A Refinement of the 1:12-Benzperylene Structure

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The structure of 1:12-benzperylene, $C_{22}H_{12}$, has been refined by two-dimensional $(F_o - F_c)$ syntheses, and the measured bond lengths have been compared with those derived by valence-bond and molecular-orbital calculations.

Introduction

A detailed X-ray investigation of the crystal structure of 1:14-benzbisanthrene, $C_{30}H_{14}$ (Fig. 1), has revealed some interesting bond length variations in this molecule, these variations being very similar to those predicted by a simple valence-bond calculation based on only the 30 non-excited structures (Trotter, 1958). Particularly marked is the increase in the length of the central bonds on proceeding from the 'closed' to the 'open' end of the molecule

$$(1\cdot40 \rightarrow 1\cdot44 \rightarrow 1\cdot47 \rightarrow 1\cdot49 \text{ Å}),$$

while the lengths of the bonds at the open side afford an explanation of the facile addition of maleic anhydride. The measured bond lengths have also been compared with the lengths calculated by the molecular orbital method (Pauncz & Berencz, 1954; Ali, 1959); the variations in the observed lengths are again closely reproduced, but the individual agreement for the shorter and longer bonds is not as good as with the valence-bond method. As is usual in the m.o. calculations for this type of molecule, the calculations underestimate the extremes of bond length variation, the calculated lengths of the longer bonds being less, and of the shorter bonds greater, than those observed. Ali has pointed out that some of this disagreement may be due to uncertainties in the order-length correlation curve in the regions of lower bond order, and to the approximations of the simple linear combination of atomic orbitals method.

A similar type of bond length variation is to be expected in 1:12-benzperylene, $C_{22}H_{12}$ (Fig. 1). A detailed X-ray investigation of the structure of this molecule has been carried out (White, 1948) and many of the bond lengths determined, but unfortunately the more interesting bonds, those on the 'open' side of the molecule, are obscured in projection by overlapping of other molecules in the unit cell. White points out that a complete and accurate determination of all the bond lengths would require a full three-dimensional analysis of the structure. However it might be possible, by using two-dimensional $(F_o - F_c)$
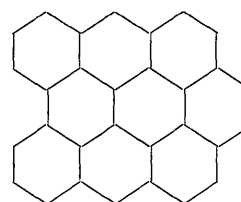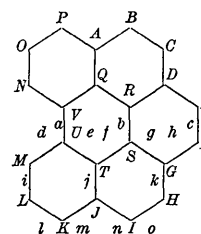
Fig. 1. (*a*) 1:14-Benzbisanthrene; (*b*) 1:12-benzperylene.

syntheses, to obtain a more extensive account of the positional parameters than that given by the original F_o syntheses method, and thus extend the bond length measurements without the labour of a three-dimensional analysis. The present paper describes such a refinement, using White's data, and the final measured bond lengths are compared with those calculated by both valence-bond and molecular-orbital methods.

Refinement of the structure

Crystals of 1:12-benzperylene are monoclinic with four molecules in a unit cell of dimensions $a = 11\cdot72$, $b = 11\cdot88$, $c = 9\cdot89$ Å, $\beta = 98\cdot5°$, space group $P2_1/a$.

The $h0l$ structure factors were calculated using White's final coordinates and Robertson's empirical scattering curve (White, 1948); the values of F_c were essentially identical with those given by White, with some differences of one unit in structure factor due to rounding-off differences. These small differences however were such as to increase the discrepancy factor, R, from $16\cdot6\%$ to $19\cdot7\%$. The structure factors were then recalculated using the same positional parameters, but with McWeeny's (1951) scattering factor

for carbon corrected for thermal vibration as usual, taking $B = 4\cdot8$ Å². Since many of the hydrogen atoms lie close to the carbon atoms in projection it was important that allowance be made for the hydrogens, and a contribution from them was included in the structure factor calculation; coordinates were obtained by assuming C–H distances of $1\cdot08$ Å, and McWeeny's hydrogen curve with $B = 5\cdot5$ Å² was used. The discrepancy factor was $21\cdot9\%$.

