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The Crystal Structure of 2:13-Benzfluoranthene

By H. W. Ehrlich and C. A. Beevers

Chemistry Department, King's Buildings, Edinburgh 9, *Scotland*

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The crystal structure of the hydrocarbon 2:13-benzfluoranthene, $C_{18}H_{10}$, has been determined. This molecule consists of four six-membered rings linked to form a five-membered ring, and the molecule is thus in a state of considerable strain. The structure was solved by a consideration of the Patterson projection and by trial-and-error methods. The molecule was found to be flat and to have the strains distributed throughout the whole molecule. The interatomic distances show that all the bonds in the five-membered ring are long, whilst in the six-membered rings there is a Kekulé arrangement of alternating long and short bonds.

Introduction

The high degree of rigidity possessed by aromatic molecules is of considerable interest to chemists. A good deal of study has been made of the strain and distortion in aromatic systems, and much has been said of the effect of 'steric hindrance' on molecular structure. Investigations of crystal structure are of great value in this subject. However, structures of this type which have so far been determined have been those in which atoms are forced to be too close to one another according to van der Waals distances. One of these substances is 3:4-benzphenanthrene (Herbstein & Schmidt, 1954), in which two unbonded carbon atoms in a strainless molecule would be about 2·4 Å apart. This distance is, of course, considerably less than the sum of the van der Waals radii, and it is also much greater than a covalent bond distance. The purpose of the present study was to determine the effect on the molecule of making this into a covalent bond, a process which changes 3:4-benzphenanthrene into the compound 2:13-benzfluoranthene. A study of the structure of acenaphthene (Kitaigorodski, 1949), which is a similarly strained molecule, had indicated that the stress might be considerable, as the length of the aliphatic single bond in this compound was found to be 1·64 Å instead of the usual 1·54 Å. We now find that, although the equivalent bond in 2:13-benzfluoranthene is significantly longer than an average aromatic bond (1·39 Å), it is not excessively so, and the stress is evenly distributed over the whole molecule.

Crystal data

2:13-Benzfluoranthene, $C_{18}H_{10}$, (m.p. 148° C.) is monoclinic, with absent spectra ($h0l$) when h is odd, and ($0k0$) when k is odd. The space group is $P2_1/a-C_{2h}^5$ with $Z = 4$. The cell dimensions are given in Table 1. A comparison of low- and high-temperature values shows that the thermal expansion is not isotropic.

Table 1. *Crystallographic data*

	At −97° C.	At +23° C.	Accuracy
a (Å)	18·83	19·03	±0·03
b (Å)	4·733	4·762	±0·005
c (Å)	15·69	15·81	±0·03
β	129° 3′	128° 53′	±3′
Cell volume (Å^3)	1086	1115	±4
d_c (g.cm.$^{-3}$)	1·384	1·348	±0·005
d_o (g.cm.$^{-3}$)	—	1·345	±0·013

The crystals, which were kindly provided by Dr O. Kruber of the Gesellschaft für Teerverwertung m.b.H., Duisburg-Meiderich, were long yellow needles, with the needle axis parallel to the b axis. Predominant faces are $\{10\overline{1}\}$, $\{001\}$ and $\{100\}$. The needles have no clear end face, but sometimes there is a fracture parallel to $\{010\}$.

Experimental

All the intensity data were obtained from Weissenberg photographs, using filtered Cu $K\alpha$ radiation. The multiple-film technique was used, employing an Ilford Industrial G film in front of three Ilford Industrial B films. Ratios that were thus obtained between successive films were $83:6\frac{1}{4}:2\frac{1}{2}:1$. The intensities were estimated visually by comparison against a calibrated scale.

Structure determination

All the early work was done from data obtained at room temperature. The short b axis suggested that the structure might resemble that of other large flat molecules, such as coronene (Robertson & White, 1945) ovalene (Donaldson & Robertson, 1953) and phthalocyanine (Robertson, 1936), which also have a b axis of about 4·7 Å. The weighted reciprocal lattice of the $h0l$ reflexions indicated the presence of nearly parallel benzene rings. The Patterson projection down the b axis confirmed this.

