homogeneous, rigid solvent has been studied theoretically and experimentally. Most of the experiments were made with fluorescein in boric acid glass. Here, as in many similar phosphors, there are two emission bands (alpha and beta) associated with two different processes by which the phosphorescent state may return to the normal state. These two processes are both unimolecular. The rate of the beta process has been studied down to 20°K. and presumably would be little changed by proceeding to the absolute zero. As to the nature of the phosphorescent state and of the beta process two possible interpretations are offered. The alpha process obeys the Arrhenius equation and the heat of activation is found to be 8 ± 1 kcal., which agrees with the spectroscopic value of 9 kcal. found for the difference in energy of the fluorescent and phosphorescent states. A full energy diagram of the several states is given.

With intense illumination the phosphorescence approaches a maximum and a new absorption spectrum appears which belongs to the phosphorescent state. By slight extrapolation it has been found possible to obtain the pure spectrum of that state.

Our experiments indicate that excitation by light does not cause appreciable turning of the dye molecule in its rigid environment. This accounts for our observations on the polarization of the phosphorescent light, and leads to a new kind of dichroism. From quantitative measurements of this dichroism we have been able to calculate the degree of orientation of the molecules in the phosphorescent and in the normal states.

BERKELEY, CALIF. RECEIVED JULY 7, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ultraviolet Absorption Spectra of Organic Molecules. II. The Effect of Substituent Groups upon the Absorption of Biphenyl

BY BARBARA WILLIAMSON AND WORTH H. RODEBUSH

In the preceding paper of this series,[1] ultraviolet absorption was shown to be a reliable measure of the existence of conjugation and the resulting resonance in organic molecules where these effects are pronounced. The degree of correlation between the absorption and the possibility of resonance structures was surprisingly high; in fact, it is probable that the absorption is a more direct measure of resonance than any other property. Chemical reactivity, for example, is affected by many variables and often depends upon several different mechanisms so that a good correlation with the predicted resonance structures is unlikely.

The article referred to above showed the effect of restricted rotation with the resultant displacement from coplanarity upon the resonance as measured by the ultraviolet absorption. The general conclusions of this paper may be stated in the following way: molecules involving saturated carbon chains or rings show absorption in the Schumann region below 2000 Å. If, however, the structure is one in which resonance structures are possible, the absorption is shifted to longer wave lengths which fall within the range of the quartz spectrograph. For many molecules one or more maxima are observed in the range mentioned above and it becomes possible, by comparing the spectra obtained for these molecules modified by further substitution, to study two effects—the change in extinction coefficient and the shift in wave length of the absorption maximum. These effects were interpreted in the paper referred to as being due to a change in the extent or number of resonance structures. It will be recognized, of course, that, according to this way of looking at things, an absorption maximum is not to be identified as belonging to any particular functional group but is to be considered as a property of the molecule as a whole or of such parts of the molecule as are capable of conjugation with each other. Naturally, in the case of a molecule such as phenyl acetic acid we should have two distinct resonance units, a phenyl group and a carboxyl group, and the absorption observed would be that resulting from the superposition of the effects due to these two units.

As a continuation of the work described in the paper referred to we have studied the dependence of extinction coefficient and wave length of the ab-

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[1] M. T. O'Shaughnessy and W. H. Rodebush, THIS JOURNAL, 62, 2906 (1940).

