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The Crystal and Molecular Structure of Pyrene

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Crystals of pyrene, $C_{16}H_{10}$, are monoclinic with four molecules in a unit cell of dimensions $a=13\cdot64_9$, $b=9\cdot25_6$, $c=8\cdot47_0$ Å, $\beta=100\cdot28°$, space group $P2_1/a$. The intensities of the reflexions were measured with a scintillation counter and Mo $K\alpha$ radiation. Starting with the parameters of a previous two-dimensional study, the positional and anisotropic thermal parameters of the carbon atoms were refined by differential syntheses and least squares; contributions from the hydrogen atoms were included in the structure calculations, but the parameters were not refined. The thermal motion was interpreted in terms of rigid body vibrations, and small corrections were made in the bond lengths to correct errors due to rotational oscillations. The general variation of the mean bond distances is in agreement with the trends predicted by valence-bond and molecular-orbital calculations, but the individual agreements are not very good; in particular the shortest bonds in the molecule measure 1·32 Å, less than either calculated value, but similar to corresponding bonds in other molecules. The molecule is slightly non-planar, probably as a result of crystal packing forces. All the intermolecular separations correspond to normal van der Waals interactions; the perpendicular distance between mean molecular planes is 3·53 Å.

Introduction

The crystal structure of pyrene was determined by Robertson & White (1947) from two projections, but resolution of the individual atoms was poor in both projections. As a result the accuracy was not very high, and the present paper describes a more detailed analysis based on new three-dimensional data.

Experimental

Crystals of pyrene are thick colourless plates with (001) developed, and smaller {110} forms. The unit cell parameters were determined by least-squares treatment of the $\sin^2\theta$ values of the α_1, α_2-doublets of a number of high-angle reflexions, for which the Bragg angles were measured on a G. E. Spectrogoniometer with Cu $K\alpha$ radiation.

Crystal data ($\lambda(\text{Cu } K\alpha_1)=1\cdot54051$ Å, $\lambda(\text{Cu } K\alpha_2)$
$=1\cdot54433$ Å).
Pyrene, $C_{16}H_{10}$; $M=202\cdot2$; m.p. = 150 °C.
Monoclinic, $a=13\cdot64_9\pm0\cdot01$, $b=9\cdot25_6\pm0\cdot01$,
$c=8\cdot47_0\pm0\cdot01$ Å, $\beta=100\cdot28°\pm0\cdot04°$.
$U=1052\cdot9$ Å^3.
$D_m=1\cdot27$, $Z=4$, $D_x=1\cdot275$ g.cm^{-3}.
Absorption for X-rays,
$\lambda=1\cdot5418$ Å, $\mu=5\cdot6$ cm^{-1}.
$\lambda=0\cdot7107$ Å, $\mu=0\cdot8$ cm^{-1}.
$F(000)=424$.
Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd.
Space group is $P2_1/a$ (C_{2h}^5).

Weissenberg films indicated a rapid fall off in intensity with increasing Bragg angle. The intensities were measured on a G. E. Spectrogoniometer with a scintillation counter and Mo $K\alpha$ radiation, exactly as for perylene (Camerman & Trotter, 1964). 965 reflexions in the range $0<2\theta(\text{Mo } K\alpha)\leq50\cdot2°$ (corresponding to a minimum interplanar spacing $d=0\cdot84$ Å) were observed, 59 % of the total number of reflexions in this range, but since the weak intensities were not considered to be very reliable, the structure refinement was based principally on those 550 reflexions with intensity greater than twice the background.

Refinement of the structure

The carbon positional parameters of Robertson & White (1947) were used as the starting point in the refinement, with the scattering factor for carbon of *International Tables for X-ray Crystallography* (1962), with $B=4\cdot0$ Å^2. The discrepancy index, R, was 0·20 for the 550 reflexions included in the refinement. The positional and isotropic thermal parameters of the carbon atoms were refined as for perylene (Camerman & Trotter, 1964), firstly by differential syntheses. Contributions from hydrogen atoms were included after three cycles, assuming ideal positions on the ring diagonals with C–H = 1·08 Å, and $B=8\cdot0$ Å. The hydrogen atom positional parameters were refined in the fourth cycle; the peak electron densities were reasonable (Table 1), but some of the curvatures were positive, so that the shifts were not considered to be very reliable, and in subsequent cycles the H atoms were kept in ideal positions. Refinement was complete after seven cycles, and R was 0·12.

Table 1. *Hydrogen atom peak electron densities* (e.Å^{-3}) *in fourth differential cycle*

Atom	Obs.	Calc.	Atom	Obs.	Calc.
H(1)	0·59	0·73	H(8)	0·48	0·67
H(2)	0·86	1·01	H(9)	0·48	0·56
H(4)	0·43	0·57	H(11)	0·45	0·50
H(5)	0·40	0·56	H(12)	0·56	0·49
H(7)	0·47	0·45	H(14)	0·68	0·62

The observed and calculated electron densities and curvatures at the carbon positions are listed in Table 2. The values suggested that the atomic vibrations are slightly anisotropic, and anisotropic thermal parameters were obtained approximately from the differences between the observed and calculated second derivatives (Cruickshank, 1956*a*). At this stage facilities for carrying out anisotropic (block-diagonal) least-squares refinement became available to us, and the carbon atom positional and anisotropic thermal parameters were further refined. The function minimized was $\Sigma w(F_o-F_c)^2$, with $\sqrt{w}=|F_o|/34$ when $|F_o|<34$, and $\sqrt{w}=34/|F_o|$ when $|F_o|\geq 34$. Three cycles were carried out; the positional parameter shifts were not significant, and the coordinates of the seventh differential cycle were retained; the anisotropic thermal parameters required a fudge factor of 0·2 to ensure convergence. R decreased by 1% in the anisotropic refinement.

The observed and calculated structure factors after the differential syntheses refinement are listed in Table 3; the R index for the 550 observed reflexions which were included in the refinement is 0·12 (reduced to 0·11 by using anisotropic thermal parameters). Also included in Table 3 are F_o and F_c values for all the weak reflexions and for some of the unobserved reflexions, which were omitted from the refinement process.

The refinement was repeated with various other weighting schemes (Cruickshank, 1961), and using all 965 observed reflexions, but the results were never significantly different from those obtained as described above, and indeed bonds 4–5 and 11–12 were usually a little shorter than in the above refinement.

Coordinates and molecular dimensions

The final positional and isotropic thermal parameters are given in Table 4. The coordinates and temperature factors for carbon are those of the seventh differential cycle, and the hydrogen atoms have been placed on the ring diagonals with C–H about 1·08 Å. The standard deviations calculated from Cruickshank's (1949) formulae, with the reflexions used in the refinement process only, are also given in Table 4. Since a large number of weak and unobserved reflexions have been omitted from the analysis, these values of the standard deviations are almost certainly over-optimistic (Sparks, 1958), and in discussing the accuracy of the molecular dimensions these σ values have been arbitrarily doubled.

The anisotropic thermal parameters are listed in Table 5, B_{ij} being the coefficients in the expression:

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

The bond distances and valency angles in the molecule and their standard deviations, calculated using twice the positional standard deviations of Table 4 as a more realistic estimate of the accuracy, are given in Fig. 1. The standard deviations of the bond distances and valency angles were also computed from the least-squares residuals, and the values were in good agreement with those given in Fig. 1. Before averaging for comparison with theoretical predictions, the bond distances were corrected for small errors due to rotational oscillations, as described later.

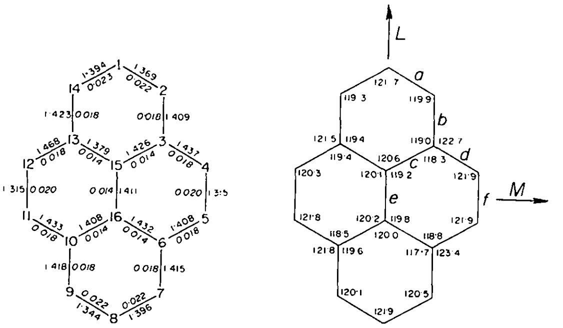

Fig. 1. (*a*) Measured bond lengths (Å), before application of the small rotational corrections, and standard deviations. (*b*) Measured valency angles (degrees). $\sigma=1{\cdot}0\text{–}1{\cdot}4°$.