When vectors from two benzene rings to their centrosymmetric partners are plotted, it is found that a concentration of vectors occurs at three sites, giving rise to three large peaks in a straight line in a Patterson

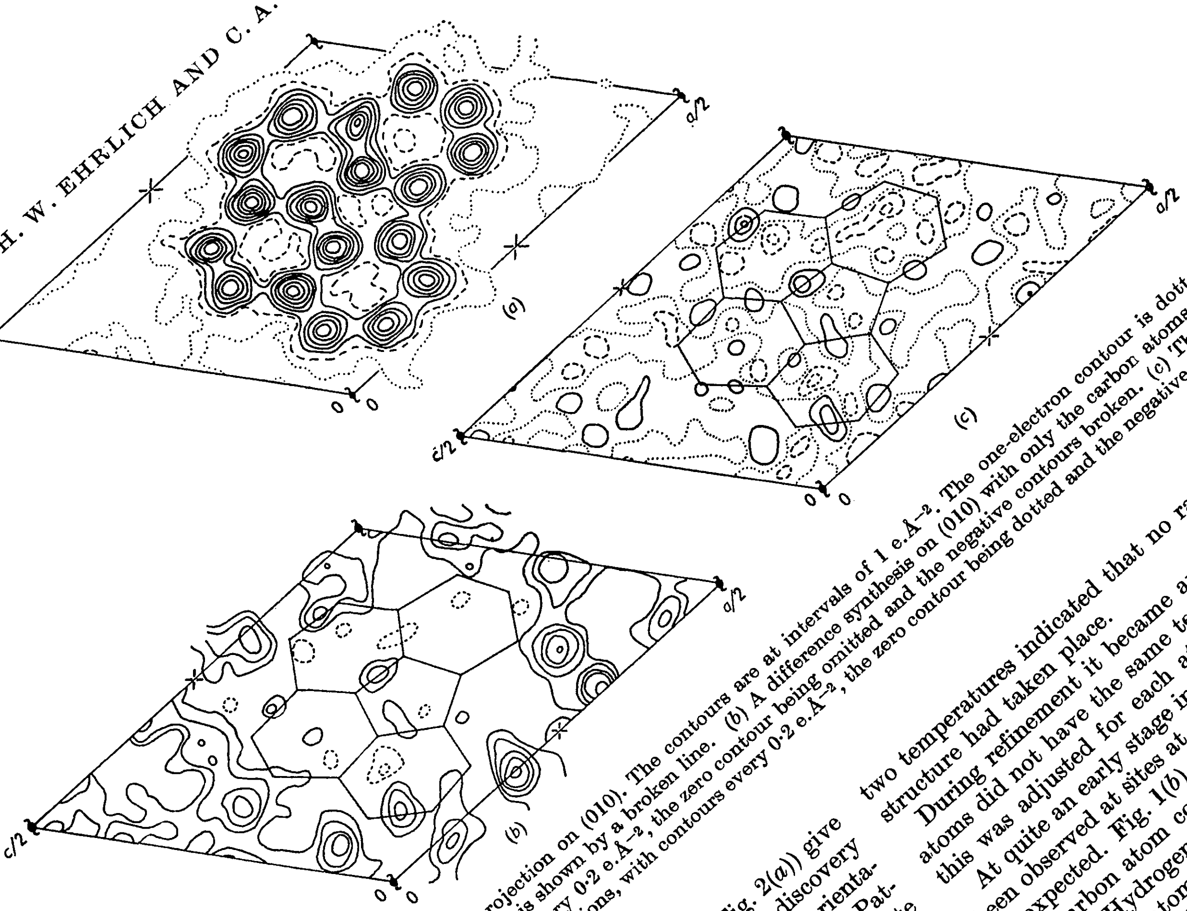


Fig. 1. (*a*) Electron-density projection on (010). The contours are at intervals of 1 e.Å^{-2}. The one-electron contour is dotted, and the two-electron contour is shown by a broken line. (*b*) A difference synthesis on (010) with only the carbon atoms subtracted. Contours are drawn every 0·2 e.Å^{-2}, the zero contour being omitted and the negative contours broken. (*c*) The final F_o-F_c synthesis of the ($h0l$) reflexions, with contours every 0·2 e.Å^{-2}, the zero contour being dotted and the negative contours broken.

map. Rings *A* and *D*, and *B* and *C* (see Fig. 2(*a*)) give rise to parallel lines of such peaks, and the discovery of such lines of peaks indicated the probable orientation of the molecule. A molecule which fitted the Patterson map was then deduced. This approximate structure was used to give signs to certain very strong high-order reflexions, which enabled the atoms to be fixed with greater accuracy. The planes which were used were $14,0,\overline{13}$, $14,0,\overline{10}$, $14,0,3$, $0,0,14$ and $2,0,\overline{14}$. The structure thus obtained was refined by means of (F_o-F_c) maps.

