sulting solution was stirred for 30 minutes with 350 g. of Dowex-50 (hydrogen ion form) which changed the *p*H of the solution to 1.0 or less; the resin was removed and the solution was evaporated to dryness. The residue was extracted with ether in a soxhlet apparatus until the material in the thimble gave no acid reaction. *o*-Nitrophenylphosphonic acid crystallized readily from the ether solution, and a second crop could be obtained by evaporating the ether to a small volume. The yield of pale yellow crystals was 5.6 g., m.p. 200–203°. Mixed m.p. with *p*-nitrophenylphosphonic acid was 159.5–165°; mixed m.p. with *m*-nitrophenylphosphonic acid was 133–137°.

Anal. Calcd. for $C_6H_6NO_5P$: N, 6.90; P, 15.25; neut. equiv., 101.5. Found: N, 6.84; P, 15.18; neut. equiv., 101.5.

The magnesium salt of *m*-nitrophenylphosphonic acid was converted to the free acid in the following manner. A suspension of 41 g. of the salt in 250 ml. of 6% sodium hydroxide solution was heated to boiling and then allowed to cool. The precipitated magnesium hydroxide was removed by filtration, and the filtrate was stirred with 350 g. of Dowex-50 (hydrogen ion form) which changed the *p*H of the solution to 1.0 or less. The resin was removed, and about 25 ml. of concentrated hydrochloric acid was added to the resulting solution, which was then evaporated to dryness. The residue was extracted with ether in a soxhlet apparatus. When the ethereal solution was concentrated to incipient crystallization and cooled, there was obtained 23.3 g. of *m*-nitrophenylphosphonic acid. This was identified by analysis, by mixed m.p. with an authentic sample and by ultraviolet absorption.

Physical Measurements.—The acid dissociation constants were determined by potentiometric titration in water as described in an earlier paper.[4e]

The ultraviolet absorption spectra were determined in 95% ethyl alcohol by the procedure previously used.[9] All measurements were made at room temperature with 1.0-cm. silica cells. The molar extinction coefficient, ϵ, was calculated from the equation: $\epsilon = D/lc$, where D = optical density, l = absorption cell thickness in cm., and c = the concentration of the sample in moles per liter.

Acknowledgments.—The authors wish to thank Miss Betty Jean Pegram for performing the analyses necessary for this investigation and Mr. Edward L. Petit for skilled technical assistance.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra of Some Biphenyl Derivatives of Phosphorus and Arsenic

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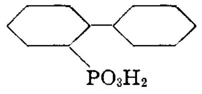
The ultraviolet absorption spectra of a number of biphenyl derivatives of phosphorus and arsenic have been determined. These spectra indicate that the *o*-PO_3H_2 and the *o*-AsO_3H_2 groups are very effective in restricting rotation around the carbon–carbon bond joining the two rings in the biphenyl molecule. The spectrum of arsafluorinic acid exhibits the intensity and the prominent fine structure characteristic of fluorene derivatives.

Biphenyl and its *meta* and *para* substituted derivatives have intense absorption ($\epsilon_{max.} > 10{,}000$) near 250 mμ, due mainly to extensive resonance between the two phenyl rings.[1] *Ortho* substituents may hinder the attainment of a planar arrangement of the two rings and thus cause a considerable change in the ultraviolet absorption. For example, the presence of two bulky *ortho* substituents in 2,2′-dimethylbiphenyl reduces the molecular extinction coefficient enormously.[1b] A single *ortho* substituent ordinarily has comparatively little effect.[1d]

In a recent communication[2] from this Laboratory, evidence was presented which indicated that the two phenyl rings in *o*-biphenylylphosphonic acid(I)


I

(and in *o*-biphenylarsonic acid) are almost perpendicular to each other. This configuration, it was concluded, is reinforced by a hydrogen bond between the PO_3H_2 (or AsO_3H_2) group and one of the benzene rings. If these deductions are correct, the ultraviolet absorption spectra of these compounds should differ markedly from the spectrum of biphenyl. Table I lists the wave lengths of the absorption maxima and the corresponding molar extinction coefficients for these compounds and several related biphenyl derivatives.

TABLE I

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF SOME BIPHENYL DERIVATIVES

Compound	$\lambda_{max.}$, mμ	$\epsilon_{max.}$
Biphenyl	248	16,600
p-Biphenylylphosphonic acid	255	21,900
3,3′-Biphenyldiphosphonic acid	250.5	15,600
4.4′-Biphenyldiphosphonic acid	262.5	23,300
o-Biphenylylphosphonic acid	237	8,220
	274.5	2,030
o-Biphenylarsonic acid	239	8,510
	276	2,890
Arsafluorinic acid	226	25,700
	232.5	29,600
	240	28,000
	276.5	8,210
	287.5	6,870

The ultraviolet absorption spectra of *p*-biphenylylphosphonic, 3,3′-biphenyldiphosphonic and 4,4′-biphenyldiphosphonic acids are very similar to the

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[1] See, for example (a) L. W. Pickett, G. F. Walter and H. France, THIS JOURNAL, **58**, 2296 (1936); (b) M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940); (c) B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941); (d) R. A. Friedel, M. Orchin and L. Reggel, *ibid.*, **70**, 199 (1948); (e) G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2888 (1949); (f) A. J. Bilbo and G. M. Wyman, THIS JOURNAL, **75**, 5312 (1953). This last paper discusses spectral and chemical effects associated with the degree of planarity of certain biphenyl derivatives.

