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The Crystal and Molecular Structure of Pentacene

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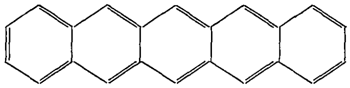
Crystals of pentacene are triclinic, with two molecules in a unit cell of dimensions $a = 7{\cdot}93$, $b = 6{\cdot}14$, $c = 16{\cdot}03$ Å, $\alpha = 101{\cdot}9°$, $\beta = 112{\cdot}6°$, $\gamma = 85{\cdot}8°$, space group $P\bar{1}$. The structure, which has been determined from projections along the a and b crystal axes, is very similar to the structures of naphthalene, anthracene and tetracene. The two molecules in the unit cell are situated on independent centres of symmetry, the asymmetric unit consisting of two half-molecules. Both molecules are completely planar. Details of the molecular dimensions and of the intermolecular separations have been obtained.

Introduction

A detailed X-ray investigation of the crystal and molecular structure of pentacene (I), the next higher benzologue in the naphthalene–anthracene–tetracene series, has been undertaken to obtain an accurate account of the dimensions of the molecule, and of the intermolecular separations. The structure is closely related to the lower members of the series.


(I)

As in the analysis of the tetracene structure (Robertson, Sinclair & Trotter, 1961), only a small proportion of the theoretically-observable intensities have been recorded, and the analysis has again been confined to the projections along the a and b crystal axes. The bond lengths in the pentacene molecule have been determined with sufficient accuracy for comparison with the distances calculated by quantum-mechanical theories.

Experimental

Crystals of pentacene obtained by crystallization from trichlorobenzene consisted of extremely thin deep violet-blue leaflets, with only the (001) face developed. Attempts to grow thicker specimens by recrystallization from trichlorobenzene in an atmosphere of carbon dioxide yielded only similar very thin plate-like crystals.

The unit-cell dimensions were determined from rotation, oscillation and Weissenberg photographs of crystals rotating about the a, b and c axes and various diagonals. The density was determined by flotation in aqueous potassium-iodide solution. The crystal data were:

Pentacene, $C_{22}H_{14}$; molecular weight = 278·3; high melting point.
Triclinic,

$$a = 7{\cdot}93 \pm 0{\cdot}02,\ b = 6{\cdot}14 \pm 0{\cdot}02,\ c = 16{\cdot}03 \pm 0{\cdot}05 \text{ Å};$$
$$\alpha = 101{\cdot}9 \pm 0{\cdot}5°,\ \beta = 112{\cdot}6 \pm 0{\cdot}5°,\ \gamma = 85{\cdot}8 \pm 0{\cdot}5°.$$

Volume of the unit cell = 705·0 Å^3.
Density, calculated (with $Z = 2$) = 1·303, measured = 1·30 g.cm.$^{-3}$.
Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 6{\cdot}80$ cm.$^{-1}$.
Total number of electrons per unit cell = $F(000) = 292$.
No systematic absences; space group is either $P1\text{–}C_1^1$ or $P\bar{1}\text{–}C_i^1$.

The intensities of the $0kl$ and $h0l$ reflexions were recorded on Weissenberg films of the equatorial layers for crystals rotating about the a and b crystal axes, using Cu $K\alpha$ radiation. The multiple-film technique (Robertson, 1943) was used to correlate strong and weak reflexions. The range of intensities measured was about 1000 to 1 for the $0kl$ zone and 3000 to 1 for the $h0l$ zone, the estimates being made visually. The crystal used for the $0kl$ zone photographs had a cross-section normal to the a-axis of 0·53 × 0·005 mm., while that used for the $h0l$ zone films had a cross-section normal to the b-axis of 1·06 × 0·005 mm. Due to the extreme thinness of the crystals, however, the mean path through the specimens was almost constant for all planes, and no absorption corrections were applied.

The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors.

61 $0kl$ and 65 $h0l$ reflexions were observed, representing about 26 and 21% respectively of the possible numbers observable under the experimental conditions. The small proportion of reflexions observed is a consequence of the rather poor quality of the very thin crystal specimens.

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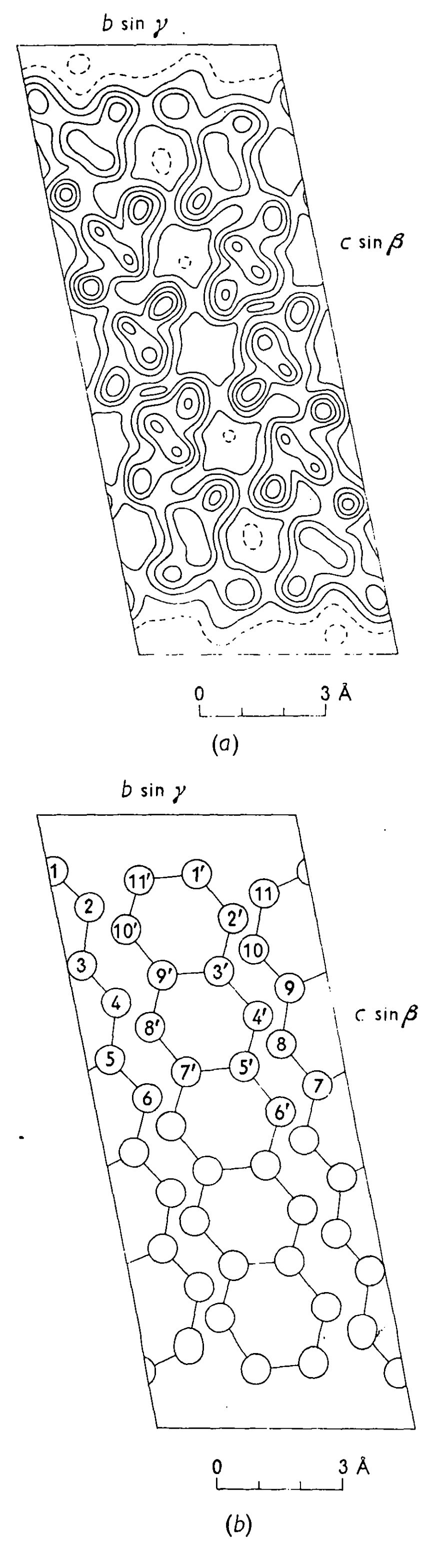

