produced when the heavy atoms are in special positions.

The acid salt rubidium hydrogen di-o-nitrobenzoate provides such an example, being triclinic with one molecule in the unit cell. The experimentally determined value of ϱ is 0·76 (Speakman, 1957), suggesting that the space group is $P1$. Interpolation in Table 1, however, for $r = 1\cdot77$ (Sim, 1958) gives

$$\text{max.}\varrho_{\bar{1}, r=1\cdot77} = 0\cdot784 ,$$

$$\text{max.}\varrho_{1, r=1\cdot77} = 0\cdot892 ,$$

indicating that the space group is really $P\bar{1}$.

It is also obvious from Table 1 that for large values of r it may be difficult to distinguish between a centrosymmetric and non-centrosymmetric structure, even when accurate intensity measurements are available. For triclinic cells containing one or two heavy atoms the value of r at which this difficulty arises is about $r \approx 2\cdot5-3\cdot0$.

If we consider as an example a molecule consisting of M carbon atoms (hydrogen atoms may safely be neglected), and a halogen atom, then this limiting value of r corresponds approximately to the following numbers of carbon atoms:

Halogen	M
Cl	2
Br	6
I	12

In the case of rectangular projections this difficulty should arise only for cells containing fewer than four heavy atoms (or eight in the case of the choice between cmm and cm).

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# The Crystal Structure of 1:14-Benzbisanthrene

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The crystal structure of the aromatic hydrocarbon 1:14-benzbisanthrene, $C_{30}H_{14}$, has been determined from the projection down the short crystal axis ($c = 4\cdot68$ Å) by use of the Patterson synthesis and trial methods. The structure is rather unusual in having two molecules in the asymmetric unit. All the atoms are well resolved in projection, and the measured bond lengths compare well with those predicted by superposition of Kekulé structures.

Introduction

Bisanthrene (I) readily adds maleic anhydride to form an adduct, which yields 1:14-benzbisanthrene (II) on decarboxylation (Clar, 1957), exactly analogous to the conversion of perylene into 1:12 benzperylene. However, while benzperylene can be converted into
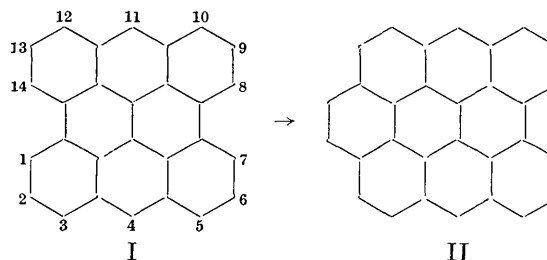
I   II

coronene only under the most forcing conditions, benzbisanthrene readily adds another molecule of maleic anhydride, forming an adduct which, on decarboxylation, yields ovalene. This facile addition of maleic anhydride suggests a rather greater fixation of single and double bonds at the 'open' side of the molecule in benzbisanthrene than in benzperylene, and the present investigation was undertaken to study the bond-length variations in the benzbisanthrene molecule.

Experimental

Crystals of benzbisanthrene are deep red-violet in colour, and consist of elongated plates with {010} developed, and with small {100} and {001} faces. They cleave very readily along the {100} face. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs about the a, b and c axes, and moving-film photographs of the $(h0l)$, $(hk0)$ and (hkl) zones.

Crystal data

1:14-Benzbisanthrene $C_{30}H_{14}$; $M = 374.4$; m.p. 452 °C. Monoclinic, $a = 36.13\pm0.10$, $b = 10.26\pm0.04$, $c = 4.68\pm0.01$ Å, $\beta = 90.0°\pm0.5°$. Volume of the unit cell = 1734.8 Å^3. Density, calculated (with four molecules per unit cell) = 1.425, measured = 1.413 g.cm.$^{-3}$. Absorption coefficient for X-rays, $\lambda = 1.542$ Å, $\mu = 7.54$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 776$. Absent spectra: $(h0l)$ when $h = 2n+1$. Space group is C_s^2–Pa or C_{2h}^4–$P2/a$.

