Acknowledgment.—I wish to thank Professor Hildebrand for his valuable suggestions and helpfulness during the course of this investigation, and Mr. John Lyman for his assistance in making the heat of fusion determinations.

Summary

The melting point of stannic iodide has been determined by the cooling method, and the value obtained was 144.5 ± 0.1°.

The vapor pressure of stannic iodide from its melting point to 250° has been determined by means of a glass click gage. The molal heat of vaporization calculated from the vapor pressure is 13,750 ± 50 cal. per mole at 25° and varies but little with temperature.

The heat of fusion of stannic iodide was found to be 4600 ± 20 cal. per mole at the melting point. The molal heat capacity of the solid can be expressed within 0.8% of the measured values in the temperature range 25° to the melting point by C_p 19.4 + 0.036T, while that of the liquid, from the melting point to 170° is 40.1 ± 0.5 cal. per mole.

BERKELEY, CALIFORNIA RECEIVED JULY 28, 1936

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

The Ultraviolet Absorption Spectra of Substituted Biphenyls[1]

BY LUCY W. PICKETT, GERTRUDE F. WALTER AND HELEN FRANCE

Investigations by Adams and others[2] have shown that those unsymmetrical derivatives of biphenyl which have substituents above a certain limiting size in the positions adjacent to the bond joining the two benzene nuclei may be resolved into stereoisomers. This phenomenon is explained as a result of the restriction of the rotation of the two benzene rings by the interference of the substituting groups. Some absorption spectra measurements made in a study of the physical properties of biphenyl derivatives showed unexpected differences in absorption which led to further investigation.

Methyl and chloro derivatives of biphenyl were chosen for the comparison because these groups do not show selective absorption in the region under investigation and are known to introduce comparatively slight modifications in the spectrum of benzene. Furthermore, these groups are sufficiently large to restrict the rotation of the benzene nuclei when they are in the 2,2′,6,6′-positions. The spectroscopic study was made with the simplest compounds available which had the above characteristics.

Experimental

Preparation of Compounds.—After purification the compounds were in each case crystallized from the optically pure solvent used in the measurements. After the absorption spectrum had been photographed, the material from which the sample was taken was further distilled or crystallized and photographs again taken. The second results agreed with the first in all cases except one as noted below in the discussion of the source and treatment of individual substances.

Biphenyl, m. p. 69–69.5°, obtained from Eastman Kodak Co., was purified by vacuum distillation and repeated crystallization from alcohol.

3,3′-Bitolyl,[3] b. p. 154° at 14 mm., was prepared by the condensation of *p*-iodotoluene with activated copper bronze and purified by two vacuum distillations. Although the product boiled constantly, a photograph taken at this time indicated slightly different absorption from that which was obtained from material distilled a third time. A fourth distillation yielded material identical with the latter.

4,4′-Bitolyl, m. p. 119.5–120°, was prepared by the condensation of *p*-bromotoluene and purified by vacuum distillation and crystallization from alcohol.

Bimesityl, m. p. 100–100.5°, was prepared from bromomesitylene by the method described by Moyer and Adams[4] and crystallized repeatedly from alcohol.

4,4′-Dichlorobiphenyl, m. p. 146.5–147°, was obtained from Eastman Kodak Co. and purified by recrystallization from alcohol.

2,4,6,2′,4′,6′-Hexachlorobiphenyl, m. p. 111.5–112°, was prepared from trichloroiodobenzene by condensation with copper bronze and recrystallized from alcohol. The trichloroiodobenzene was obtained from diazotization of trichloroaniline.

***o*-, *m*- and *p*-diphenylbenzenes,** m. p. 58, 87, 211.5°, were obtained from Eastman Kodak Co., and recrystallized repeatedly from benzene and alcohol.

Mesitylene, b. p. 66.4° at 24.5 mm., was obtained from Eastman Kodak Co., and vacuum distilled.

Absorption Spectra Measurements.—The absorption measurements were made with a Hilger quartz spectro-

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[1] This paper was presented at the New York meeting of the American Chemical Society in April, 1935.

[2] An extensive review of this subject is given by Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[3] This compound was prepared and photographed by Mary Dunlap.

[4] Moyer and Adams, THIS JOURNAL, **51**, 630 (1929).

graph (E-2) using a comparison method which has been described.[5] The source of light for most of the measurements was a condensed copper spark. In order to detect the presence of weak bands in the region of the band maxima the continuous light from a discharge through hydrogen was used for a series of closely spaced exposures made through slightly varying thicknesses of solution for each compound. Both ethyl alcohol and hexane were used as solvents and it was found that the curves obtained in the two solvents agreed closely except for very slight shifts toward the visible for the alcohol solutions. The absorption curves presented show the logarithm of the molecular extinction coefficient plotted against the wave number. Each curve represents over sixty experimental points which are not shown because they are so closely spaced.

