JOURNAL
OF
THE CHEMICAL SOCIETY

---

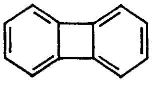
1. *The Crystal and Molecular Structure of Biphenylene.*

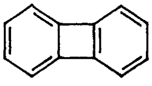
By T. C. W. Mak and J. Trotter.

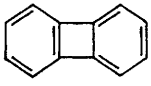
Crystals of biphenylene are monoclinic with six molecules in a unit cell of dimensions $a = 19{\cdot}66$, $b = 10{\cdot}57$, $c = 5{\cdot}85$ Å, $\beta = 91{\cdot}0°$, space group $P2_1/a$. The gross features of the structure previously determined have been confirmed, and the positional and isotropic temperature parameters of the carbon atoms have been refined from normal and generlized projections along the *c*-axis. The molecule is completely planar, and intermolecular contacts correspond to normal van der Waals interactions.

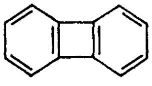
A comparison of the measured bond distances in biphenylene and those calculated by simple resonance theory and by molecular-orbital theory, indicates that the latter gives a better description of the electron distribution in the molecule. In terms of the Kekulé structures the preferred formulation is that which describes the molecule as a cyclobutane derivative. These conclusions are in agreement with the chemical behaviour of biphenylene and its derivatives.

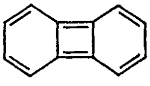
For biphenylene there is disagreement between the chemical behaviour predicted by resonance theory and by molecular-orbital calculations.[1] Five Kekulé structures may be drawn for the molecule, one of which (I) represents it as a derivative of cyclobutane, two


(I)


(II)


(III)


(IV)


(V)

(II and III) as a cyclobutene, and two (IV and V) as a cyclobutadiene. Simple resonance theory, with the five canonical forms contributing equally to the hybrid molecule, predicts that an *ortho,para*-activating group in position 2 should direct an entering substituent into position 1, while molecular-orbital calculations indicate that the substituent should be directed into position 3. It has recently been shown [2] that 2-acetamidobiphenylene undergoes monobromination as position 3. In valence-bond terminology this implies that the preferred Kekulé structure of biphenylene is (I).

Since the two methods also predict different bond-length variations for biphenylene, it should be possible to decide between them by an accurate measure of the bond distances. The structure of biphenylene has been examined by electron-diffraction of the vapour [3] and by an *X*-ray analysis of the crystalline material,[4] and indeed it was these investigations which first established the chemical structure of the molecule at a time when the formulation with a four-membered ring was considered unlikely.[5,6] In addition, these structural

[1] Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.

[2] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.

[3] Waser and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 1451.

[4] Waser and Lu, *J. Amer. Chem. Soc.*, 1944, **66**, 2035.

[5] Baker, *Nature*, 1942, **150**, 210.

[6] Coulson, *Nature*, 1942, **150**, 577.

determinations indicated that the C–C bonds in the six-membered rings had an average length of 1·39 Å, and that the bonds joining these rings were significantly longer (1·46 Å), but the measurements were not sufficiently accurate to detect the finer details of bond-length variation in the molecule. In the present paper we present a more detailed analysis to measure these distances and compare them with the various calculated bond lengths.

EXPERIMENTAL

A crystalline sample of biphenylene was made available to us by Professor J. M. Robertson. All the crystals were twinned on (100), but well-formed single crystals were obtained by recrystallization from propan-1-ol (cf. ref. 4). These consisted of pale yellow prisms elongated along the *c*-axis. The density was measured by flotation in aqueous potassium iodide.[4] The unit cell dimensions and space group were determined from rotation and oscillation photographs of crystals rotating about the *b*- and the *c*-axis, *h*0*l*, *hk*0, *hk*1, and *hk*2 Weissenberg films. No precautions were taken to prevent the crystals volatilizing, so that they disappeared in a few days.

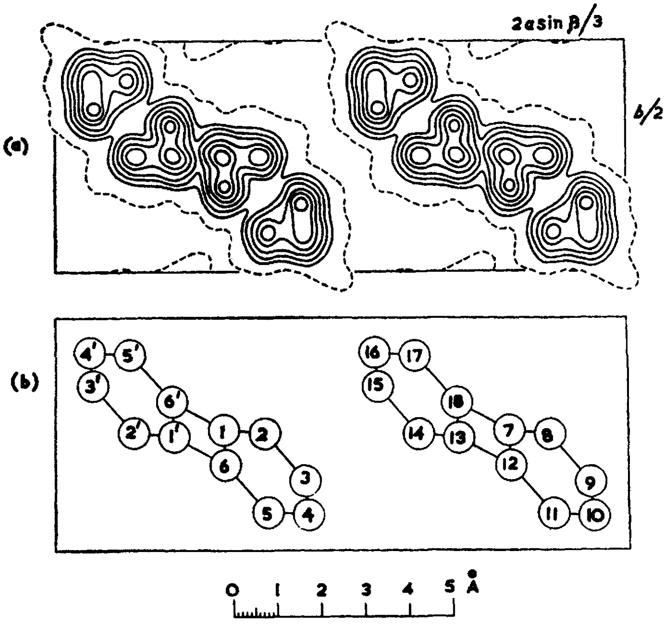


FIG. 1. (a) Electron-density projection along the *c*-axis, computed with $h = 3n$ planes only. Contours at intervals of 1 eÅ^{-2}, with the one-electron line broken.