The intensities of the $(hk0)$ and (hkl) reflexions were recorded on moving-film exposures for a crystal rotating about the c axis, the multiple-film technique (Robertson, 1943) being used to correlate strong and weak reflexions. The range of intensities measured was about 4,000 to 1, the estimates being made visually. The cross-section of the crystal, normal to the rotation axis, was 0.15×0.02 mm.; no absorption corrections were applied.

The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal. An ap-

proximately absolute scale was derived by Wilson's method (Wilson, 1942), and this scale was later adjusted by correlation with the F values calculated from the final coordinates. An approximate temperature factor ($B = 3.5$ Å^2) was also obtained.

Structure analysis

Since the unit cell contains four molecules, and Pa requires only two asymmetric units per unit cell, the space group is probably $P2/a$. When, however, the $N(z)$ test for centrosymmetry was applied (Howells, Phillips & Rogers, 1950), the intensity distribution of the $(hk0)$ zone intensities (Fig. 1) lay close to the
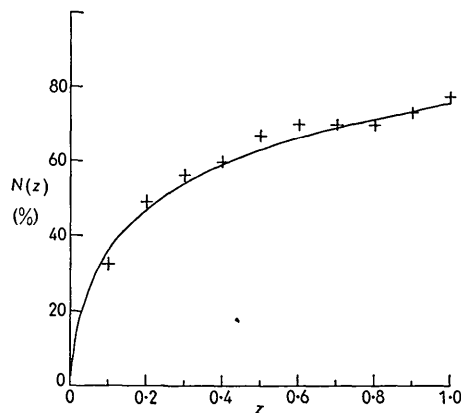
Fig. 1. Intensity distribution for the $(hk0)$ zone, compared with the theoretical curve for a centrosymmetric motif in a non-centrosymmetric arrangement.

theoretical distribution for a centrosymmetric motif in a non-centrosymmetric arrangement (Rogers & Wilson, 1953). This suggests that the asymmetric unit contains two molecules which are related by a centre of symmetry, but that this centre of symmetry is not utilized in the space group, which is non-centred. This is rather an unlikely arrangement, but the $N(z)$ test may be unreliable with a molecule of this type, which consists of regular hexagons and is almost centrosymmetric.

The structure analysis was carried out by consider-

Fig. 2. Patterson synthesis, $(hk0)$ zone. Contours at arbitrary intervals.

ing the projection down the short c axis. It was assumed initially that the space group was $P2/a$, but remembering that it was possible that the true space group might be the one of lower symmetry, namely Pa.
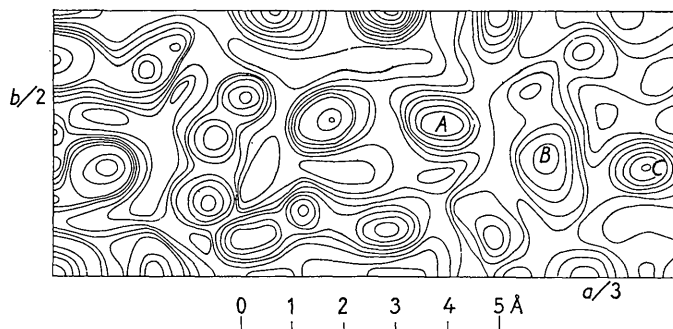
The (001) projection

An $(hk0)$ Patterson synthesis was computed (Fig. 2), and the tilt of the molecule was readily obtained from the peaks near the origin, which represent intramolecular vectors. The large peaks A, B, C correspond to the overlap of many vectors between two molecules related by a centre of symmetry, and, assuming that this centre of symmetry is coincident with one in the space group (that is, that the space group is $P2/a$), coordinates were assigned to all the atoms. Structure factors were calculated for the observed $(hk0)$ reflexions, using McWeeny's curve for carbon with $B = 3.5$ Å^2, and the discrepancy between observed and calculated values was 38%. This was a reasonable value, but there were a few very poor agreements.

