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The crystal structure of hexacene, and a revision of the crystallographic data for tetracene and pentacene.

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Crystals of tetracene and pentacene, the higher linear benzologues of the naphthalene-anthracene series, are triclinic with two molecules in the cell, but detailed structural analyses (Robertson, Sinclair & Trotter, 1961; Campbell, Robertson & Trotter, 1961) have shown that, in spite of the decrease in crystallographic symmetry, the arrangements of molecules closely resemble that in the monoclinic naphthalene and anthracene crystals.

Recently, as part of an investigation of the absorption by tetracene of plane-polarized light, Bree & Lyons (1960) determined the density of tetracene very carefully by flotation in an alcohol-chloroform mixture. The agreement with the value calculated from our cell dimensions was so poor that we felt that a complete redetermination of the crystallographic data for tetracene and pentacene was desirable.

Table 1. *Crystallographic data*

	Naphthalene	Anthracene	Tetracene	Pentacene	Hexacene
	$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	$C_{26}H_{16}$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
a (Å)	8·24	8·56	7·90	7·90	7·9
b (Å)	6·00	6·04	6·03	6·06	6·1
c (Å)	8·66	11·16	13·53	16·01	18·4
α (°)	90·0	90·0	100·3	101·9	102·7
β (°)	122·9	124·7	113·2	112·6	112·3
γ (°)	90·0	90·0	86·3	85·8	83·6
U (Å^3)	360	474	583	692	800
Z	2	2	2	2	2
$D_{\text{calc.}}$	1·17	1·24	1·29	1·33	1·35
$D_{\text{meas.}}$	1·15	1·25	1·29	1·32	1·34
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$

The reciprocal cell dimensions (a^*, b^*, c^*, β^*, γ^*) were measured from precession photographs of the $h0l$ and $0kl$ zones for crystals mounted along the a^* axis, and the angle α was determined from the precession-camera dial settings. The cell dimensions calculated from these data (Table 1) differ slightly, but significantly, from the previous measurements, and the calculated density for tetracene now agrees very well with the new measured value.

Table 2. *Orientation of the molecules in anthracene, tetracene and pentacene*

		Tetracene		Pentacene	
	Anthracene	Molecule I	Molecule II	Molecule I	Molecule II
χ_L	119·7°	105·8°	105·5°	104·4°	104·3°
ψ_L	97·0	105·5	103·6	106·4	104·0
ω_L	30·6	22·5	20·8	22·1	20·3
χ_M	71·3	69·2	115·4	67·9	118·5
ψ_M	26·6	30·1	26·0	30·7	29·2
ω_M	71·8	69·2	85·0	69·8	84·0
χ_N	36·2	26·6	30·6	26·6	32·4
ψ_N	115·5	115·2	67·8	115·7	65·0
ω_N	66·2	81·9	70·1	83·8	70·7

Table 3. *Orientation of the triclinic crystal axes in tetracene and pentacene*

	Tetracene	Pentacene
χ_a	3·7°	4·2°
ψ_a	86·3	85·8
ω_a	90·0	90·0
χ_b	90·0	90·0
ψ_b	0·0	0·0
ω_b	90·0	90·0
χ_c	112·5	111·7
ψ_c	100·3	101·9
ω_c	25·0	25·1

The values of the orientation angles for tetracene and pentacene calculated from the new crystal data are listed in Table 2, the corresponding values for anthracene being included for comparison, and the new orientations of the triclinic crystal axes with respect to the orthogonal axes are given in Table 3 (note that the previous values for ω_c were misprinted as 35·6° and 34·9° instead of 25·6° and 24·9°).

All of the molecular data given previously (Robertson, Sinclair & Trotter, 1961) should be recalculated from the fractional positional parameters, but the differences are small and, on the basis of the estimated standard deviations, not significant. The new mean bond lengths, for example, are shown in Fig. 1; the maximum differences from the previous values are 0·02 Å for the central bonds and 0·01 Å for the other bonds. There are similar small changes in valency angles and intermolecular distances; the new values can be readily calculated if required.

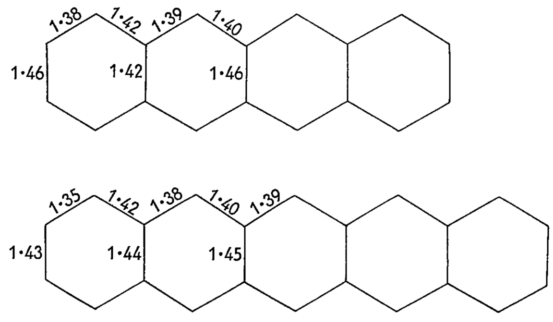
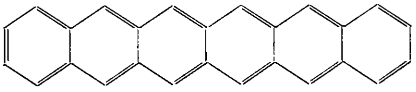


Fig. 1. Revised bond distances (Å) for tetracene and pentacene.