(b) Projection of the structure along the *c*-axis.

Crystal Data.—Biphenylene, $C_{12}H_8$; *M*, = 152·2; m. p. 110°. Monoclinic, $a = 19{\cdot}66 \pm 0{\cdot}06$, $b = 10{\cdot}57 \pm 0{\cdot}04$, $c = 5{\cdot}85 \pm 0{\cdot}01$ Å, $\beta = 91{\cdot}0° \pm 0{\cdot}5°$. Volume of the unit cell = 1215·5 Å^3. *d*, calc. (with $Z = 6$) = 1·240 g. cm.$^{-3}$, measured = 1·24 g. cm.$^{-3}$. Absorption coefficient for *X*-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 6{\cdot}46$ cm.$^{-1}$. Total no. of electrons per unit cell = $F(000) = 480$. Absent spectra: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group is $P2_1/a - C_{2h}^5$.

The intensities of the *hk*0 and *hk*1 reflexions were recorded on Weissenberg photographs for a crystal rotating about the *c*-axis, the equi-inclination method being used for the upper level. Cu-K_α radiation was used, with multiple-film technique to correlate strong and weak reflexions. The intensities were estimated visually, the range being about 5000—1. The values of the structure amplitudes were derived by the usual formulæ for a mosaic crystals, the absolute scale being established later by correlation with the calculated structure factors No absorption corrections were applied. 65 Independent *hk*0 reflexions with $h = 3n$ were observed (see below for discussion of " $h = 3n$ rule "), representing 71% of the total number of these reflexions theoretically observable with Cu-K_α radiation, but only 36 very weak reflexions with $h \neq 3n$

were observed (about 20% of the total). 206 *hk*1 reflexions were recorded, representing about 40% of the possible number observable.

Structure Analysis.—[001]-*Projection.* Since there are six molecules in the unit cell, two of them must be situated on centres of symmetry at 000 and $\frac{1}{2}\frac{1}{2}0$, and the other four in general positions. As pointed out by Waser and Lu [4] the *hk*0 reflexions exhibit a distinctive feature, being very weak unless $h = 3n$, and this " $h = 3n$ rule " requires that to a first approximation the atoms are grouped in threes with co-ordinates (x, y, z), $(\frac{1}{3} + x, y, r + z')$, $(\frac{1}{3} - x, \bar{y}, r - z')$, where $z' \approx \pm z$, and r is the z-co-ordinate of the centre of a molecule which is in a general position. Waser and Lu [4] obtained values for all the parameters from a consideration of the molecular Fourier transform, and from various trials.

Structure factors were calculated for all the *hk*0 reflexions with $h = 3n$ (those with $h \neq 3n$ necessarily have zero calculated value), by using the x and y parameters given by Waser and Lu,[4] with the scattering factor for carbon of Berghuis *et al.*,[7] with $B = 4{\cdot}8$ Å^2. The discrepancy factor for the observed reflexions was $R = 20{\cdot}4\%$. Refinement proceeded by computing Fourier and difference syntheses, and adjusting the positional parameters. After one cycle R had been reduced to 18·2%.

Further refinement then required consideration of planes for which $h \neq 3n$. The " $h = 3n$ rule " had been very useful in establishing the correct trial structure in the first instance, but at this stage of the analysis it proved troublesome, since it was very difficult to decide just what the small deviations of atomic position were which gave rise to the observation of *hk*0 reflexions with $h \neq 3n$. These reflexions were all so weak that it was impossible to deduce from the magnitudes of these structures factors what small displacements were involved. Refinement of the *hk*0 data was therefore terminated at this point, and attention was turned to the *hk*1 zone in which there are no systematically weak reflexions.

The positional parameters at this stage of the analysis are listed in the second and the third column of Table 1, and the measured structure factors are compared with the calculated values, $F_c(1)$, in Table 2 ($R = 18{\cdot}2\%$). An electron-density projection along the c-axis, computed with measured structure amplitudes and calculated signs for $h = 3n$ reflexions only, is shown in Fig. 1.

hkl *Refinement.* Since no resolution of the individual atoms could be expected in projections down the *a*- and *b*-crystal axes, the problems of finding the z-co-ordinates and of refining the x- and y-parameters further was approached by considering the *hk*1 structure factors. Structure factors were calculated for these reflexions by using the x, y, and B parameters from the *hk*0 refinement and the z-co-ordinates given by Waser and Lu.[4] The discrepancy factor was 24·8%. Refinement proceeded by computing cosine and sine difference generalized projections,[8] refining all three positional parameters x, y, z, and the isotropic temperature parameters, B, simultaneously. The first set of difference maps indicated small shifts in x and y parameters, the new co-ordinates violating the " $h = 3n$ rule; " a reduction of B to 4·5 Å^2 for all atoms; and slightly larger z-co-ordinate shifts (maximum 0·09 Å). Structure factors were recalculated, and the R value had been reduced to 20·0%. A second set of difference generalized projections was computed, but no further significant changes in parameters were indicated. Measured and calculated *hk*1 structure factors are listed in Table 3.

