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The Crystal and Molecular Structure of Tetracene

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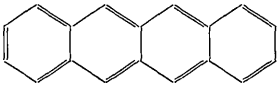
Crystals of tetracene are triclinic, with two molecules in a unit cell of dimensions $a = 7\cdot98$, $b = 6\cdot14$, $c = 13\cdot57$ Å, $\alpha = 101\cdot3°$, $\beta = 113\cdot2°$, $\gamma = 87\cdot5°$, space group $P\bar{1}$. The structure, which has been determined from projections along the a and b axes, is closely related to the structures of naphthalene and anthracene. 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 tetracene (I), the next higher benzologue in the naphthalene–anthracene series, has been undertaken to obtain an accurate account of the dimensions of the molecule, and of the intermolecular separations. The crystals of tetracene are triclinic, but the structure is closely related to the monoclinic naphthalene and anthracene structures; in particular the long axes of the molecules lie close to the c-axis, as in the two lower members of the series.


(I)

Crystals of tetracene consisted of extremely thin plates with only the (001) face developed, and it was possible to record only a rather small proportion of the reflexions theoretically observable. As efforts to grow better crystal specimens were unsuccessful, the paucity of data has precluded the attainment of results as accurate as in the naphthalene and anthracene analyses (Abrahams, Robertson & White, 1949; Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956, 1957*a*, *b*), and the present analysis of the tetracene structure has been confined to the projections along the a and b crystal axes. Nevertheless the bond lengths in the tetracene molecule have been determined with sufficient accuracy to allow a comparison to be made with the distances predicted by quantum-mechanical theories.

Experimental

Crystals of tetracene obtained by crystallization from xylene (Clar, 1942) consisted of extremely thin orange-red leaflets. Recrystallization from tetralin gave very small, more evenly developed specimens, but these were invariably twinned. Slow sublimation at 170 °C. also gave twinned crystals. The crystals were very friable, and attempts to separate the twins by mechanical means were unsuccessful. The very thin plate-like crystals obtained from xylene, in which (001) is the only face developed, were therefore used in the X-ray investigation.

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 values obtained for the axial lengths were in good agreement with previous results (Hertel & Bergk, 1936). The density was determined by flotation in aqueous potassium–iodide solution. The crystal data were:

Tetracene, $C_{18}H_{12}$; molecular weight $= 228\cdot3$; melting point $= 357$ °C.
Triclinic,

$$a = 7\cdot98 \pm 0\cdot02,\; b = 6\cdot14 \pm 0\cdot02,\; c = 13\cdot57 \pm 0\cdot04 \text{ Å};$$
$$\alpha = 101\cdot3 \pm 0\cdot5°,\; \beta = 113\cdot2 \pm 0\cdot5°,\; \gamma = 87\cdot5 \pm 0\cdot5°.$$

Volume of the unit cell $= 599\cdot2$ Å^3.
Density, calculated (with $Z = 2$) $= 1\cdot257$, measured $= 1\cdot24$ g.cm.$^{-3}$.
Absorption coefficient for X-rays, $\lambda = 1\cdot542$ Å, $\mu = 6\cdot55$ cm.$^{-1}$.
Total number of electrons per unit cell $= F(000) = 240$.
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 was used to correlate strong and weak reflexions (Robertson, 1943). The range of intensities measured was about 1500 to 1 for the $0kl$ zone and 2000 to 1 for the $h0l$ zone, the estimates being made visually. The crystal used for the $0kl$ photographs had a cross-section normal to the a-axis of $0\cdot81 \times 0\cdot005$ mm., while that used for the $h0l$ films had a cross-section normal to the b-axis of $0\cdot86 \times 0\cdot005$ mm. It was therefore considered that it would be important to apply cor-

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rections for absorption. However it was found that, due to the extreme thinness of the crystal specimens, the mean path through the crystal was almost constant for all the observed reflexions, with the exception of six. Approximate absorption corrections were therefore made for only these six planes.

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.

52 *0kl* and 71 *h0l* reflexions were observed, representing about 27 and 30% 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.

Structure analysis

Determination of the space group

Since crystals of tetracene belong to the triclinic system, the space group must be $P1$ or $P\bar{1}$, and these cannot be distinguished from their diffraction patterns. A pyroelectric test did not give a conclusive result. An attempt was therefore made to determine the space group on the basis of a close similarity to the naphthalene and anthracene structures.

It is interesting that there should be a change in the crystal structure from monoclinic to triclinic on passing from anthracene to tetracene and pentacene (which is described in the following paper). The change in molecular structure is precisely the same as that between naphthalene and anthracene, which are crystallographically very similar, and show the gradation in properties to be expected from a benzologous series. A comparison of the axial lengths of the four compounds, however, reveals quite definite similarities (Table 1). The *a*-axis shows a slight variation, due to slightly different tilts of the molecules, and the *b*-axis remains practically constant. The *c*-axis, however, expands by an increment of approximately 2·45 Å in passing to successive members of the series, and this is just sufficient to accommodate the extra benzene ring if the long axes of the molecules lie close to the *c*-axes in every case. With regard to the angles, the similarity is again revealed by the fact that the α and γ angles in tetracene and pentacene differ from right angles by relatively small amounts. A comparison of the melting points (Table 1) also shows the continuous gradation to be expected from a benzologous series.