A difference synthesis was computed, using $(F_o - F_c)$ as coefficients, and this map indicated that some small changes in the positional parameters of the carbon atoms were required to minimize the slopes at the atomic centres. In addition the usual temperature factor variation was apparent, the atoms near the centre of the molecule having the smallest B values (they lie on small peaks on the difference map), and those at the periphery of the molecule lying in slight troughs, indicating that they are executing rather larger thermal vibrations. The carbon atoms were shifted to minimize the electron-density slopes at the atomic centres, but no allowance was made for temperature factor variation. Structure factors were recalculated, a second $(F_o - F_c)$ synthesis computed, and further small changes made in the positional parameters of the carbon atoms. Recalculation of the structure factors showed that R had dropped to $20\cdot6\%$. This would appear to be still rather worse than the agreement given by White's coordinates and scattering factor, but $3\cdot6\%$ of the discrepancy is due to the planes 001, 200, 201, 20$\bar{1}$, for which the measured values may be slightly in error due to extinction (the empirical scattering curve is chosen to give a best fit between observed and calculated data in this type of molecule, and so tends to make an allowance for this effect in the calculated structure factors). The final coordinates then are probably of about the same order of accuracy as those given by White, and

of course independent estimates have now been obtained of the coordinates of those atoms which are not separately resolved in the F_o synthesis. Observed and calculated structure factors are listed in Table 3, the scale of the measured values being chosen so that $\Sigma|F_o| = \Sigma|F_c|$.

Coordinates and molecular dimensions

The projection of the structure on (010) allows two coordinates for each carbon atom to be determined, but of course gives no information about the third coordinate. White's y-coordinates were used, together with the present x- and z-coordinates, to calculate the equation of the mean molecular plane; the best plane, obtained by the least-squares method, is

$$0\cdot8343X' - 0\cdot5267Y - 0\cdot1629Z' - 1\cdot6964 = 0$$

where X', Y, Z' are coordinates expressed in Å units, and referred to the axes a, b and c', where c' is perpendicular to a and b. The deviations of the atoms from this plane are listed in the final column of Table 1, the maximum deviation being $0\cdot025$ Å, and the root mean square deviation $0\cdot015$ Å. These quite small deviations from complete coplanarity suggested that White's y-coordinates were sufficiently accurate for determining the bond lengths, and no refinement of the $hk0$ zone was attempted.

The final coordinates of the carbon atoms are listed in Table 1, the coordinates x, y, z being referred to the monoclinic axes, and expressed as fractions of the unit-cell edges. The bond lengths in the benzperylene molecule were calculated from these coordinates and are listed in Table 2, together with the values obtained by White; the mean values were obtained by averaging the values for chemically-equivalent bonds. The bond lengths are quoted to $0\cdot001$ Å for comparison

Table 1. *Coordinates of the carbon atoms (and deviations, Δ, from the mean plane)*

Atom	x	y	z	X'	Y	Z'	Δ (Å)
A	0·1597	−0·1755	0·3357	1·381	−2·085	3·284	+0·019
B	0·2318	−0·0885	0·3943	2·141	−1·051	3·857	+0·015
C	0·2620	−0·0014	0·3150	2·611	−0·017	3·081	−0·011
D	0·2263	0·0029	0·1683	2·406	0·034	1·646	+0·025
E	0·2546	0·0902	0·0862	2·858	1·072	0·844	−0·014
F	0·2167	0·0928	−0·0525	2·617	1·102	−0·513	−0·010
G	0·1438	0·0081	−0·1173	1·856	0·096	−1·147	−0·012
H	0·1057	0·0090	−0·2632	1·624	0·107	−2·574	+0·021
I	0·0358	−0·0755	−0·3173	0·884	−0·897	−3·104	+0·019
J	−0·0011	−0·1651	−0·2402	0·338	−1·961	−2·350	+0·001
K	−0·0742	−0·2508	−0·2991	−0·433	−2·979	−2·926	−0·012
L	−0·1051	−0·3397	−0·2190	−0·912	−4·036	−2·142	+0·017
M	−0·0693	−0·3423	−0·0754	−0·702	−4·067	−0·738	−0·020
N	0·0151	−0·3476	0·2139	−0·136	−4·129	2·092	+0·024
O	0·0500	−0·3502	0·3575	0·063	−4·160	3·497	−0·022
P	0·1235	−0·2637	0·4130	0·843	−3·133	4·040	−0·001
Q	0·1170	−0·1734	0·1920	1·090	−2·060	1·878	−0·008
R	0·1498	−0·0842	0·1085	1·597	−1·000	1·061	−0·010
S	0·1104	−0·0816	−0·0339	1·344	−0·970	−0·331	−0·010
T	0·0367	−0·1680	−0·0985	0·574	−1·996	−0·963	−0·009
U	0·0032	−0·2563	−0·0180	0·064	−3·045	−0·176	−0·011
V	0·0444	−0·2588	0·1306	0·329	−3·075	1·278	−0·011

Table 2. Measured and calculated bond lengths (Å)

