The writers wish to express their appreciation to Dr. E. P. Carr and Dr. H. Stücklen for helpful suggestions.

Summary

Absorption curves showing molecular extinction coefficients in the region 32–46,000 cm.$^{-1}$ are given for five methyl and chloro derivatives of biphenyl and three diphenylbenzenes.

The compounds with restricted rotation differ markedly in the intensity and structure of the absorption band from those capable of free rotation.

SOUTH HADLEY, MASS. RECEIVED AUGUST 3, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

An X-Ray Study of Substituted Biphenyls

BY LUCY W. PICKETT

The explanation advanced for the stereoisomerism observed in certain unsymmetrical derivatives of biphenyl[1] is that the rotation of the benzene rings is restricted by the interference of sufficiently large groups in the 2,2′,6,6′-positions. The crystal structure of biphenyl derivatives with restricted rotation is thus of interest in confirming this explanation but so far no derivatives of this type have been solved completely. Magnetic measurements have been published recently[2] which may offer a clue to the orientation of the molecules and it thus seems advisable to make available the x-ray findings on substances of this type. The results of a continued investigation of some derivatives of biphenyl which were described in an earlier paper by Clark and Pickett[3] are here presented together with measurements on two similar compounds, racemic 3,3′-diaminobimesityl and quaterphenyl.

Experimental

Well-known experimental methods using single crystals and the Kα radiation of copper were employed. Rotation and Weissenberg photographs were used in the interpretation, and measurements of the relative intensity of reflections were made with the integrating photometer designed by Robinson.[4] Since the measurements made in this way are relative, the structure factors given in the paper include arbitrary constants. The preparation and melting points of the compounds are described in an earlier paper.[5] The optical observations were made with a Leitz petrographic microscope (GM).

The results of the unit cell and space group determinations are summarized in Table I while those results which present especial points of interest are considered individually in the following discussion. Most of the data in the table are like those presented in the earlier paper[3] but are included for convenient reference.

Bimesityl is reported in Groth[6] as monoclinic prismatic, exhibiting the forms (001), (100) and (110). A goniometric examination confirmed the angular measurements within the limits of experimental error and together with the x-ray data showed that the form designated as (110) was rather (012) (the *a*- and *c*-axes have been renamed to correspond with the usage for other biphenyls).

An optical examination of the tablets with extended (001) faces which are formed by crystallization from an alcohol–water mixture showed parallel extinction and positive elongation. The typical interference figure obtained shows one optic axis emerging at the edge of the field but by rotating the crystal on the *b*-axis an acute bisectrix figure was obtained which showed that the crystal is biaxial negative with small optic angle. The optic axes are in the (010) plane of this monoclinic crystal with the X-direction approximately 36° from the *c*-axis in the obtuse angle β.

Analysis of the x-ray photographs showed that the most probable space group is C_{2h}^5 or C_{2h}^4 depending on the questionable existence of a very weak (030) reflection. The conclusion is therefore that the *b* spacing is either exactly or practically halved. The intensities of the reflections

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(1) An extensive review of this subject was made by Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

(2) Krishnan and Banerjee, *Trans. Roy. Soc.* (London), **A234**, 265 (1935).

(3) Clark and Pickett, THIS JOURNAL, **53**, 167 (1931); Huggins, *ibid.*, **53**, 3823 (1931); Clark, *ibid.*, **53**, 3826 (1931).

(4) Robinson, *J. Sci. Instruments*, **10**, 233 (1933).

(5) Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936).

(6) Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1919, Vol. V, p. 38.

TABLE I

SUMMARY OF CRYSTAL STRUCTURE DATA

Compound	Unit cell dimensions	n	Classification of missing reflections	Crystal class	Probable space group
Bimesityl	8.19 ± 0.03				
	8.54 ± .03	4	*h*0*l*, *l* odd	Monoclinic prismatic	
	22.10 ± .08		0*k*0, *k* odd (?)		C_{2h}^5
	95°46′				
l-3,3′-Diaminodimesityl	8.28 ± .02				
	8.63 ± .03	4	None	Monoclinic sphenoidal	C_2^1[a]
	22.50 ± .08				
	90°30′				
Racemic 3,3′-diaminodimesityl	8.45 ± .02		*h*00, *h* odd		
	8.45 ± .02	4	0*k*0, *k* odd		
	22.35 ± .08		00*l*, *l* odd		
Hexachlorobiphenyl	15.82 ± 0.04				
	8.42 ± .04	8	*hkl*, *k* + *l* odd	Monoclinic prismatic	C_{2h}^6[a]
	21.50 ± .06		*h*0*l*, *h* or *l* odd		
	91°49′				
2,2′-Diphenic acid	13.70 ± .07				
	11.95 ± .05	8	*h*0*l*, *h* odd	Monoclinic prismatic	C_{2h}^5[b]
	14.05 ± .07		0*k*0, *k* odd		
	91°40′				
Quaterphenyl	8.05 ± .02	2			
	5.55 ± .02		*h*0*l*, *h* odd	Monoclinic prismatic	C_{2h}^5
	17.81 ± .05		0*k*0, *k* odd		
	95.8° (app.)				