Table 1. *Comparison of naphthalene, anthracene, tetracene and pentacene*

	Naphthalene	Anthracene	Tetracene	Pentacene
Melting point (°C.)	80	217	357	(high)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
a (Å)	8·24	8·56	7·98	7·93
b (Å)	6·00	6·04	6·14	6·14
c (Å)	8·66	11·16	13·57	16·03
α (°)	90·0	90·0	101·3	101·9
β (°)	122·9	124·7	113·2	112·6
γ (°)	90·0	90·0	87·5	85·8

More fundamental and direct evidence regarding the orientation of the molecules in these crystals is obtained from a study of the *c*-axis rotation photographs, which have already been reproduced (Robertson, 1953). In naphthalene the third and fourth layer lines are enhanced, in anthracene the fourth and fifth, in tetracene the fifth and sixth, and in pentacene the sixth and seventh. This enhancement of the reflexions occurs in precisely the same region of the photographs in each case, clearly demonstrating an invariant feature of the structure. The fundamental periodicity required is about 2·45 Å in all the structures, and this corresponds exactly to the average width of the benzene ring in aromatic structures. Further analysis of the high order reflexions shows that the smaller periodicity of 1·22 Å is also present.

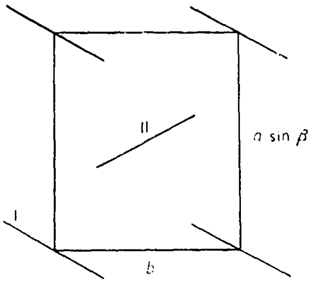


Fig. 1. Arrangement of anthracene molecules in the *c*-axis projection.

It seemed apparent therefore that the arrangement of the molecules in the crystal lattice of tetracene would be closely analogous to the arrangement in the anthracene lattice, without however maintaining the monoclinic symmetry. In anthracene the arrangement of the molecules in the projection along the *c*-axis is as shown in Fig. 1. Molecule I, which is situated on the centre of symmetry at (0, 0, 0), is transformed by the glide plane operation into molecule II on the symmetry centre at $(\frac{1}{2}, \frac{1}{2}, 0)$. The symmetry causes the *h0l* reflexions to be absent when h is odd. In tetracene although *10l* and *30l* spectra are present, they are quite weak in comparison with the *20l* reflexions. This suggests that, although the central molecule (II) in tetracene is not related to molecule I by any symmetry elements, it probably lies very close to a symmetry-related position. There would thus appear to be two unrelated molecules in the unit cell, the structure conforming to space group $P1$.

The tetracene molecule, however, possesses a centre of symmetry which may or may not be used in forming the structure. If we assume that it is used, and place the two tetracene molecules on centres of symmetry at the origin and centre in Fig. 1, that is at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0), we have an arrangement in the unit cell bearing an even closer resemblance to the anthracene structure. This structure has space group $P\bar{1}$, with pseudo $P2_1/a$ symmetry. It seemed reasonable to accept this space group of higher symmetry for at least the first trial structure. It may be noted that the asymmetric unit consists of two half-molecules.

Analysis of the structure

A comparison of Weissenberg films of anthracene and tetracene showed a marked similarity in the intensities of corresponding reflexions. This suggested a trial model having the same tilt as the anthracene molecule with respect to the (010) plane.

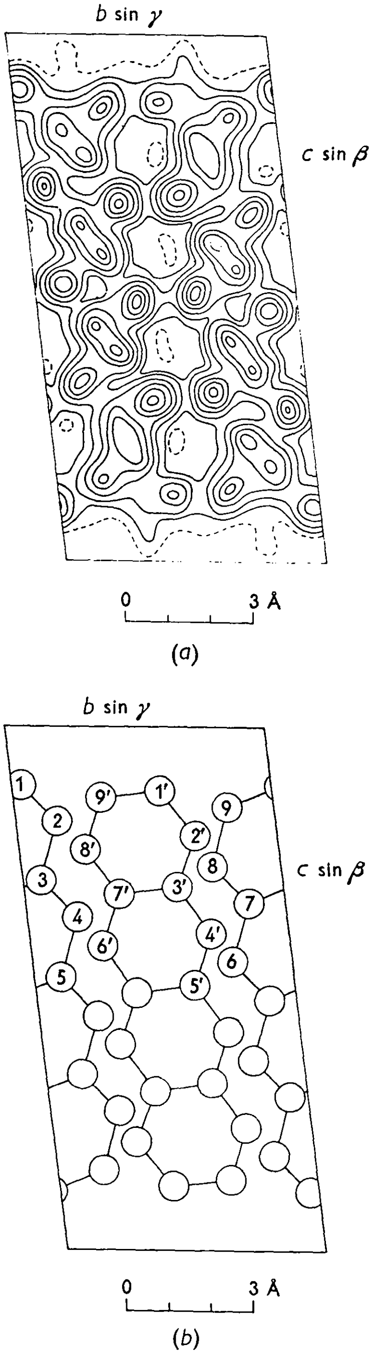
This model automatically gave rise to $h0l$ systematic absences. After several adjustments had been made in the orientations of the two half-molecules, in an attempt to increase the structure amplitudes of the h odd planes, a set of atomic coordinates was found which gave some measure of agreement between the observed and calculated values of the structure factors, the discrepancy for all the observed planes being 36·4%.

Successive electron-density projections on (010) failed to achieve any significant refinement, and attention was therefore directed to the projection on (100). An approximate orientation was taken from the best trial structure in the first projection, and adjusted to secure agreement between the observed and calculated structure factors. Atomic coordinates were found which gave a discrepancy of 32·9% over all the observed $0kl$ reflexions. A Fourier series was summed using measured structure amplitudes and calculated signs, new atomic centres were chosen on the resulting electron-density map, and structure factors were recalculated with these revised coordinates. The discrepancy factor was 27·8%. A second Fourier synthesis reduced this value to 21·0%.

The a-axis projection had thus given reliable values for the y- and z-coordinates of the atoms. Using the z-coordinates and the orientation of the molecule calculated from this projection on the basis of C–C bond distances of about 1·40 Å, approximate coordinates were obtained for the projection along the b-axis. These parameters were very similar to those of the first trial structure in the [010] projection, except that the second molecule was reversed from its previous position. Much better agreement was now obtained between measured and calculated structure factors, the discrepancy factor over the observed $h0l$ reflexions being 23·5%.