[2] H. H. Jaffé, L. D. Freedman and G. O. Doak, *ibid.*, **76**, 1548 (1954).

spectrum of biphenyl. These results are consistent with an earlier conclusion that the PO_3H_2 group causes no profound change in the general characteristic of the spectrum of the parent compound.[3] In contrast, a PO_3H_2 group in the *ortho* position of biphenyl greatly reduces the intensity of the biphenyl absorption. The effect of an o-AsO_3H_2 group is very similar. It seems clear that the o-PO_3H_2 and the o-AsO_3H_2 groups must be very effective in restricting rotation around the carbon-carbon bond joining the two rings in the biphenyl molecule.

A scale model[4] indicates that the arsafluorinic acid[5] has a planar, or near planar, structure. Thus, this compound is a biphenyl derivative in which free rotation of the rings is restricted in such a manner as to hold the phenyl groups in a planar configuration. The possibility of resonance between the rings is enhanced; and, accordingly, the ultraviolet absorption of this compound is even more intense than that of biphenyl. Jones[6] has pointed out that the methylene bridge in fluorene is associated with the production of very prominent fine structure in the spectrum of the compound. The fine structure effect is also seen in the spectrum of arsafluorinic acid.

Experimental

Materials.—With the exception of the biphenyl, all compounds studied were prepared in this Laboratory. The biphenyl was a reagent grade material (Eastman Kodak Co. 721) which was recrystallized from ethanol. *o*-Biphenylylphosphonic,[2] *p*-biphenylylphosphonic,[2] *o*-biphenylarsonic[7] and arsafluorinic[8] acids were prepared by known methods. The procedure used for preparing the diphosphonic acids is described below and is based on the method developed by Busch[9] for the catalytic reduction of bromobenzene to biphenyl.

3,3'-Biphenyldiphosphonic Acid.—*m*-Bromophenylphosphonic acid (11.9 g.) and 3.0 g. of 1% palladium-on-calcium carbonate[9b] were added to a mixture of 90 ml. of 2.2 *N* aqueous potassium hydroxide and 90 ml. of methanol in a 2-necked flask equipped with a sealed stirrer and a reflux condenser. The mixture was stirred and refluxed for 24 hours. The catalyst, which was now completely black, was removed by filtration.[10] The filtrate was acidified with 40 ml. of concentrated hydrochloric acid and then evaporated to dryness on a steam-bath. The residue was further dried in a desiccator over sodium hydroxide. The solid thus obtained was pulverized and then extracted for 48 hours with 250 ml. of ether in a Soxhlet apparatus.[11] The material in the thimble was then extracted for eight hours with 250 ml. of absolute ethanol. The alcoholic solution was evaporated to dryness, and the residue was recrystallized from dilute hydrochloric acid. The yield of white crystals was 1.8 g. (23%), m.p. 246–252°.

Anal. Calcd. for $C_{12}H_{12}O_6P_2$: P, 19.72; neut. equiv., 78.5. Found: P, 19.11; neut. equiv., 78.8.

4,4'-Biphenyldiphosphonic Acid.—*p*-Bromophenylphosphonic acid (11.9 g.) was reduced by the method described for the *m*-isomer. After the catalyst was removed by filtration, the filtrate was acidified with 17 ml. of concentrated hydrochloric acid. A potassium salt of the diphosphonic acid immediately precipitated. The mixture was cooled and the salt removed by filtration. In order to isolate the free diphosphonic acid, the salt was dissolved in a boiling mixture of five volumes of alcohol and seven volumes of 9 *N* hydrochloric acid; the crystalline acid separated when the solution was cooled. The yield was 2.2 g. (28%), m.p. $> 300°$.

Anal. Calcd. for $C_{12}H_{12}O_6P_2$: P, 19.72; neut. equiv., 78.5. Found: P, 19.21; neut. equiv., 78.2.

Attempted Synthesis of 2,2'-Biphenyldiphosphonic Acid.—*o*-Bromophenylphosphonic acid could not be reduced to a biphenyl derivative by the procedure used for reducing *m*- and *p*-bromophenylphosphonic acids.

Absorption Spectra Measurements.—The ultraviolet absorption spectra were determined in 95% ethyl alcohol by the procedure previously used.[3] All measurements were made at room temperature with 1.0 cm. silica cells. The molar extinction coefficient, ϵ, was calculated from the equation $\epsilon = D/lc$, where D = optical density, l = absorption cell thickness in cm., and c = concentration of the sample in moles per liter.

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[3] H. H. Jaffé and L. D. Freedman, THIS JOURNAL, **74**, 1069 (1952); **74**, 2930 (1952). It has also been shown that the effect of an AsO_3H_2 group is almost the same as that of a PO_3H_2 group; *cf.*, H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

[4] Constructed with an atom model set manufactured by Waltham Enterprises, Ltd., in England.

[5] F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth and Silicon," Interscience Publishers, Inc., New York, N. Y., 1950, p. 37.

[6] R. N. Jones, THIS JOURNAL, **67**, 2127 (1945).

[7] G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2895 (1949).

[8] J. A. Aeschlimann, N. D. Lees, N. P. McCleland and G. N. Nicklin, *ibid.*, **127**, 66 (1925).

[9] (a) M. Busch and W. Weber, *J. prakt. Chem.*, **146**, 1 (1936); (b) see also F. R. Mayo and M. D. Hurwitz, THIS JOURNAL, **71**, 776 (1949).

[10] Bromide ion analyses on aliquots from the filtrate showed that all of the bromine had been split from the ring.

[11] This step removed the phenylphosphonic acid formed in the reaction. When the ethereal solution was evaporated to dryness and the residue recrystallized from dilute hydrochloric acid, we obtained 2.6 g. of pure phenylphosphonic acid. This was identified by analysis, by mixed m.p. with an authentic sample, and by ultraviolet absorption.