[a] The space group assignments differ from those in the early paper by Clark and Pickett,[3] *cf.* discussion. [b] This space group is the second alternative suggested by Clark.[3]

from a large number of planes have been measured and structure factors calculated therefrom. Attempts have been made to locate the positions of the individual atoms but the results thus far have been negative. Trial and error analyses show that the length of the molecule is not parallel to the *c*-axis although the unit cell dimensions indicate that the length is more or less parallel to this direction. One-dimensional Fourier projections of the density of the scattering matter along the normal to the (001) plane were made using all possible combinations of signs of terms but none of the contour maps obtained suggested the form of the molecule, probably because the projections so obtained were confused composites of more than one molecule.

***l*-3,3′-Diaminobimesityl** was prepared by Moyer and Adams.[7] Not only in unit cell dimensions but in the intensity of reflections from corresponding planes does this compound show a striking resemblance to bimesityl. It was first observed that like bimesityl the (*h*0*l*) and (0*k*0) planes where *l* and *k* are odd were missing but with long exposures, faint (101) and (010) reflections were unmistakably found. Since no other spacings were consistently halved, the space group C_2^1 was indicated with the molecules occupying two sets of equivalent positions, a possibility suggested by Dr. Huggins.[3] The evidence of the similar intensities shows that the molecules of the two compounds, bimesityl and *l*-3,3′-diaminobimesityl, must have very similar spatial arrangements. The two are alike in chemical structure except for the substitution of two hydrogen atoms by amino groups in the second. This suggests that whereas the second molecule of bimesityl in the unit cell may be derived from the first by reflection and a translation of one-half, corresponding molecules of the optically active compound would bear the same relation if the NH_2 groups could be ignored, thus simulating the C_{2h}^5 symmetry. The presence of the asymmetrically placed amino groups makes reflection of the entire molecule impossible and lower real symmetry exists.

Racemic 3,3′-diaminobimesityl also prepared by Moyer and Adams[7] yields ambiguous results. Recrystallized from alcohol on a microscope slide, it forms square or rectangular tablets with parallel extinction and positive elongation from which acute bisectrix interference figures are obtained which indicate that the crystal is biaxially nega-

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(7) Moyer and Adams, THIS JOURNAL, **51**, 630 (1929).

tive. A Laue photograph with the x-ray beam parallel to the *a*-axis showed the two-fold symmetry. However Weissenberg photographs about perpendicular *a*- and *b*-axes appeared identical. It is possible that some type of twinning might give rise to these anomalous results.

2,4,6,2′,4′,6′-Hexachlorobiphenyl crystallizes from alcohol to form crystals with (001), (101), (111), (100) and (011) faces. Since no measurements of its crystal form have been reported,[8] goniometric measurements were made on six crystals which showed good reflections and the angular measurements recorded in Table II.

TABLE II

ANGULAR MEASUREMENTS OF HEXACHLOROBIPHENYL

Angle	No. of measurements	Range	Mean observed	Average deviation	Calculated value
(100):(001)	16	91°41′-91°56′	91°49′	4′	
(101):(111)	14	56°01′-56°11′	56°08′	3′	
(001):(101)	6	52°25′-52°33′	52°30′	2′	
(101):(100)	5	35°37′-35°46′	35°41′	4′	35°41′
(001):(011)	4	68°34′-68°47′	68°40′	4′	68°36′
(100):(011)	2	90°00′-90°34′	90°17′	17′	90°16′
(100):(111)	3	62°57′-63°11′	63°03′	5′	63°05′

These showed that the crystal is monoclinic prismatic with an angle β of 91°49′ and an axial ratio 1.8785:1:2.554. Extinction is unsymmetrical in the principal views. An acute bisectrix figure may be seen from the (101) face, which shows that the crystal is negative with a small optic angle. Examination of the x-ray photographs showed that of the planes with indices up to and including $h = 6$, $k = 3$, $l = 7$, those which may be classified as (hkl) where $k + l$ is odd and $(h0l)$ where h or l is odd are missing. This led to the assignment of space group C_{2h}^{6} instead of that reported in the earlier paper.