TABLE I

No.	Biphenyl compound	Source	Purification, recryst. from	M. p., cor., °C.	Max. λ, Å.	Max., ϵ
1	2,2'-Dimethoxy[a]	Prepd. by one of writers	Benzene after vac. subl.	154.5–155.5	2767	6,000
2	4,4'-Dimethoxy[a]	Prepd. by one of writers	Benzene after vac. subl.	176.5–177.0	2630	21,700
3	2,2'-Dihydroxy	Prepd. by one of writers	Water, then toluene	107.0–107.5	2420 2850	10,000 6,000
4	3,3'-Dihydroxy	Prepd. by one of writers	Water	124.0–125.0	2550	12,000
5	4,4'-Dihydroxy	Stock	Alcohol	280.5	2650	22,400
6	2,2'-Dicarboxy	Mr. E. C. Dunlop	Alcohol	231.5	2800	2,200
7	3,3'-Dicarboxy	Dr. L. A. Brooks	Alcohol	350–352	= 20,000 at 2430, falls steadily	
8	4,4'-Dicarboxy (dimethyl ester)	Mr. J. C. Robinson	Benzene	212.5–213.0	2800	30,000
9	2,2'-Diamino	Stock	Alcohol, then pet. ether	78.5	2920	5,000
10	4,4'-Diamino	Stock	Alcohol	128.0–129.0	2850	23,200
11	2,2'-Dinitro	Stock	Alcohol	124.5	2570	12,000
12	3,3'-Dinitro	Dr. R. W. Kell		198.5–199.5	3373	18,000
13	4,4'-Dinitro	Stock	Alcohol, then toluene	239.0–239.5	3050	24,000
14	Diphenyl 2,2'-disulfonic acid (disodium salt)	Prepd. by one of writers	Alcohol	...	2777	2,000
15	2,2'-Dichloro	Monsanto Chem. Co.		59.0–60.5	= 4500 at 2350, falls steadily	
16	4,4'-Dichloro	Prepd. by one of writers	Alcohol	148.0–149.0	2600	21,700
17	4,4'-Difluoro	Dr. G. C. Finger	Alcohol	88.5	2430	17,000
18	4,4'-Dibromo	Prepd. by one of writers	Benzene	166.5–167.0	2620	23,300
19	4,4'-Diiodo	Prepd. by one of writers	Pet. ether, glyc., HAc, alc.	205.5–206.0	2740	30,000

[a] Solvent for these, *n*-hexane; for others, alcohol.

sorption maximum upon the type of group substituted and the position of substitution. Certain predictions can be made from generally accepted theories in regard to these effects.

In the previous paper the theory of the absorption of light by organic molecules was presented in brief outline. The excited state of the molecule is ionic and any modification of the structure by substitution which increases the number of resonance configurations will, in general, produce a greater increase in the number of configurations for the excited ionic state than for the normal unexcited state. The result of this is a lowering of the energy of the excited state relative to that of the normal state and a shift of the absorption maximum to longer wave lengths.

The extinction coefficient depends in an indirect way upon the polarizability. But the polarizability itself must vary with the number of resonance states, so that we may expect a certain parallelism, though by no means an exact correlation, between the change in extinction coefficient and the shift in wave length. These relationships will be discussed in detail later in this paper.

Experimental

The source, purification and corrected melting point of the compounds studied are listed in Table I. The melting points given here include calibration and stem correction as determined by a set of Central Scientific Company calibrating thermometers.

Preparations.—Since all the compounds synthesized by the writers were prepared according to previously established procedures, only references to the procedures used are made, with a statement of any departures therefrom.

2,2'-Dimethoxybiphenyl was prepared by the Ullmann[2] reaction following O'Shaughnessy's[3] directions from *o*-iodomethoxybenzene according to Holmes.[4] 4,4'-Dimethoxybiphenyl was prepared by the Ullmann reaction, according to O'Shaughnessy's directions, from *p*-iodomethoxybenzene obtained from stock. 2,2'-Dihydroxybiphenyl (and 4,4'-dihydroxybiphenyl) were prepared by the demethylation of 2,2'-dimethoxybiphenyl and 4,4'-dimethoxy biphenyl, respectively, according to Adams and Kornblum.[5] The disodium salt of diphenyl-2,2'-disulfonic acid was obtained from a sample of diphenyl-2,2'-disulfonic acid, prepared by Stanley,[6] by titrating the aqueous solution with dilute sodium hydroxide. 4,4'-Dibromobiphenyl was prepared according to Carnelley and Thomson.[7] 4,4'-Diiodobiphenyl was prepared from benzidine by diazotization and addition of potassium iodide according to directions in Holmes'[4] thesis. The crude product was washed successively with sodium bisulfite, sodium hydroxide, and hydrochloric acid before successive recrystallization from petroleum ether, glacial acetic acid and alcohol.

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(2) F. Ullmann, *et al.*, *Ann.*, **332**, 67 (1904).

(3) M. T. O'Shaughnessy, Doctor's Thesis, Urbana, Illinois, 1940.

(4) D. F. Holmes, Doctor's Thesis, Urbana, Illinois, 1934.

