$$V = \left[1 + \frac{\frac{1-c}{c}\left(1+\frac{c'}{1-c'}\right)\frac{\delta_a}{\delta_e}}{1+\frac{c'}{1-c'}\frac{\delta_a}{\delta_e}} \right]^{-1}$$

Le modèle de structure fournit la relation:

$$V = \frac{1}{a^3}\cdot\frac{4\pi R^3}{3}\cdot 4$$

d'où:

$$R = a\left[\frac{16\pi}{3} \frac{\frac{1-c}{c}\left(1+\frac{c'}{1-c'}\right)\frac{\delta_a}{\delta_e}}{1+\frac{c'}{1-c'}\frac{\delta_a}{\delta_e}} \right]^{-\frac{1}{3}} .$$

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The Crystal Structure of Pyracene*

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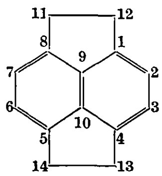
The crystal structure of pyracene has been determined by two-dimensional X-ray diffraction methods. The monoclinic cell has

$$a_0 = 12{\cdot}56,\ b_0 = 5{\cdot}03,\ c_0 = 7{\cdot}32\ \text{Å};\ \beta = 96°\ 14',$$

and contains 2 molecules. The space group is $P2_1/n$. The strain in the *peri*-ring is almost entirely taken up in distortion of bond angles, both in the peri-ring and in the naphthalene rings. The aliphatic C–C bond has a length of 1·59 Å with a standard deviation of 0·03 Å.

Introduction



Pyracene, which was first synthesized by Anderson & Wade (1952), affords an example in which to compare the relative resistance of bond lengths and bond angles to distortion. Accordingly, we have determined its crystal structure by 2-dimensional X-ray diffraction methods.

Experimental

The sample of pyracene was obtained from Dr A. G. Anderson and suitable single crystals were grown by slowly cooling a hot saturated solution in benzene. The crystals were monoclinic needles, elongated in the [010] direction.

Cell dimensions and space group were determined from rotation, equi-inclination Weissenberg, and precession photographs using Cu $K\alpha$ radiation (λ = 1·5418 Å). The rotation pattern of a sodium chloride

Table 1. *Atomic coordinates and individual temperature factor parameters of pyracene*

Atom	x/a	y/b	z/c	B
C_1	0·1228	0·1970	−0·0280	2·70
C_2	0·1443	0·0960	−0·1960	3·00
C_3	0·0761	−0·1020	−0·2900	2·95
C_8	0·0112	0·1970	0·2174	3·00
C_9	0·0321	0·0908	0·0450	2·72
C_{11}	0·0980	0·4078	0·2705	3·20
C_{12}	0·1722	0·4093	0·1073	3·02
H_1	0·0948	−0·1762	−0·4206	2·95
H_2	0·2130	0·1666	−0·2572	3·00
H_3	0·0620	0·5998	0·2837	3·20
H_4	0·1440	0·3554	0·3980	3·20
H_5	0·1709	0·6012	0·0425	3·02
H_6	0·2533	0·3582	0·1573	3·02

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Table 2. *Observed and calculated structure factors for pyracene*

