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A Refinement of the Crystal and Molecular Structure of Acenaphthene

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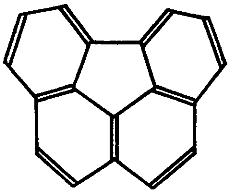
The refinement of the crystal and molecular structure of acenaphthene was undertaken with a view to determining the effects of 'mechanical' strain in an aromatic molecule. Geiger-counter intensity measurements were made of one zone of reflexions, while photographic data were used for the refinement of the other two projections. The results show that bond lengths remain practically unaltered, so that even the bonds in the naphthalene nucleus are not significantly different from those in naphthalene itself. The analysis of the packing of the molecules shows that minimum approach distances can also be considered as constant if the hydrogen atoms are not omitted from the examination of the intermolecular contacts.

Introduction

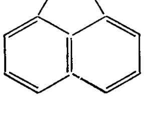
Hydrocarbon molecules in which five-membered rings are fused to six-membered aromatic rings must either be non-planar, have unusual bond lengths, have bond angles differing from 120°, or have some combination of these three features.

A molecule in which any of these distortions might occur, is 2:13-benzfluoranthene,



which has recently been investigated (Ehrlich & Beevers, 1956). The analysis revealed a planar molecule, with large deviations from 120° in the bond angles. The longest bond is that one of the five membered ring which is on the open side of the molecule; its length is 1·49 Å. In none of the Kekulé structures for this molecule, however, can this linkage ever be a double bond, and its length compares favourably with those of other 'aromatic single' bonds. Examples of these are found in perylene (1·50 Å) (Donaldson & Robertson, 1953), indanthrone (1·48, 1·49, 1·50, 1·50 Å) (Bailey, 1955), and in molecules where two aromatic systems are joined by a (chemically) single bond, e.g. diphenyl (1·48 Å) (Dhar, 1932), *p*-diphenyl benzene (1·48 Å) (Pickett, 1933) and 2:2'-bipyridine (1·50 Å) (Merritt & Schroeder, 1956). There is therefore no evidence for any bond lengthening in the 2:13-benzfluoranthene molecule.

In acenaphthene,



the single bond is under less strain than the equivalent one in 2:13-benzfluoranthene, but in all its determinations it has been reported as being significantly longer than a normal single bond (2·01 Å by Bannerjee & Sinha, 1937; 1·80 Å by Kitaigorodskii, 1947; and 1·64 Å by Kitaigorodskii, 1949). This, therefore, led to the present re-examination.

Summary of previous work

The first published structure determination of acenaphthene was by Bannerjee & Sinha, whose analysis was the result of X-ray diffraction and magnetic measurements. Kitaigorodskii showed that this structure was wrong, and solved it himself on one projection only. Then, by means of the one-dimensional $F(0k0)$'s, he determined the aliphatic bond length, since this is dependent only on the y coordinate of one atom. Using accurate experimental data, obtained by means of an ionization chamber, he confirmed his results by carrying out comparisons between two-dimensional F_o and F_c syntheses. Because of the use of the ionization chamber, he was not able to measure all the reflexions inside the limiting circle for Cu $K\alpha$ radiation, thus reducing the resolving power of the analysis.

Crystal data

Acenaphthene, $C_{12}H_{10}$, (m.p. 95° C.), is orthorhombic with absent spectra $0kl$ when l is odd. The space group (as determined by Kitaigorodskii) is $Pcm2_1$–C_{2v}^2 with $Z = 4$. This space group has no centre of symmetry, but the (001) projection is centro-symmetric. Kitaigorodskii rejected the other two possible space groups, *Pcmm* and *Pc2m*, on the grounds that these are forbidden to hydrocarbons (Kitaigorodskii, 1948).

The cell dimensions at 15° C. are

$$a = 8{\cdot}290 \pm 0{\cdot}004,\; b = 14{\cdot}000 \pm 0{\cdot}007,\; c = 7{\cdot}225 \pm 0{\cdot}004\ \text{Å}\,.$$

The calculated and observed densities are 1·22 g.cm.$^{-3}$ and 1·19 g.cm.$^{-3}$ respectively.

The $0k0$ reflexions also appear to be systematically absent when k is odd, but long-exposure (6 hr.) photographs of large crystals (1·3 mm. diameter) show a weak 0,15,0 reflexion.

A spot of a different shape from the others was observed at the point where the 220 reflexion is expected, and this is thought to be due to double reflexion off the planes (300) and $(\bar{1}20)$.

Acenaphthene grows in long flat needles from most solvents, but square prismatic specimens can be obtained by allowing a solution in a mixture of ethyl acetate and carbon tetrachloride to evaporate slowly. The flat crystals have a predominant (010) face, the needle axis being parallel to the crystallographic c axis.

Experimental

The $h0l$ and $0kl$ intensities were obtained from Weissenberg photographs, using filtered Cu $K\alpha$ radiation. The multiple-film technique was used, and the intensities were estimated by visual comparison against a calibrated scale.

The $hk0$ intensities were measured both photographically and by means of a Geiger counter. In the Geiger-counter experiment, the integrated intensity was obtained by oscillating the crystal through the reflecting position, and counting the total number of pulses, but the dead-time corrections applied differed from those suggested by Cochran (1950). Cochran found that the integrated intensity of a reflexion could be obtained from the total number of counts, by using a different dead time for the counter. The dead time increases by a factor K, and K was found to be constant for all reflexions.