Structure factors were then calculated for all the *hk*0 reflexions with the parameters determined from the *hk*1 refinement, and these calculated values, $F_c(2)$, are compared with $F_c(1)$ and with the measured structure factors in Table 2. For the reflexions with $h = 3n$, the R value had been reduced from 18·2% to 14·5%, a significant improvement. For the $h \neq 3n$ reflexions the $F_c(2)$ values differ from zero, and hence compare better with the measured structure amplitudes than do the $F_c(1)$ structure factors, but there is no real quantitative agreement. In general the calculated values are too low, indicating that further deviations from the idealized $h = 3n$ positions are probably necessary. In addition, inclusion of other factors which we have not considered, such as thermal anisotropy, would probably help to improve the agreement.

Any further refinement would have to utilize the complete three-dimensional data, and since our computing facilities did not allow us to undertake this work (most of the calculations were performed on a desk calculator, with Beevers–Lipson strips for Fourier summation), refinement

---

[7] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[8] Rossmann and Shearer, *Acta Cryst.*, 1958, **11**, 829.

TABLE 1.

Positional parameters.

Atom	*hk*0, *h* = 3*n* *x*	*y*	Final, from *hkl* *x*	*y*	*z*	Δ (Å)
1	0·0300	0·0072	0·0294	0·0047	−0·146	−0·011
2	0·0765	0·0000	0·0743	−0·0007	−0·318	+0·026
3	0·1236	−0·1001	0·1237	−0·1006	−0·302	−0·008
4	0·1275	−0·1750	0·1250	−0·1782	−0·117	−0·022
5	0·0810	−0·1695	0·0821	−0·1696	0·062	+0·015
6	0·0314	−0·0677	0·0313	−0·0690	0·045	+0·035
7	0·3633	0·0072	0·3637	0·0050	0·587	−0·025
8	0·4098	0·0000	0·4081	0·0008	0·753	+0·027
9	0·4569	−0·1001	0·4585	−0·1013	0·729	−0·021
10	0·4605	−0·1750	0·4619	−0·1731	0·541	+0·024
11	0·4140	−0·1695	0·4142	−0·1675	0·364	−0·028
12	0·3647	−0·0677	0·3665	−0·0700	0·393	+0·006
13	0·3033	−0·0072	0·3048	−0·0035	0·282	+0·034
14	0·2568	0·0000	0·2599	0·0012	0·113	−0·012
15	0·2097	0·1001	0·2092	0·0999	0·137	+0·009
16	0·2058	0·1750	0·2058	0·1748	0·326	−0·017
17	0·2523	0·1695	0·2529	0·1684	0·511	+0·001
18	0·3019	0·0677	0·3042	0·0682	0·478	+0·001

TABLE 2.

Measured and calculated *hk*0 structure factors.