A Fourier synthesis was computed, using as coefficients observed structure factors and calculated signs (Fig. 3). All the atoms were reasonably well resolved, with only a little spurious density, and new centres were chosen. Recalculation of the structure factors led to no improvement in the agreement between F_o and F_c.

Since it was obvious that this structure was not refining, and could not be the correct one, a new

structure had to be obtained. The Patterson synthesis requires that two molecules be in the present relative

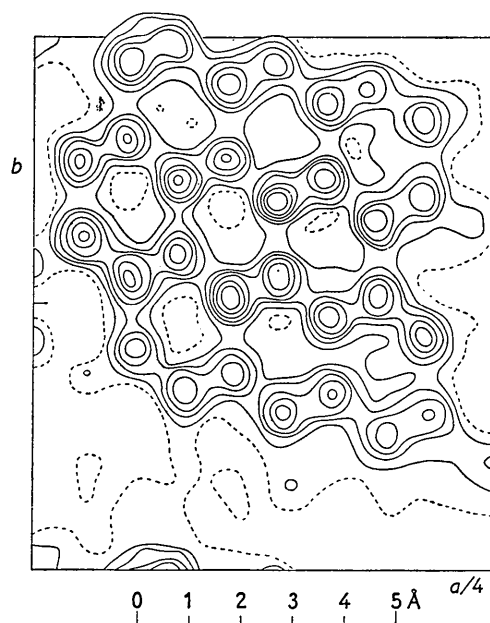
Fig. 3. Electron-density projection on (001), assuming space group $P2/a$. Contours at intervals of 1 e.Å^{-2}, with the one-electron line broken.

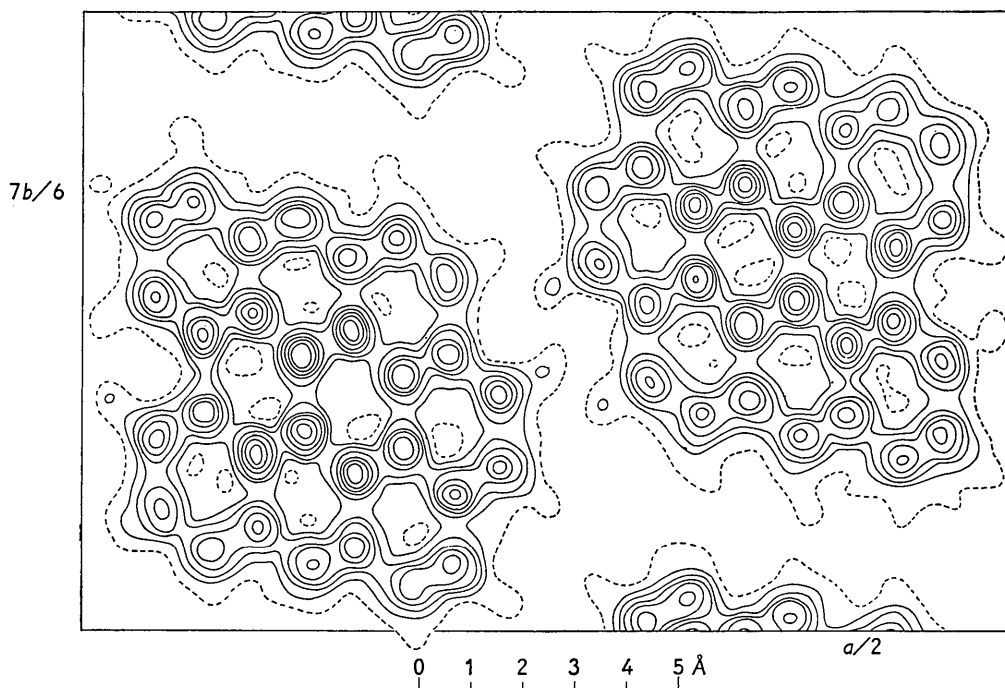positions, so that the space group must be Pa, and the centre of symmetry between the two molecules

Fig. 4. Electron-density projection on (001) with space group Pa. Contours at intervals of 1 e.Å^{-2}, with the one-electron line broken.