Fig. 1. (*a*) Electron-density projection along the *a*-axis. Contours at intervals of 1 e.Å^{-2}, with the one-electron line broken. (*b*) Projection of the structure along [100].

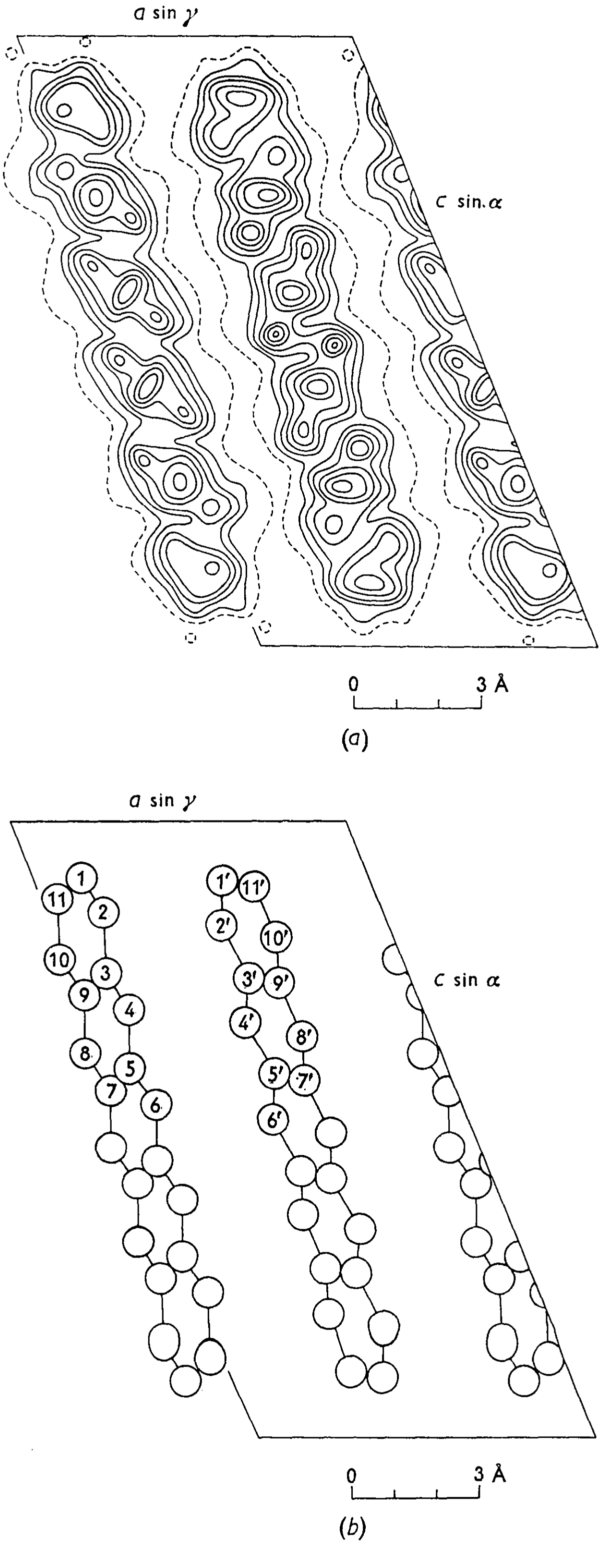

Fig. 2. (*a*) Electron-density projection along the *b*-axis. Contours as in Fig. 1. (*b*) Projection of the structure along [010].

Structure analysis

A clue to the arrangement of the molecules in the pentacene crystal was provided in cell dimensions and by the characteristic appearance of the c-axis rotation photograph, as explained in the tetracene analysis (Robertson, Sinclair & Trotter, 1961). A comparison of Weissenberg films of tetracene and pentacene also showed a marked similarity in the intensities of corresponding reflexions. The $10l$ and $30l$ reflexions are quite weak in comparison with the $20l$ planes, and this pseudo-monoclinic symmetry suggested that the two pentacene molecules in the unit cell were situated on centres of symmetry at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$ in space group $P\bar{1}$, as is the case in crystals of tetracene.

A trial structure was therefore set up, having the same molecular orientations as in tetracene, and structure factors were calculated for the $0kl$ and $h0l$ reflexions using the scattering curve for carbon of Berghuis *et al.* (1955), corrected for thermal vibration with $B = 4{\cdot}2$ Å^2 for all the atoms. The discrepancy between measured and calculated structure factors was 30·2% for the observed $0kl$ planes and 36·3% for the $h0l$ reflexions.