*h*0*l*	F_o	F_c
2,0	298	384
4,0	267	−281
6,0	89	92
8,0	80	73
10,0	<28	14
12,0	<30	33
14,0	<27	−6
1,1	313	402
−1,1	329	431
3,1	113	−106
−3,1	161	−163
5,1	<17	36
−5,1	198	192
7,1	89	85
−7,1	227	218
9,1	<25	−12
−9,1	<24	−8
11,1	111	−112
−11,1	<27	41
13,1	141	−136
−13,1	47	50
15,1	<16	−4
−15,1	33	−34
0,2	292	−284
2,2	173	−168
−2,2	81	−90
4,2	<17	−4
−4,2	51	43
6,2	91	−84
−6,2	268	268
8,2	51	−41
−8,2	48	55
10,2	<27	3
−10,2	103	−114
12,2	134	−129
−12,2	56	−60
14,2	95	−90
−14,2	32	−34
1,3	<16	8
−1,3	258	250
3,3	90	91
−3,3	<17	4
5,3	126	−119
−5,3	191	−182
7,3	224	−225
−7,3	40	54
9,3	<27	20
−9,3	44	43
11,3	56	58
−11,3	77	−93
13,3	41	−32
−13,3	56	−56
−15,3	<16	−3
0,4	233	227
2,4	108	104
−2,4	254	254
4,4	26	25
−4,4	85	−96
6,4	79	−72
−6,4	62	−65
8,4	<27	−1
−8,4	151	165
10,4	39	29
−10,4	59	61
12,4	<21	−19
−12,4	<25	−20
−14,4	27	31
1,5	41	34
−1,5	<23	9
3,5	<25	−12
−3,5	68	72
5,5	27	−24
−5,5	111	112
7,5	70	72
−7,5	189	191
9,5	40	29
−9,5	90	91
11,5	82	−81
−11,5	41	−36
−13,5	<19	31
0,6	45	−46
2,6	41	48
−2,6	85	−96
4,6	108	−111
−4,6	83	87
6,6	108	−109
−6,6	122	125
8,6	<24	12
−8,6	40	43
10,6	37	−26
−10,6	32	−26
−12,6	26	−18
1,7	68	77
−1,7	71	−79
3,7	<26	7
−3,7	68	−75
5,7	154	−150
−5,7	<27	−1
7,7	92	−89
−7,7	44	−40
9,7	<14	−8
−9,7	<22	8
−11,7	43	36
0,8	<24	−21
2,8	<22	3
−2,8	46	−52
4,8	<19	−17
−4,8	<23	1
6,8	<15	−12
−6,8	<21	1
−8,8	<17	−5
1,9	25	−24
−1,9	<16	−8
−3,9	<16	4
−5,9	50	59
*hk*0		
1,1	264	271
2,1	396	−407
3,1	213	211
4,1	61	68
5,1	<23	8
6,1	73	76
7,1	44	51
8,1	110	−107
9,1	<30	7
10,1	108	−110
11,1	72	−82
12,1	49	−53
13,1	<33	15
14,1	<32	−9
15,1	40	36
0,2	<24	23
1,2	51	49
2,2	48	−43
3,2	<25	26
4,2	52	−51
5,2	<27	27
6,2	29	−28
7,2	78	−72
8,2	94	−94
9,2	177	−188
10,2	34	−37
11,2	80	−75
12,2	35	22
13,2	45	45
14,2	<30	−15
15,2	<22	−7
1,3	147	−141
2,3	100	−115
3,3	31	−26
4,3	67	69
5,3	<30	—
6,3	<31	3
7,3	53	−49
8,3	80	−78
9,3	38	−46
10,3	<33	−9
11,3	<33	7
12,3	<32	−24
13,3	<29	−3
14,3	31	−25
0,4	177	−161
1,4	72	64
2,4	<32	−21
3,4	59	56
4,4	51	50
5,4	34	−20
6,4	<33	8
7,4	42	−40
8,4	34	31
9,4	34	−39
10,4	<31	17
11,4	<29	14
12,4	<24	−21
1,5	<33	17
2,5	<33	−19
3,5	<33	−33
4,5	<32	−4
5,5	<32	5
6,5	<31	−5
7,5	33	30
8,5	<29	−6
9,5	55	46
10,5	<16	4
0,6	104	−76
1,6	39	−22
2,6	29	−12
3,6	<26	−29
4,6	26	25
5,6	<22	−2

crystal ($a_0 = 5{\cdot}6387$ Å) was superimposed for calibration on the films used for measurement of cell dimensions, giving

$$a_0 = 12{\cdot}56 \pm 0{\cdot}02,\quad b_0 = 5{\cdot}03 \pm 0{\cdot}02,\quad c_0 = 7{\cdot}32 \pm 0{\cdot}01\ \text{Å};$$
$$\beta = 96°\ 14' \pm 5'.$$

The cell contains two molecules.

$$\text{Density (calc.)} = 1{\cdot}30\ \text{g.cm.}^{-3},$$
$$\text{density by flotation} = 1{\cdot}29\ \text{g.cm.}^{-3}.$$

Systematic absences were observed in (*h*0*l*) for $h+l$ odd and in (0*k*0) for k odd, indicating the space group $P2_1/n$.