Refinement of the structure

From this point further refinement proceeded by computing successive difference syntheses, with $(F_o - F_c)$ as coefficients, the scattering curve for carbon of Berghuis *et al.* (1955) being introduced, corrected for thermal vibration with $B = 4{\cdot}2$ Å^2 for all the atoms. The positional and isotropic temperature parameters were then altered to minimize the slopes and difference electron-densities at the atomic centres. Both projections were refined simultaneously, the mean values of the shifts in z-coordinates being taken at each stage. The first difference map revealed regions



(a)

(b)

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

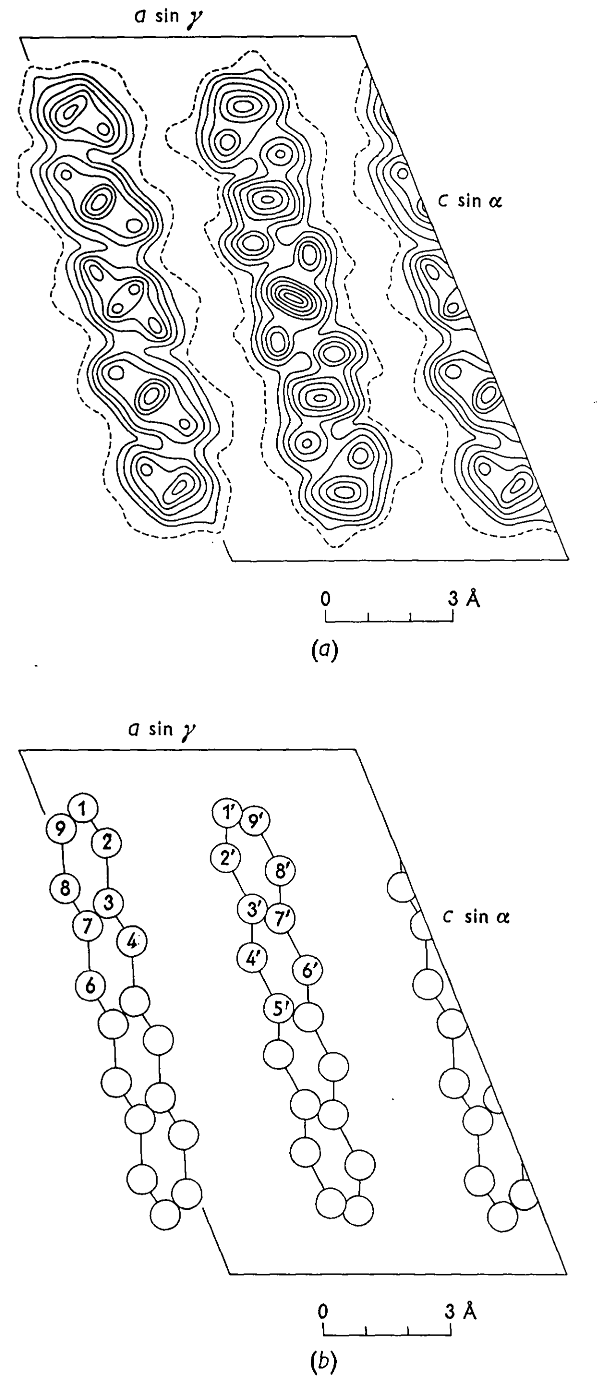


Fig. 3. (*a*) Electron-density projection along the *b*-axis. Contours as in Fig. 2. (*b*) Projection of the structure along [010].

of positive density close to the positions expected for hydrogen atoms, and a contribution from the hydrogens was therefore introduced, coordinates (Table 2) being chosen by assuming that they lay on the ring diagonals with C–H distances of 1·08 Å. After three cycles of refinement the discrepancy factors were reduced to 10·7% for the 0*kl* zone and 9·8% for the *h*0*l* zone, and no further significant changes in positional or temperature parameters were indicated. Final measured and calculated structure factors are listed in Table 7, and final F_o syntheses, computed with measured structure amplitudes and calculated signs, are shown in Figs. 2 and 3.

Table 2. *Assumed hydrogen fractional coordinates*

Atom	x	y	z
H 1	0·168	0·100	0·470
2	0·212	0·317	0·349
4	0·176	0·354	0·165
6	−0·134	−0·388	0·022
8	−0·095	−0·425	0·202
9	0·011	−0·279	0·400
1′	0·531	0·650	0·454
2′	0·425	0·852	0·305
4′	0·386	0·870	0·114
6′	0·649	0·113	0·072
8′	0·685	0·089	0·253
9′	0·655	0·246	0·425

Coordinates, molecular dimensions and orientation

The final positional and temperature parameters of the carbon atoms are listed in Table 3, 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'. The orthogonal axes consisted of the b crystal axis, a' the projected a-axis ($a \sin \gamma$), and a third axis c' perpendicular to a' and b.

The equations of the mean molecular planes are

Molecule I at (0, 0, 0):

$$0{\cdot}8936X' - 0{\cdot}4293Y' + 0{\cdot}1314Z' = 0$$

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

$$0{\cdot}8453X' + 0{\cdot}3987Y' + 0{\cdot}3556Z' = 4{\cdot}6628$$

and the deviations of the atoms from these planes are listed in the final column of Table 3.

The bond lengths and valency angles, calculated from the coordinates of Table 3, are shown in Fig. 4(*a*). These values suggested that the symmetry of the tetracene molecule did not differ from *mmm*, and the mean values of the bond distances and angles are shown in Fig. 4(*b*).