Unfortunately, acenaphthene exhibits diffuse scattering of X-rays, and the background is therefore considerable. For a very weak reflexion, therefore, K must be very nearly equal to unity, and for large reflexions K was found to be about 3. An empirical curve relating K to the ratio

$$\frac{\text{total number of counts for the sweep}}{\text{background at either extreme of oscillation}}$$

was obtained, K being determined from the profile of several reflexions of various sizes. The average background was subtracted from the integrated intensity to give the intensity of the reflexion itself.

To correct for fluctuations in the performance of the X-ray tube, and for sublimation of the crystal, all readings were related to measurements of one reflexion, which was taken as a standard.

Intensities of very weak reflexions are not very accurately measured by this method, and those values obtained photographically were preferred. Also for reflexions with $\sin\theta > 0{\cdot}845$, no Geiger-counter measurements were available because of the construction of the spectrometer. For these reflexions, 'photographic' intensities were also used. Since only weak reflexions were estimated photographically, the absolute error in F_o is not very large.

Determination of the z parameters

The structure proposed by Kitaigorodskii was used as the starting point of the refinement. The fact that it did refine confirmed that the crystal structure was essentially correct, and consisted of one molecule (A) lying parallel to the (001) face, and one (B) at 62° to it, but the relative z coordinates of the two molecules were still unknown. A (100) Patterson projection was then calculated, and solved by using the Buerger minimum-function technique (1951), the resolved molecule being used as an image-seeking function.

Refinement of the crystal structure

The $hk0$ projection was refined by means of $F_o - F_c$ maps; contributions from hydrogen atoms were included in the F_c's at the second cycle of refinement,

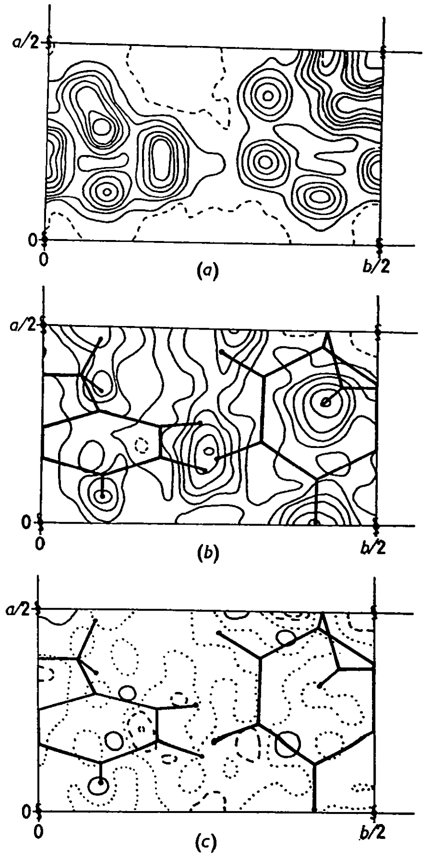


Fig. 1. (a) Electron-density projection on (001). Contours are at intervals of 1 e.Å^{-2}, the one-electron contour being broken. (b) Difference synthesis on (001) with only the carbon atoms subtracted. Contours every 0·2 e.Å^{-2}, positive contours in full lines, negative contours broken and zero contour omitted. (c) Final ($F_o - F_c$) synthesis for $hk0$'s. Contours every 0·2 e.Å^{-2}, with positive contours in full lines, negative contours broken and zero contour dotted.

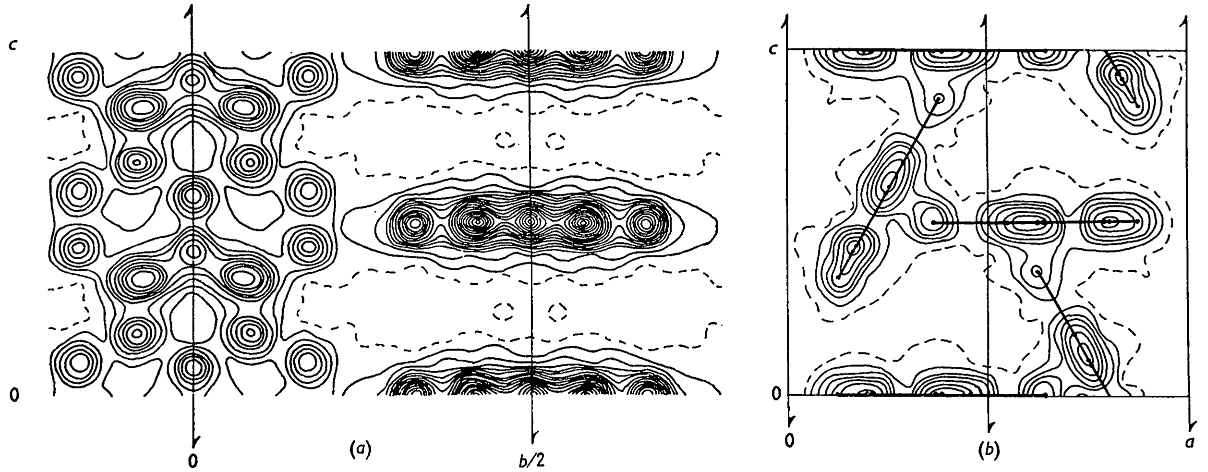


Fig. 2. (a) Electron-density projection on (100). Contours are at intervals of 1 e.Å^{-2}, the one-electron contour being broken. (b) Electron density projection on (010). Contours are at intervals of 3 e.Å^{-2}, the three-electron contour being broken.