Photographs of the solid biphenyl were made by mounting a very thin uniform crystal on a fluorite plate placed before the slit of the spectrograph normal to the light beam. The thickness was calculated from the interference color between crossed nicol prisms using the refractive indices determined by Hendricks and Jefferson.[6]

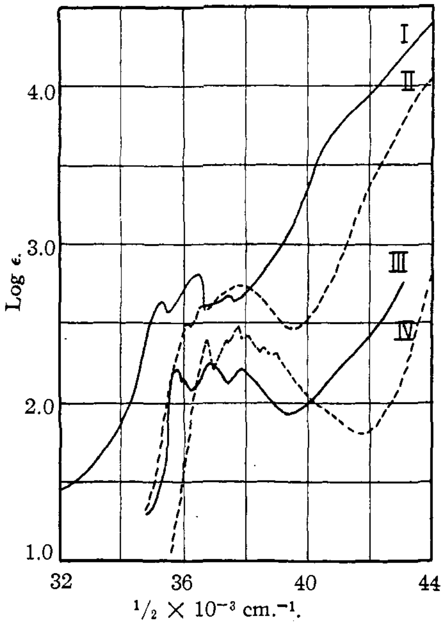
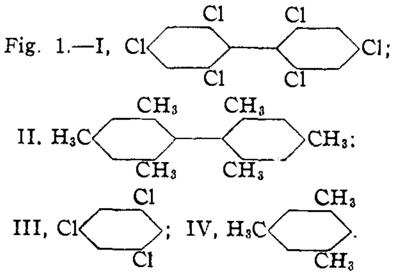


Fig. 1.—I,



Discussion of Results

The absorption curves of 2,4,6,2′,4′,6′-hexachlorobiphenyl and bimesityl in alcohol solution are shown in Fig. 1. Each has a group of three absorption bands whose positions are as follows

Compound	Band maxima (1/λ cm.$^{-1}$)		
Bimesityl	36070	36480	37800
Hexachlorobiphenyl	35260	36350	37360

The position of the bands is practically the same in hexane and alcohol solutions, the difference being less than the error of measurement. It was especially noticeable in the chlorine compound that the bands had very sharp edges on the short wave length side.

For comparison are shown the absorption curves of the corresponding benzene derivatives, 1,3,5-trichlorobenzene and mesitylene as measured by Conrad-Billroth[7] and Wolf and Strasser.[8] The curve of the second compound is continued into the shorter wave region from data obtained in this Laboratory. It will be noticed that the band maxima of the most intense bands in the benzene derivative correspond to similar ones in the biphenyl compound which are displaced toward the visible. This shift is small and fairly constant (340, 350, 300 cm.$^{-1}$) for the chloro compounds but larger for those with methyl groups so that the second band of bimesityl almost coincides in frequency with the first band of mesitylene. The extinction coefficient of the band maxima of the biphenyl derivative is two or three times that of the corresponding benzene indicating that the absorption is nearly additive for the two benzene rings.

A similar comparison would be expected between monosubstituted derivatives of benzene and disubstituted derivatives of biphenyl but Fig. 2 shows that the curves for 3,3′- or 4,4′-bitolyl and 4,4′-dichlorobiphenyl in alcohol solution differ markedly from those of toluene[9] and monochlorobenzene.[10] In each case the narrow band structure is lost completely and the intensity increase is of the order of 100-fold. A difference of this kind is known to exist between benzene and biphenyl[11] and a recent article[12] by Seshan notes that the loss of banded structure is characteristic of the absorption of terphenyl and *s*-triphenylbenzene as well.

A study of the *o*-, *m*- and *p*-diphenylbenzenes in hexane solution with biphenyl included for com-

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(5) Carr, THIS JOURNAL, **51**, 3041 (1929).

(6) Hendricks and Jefferson, *J. Optical Soc. Am.*, **23**, 299 (1933); *cf.* Narasimham, *Indian J. Physics*, **6**, 233 (1931); Sundarajan, *Z. Krist.*, **93**, 238 (1936).

(7) Conrad-Billroth, *Z. physik. Chem.*, **B19**, 76 (1932); **B29**, 170 (1935); **B31**, 475 (1936).

(8) Wolf and Strasser, *ibid.*, **B21**, 389 (1933).

(9) Wolf and Herold, *ibid.*, **B13**, 201 (1931).

(10) Conrad-Billroth, *ibid.*, **B19**, 76 (1932).

(11) "International Critical Tables," Vol. V, p. 359.

(12) Seshan, *Proc. Indian Acad. Sci.*, **3A**, 148 (1936).