The *c*-axis projection was solved by a Patterson map which showed, by the absence of high ground at $(0, \frac{1}{2})$, that in this projection the molecules must lie about a centre of symmetry, and not about a screw axis. The angle of tilt of the molecule could be estimated from the *b*-axis projection. Confirmation was obtained from the *c*-axis Patterson projection, and an approximately planar molecule was used for a trial structure. All the evidence so far had indicated that the molecule might be flat. The *c*-axis projection was also refined by means of (F_o-F_c) maps.

Low-temperature photographs were then used for further refinement. The reduced vibrations enabled us o obtain more accurate atomic coordinates. A com- ison of the intensities of photographs taken at the two temperatures indicated that no radical change in structure had taken place.

During refinement it became apparent that all the atoms did not have the same temperature factor, and this was adjusted for each atom.

At quite an early stage in the refinement, peaks had been observed at sites at which hydrogen atoms might be expected. Fig. 1(*b*) shows an (F_o-F_c) map where only carbon atom contributions to F_c have been considered. Hydrogen atom contributions were then calculated for atoms whose positions were placed so as to make the C–H bond about 1 Å long and collinear with the long diagonal of the benzene ring.

The final (F_o-F_c) map (Fig. 1(*c*)), using F_c with contributions from both carbon and hydrogen atom shows the carbon atoms at positions where the little or no slope, and where the electron densit significant. The larger peaks can be accounte assuming that some of the atoms vibrate cally.

Because of poor resolution of the at *c*-axis projections are not as accu projection, although some high gr maps is found at sites where h be expected.

The value of $R = \Sigma|F$

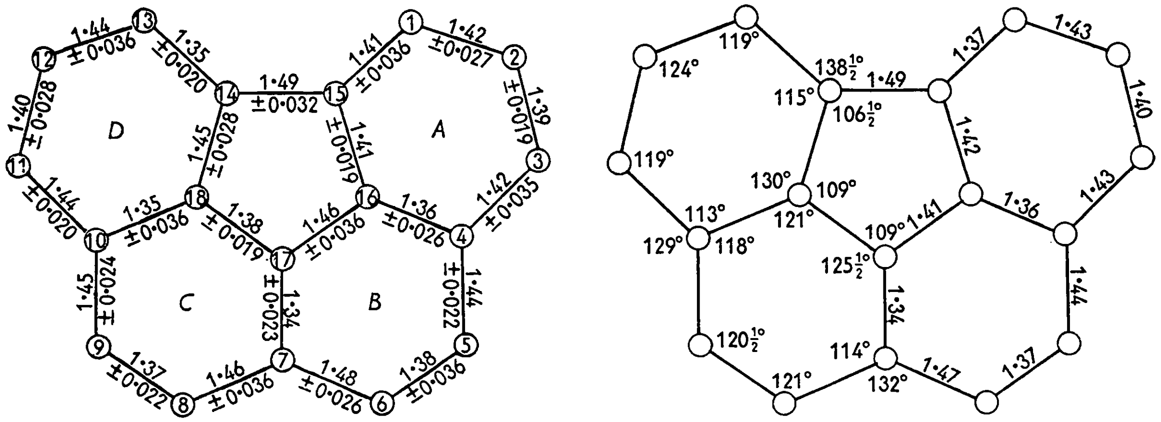


Fig. 2. (*a*) The bond lengths and their standard deviations. (*b*) Mean bond lengths and angles.

Table 2. *Final coordinates*

Atom	x	y	z	B (Å^2)	Deviation of D from 2·191	Displacement from the plane (Å)
1	0·931	0·428	0·058	3·00	−0·020	0·013
2	0·858	0·563	0·047	2·85	−0·012	0·008
3	0·834	0·504	0·113	3·00	−0·031	0·019
4	0·886	0·313	0·200	2·37	0·062	0·039
5	0·875	0·206	0·277	3·15	−0·017	0·011
6	0·930	0·003	0·355	2·85	−0·034	0·021
7	0·005	0·875	0·362	2·85	−0·018	0·011
8	0·073	0·662	0·435	3·00	−0·013	0·008
9	0·138	0·576	0·427	3·15	0·027	0·017
10	0·140	0·692	0·343	3·00	0·022	0·014
11	0·201	0·624	0·320	3·75	0·011	0·007
12	0·189	0·756	0·232	3·50	−0·062	0·039
13	0·121	0·970	0·167	3·25	0·002	0·001
14	0·063	0·041	0·187	2·85	0·034	0·021
15	0·983	0·228	0·143	3·00	0·008	0·005
16	0·955	0·192	0·207	2·37	0·065	0·041
17	0·012	0·970	0·287	2·37	−0·032	0·020
18	0·076	0·888	0·276	2·85	0·007	0·004

