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The Crystal and Molecular Structure of Phenanthrene

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Crystals of phenanthrene are monoclinic with two molecules in a unit cell of dimensions $a = 8{\cdot}46$, $b = 6{\cdot}16$, $c = 9{\cdot}47$ Å, $\beta = 97{\cdot}7°$, space group $P2_1$. The positional parameters of a previous two-dimensional investigation have been refined using three-dimensional data, and least-squares and Fourier methods. Apart from small deviations from complete planarity, the molecule does not deviate significantly from C_{2v} symmetry, and the general variation of bond distances is similar to that predicted by quantum mechanical methods; there are however two bonds for which the measured and calculated values appear to differ significantly. All the intermolecular contacts correspond to normal van der Waals interactions.

A previous two-dimensional analysis of the crystal structure of phenanthrene (Basak, 1950) was not sufficiently precise to measure the bond distances accurately. The present paper describes a more detailed analysis based on three-dimensional data.

Experimental

Crystal data (λ, Cu $K\alpha = 1{\cdot}542$ Å)

Phenanthrene, $C_{14}H_{10}$; $M = 178{\cdot}2$; m.p. = 101 °C.
Monoclinic, $a = 8{\cdot}46$, $b = 6{\cdot}16$, $c = 9{\cdot}47$ Å; $\beta = 97{\cdot}7°$.
$U = 489$ Å^3. D_c (with $Z = 2$) = 1·203.
Absorption coefficient for X-rays, $\mu = 6{\cdot}4$ cm^{-1}.
$F(000) = 188$.
Absent reflexions: $0k0$ when k is odd; space group $P2_1$($P2_1/m$ being excluded from packing considerations (Basak, 1950)).

The intensities of the hkl reflexions were recorded on Weissenberg films of the $h0l$...$h5l$ zones, estimated visually, and the structure amplitudes derived. The various layers were brought to approximately the same scale by comparison with Basak's (1950) structure factors and to an approximately absolute scale by Wilson's (1942) method. The scale of each layer was refined individually in the least-squares cycles. 560 reflexions were observed, about one-half of those within the Cu $K\alpha$ sphere.

Structure refinement

Initial positional parameters for the carbon atoms were derived from those given by Basak (1950), and for the hydrogen atoms by assuming C–H bond distances of 1·08 Å, and structure factors were calculated using the scattering factor for carbon of Berghuis *et al.* (1955) and McWeeny's (1951) curve for hydrogen, each corrected for thermal vibration with $B = 4{\cdot}5$ Å^2 for all atoms. The R-factor ($\Sigma||F_o|-|F_c||/\Sigma|F_o|$) was 0·550, but the scale factor was in error by a factor of about two, so that the agreement was much better than the value of R suggested.

Refinement of the positional and isotropic temperature parameters of the carbon atoms then proceeded by successive cycles of full-matrix least squares, minimizing $\Sigma w(|F_o|-|F_c|)^2$ using Busing & Levy's (1959) IBM 704 program, simulated on the IBM 709. The weighting scheme of Hughes (1941) was used, and unobserved reflexions were included in the refinement as long as F_c was greater than the threshold value of F_o. The origin was chosen by fixing (*i.e.* not refining) the y-coordinate of atom C1. Three cycles of refinement reduced R, for the observed reflexions, to 0·154 (Table 1), but the y-coordinate shifts in the final cycle were still appreciable. Examination of the parameter changes in the second and third cycles suggested that application of 1·6 times the y-shifts would give convergence. Recalculation of structure factors with these coordinates, and with revised hydrogen positions, showed that R had been reduced to 0·140.

Table 1. *Progress of the refinement*

Parameters from	R	$\Sigma w.\Delta F^2$
Basak (1950) + estimated H positions	(0·550)	(24·300)
First L.S. cycle	0·220	1·050
Second L.S. cycle	0·159	563
Third L.S. cycle	0·154	533
Third L.S. + 1·6 y-shifts + new H positions	0·140	—
($F_o - F_c$) synthesis	0·137	—

Further refinement by least-squares methods required introduction of anisotropic thermal parameters and since 709 computer time was not available for this further work, refinement was completed by an ($F_o - F_c$) synthesis, calculated on the IBM 1620 computer. This synthesis suggested only small shifts in the carbon atom positional parameters, which reduced R to 0·137 (Table 1). Structure factors are listed in Table 4.