Quaterphenyl,[9] m. p. 310°, was kindly supplied by Dr. Robertson. It is very difficultly soluble and was finally crystallized in tiny flakes with (001) faces from monobromobenzene. Optical examination showed that the crystal is biaxially positive with the direction of vibration of the slow ray that which was later known to be the long axis of the molecule. The unit cell whose dimensions are shown in Table I is similar to those of biphenyl[8,10] or terphenyl[11] differing only in the length of the *c*-axis. Hertel and Römer[12] have reported the unit cell dimensions and space group of quaterphenyl.

The extremely small size of the crystal made it difficult to obtain reflections of measurable intensity from more than a small number of planes. Relative intensity values, measured photometrically are listed in Table III together with visual estimates of intensity of those reflections not suitable for measurement.

TABLE III

OBSERVED AND CALCULATED INTENSITIES OF REFLECTIONS FROM QUATERPHENYL

Plane hkl	$2 \sin \theta$	Observed intensity Visual	Observed intensity Measured	Calcd. intensity $\theta = 34°$ $\phi = 12°$
001	0.086	Strong	42	98
002	.173	Medium	21	55
003	.259	Medium	20.1	51
004	.346	Strong	72	128
005	.432	Missing	0	0
006	.519	V. weak	1.5	3
007	.605	Weak	4.3	5
008	.692	Medium	21.6	22
009	.778	Medium	21.6	22
0010	.865	V. weak	1.7	1
200	.380	Weak		12
$20\bar{1}$	.385	Weak		7
$20\bar{2}$	.407	Weak		9
$20\bar{3}$	.444	Medium		20
$20\bar{4}$	.490	Missing		1
$20\bar{5}$	.550	Missing		3
$20\bar{6}$	.620	V. weak		5
$20\bar{7}$	.680	Medium	15.0	17
$20\bar{8}$	.760	M. strong	32.0	33
$20\bar{9}$	.837	Missing		0
$20\overline{10}$	.910	Missing		0
$20\overline{11}$	.990	Missing		0
$20\overline{12}$	1.070	V. weak		5
201	0.388	V. strong		682
202	.429	Missing		9
203	.475	Missing		1
204	.532	Missing		0
205	.598	Missing		0
206	.665	Missing		3
207	.740	Missing		1
208	.814	Missing		0
209	.890	Missing		2
2010	.964	Missing		0
2014	1.130	Weak		10
406	0.963	Weak		10

The position of the individual molecules in the unit cell was found through the assumption that their orientations are similar to biphenyl and terphenyl with a probable slighter tilt to the *c*-axis. After some trial and error experimentation, planar molecules with a carbon–carbon distance of 1.42

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[8] A private communication from Dr. Wherry which stated that the crystal was monoclinic with β = about 92° agrees with the present finding.

[9] This report was presented at a meeting of the American Chemical Society in September, 1933.

[10] Dhar, *Indian J. Physics*, VII (1), 43 (1932).

[11] Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933); Hertel and Römer, *Z. physik. Chem.*, **B21**, 292 (1933).

[12] Hertel and Römer, *ibid.*, **B23**, 226 (1933).

Å. in the ring and 1.48 Å. between rings were postulated, with centers of symmetry at the coördinates (000) and (1/2,1/2,0) and rotated 34° (θ) about the *c*-axis and 12° (ϕ) about the *b*-axis from an original position in the (100) plane with length parallel to the *c*-axis. The intensity of reflections from such a structure agreed well with the experimental values as shown in Table III. The lack of agreement in the lower orders of the (001) planes is not significant as the factors used in the calculation are uncertain in this region.