The orientations of the molecules in the crystal are given in Table 4, 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. 4) 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 1–9 and 1′–9′, and axes M through the molecular centres and atoms 5 and 5′. The orientation angles in anthracene, referred to analogous orthogonal axes (Sinclair, Robertson & Mathieson, 1950) are included in Table 4 for comparison. The

Table 3. *Final positional and temperature parameters, and deviations* (Δ) *from the mean planes*

Atom	x	y	z	X'	Y'	Z'	B	Δ
C 1	0·1194	0·0331	0·3890	−1·080	−0·787	4·761	4·6 Å^2	−0·002 Å
2	0·1494	0·1564	0·3219	−0·491	0·159	3·940	4·6	+0·011
3	0·0811	0·0724	0·2040	−0·419	−0·068	2·497	4·6	−0·017
4	0·1094	0·1899	0·1360	0·162	0·843	1·665	4·2	+0·002
5	0·0467	0·1089	0·0211	0·262	0·629	0·258	4·2	−0·002
6	−0·0691	−0·2228	0·0516	−0·821	−1·529	0·632	4·2	+0·006
7	−0·0035	−0·1405	0·1637	−0·883	−1·298	2·004	4·6	+0·032
8	−0·0378	−0·2646	0·2355	−1·532	−2·262	2·883	4·6	−0·019
9	0·0267	−0·1832	0·3483	−1·607	−2·039	4·263	4·6	−0·001
1′	0·5428	0·5680	0·3787	2·349	2·672	4·635	4·6	+0·036
2′	0·4799	0·6861	0·2930	2·295	3·603	3·586	4·6	−0·011
3′	0·4997	0·5864	0·1947	2·967	3·258	2·383	4·6	−0·008
4′	0·4425	0·7007	0·1048	2·980	4·178	1·283	4·2	−0·022
5′	0·4638	0·6140	0·0052	3·671	3·918	0·064	4·2	+0·025
6′	0·5948	0·2758	0·0832	4·307	1·680	1·018	4·2	+0·010
7′	0·5758	0·3649	0·1811	3·644	1·961	2·217	4·6	−0·012
8′	0·6306	0·2568	0·2685	3·625	1·084	3·287	4·6	+0·002
9′	0·6148	0·3374	0·3645	2·997	1·319	4·462	4·6	−0·017

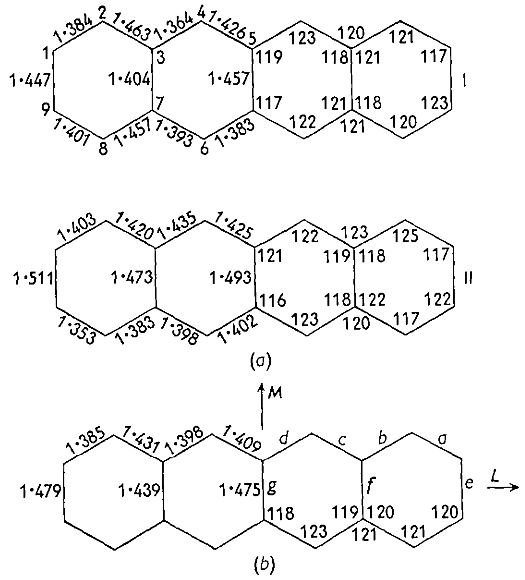


Fig. 4. (*a*) Measured bond lengths (Å) and valency angles (degrees). (*b*) Mean bond lengths and valency angles.

angles which the triclinic axes make with the orthogonal reference axes are given in Table 5.

Table 4. *Orientation of the molecules in tetracene and anthracene*

	Tetracene		
	Molecule I	Molecule II	Anthracene
χ_L	105·9°	105·6°	119·7°
ψ_L	106·7	104·8	97·0
ω_L	23·4	21·7	30·6
χ_M	68·9	115·0	71·3
ψ_M	30·3	25·5	26·6
ω_M	69·3	85·1	71·8
χ_N	26·7	32·3	36·2
ψ_N	115·4	66·5	115·5
ω_N	82·4	69·2	66·2

Table 5. *Orientation of the triclinic crystal axes in tetracene*

$\chi_a = 2·5°$	$\chi_b = 90·0°$	$\chi_c = 112·7°$
$\psi_a = 87·5$	$\psi_b = 0·0$	$\psi_c = 101·3$
$\omega_a = 90·0$	$\omega_b = 90·0$	$\omega_c = 35·6$

Intermolecular distances

All the intermolecular separations correspond to normal van der Waals interactions. The shortest distance between molecule I and molecule II is 3·70 Å. Between molecules related by translation *b*, the minimum separation is 3·68 Å, and between those related by translation *c*, 3·86 Å. The minimum distance between molecules I and II and the molecules II or I one translation along *c* is 3·75 Å.

Table 6. *Measured and calculated bond distances* (*Å*) *in tetracene*

		Kekulé structures		M.O. calculations	
Bond (Fig. 4(*b*))	Measured	Calculated	Δ	Calculated	Δ
a	1·385	1·355	0·030	1·369	0·016
b	1·431	1·450	0·019	1·431	0
c	1·398	1·378	0·020	1·400	0·002
d	1·409	1·409	0	1·411	0·002
e	1·479	1·450	0·029	1·413	0·066
f	1·439	1·450	0·011	1·457	0·018
g	1·475	1·450	0·025	1·463	0·012
R.m.s. Δ over whole molecule			0·021		0·022

The corresponding minimum intermolecular approach distances in anthracene are 3·77, 3·80, 4·06 and 3·67 Å (Robertson, 1933).