h	*k*	*F*o	*F*c(1)	*F*c(2)	*h*	*k*	*F*o	*F*c(1)	*F*c(2)	*h*	*k*	*F*o	*F*c(1)	*F*c(2)
							h = 3*n*							
0	2	97·8	+112·1	+111·0	6	11	10·4	−6·9	−7·5	15	3	21·9	−19·1	−18·4
	4	9·4	+11·2	+9·7		12	<2·7	−4·7	−5·0		4	5·2	−6·7	−6·1
	6	42·9	+54·7	+50·6		13	5·1	−7·5	−7·9		5	3·7	+2·6	+3·7
	8	4·2	−1·7	−0·3	9	1	4·9	+4·4	+1·4		6	<3·7	+3·1	+3·0
	10	14·0	+14·8	+17·2		2	30·8	+36·9	+30·8		7	6·2	+4·1	+5·4
	12	18·9	+17·2	+19·9		3	34·7	−28·9	−33·0		8	9·5	+4·8	+5·7
3	1	45·0	+53·8	+55·5		4	32·8	+25·4	+28·4		9	<3·0	0	+0·8
	2	116·7	+134·0	+134·6		5	12·4	−12·8	−14·2		10	<2·4	−2·1	−2·2
	3	89·1	+95·5	+96·1		6	<3·3	0	+1·3		11	<1·4	+2·7	+3·2
	4	21·7	−26·9	−22·1		7	6·2	−5·3	− 6·6	18	0	30·2	−28·3	−29·6
	5	24·7	+20·6	+20·4		8	15·6	−15·3	−14·2		1	11·7	+11·4	+12·5
	6	<3·1	+1·0	+1·4		9	<3·7	−0·7	−1·9		2	14·0	−11·3	−11·4
	7	3·2	+3·3	+4·7		10	9·7	−5·9	−6·0		3	<3·7	+2·8	+3·3
	8	7·0	+1·9	+3·1		11	<3·0	+2·2	+2·0		4	5·8	−6·9	−6·0
	9	5·2	+3·0	+4·0		12	<2·3	−0·7	−0·8		5	7·1	−6·0	−7·1
	10	11·4	−15·9	−16·5	12	0	30·4	−27·5	−30·1		6	10·5	−10·0	−10·2
	11	<3·4	−1·7	−0·8		1	<3·0	0	+0·5		7	<3·0	+1·1	+1·1
	12	<3·0	+1·8	+2·6		2	11·8	−8·4	−9·4		8	<2·6	+0·5	+0·6
	13	8·6	+4·9	+6·6		3	10·9	+9·2	+11·2		9	<2·0	−1·8	−2·2
6	0	46·8	−53·2	−49·5		4	14·0	+13·4	+13·7	21	1	19·8	−13·5	−16·9
	1	48·6	−48·1	−47·1		5	8·8	+7·9	+8·9		2	16·8	−11·7	−14·0
	2	2·1	+6·6	+8·9		6	19·4	+16·2	+17·1		3	5·5	−2·6	−4·0
	3	3·1	0	+1·0		7	4·5	−4·7	−3·8		4	<3·0	+2·7	+2·6
	4	<2·5	−4·1	−3·1		8	6·4	+5·4	+5·3		5	<2·8	−2·8	−4·5
	5	30·7	+26·6	+29·0		9	6·9	−3·5	−3·8		6	7·2	−1·0	−0·9
	6	31·2	−28·9	−30·9		10	6·5	−2·9	−4·8		7	<2·0	−2·2	−3·3
	7	<3·3	−1·2	−0·3		11	3·0	−2·9	−2·6	24	0	10·4	+9·6	+9·5
	8	3·6	−4·1	−4·0		12	<1·4	−0·1	−0·5		1	2·9	−1·4	−1·6
	9	<3·6	+0·7	+1·5	15	1	<3·5	−3·0	−0·6		2	3·7	−1·1	−2·7
	10	3·6	−2·6	−2·0		2	3·5	−2·5	−2·3		3	6·2	−2·8	−3·1
							h ≠ 3*n*							
5	0	5·9	0	0	10	2	4·4	0	−0·3	5	4	6·9	0	+0·8
8		4·0	0	+1·3	11		4·1	0	+3·0	7		4·6	0	+0·1
10		2·6	0	+4·0	16		5·2	0	+1·1	8		3·4	0	−0·5
11		2·8	0	0	2	3	10·6	0	−0·7	5	5	6·7	0	−1·6
2	1	2·1	0	+1·3	4		2·1	0	−1·3	7		2·1	0	+0·6
4		2·5	0	+0·9	5		6·2	0	+1·7	8		5·3	0	+1·7
7		2·2	0	−1·1	7		3·5	0	+1·4	16		2·7	0	+0·8
8		2·8	0	−1·8	8		6·3	0	+1·1	1	6	7·0	0	−0·8
16		4·4	0	−1·5	10		3·6	0	−2·1	5		3·7	0	−0·6
2	2	8·8	0	+0·6	13		3·4	0	+1·4	7		6·0	0	−1·3
4		3·1	0	0	17		5·3	0	−1·5	10	8	3·8	0	−0·9
5		6·2	0	+1·5	4	4	1·6	0	−1·2	11		5·3	0	−0·3

was not carried any further, the final parameters being taken as those determined from the *hk*1 generalized projections.

Co-ordinates, Molecular Dimensions, and Orientation.—The final positional parameters of the carbon atoms are listed in Table 1, x, y, z being co-ordinates referred to the monoclinic crystal axes and expressed as fractions of the unit-cell edges.

TABLE 3.

Measured and calculated *hk*1 structure factors.