Table 2. *Carbon peak electron densities* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *from seventh differential cycle*

	ϱ		$-\partial^2\varrho/\partial x^2$		$-\partial^2\varrho/\partial y^2$		$-\partial^2\varrho/\partial z^2$	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C(1)	4·16	4·31	24·2	24·5	21·0	21·2	18·3	20·8
C(2)	4·45	4·67	29·1	28·6	23·9	24·0	20·9	24·6
C(3)	5·45	5·56	38·5	37·1	34·2	32·0	29·9	32·4
C(4)	4·72	4·81	31·1	29·9	30·0	27·6	21·8	24·1
C(5)	4·70	4·81	27·9	27·7	25·0	24·1	26·1	27·5
C(6)	5·32	5·38	36·9	34·8	32·2	30·3	30·8	31·7
C(7)	4·37	4·46	25·1	24·7	21·4	21·6	25·1	25·8
C(8)	4·16	4·26	25·2	24·6	20·2	20·2	17·9	19·5
C(9)	4·39	4·50	28·2	26·5	23·1	22·7	19·4	22·9
C(10)	5·52	5·56	37·8	35·8	36·3	33·5	29·8	31·8
C(11)	4·62	4·65	30·4	28·0	27·9	25·8	21·4	23·5
C(12)	4·78	4·80	29·0	27·9	26·2	24·5	25·6	26·8
C(13)	5·09	5·15	33·4	31·9	27·8	27·0	27·7	29·3
C(14)	4·47	4·54	25·4	25·9	22·6	21·8	25·1	26·3
C(15)	6·06	6·28	43·7	42·7	38·2	36·7	37·3	39·7
C(16)	6·09	6·07	44·2	41·6	40·0	36·1	36·0	37·5

Table 3. *Measured and calculated structure factors*

The reflexions used in the refinement are listed first. Unobserved reflexions, for which F_o is listed as 0·0, have threshold values in the range 1·5–3·0. Columns are in the order *h*, *k*, *l*, F_o, F_c.