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

$\sigma(x) = \sigma(y) = \sigma(z) = 0·020$ Å, so that the estimated standard deviations of the measured bond lengths are

Table 7. *Measured and calculated structure factors*

h k l	$\lvert F_o\rvert$	F_c
1 0 0	< 1·4	− 3·4
2	87·2	+86·3
3	< 2·4	− 5·7
4	3·8	− 3·5
5	< 3·5	+ 0·1
6	< 4·0	− 1·8
7	< 4·1	+ 0·4
8	< 3·7	+ 1·0
0 1 0	< 1·8	+ 1·5
2	39·9	−38·2
3	5·7	+ 5·5
4	8·1	− 5·8
5	< 4·9	+ 0·5
6	< 4·8	− 1·3
7	< 3·5	+ 1·5
0 0 1	35·0	+36·9
2	28·8	−30·1
3	20·9	+20·7
4	14·0	−14·7
5	16·2	+17·7
6	11·8	+11·2
7	4·4	− 5·8
8	< 3·0	+ 3·5
9	3·2	− 2·1
10	5·8	+ 4·0
11	6·9	+ 5·6
12	< 3·6	− 1·1
13	< 3·4	+ 0·6
14	< 3·0	− 0·1
15	< 2·5	+ 0·3
0 1 14	< 3·5	− 0·1
13	< 4·1	− 0·5
12	< 4·5	− 0·8
11	4·7	− 5·1
10	< 4·5	− 1·4
9	< 4·4	+ 0·5
8	< 4·0	− 2·4
7	< 3·7	+ 1·8
6	< 3·4	+ 3·7
5	< 3·1	+ 1·4
4	< 2·7	− 0·6
3	< 2·5	− 1·5
2	< 2·2	+ 2·7
1	< 1·8	− 0·6
$\bar{1}$	3·1	− 1·6
$\bar{2}$	< 1·9	− 0·5
$\bar{3}$	2·8	+ 2·9
$\bar{4}$	2·8	− 3·7
$\bar{5}$	10·9	−10·0
$\bar{6}$	3·1	− 3·0
$\bar{7}$	< 3·5	+ 1·5
$\bar{8}$	< 3·8	0
$\bar{9}$	< 4·1	+ 0·4
$\overline{10}$	4·3	− 5·0
$\overline{11}$	6·7	− 6·7
$\overline{12}$	< 4·6	+ 1·4
$\overline{13}$	< 4·4	+ 0·8
$\overline{14}$	< 3·9	− 1·4
$\overline{15}$	< 3·3	+ 1·6
0 2 14	< 2·9	− 1·1
13	< 3·6	+ 0·6
12	< 4·2	− 1·1
11	6·7	− 7·2
10	< 4·6	− 1·2
9	< 4·5	+ 0·4
8	< 4·4	− 0·8
7	< 4·1	+ 0·6
6	5·5	+ 6·7
5	16·0	+12·0
4	< 3·3	− 2·2
0 2 3	< 3·0	− 3·5
2	8·6	+ 9·6
1	26·4	−26·5
$\bar{1}$	3·5	− 2·8
$\bar{2}$	7·8	+ 8·6
$\bar{3}$	8·3	− 9·2
$\bar{4}$	5·1	+ 4·4
$\bar{5}$	35·7	+37·0
$\bar{6}$	5·8	+ 6·7
$\bar{7}$	< 3·6	− 2·5
$\bar{8}$	< 3·9	+ 1·5
$\bar{9}$	< 4·2	− 3·5
$\overline{10}$	11·8	+14·2
$\overline{11}$	6·7	+10·2
$\overline{12}$	< 4·5	− 3·1
$\overline{13}$	< 4·4	+ 1·3
$\overline{14}$	< 3·9	− 0·7
$\overline{15}$	< 3·3	+ 1·0
0 3 13	< 2·8	+ 0·2
12	< 3·5	− 0·1
11	< 4·1	+ 2·9
10	< 4·5	+ 1·4
9	< 4·5	− 1·5
8	< 4·6	+ 3·0
7	< 4·5	− 4·3
6	10·9	−11·3
5	< 4·1	− 1·5
4	< 3·9	+ 0·2
3	< 3·6	+ 0·9
2	< 3·5	− 1·2
1	5·8	− 4·3
$\bar{1}$	< 3·2	+ 0·5
$\bar{2}$	< 3·2	− 0·8
$\bar{3}$	< 3·3	− 1·3
$\bar{4}$	4·7	+ 5·2
$\bar{5}$	11·4	+10·1
$\bar{6}$	< 3·7	− 2·3
$\bar{7}$	< 4·0	+ 1·5
$\bar{8}$	< 4·2	+ 0·5
$\bar{9}$	< 4·5	− 0·6
$\overline{10}$	11·8	+13·2
$\overline{11}$	5·8	+ 7·9
$\overline{12}$	< 4·5	− 2·3
$\overline{13}$	< 4·2	+ 1·1
$\overline{14}$	< 3·7	0
$\overline{15}$	< 3·0	− 2·0
0 4 11	< 3·1	− 1·8
10	< 3·7	+ 1·8
9	< 4·2	− 2·1
8	< 4·5	+ 2·4
7	5·8	− 4·3
6	25·8	−25·0
5	8·3	− 5·9
4	< 4·5	+ 3·6
3	< 4·3	− 4·1
2	< 4·2	+ 3·6
1	8·3	− 9·8
$\bar{1}$	< 3·9	+ 3·8
$\bar{2}$	< 3·9	− 5·9
$\bar{3}$	< 4·0	+ 5·1
$\bar{4}$	4·3	− 4·8
$\bar{5}$	10·2	−11·1
$\bar{6}$	< 4·3	+ 0·7
$\bar{7}$	< 4·4	− 1·0
$\bar{8}$	< 4·5	+ 0·6
$\bar{9}$	< 4·6	− 1·5
$\overline{10}$	6·4	− 8·1
$\overline{11}$	< 4·5	− 2·5
$\overline{12}$	< 4·3	+ 1·3