h	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c
$\bar{20}$	0	4·2	−4·2	$\bar{12}$	2	3·7	+4·7	18	3	<4·4	−1·3	15	5	6·3	+7·6
$\bar{18}$		16·6	−11·4	$\bar{11}$		5·0	−4·3	19		<4·2	+1·4	$\bar{9}$	6	5·8	−5·3
$\bar{16}$		12·2	−12·6	$\bar{10}$		8·1	−12·3	20		4·0	−3·3	$\bar{8}$		4·0	+1·2
$\bar{14}$		<4·0	+0·7	$\bar{9}$		26·8	+23·2	$\bar{19}$	4	5·9	−4·4	$\bar{7}$		<3·8	+2·7
$\bar{12}$		3·6	+6·0	$\bar{8}$		<2·9	+2·3	$\bar{18}$		<4·3	+1·1	$\bar{6}$		26·7	−19·8
$\bar{10}$		<3·2	+2·8	7		10·1	−4·8	$\bar{17}$		<4·4	−3·4	$\bar{5}$		<3·6	+0·1
$\bar{8}$		<2·7	+2·0	$\bar{6}$		47·5	−45·6	$\bar{16}$		<4·5	−1·3	$\bar{4}$		14·3	−19·1
$\bar{6}$		27·6	+29·6	$\bar{5}$		4·7	+0·6	$\bar{15}$		4·4	+3·3	$\bar{3}$		3·5	−1·0
$\bar{4}$		16·7	+24·1	$\bar{4}$		80·6	+83·8	$\bar{14}$		7·5	−9·9	$\bar{2}$		<3·5	−3·2
$\bar{2}$		Not obs.		$\bar{3}$		74·9	−74·4	$\bar{13}$		5·9	+9·0	$\bar{1}$		6·8	+11·1
0		Not obs.		$\bar{2}$		<1·9	−0·8	$\bar{12}$		<4·0	+2·3	0		8·4	−6·8
2		Not obs.		$\bar{1}$		33·0	+30·2	$\bar{11}$		5·5	+5·6	1		4·8	+6·6
4		16·0	+21·7	0		4·3	+3·1	$\bar{10}$		7·4	−8·3	2		<3·5	−2·1
6		29·8	−37·5	1		5·7	+8·0	$\bar{9}$		<3·5	−3·4	3		<3·5	−2·2
8		<2·8	+3·8	2		9·6	+14·7	$\bar{8}$		<3·3	+4·1	4		<3·6	−5·7
10		4·5	+6·5	3		26·2	+36·6	$\bar{7}$		31·2	+41·0	5		5·2	+1·7
12		5·1	+4·1	4		44·1	+49·5	$\bar{6}$		58·5	−57·2	6		22·2	+23·4
14		11·4	−8·2	5		22·9	+20·7	$\bar{5}$		11·0	+5·3	7		<3·8	+1·6
16		9·7	−7·7	6		23·2	+21·4	$\bar{4}$		23·9	+27·2	8		6·0	+7·2
18		30·4	+23·1	7		3·9	−6·2	$\bar{3}$		3·9	+1·3	9		<4·1	+0·6
20		6·0	−8·1	8		8·3	+4·3	$\bar{2}$		6·0	−2·0	10		<4·2	+3·2
$\bar{22}$	1	8·9	−7·2	9		25·1	−29·4	$\bar{1}$		24·0	−26·9	11		6·1	+6·6
$\bar{21}$		<4·0	+6·5	10		7·0	−9·4	0		9·8	+6·8	$\bar{9}$	7	12·2	−4·8
$\bar{20}$		<4·2	−3·6	11		<3·5	−1·8	1		9·8	−11·6	$\bar{8}$		<4·2	−4·0
$\bar{19}$		10·7	−8·2	12		3·7	+4·8	2		10·7	−2·6	$\bar{7}$		<4·1	−4·6
$\bar{18}$		4·4	+1·4	13		7·9	+7·5	3		8·2	+13·8	$\bar{6}$		<4·1	−7·8
$\bar{17}$		6·3	−9·5	14		21·0	−21·4	4		14·4	+18·7	$\bar{5}$		9·8	−8·2
$\bar{16}$		<4·3	+5·4	15		13·5	−15·7	5		17·4	+18·9	$\bar{4}$		3·7	+7·7
$\bar{15}$		4·2	+4·7	16		9·8	−5·9	6		37·1	+43·6	$\bar{3}$		13·5	−13·2
$\bar{14}$		<4·0	+1·3	17		<4·5	+6·9	7		24·5	+22·3	$\bar{2}$		12·2	+8·8
$\bar{13}$		26·5	−19·8	18		6·3	+5·5	8		19·1	+12·5	$\bar{1}$		<3·8	0
$\bar{12}$		22·9	−22·0	19		<4·3	−1·1	9		<3·5	−5·3	0		10·8	+12·4
$\bar{11}$		4·8	−7·3	20		<4·1	+2·0	10		3·7	−6·9	1		<3·8	−0·3
$\bar{10}$		7·8	+5·2	21		6·7	+6·1	11		7·8	+9·8	2		21·8	+22·0
$\bar{9}$		20·6	−18·7	$\bar{19}$	3	4·3	+5·7	12		5·7	+3·9	3		26·6	+19·6