planes included

H	K	L	F OBS	F CALC
2	0	0	7.6	6.9
4	0	0	45.3	48.3
8	0	0	4.3	-3.0
14	0	0	7.3	5.2
-8	0	1	29.3	30.9
-6	0	1	8.8	-8.7
-4	0	1	34.4	35.8
-2	0	1	46.2	50.2
0	0	1	77.3	78.2
2	0	1	7.6	6.6
4	0	1	20.5	-21.4
12	0	1	25.1	25.7
14	0	1	5.7	2.8
-10	0	2	18.9	19.3
-8	0	2	18.1	18.6
-6	0	2	4.3	-2.4
-4	0	2	14.3	14.3
-2	0	2	37.5	-38.1
0	0	2	31.2	-33.1
2	0	2	19.9	-19.5
4	0	2	25.6	27.5
6	0	2	14.7	-15.3
8	0	2	8.5	8.1
10	0	2	4.3	2.1
12	0	2	17.5	16.7
-6	0	3	4.8	-2.9
-4	0	3	4.3	-3.7
-2	0	3	15.0	12.8
0	0	3	5.0	2.9
2	0	3	20.5	20.4
4	0	3	36.3	39.0
6	0	3	10.1	-10.3
8	0	3	4.7	5.0
-10	0	4	4.0	-2.3
-6	0	4	16.0	-15.3
-4	0	4	3.6	2.0
-2	0	4	19.8	19.6
2	0	4	6.8	7.4
6	0	4	3.7	1.4
-14	0	5	5.0	-2.7
-12	0	5	12.2	11.3
-10	0	5	5.7	6.6
-6	0	5	14.0	-17.9
-4	0	5	7.6	7.9
-2	0	5	4.5	-4.3
2	0	5	9.6	-7.5
10	0	5	6.5	8.4
-14	0	6	5.6	-4.9
-12	0	6	17.8	16.0
0	0	6	7.9	11.4
2	0	6	19.4	21.3
-2	0	7	8.1	-7.6
0	0	7	27.9	34.9
2	0	7	7.8	8.5
-8	0	8	6.2	9.1
-8	0	9	5.0	5.6
1	1	0	50.8	55.6
2	1	0	46.2	51.4
3	1	0	25.0	-26.9
4	1	0	11.9	-9.5
5	1	0	9.5	-8.2
6	1	0	9.0	-7.8
7	1	0	3.7	2.0
13	1	0	4.7	4.0
15	1	0	5.9	-4.6
-9	1	1	10.9	10.4
-8	1	1	10.1	9.0
-7	1	1	15.3	-16.4
-6	1	1	27.0	28.2
-5	1	1	2.9	-2.0
-4	1	1	17.7	-18.2
-3	1	1	73.0	-79.0
-2	1	1	31.9	-36.7
-1	1	1	47.6	53.2
0	1	1	12.9	13.4
1	1	1	14.7	-12.8
2	1	1	20.0	-18.3
3	1	1	4.3	1.9
5	1	1	3.7	4.5
6	1	1	3.6	2.8
7	1	1	7.3	-7.1
8	1	1	6.8	6.5
12	1	1	5.6	3.2
13	1	1	10.9	11.2
14	1	1	8.7	7.5
15	1	1	6.8	-5.6
-11	1	2	4.2	-4.2
-10	1	2	3.7	1.4
-9	1	2	19.1	19.8
-8	1	2	14.6	13.6
-7	1	2	12.6	-13.2
-6	1	2	11.3	9.4
-5	1	2	4.0	5.2
-4	1	2	5.4	3.2
-2	1	2	17.2	17.1
-1	1	2	31.3	-32.3
0	1	2	3.3	-0.1
1	1	2	17.4	19.7
2	1	2	8.2	7.6
3	1	2	4.8	-5.2
4	1	2	15.5	15.1
6	1	2	23.6	24.4
7	1	2	12.2	-12.7
8	1	2	4.7	3.6
9	1	2	6.7	-7.6
10	1	2	5.1	-4.7
11	1	2	7.1	5.3
12	1	2	5.0	5.9
-10	1	3	8.4	5.3
-7	1	3	3.6	2.8
-3	1	3	22.3	23.2
-2	1	3	25.1	-25.5
-1	1	3	13.2	12.0
0	1	3	8.7	9.2
1	1	3	5.4	-4.3
2	1	3	2.8	2.3
3	1	3	35.0	36.3
4	1	3	27.9	29.6
5	1	3	9.1	-9.1
6	1	3	11.5	12.6
9	1	3	4.2	-2.4
-7	1	4	3.9	3.9
-6	1	4	13.3	-13.6
-5	1	4	20.5	-21.5
-4	1	4	30.1	-30.7
-3	1	4	30.4	33.8
-2	1	4	15.7	-17.2
-1	1	4	4.0	-3.1
0	1	4	7.9	-7.2
2	1	4	8.1	9.1
3	1	4	6.7	8.4
4	1	4	3.4	1.7
-11	1	5	11.6	12.3
-10	1	5	4.5	-3.4
-9	1	5	5.7	-6.1
-6	1	5	13.3	-14.0
-5	1	5	10.4	-9.4
-4	1	5	7.8	-9.5
-3	1	5	3.3	3.4
0	1	5	4.7	5.0
1	1	5	5.1	-3.4
3	1	5	3.7	-4.5
8	1	5	5.1	-6.5
-14	1	6	8.5	-6.9
-12	1	6	7.6	-7.0
-11	1	6	6.2	4.6
0	1	6	6.2	-7.1
1	1	6	14.3	18.8
3	1	6	6.8	-9.7
4	1	6	5.9	4.5
6	1	6	4.8	-6.7
-3	1	7	4.5	-2.5
-2	1	7	12.6	-13.8
-1	1	7	5.1	-6.3
0	1	7	11.0	-12.5
1	1	7	14.9	17.9
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2	2	0	120.4	-122.5
3	2	0	37.4	38.9
4	2	0	2.8	1.8
5	2	0	6.7	-8.3
6	2	0	13.0	-12.7
15	2	0	6.0	5.4
-10	2	1	5.1	-4.4
-8	2	1	4.2	-4.6
-7	2	1	11.8	12.4
-6	2	1	37.0	-39.6
-5	2	1	10.2	11.1
-4	2	1	25.6	-25.8
-3	2	1	93.8	-105.0
-2	2	1	105.1	-106.2
-1	2	1	7.3	-10.7
1	2	1	34.6	-33.7
2	2	1	18.3	16.6
3	2	1	4.7	-5.5
5	2	1	3.1	-4.1
6	2	1	7.4	7.2
9	2	1	5.6	-5.4
10	2	1	9.0	-9.0
11	2	1	7.6	-7.5
13	2	1	5.0	4.2
14	2	1	9.8	-7.0
15	2	1	5.0	4.0
-12	2	2	7.8	-8.1
-11	2	2	8.7	-7.9
-10	2	2	6.2	-5.4
-8	2	2	5.9	-6.9
-6	2	2	5.1	-4.2
-5	2	2	3.1	-3.2
-4	2	2	9.0	-10.6
-3	2	2	5.9	-5.3
-2	2	2	7.6	5.6
0	2	2	8.8	9.5
1	2	2	8.1	7.3
4	2	2	5.9	6.1
5	2	2	9.5	9.3
6	2	2	22.6	-22.9
7	2	2	5.7	6.8
9	2	2	17.5	-20.1
10	2	2	19.7	-21.2
11	2	2	6.2	-5.6
-12	2	3	5.9	-5.1
-11	2	3	4.8	-4.7
-8	2	3	4.5	4.3
-7	2	3	8.2	-7.5
-5	2	3	6.7	5.5
-4	2	3	13.5	14.0
-3	2	3	4.7	-2.0
-2	2	3	10.7	11.7
-1	2	3	14.4	15.3
0	2	3	22.0	-21.9
1	2	3	9.1	-11.5
2	2	3	16.4	-16.5
3	2	3	5.7	5.3
5	2	3	5.1	5.3
6	2	3	9.1	-9.4
8	2	3	4.8	-3.6
9	2	3	6.5	-6.8
10	2	3	4.7	-3.2
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2	2	4	3.7	-4.1
4	2	4	3.9	4.0
5	2	4	7.3	-6.3
-12	2	5	5.1	3.0
-10	2	5	11.0	-11.3
-9	2	5	17.4	18.6
-6	2	5	7.6	-8.8
-5	2	5	4.5	-5.1
4	2	5	6.4	-7.2
5	2	5	5.6	6.4
-14	2	6	7.4	-5.3
-10	2	6	5.0	-5.6
-9	2	6	6.7	4.9
2	2	6	8.1	-9.8
3	2	6	18.3	20.2
4	2	6	10.5	-10.3
5	2	6	4.7	4.7
-2	2	7	11.3	-15.5
-1	2	7	13.0	-11.9
2	2	7	8.2	-11.6
3	2	7	5.6	7.2
-5	2	8	6.7	6.4
-3	2	8	6.8	-7.4
-2	2	8	9.0	-12.6
1	3	0	12.9	-12.9
2	3	0	30.8	33.2
3	3	0	22.8	23.5
4	3	0	19.4	19.2
5	3	0	4.2	2.0
-7	3	1	10.9	-11.7
-6	3	1	13.8	13.3
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-2	3	1	33.6	-35.9
-1	3	1	5.1	9.9
0	3	1	2.6	-0.9
1	3	1	13.5	12.2
2	3	1	3.7	-4.9
4	3	1	5.3	5.0
5	3	1	3.4	2.9
8	3	1	6.7	-5.9
9	3	1	11.5	10.7
10	3	1	10.7	-9.5
11	3	1	6.5	-6.0
-13	3	2	4.7	-4.2
-11	3	2	8.1	-7.3
-10	3	2	4.3	-3.4
-7	3	2	3.7	1.5
-6	3	2	18.8	18.4
-5	3	2	17.5	17.0
-4	3	2	3.1	-1.3
-3	3	2	3.9	-6.3
-2	3	2	6.8	6.5
-1	3	2	2.8	-4.4
0	3	2	10.2	9.5
1	3	2	5.3	-4.1
5	3	2	4.2	-4.3
7	3	2	11.2	13.0
8	3	2	7.4	-4.4
10	3	2	14.3	-15.5
11	3	2	4.5	-5.9
-12	3	3	5.6	-5.1
-11	3	3	5.6	-4.7
-7	3	3	3.9	-2.7
-6	3	3	4.8	-4.9
-5	3	3	9.0	-7.9
-4	3	3	9.6	9.1
-1	3	3	28.1	-30.3
0	3	3	29.0	30.6
1	3	3	26.8	-28.0
2	3	3	19.4	-19.8
3	3	3	5.4	-5.4
5	3	3	5.0	-4.8
6	3	3	3.6	3.6
7	3	3	8.1	10.1
9	3	3	7.9	-6.5
-10	3	4	6.7	4.0
-9	3	4	10.5	-11.3
-8	3	4	10.4	12.2
-7	3	4	4.7	5.0
-5	3	4	4.8	-6.0
-2	3	4	12.4	13.2
-1	3	4	12.6	-14.7
0	3	4	8.8	-8.0
1	3	4	18.4	-20.9
2	3	4	6.0	-7.3
4	3	4	5.7	-4.9
-10	3	5	12.1	12.9
-9	3	5	10.1	-11.7
-8	3	5	14.1	13.8
-7	3	5	13.8	12.8
-3	3	5	3.4	1.8
4	3	5	6.7	8.9
6	3	5	5.9	-5.6
0	3	6	4.2	3.3
2	3	6	9.0	8.1
3	3	6	13.8	-14.5
4	3	6	10.2	13.3
5	3	6	8.8	11.8
-3	3	7	6.4	9.4
-1	3	7	5.4	-4.0
2	3	7	5.0	5.8
-6	3	8	5.3	4.6
-5	3	8	7.9	7.6
-4	3	8	6.2	6.8
0	4	0	18.3	18.8
1	4	0	14.0	-13.2
2	4	0	3.7	-3.2
3	4	0	17.1	17.7
4	4	0	29.3	30.7
5	4	0	10.9	8.9
-8	4	1	5.7	4.8
-6	4	1	18.4	17.8
-5	4	1	35.2	31.8
-4	4	1	58.4	59.0
-3	4	1	5.0	4.2
-2	4	1	2.8	-2.2
-1	4	1	16.6	16.8
0	4	1	8.2	9.3
1	4	1	6.4	-5.5
3	4	1	13.3	13.4
4	4	1	9.6	-10.0
8	4	1	5.1	2.8
9	4	1	4.5	-5.0
-13	4	2	7.8	6.6
-9	4	2	4.5	4.8
-7	4	2	5.7	4.2
-6	4	2	24.8	22.8
-5	4	2	37.7	38.9
-4	4	2	4.8	5.4
-2	4	2	4.7	4.6
0	4	2	11.9	-9.9
2	4	2	8.1	8.2
3	4	2	14.1	-17.4
4	4	2	6.8	4.9
7	4	2	5.0	8.0
8	4	2	24.8	25.6
9	4	2	4.5	3.0
-13	4	3	5.3	4.6
-5	4	3	6.5	-8.4
-3	4	3	4.0	-4.1
-2	4	3	3.4	-3.5
-1	4	3	11.2	11.0
0	4	3	7.0	-7.5
1	4	3	9.5	-9.3
2	4	3	8.1	8.7
6	4	3	9.8	11.4
7	4	3	19.7	21.6
8	4	3	8.2	10.2
-9	4	4	5.9	4.7
-8	4	4	3.9	3.2
-7	4	4	17.7	-20.3
-6	4	4	13.8	16.5
-2	4	4	10.2	9.9
-1	4	4	18.8	22.0
1	4	4	6.0	-6.2
3	4	4	4.7	4.3
-8	4	5	11.8	11.8
-7	4	5	6.0	-6.7
-6	4	5	7.8	4.4
-3	4	5	4.5	5.7
-2	4	5	9.0	8.0
5	4	5	9.3	-10.1
6	4	5	11.6	11.4
-3	4	6	4.0	-4.4
2	4	6	4.2	-3.1
4	4	6	6.8	7.2
-5	4	8	5.0	4.0
-4	4	8	11.2	12.8
1	5	0	19.8	-19.4
2	5	0	15.3	-17.0
3	5	0	7.4	-6.1
4	5	0	9.5	8.2
6	5	0	6.5	-5.3
-11	5	1	4.7	4.8
-10	5	1	6.0	-6.8
-9	5	1	4.0	5.2
-7	5	1	9.8	-9.7
-6	5	1	4.0	-3.9
-5	5	1	16.9	16.8
-4	5	1	15.2	12.9
-3	5	1	5.4	-5.1
0	5	1	9.3	-10.2
1	5	1	15.5	-14.5
2	5	1	4.3	-4.6
10	5	1	5.4	3.5
-9	5	2	4.5	-2.3
-8	5	2	16.3	-14.8
-7	5	2	16.7	-15.1
-6	5	2	9.8	9.4
-5	5	2	11.9	10.7
1	5	2	9.3	9.3
2	5	2	18.3	-17.0
3	5	2	14.7	14.6
7	5	2	7.3	7.4
8	5	2	9.3	9.6
-8	5	3	7.8	-5.0
-7	5	3	6.0	3.1
-6	5	3	8.5	-7.0
-2	5	3	4.3	-6.0
-1	5	3	3.9	4.3
0	5	3	3.9	4.0
1	5	3	13.0	13.8
2	5	3	13.3	-13.8
3	5	3	7.6	7.1
5	5	3	8.2	-10.3
7	5	3	10.4	11.8
8	5	3	6.5	8.2
-8	5	4	6.0	-4.8
-7	5	4	17.4	19.3
-6	5	4	14.0	-15.5
-4	5	4	6.2	5.0
-2	5	4	5.0	5.1
-1	5	4	12.7	13.0
4	5	4	5.4	-4.4
-8	5	5	6.2	-8.3
-7	5	5	8.2	9.2
-5	5	5	5.0	-3.1
-2	5	5	7.9	8.4