$\overline{13}$	< 3·8	− 0·6
0 4 $\overline{14}$	< 3·3	− 0·4
0 5 9	< 3·1	+ 0·3
8	< 3·6	− 0·7
7	< 4·0	+ 1·2
6	6·3	+ 5·9
5	< 4·5	+ 2·7
4	< 4·5	− 1·9
3	< 4·6	+ 1·1
2	< 4·6	+ 0·1
1	< 4·5	− 0·4
$\bar{1}$	< 4·5	− 2·2
$\bar{2}$	< 4·5	+ 2·3
$\bar{3}$	< 4·5	− 0·3
$\bar{4}$	< 4·5	− 3·2
$\bar{5}$	7·4	+ 7·3
$\bar{6}$	< 4·6	+ 1·1
$\bar{7}$	< 4·6	− 2·3
$\bar{8}$	< 4·5	+ 2·1
$\bar{9}$	< 4·5	− 3·0
$\overline{10}$	< 4·4	− 4·0
$\overline{11}$	< 4·1	− 1·3
$\overline{12}$	< 3·6	+ 0·5
$\overline{13}$	< 3·1	+ 0·1
0 6 6	< 3·2	+ 3·4
5	< 3·5	+ 0·2
4	< 3·9	− 0·5
3	< 4·1	+ 1·6
2	< 4·3	− 1·5
1	6·5	− 6·7
$\bar{1}$	< 4·5	+ 0·6
$\bar{2}$	< 4·5	+ 0·2
$\bar{3}$	< 4·5	+ 0·6
$\bar{4}$	14·3	−11·2
$\bar{5}$	7·8	− 8·1
$\bar{6}$	< 4·4	+ 2·2
$\bar{7}$	< 4·3	− 1·2
$\bar{8}$	< 4·1	+ 0·7
$\bar{9}$	< 3·9	− 0·5
$\overline{10}$	< 3·5	− 2·7
$\overline{11}$	< 3·1	+ 0·7
0 7 2	< 2·9	− 0·8
1	< 3·2	− 0·5
$\bar{1}$	< 3·5	− 0·2
$\bar{2}$	< 3·5	− 1·0
$\bar{3}$	< 3·5	+ 0·8
$\bar{4}$	< 3·5	− 3·2
$\bar{5}$	< 3·5	− 3·0
$\bar{6}$	< 3·3	+ 0·2
$\bar{7}$	< 3·1	− 0·3
$\bar{8}$	< 2·8	+ 0·2
1 0 14	< 2·7	− 0·4
13	< 3·5	− 0·4
12	< 3·9	+ 1·9
11	12·6	−13·2
10	17·9	−14·9
9	< 3·9	+ 2·4
8	< 3·7	− 0·3
7	5·3	− 5·0
6	12·0	+12·0
5	21·4	+20·5
4	4·7	+ 3·7
3	6·7	− 6·6
2	< 1·9	+ 3·9
1	< 1·7	+ 0·4
$\bar{1}$	1·3	+ 4·6
$\bar{2}$	2·2	− 2·6
$\bar{3}$	< 1·8	+ 0·7
$\bar{4}$	< 2·0	− 0·3
$\bar{5}$	< 2·3	− 1·8
$\bar{6}$	3·8	+ 2·7
1 0 $\bar{7}$	< 2·9	+ 0·8
$\bar{8}$	< 3·3	− 1·3
$\bar{9}$	< 3·6	+ 1·3
$\overline{10}$	5·5	− 4·7
$\overline{11}$	12·0	− 9·8
$\overline{12}$	< 4·1	− 1·8
$\overline{13}$	< 3·9	+ 1·3
$\overline{14}$	< 3·6	− 1·0
$\overline{15}$	< 2·9	+ 0·5
2 0 13	< 2·8	+ 0·2
12	< 3·5	− 1·3
11	< 3·9	+ 2·2
10	7·0	+ 5·7
9	< 4·1	− 1·0
8	< 4·0	+ 0·5
7	< 3·6	− 1·5
6	< 3·5	+ 1·2
5	25·0	+23·3
4	2·9	+ 3·1
3	4·3	− 4·0
2	5·7	+ 6·6
1	12·7	−16·8
$\bar{1}$	74·8	+75·5
$\bar{2}$	23·2	−28·3
$\bar{3}$	12·6	+14·5
$\bar{4}$	4·8	− 5·6
$\bar{5}$	< 2·4	+ 1·9
$\bar{6}$	18·5	+20·1
$\bar{7}$	4·2	− 4·5
$\bar{8}$	< 3·2	+ 1·9
$\bar{9}$	< 3·6	+ 1·3
$\overline{10}$	< 3·8	− 1·4
$\overline{11}$	8·0	+ 6·9
$\overline{12}$	< 4·1	+ 0·6
$\overline{13}$	< 4·1	+ 0·5
$\overline{14}$	< 3·8	+ 0·6
$\overline{15}$	< 3·2	− 0·6
3 0 12	< 2·8	+ 1·3
11	3·5	− 3·2
10	12·0	−11·2
9	< 4·1	− 1·3
8	< 4·1	+ 1·1
7	< 4·0	− 3·2
6	< 3·8	+ 2·5
5	4·4	+ 5·8
4	< 3·3	+ 4·5
3	< 3·0	− 1·8
2	< 2·8	− 2·1
1	< 2·6	+ 4·6
$\bar{1}$	< 2·3	+ 1·2
$\bar{2}$	< 2·3	− 0·4
$\bar{3}$	< 2·3	− 1·5
$\bar{4}$	4·0	+ 3·6
$\bar{5}$	9·2	− 9·4
$\bar{6}$	19·5	−18·9
$\bar{7}$	4·4	− 5·2
$\bar{8}$	< 3·4	+ 4·9
$\bar{9}$	< 3·6	− 2·3
$\overline{10}$	< 3·9	− 1·4
$\overline{11}$	7·0	+ 8·8
$\overline{12}$	< 4·1	+ 4·9
$\overline{13}$	< 4·1	− 1·3
$\overline{14}$	< 3·9	+ 0·4
$\overline{15}$	< 3·4	− 0·4
$\overline{16}$	< 2·7	− 0·3
4 0 11	< 2·5	0
10	< 3·3	+ 2·3
9	< 3·8	+ 0·9
8	< 4·0	− 1·0
7	< 4·1	+ 0·1