and corrections for anisotropic thermal vibrations at the third cycle. The latter were only made to correct for atoms with the directions of maximum and minimum vibration parallel to the crystal axes, as such corrections can be made very conveniently. Since the atoms do not, in fact, behave in this manner, the corrections cannot be considered as complete, and the electron-density detail in the difference map in Fig. 1(c) shows that there is still some anisotropic motion for which no correction has been made.

At a later stage in the refinement corrections were made for secondary extinction, the extinction coefficient being found by trial.

The final F_o synthesis and the difference synthesis with only the carbon atom contributions subtracted are shown in Fig. 1(a) and 1(b).

The refinement of the other two projections followed along similar lines, but only the z parameters were adjusted to improve the agreement, the x and y parameters being more accurately determinable from the centrosymmetric (001) projection.

After the penultimate cycle of refinement of the z parameters, the bond lengths were calculated for molecules A and B. The mean plane through the atoms of molecule B was also determined by least squares. No significant deviation from planarity was observed, and when the z coordinates were adjusted to improve the fit of the atoms on to the plane, the agreement in bond lengths between corresponding bonds in molecules A and B improved. Although these shifts had not been indicated by the F_o-F_c map, the agreement between F_o and F_c was better, i.e. $\Sigma(F_o-F_c)^2$ became smaller, for both projections. $\Sigma l^2(F_o-F_c)^2$, however, increased for both projections. The planar molecule was chosen as a final model because of the better agreement in bond lengths between the molecules A and B, there being otherwise no discriminating factor.

The final F_o syntheses for the (100) and (010) projections are shown in Figs. 2(a) and 2(b). The final values of $R = 100(\Sigma||F_o|-|F_c||)\div\Sigma|F_o|$ for the (100), (010) and (001) projections were 8·5, 8·1 and 9·2 respectively. Table 1 shows the agreement between F_c and F_o.

Corrections for anisotropic thermal vibration

The conventional method for this correction treats each atom individually. The trigonometric function must be calculated and multiplied by the corresponding temperature factor for each atom before any summation can be made. The procedure discussed here enables one to deal with all atoms of the same element at once, by reducing the exponential term to a product of univariant terms.

For isotropically vibrating atoms in acenaphthene we have

$$F(hk0) = \Sigma F_j = 4\Sigma f_{o_j} \times [\Sigma \exp(-B_i\lambda^{-2}\sin^2\theta)\cos(2\pi hx_i)\cos(2\pi ky_i)]\,,$$

where j refers to an atomic species and i refers to an individual atom of that species.

Since the lattice is orthogonal, we have

$$4\sin^2\theta = (ha^*)^2+(kb^*)^2\,,$$

and hence

$$F(hk0) = 4\Sigma f_{o_j}\left[\Sigma \exp\left(\frac{-B_{x_i}a^{*2}}{4\lambda^2}h^2\right)\cos(2\pi hx_i) \times \exp\left(\frac{-B_{y_i}b^{*2}}{4\lambda^2}k^2\right)\cos(2\pi ky_i)\right].$$

For isotropy $B_x = B_y$, but if these terms are not equal, anisotropy parallel to the crystallographic axes is produced.

Thus $F(hk0)$ is obtained as the sum of products of two univariant terms in h and k. The procedure has application to all orthogonal lattices, and the products can be formed and summed very rapidly on an ordinary desk calculator.

Table 1. *Calculated and observed values of F*

hk0 reflexions.