Table 3 (*cont.*)

H	K	L	F OBS	F CALC
-1	5	5	4.2	5.6
5	5	5	8.1	7.9
1	6	0	16.0	-15.0
2	6	0	15.8	-16.9
5	6	0	5.3	-3.7
7	6	0	5.4	-6.2
-8	6	1	5.1	-5.5
-7	6	1	8.7	-6.3
-6	6	1	10.2	-8.3
-5	6	1	7.1	-6.7
0	6	1	7.3	-6.0
1	6	1	13.6	-13.3
2	6	1	3.9	-4.0
-8	6	2	17.7	-14.3
-7	6	2	25.0	-21.5
-6	6	2	9.0	-7.8
-4	6	2	3.6	-1.8
-3	6	2	4.3	-4.4
2	6	2	9.1	8.3
3	6	2	3.7	-2.3
4	6	2	6.5	-5.6
5	6	2	5.6	4.9
6	6	2	8.8	-6.5
-9	6	3	7.9	-5.3
-8	6	3	10.1	-9.2
-7	6	3	7.6	-4.5
-5	6	3	6.4	6.6
-4	6	3	13.8	-15.7
-3	6	3	10.7	12.9
1	6	3	5.9	-5.5
4	6	3	10.7	-11.9
5	6	3	17.8	-18.9
6	6	3	10.2	-10.6
-7	6	4	4.5	-4.5
-5	6	4	14.4	15.8
-4	6	4	15.5	-14.8
-1	6	4	5.3	4.4
3	6	4	5.0	-4.7
4	6	4	10.7	-10.9
5	6	4	7.4	-8.1
8	6	4	5.7	-5.0
-4	6	5	9.5	-6.8
1	7	0	8.5	5.7
2	7	0	5.6	-4.5
3	7	0	3.9	-1.5
-9	7	1	4.7	-3.3
-8	7	1	4.5	5.6
-7	7	1	4.8	-4.5
-2	7	1	7.3	7.0
-1	7	1	11.9	11.1
0	7	1	8.2	7.1
1	7	1	5.9	-4.3
4	7	1	4.8	4.7
5	7	1	7.8	-6.1
6	7	1	5.3	3.8
-10	7	2	6.8	5.6
-9	7	2	4.7	3.5
-7	7	2	9.9	-6.9
-2	7	2	6.8	5.4
-1	7	2	3.9	3.8
3	7	2	4.8	-4.7
4	7	2	10.9	9.2
5	7	2	9.3	-7.7
-11	7	3	5.9	3.8
-10	7	3	8.1	5.7
-5	7	3	10.1	-8.1
-4	7	3	15.7	15.5
-3	7	3	6.0	-6.5
-2	7	3	6.2	-5.9
5	7	3	10.1	-10.0
6	7	3	5.1	-6.6
-5	7	4	10.5	-12.0
-4	7	4	6.4	6.6
-3	7	4	5.6	-3.8
-2	7	4	5.3	-3.1
2	7	4	6.8	7.4
3	7	4	5.0	4.6
0	8	0	5.1	4.8
-2	8	1	4.0	2.8
-1	8	1	12.2	11.2
0	8	1	4.8	3.9
7	8	1	5.6	-4.0
-10	8	2	6.5	3.8
-9	8	2	9.3	6.9
-2	8	2	10.2	9.3
-1	8	2	5.7	-5.4
-10	8	3	11.2	7.5
-9	8	3	5.9	3.0
-3	8	3	6.2	-5.1
-2	8	3	13.5	13.1
-1	8	3	10.1	-8.5
2	8	3	4.5	4.0
-3	8	4	6.7	-5.4
-2	8	4	5.4	3.9
-3	9	1	5.4	-4.3
7	9	1	5.3	4.4
-1	9	2	8.8	7.7
-2	9	3	10.5	-9.3
-1	9	3	6.2	4.8
0	10	2	6.5	-5.0
0	10	3	6.2	-4.5
-12	0	1	2.2	-1.0
-10	0	1	3.4	2.2
6	0	1	1.6	-0.3
8	0	1	1.6	0.5
10	0	1	1.2	-0.9
-12	0	2	1.9	0.4
-12	0	3	3.3	0.2
-10	0	3	1.7	1.0
-8	0	3	0.0	-1.4
10	0	3	2.3	-1.1
-12	0	4	0.0	-0.3
-8	0	4	2.5	0.7
0	0	4	1.9	-0.4
4	0	4	0.0	0.7
8	0	4	3.1	-1.8
10	0	4	2.0	1.7
-8	0	5	3.4	4.6
4	0	5	0.0	-0.1
6	0	5	2.5	-1.7
8	0	5	2.3	-1.6
-10	0	6	1.9	-0.3
-8	0	6	0.0	1.4
-6	0	6	2.5	-0.3
-4	0	6	2.6	-2.2
-2	0	6	2.6	3.3
4	0	6	2.2	1.6
6	0	6	2.8	-1.8
-12	0	7	3.7	1.7
-8	0	7	2.3	0.8
-6	0	7	1.2	2.6
-4	0	7	2.5	4.9
4	0	7	2.8	3.4
-2	0	8	2.8	-2.2
8	1	0	1.9	-0.0
9	1	0	2.2	-0.9
10	1	0	1.7	1.6
11	1	0	2.2	-1.0
12	1	0	1.9	-0.0
14	1	0	4.7	2.5
-12	1	1	1.2	0.4
-11	1	1	1.7	-1.1
-10	1	1	2.6	0.8
4	1	1	1.4	1.6
9	1	1	2.8	1.8
10	1	1	2.2	-2.9
11	1	1	3.4	-1.4
-12	1	2	2.6	-1.3
-3	1	2	0.8	1.5
5	1	2	2.3	1.8
-12	1	3	1.2	-1.6
-11	1	3	2.8	-1.6
-9	1	3	2.3	2.3
-8	1	3	0.0	-1.5
-6	1	3	0.0	-2.3
-5	1	3	1.2	2.6
-4	1	3	0.8	0.9
7	1	3	1.6	0.7
8	1	3	1.7	0.4
10	1	3	1.9	1.2
-12	1	4	0.0	0.8
-11	1	4	2.6	0.8
-10	1	4	3.7	-2.9
-9	1	4	3.1	-3.2
-8	1	4	2.5	-0.5
1	1	4	1.7	1.0
5	1	4	3.1	2.9
6	1	4	2.3	-1.5
7	1	4	0.0	0.6
8	1	4	0.0	0.5
9	1	4	2.3	3.6
-14	1	5	3.9	-2.1
-8	1	5	1.7	-0.7
-7	1	5	2.3	-0.5
-2	1	5	0.0	-0.1
-1	1	5	2.8	3.2
2	1	5	3.3	-3.5
4	1	5	0.0	-0.1
5	1	5	1.7	2.0
6	1	5	3.1	-4.8
7	1	5	3.6	-6.8
-10	1	6	1.4	-0.3
-9	1	6	3.3	-0.5
-8	1	6	1.2	-1.4
-7	1	6	2.5	-1.9
-6	1	6	1.7	-0.7
-5	1	6	0.0	0.1
-4	1	6	2.6	3.4
-3	1	6	0.0	0.1
-2	1	6	0.0	0.6
-1	1	6	1.9	-4.5
2	1	6	3.3	-4.7
5	1	6	0.0	1.6
-8	1	7	0.0	0.8
-7	1	7	0.0	2.9
-6	1	7	0.0	2.0
-5	1	7	3.1	-4.3
-4	1	7	0.0	1.3
2	1	7	2.6	0.4
4	1	7	2.0	-0.1
-6	1	8	3.3	2.6
0	1	8	3.7	0.1
0	2	0	0.6	0.9
7	2	0	3.9	-2.5
8	2	0	2.2	1.0
9	2	0	2.0	0.6
10	2	0	3.6	5.1
11	2	0	2.8	1.9
12	2	0	2.3	-0.1
14	2	0	4.2	-3.3
-12	2	1	0.0	-0.2
-11	2	1	1.2	0.4
-9	2	1	0.0	-0.1
0	2	1	0.0	-0.6
4	2	1	1.4	0.2
7	2	1	3.1	3.4
8	2	1	1.9	0.7
12	2	1	3.4	-0.5
-9	2	2	2.6	2.8
-7	2	2	1.1	-0.1