Table 7 (*cont.*)

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
4 0	6	< 4·1	− 1·0	5 0	2	< 3·9	− 1·5	6 0	$\bar{5}$	< 3·9	− 3·2	7 0	$\bar{14}$	< 3·0	− 1·9
	5	9·5	+ 9·6		1	< 3·7	+ 0·3		$\bar{6}$	10·8	+ 10·9		$\bar{15}$	< 2·5	+ 1·2
	4	11·8	+ 12·1		$\bar{1}$	< 3·5	− 2·0		$\bar{7}$	11·1	+ 11·5	8 0	2	< 3·0	+ 0·4
	3	< 3·6	− 3·9		$\bar{2}$	< 3·4	+ 0·6		$\bar{8}$	< 4·0	− 1·3		1	< 3·4	− 0·8
	2	< 3·4	+ 1·3		$\bar{3}$	< 3·4	− 1·0		$\bar{9}$	< 4·1	+ 0·9		$\bar{1}$	8·0	− 5·2
	1	< 3·2	+ 1·4		$\bar{4}$	< 3·4	+ 0·5		$\bar{10}$	< 4·1	− 0·3		$\bar{2}$	9·4	− 7·6
	$\bar{1}$	< 3·0	+ 5·0		$\bar{5}$	< 3·5	− 3·0		$\bar{11}$	< 4·1	− 0·2		$\bar{3}$	< 3·9	+ 0·7
	$\bar{2}$	3·5	− 3·4		$\bar{6}$	3·5	− 5·2		$\bar{12}$	4·0	+ 4·8		$\bar{4}$	< 4·0	0
	$\bar{3}$	< 2·8	+ 3·6		$\bar{7}$	3·7	− 4·8		$\bar{13}$	< 3·8	+ 1·6		$\bar{5}$	< 4·0	− 1·6
	$\bar{4}$	< 2·9	− 0·9		$\bar{8}$	< 3·8	+ 1·1		$\bar{14}$	< 3·5	− 0·1		$\bar{6}$	< 4·0	+ 2·2
	$\bar{5}$	< 3·0	− 2·4		$\bar{9}$	< 3·9	+ 1·3		$\bar{15}$	< 2·9	+ 0·5		$\bar{7}$	< 4·0	+ 4·0
	$\bar{6}$	21·7	+ 21·8		$\bar{10}$	< 4·1	− 4·4	7 0	5	< 2·9	− 1·5		$\bar{8}$	< 3·9	+ 1·5
	$\bar{7}$	5·7	+ 5·7		$\bar{11}$	10·0	+ 9·5		4	8·4	− 7·8		$\bar{9}$	< 3·9	− 0·5
	$\bar{8}$	3·2	− 2·5		$\bar{12}$	15·6	+ 16·4		3	< 3·7	− 1·6		$\bar{10}$	< 3·7	+ 0·1
	$\bar{9}$	< 3·7	+ 3·7		$\bar{13}$	< 4·0	+ 0·3		2	< 3·9	+ 1·0		$\bar{11}$	< 3·5	− 0·2
	$\bar{10}$	< 3·9	− 3·2		$\bar{14}$	< 3·7	− 1·2		1	< 4·1	− 1·5		$\bar{12}$	< 3·2	+ 0·4
	$\bar{11}$	5·0	+ 4·4		$\bar{15}$	< 3·3	+ 1·1		$\bar{1}$	< 4·1	− 0·2		$\bar{13}$	< 2·8	+ 1·3
	$\bar{12}$	3·8	+ 5·2		$\bar{16}$	< 2·6	− 1·5		$\bar{2}$	< 4·1	0	9 0	$\bar{1}$	< 2·7	+ 0·3
	$\bar{13}$	< 4·1	− 0·2	6 0	7	< 3·0	− 0·4		$\bar{3}$	< 4·1	− 0·6		$\bar{2}$	< 3·0	+ 0·3
	$\bar{14}$	< 3·8	+ 1·1		6	< 3·5	+ 0·3		$\bar{4}$	< 4·1	− 0·4		$\bar{3}$	< 3·2	− 0·3
	$\bar{15}$	< 3·5	− 0·7		5	< 3·9	+ 0·8		$\bar{5}$	< 4·1	− 1·5		$\bar{4}$	< 3·3	− 0·6
	$\bar{16}$	< 2·7	+ 1·9		4	< 4·1	+ 3·6		$\bar{6}$	< 4·1	+ 1·2		$\bar{5}$	< 3·3	− 0·5
5 0	9	< 2·9	− 0·7		3	< 4·1	+ 1·7		$\bar{7}$	6·1	+ 4·9		$\bar{6}$	< 3·4	+ 0·5
	8	< 3·5	+ 0·4		2	< 4·1	− 1·9		$\bar{8}$	< 4·1	− 0·5		$\bar{7}$	8·4	+ 5·3
	7	< 3·9	− 1·6		1	< 4·1	+ 2·2		$\bar{9}$	< 4·1	0		$\bar{8}$	< 3·3	+ 3·0
	6	< 4·1	+ 1·8		$\bar{1}$	14·1	− 13·9		$\bar{10}$	< 4·1	− 0·6		$\bar{9}$	< 3·2	− 1·7
	5	5·7	− 3·8		$\bar{2}$	8·6	− 7·4		$\bar{11}$	< 3·8	+ 0·5		$\bar{10}$	< 2·9	+ 0·7
	4	6·3	− 5·5		$\bar{3}$	< 3·9	+ 3·3		$\bar{12}$	11·8	+ 10·4		$\bar{11}$	< 2·6	− 0·3
	3	< 4·0	+ 1·6		$\bar{4}$	< 3·9	− 0·7		$\bar{13}$	3·5	+ 4·6				

0·028 Å. This value may be compared with the r.m.s. deviation of the individual bond lengths from the mean distances, which is 0·026 Å. The standard deviations of the mean bond distances are 0·014 Å for bonds *a*, *b*, *c*, *d* and 0·020 Å for bonds *e*, *f*, *g*.