hkl	F_c	$\|F_o\|$	*hkl*	F_c	$\|F_o\|$	*hkl*	F_c	$\|F_o\|$
000	328.0	-	310	-3.6	4.4	650	0.0	<0.9
010	0.0	<0.2	320	13.3	13.3	660	-0.8	<0.9
020	64.8	67.3	330	2.1	1.1	670	0.4	<0.9
030	-0.2	<0.3	340	5.8	5.7	680	0.0	1.8
040	-23.0	23.7	350	-17.6	18.2	690	-0.9	<0.9
050	-0.6	<0.5	360	-8.6	8.3	6,10,0	0.0	<0.9
060	1.5	<0.5	370	-11.6	11.3	6,11,0	0.1	<0.8
070	-0.5	<0.6	380	-6.8	7.6	6,12,0	-0.3	0.7
080	-26.4	26.1	390	2.0	1.5	6,13,0	-0.9	1.3
090	0.0	<0.7	3,10,0	-10.1	10.3	6,14,0	0.7	<0.5
0,10,0	9.4	9.2	3,11,0	-0.2	0.9			
0,11,0	0.6	<0.8	3,12,0	-8.3	7.7	700	-0.5	<0.9
0,12,0	29.0	28.7	3,13,0	1.1	1.8	710	12.4	11.8
0,13,0	0.1	<0.9	3,14,0	1.7	1.6	720	-1.2	<0.9
0,14,0	0.6	<0.9	3,15,0	0.1	<0.7	730	-0.5	<0.9
0,15,0	-0.6	2.0	3,16,0	1.5	1.8	740	-7.6	8.7
0,16,0	1.6	1.4	3,17,0	-3.8	4.2	750	3.1	3.4
0,17,0	-0.7	<0.6				760	-10.4	9.0
0,18,0	4.6	4.6	400	-26.5	27.1	770	0.1	<0.9
			410	12.2	12.6	780	1.2	2.4
100	-24.0	23.5	420	-17.2	17.4	790	-2.4	2.4
110	30.0	28.9	430	-2.2	1.6	7,10,0	5.0	4.7
120	-20.2	18.8	440	0.9	<0.7	7,11,0	4.6	4.5
130	-10.1	10.5	450	8.5	8.4	7,12,0	2.6	1.4
140	-6.0	6.3	460	8.8	9.5	7,13,0	3.0	3.1
150	7.4	7.5	470	4.7	5.2			
160	7.5	7.2	480	4.6	3.5	800	11.3	11.3
170	1.4	<0.6	490	-2.0	2.0	810	-0.8	<0.9
180	12.7	13.3	4,10,0	2.6	3.1	820	4.8	5.0
190	-2.0	1.6	4,11,0	3.4	2.6	830	0.7	<0.9
1,10,0	7.5	7.6	4,12,0	2.2	2.0	840	-1.9	1.1
1,11,0	7.3	7.4	4,13,0	2.4	2.3	850	1.1	<0.8
1,12,0	0.4	<0.9	4,14,0	0.5	<0.8	860	-2.0	1.9
1,13,0	3.8	3.9	4,15,0	0.2	<0.7	870	1.5	2.6
1,14,0	-2.3	2.4	4,16,0	-1.5	<0.5	880	-2.3	2.5
1,15,0	-0.8	1.0				890	2.0	1.1
1,16,0	-1.1	1.4	500	8.4	8.4	8,10,0	-0.3	<0.6
1,17,0	0.9	1.3	510	-10.3	11.2	8,11,0	0.8	<0.5
			520	-5.8	5.2	8,12,0	0.9	1.2
200	-69.0	68.3	530	5.0	5.3			
210	-34.7	33.8	540	12.7	12.6	900	-1.4	<0.8
220	0.9	-	550	-2.7	1.9	910	-5.4	6.0
230	9.1	9.4	560	27.2	27.2	920	0.7	<0.8
240	-7.1	6.8	570	-0.6	1.6	930	0.8	<0.8
250	6.4	7.3	580	-1.4	<0.9	940	-1.7	2.1
260	-30.5	29.1	590	1.8	1.9	950	1.5	1.8
270	6.8	7.5	5,10,0	-5.4	5.1	960	-3.8	4.2
280	3.3	2.1	5,11,0	-4.8	3.7	970	1.9	2.0
290	0.5	0.9	5,12,0	0.8	<0.8	980	0.9	<0.5
2,10,0	-2.1	2.0	5,13,0	-2.6	2.7	990	0.6	<0.4
2,11,0	-9.4	9.2	5,14,0	-1.8	2.5			
2,12,0	-10.5	10.8	5,15,0	0.7	0.6	10,0,0	-2.8	2.5
2,13,0	-5.9	5.7	5,16,0	3.7	3.6	10,1,0	0.1	<0.6
2,14,0	0.9	1.9				10,2,0	-2.4	2.1
2,15,0	1.0	0.9	600	4.3	4.1	10,3,0	1.7	1.2
2,16,0	-1.8	2.8	610	-4.2	4.6	10,4,0	-1.9	0.9
2,17,0	1.3	<0.5	620	5.4	5.5	10,5,0	-5.5	5.3
			630	-4.7	4.6	10,6,0	-1.1	0.9
300	-19.2	18.5	640	3.0	2.6			

h0l and 0kl reflexions.