(which need not now be exact) is not utilized—as suggested by the $N(z)$ test above.

The agreement between the observed and calculated structure factors of the $(h00)$ reflexions was extremely good at this stage, so that the x coordinates of the carbon atoms were probably close to the correct values, and the coordinates of the pseudo-centre could be taken as $(0, y_c)$. Structure factors for the $(0k0)$ reflexions were computed using Beevers-Lipson strips, for values of y_c from $(0/120)b$ to $(120/120)b$. Best agreement between F_o and F_c was obtained when y_c was taken as $(8\frac{1}{2}/120)b$. The pseudo-centre was therefore shifted from $(0, 0)$ to $(0, 8\frac{1}{2}/120)$ and structure factors were calculated for all the $(hk0)$ reflexions; the discrepancy between F_o and F_c was 22% and there were no gross anomalies, so that it appeared that this structure was almost certainly correct.

A Fourier series was computed (Fig. 4) using as coefficients observed structure factors with calculated phase angles. The a axis was subdivided into 120 parts, interval 0·301 Å, and the b axis into 60 parts, interval 0·171 Å. All the carbon atoms were well resolved, and the map generally is a little better than Fig. 3. New centres were chosen, and structure factors were recalculated; the discrepancy was 15% over the observed planes. The Fourier map shows distinct evidence of the hydrogen atoms, and if these were included in the structure-factor calculations, the discrepancy would probably be reduced somewhat. The values of F_o and $|F_c|$, together with the calculated phase constants, are listed in Table 3. The observed value of the (400) structure factor is possibly slightly in error owing to extinction.

The structure now has 120 carbon positional parameters, and there are only 150 independent observed $(hk0)$ reflexions, so that further refinement is not justified. There are about 500 possible independent reflexions in this zone, but even with long exposures, no more than 150 have been observed.

Coordinates and molecular dimensions

The final coordinates of the carbon atoms are listed in Table 1 (the numbering of the atoms was chosen for convenience in the structure-factor calculations). The bond lengths projected on (001) were calculated from these coordinates, but to find the true bond lengths some information must be obtained about the tilt of the molecule, or about the third coordinates of the atoms. The amount of data available, even in the $(hk1)$ zone, scarcely justifies the labour involved in refining the z coordinates unless a three-dimensional analysis had been contemplated. In the present case, the tilt of the molecule was obtained and the projected bond lengths were converted into true bond lengths by assuming that the molecule was completely planar and that the average observed bond length was equal to the average bond length calculated by superposition of Kekulé structures (the planarity of the molecule

Table 1. Coordinates of the carbon atoms

Atom	x/a	y/b	Atom	x/a	y/b
C 1	+0·0268	+0·1988	C 1'	−0·0263	−0·0530
2	+0·0252	+0·3339	2'	−0·0260	−0·1879
3	+0·0536	−0·0275	3'	−0·0542	+0·1672
4	+0·0523	+0·1158	4'	−0·0533	+0·0253
5	+0·0503	+0·3770	5'	−0·0505	−0·2409
6	+0·0520	+0·5173	6'	−0·0502	−0·3811
7	+0·0806	−0·0971	7'	−0·0799	+0·2458
8	+0·0786	+0·1632	8'	−0·0788	−0·0181
9	+0·0782	+0·3031	9'	−0·0774	−0·1571
10	+0·0758	+0·5659	10'	−0·0753	−0·4214
11	+0·1082	−0·0589	11'	−0·1078	+0·2037
12	+0·1055	+0·0780	12'	−0·1056	+0·0653
13	+0·1046	+0·3452	13'	−0·1031	−0·2025
14	+0·1051	+0·4864	14'	−0·1035	−0·3421
15	+0·1331	−0·1388	15'	−0·1334	+0·2846
16	+0·1314	+0·1197	16'	−0·1316	+0·0209
17	+0·1307	+0·2616	17'	−0·1299	−0·1214
18	+0·1303	+0·5314	18'	−0·1287	−0·3840
19	+0·1590	−0·0957	19'	−0·1591	+0·2407
20	+0·1584	+0·0400	20'	−0·1581	+0·1016
21	+0·1565	+0·3051	21'	−0·1555	−0·1645
22	+0·1556	+0·4421	22'	−0·1549	−0·3041
23	+0·1850	−0·1811	23'	−0·1863	+0·3214
24	+0·1833	+0·0856	24'	−0·1852	+0·0591
25	+0·1851	+0·2287	25'	−0·1845	−0·0860
26	+0·1817	+0·4897	26'	−0·1813	−0·3503
27	+0·2090	−0·1281	27'	−0·2110	+0·2745
28	+0·2099	+0·0117	28'	−0·2106	+0·1355
29	+0·2096	+0·2795	29'	−0·2090	−0·1341
30	+0·2088	+0·4189	30'	−0·2077	−0·2715