the *b*-axis projection (contributions from 200, 002, 20$\bar{2}$ and 20$\bar{4}$ were omitted, as these differences are considered to be mainly due to extinction effects). If the unobserved reflexions are given a value of $\frac{1}{2}\sqrt{2}\times$(minimum observed), this quantity is reduced to 11·8%.

The reliability indices, R, for the a- and c-axis projections are 17·1% and 19·8% respectively (differences that are thought to be due to extinctions are again omitted, the reflexions involved being 002, 012 and 200). If the unobserved reflexions are corrected for, as previously, the values become 13·9% and 13·2%. Table 4 shows the agreement between observed and calculated values of F.

Atomic coordinates and molecular dimensions

The final atomic coordinates are listed in Table 2, where x, y and z are fractions of the monoclinic axes a, b and c. The scattering curve for carbon used was that of Hoerni & Ibers (1954), modified by a temperature factor of $\exp(-B\sin^2\theta/\lambda^2)$. The value of B for each atom is also shown in Table 2.

The mean plane of the molecule was determined by the method of least squares, after the coordinates of the atoms had been referred to orthogonal axes. The atoms can be fitted on to a plane $Ax+By+Cz=D$, where $A = 8{\cdot}7599$, $B = 5{\cdot}433$, $C = 7{\cdot}7587$, $D = 2{\cdot}191$ and x, y, z are again the fractional coordinates referred to the monoclinic axes a, b and c. The deviations of D for each atom from 2·191 are listed in Table 2.

The bond lengths and their standard deviations are shown in Fig. 2(*a*). Assuming that chemically similar

Table 3. *Hydrogen coordinates*

Atom	120x	120y	120z
1	114	56	1
2	21	36	1
3	93	72	12
5	99	36	33
6	110	112	49
8	9	70	59
9	22	52	58
11	30	56	44
12	28	86	27
13	14	10	12

Table 4

hk0 reflexions

	F_o	F_o
k=1		
h=1	32.8	34.2
2	111.7	105.0
3	88.7	82.9
4	21.8	23.0
5	-3.9	5.6
6	10.2	9.6
7	-9.4	9.5
8	2.9	4.2
9	13.8	13.2
10	10.6	10.6
11	10.1	9.2

	F_o	F_o
12	5.1	6.4
13	0.7	<4.0
14	-7.1	7.2
15	4.4	<3.7
16	6.8	7.1
17	8.6	7.1
18	7.6	6.2
k=2		
h=0	19.5	21.2
1	-16.1	15.1
2	12.3	15.1

	F_o	F_o
3	-6.2	3.4
4	-9.1	10.2
5	2.9	<2.9
6	-8.4	10.4
7	5.4	5.5
8	-7.3	7.0
9	12.2	11.6
10	-9.5	10.1
11	4.9	6.0
12	12.5	11.5
13	8.3	8.9
14	11.7	9.7

	F_o	F_o
15	1.7	3.4
16	1.5	<3.0
17	-1.2	<2.4
k=3		
h=1	10.0	9.6
2	-4.8	<3.2
3	-5.1	4.5
4	8.9	11.5
5	-14.3	14.0
6	2.2	<3.7
7	-10.7	11.2

	F_c	F_o
8	-9.1	9.9
9	6.3	3.4
10	-6.4	6.8
11	0.4	<3.9
12	-2.6	<3.8
13	0.4	<3.5
14	3.2	<3.2
15	7.6	9.2
16	4.7	3.0
k=4		
h=0	10.7	11.2

	F_c	F_o
1	4.0	4.5
2	1.1	<3.9
3	-1.6	<3.9
4	-2.7	3.5
5	-12.5	13.1
6	7.3	5.5
7	-8.9	9.0
8	1.1	<3.9
9	2.0	<3.7
10	-2.8	<3.6
11	3.1	<3.3
12	-1.0	<3.0