Discussion

The most interesting feature of the crystal structure of tetracene is the close similarity to the two preceding members of the benzologous series, naphthalene and anthracene. Although there are definite variations in orientation, the general arrangement of the tetracene molecules in the unit cell is very like that of anthracene. It is therefore surprising that the crystal system should change from monoclinic to triclinic in passing from anthracene to tetracene, and also that the appearance of the crystals should change from colourless to bright orange-red.

The crystal system is determined by the packing of the molecules, and the arrangement which gives the lowest lattice energy will be the one normally adopted. An example of a slight departure from higher symmetry resulting in a lower lattice energy was encountered in crystals of hexamethylbenzene (Brockway & Robertson, 1939). In this structure, which is triclinic, the (001) plane approaches very closely to hexagonal symmetry ($a=8{\cdot}92$, $b=8{\cdot}86$ Å, $\gamma=119°\ 34'$), and it was shown that this slight departure from the higher symmetry resulted in a much closer packing of the molecules in the crystal lattice, and an increase in density of 9%. The small deviation from monoclinic symmetry in tetracene could be given a similar explanation. The deviations of the α and γ angles from 90° result in an increase in density, but only of about 2%, and a corresponding closer packing of the tetracene molecules in the crystal, but without causing any unusually close intermolecular contacts.

Some elucidation of the remarkable change in colour can be obtained from spectroscopic studies of naphthalene, anthracene and tetracene. The investigation of the absorption spectra of the three substances in solution emphasizes their close similarity in structure. It has been shown (Clar, 1932; Seshan, 1936) that the band spectrum becomes more diffuse on passing from naphthalene to tetracene, and shifts continuously towards the red end of the spectrum. The shift from naphthalene to anthracene is about 4970 cm.$^{-1}$ and from anthracene to tetracene 5230 cm.$^{-1}$. These studies also show that there is a slight shift towards the red end of the spectrum in passing from the vapour state to solution and again in passing from solution to the crystalline state. In tetracene and anthracene this shift is of the order of 200 Å. The first band of tetracene in solution is at 4680 Å, and in the solid state at 4850 Å.

A noticeable feature of the absorption spectrum of crystalline tetracene is the presence of another band at 5250 Å (Schiebe, Muller & Schiffmann, 1941) which is completely absent in the vapour phase and in solution. This additional band accounts for the fact that crystals of tetracene are bright red in colour, whilst the solution is pale yellow. Similar bands are observed in the higher members of the series, pentacene and hexacene, but are completely absent in naphthalene and anthracene. It has been suggested that the appearance of this band in tetracene may be due to an arrangement whereby the molecules are more nearly parallel than in the anthracene structure, and some form of coupling can take place in the direction parallel to the N axes of the molecules. No evidence in support of this theory has, however, been given by the present crystal-structure determination.

Both tetracene molecules in the unit cell are completely planar within the limits of experimental error, the maximum deviation from the mean molecular planes being 0·036 Å, and the root-mean-square deviation 0·017 Å. Very accurate refinements of the crystal structures of naphthalene and anthracene (Cruickshank, 1956, 1957*a*, *b*) have shown that small deviations from planarity previously observed (Abrahams, Robertson & White, 1949; Sinclair, Mathieson & Robertson, 1950) are highly significant, and are caused by the close approach of neighbouring molecules in the crystals. While similar effects might be present in tetracene, the present analysis is not accurate enough to detect them.

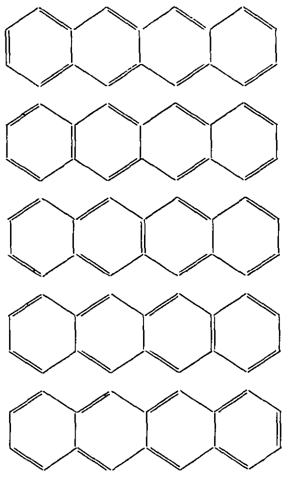


Fig. 5. Kekulé structures for tetracene.

On the basis of the standard deviations of the bond distances, it was not considered that the molecular symmetry differed from *mmm*, and the mean bond lengths and valency angles are shown in Fig. 4(*b*). The bond distances are quoted to 0·001 Å for comparison with the calculated values below, but the third place is not, of course, significant. A calculation of the bond lengths for comparison with the measured distances was made from the five non-excited valence bond structures for tetracene (Fig. 5). 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; Berthier, Coulson, Greenwood & Pullman, 1948) and calculated bond distances were obtained from the correlation curve described by Goodwin & Vand (1955). The bond lengths calculated by the valence bond and by the molecular orbital methods are compared in Table 6 with the measured distances; the differences (Δ) between measured and calculated values are included in the table. The general variation of the aromatic C–C distances measured in the present X-ray analysis is well reproduced in both sets of calculated lengths. 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 0·021 Å, while the corresponding deviations for the molecular orbital method are 0·066 and 0·022 Å. Both sets of calculated distances therefore agree equally well with the measured values.

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