hkl	A_c	B_c	$\|F_o\|$	$\|F_o\|$	*hkl*	A_c	B_c	$\|F_c\|$	$\|F_o\|$
101	21.3	-4.6	21.8	20.7	607	-0.7	1.1	1.3	2.2
201	-49.3	-20.5	53.4	49.4	707	3.1	1.3	3.4	1.9
301	-23.2	37.1	43.8	40.7					
401	12.9	-17.4	21.7	23.1	008	8.8	-3.2	9.4	9.2
501	13.7	2.1	13.9	14.6	108	-7.0	-0.2	7.0	6.3
601	1.9	4.9	5.3	5.3	208	4.1	0.4	4.1	2.7
701	-3.4	0.5	3.4	4.3	308	0.8	0.3	0.9	1.3
801	0.8	-7.4	7.4	9.2	408	-4.4	0.8	4.5	3.6
901	-0.6	-2.6	2.6	2.8	508	4.1	-0.1	4.1	4.1
10,0,1	-2.5	2.9	3.8	3.1					
					109	-1.0	7.4	7.5	5.3
002	110.5	-17.1	111.8	113.4	209	1.4	3.7	4.0	2.1
102	-20.3	-11.7	23.4	25.3					
202	-13.4	-22.0	25.8	27.1	012	-85.1	-15.9	86.6	85.8
302	-17.2	20.9	27.1	29.2	022	10.4	-12.5	16.3	16.3
402	-13.9	33.9	36.6	33.8	032	2.6	-7.1	7.6	7.5
502	19.4	-7.6	20.8	21.0	042	1.7	-0.6	1.8	2.4
602	5.0	-13.4	14.3	13.6	052	20.2	4.4	20.7	23.5
702	-10.3	0.4	10.3	11.1	062	26.2	5.7	26.8	29.5
802	4.9	0.5	4.9	4.5	072	19.2	4.5	19.7	21.7
902	1.9	-0.2	1.9	3.0	082	-7.9	3.1	8.5	7.8
10,0,2	-3.1	0.4	3.1	4.0	092	5.3	2.4	5.8	6.5
					0,10,2	3.2	2.5	4.1	3.5
103	3.1	46.7	46.8	46.5	0,11,2	-10.9	2.7	11.2	11.0
203	-15.2	20.5	25.5	27.2	0,12,2	14.2	2.7	14.5	15.9
303	-9.0	0.8	9.0	11.6	0,13,2	-6.6	2.2	7.0	7.6
403	8.3	-9.9	12.9	14.3	0,14,2	-0.7	1.1	1.3	<1.5
503	13.0	5.7	14.2	13.2	0,15,2	0.6	-0.1	0.6	<1.4
603	1.6	-14.0	14.1	15.3	0,16,2	2.6	-1.0	2.8	3.8
703	-8.7	-2.1	8.9	10.0	0,17,2	-0.2	-1.5	1.5	<1.0
803	-3.7	1.1	3.9	3.6					
903	3.1	-0.3	3.1	4.0	014	-57.6	1.9	57.6	57.5
10,0,3	2.3	2.6	3.5	3.6	024	6.1	4.6	7.6	10.1
					034	5.9	4.8	7.6	7.5
004	24.6	0.3	24.6	25.1	044	-3.3	1.9	3.8	2.4
104	-12.9	-1.6	13.0	12.7	054	-3.9	-1.1	4.1	5.6
204	10.9	4.6	11.8	13.3	064	0.9	-1.7	1.9	<1.4
304	-2.4	1.8	3.0	2.9	074	4.8	0.2	4.8	4.3
404	-11.2	-1.5	11.3	10.2	084	-3.5	1.7	3.9	4.9
504	8.3	-0.1	8.3	10.7	094	8.5	1.1	8.6	8.8
604	3.6	-7.0	7.9	6.7	0,10,4	2.2	-1.1	2.5	3.1
704	-8.4	-3.8	9.2	11.1	0,11,4	-12.9	-2.8	13.2	15.0
804	1.4	7.5	7.6	10.1	0,12,4	5.2	-2.9	6.0	7.2
904	2.9	5.1	5.9	7.6	0,13,4	-7.2	-1.6	7.4	8.4
					0,14,4	0.4	-0.2	0.4	<1.2
105	-7.4	22.9	24.1	22.8	0,15,4	1.0	0.5	1.1	2.9
205	-7.0	8.3	10.9	10.9	0,16,4	0.5	0.6	0.8	<0.7
305	2.3	-0.5	2.4	<1.1					
405	-0.1	-17.1	17.1	15.0	016	-17.1	1.9	17.2	15.3
505	1.5	4.4	4.7	4.6	026	13.4	4.8	14.2	14.6
605	-1.9	2.2	2.9	2.2	036	4.9	4.8	6.9	6.1
705	-4.0	0.1	4.0	3.5	046	-8.3	1.0	8.4	7.4
805	-2.9	-2.2	3.6	2.8	056	-15.3	-3.5	15.7	15.3
905	2.5	1.6	3.0	2.9	066	-16.5	-5.0	17.2	15.9
					076	-8.7	-2.9	9.2	10.2
006	27.9	0.2	27.9	25.4	086	-5.5	0.2	8.5	9.3
106	-11.0	-2.2	11.2	12.4	096	4.4	1.3	4.6	4.9
206	3.1	1.5	3.4	4.1	0,10,6	2.1	0.3	2.1	2.4
306	4.3	2.9	5.2	4.1	0,11,6	-7.7	-1.0	7.8	9.7
406	-12.2	-1.7	12.3	13.2	0,12,6	5.2	-0.9	5.3	5.0
506	-2.2	-1.2	2.5	2.4	0,13,6	-3.5	0.3	3.5	3.7
606	1.7	0.2	1.7	2.1					
706	-1.5	0.3	1.5	3.3	018	-16.9	-2.6	17.1	15.5
806	4.2	0.0	4.2	4.9	028	2.9	-1.3	3.2	2.5
					038	1.3	-0.2	1.3	<1.2
107	-0.1	13.6	13.6	13.1	048	-0.2	0.1	0.2	<1.2
207	-4.6	2.3	5.1	3.3	058	1.2	-0.1	1.2	<1.1
307	-1.1	0.8	1.4	2.0	068	0.2	0.2	0.3	<1.1
407	2.4	-9.9	10.2	9.9	078	2.8	0.0	2.8	3.6
507	-0.3	1.8	1.8	1.7	088	-2.7	0.3	2.7	<0.8
					098	2.0	0.4	2.0	1.6

For three-dimensional F's, new preliminary tables must be calculated for each value of l, since products of three terms cannot simultaneously be formed and summed on a desk calculator.