	F_c	F_o
13	3.3	<2.5
14	-4.6	4.5
k=5		
h=1	6.6	6.3
2	-2.7	<3.6
3	4.2	<3.6
4	-2.9	<3.5
5	1.6	<3.4
6	-0.3	<3.2
7	-2.6	<3.0
8	2.1	<2.8

	F_c	F_o
9	-1.1	<2.5
10	4.1	4.1
k=6		
h=0	3.3	<2.0
1	1.7	<2.0
2	2.5	<1.8
3	-1.9	<1.6

h0ℓ reflexions

	F_c	F_o
h=0		
ℓ=0	472.0	-
1	5.8	-
2	-100.3	73.0
3	13.1	12.2
4	-11.0	12.5
5	10.7	9.0
6	7.2	7.4
7	-3.9	3.4
8	-22.6	23.9
9	-1.9	<3.1
10	-8.7	9.9
11	7.7	7.4
12	-11.1	11.2
13	-19.9	20.4
14	14.3	14.6
15	-0.3	<2.1
h=2		
ℓ=0	89.8	70.0
1	-21.9	19.5
2	33.7	33.9
3	3.0	<1.9
4	27.9	33.7
5	23.1	22.7
6	29.2	29.9
7	-4.9	5.3
8	-8.9	8.7
9	-8.4	9.5
10	-6.9	8.2
11	26.0	29.9
12	-11.8	14.1
13	-14.8	16.3
14	4.1	5.6
-1	14.6	13.6
-2	-98.6	68.5
-3	-20.6	17.7
-4	-67.7	55.8
-5	6.0	4.9
-6	-18.6	20.2
-7	16.3	17.2
-8	-3.1	<2.7

	F_o	F_o
-9	-28.8	29.9
-10	1.8	3.6
-11	-4.9	4.4
-12	-9.3	9.2
-13	5.7	5.3
-14	28.5	33.9
-15	5.6	6.0
-16	-4.0	<2.0
h=4		
ℓ=0	-60.0	52.7
1	12.6	8.7
2	-24.3	24.6
3	1.8	<2.3
4	2.3	<2.5
5	-15.5	16.2
6	31.4	36.5
7	4.9	3.6
8	-2.7	<3.3
9	4.9	4.9
10	11.2	11.1
11	-6.4	6.5
12	-14.8	17.6
13	7.3	10.7
-1	-37.3	35.0
-2	6.0	6.9
-3	23.7	22.7
-4	-28.8	26.5
-5	0.4	3.1
-6	-36.3	36.1
-7	-18.7	19.0
-8	59.8	60.2
-9	-5.4	5.3
-10	-12.8	11.9
-11	5.8	6.4
-12	13.3	11.3
-13	22.1	23.1
-14	5.0	4.4
-15	-7.5	6.7
-16	-2.3	<2.6
-17	-2.6	2.5

	F_o	F_o
h=6		
ℓ=0	11.2	12.7
1	-6.7	8.7
2	2.2	<2.5
3	35.0	36.5
4	-23.5	26.2
5	-30.0	32.4
6	5.4	4.4
7	4.3	<3.4
8	7.5	7.4
9	8.5	9.0
10	2.0	<2.9
11	-13.3	16.0
12	-3.7	2.5
-1	27.1	24.5
-2	-16.6	16.6
-3	-38.5	40.0
-4	5.5	4.1
-5	12.8	13.3
-6	-0.3	<2.0
-7	15.7	15.4
-8	39.9	40.2
-9	3.5	<2.7
-10	-9.4	12.1
-11	4.1	3.4
-12	-3.0	<3.2
-13	4.9	5.3
-14	-3.6	<3.4
-15	-15.9	15.7
-16	-3.7	2.6
-17	3.9	3.5
-18	-0.2	<1.7
h=8		
ℓ=0	1.4	<2.5
1	7.6	8.4
2	17.2	20.9
3	3.6	<3.1
4	-9.5	11.7
5	1.2	<3.4
6	0.6	<3.4
7	7.8	6.7