and the calculated bond lengths will be discussed later). Small errors in the tilt of the molecule would alter the bond lengths by only small amounts. The lines X, Y and Z, which are taken in the plane of the molecule, and the lines in the other molecule, which are in the same directions, are inclined to (001) at angles of 6·6°, 42·4° and 25·3° respectively.
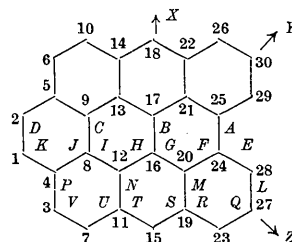
Table 2. Observed and calculated bond lengths

Bond*	Observed	Calculated	Bond*	Observed	Calculated
A	1·49 Å	1·50 Å	L	1·43	1·42
B	1·47	1·47	M	1·42	1·43
C	1·44	1·43	N	1·44	1·45
D	1·40	1·39	P	1·46	1·47
E	1·36	1·37	Q	1·37	1·37
F	1·43	1·43	R	1·43	1·42
G	1·40	1·41	S	1·40	1·41
H	1·41	1·39	T	1·37	1·38
I	1·43	1·43	U	1·47	1·47
J	1·42	1·41	V	1·35	1·35
K	1·39	1·39			

Root-mean-square $\Delta = 0\cdot01$ Å.

* See Table 1 for key.