Relative intensities were obtained from multiple film photographs using copper radiation filtered through nickel in a Nonius Integrating Weissenberg camera for (*h*0*l*) data and molybdenum radiation filtered through zirconium in an integrating precession camera for (*hk*0) data. In both cases the camera integration was carried out in one direction only. Each diffraction spot within the linear response range of the film was then scanned in the other direction using a Moll type microphotometer and a Leeds and Northrup amplifier and recorder with a logarithmic slide wire. The areas under the tracings were used directly as relative intensities. Lorentz and polarization factors were applied and the resulting observed structure factors were placed on an absolute scale by comparison with calculated structure factors at a later stage in the determination of the structure. Since the crystal used had dimensions of 0·1 × 0·1 × 5 mm., absorption was neglected.

Determination of structure

The Patterson projection $P(x, z)$ was interpreted by comparison with a molecular model. Two Fourier projections followed by three difference syntheses reduced R to 0·15. Structure factors were calculated using McWeeny (1951) scattering factors. At this point the x and z coordinates were used in conjunction with a planar molecular model to calculate approximate y coordinates and the projection along [001] was refined by difference syntheses to $R=0{\cdot}15$. Hydrogen atom coordinates were calculated using a C–H distance of 1·075 Å and the two projections, along [010] and along [001], were refined together by difference syntheses, using individual atomic isotropic temperature factors. Comparison of observed and calculated structure factors during the later stages of the refinement of the structure indicated that the reflections (101) and ($\bar{1}01$) were appreciably affected by secondary extinction. They were therefore omitted from difference Fourier and reliability index calculations and were replaced by the calculated values in Fourier syntheses. No further correction was made for secondary extinction. The final values of the reliability index are $R_{h0l}=0{\cdot}060$ and $R_{hk0}=0{\cdot}077$.

The final values of the atomic coordinates and temperature factors are given in Table 1 and observed and calculated structure factors are given in Table 2.

Discussion

The packing of the molecules of pyracene is similar to that found for naphthalene (Cruickshank, 1957) and many other planar molecules.

Bond distances and angles in the pyracene molecule are given in Table 3. The standard deviation of the bond lengths is 0·03 Å, except for C_9–C_{10}, for which it is 0·05 Å, and that of the angles is 1·0°, calculated by the method of Cruickshank (1949).

None of the carbon atoms of the molecule deviates by more than 0·02 Å from a least-squares plane through the entire molecule, therefore, although the aliphatic bridge atoms lie out of the least-squares plane through the central 'naphthalene' portion of the molecule by 0·05 Å, this apparent deviation from planarity is of doubtful significance.

Table 3. *Bond lengths and angles in pyracene*

1–2	1·38 Å	9–1–2	116°
2–3	1·44	1–2–3	121
3–4	1·36	2–3–4	121
4–10	1·42	3–4–10	117
1–9	1·41	4–10–9	122
1–12	1·54	1–9–10	123
8–11	1·54	1–9–8	115
11–12	1·59	9–1–12	108
9–10	1·34	1–12–11	105
		8–11–12	106
		9–8–11	107

The aliphatic C_{11}–C_{12} bond in the *peri*-ring has a length of 1·59 Å, which is less than two standard deviations longer than the normal length of 1·54 Å and should not, therefore, be considered to be significantly lengthened, although the length of 1·64 ± 0·04 Å reported by Kitaigorodskii (1949) for the corresponding bond length in acenaphthene suggests that there is some stretching of this bond. Thus, the strain in the *peri*-ring is almost entirely in the angles C_9–C_8–C_{11}, etc., which are significantly reduced from the 'normal' 120° to 107° or 108°. Further influence of the strain is shown by the significant reduction of the angles C_1–C_9–C_8, C_2–C_1–C_9, etc.

The apparent shortening of the central C_9–C_{10} bond from 1·41 Å in naphthalene to 1·34 Å is probably not significant (less than two standard deviations), and all other bond lengths are equal to those in naphthalene within one standard deviation.

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