	F_o	F_o
8	4.7	6.2
9	-6.3	6.2
10	2.0	<2.0
-1	-15.9	16.6
-2	-39.0	42.2
-3	5.8	5.1
-4	-20.9	20.7
-5	-11.0	10.2
-6	33.1	32.8
-7	25.7	24.3
-8	-4.4	<2.5
-9	-29.0	27.2
-10	-18.3	17.4
-11	0.6	<3.0
-12	3.9	<3.2
-13	-2.5	<3.4
-14	8.5	7.6
-15	4.5	3.8
-16	-14.0	14.8
-17	1.7	<2.8
-18	4.7	4.4
-19	-1.9	<1.3
h=10		
ℓ=0	-4.5	5.0
1	-0.9	<3.2
2	-5.9	6.[illegible]
3	-14.8	14.4
4	-10.4	10.7
5	5.2	4.4
6	1.2	<3.1
7	4.3	4.0
8	8.7	9.0
9	-4.5	2.2
-1	-17.4	18.0
-2	-33.4	32.9
-3	36.7	37.9
-4	29.6	28.2
-5	-47.2	45.2
-6	15.5	12.3
-7	11.3	12.1
-8	2.2	<2.7

	F_c	F_o
-9	1.5	<2.8
-10	2.7	<2.9
-11	-12.6	12.3
-12	-1.2	<3.2
-13	28.3	26.8
-14	6.5	5.3
-15	-5.2	6.2
-16	-18.2	16.0
-17	-4.2	4.4
-18	4.5	4.0
-19	-1.2	<1.9
h=12		
ℓ=0	-0.2	<3.4
1	-2.7	<3.4
2	8.4	8.7
3	7.2	6.9
4	-21.8	21.2
5	-12.3	11.3
6	-9.3	7.3
7	3.7	2.7
-1	-5.2	4.4
-2	12.2	12.9
-3	10.6	11.5
-4	22.0	23.6
-5	-5.4	3.1
-6	3.9	<2.9
-7	3.9	<2.9
-8	20.9	20.9
-9	11.3	9.2
-10	-17.4	16.0
-11	15.0	12.0
-12	-27.4	25.0
-13	-7.4	4.4
-14	14.9	16.0
-15	-12.6	8.6
-16	-10.7	9.2
-17	1.0	<3.0
-18	4.0	<2.7
-19	-2.7	2.2
-20	6.4	4.9

	F_c	F_o
h=14		
ℓ=0	21.8	20.8
1	-8.0	6.7
2	13.1	12.6
3	21.4	22.8
4	-8.8	8.7
5	-9.7	9.2
-1	-11.9	10.9
-2	-3.4	<3.4
-3	12.0	12.3
-4	0.4	<3.3
-5	12.6	11.7
-6	5.4	6.4
-7	0.0	<3.2
-8	-9.9	8.0
-9	-18.4	14.8
-10	-46.2	42.9
-11	22.6	22.7
-12	14.0	13.8
-13	-37.7	35.5
-14	4.9	4.9
-15	5.8	7.1
-16	8.3	8.2
-17	4.3	<3.1
-18	1.1	<2.7
-19	-2.3	<2.3
-20	-0.4	<1.5
h=16		
ℓ=0	19.5	18.8
1	-15.9	18.6
2	0.6	<2.3
3	6.7	4.9
-1	12.6	11.8
-2	-22.0	23.7
-3	-6.8	7.1
-4	-3.1	<3.4
-5	11.4	12.3
-6	-6.3	5.6
-7	-6.5	4.9
-8	-18.2	15.4
-9	-30.1	27.9

	F_c	F_o
-10	0.4	<3.4
-11	24.5	22.8
-12	22.3	19.5
-13	-11.5	8.2
-14	3.9	4.4
-15	2.4	<3.3
-16	5.6	4.9
-17	7.7	6.9
-18	-2.9	3.1
-19	5.8	7.1
-20	-3.5	3.4
h=18		
ℓ=0	-1.4	<2.1
1	-0.2	<1.4
-1	9.9	8.2
-2	-3.5	<2.8
-3	-14.7	15.1
-4	-15.0	14.3
-5	10.9	9.8
-6	6.3	6.4
-7	-5.7	4.9
-8	6.0	3.8
-9	-10.0	8.1
-10	14.2	12.3
-11	21.0	18.7
-12	0.3	<3.4
-13	-1.8	<3.4
-14	2.9	4.6
-15	3.0	<3.2
-16	-2.1	<3.0
-17	-0.7	<2.8
-18	-6.1	4.6
-19	7.1	9.4
-20	0.2	<1.0
h=20		
ℓ=-2	0.0	<1.7
-3	-1.3	<2.1
-4	1.4	<2.4
-5	5.9	3.4
-6	5.2	5.1