Table 1. *Assumed hydrogen fractional coordinates*

Atom	x	y	z
H 1	0·202	0·087	0·482
2	0·246	0·294	0·370
4	0·202	0·321	0·218
6	0·162	0·362	0·061
8	−0·122	−0·395	0·098
10	−0·085	−0·427	0·251
11	0·033	−0·272	0·420
1′	0·553	0·661	0·475
2′	0·447	0·853	0·335
4′	0·401	0·873	0·178
6′	0·362	0·887	0·020
8′	0·673	0·104	0·142
10′	0·718	0·088	0·304
11′	0·700	0·265	0·453

Refinement of the positional and temperature parameters proceeded by computing successive difference syntheses, with $(F_o - F_c)$ as coefficients, and minimizing the slopes and difference electron-densities at the atomic centres. Both projections were refined simultaneously, the mean values of the shifts in z-coordinate being taken at each stage. The first difference map revealed regions of positive density close to the positions expected for hydrogen atoms, and a contribution from the hydrogens was therefore introduced, coordinates (Table 1) being obtained by assuming that they lay on the ring diagonals with C–H distances of 1·08 Å. After four cycles of refinement the discrepancies were reduced to 10·4% for the $0kl$ zone and 18·2% for the $h0l$ zone, 3·8% of this latter figure being due to the $20\bar{1}$ plane, which might be affected by extinction. Final $(F_o - F_c)$ syntheses indicated no further significant changes in positional or temperature parameters. The values of the measured and calculated structure factors are listed in Table 6, and final F_o syntheses, computed with measured structure amplitudes and calculated signs, are shown in Figs. 1 and 2.

Coordinates, molecular dimensions and orientation

The final positional and temperature parameters of the carbon atoms are listed in Table 2, x, y and z being coordinates referred to the triclinic crystal axes, and expressed as fractions of the unit-cell edges, and X', Y' and Z' coordinates in Ångström units referred to orthogonal axes a', b and c'. These orthogonal axes consisted of the b crystal axes, a' the projected a-axis

Table 2. *Final positional and temperature parameters, and deviations (Δ) from the mean planes*

Atom	x	y	z	X'	Y'	Z'	B	Δ
C 1	0·1484	0·0183	0·4071	−1·239	−1·152	5·911	4·8 Å^2	+0·042 Å
2	0·1707	0·1361	0·3491	−0·719	−0·223	5·069	4·8	+0·011
3	0·1030	0·0604	0·2508	−0·672	−0·401	3·641	4·8	−0·026
4	0·1274	0·1650	0·1894	−0·115	0·459	2·750	4·8	+0·001
5	0·0572	0·0951	0·0950	−0·111	0·302	1·379	4·8	−0·079
6	0·0925	0·2095	0·0335	0·533	1·229	0·486	4·8	−0·003
7	−0·0227	−0·1227	0·0567	−0·516	−0·955	0·823	4·8	+0·043
8	−0·0540	−0·2325	0·1225	−1·153	−1·866	1·779	4·8	−0·026
9	0·0150	−0·1516	0·2149	−1·155	−1·635	3·120	4·8	+0·020
10	−0·0152	−0·2634	0·2786	−1·772	−2·551	4·045	4·8	−0·033
11	0·0519	−0·1800	0·3706	−1·786	−2·305	5·381	4·8	−0·005
1′	0·5627	0·5733	0·4014	2·071	2·516	5·828	4·8	+0·006
2′	0·5035	0·6805	0·3286	2·034	3·381	4·771	4·8	−0·016
3′	0·5210	0·5876	0·2434	2·678	3·104	3·534	4·8	−0·003
4′	0·4582	0·7010	0·1686	2·624	4·012	2·448	4·8	−0·031
5′	0·4810	0·6062	0·0846	3·303	3·722	1·228	4·8	+0·013
6′	0·4231	0·7138	0·0100	3·287	4·596	0·145	4·8	+0·003
7′	0·5622	0·3794	0·0754	3·999	2·407	1·095	4·8	+0·004
8′	0·6103	0·2743	0·1483	3·948	1·548	2·153	4·8	−0·045
9′	0·6061	0·3652	0·2342	3·405	1·819	3·400	4·8	+0·027
10′	0·6549	0·2570	0·3094	3·345	0·933	4·492	4·8	−0·029
11′	0·6496	0·3487	0·3925	2·811	1·217	5·699	4·8	+0·043
Molecular centre I	0	0	0	0	0	0	—	0
Molecular centre II	0·5000	0·5000	0	3·954	3·361	0	—	0

($a \sin \gamma$), and a third axis c' perpendicular to a' and b.

The equations of the mean molecular planes are Molecule I at (0, 0, 0):

$$0{\cdot}8942X' - 0{\cdot}4339Y' + 0{\cdot}1100Z' = 0$$

Molecule II at ($\frac{1}{2}$, $\frac{1}{2}$, 0):

$$0{\cdot}8840X' + 0{\cdot}4193Y' + 0{\cdot}3345Z' = 4{\cdot}7464$$

and the deviations of the atoms from these planes are listed in the final column of Table 2.

The bond lengths and valency angles, calculated from the coordinates of Table 2, are shown in Fig. 3(*a*). These values suggested that the symmetry of the pentacene molecule did not differ from *mmm*, and the mean values of the bond distances and angles are shown in Fig. 3(*b*).

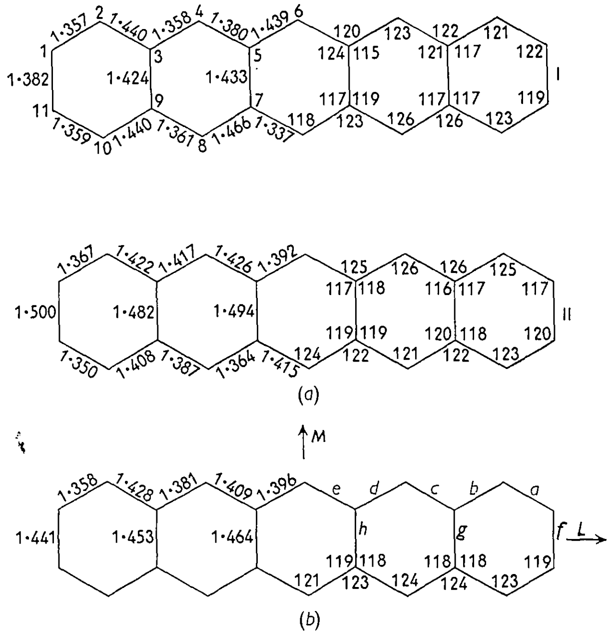

Fig. 3. (*a*) Measured bond lengths (Å) and valency angles (degrees). (*b*) Mean bond lengths and valency angles.