The crystal structure of hexacene

Hexacene (I), $C_{26}H_{16}$, the next member in the series, has been obtained in a pure state, but decreasing stability and increasing ease of oxidation, with increase in the number of rings, preclude the preparation of heptacene and higher benzologues (Clar, 1952). The following paragraphs describe an investigation of the hexacene structure.



(I)

All the crystals of hexacene which we obtained were small, extremely thin, almost-black plates, with (001) developed; they were invariably twinned. The unit-cell dimensions, determined from various rotation and Weissenberg photographs, and the density, measured by flotation in aqueous potassium iodide solution, are compared in Table 1 with the revised data for the other members of the series; the comparison indicates that hexacene has a crystal structure very similar to the lower benzologues, the only significant difference in cell dimensions being a further increase of 2·4 Å in the c-axis to accommodate the extra ring.

As a preliminary to complete structure analysis the intensities of the $0kl$ and $h0l$ reflexions were recorded on Weissenberg films with Cu $K\alpha$ radiation. As a result of the rather poor quality of the crystal specimens the proportion of the possible reflexions observed was even smaller than for tetracene and pentacene; only 17 independent $0kl$ reflexions and 16 $h0l$ reflexions were measurable. Since there are 78 carbon atom positional parameters the data were clearly insufficient for any detailed analysis of the structure. Comparison of the Weissenberg photographs with the corresponding films for tetracene and pentacene showed marked similarities, the strong reflexions being in the same regions of reciprocal space in each case. The orientations of the hexacene molecules in the unit cell are therefore very similar to those in the other members of the series, but no detailed determination of the molecular dimensions is possible.

We thank Dr E. Clar for the crystal sample. One of us (R. B. C.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

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The unit cell dimensions and crystal structure of KBaPO$_4$.

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The low temperature form of KBaPO$_4$ has been reported to be orthorhombic (Klement & Uffelmann, 1941), with

$$a = 5{\cdot}61_5,\ b = 11{\cdot}09,\ c = 7{\cdot}62\ \text{Å}\ .$$

Several polycrystalline samples of this phase have been made here recently, using for raw materials either KNO$_3$ + BaHPO$_4$ or $\frac{1}{2}$ K$_2$CO$_3$ + BaHPO$_4$, and firing in N$_2$ at temperatures from 900 to 1250 °C. for 3–24 hours. We have annealed the phase for one week at 600 °C.

All samples prepared in these ways have given identical X-ray diffraction patterns, which can be indexed on the basis of an orthorhombic unit cell, with

$$a = 5{\cdot}66_6 \pm 0{\cdot}005,\ b = 9{\cdot}95_9 \pm 0{\cdot}010,\ c = 7{\cdot}69_7 \pm 0{\cdot}008\ \text{Å}\ .$$

Our a and c axes are quite close to the dimensions of Klement & Uffelmann but b is appreciably different.

Table 1. *Coordinates of the atoms in* KBaPO$_4$

Atom	x	y	z
K	0·250	0·415	−0·330
Ba	0·250	−0·312	0·000
P	0·250	0·425	0·267
O$_1$	0·250	0·432	0·046
O$_2$	0·250	−0·417	0·350
O$_3$	0·005	0·343	0·337

In our data, the unobserved reflections are consistent with the space group $Pmcn$ (D_{2h}^{16}). The cell dimensions and space group are highly suggestive of the β-K$_2$SO$_4$ structure (Ehrenberg & Hermann, 1929). This structure requires four formula units per unit cell with 4K, 4Ba, 4P, and 8O atoms in positions (c) $\frac{1}{4}, y, z$; $\frac{1}{4}, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{3}{4}, \bar{y}, \bar{z}$; $\frac{3}{4}, \frac{1}{2}+y, \frac{1}{2}-z$ and 8O atoms in (d) $\pm x, y, z$; $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}+x, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ with the parameters as given in Table 1. The intensities of the first 56 lines recorded on a powder diffraction photograph (Cu $K\alpha$ radiation) were estimated visually using a multiple film technique. Of these lines 31 are separately resolved reflections and 25 may be composed of overlapping reflections. A Patterson section at $x = 0$ showed clearly the barium and potassium atom positions and several electron density maps of the plane $x = \frac{1}{4}$ were computed, in which the intensities of overlapping lines were divided in the ratio of the calculated contributions, and an artificial temperature factor was used for convergence of the rather short series. The oxygen parameters were obtained by assuming a regular tetrahedron for the phosphate group and rotating about the P position to obtain the best fit with the observed electron density.

The observed and calculated values of the lattice spacings and intensities are listed in Table 2. For the calculated intensities the scattering factors given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. II (1935) have been used. The observed intensities have been modified by a cylindrical absorption correction chosen to give the best fit with the calculated data and since the latter are for atoms at rest the tem-