	F_o	F_o
-7	-5.1	3.1
-8	7.7	5.8
-9	3.6	3.6
-10	-7.0	6.0
-11	-1.8	<3.1
-12	0.3	<3.1
-13	5.5	5.3
-14	-2.0	<3.0
-15	-3.5	3.6
-16	0.6	<2.6
-17	-4.3	<2.4
-18	-7.4	11.4
-19	1.9	<1.5
h=22		
ℓ=-5	1.3	<1.3
-6	-3.0	2.5
-7	-6.5	6.0
-8	-2.1	<2.3
-9	2.0	<2.4
-10	-1.7	<2.5
-11	1.9	<2.6
-12	5.7	7.2
-13	-0.5	<2.6
-14	0.3	<2.4
-15	-2.0	<2.3
-16	-10.2	11.4
-17	0.9	<1.8
-18	6.3	4.7
h=24		
ℓ=-11	6.5	5.6
-12	2.5	<1.5
-13	-5.9	6.0
-14	-4.1	3.4
-15	4.4	1.8

0kℓ reflexions

	F_o	F_o
k=1		
ℓ=1	13.6	13.5
2	-82.9	66.8
3	24.6	26.7
4	22.7	21.7
5	5.4	3.3
6	-5.1	4.0
7	-2.3	3.8
8	-8.0	8.1
9	7.9	7.0

	F_c	F_o
10	9.3	9.8
11	-15.2	15.2
12	3.1	<4.4
13	5.0	<3.9
14	7.0	7.2
15	-1.2	<2.4
k=2		
ℓ=1	12.3	12.2
2	31.5	33.3

	F_c	F_o
3	12.9	15.8
4	-20.9	22.2
5	-12.2	13.0
6	3.8	4.3
7	3.4	<4.0
8	-7.5	8.3
9	-15.2	17.2
10	-0.3	<4.5
11	7.2	7.2
12	0.1	<4.0

	F_c	F_o
13	-5.7	5.1
14	-5.4	5.7
k=3		
ℓ=1	26.1	25.8
2	-9.0	9.3
3	1.7	<3.9
4	1.9	<3.9
5	-1.1	<4.3
6	-14.8	14.1

	F_c	F_o
7	2.6	<4.4
8	15.8	17.0
9	-0.7	<4.4
10	-1.3	<4.2
11	2.9	<3.8
12	5.3	4.4
13	-6.7	7.6
k=4		
ℓ=1	12.3	13.4

	F_c	F_o
2	-10.1	12.3
3	-12.0	14.5
4	-2.7	<4.5
5	0.6	<4.5
6	4.0	<4.4
7	0.1	<4.3
8	5.9	7.0
9	0.0	<3.8
10	0.7	<3.3
11	0.0	<2.7

	F_c	F_o
12	-1.4	<1.4
k=5		
ℓ=1	-0.7	<4.1
2	3.7	3.3
3	-5.2	3.3
4	-1.3	<3.8
5	6.2	6.6
6	1.6	<3.3
7	-1.4	<3.0

	F_c	F_o
8	1.8	<2.4
9	-1.6	<1.4
k=6		
ℓ=1	-3.2	2.6
2	-4.3	4.0
3	-1.3	<1.9

bonds have equal bond lengths, the final model is as shown in Fig. 2(*b*), where the weighted mean is used to obtain final bond lengths. The angles quoted are the means of chemically equivalent angles.

The hydrogen atom coordinates listed in Table 3 are those used for the calculation of *F*'s, and have no value for the calculation of C–H bond lengths The numbering of a hydrogen atom is determined by the number of the carbon atom to which it is attached.

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

$$\sigma(x) = \sigma(z) = 0{\cdot}012 \text{ Å}, \quad \sigma(y) = 0{\cdot}025 \text{ Å};$$
$$\sigma(\varrho_0) = 0{\cdot}34 \text{ e.Å}^{-2} \quad \text{for the (010) projection,}$$
$$\sigma(\varrho_0) = 1{\cdot}07 \text{ e.Å}^{-2} \quad \text{for the (100) projection and}$$
$$\sigma(\varrho_0) = 0{\cdot}76 \text{ e.Å}^{-2} \quad \text{for the (001) projection.}$$

If contributions from reflexions considered to be unreliable because of extinction effects, are omitted, the values for the standard deviation of the electron density become 0·18, 0·41 and 0·37 e.Å^{-2} respectively. The values for atomic coordinates are not appreciably affected.