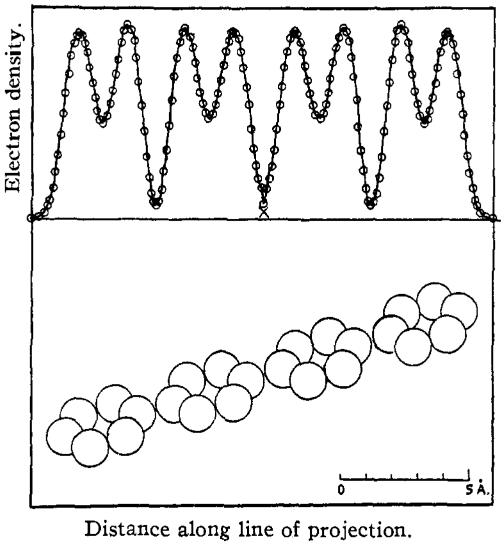

Fig. 1.—The projection of the electron density of quaterphenyl upon the line normal to the (001) plane is shown together with a diagrammatic representation of carbon atoms in an arrangement consistent with the projection. X is center of symmetry.

A one-dimensional projection of the electron density of the scattering matter in the crystal was made upon the normal to the (001) face. Relative *F* values were calculated from the measured intensities (I) of the first ten orders of the (001) planes according to the formula, $F = \left(I/1 + \frac{\cos^2 2\theta}{\sin 2\theta}\right)^{1/2}$ using the signs determined in the trial and error analysis described above. The electron density was found at points approximately 0.1 Å. apart (the unit cell length being divided into 180 parts), along the direction chosen for the projection, from the summation, $d = \Sigma F_{(001)} \cos 2\pi lz/c$. The values so obtained are plotted in Fig. 1 together with a molecular model which is consistent with the projection. The two molecules in the unit cell project as a single molecule since the atoms have like *z*-coördinates. Each peak apparently represents three unresolved atoms of carbon in each molecule.

From this experimental curve it is evident that the four benzene rings are extended coaxially while the equal width of peak suggests that the rings are coplanar. The length of projection of a single ring corresponds to that of a molecule with 1.42 Å. between the carbon atoms of the same ring and 1.48 Å. between those of adjacent rings if this molecule is placed at a tilt of 17.3° from the normal to the (001) face or 11.5° from the *c*-axis.

The above evidence does not exclude the possibility of a shorter molecule at a lesser tilt. For this reason, comparisons of observed and calculated structure factors were made for slightly differing structures (*e. g.*, for molecules with a distance between rings of 1.42 Å. and a tilt of 8.5°), using those planes which are accurately measurable and especially sensitive to change in length of the molecule, namely, (008), (009), ($20\bar{7}$) ($20\bar{8}$). The model described above with $\theta = 34°$, $\phi = 11.5°$, C–C = 1.48 Å. showed the best agreement with the experimental data. The structure factors of the above mentioned planes are insensitive to small changes in θ.

Krishnan and Banerjee[2] from measurements of magnetic susceptibilities independently reached the conclusion that the orientation of the quaterphenyl molecule was ±32° from the plane of symmetry and 17.1° from the normal to the (001) plane, results in close agreement with these.

The structure factors have been recalculated recently using the atomic *f* values for carbon in anthracene published by Robertson[13] and a carbon–carbon distance of 1.41 Å. which has been generally accepted for the aromatic carbon atom. Since there is less evidence for the distance 1.48 as existing between benzene rings these calculations were designed as a test of this distance. A comparison of structure factors for molecular models with $\theta = 32°$, $\phi = 11.3°$, a carbon–carbon distance in the ring of 1.41 Å. and the two alternatives 1.41 and 1.48 between rings is shown in Table IV with the experimental values. The results show conclusively that if the orientation of the molecule found from the magnetic susceptibility results and indicated independently by the x-ray work is correct, the distance between rings must be 1.48 rather than 1.41 Å. This is in accord with results of analyses of biphenyl[10] and terphenyl.[11]

(13) Robertson, *Proc. Roy. Soc.* (London), **A150**, 106 (1935).