This method is also applicable to lattices in which α^*, β^* and γ^* are not very different from 90°, since no large errors develop in the exponential terms by approximating to an orthogonal lattice.

Atomic coordinates and molecular dimensions

The final carbon atom parameters are listed in Table 2, and the hydrogen atom coordinates in Table 3. The

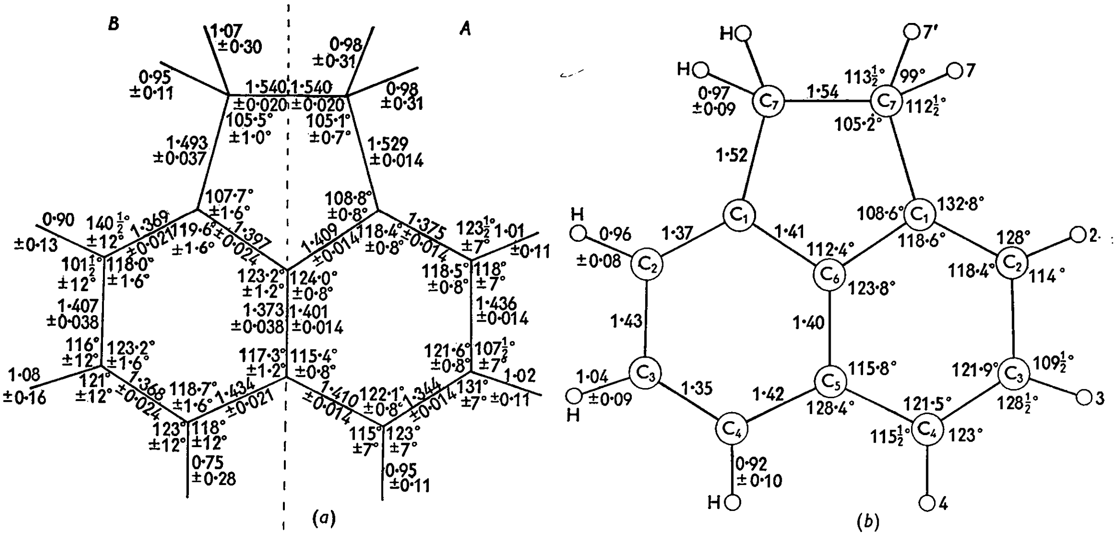


Fig. 3. (*a*) The bond lengths (Å) and angles (°), and their standard deviations in the two crystallographically independent acenaphthene molecules. (*b*) The weighted means of the bond lengths (Å) and angles (°). Also, the standard deviations (Å) of the C–H bond lengths.

Table 2. *Carbon atom parameters*

Atom	x	y	z	B_x (Å^2)	B_y (Å^2)	B_z (Å^2)
$A1$	0·460	0·4165	0·000	4·3	3·9	2·0
$A2$	0·383	0·3295	0·000	4·7	4·3	3·7
$A3$	0·210	0·3280	0·000	4·8	4·5	3·7
$A4$	0·123	0·4090	0·000	3·0	6·8	3·7
$A5$	0·196	0·5000	0·000	3·5	4·3	3·7
$A6$	0·365	0·5000	0·000	3·7	3·0	3·0
$A7$	0·638	0·4450	0·000	2·5	4·7	2·5
$B1$	0·288	0·0835	0·675	2·7	3·5	2·0
$B2$	0·252	0·1705	0·599	4·5	4·5	4·0
$B3$	0·171	0·1720	0·428	4·3	4·1	3·0
$B4$	0·127	0·0910	0·335	3·2	6·0	2·7
$B5$	0·165	0·0000	0·415	3·0	4·1	4·0
$B6$	0·244	0·0000	0·582	2·7	4·0	2·3
$B7$	0·371	0·0550	0·850	6·8	5·0	4·6

Table 3. *Hydrogen atom coordinates*

Atom	$120x$	$120y$	$120z$	Atom	$120x$	$120y$	$120z$
$A2$	53	32	0	$B2$	31	28	75
$A3$	21	31	0	$B3$	17	29	45
$A4$	1	49	0	$B4$	9	11	30
$A7$	83	50	13	$B7$	57	10	102
$A7'$	83	50	107	$B7'$	41	10	118

scattering curve used for carbon was that of Hoerni & Ibers (1954). The hydrogen atoms were assumed to be vibrating isotropically, the Debye factor, B, being 5·5 Å^2.

The two independent molecules are both planar, molecule A lying on the plane $z = 0$, and molecule B on the plane $2 \cdot 112x + 0 \cdot 0666 = z$, where x and z are the fractional coordinates of the atoms referred to a and c. The plane of the molecule B makes an angle of 61½° to (001).

The bond lengths and bond angles are shown in Fig. 3(*a*), while the weighted means of both these quantities are shown in Fig. 3(*b*).