$\bar{8}$		18·6	+7·4	$\bar{18}$		<4·4	+3·4	13		4·2	+2·9	4		5·6	+3·6
$\bar{7}$		18·2	+13·9	$\bar{17}$		4·4	−2·4	14		13·0	−13·7	5		8·0	−7·2
$\bar{6}$		21·5	+14·1	$\bar{16}$		<404	−3·1	15		<4·4	−2·0	$\bar{8}$	8	<4·2	−0·8
$\bar{5}$		5·6	+8·4	$\bar{15}$		11·4	−12·2	16		<4·5	+0·7	$\bar{7}$		14·0	−11·0
$\bar{4}$		50·2	+50·9	$\bar{14}$		<4·2	+4·0	17		4·4	−8·4	$\bar{6}$		12·4	−16·1
$\bar{3}$		109·9	−101·2	$\bar{13}$		9·9	−14·9	$\bar{16}$	5	6·3	−5·3	$\bar{5}$		<4·3	−1·1
$\bar{2}$		18·2	+26·8	$\bar{12}$		3·9	−10·8	$\bar{15}$		4·4	−10·1	$\bar{4}$		12·7	+13·7
$\bar{1}$		Not obs.		$\bar{11}$		7·3	−0·2	$\bar{14}$		4·4	+1·9	$\bar{3}$		<4·2	−0·4
0		Not obs.		$\bar{10}$		9·2	+7·7	$\bar{13}$		<4·3	−2·6	$\bar{2}$		<4·2	−7·6
1		Not obs.		$\bar{9}$		30·1	+24·4	$\bar{12}$		10·3	+8·1	$\bar{1}$		9·3	+10·4
2		61·4	+60·4	$\bar{8}$		7·6	+13·3	$\bar{11}$		<4·1	−0·6	0		<4·2	0
3		70·2	+72·1	$\bar{7}$		27·8	+29·0	$\bar{10}$		5·6	+9·7	1		7·2	+6·2
4		25·1	+34·3	$\bar{6}$		23·1	−14·0	$\bar{9}$		3·8	−3·7	2		5·9	−11·9
5		26·0	+25·4	$\bar{5}$		2·6	+8·5	$\bar{8}$		<3·6	+5·6	3		10·3	−6·9
6		16·9	−12·1	$\bar{4}$		28·8	+29·5	$\bar{7}$		22·2	+17·5	4		7·4	+9·0
7		2·6	+3·5	$\bar{3}$		47·7	−52·0	$\bar{6}$		28·4	−17·2	5		6·1	−3·0
8		<2·8	+3·1	$\bar{2}$		5·6	−6·2	$\bar{5}$		9·8	−16·2	6		17·3	+13·2
9		20·6	+19·4	$\bar{1}$		24·3	−28·5	$\bar{4}$		3·2	−2·9	$\bar{4}$	9	8·9	−5·7
10		<3·2	+1·8	0		21·5	−19·9	$\bar{3}$		8·2	−15·8	$\bar{3}$		16·5	−18·9
11		10·8	−13·6	1		14·1	−13·8	$\bar{2}$		4·3	−12·1	$\bar{2}$		<4·4	−2·7
12		25·0	+25·2	2		11·2	−5·9	$\bar{1}$		9·1	+15·8	$\bar{1}$		15·3	−14·1
13		10·9	−11·3	3		21·7	+27·2	0		7·4	+10·8	0		<4·4	0
14		4·0	+3·2	4		20·1	+18·6	1		9·6	+9·4	1		<4·4	0
15		4·2	+3·5	5		33·9	+42·2	2		21·0	−19·9	2		6·2	−5·0
16		<4·4	+0·3	6		<2·8	−4·7	3		23·1	+23·6	3		17·7	+16·4
17		15·3	−15·4	7		21·0	+19·0	4		<3·2	−2·1	4		4·4	−4·8
18		<4·4	−4·7	8		24·5	+23·6	5		18·0	−20·1	5		7·7	+9·1
19		<4·4	−3·2	9		24·5	−24·8	6		<3·4	+2·9	$\bar{4}$	10	6·2	+7·0
20		5·1	−5·4	10		<3·5	+3·9	7		10·0	+10·0	$\bar{3}$		<4·4	+7·0
21		5·6	−4·9	11		11·1	−8·1	8		18·7	+15·8	$\bar{2}$		<4·4	−4·9
$\bar{18}$	2	4·4	−4·7	12		<3·9	+4·6	9		<3·8	−0·6	$\bar{1}$		4·4	−7·5
$\bar{17}$		6·3	+6·5	13		9·1	−5·9	10		7·9	+5·1	$\bar{3}$	11	11·5	−10·3
$\bar{16}$		12·4	−13·8	14		<4·2	+7·7	11		<4·1	−3·1	$\bar{2}$		<4·1	−3·3
$\bar{15}$		7·4	+10·1	15		32·1	+25·8	12		16·9	−15·4	$\bar{1}$		5·8	+6·6
$\bar{14}$		13·0	−11·4	16		<4·4	−2·3	13		<4·3	−1·0	0		5·8	−3·9
$\bar{13}$		3·9	+7·9	17		<4·5	−3·6	14		<4·4	+1·9	1		7·1	+4·4
												2		5·8	−7·1