TABLE IV

hkl	F, exptl.	F, calcd. C–C = 1.48	F, calcd. C–C = 1.41
008	49.5	49.3	37.4
009	53.0	53.1	65.0
$20\bar{7}$	40.5	38.1	27.3
$20\bar{8}$	63.6	66.0	75.3

Probable positions for the 48 carbon atoms in the unit cell are x,y,z; $\bar{x},\bar{y},\bar{z}$; $^1/_2 + x$, $^1/_2 - y,z$; $^1/_2 - x$, $^1/_2 + y,\bar{z}$; the values of x,y,z for the twelve carbon atoms in the half molecule are as follows

Atom	x	y	z
1	−0.018	0	0.040
2	+ .043	+0.186	.089
3	+ .009	+ .186	.165
4	− .087	0	.192
5	− .149	− .186	.144
6	− .115	− .186	.067
7	− .123	0	.272
8	− .061	+ .186	.321
9	− .096	+ .186	.398
10	− .192	0	.425
11	− .254	− .186	.376
12	− .220	− .186	.300

The writer wishes to acknowledge with appreciation the grant of the European Fellowship from the American Association of University Women which made possible the work; and to express to Sir William Bragg and the Managers of the Royal Institution her thanks for the privilege of making the measurements in the Davy Faraday Laboratory, and to Dr. K. Lonsdale for her helpful interest in the work.

Summary

Additional experimental data concerning the crystal structures of five biphenyl derivatives are presented.

The unit cell of quaterphenyl has the dimensions $a = 8.05$ Å., $b = 5.55$ Å., $c = 17.81$ Å., $\beta =$ approximately 95.8° and contains two centrosymmetrical molecules. Trial and error analyses together with a one-dimensional Fourier projection indicate that the molecules are oriented at an angle of 17.3° to the normal to the (001) plane in the acute angle β and that the carbon–carbon distance between benzene rings is 1.48 Å.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

Ultraviolet Absorption and Rotatory Dispersion of 3-Methylcyclohexanone[1]

BY H. S. FRENCH AND M. NAPS

The rotatory dispersion within an absorption band has thus far been recorded for only a limited number of compounds. We have been especially interested in such work on compounds containing the carbonyl group. It has been proved conclusively for several of these carbonyl compounds, especially camphor,[2] camphor-β-sulfonic acid,[3] and carvomenthone,[4] that the zero molecular rotation (and also the maximum of circular dichroism) occurs at a wave length greater by 60 to 110 Å. than the wave length of the maximum for the carbonyl absorption band. At least a slight shift in this direction may be noted in almost all the carbonyl compounds[5] thus far reported upon, although it is not so marked in the simpler ketones. This shift has been interpreted by some investigators[2,6] to mean an induced dissymmetry of the chromophore and a difference between the two carbon–oxygen valences. The use of rotatory dispersion curves in these cases shows therefore the non-homogeneity of an absorption band, or the fact that it is actually made up of two overlapping bands.

The present study was undertaken in order to collect further evidence concerning the carbonyl group by the use of a different cyclic ketone, 3-methylcyclohexanone,[7] simpler in structure than most of the carbonyl compounds previously used.

Previous determinations of the absorption spectrum of 3-methylcyclohexanone[8] were done

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(1) This work is included in a thesis submitted by Miss Naps to the Faculty of Wellesley College in partial fulfillment of the requirements for the degree of Master of Arts.

(2) Kuhn and Gore, *Z. physik. Chem.*, **B12**, 389 (1931).

(3) Lowry and French, *J. Chem. Soc.*, 2654 (1932).

(4) Lowry and Lishmund, *ibid.*, 709 (1935).

(5) Lowry and Gore, *Proc. Roy. Soc.* (London), **A135**, 13 (1932); Hudson, Wolfrom and Lowry, *J. Chem. Soc.*, 1179 (1933); Baldwin, Wolfrom and Lowry, *ibid.*, 696 (1935); Mathieu and Perrichtet, *Compt. rend.*, **200**, 1583 (1935); *J. phys. radium*, **7**, 138 (1936); Levene and Rothen, *J. Org. Chem.*, **1**, 116 (1936); *J. Chem. Phys.*, **4**, 48 (1936).

(6) Lowry and Walker, *Nature*, **113**, 565 (1924); Kuhn and Lehmann, *Z. Elektrochem.*, **37**, 549 (1931); Lowry, *ibid.*, **40**, 475 (1934); *Chemistry and Industry*, 477 (1935); Lowry and Allsopp, *Proc. Roy. Soc.* (London), **A146**, 313 (1934).

(7) This compound was kindly suggested to one of us by Professor T. M. Lowry of Cambridge University.

(8) Gelbke, *Jahrb. Radioakt. Elektronik*, **10**, 1 (1913); Henderson, Henderson and Heilbron, *Ber.*, **47**, 876 (1914); Purvis, *Proc. Cambridge Phil. Soc.*, **23**, 588 (1927).