-1	2	2	0.0	1.1
2	2	2	2.5	5.2
3	2	2	0.0	-0.7
8	2	2	2.8	2.0
-10	2	3	0.0	-0.5
-9	2	3	1.1	-1.2
-6	2	3	0.0	-0.1
4	2	3	2.0	1.8
7	2	3	1.7	0.0
-11	2	4	1.9	0.0
-10	2	4	2.2	-1.3
-8	2	4	2.8	-5.5
-6	2	4	1.9	-1.9
-4	2	4	1.4	0.4
-2	2	4	1.6	1.7
3	2	4	1.1	1.6
6	2	4	0.0	0.6
7	2	4	1.7	1.4
8	2	4	2.3	1.5
9	2	4	1.9	1.5
-11	2	5	2.3	-1.3
-8	2	5	2.9	2.1
-7	2	5	3.6	3.0
-4	2	5	0.0	3.8
-3	2	5	0.0	-0.8
-2	2	5	0.0	-0.1
-1	2	5	0.0	-1.1
0	2	5	2.9	1.7
1	2	5	3.3	3.1
2	2	5	0.0	0.2
3	2	5	0.0	3.2
6	2	5	1.2	0.5
7	2	5	2.3	-1.2
8	2	5	2.8	-3.0
-13	2	6	4.7	-4.8
-8	2	6	2.6	3.6
-7	2	6	1.9	-1.0
-6	2	6	1.2	0.2
-5	2	6	2.5	1.0
-4	2	6	2.3	-2.8
-3	2	6	0.0	0.2
-2	2	6	2.0	0.5
-1	2	6	3.1	2.4
0	2	6	1.7	-0.9
1	2	6	2.0	-1.7
6	2	6	2.5	-3.0
-7	2	7	2.8	-0.0
-6	2	7	2.9	-3.3
-5	2	7	2.9	4.8
-4	2	7	1.9	-0.9
-3	2	7	2.6	-2.6
0	2	7	2.6	-0.1
1	2	7	3.4	1.2
-6	2	8	4.3	-7.2
6	3	0	1.4	-1.2
7	3	0	2.8	1.6
8	3	0	2.9	2.4
9	3	0	2.9	-0.6
10	3	0	2.8	-0.9
11	3	0	2.9	2.8
12	3	0	0.0	1.0
-13	3	1	3.3	-1.7
-12	3	1	2.3	3.0
-11	3	1	2.8	-2.7
-10	3	1	2.6	-2.1
-9	3	1	2.3	2.7
-8	3	1	1.6	0.2
3	3	1	1.2	-0.8
6	3	1	2.8	-3.1
7	3	1	2.6	-4.0
-12	3	2	1.4	2.1
-9	3	2	2.6	2.0
-8	3	2	3.4	-2.3
2	3	2	2.3	-2.5
3	3	2	2.6	-2.8
4	3	2	2.9	-1.1
6	3	2	1.9	-0.3
9	3	2	3.4	-0.1
-14	3	3	4.3	4.2
-10	3	3	0.0	-0.5
-9	3	3	0.0	2.8
-8	3	3	3.4	-3.9
-3	3	3	2.5	1.0
-2	3	3	1.6	-2.2
4	3	3	2.9	2.4
8	3	3	3.1	-0.1
10	3	3	2.8	-3.9
-11	3	4	0.0	-0.0
-6	3	4	0.0	-3.4
-4	3	4	1.1	2.8
-3	3	4	0.0	-0.3
3	3	4	1.9	1.5
5	3	4	0.0	-2.[illegible]
6	3	4	2.2	-0.5
7	3	4	2.2	-2.2
8	3	4	2.6	2.1
9	3	4	2.0	1.1
-11	3	5	3.7	-2.5
-6	3	5	1.7	3.1
-5	3	5	3.1	-4.[illegible]
-4	3	5	1.9	1.4
-2	3	5	0.0	0.6
-1	3	5	0.0	1.5
0	3	5	2.5	-3.1
1	3	5	2.0	0.1
2	3	5	1.7	-1.1
3	3	5	3.6	-4.6
5	3	5	2.2	1.8
7	3	5	3.9	1.2
-9	3	6	3.3	3.6
-8	3	6	3.9	4.2
-7	3	6	2.9	1.0
-6	3	6	2.2	-1.1
-5	3	6	1.2	0.5
-4	3	6	2.2	-1.0
-3	3	6	0.0	0.1
-2	3	6	0.0	-4.4
-1	3	6	0.0	0.5
1	3	6	2.2	2.5
-6	3	7	2.8	0.8
-5	3	7	2.6	-1.7
-4	3	7	2.9	3.1
-2	3	7	4.0	-3.8
0	3	7	1.9	0.9
1	3	7	2.3	-0.2
-3	3	8	3.3	3.3
-2	3	8	4.0	-3.3
-5	3	9	3.4	4.3
6	4	0	2.2	-1.0
7	4	0	1.1	1.2
8	4	0	1.7	-3.0
9	4	0	1.2	-0.1
10	4	0	1.2	0.8
11	4	0	0.0	1.1
-11	4	1	1.9	-0.2
-10	4	1	2.5	3.7
-9	4	1	2.0	-1.9
-7	4	1	0.0	-1.0
2	4	1	1.4	1.4
5	4	1	1.1	0.5
6	4	1	1.9	-1.1
7	4	1	1.1	-2.0
10	4	1	2.3	0.5
11	4	1	2.8	2.8
-11	4	2	1.9	-2.5
-10	4	2	3.6	3.6
-8	4	2	2.8	-1.2
-3	4	2	0.9	0.1
-1	4	2	1.9	2.7
1	4	2	2.2	1.6
5	4	2	1.6	0.4
6	4	2	2.8	2.5
10	4	2	3.1	-3.7
-14	4	3	3.9	2.4
-11	4	3	2.9	0.3
-10	4	3	0.0	0.7
-9	4	3	2.2	1.4
-8	4	3	2.0	0.4
-7	4	3	2.6	-0.1
-6	4	3	2.2	2.6
-4	4	3	1.7	-2.0
3	4	3	2.5	2.3
4	4	3	2.8	1.2
5	4	3	1.7	0.0
9	4	3	2.0	0.3
-10	4	4	2.3	-0.2
-5	4	4	2.2	-3.8
-4	4	4	0.0	-0.1
-3	4	4	2.3	-3.5
0	4	4	0.0	1.4
2	4	4	1.6	-0.6
4	4	4	1.7	0.9
5	4	4	3.1	2.0
6	4	4	3.4	3.4
7	4	4	2.3	-1.3
8	4	4	2.0	0.0
-9	4	5	2.6	1.8
-5	4	5	1.2	0.9
-4	4	5	0.0	1.5
-1	4	5	2.0	2.4
[illegible]	4	5	3.1	-1.1
1	4	5	0.0	0.2
2	4	5	3.6	3.1
3	4	5	1.9	0.6
4	4	5	2.2	-0.0
-8	4	6	2.8	2.4
-7	4	6	1.9	2.1
-6	4	6	1.9	-0.6
-5	4	6	1.9	0.7
-4	4	6	2.6	-1.6
-2	4	6	0.0	2.5
-1	4	6	0.0	-1.6
0	4	6	2.2	1.1
1	4	6	2.2	-3.2
3	4	6	1.9	0.8
-4	4	7	3.6	8.6
-3	4	7	2.3	-3.9
-2	4	7	3.4	3.4
-1	4	7	0.0	0.5
0	4	7	1.4	2.3
-3	4	8	3.3	2.3
-5	4	9	4.8	4.5
5	5	0	0.0	0.5
7	5	0	3.1	1.5
8	5	0	0.0	1.0
9	5	0	2.6	0.8
10	5	0	1.9	0.4
-8	5	1	2.8	-1.7
-2	5	1	1.4	0.4
-1	5	1	0.0	-0.1
2	5	1	1.6	0.9
4	5	1	1.6	0.2
5	5	1	1.6	0.6
6	5	1	2.2	1.6
7	5	1	2.2	-0.8
8	5	1	0.0	-1.9
9	5	1	0.0	-0.0
-10	5	2	1.9	-1.1
-4	5	2	2.2	0.3
-3	5	2	0.0	-0.6
-2	5	2	3.1	-4.3
-1	5	2	0.0	1.1
0	5	2	2.3	-1.2
4	5	2	1.6	1.3
5	5	2	2.6	-2.1
6	5	2	3.4	-3.7