Estimation of accuracy

The standard deviations of the atomic coordinates and electron densities were estimated by the method of Cruickshank (1949). The values obtained were

$$\sigma(x) = \sigma(y) = 0 \cdot 010 \text{ Å}, \quad \sigma(z) = 0 \cdot 030 \text{ Å} \text{ for C atoms,}$$

and

$$\sigma(x) = \sigma(y) = 0 \cdot 11 \text{ Å}, \quad \sigma(z) = 0 \cdot 33 \text{ Å} \text{ for H atoms.}$$

$$\sigma(\varrho) = 0 \cdot 36 \text{ e.Å}^{-2} \text{ for the (100) projection,}$$

$$\sigma(\varrho) = 0 \cdot 79 \text{ e.Å}^{-2} \text{ for the (010) projection,}$$

and

$$\sigma(\varrho) = 0 \cdot 13 \text{ e.Å}^{-2} \text{ for the (001) projection.}$$

The high value for the standard deviation of the electron density for the (010) projection is explained by the fact that there is a mirror plane parallel to (010), so that in this projection all the electron density is doubled.

From these figures, the values of the standard deviations quoted in Fig. 3(*a*) were derived. The standard deviations of the dimensions in Fig. 3(*b*) are

0·014 Å for bond C_7–C_7, 0·013 Å for bonds C_1–C_7, C_2–C_3, C_5–C_6, 0·012 Å for the other C–C bonds, 0·6° for the C_7–C_7–C_1 angle, 0·7° for all the other C–C–C angles, 6° for all C–C–H angles and 17° for the H–C–H angle.

Discussion of structure

Crystal structure

The packing of the acenaphthene molecules is very interesting. In the unit cell there are four molecules, which fall into two crystallographically independent sets, all the molecules lying about special positions,

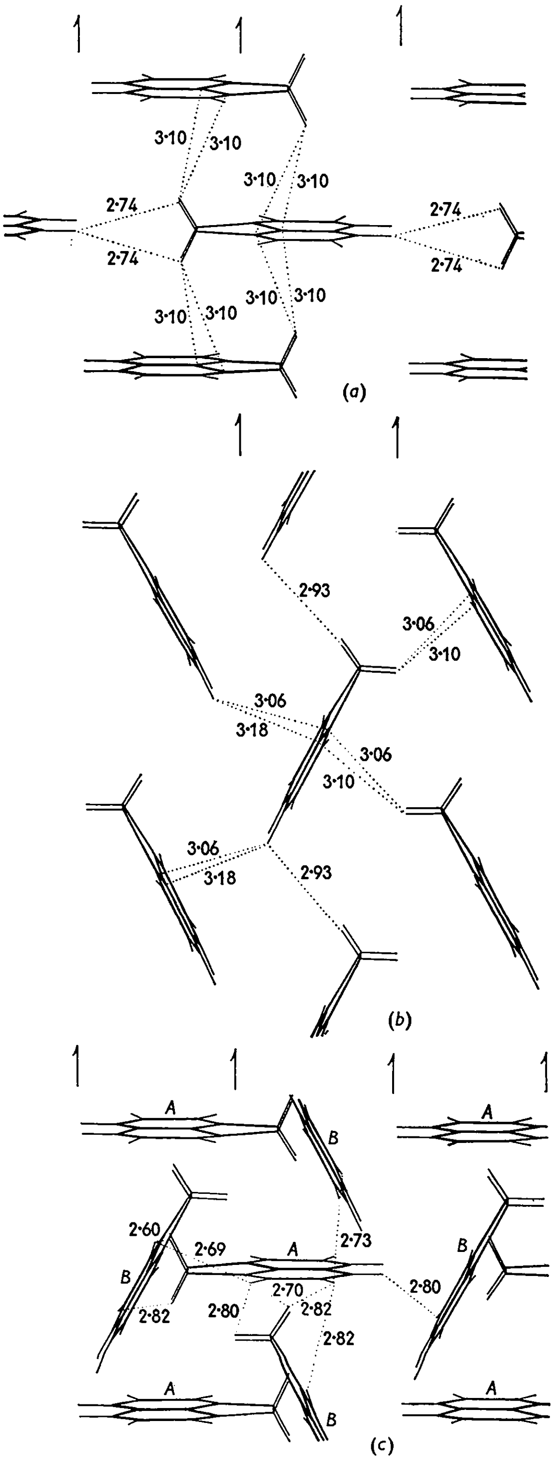


Fig. 4. (*a*) The intermolecular contacts in a sheet of only *A* molecules. (*b*) The intermolecular contacts in a sheet of only *B* molecules. (*c*) The intermolecular contacts between sheets.

i.e. the molecular and crystallographic mirror planes coincide. Thus there are sheets of molecules parallel to the mirror planes. One sheet has only *A* molecules, which pack in a way similar to graphite. Some stability is given to this structure by the hydrogens of the CH_2 group, which fit into the hollows at the centres of the benzene rings of adjacent molecules. The other sheet consists only of *B* molecules, which pack in a way reminiscent of flat molecules of finite size. The *A* sheet fits on to the *B* sheet in such a way that the protuberances of one fit into the hollows of the other, and the crystal is built up of alternate *A* and *B* sheets. The contacts between molecules in the two sheets are shown in Figs. 4(*a*) and 4(*b*), and the contacts between sheets can be seen in Fig. 4(*c*).