Table 3. *Orientation of the molecules in pentacene and tetracene*

	Pentacene		Tetracene	
	Molecule I	Molecule II	Molecule I	Molecule II
χ_L	104·4°	104·3°	105·9°	105·6°
ψ_L	106·5	104·1	106·7	104·8
ω_L	22·2	20·3	23·4	21·7
χ_M	68·0	118·2	68·9	115·0
ψ_M	30·4	28·9	30·3	25·5
ω_M	70·1	84·1	69·3	85·1
χ_N	26·6	32·4	26·7	32·3
ψ_N	115·7	65·2	115·4	66·5
ω_N	83·7	70·5	82·4	69·2

The orientations of the molecules in the crystal are given in Table 3, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; and χ_N, ψ_N, ω_N are the angles which the molecular axes, L, M (see Fig. 3) and the plane normals N make with the orthogonal axes a', b and c'. The axes L were taken through the molecular centres and the mid-points of bonds 1–11 and 1′–11′, and axes M through the molecular centres and atoms 6 and 6′. The orientation angles in tetracene, referred to analogous orthogonal axes, are included in Table 3 for comparison. The angles which the triclinic axes make with the orthogonal reference axes are given in Table 4.

Table 4. *Orientation of the triclinic crystal axes in pentacene*

$\chi_a = 4{\cdot}2°$
$\psi_a = 85{\cdot}8$
$\omega_a = 90{\cdot}0$

$\chi_b = 90{\cdot}0°$
$\psi_b = 0{\cdot}0$
$\omega_b = 90{\cdot}0$

$\chi_c = 111{\cdot}7°$
$\psi_c = 101{\cdot}9$
$\omega_c = 34{\cdot}9$

Intermolecular distances

All the intermolecular separations correspond to normal van der Waals interactions. The shortest

Table 5. *Measured and calculated bond distances in pentacene*

		Kekulé structures		M.O. calculations	
Bond (Fig. 3)	Measured	Calculated	Δ	Calculated	Δ
a	1·358 Å	1·351 Å	0·007 Å	1·369 Å	0·011 Å
b	1·428	1·458	0·030	1·431	0·003
c	1·381	1·370	0·011	1·399	0·018
d	1·409	1·420	0·011	1·413	0·004
e	1·396	1·392	0·004	1·408	0·012
f	1·441	1·458	0·017	1·413	0·028
g	1·453	1·458	0·005	1·458	0·005
h	1·464	1·458	0·006	1·465	0·001
R.m.s. Δ over whole molecule			0·015		0·013

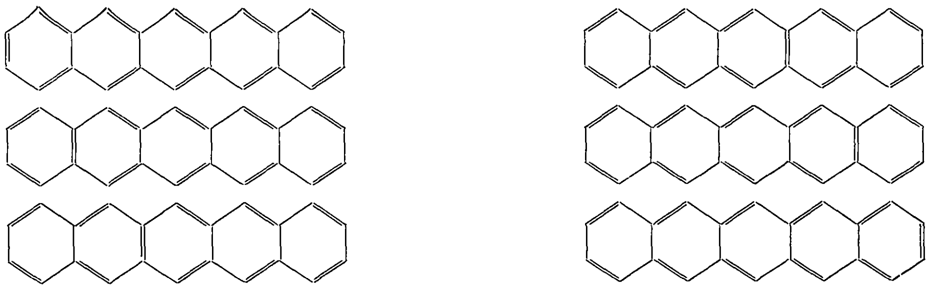

Fig. 4. Kekulé structures for pentacene.