Table 3. *Observed and calculated structure factors and calculated phase angles*

h	k	F_o	$\|F_c\|$	α (°)	h	k	F_o	$\|F_c\|$	α (°)	h	k	F_o	$\|F_c\|$	α (°)	h	k	F_o	$\|F_c\|$	α (°)
0	0	—	776	—	6	2	18	18	175	5	4	9	10	305	3	7	< 7	2	342
2		*	5	6	7		< 4	5	277	6		7	3	108	4		7	7	331
4		143	168	181	8		16	15	247	7		< 5	2	161	5		10	8	12
6		11	14	354	9		29	22	247	8		< 5	5	95	6		< 7	8	197
8		107	108	179	10		17	14	186	9		< 5	0	296	7		< 7	5	316
10		20	14	358	11		4	3	222	10		< 5	1	256	8		< 7	5	185
12		63	57	179	12		13	15	279	11		< 5	2	192	9		< 7	2	20
14		16	12	1	13		17	13	217	12		10	12	85	10		10	14	180
16		9	7	194	14		17	12	191	13		< 6	2	211	11		13	15	1
18		< 6	1	139	15		5	2	174	14		8	11	268	12		8	12	174
20		< 6	6	9	16		42	33	312	15		13	15	74	13		35	36	183
22		9	15	186	17		69	53	139	16		11	11	255	14		60	63	1
24		< 7	6	6	18		59	46	293	17		6	1	77	15		43	52	178
26		9	14	176	19		< 6	5	99	18		7	7	71	16		< 8	5	177
28		< 8	5	356	20		37	33	84	19		11	15	260	17		16	12	0
30		12	22	175	21		37	32	24	34		11	7	82	18		17	14	185
32		< 8	2	210	22		18	18	59	35		11	5	258	19		< 8	2	37
34		23	21	186	23		< 7	4	90						20		9	6	184
36		< 8	6	182	24		6	4	153	0	5	26	28	180	21		9	10	184
38		63	70	1	25		7	9	322	1		14	10	28	22		9	10	181
40		< 7	6	19	26		7	7	94	2		58	53	316	23		21	31	1
42		9	13	188						3		89	83	307	24		24	35	359
					0	3	10	9	180	4		62	57	296	25		14	21	5
0	1	106	109	0	1		43	41	259	5		11	16	64					
1		63	71	153	2		42	37	267	6		33	34	136	0	8	< 7	2	0
2		39	41	257	3		9	10	99	7		21	29	133	1		< 7	3	234
3		67	68	198	4		20	22	79	8		7	6	163	2		< 7	6	198
4		22	26	222	5		25	25	76	9		8	11	54	3		< 7	5	287
5		32	28	164	6		7	9	65	10		8	10	170	4		< 7	2	10
6		19	20	307	7		8	10	118	11		11	13	136	5		< 7	2	35
7		42	34	189	8		8	12	272	12		< 6	6	106	6		< 7	6	176
8		16	16	220	9		< 5	6	283	13		< 6	5	27	7		< 8	5	304
9		24	20	174	10		10	14	93	14		< 7	5	206	8		< 8	3	122
10		13	13	312	11		< 5	1	258	15		< 7	5	167	9		< 8	4	31
11		25	21	185	12		11	14	265	16		10	11	79	10		13	11	151
12		10	12	213	13		18	21	267	35		10	14	235	11		19	21	329
13		14	10	187	14		31	32	102	41		9	10	307	12		19	26	157
14		7	4	296	15		24	30	287						13		< 8	6	17
15		7	7	185	16		8	4	194	0	6	9	4	0	14		18	20	333
16		7	9	212	17		12	14	118	1		8	5	274	15		24	32	161
17		5	4	299	18		37	37	281	2		14	15	352	16		13	15	322
36		10	8	40	19		49	44	93	3		< 6	5	258	17		< 8	0	219
37		23	18	33	20		51	39	77	4		< 6	7	40	18		< 8	6	28
38		21	13	15	21		37	24	68	5		12	12	180	19		< 8	4	84
39		< 7	3	351	22		< 7	2	85	6		9	9	111	20		< 8	6	309
40		8	8	212	23		15	15	254	7		11	11	175	21		< 8	3	156
41		10	11	204	24		20	20	262	8		< 7	3	74	22		17	17	37
					25		7	12	265	9		8	9	173	23		29	30	25
0	2	19	14	180						10		< 7	4	119	24		23	22	21
1		54	55	358	0	4	9	11	180	11		7	10	180	25		< 8	1	168
2		79	77	77	1		28	30	93						26		15	18	206
3		25	26	36	2		< 5	2	82	0	7	< 7	3	0	27		15	17	212
4		16	19	223	3		27	26	282	1		< 7	2	12	28		7	9	206
5		38	37	257	4		30	35	279	2		14	17	187					

* Not observed.

There are four independent measured values of each chemically identical bond (except for the central bonds, where there are only two independent values) and the mean bond lengths are given in Table 2. The root-mean-square deviation of the individually-determined lengths of the bonds from the mean lengths is 0·016 Å.

The perpendicular distance between the planes of molecules related by translation b is about 3·4 Å, as is usual for aromatic hydrocarbons with this type of crystal structure.

Discussion

In the final Fourier map (Fig. 4) all the carbon atoms are well resolved, and the one-electron contour reveals the hydrogen atoms, although these are not of course separately resolved. Better resolution of the hydrogens might have been obtained if a contribution from them had been included in the calculated structure factors, and hence in the phase angles. The positions of the atoms in projection on (001) indicate that the carbon atoms all lie at least approximately in one plane,

although the mean C(28)–C(29) distance is only 2·78 Å. If the hydrogen atoms attached to C(28) and C(29) lie in the plane of the carbon atoms, they will approach to within the normal van der Waals distance. There is some indication on the Fourier map that these hydrogen atoms deviate from the C(19)–C(28) and C(22)–C(29) diagonals in such a way that they are pushed out of the carbon plane in opposite directions. This evidence is of course not very definite, but it does appear likely that while the carbon atoms all lie in one plane, the 'over-crowded' hydrogen atoms are pushed apart to increase the separation between them to the usual van der Waals distance.