The co-ordinates of the atoms in each molecule can be fitted to an equation of the form, $X' + mY + nZ' + p = 0$, where X', Y, Z' are co-ordinates expressed in Å and referred to orthogonal axes *a*, *b*, and *c*′. The equations of these mean molecular planes are:

Molecule I (atoms C_1–C_6 and C_1'–C_6'):

$$0{\cdot}6109X' + 0{\cdot}6353Y + 0{\cdot}4718Z' = 0.$$

Molecule II (atoms C_7–C_{18}):

$$0{\cdot}6035X' + 0{\cdot}6582Y - 0{\cdot}4500Z' - 2{\cdot}8008 = 0.$$

The deviations of the atoms from these planes are listed in the last column of Table 1.

The bond lengths and valency angles, calculated from the final *x*, *y*, *z* co-ordinates of Table 1, are shown in Fig. 2. The mean values of the distances and angles, with symmetry *mmm* assumed (this assumption is discussed below), are shown in Fig. 3.

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. 3) and the plane normals N make with the orthogonal axes a, b, and c'. The axes L were taken through the molecular centre and the mid-point of bond 3—4 for molecule (I), and through the mid-points of bonds 9—10 and 15—16 for molecule (II); and axes M through the molecular centre and the mid-point of 1–6′, and through the mid-points of bonds 12–13 and 18–7. L, M, and N are thus not accurately mutually perpendicular, the angles being $\angle LM = 90{\cdot}6°$, $\angle MN = 91{\cdot}9°$, and $\angle LN = 93{\cdot}2°$ for molecule (I), and 88·6°, 88·6°, 90·6° for the corresponding angles for molecule (II). The orientation angles differ from those given by Waser and Lu [4] by a maximum of 5·3°, and a mean of 2·1°. The angle between the plane of the molecule and the (001) plane, ω_N, is 61·8° for molecule (I) and 63·3° for molecule (II).

TABLE 4.

Orientation of the molecules in the unit cell.

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)
χ_L	40·9°	37·2°	χ_M	90·9°	92·0°	χ_N	52·3°	127·1°
ψ_L	122·4	117·9	ψ_M	55·1	55·8	ψ_N	50·6	131·2
ω_L	112·1	67·6	ω_M	145·1	34·2	ω_N	61·8	63·3

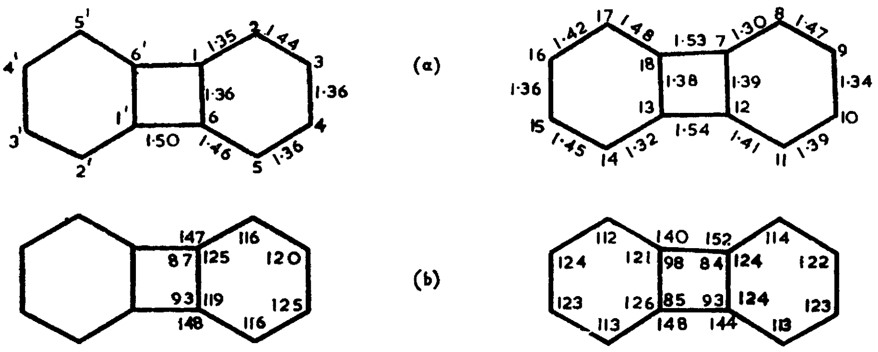
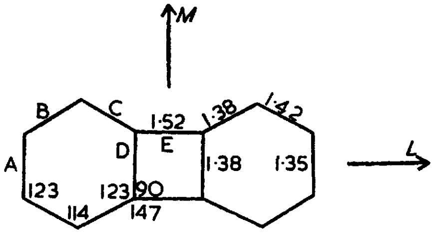


FIG. 2. (a) Measured bond lengths and (b) valency angles in biphenylene.

FIG. 3. Mean bond distances and valency angles.



Standard Deviations.—The standard deviations of the atomic positions were calculated from Cruickshank's formulæ.[9] The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}022$ Å, so that the standard deviations of the individual bond distances are 0·031 Å. This value may be compared with the root mean square deviation of the individual bond lengths from the mean distances, which is 0·043 Å.

Intermolecular Distances.—All the intermolecular separations correspond to normal van der Waals interactions. The shorter contacts are illustrated in Fig. 4.

General Structure.—Both of the crystallographically independent biphenylene molecules in the asymmetric crystal unit are completely planar within the limits of experimental error, the

[9] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

maximum deviation from the mean planes being 0·035 Å and the root mean square deviation 0·02 Å, in comparison with a standard deviation in atomic co-ordinate of 0·02 Å.

On the basis of the standard deviations of the measured bond distances (0·03 Å), some of the differences between chemically identical but crystallographically distinct bonds are significant, particularly the large discrepancy between bonds 7–8 and 17–18. However, detailed examination of all the bond distances (Fig. 2a) indicates that in general bonds parallel to 7–8 all have rather short measured distances, while those parallel to 17—18 are much longer. This suggests that there are systematic errors in molecular orientation.

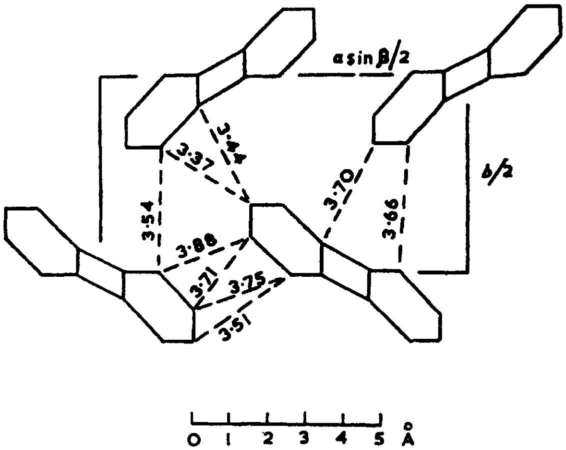


FIG. 4. Projection of the structure along [001], showing the shorter intermolecular contacts.

Since it was considered that these differences between chemically similar bonds could scarcely be real, mean values were obtained by assuming symmetry *mmm* for the molecule. The root mean square difference between the individual bond distances and the corresponding mean values is 0·04 Å, a little greater than the estimated standard deviation of bond length. Fortunately there are six independent estimates for bonds of type B and C, and three independent measurements for bond A, D, and E, so that the mean distances are considerably more accurate than the individual measurements. The standard deviations of the mean bond distances, estimated from the root mean square deviations of the individual lengths from the corresponding mean values, are: 0·01 Å for bonds A, D, and E; 0·02 Å for bond B; and 0·03 Å for bond C.