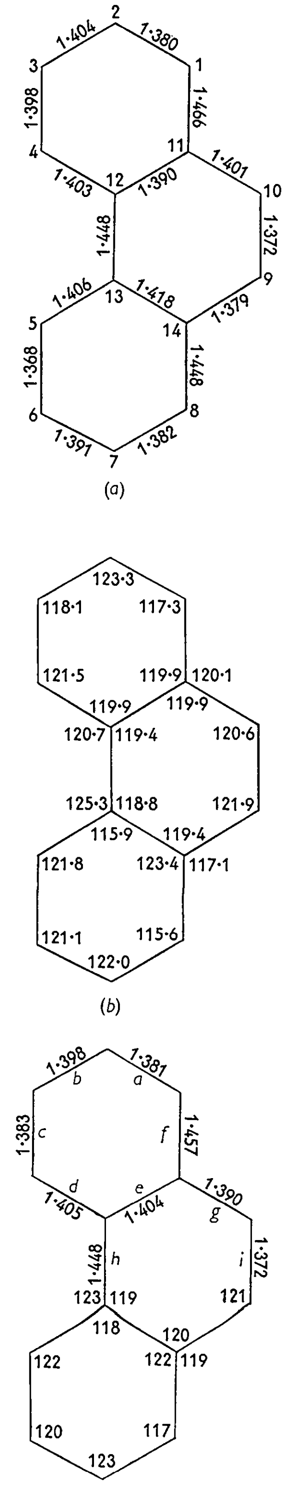

Fig. 1. (*a*) Measured bond lengths (Å). (*b*) Measured valency angles (degrees). (*c*) Mean bond lengths and valency angles.

Coordinates and molecular dimensions

The final positional and thermal parameters of the carbon atoms are listed in Table 2, x, y, z being fractional coordinates referred to the crystallographic axes. The standard deviations of the positional parameters were calculated from the diagonal elements of the inverse matrix in the third least-squares cycle. The mean values are $\sigma(x)=\sigma(y)=\sigma(z)=0{\cdot}014$ Å. The thermal parameters (mean $\sigma=0{\cdot}35$ Å^2) indicate that as usual in a molecule of this type, the atoms at the periphery are executing rather larger thermal vibrations than those nearer the centre.

The best plane through all the atoms has equation:

$$0{\cdot}8217X'-0{\cdot}4879Y-0{\cdot}2947Z'-0{\cdot}8785=0$$

where X', Y', Z' are coordinates in Å referred to orthogonal axes a', b and c. The displacements of the atoms from this plane (Δ_1 in Table 2), although quite small, appear to be significant since $\chi^2=27$, and are probably the result of slight intramolecular overcrowding involving the hydrogen atoms bonded to C4 and C5. This is supported by an examination of the deviations (Δ_2 in Table 2) of the atoms from the plane of the central ring, C9–C14; these indicate that the other two rings are displaced in opposite directions from this plane.

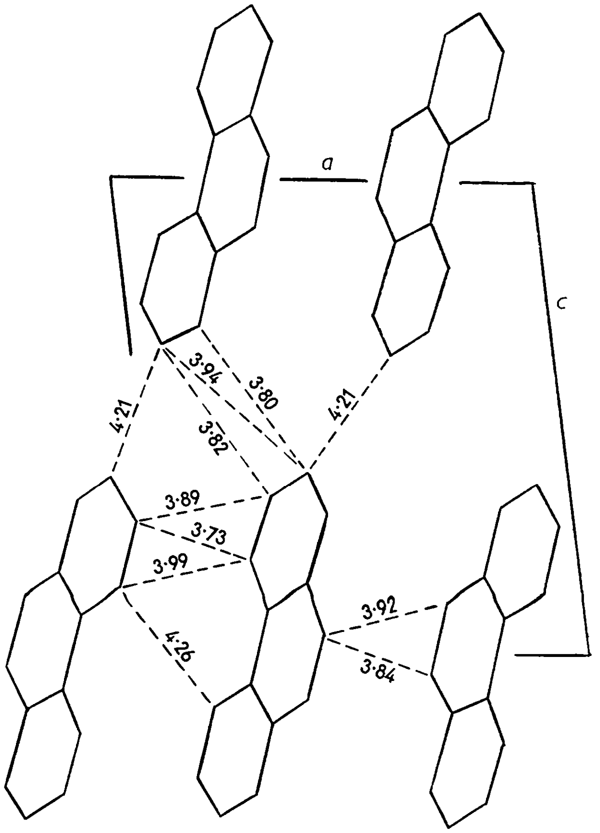

Fig. 2. Projection of the structure along the *b*-axis showing the shorter intermolecular contacts.