Bond	Measured White (1948)	Present analysis Upper	Present analysis Lower	Present analysis Mean	Calculated Valence Bond	Δ	Calculated Molecular Orbital	Δ
a	—	1·478	—	1·478	1·479	−0·001	1·443	+0·035
b	1·42	1·415	—	1·415	1·429	−0·014	1·424	−0·009
c	—	1·379	—	1·379	1·375	+0·004	1·384	−0·005
d	—	1·411	1·395	1·403	1·383	+0·020	1·404	−0·001
e	—	1·403	1·407	1·405	1·415	−0·010	1·421	−0·016
f	1·43	1·431	1·430	1·430	1·429	+0·001	1·425	+0·005
g	1·42	1·437	1·437	1·437	1·403	+0·034	1·419	+0·018
h	—	1·387	1·412	1·400	1·415	−0·015	1·418	−0·018
i	—	1·419	1·420	1·420	1·403	+0·017	1·399	+0·021
j	1·41	1·436	1·407	1·422	1·415	+0·007	1·422	0
k	1·43	1·450	1·446	1·448	1·444	+0·004	1·424	+0·024
l	—	1·399	1·401	1·400	1·383	+0·017	1·392	+0·008
m	1·40	1·400	1·401	1·401	1·403	−0·002	1·413	−0·012
n	1·41	1·405	1·414	1·410	1·443	−0·033	1·425	−0·015
o	1·38	1·376	1·355	1·366	1·360	+0·006	1·379	−0·013
Mean bond lengths over whole molecule				1·413	1·410		1·412	
R.m.s. Δ over whole molecule						0·017		0·015

Table 3. Observed and calculated h0l structure factors

hl	F_o	F_c	hl	F_o	F_c	hl	F_o	F_c	hl	F_o	F_c
01	92	+104	2,11	1	0	$6\bar1$	2	+1	$10,\bar8$	2	+3
02	47	−51	$4,\overline{11}$	1	0	60	15	−18	$10,\bar7$	2	−4
03	30	+34	$4,\overline{10}$	3	−1	61	5	+1	$10,\bar6$	4	+5
04	30	−33	$4\bar9$	3	−1	62	1	−1	$10,\bar5$	18	+16
05	13	−15	$4\bar8$	4	−4	63	6	−5	$10,\bar4$	4	0
06	11	−10	$4\bar7$	4	−5	64	5	+6	$10,\bar3$	4	−5
07	7	−8	$4\bar6$	9	+11	65	10	+9	$10,\bar2$	3	−4
08	1	−3	$4\bar5$	3	+4	66	4	+4	$10,\bar1$	3	0
09	11	+9	$4\bar4$	4	+2	67	4	+5	10,0	9	−7
0,10	7	+7	$4\bar3$	23	+21	68	1	+3	10,1	4	+4
0,11	5	−4	$4\bar2$	16	+19	69	1	0	10,2	4	−2
0,12	2	+1	$4\bar1$	24	+30	$8,\overline{11}$	4	−4	10,3	4	+2
$2,\overline{11}$	1	0	40	22	+25	$8,\overline{10}$	6	+6	10,4	44	+40
$2,\overline{10}$	1	+1	41	4	−6	$8\bar9$	14	+10	10,5	19	+16
$2\bar9$	2	+1	42	8	−7	$8\bar8$	5	0	10,6	5	−6
$2\bar8$	2	+1	43	10	+4	$8\bar7$	1	+2	10,7	2	+3
$2\bar7$	1	−1	44	1	−6	$8\bar6$	4	−4	10,8	2	−2
$2\bar6$	5	+8	45	6	−6	$8\bar5$	27	+22	$12,\bar7$	1	0
$2\bar5$	11	−9	46	2	0	$8\bar4$	28	+24	$12,\bar6$	1	+1
$2\bar4$	1	+2	47	2	−4	$8\bar3$	3	−5	$12,\bar5$	1	0
$2\bar3$	17	+14	48	4	+1	$8\bar2$	6	−6	$12,\bar4$	1	0
$2\bar2$	52	−56	49	1	−1	$8\bar1$	9	+7	$12,\bar3$	1	−1
$2\bar1$	74	+89	4,10	2	0	80	32	+31	$12,\bar2$	1	+1
20	44	+53	4,11	2	−1	81	9	+8	$12,\bar1$	9	−3
21	36	−46	$6,\overline{11}$	2	−1	82	1	−2	12,0	2	−1
22	13	−15	$6,\overline{10}$	2	−5	83	5	−6	12,1	2	+3
23	3	+2	$6\bar9$	28	+25	84	1	0	12,2	2	−4
24	55	+57	$6\bar8$	20	+18	85	13	+9	12,3	12	+7
25	26	+22	$6\bar7$	2	−4	86	1	−6	12,4	10	+8
26	14	−12	$6\bar6$	1	+3	87	1	0	12,5	1	−3
27	1	−1	$6\bar5$	2	−1	88	2	+2	$14,\bar3$	1	−2
28	13	+15	$6\bar4$	2	+1	89	3	−3	$14,\bar2$	2	+3
29	21	+19	$6\bar3$	11	−10	$10,\overline{10}$	5	−3	$14,\bar1$	2	+2
2,10	2	0	$6\bar2$	4	+3	$10,\bar9$	6	−4	14,0	1	−1

with the calculated values, but the third place is not of course significant.