planes omitted

H	K	L	F OBS	F CALC
6	0	0	0.0	-2.1
10	0	0	2.0	-0.2
12	0	0	3.3	0.6
-13	0	1	0.0	0.0

Table 3 (*cont.*)

H	K	L	F OBS	F CALC
9	5	2	3.7	3.4
-14	5	3	3.6	2.8
-10	5	3	0.0	1.3
-9	5	3	3.9	-3.1
-5	5	3	0.0	2.9
-4	5	3	2.5	5.2
-3	5	3	1.9	0.8
4	5	3	3.3	-5.0
6	5	3	3.4	1.5
-9	5	4	2.6	1.6
-5	5	4	2.3	0.2
-3	5	4	1.2	3.4
0	5	4	0.0	4.0
1	5	4	0.0	1.3
2	5	4	2.8	2.8
3	5	4	0.0	-0.0
5	5	4	3.4	-3.0
6	5	4	3.1	0.6
7	5	4	3.1	4.3
-6	5	5	2.2	-1.3
-4	5	5	1.9	-3.0
-3	5	5	2.8	3.0
0	5	5	3.7	2.8
1	5	5	0.0	-2.1
2	5	5	1.2	1.1
3	5	5	0.0	1.1
4	5	5	2.3	1.2
-6	5	6	1.4	0.1
-5	5	6	0.0	-0.2
-4	5	6	1.9	1.4
-3	5	6	2.3	1.1
-2	5	6	2.6	-1.9
-1	5	6	0.0	-3.7
0	5	6	2.6	4.5
1	5	6	1.9	-0.8
2	5	6	2.5	-3.5
-4	5	8	3.4	1.6
0	6	0	0.0	1.1
3	6	0	3.4	-4.0
4	6	0	2.6	-0.1
6	6	0	2.9	0.8
8	6	0	0.0	-0.9
9	6	0	1.9	0.7
-11	6	1	3.4	-2.5
-10	6	1	4.0	4.6
-9	6	1	2.6	0.0
-5	6	1	3.3	-0.3
-4	6	1	2.0	-0.2
-2	6	1	1.9	1.2
-1	6	1	2.3	3.3
3	6	1	2.0	-1.2
4	6	1	0.0	-0.9
5	6	1	3.6	4.5
6	6	1	2.2	0.9
7	6	1	2.3	1.9
8	6	1	0.0	0.2
9	6	1	0.0	0.3
-11	6	2	4.0	-4.1
-9	6	2	3.6	-2.0
-5	6	2	2.3	0.3
-2	6	2	1.9	1.6
-1	6	2	0.0	-0.7
0	6	2	3.4	-3.1
1	6	2	2.0	0.1
7	6	2	2.6	-1.8
8	6	2	2.5	1.2
-6	6	3	3.7	2.5
-2	6	3	1.2	-0.8
-1	6	3	2.3	2.7
0	6	3	2.9	-1.4
2	6	3	2.8	4.0
3	6	3	2.5	1.1
7	6	3	2.5	0.3
-8	6	4	3.6	2.7
-6	6	4	2.9	-1.0
-3	6	4	1.7	-2.4
-2	6	4	0.0	0.3
0	6	4	2.8	-1.1
1	6	4	2.2	-3.1
2	6	4	1.9	0.4
-6	6	5	3.1	-2.4
-5	6	5	3.6	-2.7
-3	6	5	3.7	-4.5
-2	6	5	0.0	2.4
-1	6	5	0.0	-0.0
0	6	5	3.6	-3.5
1	6	5	0.0	1.2
2	6	5	2.8	-0.1
3	6	5	0.0	0.4
0	6	6	4.0	-4.7
4	7	0	0.0	0.7
5	7	0	3.1	2.1
6	7	0	3.9	-3.3
7	7	0	4.0	-4.7
8	7	0	3.7	-3.6
-6	7	1	3.4	-1.2
-5	7	1	3.1	1.4
-4	7	1	1.7	-0.1
-3	7	1	3.4	2.5
2	7	1	0.0	-0.7
3	7	1	1.9	0.4
7	7	1	1.4	1.1
-8	7	2	4.3	-3.7
-6	7	2	2.6	-1.2
-5	7	2	1.9	2.1
-4	7	2	3.6	0.6
-3	7	2	2.2	-0.7
0	7	2	2.8	0.8
1	7	2	2.5	-2.5
2	7	2	2.2	-1.0
6	7	2	2.5	-0.7
-8	7	3	4.3	-3.5
-7	7	3	2.3	-1.9
-6	7	3	3.6	1.4
-1	7	3	2.2	1.7
0	7	3	2.6	2.8
1	7	3	2.6	-2.6
2	7	3	0.0	1.3
3	7	3	3.6	2.2
4	7	3	3.1	1.1
-1	7	4	2.6	-0.6
0	7	4	2.6	-0.6
1	7	4	0.0	1.7
1	8	0	3.4	-0.8
2	8	0	1.9	-0.0
3	8	0	4.0	1.1
4	8	0	0.0	1.7
5	8	0	2.8	3.6
8	8	0	3.6	-2.7
0	10	4	6.0	-4.3
-8	8	1	3.7	-3.3
-5	8	1	1.4	2.0
-4	8	1	2.9	-1.8
-3	8	1	2.3	-2.2
1	8	1	2.6	1.1
2	8	1	0.0	0.5
3	8	1	0.0	0.6
4	8	1	2.8	-0.5
5	8	1	3.7	3.5
-8	8	2	3.7	1.7
-5	8	2	1.4	1.3
-4	8	2	3.9	-2.3
-3	8	2	2.6	0.8
0	8	2	3.6	3.3
1	8	2	0.0	-0.1
2	8	2	2.3	0.5
3	8	2	2.0	-1.9
4	8	2	4.3	-4.0
0	8	3	2.3	0.6
1	8	3	0.0	-0.6
-10	8	4	4.8	3.8
5	9	0	3.6	4.4
6	9	0	3.7	3.5
-4	9	1	3.9	-2.8
-9	9	2	4.0	1.7
0	9	3	3.3	2.3
-3	10	1	4.2	-2.9
-1	10	3	3.6	2.1

