 0·05 e.Å⁻³. The broken contours show negative values. The difference Fourier sections bisecting the C≡N triple bonds are also illustrated in the rectangles with a contour of 0·04 e.Å⁻³ (f).

rigid body thermal parametres and the thermal ellipsoid of the anthracene molecule have real significance.

The final difference map of the TCNB molecule is presented in Fig. 6. There are maxima at the middle of the bonds, whereas minima appear at the middle of the $C\equiv N$ bond and at both ends of the bonds. The height of the positive regions is approximately 0.18 e.$Å^{-3}$ for $C_{ar}-C_{ar}$, 0.11 e.$Å^{-3}$ for $C_{ar}-C$ and 0.10 e.$Å^{-3}$ for $C_{ar}-H$: the minima range from -0.08 to -0.20 e.$Å^{-3}$. The systematic arrangement of the maxima and minima seems to suggest that electron density has moved to the centre of the bonds. In the middle of the $C\equiv N$ bond no maximum appears as in the case of cis-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966). This might be related to the fact that the $C\equiv N$ bond length is shorter when measured with X-rays than when measured with neutrons or when determined spectroscopically (Little, Paulter & Coppens, 1971). But the section perpendicular to and through the midpoint of the $C\equiv N$ bond shows the residual electron density surrounding the bond in the form of a torus.

The maximum is 0.07 e.$Å^{-3}$ and lies at a distance of 0.7 Å from the $C\equiv N$ bond. It may be noted that the π-electron density calculation on the basis of a wave function of the form $\varphi(2p_x) = Nx \cdot \exp(-cr/2)$ (Coulson, 1961) shows a maximum of 0.12 e.$Å^{-3}$ 0.70 Å from the midpoint of the carbon and nitrogen atoms.

The calculations were carried out on the FACOM 270-30 computer at this Institute with a local version of the Universal Crystallographic Computation Program System, UNICS (Crystallographic Society of Japan, 1967). This research was aided in part by a Scientific Research Grant of the Ministry of Education.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1952). Acta Cryst. 5, 852.
BROWN, D. S., WALLWORK, S. C. & WILSON, A. (1964). Acta Cryst. 17, 168.
COULSON, C. A. (1961). Valence. Oxford: Clarendon Press.
CRUICKSHANK, D. W. J. (1965a). Acta Cryst. 9, 747, 754.
CRUICKSHANK, D. W. J. (1956b). Acta Cryst. 9, 915.
CRUICKSHANK, D. W. J. (1961). Acta Cryst. 14, 896.
Crystallographic Society of Japan (1967). 5020 UNICS, The Universal Crystallographic Computation Program System.
HARTMAN, A. & HIRSHFELD, F. L. (1966). Acta Cryst. 20, 80.
International Tables For X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). ORTEP. Report No. ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
KUMAKURA, S., IWASAKI, F. & SAITO, Y. (1967). Bull. Chem. Soc. Japan, 40, 1826.
LITTLE, R. G., PAULTER, D. & COPPENS, P. (1971). Acta Cryst. B27, 1493.
NIIMURA, N., OHASHI, Y. & SAITO, Y. (1968). Bull. Chem. Soc. Japan, 41, 1815.
OHASHI, Y., IWASAKI, H. & SAITO, Y. (1967). Bull. Chem. Soc. Japan, 40, 1789.
SINCLAIR, V. C., MATHIESON, A. McL. & ROBERTSON, J. M. (1950). Acta Cryst. 3, 251.
WILLIAMS, R. M. & WALLWORK, S. C. (1968). Acta Cryst. B24, 168.

The Crystal and Molecular Structure of Bis[bis(dicyclohexylphosphino)methane]nickel

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Bis[bis(dicyclohexylphosphino)methane]nickel, $\{[(C_6H_{11})_2P]_2CH_2\}_2Ni$, crystallizes in the space group $P2_1/c$ with the unit-cell constants $a = 19.404$ (5), $b = 12.193$ (5), $c = 22.310$ (6) Å, $\beta = 100.41$ (3)°, $Z = 4$, $D_c = 1.12$ g.cm^{-3}. Integrated intensities of 5844 unique reflexions were collected at room temperature with a computer-controlled Siemens–Hoppe diffractometer, using Cu $K\alpha$ radiation. The structure was solved by a combination of direct and Fourier methods and refined by full-matrix least-squares calculations to a reliability index $R = 0.069$, using 3982 observed reflexions. The coordination around the nickel is distorted-tetrahedral. The presence of bent Ni–P bonds is indicated by comparison of the bond angles about the nickel atom with those of the ideal sp^3 hybridization. All cyclohexyl rings are in the chair conformation and bonded equatorially to the phosphorus.

Introduction

Low valent nickel is known to form phosphine-adducts of variable stoichiometry $Ni(PR_3)_n$, $n = 2,3,4$, (Wilke, Englert & Jolly, 1971; Jolly, Jonas, Krüger & Tsay, 1971; Heimbach, 1964), depending on experimental conditions and ligand properties. Structural determinations have been reported for $(PF_3)_4Ni$ (Marriott, Salthouse, Ware & Freeman, 1970; Almenningen, Andersen & Astrup, 1970) and in part for (piperidine-