The usual formulae for estimating the standard deviations of the atomic coordinates and bong lengths (Cruickshank, 1949) are not strictly applicable here due to the overlap in projection, but they give an approximate measure of the accuracy. The estimated standard deviations of the x- and z-coordinates are $\sigma(x)=\sigma(z)=0.015$ Å, so that the standard deviations of the mean bond lengths are about 0·015 Å for all the bonds except the central bonds (a, b, c), for which the standard deviations are about 0·02 Å.

A calculation of the bond lengths for comparison with the measured distances was made from the 14 non-excited valence bond structures for benzperylene (Fig. 2). The percentage double-bond character was
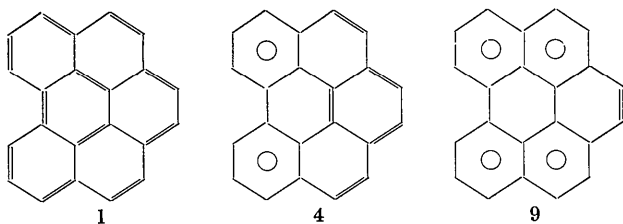
Fig. 2. Kekulé structures for 1:12-benzperylene.

calculated for each bond in the molecule, and the corresponding bond lengths derived from a bond order-bond length correlation curve drawn through the points (0, 1·50), (0·33, 1·42), (0·5, 1·39) and (1·0, 1·34). Bond lengths calculated by the linear combination of atomic orbitals molecular orbital method are also available (Pauncz & Berencz, 1953, 1954). The bond lengths calculated by the valence bond and by the molecular orbital methods are compared in Table 2 with the measured lengths; the differences (Δ) between measured and calculated distances are included in the table.

Discussion

The bond length variations in 1:12-benzperylene are very similar to those in 1:14-benzbisanthrene, the variations in bond distance along the central bonds (1·38 → 1·42 → 1·48 Å) being especially marked. Since the e.s.d.'s of these bonds are about 0·02 Å, the differences are significant. The variations in the bond lengths calculated both by the valence bond method and by the molecular orbital method are similar to the observed variations, but as with 1:14-benzbisanthrene, the linear combination of atomic orbitals method tends to underestimate the extremes of bond length variation. The root mean square difference between the measured and calculated bond lengths is 0·017 Å for the valence bond method and 0·015 Å for the molecular orbital calculation, so that both methods give about the same order of agreement with the observed distances. The mean observed bond length, 1·413 Å, is very similar to the mean calculated distances, 1·410 Å and 1·412 Å.

Comparison of the bond lengths at the 'open' ends of both molecules affords an explanation of the different ease of reaction with maleic anhydride. Benzbisanthrene readily takes up one molecule of

maleic anhydride, forming an adduct which yields ovalene on decarboxylation and dehydrogenation. The corresponding conversion of benzperylene into coronene proceeds only under the most forcing conditions. The addition of maleic anhydride to a system of this type (Diels–Alder reaction) can be represented as:
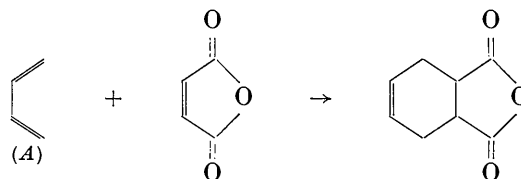
The reaction will proceed more readily the greater the amount of double and single bond fixation in the system A. The measured bond lengths in the corresponding parts of the benzbisanthrene and benzperylene molecules are shown in Fig. 3; since the
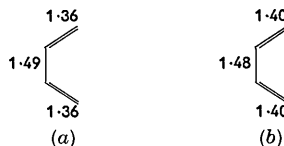

Fig. 3. Bond lengths at 'open' sides in
(a) 1:14-benzbisanthrene, (b) 1:12-benzperylene.

fixation of the double and single bonds is greater in benzbisanthrene, we would expect that this molecule would react with maleic anhydride more easily than would benzperylene. This is in agreement with the observed behaviour. The bond lengths calculated by the valence bond method lead to an exactly similar conclusion, but the molecular orbital distances, since they underestimate the bond length variation, show little difference for the two molecules.

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