Table 6. *Measured and calculated structure factors*

$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
1 0 0	< 1·7	− 3·1	0 2 4	< 3·2	− 0·4	0 4 $\bar{13}$	< 4·7	− 2·5	1 0 $\bar{4}$	< 2·4	+ 0·7
2	83·0	+ 86·1	3	4·8	− 4·0	$\bar{14}$	< 4·5	+ 1·1	$\bar{5}$	< 2·7	− 0·7
3	< 3·1	− 2·7	2	10·4	+ 9·7	0 5 9	< 4·0	− 0·5	$\bar{6}$	< 3·0	+ 5·9
4	4·4	− 3·8	1	29·6	− 29·6	8	< 4·3	+ 1·5	$\bar{7}$	3·3	− 1·1
5	< 4·5	+ 1·4	$\bar{1}$	< 2·6	− 3·6	7	4·8	− 5·1	$\bar{8}$	< 3·7	+ 0·2
6	< 5·0	+ 2·9	$\bar{2}$	7·2	+ 7·1	6	< 4·8	− 5·3	$\bar{9}$	< 4·0	+ 0·9
7	< 5·3	+ 0·2	$\bar{3}$	8·0	− 9·7	5	< 4·9	+ 2·3	$\bar{10}$	< 4·3	− 3·0
8	< 4·6	+ 0·5	$\bar{4}$	7·2	+ 7·5	4	< 4·9	− 2·4	$\bar{11}$	< 4·6	+ 3·0
0 1 0	< 1·8	+ 4·1	$\bar{5}$	3·8	− 3·3	3	< 4·9	+ 0·7	$\bar{12}$	< 4·9	− 4·9
2	41·9	− 43·5	$\bar{6}$	40·8	− 43·4	2	< 4·8	+ 0·9	$\bar{13}$	13·7	− 11·2
3	7·1	+ 8·2	$\bar{7}$	8·9	− 7·1	1	< 4·8	− 0·8	$\bar{14}$	< 5·2	− 0·4
4	11·5	− 8·9	$\bar{8}$	< 4·3	+ 1·1	$\bar{1}$	< 4·7	− 2·7	$\bar{15}$	< 5·1	+ 0·8
5	< 4·8	+ 0·9	$\bar{9}$	< 4·0	− 2·3	$\bar{2}$	< 4·7	+ 1·9	2 0 13	< 4·9	− 1·1
6	< 3·9	− 1·8	$\bar{10}$	< 4·3	+ 1·4	$\bar{3}$	< 4·7	− 1·6	12	6·5	+ 6·4
7	< 3·7	+ 2·3	$\bar{11}$	< 4·6	− 4·8	$\bar{4}$	< 4·7	+ 1·8	11	< 5·2	+ 1·7
0 0 1	Not obs.	+ 36·1	$\bar{12}$	16·0	+ 15·8	$\bar{5}$	< 4·8	+ 3·8	10	< 5·1	− 0·9
2	32·6	− 30·0	$\bar{13}$	10·4	+ 10·9	$\bar{6}$	8·7	− 10·1	9	< 4·9	+ 0·3
3	24·7	+ 24·1	$\bar{14}$	< 4·8	− 2·8	$\bar{7}$	< 4·9	+ 0·5	8	< 4·6	+ 0·2
4	17·7	− 17·3	$\bar{15}$	< 4·7	+ 1·7	$\bar{8}$	< 4·9	+ 1·2	7	< 4·3	+ 1·1
5	12·7	+ 13·4	0 3 13	< 4·2	+ 3·3	$\bar{9}$	< 4·9	− 1·1	6	23·6	− 23·7
6	16·5	− 17·2	12	< 4·6	+ 1·7	$\bar{10}$	< 4·8	+ 3·4	5	< 3·7	− 7·5
7	10·2	− 10·6	11	< 4·8	− 2·0	$\bar{11}$	< 4·7	− 3·2	4	4·4	+ 5·8
8	5·4	+ 5·3	10	< 4·9	+ 3·3	$\bar{12}$	< 4·5	− 3·7	3	6·1	− 7·6
9	< 3·9	− 3·3	9	< 4·8	− 2·7	$\bar{13}$	< 4·3	− 0·7	2	10·0	+ 11·5
10	< 4·2	+ 2·3	8	< 4·7	+ 4·2	0 6 7	2·9	− 2·8	1	18·4	− 21·0
11	< 4·5	− 3·1	7	13·1	+ 12·4	6	< 3·8	− 0·4	$\bar{1}$	70·1	+ 101·1
12	4·7	+ 6·6	6	< 4·3	− 0·9	5	< 4·1	+ 0·2	$\bar{2}$	31·3	− 32·8
13	5·5	+ 4·3	5	< 4·1	+ 0·4	4	< 4·3	− 1·1	$\bar{3}$	16·2	+ 14·6
14	< 4·8	− 2·5	4	< 3·9	− 0·3	3	< 4·5	+ 0·7	$\bar{4}$	7·3	− 5·2
15	< 4·6	+ 1·0	3	< 3·7	+ 2·2	2	< 4·6	− 0·4	$\bar{5}$	3·3	+ 0·1
			2	< 3·6	− 1·3	1	7·3	− 5·9	$\bar{6}$	< 3·1	+ 1·7
0 1 14	< 4·7	− 1·1	1	6·9	− 9·5	$\bar{1}$	< 4·8	− 0·6	$\bar{7}$	20·8	− 21·7
13	4·8	− 7·3	$\bar{1}$	< 3·3	+ 1·7	$\bar{2}$	< 4·8	0	$\bar{8}$	3·6	+ 3·8
12	< 4·8	− 1·3	$\bar{2}$	< 3·3	+ 0·5	$\bar{3}$	< 4·8	− 0·5	$\bar{9}$	< 4·0	− 1·7
11	< 4·7	+ 2·2	$\bar{3}$	< 3·4	− 0·9	$\bar{4}$	< 4·8	− 1·8	$\bar{10}$	< 4·3	− 0·2