The standard deviations for the individual bonds are as shown in Fig. 2(*a*), and in the final model the standard deviations are of the order of 0·02 Å, except for the bond C_{14}–C_{15}, which has a standard deviation of 0·03 Å. The standard deviation of the mean angles is about 1½°.

Discussion of the structure

The molecule appears to be quite flat, since the deviations from the mean plane average 0·017 Å (maximum 0·041 Å), while the standard deviation of the carbon atom position is 0·028 Å. Furthermore, the molecule is most probably symmetrical about the line joining C_7 to C_{17}, since, for the most part, the bond lengths and angles are not significantly different in the two halves. Only in the case of one pair of bonds does the difference fall in the region of 'possibly significant' (Cruickshank, 1949).

Hence we consider the molecule to be planar and symmetrical, and we can take the average bond lengths

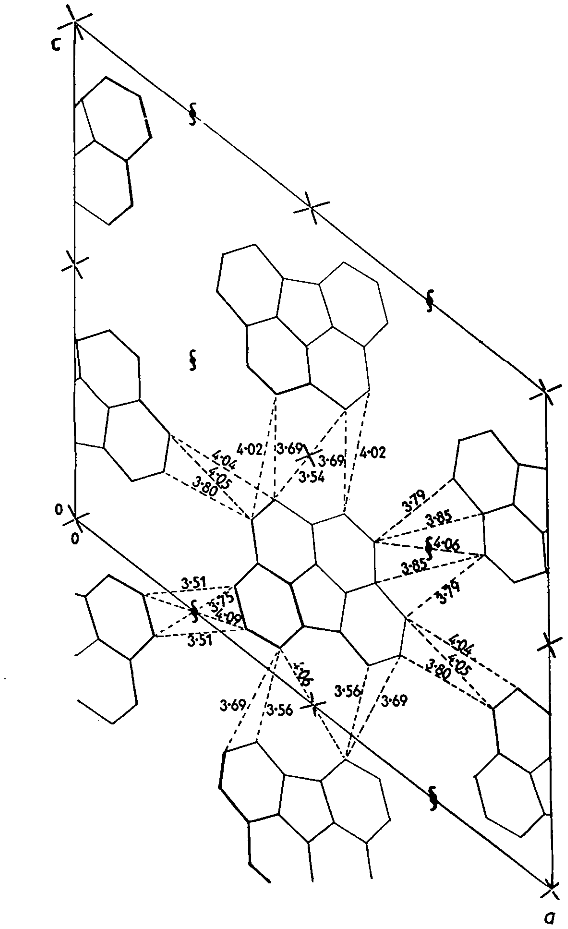
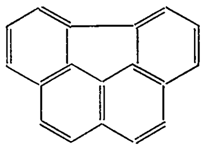


Fig. 3. The arrangement of the molecules in the (010) projection, showing the lengths of the van der Waals contacts in Ångström units.

and angles on the two sides as being more reliable than the individual values. These mean values are shown in Fig. 2(*b*).

Although most of the bond lengths are not significantly different from the average aromatic bond length of 1·39 Å, there are three bonds, namely, C_{14}–C_{15}, C_4–C_5 and C_6–C_7, which are significantly longer. The molecule, as a whole, has a marked tendency towards the structure with the maximum number of Kekulé type rings



the long bonds occurring where single bonds are found in the hypothetical molecule. The stress seems to be mainly in the bond-angle distortions.

The plane of the molecule makes an angle of 44·2° with the (010) plane. The corresponding values for coronene, ovalene and phthalocyanine are 43·7°, 42·9° and 44·2° respectively. Unlike these substances, however, the plane of the molecule does not pass through the centre of symmetry.

The slope of the molecule gives the thickness of a molecule as

$$b \cos 44{\cdot}2^\circ = 3{\cdot}40\ \text{Å}\ .$$

Fig. 3 shows all other close approaches between different molecules that are less than 4·10 Å. None of these conflicts with our knowledge of van der Waals radii.

In conclusion, we would like to thank Dr O. Kruber, who provided the crystals. One of us (H. W. E.) is indebted to the University of Edinburgh for an award of a Post-Graduate Studentship, and we are also grateful to the Moray Fund for financial assistance.

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