If the van der Waals radius of a carbon atom in an aromatic molecule is 1·70 Å, the semi-thickness of such a molecule, the hydrogen-atom van der Waals radius may be evaluated both from the C–H contacts and the H–H contacts. The average of the 17 independent measurements in this structure has the value 1·39 Å, which agrees well with the average of 7 hydrogen-atom van der Waals radii in the anthracene crystal, namely 1·36 Å (Cruickshank, 1956).

The maximum deviation from this mean is 0·09 Å, which is certainly not a significant difference. Therefore it appears that the minimum approach distance is the same at all points of contact. This property is usually obscured when the distances between only the carbon atoms are considered.

Molecular structure

The analysis reveals a planar molecule with no unusual bond lengths. The aliphatic CH_2–CH_2 bond is the length normally expected of a single bond. The C_7–C_1 bond length ($1{\cdot}524 \pm 0{\cdot}013$ Å) does not indicate whether there is any bond shrinking due to hyperconjugation, since the value is not significantly different either from 1·54 Å or from 1·51 Å, the corresponding bond length in toluene (Keidel & Bauer, 1956).

It is interesting to note that the bond lengths in the aromatic part of the molecule are still very similar to those in naphthalene (Cruickshank, 1957). A comparison of the results is shown in Table 4.

Table 4. *Comparison between bond lengths in acenaphthene and naphthalene*

Bond	Acenaphthene	Corresponding bond in naphthalene
1–2	1·37 Å	1·36 Å
2–3	1·43	1·42
3–4	1·35	1·36
4–5	1·42	$1{\cdot}42_5$
5–6	1·40	1·41
6–1	1·41	$1{\cdot}42_5$

The main changes are in the bond angles. The angular stress has been evenly shared out over the three rings, one angle in the five-membered ring increasing by 4°, and two of the angles in each of the benzene rings also changing by that amount.

Therefore it appears that purely 'mechanical' forces do not appreciably affect bond length, whereas bond angles are not as rigorous in their demands for constancy.

I should like to conclude by thanking Dr C. A. Beevers for much helpful discussion and advice, and also to express my gratitude to the University of Edinburgh for an award of a Post-Graduate Studentship.

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The Crystallographic, Elastic, and Piezoelectric Properties of Ammonium Pentaborate and Potassium Pentaborate

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The crystallographic descriptions of potassium and ammonium pentaborate are given, including a review of previous conflicting data. The full set of elastic, piezoelectric, and dielectric coefficients of potassium pentaborate were obtained, as well as piezoelectric and dielectric data for ammonium pentaborate.

Potassium pentaborate ($KB_5O_8.4\,H_2O$) and its isomorphous compounds form well defined orthorhombic crystals. The early crystallographic literature (Groth, 1908) indicated central symmetry, but a structure determination by Zachariasen (1937) led to the polar space group C_{2v}^{17}–Aba. At the suggestion of Prof. Zachariasen (1941), we studied the piezoelectric effect in this crystal group, and we found the effect at a substantial level as well as a somewhat unusual elastic behavior. These studies were given in a government report (Jaffe, 1948). The purpose of the present note is to make these results generally available as well as to clarify discrepancies in the crystallographic descriptions of this crystal type. These discrepancies were brought to our attention especially by correspondence with Prof. A. N. Winchell.

Potassium pentaborate is orthorhombic, class C_{2v},

$$a = 11{\cdot}065 \pm 0{\cdot}002, \quad b = 11{\cdot}171 \pm 0{\cdot}001,$$
$$c \text{ (polar axis)} = 9{\cdot}054 \pm 0{\cdot}0006 \text{ Å},$$
$$\text{axial ratio } 0{\cdot}9905:1:0{\cdot}8105\,.$$

Zachariasen (1937) found the space group to be C_{2v}^{17}–Aba and dimensions close to those here reported; our choice of axes agrees with his. The crystal is biaxial positive, optic plane 010,

$$N_\alpha = 1{\cdot}422, \quad N_\beta = 1{\cdot}436, \quad N_\gamma = 1{\cdot}480\,,$$
$$c = X(\alpha), \quad b = Y(\beta), \quad a = Z(\gamma)\,.$$

Predominant crystal forms are {111}, {100}, and $\{00\overset{+}{1}\}$, with perfect 010 and distinct 100 cleavage; generally twinned on $01\bar{1}$ and occasionally on $00\bar{1}$. The density is 1·740 g.cm.$^{-3}$, and the hardness is $2\frac{1}{2}$ on Mohs scale.

Ammonium pentaborate is orthorhombic, class C_{2v},

$$a = 11{\cdot}324 \pm 0{\cdot}002, \quad b = 11{\cdot}029 \pm 0{\cdot}001,$$
$$c = 9{\cdot}235 \pm 0{\cdot}004 \text{ Å}\,,$$
$$\text{axial ratio } 0{\cdot}9740:1:0{\cdot}8155\,.$$

The crystal is biaxial positive, optic plane 010,

$$N_\alpha = 1{\cdot}427, \quad N_\beta = 1{\cdot}431, \quad N_\gamma = 1{\cdot}486,$$
$$c = X(\alpha), \quad b = Y(\beta), \quad a = Z(\gamma)\,.$$

Predominant crystal forms are {100}, {111}, $\{00\overset{+}{1}\}$, with distinct 100 and 010 cleavage; generally twinned