10	< 4·5	− 2·3	$\bar{4}$	< 3·5	+ 1·5	$\bar{5}$	11·3	+ 12·7	$\bar{11}$	< 4·6	+ 0·8
9	4·1	+ 2·3	$\bar{5}$	5·4	− 6·7	$\bar{6}$	8·5	+ 8·4	$\bar{12}$	< 4·9	− 2·9
8	< 3·8	− 1·5	$\bar{6}$	11·7	− 13·1	$\bar{7}$	< 4·7	− 2·7	$\bar{13}$	7·2	+ 7·5
7	3·5	− 5·7	$\bar{7}$	< 3·9	+ 2·9	$\bar{8}$	< 4·6	+ 1·7	$\bar{14}$	< 5·2	+ 1·1
6	< 3·3	+ 3·6	$\bar{8}$	< 4·1	− 2·0	$\bar{9}$	< 4·5	− 0·4	$\bar{15}$	< 5·2	− 0·1
5	< 3·0	+ 2·6	$\bar{9}$	< 4·4	+ 0·5	$\bar{10}$	< 4·3	+ 0·9	3 0 12	11·1	− 12·5
4	< 2·7	− 0·4	$\bar{10}$	< 4·6	− 1·1	$\bar{11}$	< 4·0	− 0·4	11	< 5·1	− 3·9
3	< 2·4	− 1·5	$\bar{11}$	< 4·7	− 2·9	0 7 2	< 3·3	− 1·7	10	< 5·2	+ 3·5
2	< 2·2	+ 0·2	$\bar{12}$	16·4	+ 16·5	1	< 3·6	− 0·3	9	< 5·1	− 2·4
1	< 1·9	+ 4·0	$\bar{13}$	9·1	+ 7·6	$\bar{1}$	< 3·8	− 0·9	8	< 5·0	+ 2·0
$\bar{1}$	< 1·8	− 4·9	$\bar{14}$	< 4·8	− 3·1	$\bar{2}$	< 3·9	0	7	< 4·8	− 1·9
$\bar{2}$	< 2·0	− 0·1	$\bar{15}$	< 4·5	+ 2·5	$\bar{3}$	< 3·9	− 0·1	6	5·2	− 8·4
$\bar{3}$	< 2·2	+ 3·3	0 4 11	< 4·2	− 1·5	$\bar{4}$	< 3·9	− 1·5	5	< 4·2	− 4·4
$\bar{4}$	< 2·4	− 3·2	10	< 4·6	+ 1·3	$\bar{5}$	6·2	+ 4·9	4	< 4·0	+ 2·3
$\bar{5}$	< 2·7	+ 3·9	9	< 4·8	− 2·1	$\bar{6}$	4·3	+ 2·6	3	< 3·7	+ 1·7
$\bar{6}$	13·0	+ 12·5	8	4·4	+ 3·2	$\bar{7}$	< 3·6	− 0·8	2	< 3·5	− 3·1
$\bar{7}$	4·9	+ 2·1	7	26·2	+ 26·4	$\bar{8}$	< 3·5	+ 0·7	1	< 3·3	+ 4·6
$\bar{8}$	< 3·6	− 1·9	6	7·7	+ 7·0				$\bar{1}$	< 3·0	+ 1·6
$\bar{9}$	< 3·9	− 0·7	5	4·6	− 4·3	1 0 14	< 5·0	+ 3·0	$\bar{2}$	< 3·0	− 0·8
$\bar{10}$	< 4·3	− 0·2	4	< 4·6	+ 4·1	13	13·9	− 12·1	$\bar{3}$	< 3·0	− 2·0
$\bar{11}$	< 4·5	+ 0·6	3	< 4·4	− 2·8	12	14·5	− 19·3	$\bar{4}$	< 3·1	+ 4·0
$\bar{12}$	7·1	− 7·7	2	3·5	+ 3·8	11	< 5·0	+ 3·8	$\bar{5}$	4·5	− 5·7
$\bar{13}$	6·8	− 5·4	1	12·6	− 11·2	10	< 4·8	+ 0·6	$\bar{6}$	8·0	+ 7·9
$\bar{14}$	< 4·9	+ 2·6	$\bar{1}$	4·6	+ 5·3	9	< 4·5	− 3·8	$\bar{7}$	21·4	+ 22·3
$\bar{15}$	< 4·7	− 0·8	$\bar{2}$	3·3	− 3·5	8	6·3	+ 5·5	$\bar{8}$	4·4	+ 5·4
0 2 14	< 4·4	− 0·6	$\bar{3}$	3·4	+ 4·0	7	12·0	− 11·5	$\bar{9}$	4·1	− 4·1
13	6·6	− 7·8	$\bar{4}$	3·4	− 2·8	6	22·5	− 23·5	$\bar{10}$	< 4·3	+ 1·5
12	< 4·9	− 2·1	$\bar{5}$	4·2	+ 2·5	5	3·6	− 2·1	$\bar{11}$	< 4·6	− 0·3
11	< 4·9	+ 1·3	$\bar{6}$	13·5	+ 11·4	4	4·3	+ 6·3	$\bar{12}$	< 4·9	− 2·7
10	< 4·8	+ 0·1	$\bar{7}$	< 4·5	+ 1·8	3	3·2	− 3·1	$\bar{13}$	7·2	+ 8·7
9	< 4·6	+ 0·5	$\bar{8}$	< 4·6	0	2	< 2·2	+ 0·4	$\bar{14}$	6·0	+ 7·5
8	< 4·3	+ 2·0	$\bar{9}$	< 4·7	− 0·4	1	< 1·9	+ 3·3	$\bar{15}$	< 5·2	− 1·5
7	9·1	− 9·3	$\bar{10}$	< 4·8	+ 1·2	$\bar{1}$	< 1·6	+ 5·6	$\bar{16}$	< 5·0	+ 0·5
6	13·4	− 14·7	$\bar{11}$	< 4·9	− 1·8	$\bar{2}$	< 1·8	− 3·6	4 0 11	< 4·6	+ 2·3
5	4·9	+ 6·1	$\bar{12}$	6·8	− 8·4	$\bar{3}$	< 2·1	+ 2·3	10	< 5·4	− 0·1