The mean values of the bond angles indicate that there are deviations from 120° in the six-membered rings, but that the angles in the four-membered ring do not differ significantly from 90°.

DISCUSSION

The measured C–C bond distances in biphenylene are listed in the first row of Table 5. Bond lengths calculated from simple resonance theory, with the five Kekulé structures given equal weight, are those listed for model *a*. In deriving these distances, the double-bond character was correlated with bond length by using a curve based on the points (0, $1{\cdot}52_7$ Å), (0·33, $1{\cdot}42_1$), (0·50, $1{\cdot}39_2$), (1·00, $1{\cdot}33_9$). This is similar to the original correlation curve given by Pauling[10] except for a small change in the value used for the single-bond distance. Coulson[11] has suggested that the usual 1·54 Å single-bond length observed in diamond and in aliphatic molecules (sp^3 hybrid orbitals) should be reduced to 1·50 Å in aromatic molecules to allow for the change to sp^2-hybridization. Recent accurate measurements[12] of the lengths of formally single bonds in quaterylene suggest, however, that the pure single-bond distance in polynuclear aromatic hydrocarbons is greater than 1·50 Å, and we have used the mean value for the six single bonds in quaterylene in deriving the correlation curve.

---

[10] Pauling, " The Nature of the Chemical Bond," Oxford, 1950.

[11] Coulson, in the " V. Henri Memorial Volume," Desoer, Liége, 1948.

[12] Shrivastava and Speakman, *Proc. Roy. Soc.*, 1960, *A*, **257**, 477.

There are marked discrepancies between these bond lengths predicted by the simplest resonance theory and those observed. The predicted lengths of bonds A, B, C vary in the order long-short-long, and this is just the opposite of the measured order.

TABLE 5.

Measured and calculated bond lengths (Å) in biphenylene.

						A	B	C	D	E
					Measured:	1·35	1·42	1·38	1·38	1·52
Valence-bond Theory										
	Weights of Kekulé structures									
	I	II	III	IV	V					
a	1	1	1	1	1	1·41	1·38	1·41	1·41	1·45
b	1	1	1	1	0	1·39	1·39	1·39	1·39	1·53
c	4	2	2	1	1	1·38	1·41	1·38	1·43	1·48
d	4	2	2	1	0	1·37	1·42	1·37	1·42	1·53
e	2	1	1	0	0	1·36	1·44	1·36	1·44	1·53
f	1	0	0	0	0	1·34	1·53	1·34	1·53	1·53
M.O. Theory										
g						1·38	1·40	1·38	1·41	1·47
h						1·39	1·41	1·39	1·41	1·47
i						1·39	1·40	1·39	1·41	1·53

Molecular-orbital calculations for biphenylene were first carried out about eighteen years ago,[3] and the calculated bond distances (model *g*) do not differ significantly from those (model *h*) of a more recent calculation.[13] Model *i* has been derived from the calculated bond orders [13] by using a correlation curve passing through the usual points ($0{\cdot}525$, $1{\cdot}42_1$), ($0{\cdot}667$, $1{\cdot}39_2$) and ($1{\cdot}000$, $1{\cdot}33_9$), and extrapolated to lower bond orders. The agreement between measured and calculated distances is much more satisfactory than for the simple valence-bond method, the variation of the predicted bond distances A, B, C being in the same order as the observed variation.

The measured bond lengths then are in agreement with the chemical reactivity in suggesting that the molecular-orbital method gives a better estimation of the electron distribution in the molecule than does simple resonance theory. In terms of the Kekulé structures, it appears that all five do not contribute equally to the hybrid molecule, but that the preferred structure is (I). The bond distances for (I) (model *f*) obviously represent too severe a fixation of double and single bonds, and by varying the weights (Table 5) best agreement is obtained for model *d*, that is with maximum weight given to the cyclobutane formulation (I), less weight to the cyclobutene structures (II and III), and only a little weight to the cyclobutadiene structures.

It is apparent that in all the models bond D has calculated values which are considerably greater than the measured distance. Now in all the bond-length calculations, no account has been taken of the strain introduced in forming the four-membered ring (it might be recalled that the correct molecular structure was previously discounted [5,6] because of the high value expected for this strain energy). The distortion involved in decreasing two valency angles at *ortho*-positions in each benzene ring from 120° to 90° would obviously result in a considerable compressive force on bond D, and a shortening below the distances predicted by neglecting the effect of strain, in agreement with the short measured length. Best agreement with measured bond distances is obtained by using model *d* or *e* and applying a correction to bond D for compression due to the formation of the four-membered ring; the other bonds in the six-membered rings are, of course, also affected by this strain but probably to a smaller extent.

We are indebted to the National Research Council of Canada for grants-in-aid of this work, and for the award of a research bursary (to T. C. W. M.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, CANADA.

[*Received, May 29th,* 1961.]

[13] Ali and Coulson, *Tetrahedron*, 1960, **10**, 41.