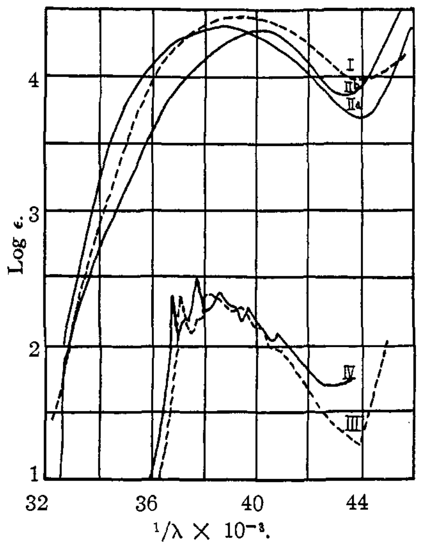
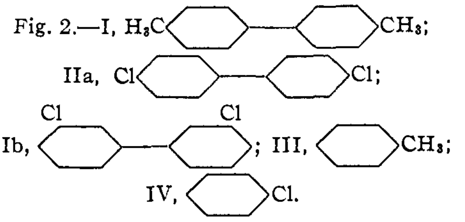


Fig. 2.—



parison is illustrated in Fig. 3. The absorption band of the meta compound is similar in position to that of biphenyl but of greater intensity while that of the para compound is displaced toward the visible and still slightly higher. In the ortho compound there is a second rise in absorption overlapping the band so that the minimum is not developed but the band which corresponds to those of the other isomers is of lower intensity.

In a study of several complete series of halogenated and methylated benzenes, Conrad-Billroth[7,13] has shown that the number and position of substituting groups causes some modification in the position and intensity of the absorption bands and has called attention to the para effect, namely, a heightened intensity exhibited by para compounds. The variation among biphenyl, dichlorobiphenyl and the bitolyls is of this order and is probably due to a similar cause. The magnitude of the intensity difference noted in the present paper is thought to require a different explanation.

An attempt at such explanation is hardly justified at present. The evidence shows that a molecule such as bimesityl absorbs light as two mesitylene molecules while bitolyl has a greatly increased probability of absorption compared to two toluene molecules. If the increased intensity of absorption directly results from the free rotation of the molecule, solid biphenyl should show less intense absorption than in solution. Measurements of single crystals showed that the absorption curve of solid biphenyl was shifted toward the visible by about 550 cm.$^{-1}$ from that of the solution and although the measurements did not extend to the top of the band there was no evidence of decrease in intensity of absorption. It is possible that the increased absorption may be dependent on the planar form of the molecule[14] since the most stable position for biphenyl in solution is probably planar, a form which the 2,2′,6,6′-derivatives cannot assume because of the interference of substituting groups. Similarly, *o*-diphenylbenzene is less likely to be planar than the *m*- or *p*-isomers. Regardless of explanation, these results suggest a possible means of distinguishing compounds of restricted rotation.

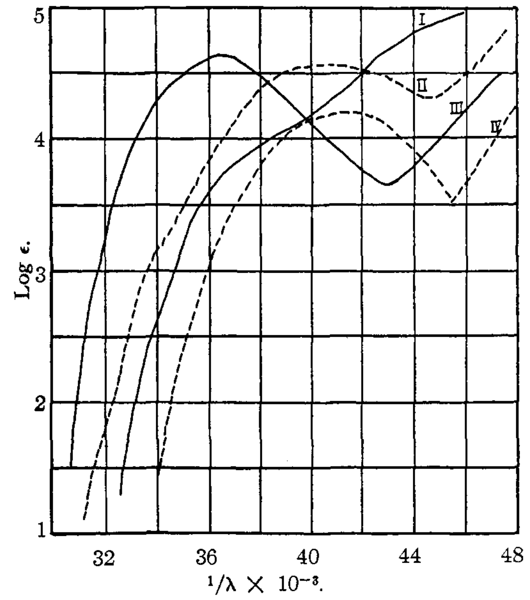


Fig. 3.—I, *o*-Diphenylbenzene; II, *m*-diphenylbenzene; III, *p*-diphenylbenzene; IV, biphenyl.

The effect of substitution of chloro and methyl groups on the wave length of the band maxima is just that which would be predicted from the results of a study of benzene derivatives.[13] The band is displaced toward the visible in all cases. This shift is greater for the chloro than the methyl derivatives, greater for the para than the meta compound, and approximately twice as great for the hexasubstituted as for the disubstituted compounds.

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(13) Also *Z. physik. Chem.*, **B20**, 222, 227 (1933).

(14) We are indebted to Dr. G. B. Kistiakowsky for suggesting this possibility.

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.