Table 4. *Final positional parameters (fractional), standard deviations* (Å), *isotropic thermal parameters* (Å^2), *and displacements* (Å) *from the mean molecular plane*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B(Å^2)	Δ(Å)
C(1)	0·2817	−0·0402	0·4119	0·007	0·008	0·010	7·05	0·007
C(2)	0·2947	0·0246	0·2717	0·006	0·007	0·008	5·95	0·003
C(3)	0·2296	−0·0077	0·1274	0·005	0·005	0·006	4·88	0·004
C(4)	0·2389	0·0567	−0·0238	0·006	0·006	0·008	5·82	0·003
C(5)	0·1783	0·0237	−0·1578	0·006	0·007	0·007	6·06	−0·015
C(6)	0·0990	−0·0738	−0·1606	0·005	0·005	0·006	5·39	0·001
C(7)	0·0316	−0·1103	−0·3020	0·007	0·008	0·007	7·15	0·000
C(8)	−0·0449	−0·2090	−0·2966	0·007	0·009	0·010	7·26	0·003
C(9)	−0·0566	−0·2746	−0·1594	0·006	0·008	0·009	6·62	−0·016
C(10)	0·0071	−0·2396	−0·0131	0·005	0·005	0·006	5·34	0·018
C(11)	−0·0030	−0·3070	0·1356	0·006	0·006	0·008	6·53	0·000
C(12)	0·0575	−0·2772	0·2706	0·006	0·007	0·007	6·07	−0·001
C(13)	0·1389	−0·1735	0·2723	0·005	0·006	0·006	5·19	0·004
C(14)	0·2066	−0·1412	0·4161	0·007	0·008	0·007	7·06	−0·020
C(15)	0·1514	−0·1091	0·1303	0·004	0·005	0·005	4·01	−0·002
C(16)	0·0854	−0·1409	−0·0136	0·004	0·004	0·005	4·62	0·011
H(1)	0·33	−0·03	0·52	0·07	0·07	0·10	8·0	
H(2)	0·36	0·10	0·27					
H(4)	0·30	0·13	−0·03					
H(5)	0·19	0·08	−0·27					
H(7)	0·04	−0·06	−0·41					
H(8)	−0·10	−0·24	−0·41					
H(9)	−0·12	−0·35	−0·16					
H(11)	−0·06	−0·38	0·14					
H(12)	0·05	−0·33	0·38					
H(14)	0·20	−0·19	0·53					

The best plane through the carbon atoms has equation:

$$-0{\cdot}64213\ X'+0{\cdot}74683\ Y+0{\cdot}17291\ Z'+1{\cdot}76738=0\ ,$$

where X', Y, Z' are coordinates in Å, referred to orthogonal axes a, b and c^*. The deviations of the atoms from this plane are listed in the last column of Table 4.

The orientation of the molecule in the unit cell is given in Table 6 in terms of the angles which the molecular axes L, M (Fig. 1), and the plane normal, N, make with the orthogonal crystal axes. L was taken through atoms 1 and 8, and M through the mid points of bonds 4–5 and 11–12. L, M and N are almost exactly mutually perpendicular, the angles between them being $\angle\ LM=89{\cdot}5°$, $\angle\ MN=90{\cdot}0°$, and $\angle\ LN=90{\cdot}0°$. Previous values of the orientation angles (Robertson & White, 1947) are included in Table 6 for comparison.

Table 5. *Anisotropic thermal parameters for the carbon atoms* (× 10^4)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(1)	98	204	277	−29	48	9
C(2)	88	162	249	5	52	4
C(3)	64	138	197	−15	45	1
C(4)	85	150	235	6	57	−10
C(5)	81	169	243	13	52	8
C(6)	72	158	234	−5	54	21
C(7)	96	214	284	−5	63	37
C(8)	103	196	298	−23	54	13
C(9)	89	185	271	−22	43	9
C(10)	77	148	209	−7	50	10
C(11)	91	174	264	−8	48	3
C(12)	88	164	240	0	64	16
C(13)	67	147	210	−7	40	15
C(14)	100	207	281	32	65	33
C(15)	54	118	171	4	46	17
C(16)	59	137	188	−6	45	14

Table 6. *Orientation of the molecule in the crystal*

	Robertson & White (1947)	Present analysis
χL	61·1°	60·9°
ψL	77·7	77·1
ωL	31·9	32·5
χM	52·2	53·3
ψM	52·4	51·1
ωM	120·1	120·0
χN	128·7	130·0
ψN	40·2	41·7
ωN	80·5	80·0

All the carbon–carbon intermolecular separations less than 4 Å were calculated; all these contacts correspond to normal van der Waals interactions. The shortest distances are between molecules related by a centre of symmetry; the planes of these molecules are parallel and separated by 3·53 Å, and there are 59 contacts less than 4 Å, those less than 3·6 Å being listed in Table 7. The shortest lateral C...C contacts and the most significant C...H and H...H contacts, are also given in Table 7.

Table 7. *Shortest intermolecular contacts* (Å)

All C...C contacts ≤4·0 Å between a standard molecule (1) and neighbouring molecules were calculated, but only the most significant separations are listed. The shortest C...H and H...H contacts are also given

	Atom (molecule 1)	to Atom	in Molecule	d
C...C	3	9	3	3·55
	5	11	3	3·58
	6	10	3	3·67
	7	13	3	3·56
	8	15	3	3·67
	16	16	3	3·53
	2	11	12	3·78
	4	15	5	3·64
	4	16	5	3·68
	14	7	2	3·67
C...H	C(2)	H(11)	12	2·8
	H(4)	C(10)	5	2·9
	H(4)	C(15)	5	2·7
	H(4)	C(16)	5	2·6
H...H	1	12	6	2·5
	2	11	12	2·6
	2	14	6	2·8
	11	7	2	2·6

Molecule				
	1	x	y	z
	2	x	y	$1+z$
	3	$-x$	$-y$	$-z$
	5	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$
	6	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$
	12	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	z

Discussion

The deviations of the carbon atoms from the mean molecular plane (Table 4) are smaller than the displacements in perylene (Camerman & Trotter, 1964), and on the basis of the standard deviations are not significant. The displacement are suggestive of a small bending of the molecule, similar to that in perylene, and this, if real, is probably a result of crystal packing forces.

The anisotropic thermal parameters, B_{ij}, were transformed to U_{ij} referred to the orthogonal crystal axes a, b and c^* (Rollett & Davies, 1955), and then to U tensors referred to the molecular axes L, M and N. The thermal motion was analysed in terms of the rigid-body vibrations of the molecule (Cruickshank, 1956*b*). The **T** and **ω** tensors are:

$$\mathbf{T}=\begin{pmatrix} 0\cdot0589 & -0\cdot0067 & 0\cdot0076 \\ & 0\cdot0501 & 0\cdot0025 \\ & & 0\cdot0500 \end{pmatrix} \text{Å}^2$$

$$\boldsymbol{\omega}=\begin{pmatrix} 14\cdot56 & 0\cdot55 & -0\cdot42 \\ & 10\cdot67 & -1\cdot37 \\ & & 17\cdot18 \end{pmatrix} \text{deg}^2$$

The r.m.s. amplitudes of translational oscillation in the directions of the molecular axes are 0·24, 0·22, and 0·22 Å respectively, and the corresponding amplitudes of angular oscillation are 3·8°, 3·3°, and 4·1°. These values are of the same magnitude as those found for anthracene (Cruickshank, 1956*d*) and illustrate that the molecule seems to move most easily in the directions offering least resistance, *i.e.* greatest translational motion in the direction of the long axis and greatest rotational oscillations about axes N and L.