The differences between the observed lengths of crystallographically different but chemically equivalent bonds are in some cases quite large (maximum 0·09 Å), but the mean lengths will be more accurate than the individually determined lengths. The root-mean-square deviation of the bond lengths from the mean lengths is 0·016 Å, so that the standard deviation of the mean bond lengths is 0·008 Å for all the bonds except the central bonds, for which the standard deviation is 0·011 Å. Errors in the molecular orientation will, of course, cause errors in the observed bond lengths, but these are likely to be small.

A rough calculation of the bond distances for comparison with the observed distances was made from the 30 non-excited valence bond structures for benzbisanthrene (Fig. 5). The percentage double-bond
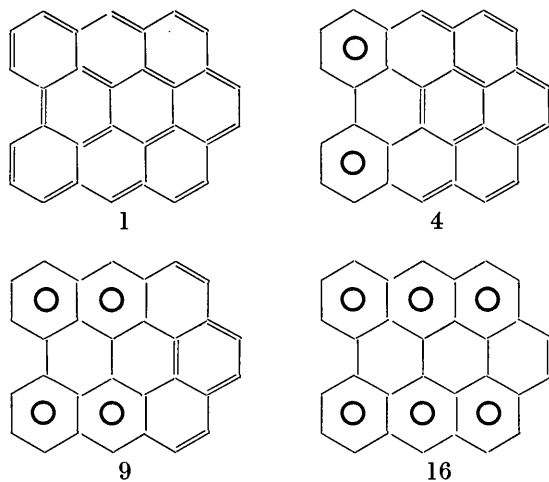

Fig. 5. Kekulé structures for benzbisanthrene.

character was calculated for each bond in the molecule, and the corresponding bond lengths were obtained from the usual valence bond correlation curve. The calculated and observed bond lengths are compared in Table 2.

The agreement between observed and calculated bond lengths is very good, with root-mean-square deviation only 0·01 Å. The mean observed bond length

over the whole molecule is 1·415 Å, and this is of course equal to the mean calculated length, since this assumption was made initially. The variations in calculated bond lengths within the molecule follow closely the variations in observed lengths. The bond length variation along the central bonds

$$(1·40 \rightarrow 1·44 \rightarrow 1·47 \rightarrow 1·49 \text{ Å})$$

is specially marked, and the fixation of double and single bonds at the 'open' end of the molecule affords an explanation of the facile addition of maleic anhydride.

The longest bond in the molecule is A, observed length 1·49 Å and percentage double-bond character 3·3, and the shortest V, observed length 1·35 Å and percentage double-bond character 86·7.

The magnitudes of the tilts of the two molecules in the asymmetric unit are equal, and so it seems probable that the planes of the molecules are parallel, and that the pseudo-centre is not restricted to the (001) projection, but present also in three dimensions. In further refinement a set of trial z coordinates could be obtained by establishing the distance of the molecular planes from the pseudo-centre, and this involves finding only one parameter. It is, of course, not impossible that the molecules are tilted in opposite directions and that the pseudo-centre is present only in projection along the c axis, but even then trial z coordinates could still be obtained without much difficulty. Since the number of reflexions observed in each zone is only of the same order as the number of parameters, further refinement would involve the use of three-dimensional data. Since there are 60 atoms in the asymmetric unit and the space group is non-centred, this is a formidable task, and no further work is contemplated at the moment.

The present analysis has yielded an accurate account of the bond lengths in the molecule, but, since z coordinates have not been obtained, the intermolecular approach distances are not accurately known. However, examination of the distances between the molecules in projection on (001) indicates that all intermolecular contacts correspond to normal van der Waals interactions.

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