Table 6 (*cont.*)

h k	*l*	F_o	F_c
4 0	9	< 5·2	+ 0·2
	8	< 5·2	0
	7	< 5·1	+ 1·0
	6	8·1	− 6·7
	5	11·7	−15·3
	4	< 3·8	+ 1·6
	3	< 4·3	+ 1·2
	2	< 4·1	− 2·8
	1	< 4·0	+ 3·4
	$\bar{1}$	< 3·7	+ 1·8
	$\bar{2}$	< 3·7	+ 0·2
	$\bar{3}$	< 3·6	+ 1·5
	$\bar{4}$	< 3·7	+ 0·5
	$\bar{5}$	< 3·7	− 3·6
	$\bar{6}$	< 3·8	+ 4·3
	$\bar{7}$	22·7	−22·0
	$\bar{8}$	7·6	−12·0
	$\bar{9}$	< 4·4	+ 4·4
	$\overline{10}$	< 4·6	− 3·4
	$\overline{11}$	< 4·8	+ 2·7
	$\overline{12}$	< 5·0	− 3·0
	$\overline{13}$	< 5·1	+ 0·8
	$\overline{14}$	5·3	+ 7·6
	$\overline{15}$	< 5·2	+ 0·8
	$\overline{16}$	< 5·0	− 0·2
5 0	9	< 4·6	− 0·8
	8	< 5·0	+ 1·5
	7	< 5·1	− 0·7
	6	5·2	+ 0·4
	5	5·9	+ 6·0
5 0	4	< 5·2	− 0·1
	3	< 4·9	0
	2	< 4·8	+ 0·2
	1	< 4·6	+ 0·2
	$\bar{1}$	< 4·4	+ 0·3
	$\bar{2}$	< 4·3	+ 1·6
	$\bar{3}$	< 4·3	− 2·3
	$\bar{4}$	< 4·2	+ 1·5
	$\bar{5}$	< 4·3	− 1·7
	$\bar{6}$	< 4·3	+ 1·0
	$\bar{7}$	4·4	+ 4·7
	$\bar{8}$	4·5	+ 1·2
	$\bar{9}$	< 4·7	− 1·5
	$\overline{10}$	< 4·9	− 1·6
	$\overline{11}$	< 5·0	+ 2·5
	$\overline{12}$	< 5·1	− 3·7
	$\overline{13}$	8·9	+ 4·4
	$\overline{14}$	16·2	+19·5
	$\overline{15}$	< 5·1	+ 2·5
	$\overline{16}$	< 4·8	− 2·4
6 0	7	< 4·5	0
	6	< 4·9	− 0·8
	5	< 5·1	− 2·1
	4	< 5·2	− 3·0
	3	< 5·2	+ 1·8
	2	< 5·2	− 0·4
	1	< 5·1	− 1·1
	$\bar{1}$	17·0	−13·4
	$\bar{2}$	7·9	−12·8
	$\bar{3}$	< 4·9	+ 5·5
6 0	$\bar{4}$	< 4·8	0
	$\bar{5}$	< 4·8	− 2·4
	$\bar{6}$	< 4·9	+ 2·5
	$\bar{7}$	11·9	− 8·0
	$\bar{8}$	12·1	−15·8
	$\bar{9}$	< 5·0	− 1·1
	$\overline{10}$	< 5·1	+ 1·0
	$\overline{11}$	< 5·2	− 1·2
	$\overline{12}$	< 5·2	+ 0·8
	$\overline{13}$	< 5·2	− 2·0
	$\overline{14}$	< 5·1	+ 2·8
	$\overline{15}$	< 4·9	+ 4·0
7 0	5	6·9	+ 6·3
	4	< 4·6	+ 3·9
	3	< 4·8	− 2·1
	2	< 5·0	+ 0·5
	1	< 5·2	+ 0·2
	$\bar{1}$	< 5·2	+ 0·9
	$\bar{2}$	< 5·2	+ 1·9
	$\bar{3}$	< 5·2	0
	$\bar{4}$	< 5·2	− 0·1
	$\bar{5}$	< 5·2	− 0·1
	$\bar{6}$	< 5·2	0
	$\bar{7}$	< 5·2	+ 0·6
	$\bar{8}$	7·3	− 7·8
	$\bar{9}$	< 5·2	− 3·6
	$\overline{10}$	< 5·2	+ 0·7
	$\overline{11}$	< 5·1	− 0·8
	$\overline{12}$	< 5·1	+ 0·9
7 0	$\overline{13}$	< 4·9	− 2·1
	$\overline{14}$	10·8	+ 7·9
	$\overline{15}$	< 4·4	+ 7·9
8 0	2	< 4·1	+ 0·8
	1	< 4·3	− 0·6
	$\bar{1}$	6·7	− 0·5
	$\bar{2}$	9·2	−10·1
	$\bar{3}$	< 4·9	− 1·0
	$\bar{4}$	< 5·0	+ 2·8
	$\bar{5}$	< 5·0	− 2·0
	$\bar{6}$	< 5·0	+ 1·3
	$\bar{7}$	< 5·0	− 1·6
	$\bar{8}$	< 5·0	− 4·1
	$\bar{9}$	< 4·9	− 2·7
	$\overline{10}$	< 4·9	+ 0·2
	$\overline{11}$	< 4·8	+ 0·1
	$\overline{12}$	< 4·6	− 0·6
	$\overline{13}$	< 4·4	+ 0·6
9 0	$\bar{1}$	< 3·9	+ 0·1
	$\bar{2}$	< 3·9	+ 1·1
	$\bar{3}$	< 3·9	+ 1·0
	$\bar{4}$	< 4·0	0
	$\bar{5}$	< 4·2	+ 0·1
	$\bar{6}$	< 4·2	− 0·2
	$\bar{7}$	< 4·2	+ 0·6
	$\bar{8}$	7·6	− 4·1
	$\bar{9}$	< 4·1	− 6·4
	$\overline{10}$	< 4·0	+ 0·8
	$\overline{11}$	< 4·0	− 0·1

distance between molecule I and molecule II is 3·66 Å. Between molecules related by translation *b*, the minimum separation is 3·71 Å, and between those related by translation *c*, 3·94 Å. The minimum distance between molecules I or II and the molecules II or I one translation along *c* is 3·64 Å.