Table 2. *Final positional and thermal parameters, and deviations from the mean molecular plane* (Δ_1) *and from the plane of the central ring* (Δ_2)

Atom	x	y	z	B (Å^2)	Δ_1 (Å)	Δ_2 (Å)
C1	0·1665	0·3873	−0·3081	6·3	+0·020	−0·011
2	0·0747	0·2098	−0·3549	6·3	+0·021	−0·015
3	0·0354	0·0440	−0·2641	6·1	−0·018	−0·042
4	0·0954	0·0580	−0·1194	5·0	−0·030	−0·037
5	0·2292	0·0861	0·1872	5·4	−0·004	+0·028
6	0·2967	0·1046	0·3262	6·4	+0·040	+0·089
7	0·3858	0·2864	0·3737	5·9	+0·004	+0·058
8	0·4179	0·4505	0·2823	5·6	−0·002	+0·041
9	0·3786	0·5849	0·0410	5·6	−0·016	−0·005
10	0·3228	0·5724	−0·1017	5·2	+0·016	+0·010
11	0·2278	0·3973	−0·1559	4·6	+0·008	−0·004
12	0·1919	0·2321	−0·0653	4·1	−0·008	−0·008
13	0·2544	0·2427	0·0845	4·1	−0·006	+0·012
14	0·3467	0·4255	0·1355	5·0	−0·031	−0·007

The bond lengths and valency angles in the molecule, calculated from the coordinates of Table 2, are shown in Fig. 1(*a*) and (*b*). The molecular symmetry does not appear to deviate from C_{2v} (apart from the small displacements from exact planarity noted above), since comparison of chemically equivalent bonds shows that (on seven degrees of freedom) $\chi^2 = 6{\cdot}7$. The mean distances and angles are shown in Fig. 1(*c*).

All the intermolecular approaches correspond to van der Waals interactions. The shortest distances between molecules related by translation b are 3·55 and 3·68 Å; the shorter lateral contacts are shown in Fig. 2.

Discussion

As noted above there are small distortions from complete planarity, probably a result of intramolecular overcrowding, but otherwise the phenanthrene molecule has *mm*2 symmetry.

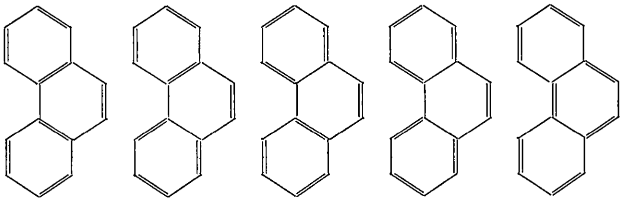

Fig. 3. Kekulé structures for phenanthrene.

Calculations of the bond lengths for comparison with the measured distances were made from the five non-excited valence bond structures (Fig. 3) and from the LCAO bond-orders (*Dictionary of Values of Molecular Constants*, 1955), and the usual correlation curves. The measured and calculated distances are compared in Table 3. The general variation of the measured distances is well reproduced in both sets of calculated values, and except for two bonds, f and g in Fig. 1(*c*), the individual agreements are also very good. Bond i (9–10) has the shortest measured length in the molecule, and this is in accord with the calculated values and with the chemical properties. Bond f is significantly longer and bond g shorter than the corresponding calculated values, suggesting that the real molecule is not adequately described by the Kekulé structures or by the LCAO approximation. Bond f has apparently less, and bond g more, aromatic character than is suggested by the theoretical calculations.

Table 3. *Means of measured, and calculated bond distances* (Å)

Bond	Means of measured (with e.s.d.)	Valence-bond		Molecular-orbital	
		Calc.	Δ	Calc.	Δ
a	1·381 ± 0·014	1·378	0·003	1·390	0·009
b	1·398 ± 0·014	1·409	0·011	1·405	0·007
c	1·383 ± 0·014	1·378	0·005	1·391	0·008
d	1·405 ± 0·014	1·409	0·004	1·411	0·006
e	1·404 ± 0·014	1·409	0·005	1·419	0·015
f	1·457 ± 0·014	1·409	0·048	1·413	0·044
g	1·390 ± 0·014	1·450	0·060	1·426	0·036
h	1·448 ± 0·020	1·450	0·002	1·434	0·014
i	1·372 ± 0·020	1·355	0·017	1·378	0·006

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Table 4. *Measured and calculated structure factors*

Columns, from left to right, are h, l, $10|F_o|$, $10|F_c|$
Unobserved reflexions, for which F_o is listed as zero, have threshold values in the range 1·0 to 2·8