Slight corrections in bond distances are necessary to allow for the angular oscillations, which cause the atoms to appear too close to the centre of the molecule (Cruickshank, 1956*c*). The bond length corrections, which vary from 0·004 to 0·006 Å, were applied to the distances of Fig. 1(*a*) before the final mean values of Table 8 were derived.

Differences between chemically equivalent bond lengths are generally small [Fig. 1(*a*)], but one or two differences are fairly large: *e.g.* bond 5–6 is shorter and bond 12–13 is longer than (with their mean about equal to) chemically equivalent bonds; bond 8–9 is very short, but its chemically equivalent bonds are also fairly short. These variations are only possibly significant and, although the differences may be real, the chemically equivalent bond distances were averaged for comparison with theoretical values. The mean bond distances are given in Table 8, together with their standard deviations, σ_m being calculated from the standard deviations of the individual distances [Fig. 1(*a*)], and σ'_m being derived from the deviations between the individual measured values and the means. The general agreement between the two different estimates of the standard deviations suggests that the accuracy quoted is realistic.

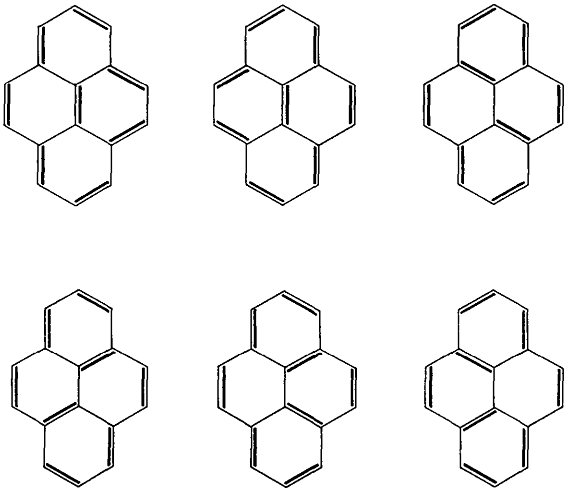

Fig. 2. Kekulé structures for pyrene.

For comparison with these measured distances the theoretical bond lengths were derived from the six non-excited valence bond structures (Fig. 2), and from the LCAO π-bond orders (*Dictionary of Values of Molecular Constants*, 1955). The correlation curve of Cruickshank & Sparks (1960) was used for the valence bond method, and for the molecular orbital method a linear correlation between (0·40, 1·46 Å) and (0·85, 1·34 Å) (Cruickshank & Sparks, 1960). The general variation of the measured distances is well reproduced in both sets of calculated values, but some of the individual agreements are not particularly good. Bond *f* is the shortest in the molecule, but the measured distance (1·320 ± 0·014 Å) is shorter than either of the calculated distances, and apparently shorter than the C=C distance in ethylene (1·337 ± 0·003 Å, Allen & Plyler, 1958). This is similar to the situation in *p*-benzoquinone (Trotter, 1960), where a similar bond has length 1·322 ± 0·008 Å, and suggests that the value in ethylene is perhaps not the normal double distance in this type of molecule (Cruickshank, 1962). Bond *a* is the next shortest bond in the molecule (measured length 1·376 Å) and bond *d* the longest bond (measured 1·437 Å), with bonds *b*, *c* and *e* of intermediate length. These features are reasonably well reproduced in the calculated distances, with the molecular orbital method giving somewhat better individual agreement, particularly for bonds *a* and *b*.

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References

Allen, H. C. & Plyler, E. K. (1958). *J. Amer. Chem. Soc.* **80**, 2673.

Camerman, A. & Trotter, J. (1964). *Proc. Roy. Soc.* A, **279**, 129.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1956*a*). *Acta Cryst.* **9**, 747.

Cruickshank, D. W. J. (1956*b*). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1956*c*). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. (1956*d*). *Acta Cryst.* **9**, 915.

Table 8. *Mean measured and calculated bond lengths* (Å) *in pyrene*

	Measured					
	l_m				Calculated	
Bond (Fig. 1*b*)	Uncorrected	Corrected for rotational oscillation	σ_m	σ_m'	V.B.	M.O.
a	1·376	1·380	0·011	0·012	1·397	1·388
b	1·416	1·420	0·009	0·003	1·397	1·408
c	1·411	1·417	0·007	0·012	1·421	1·427
d	1·437	1·442	0·009	0·012	1·448	1·433
e	1·411	1·417	0·014	—	1·421	1·424
f	1·315	1·320	0·014	—	1·355	1·360

CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. p. 41. Oxford: Pergamon Press.

CRUICKSHANK, D. W. J. (1962). *Tetrahedron*, **17**, 155.

CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc.* A, **258**, 270.

Dictionary of Values of Molecular Constants (1955). Vol. II. Centre National de la Recherche Scientifique, and I. C. I. Ltd.

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

ROBERTSON, J. M. & WHITE, J. G. (1947). *J. Chem. Soc.* p. 358.

ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.

SPARKS, R. A. (1958). *Ph. D. Thesis*, University of California, Los Angeles.

TROTTER, J. (1960). *Acta Cryst.* **13**, 86.

Acta Cryst. (1965). **18**, 643

The Crystal Structure of PNb_9O_{25}, ($P_2O_5 . 9Nb_2O_5$)

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PNb_9O_{25} crystallizes in the tetragonal system, with the lattice parameters $a = 15{\cdot}60$, $c = 3{\cdot}828$ Å and the space group $I\bar{4}$ or possibly $I4/m$. The structure, predicted from crystallochemical principles and refined by Fourier and least-squares methods, contains blocks of the ReO_3-type structure, three octahedra wide, three long and infinite in the third dimension. These blocks are joined to similar blocks at different levels along c by having octahedral edges in common, and the tetrahedral positions at the junctions are occupied in part by the phosphorus atoms, which may or may not be ordered.

Introduction

There has been a good deal of recent attention given to the compounds made by reacting niobium pentoxide with the oxides of uni-, di-, tri-, and quadrivalent elements at high temperatures. In most cases the ionic radii of these elements are equal to or greater than that of Nb^{5+} itself, and the wide variety of compounds that are formed fall into a number of different structural types which have been of independent interest to us for some little time.

Waring & Roth (1964) recently showed that both Nb_2O_5 and Ta_2O_5 form a number of isostructural compounds ANb_9O_{25} and ATa_9O_{25}, where A is one or another of the small pentavalent ions As, V, and P. The presence of isolated tetrahedrally coordinated Nb atoms in the crystal structure of the high temperature form of Nb_2O_5 (Gatehouse & Wadsley, 1964) has prompted us to examine PNb_9O_{25}, a representative member of this new group, where phosphorus might be expected to adopt positions of a similar kind in a structure related to Nb_2O_5 in some close way.

Experimental

The original specimen of PNb_9O_{25}, made in the United States by Waring & Roth (1964), was fine-grained and no single crystal could be isolated from it. A microchemical analysis of this material, kindly made by E. S. Pilkington and P. R. Smith, C.S.I.R.O. Division of Mineral Chemistry, proved that combined phosphorus is present in the correct order of magnitude. The exact composition can be inferred from the isostructural relationship with the As and V compounds, as both of these can be prepared by standard ceramic techniques as single phases with the exact formulae ANb_9O_{25}.

At the University of Stockholm low temperature Nb_2O_5 was treated with an excess of phosphoric acid in a gold capsule under hydrothermal conditions at 750 °C and 20,000 p.s.i. A number of fine needles, present in a matrix of another phase, proved to be single crystals of PNb_9O_{25} and were used for the structure determination, undertaken cooperatively in Stockholm and in Melbourne.

The crystal data are summarized in Table 1, the unit-cell dimensions being derived from a powder diffractometer pattern. Zero, first and second level

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