The corresponding minimum intermolecular approach distances in tetracene are 3·70, 3·68, 3·86 and 3·75 Å.

Standard deviations

The standard deviations of the atomic positions were calculated from Cruickshank's (1949) formulae. The r.m.s. values for all the atoms were

$$\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}030 \text{ Å},$$

so that the estimated standard deviations of the measured bond lengths are 0·042 Å. This value may be compared with the r.m.s. deviation of the individual bond distances from the mean distances, which is 0·031 Å. The standard deviations of the mean bond distances are 0·021 Å for bonds *a*, *b*, *c*, *d*, *e*, and 0·030 Å for bonds *f*, *g*, *h*.

Discussion

The close similarity to the preceding members of the benzologous series, naphthalene, anthracene and tetracene, is the most interesting feature of the crystal structure of pentacene. As with tetracene, the slight deviation from monoclinic symmetry results in a closer packing of the pentacene molecules in the crystal, and a corresponding increase in density (of about 2%).

Both pentacene molecules in the unit cell are completely planar within the limits of experimental error, the maximum deviation from the mean molecular planes being 0·079 Å, and the root-mean-square deviation 0·030 Å.

On the basis of the standard deviations of the bond distances given above, it was not considered that the molecule deviated from symmetry *mmm*, and the mean bond lengths and valency angles are shown in Fig. 3(*b*). The bond distances are quoted to 0·001 Å for comparison with the calculated distances below, although the accuracy, as indicated by the standard deviations, is not nearly as good as this. A calculation of the bond lengths for comparison with the measured distances was made from the six non-excited valence bond structures for pentacene (Fig. 4). The percentage double-bond character was calculated for each bond in the molecule, and the corresponding bond lengths derived from a correlation curve drawn through the points (0, 1·50), (0·33, 1·42), (0·5, $1{\cdot}39_2$), (1·0, $1{\cdot}33_7$). π-Bond orders calculated by the LCAO molecular orbital method are also available (*Dictionary of Values of Molecular Constants*, 1955; Baldock, Berthier & Pullman, 1949), and calculated bond distances were obtained from the order-length curve described by Goodwin & Vand (1955). The bond lengths calculated by the valency bond and by the molecular orbital methods are compared in Table 5 with the measured distances; the differences (Δ) between measured and calculated values are included in the table. The general variation of the measured bond lengths is well reproduced in both sets of calculated distances. The individual agreements are also remarkably good; for the valence-bond distances, the maximum difference between measured and calculated values is 0·030 Å, and the root-mean-square deviation 0·015 Å, while the corresponding deviations for the molecular orbital method are 0·028 and 0·013 Å. Both sets of calculated distances therefore agree equally well with the measured values.

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The Crystal Structure of *N*-Chloro-Succinimide

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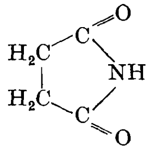
N-chloro-succinimide, $C_4H_4ClNO_2$, forms orthorhombic crystals with $a = 6{\cdot}41$, $b = 7{\cdot}11$, $c = 11{\cdot}69$ Å, space group $P2_12_12_1$ and $Z = 4$. The structure has been solved by application of the heavy-atom method to the bromine isomorph and refined by two-dimensional projections on the (100) and (010) planes. The molecular bond lengths and angles are bilaterally symmetrical, but the molecule is significantly aplanar. A 'close' intermolecular approach of 2·88 Å has been observed between Cl and O.

Introduction

Preliminary crystallographic work on the heterocyclic compound succinimide (I) and its *N*-chloro and *N*-bromo derivatives had revealed that the latter two compounds form an isomorphous pair (Brown, 1956).


(1)

Experimental

N-chloro-succinimide (N.C.S.), $C_4H_4ClNO_2$, mol. wt. 133·5, was made from succinimide by the method of Hirst & Macbeth (1922). It is a colourless crystalline solid melting at 148 °C. Crystals were obtained from benzene by slow evaporation as small orthorhombic plates tabular on {001} with the additional forms {111} (always present), {110} (common), {011} (rare) and {101} (very rare). Optic orientation: $X = a$, $Y = b$, $Z = c$; optic sign negative. Refractive indices,

$$n_X = 1{\cdot}492 \pm 0{\cdot}002,\ n_Y = 1{\cdot}625 \pm 0{\cdot}002,$$
$$n_Z = 1{\cdot}669 \pm 0{\cdot}002\ ,$$

measured by the oil-immersion method. Unit-cell dimensions, assuming the Cu $K\alpha$ wavelengths of Lonsdale (1950):

$$a = 6{\cdot}412 \pm 0{\cdot}003, b = 7{\cdot}111 \pm 0{\cdot}015, c = 11{\cdot}691 \pm 0{\cdot}004 \text{ Å}.$$

Systematic absences: $h00$, $0k0$, $00l$ for odd indices; space group $P2_12_12_1$.

$$V = 533 \text{ Å}^3,\ Z = 4,\ d(\text{calc.}) = 1{\cdot}66,\ d(\text{obs.}) = 1{\cdot}65 \text{ g.cm.}^{-3}$$
(Stefl., 1915).

Absorption coeff. for Cu $K\alpha$, $\mu = 55$ cm.$^{-1}$.

N-bromo-succinimide (N.B.S.), $C_4H_4BrNO_2$, mol.wt. 178·0, was obtained ready-made as crystals melting at 174 °C. Crystals from water were thin {001} plates showing also the faces {111} and {011}. Optic orientation: $X = b$, $Y = a$, $Z = c$; optic sign negative. Refractive indices:

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