		k=0	
0	1	332	367
	2	199	195
	3	130	111
	4	255	232
	5	180	174
	6	26	6
	7	0	6
	8	0	5
	9	16	20
1	-8	12	0
	-7	0	12
	-6	33	45
	-5	32	12
	-4	23	18
	-3	34	47
	-2	159	176
	-1	14	20
	0	17	18
	1	89	93
	2	16	13
	3	0	9
	4	38	27
	5	9	18
	6	41	45
	7	12	22
	8	0	2
	9	12	13
2	-9	24	27
	-8	34	25
	-7	12	14
	-6	17	16
	-5	46	53
	-4	33	39
	-3	0	7
	-2	56	51
	-1	710	715
	0	260	273
	1	175	181
	2	111	116
	3	228	203
	4	266	272
	5	10	5
	6	34	28
	7	16	36
	8	65	72
	9	20	27
3	-9	38	37
	-8	113	105
	-7	16	26
	-6	0	9
	-5	16	14
	-4	44	39
	-3	10	17
	-2	10	7
	-1	35	45
	0	105	126
	1	51	59
	2	0	17
	3	20	17
	4	31	33
	5	31	37
	6	0	16
4	-9	23	18
	-8	24	25
	-7	23	35
	-6	0	0
	-5	0	2
	-4	55	61
	-3	51	55
	-2	44	48
	-1	33	40
	0	39	37
	1	50	57
	2	35	40
	3	77	79
	4	0	12
	5	0	17
	6	0	9
	7	38	43
	8	28	32
5	-9	104	99
	-8	50	55
	-7	0	5
	-6	0	12
	-5	74	77
	-4	110	110
	-3	14	16
	-2	0	0
	-1	10	15
	0	71	68
5	1	19	16
	2	17	21
	3	18	17
	4	12	13
	5	0	0
6	-5	31	30
	-4	0	9
	-3	35	36
	-2	28	34
	-1	0	16
	0	41	42
6	1	0	15
	2	0	4
	3	12	13
	4	34	31
	5	0	1
7	-9	23	24
	-8	0	0
	-7	12	11
	-6	31	34
	-5	70	69
	-4	12	9
	-3	16	16
	-2	16	20
	-1	97	90
	0	56	50
	1	0	1
	2	0	8
	3	40	48
	4	73	69
	5	15	19
8	-3	0	9
	-2	12	15
	-1	20	25
	0	0	3
	1	0	0
	2	0	5
	3	34	36
	4	11	15
	5	14	20
9	-2	31	29
	-1	29	30
9	0	0	4
	1	0	9
	2	32	32
	3	63	65
	4	21	20
		k=1	
0	1	68	39
	2	21	15
	3	18	5
	4	105	100
	5	97	99
	6	27	25
	7	69	62
	8	35	33
	9	50	43
1	-9	16	15
	-8	53	55
	-7	83	92
	-6	0	10
	-5	152	124
	-4	73	74
	-3	116	106
	-2	171	166
	-1	290	320
	0	495	521
	1	250	215
	2	69	70
	3	21	17
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	5	47	48
	6	26	24
	7	15	11
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	9	24	23
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	-8	91	75
	-7	44	46
	-6	66	73
	-5	87	90
	-4	34	33
	-3	116	120
	-2	69	72
	-1	579	619
	0	313	343
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	2	19	20
	3	22	25
	4	73	69
	5	14	20
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	8	21	21
	9	23	7
3	-9	20	34
	-8	86	90
	-7	24	35
	-6	36	35
	-5	41	53
	-4	133	124
	-3	124	128
	-2	92	93
	-1	333	352
	0	44	55
	1	78	78
	2	13	14
	3	140	122
	4	56	49
	5	18	16
	6	0	7
	7	0	8
3	8	24	30
4	-9	45	45
	-8	52	47
	-7	0	9
	-6	19	13
	-5	20	25
	-4	31	92
	-3	17	29
	-2	187	192
	-1	173	174
	0	99	110
	1	61	55
	2	14	17
	3	124	127
	4	18	26
	5	81	65
	6	21	23
	7	26	33
5	-9	14	13
	-8	0	6
	-7	0	5
	-6	18	17
	-5	39	43
	-4	54	58
	-3	0	7
	-2	92	87
	-1	59	63
	0	120	120
	1	34	37
	2	60	58
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	5	68	57
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	-6	0	4
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	1	10	3
	2	13	20
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	2	171	184
	3	124	95
	4	56	52
0	5	35	34
	6	23	36
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	4	40	41
	5	33	50
	6	127	125
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	4	41	41
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	3	45	8
	4	16	19
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	6	116	112
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	-1	28	39
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	2	14	19
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	-4	19	11
6	-3	120	121
	-2	112	112
	-1	14	13
	0	0	15
	1	14	15
	2	35	36
	3	17	18
	4	0	9
	5	16	8
7	-4	35	33
	-3	32	38
	-2	30	29
	-1	14	16
	0	0	5
	1	14	21
8	-4	43	50
	-3	59	56
	-2	14	13
	-1	0	5
	0	0	10
	1	37	39
	2	20	21
9	-3	19	15
		k=4	
0	1	19	22
	2	54	43
	3	14	26
	4	13	3
	5	0	14
	6	63	57
	7	42	35
	8	14	9
1	-8	14	17
	-7	82	75
	-6	43	46
	-5	24	32
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