(5) R. Adams and N. Kornblum, THIS JOURNAL, **63**, 197 (1941).

(6) W. M. Stanley and R. Adams, *ibid.*, **52**, 4471 (1930).

(7) T. Carnelley and A. Thomson, *J. Chem. Soc.*, **47**, 587 (1885).

2,3-Diphenylbutadiene-1,3 was prepared and purified according to Allen, Eliot and Bell.[8]

Solvents.—The solvent was either *n*-hexane or 95% alcohol (see Table I). The *n*-hexane was purified with fuming sulfuric acid according to the procedure given by O'Shaughnessy and Rodebush.[1] If the compound was insoluble in *n*-hexane, then alcohol was used as a solvent. In most cases the alcohol obtained from stock was sufficiently transparent in the range investigated. If not, it was purified by allowing it to stand overnight with iodine (1 g. of iodine per l. of alcohol) and then distilling from zinc dust. In all cases the solvent was checked before use. Since it was desirable to compare the absorption curves in at least a semi-quantitative manner, alcohol was used as a solvent for almost all of the biphenyl samples even though a few of them were soluble in *n*-hexane. The dimethoxybiphenyls were run in *n*-hexane to facilitate comparison with the data of O'Shaughnessy and Rodebush.

Absorption Measurements

Apparatus.—The instrument used was a Bausch and Lomb medium quartz spectrograph fitted with a sector-photometer. The light source was a condensed spark between tungsten-steel electrodes. Two sets of optically matched, fused quartz absorption cells were used. In all calculations their length was taken as 5.0000 cm. In no case did this involve an error greater than 0.15%.

Method.—For the biphenyls duplicate samples were weighed out by the microanalyst to five significant figures. Dilutions of approximately 0.001, 0.0001 and 0.00001 mole per liter were then made up in a series of 50-ml. volumetric flasks. For the para substituted biphenyls an additional dilution was sometimes needed to cover all features of the absorption curve. One set of dilutions was run immediately; the other set was allowed to stand a week and then run. This served the double purpose of ensuring against any slow progressive reaction of the compound with the solvent and checking the absorption curve.

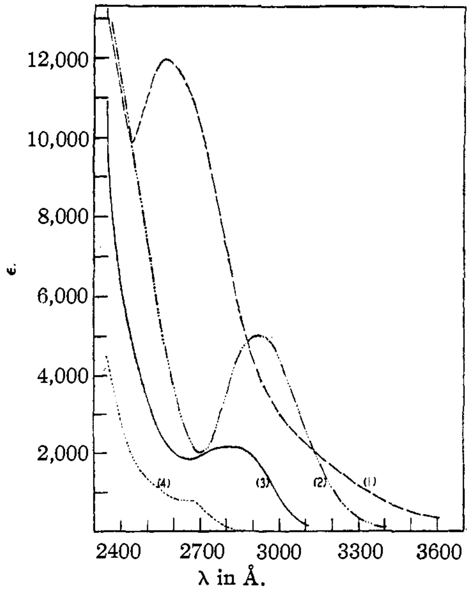

Fig. 1.—Absorption spectra: (1) 2,2′-diaminobiphenyl; (2) 2,2′-dinitrobiphenyl; (3) 2,2′-dicarboxybiphenyl; (4) 2,2′-dimethylbiphenyl.[1]

Extinction coefficients in most cases were measured throughout the entire wave length range from 2330 Å. to the wave length at which the extinction coefficient fell and remained below 10. Thirteen exposures were made through each solution, with extinction values set at 0.00, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, . . ., 1.00, on the sector scale.

Calculations.—The values of the extinction coefficient, ϵ, were determined from the extinction values of lines of equal intensity by means of the equation

$$\epsilon = E/cd$$

where E is the extinction ($= \log_{10} I_0/I$), c the molar concentration and d the cell thickness in centimeters.

Method of Plotting Results.—The data are plotted with the extinction coefficient against increasing wave length. The extinction coefficients, rather than their logarithms, have been plotted because the present work is concerned with structure studies and, as an aid to thought and a means of representing visually a physical situation, the logarithmic plots are open to serious objection.

Discussion of Results

Interference of Groups in the Ortho Position with Coplanarity of Biphenyl.—While evidence given by O'Shaughnessy and Rodebush shows that

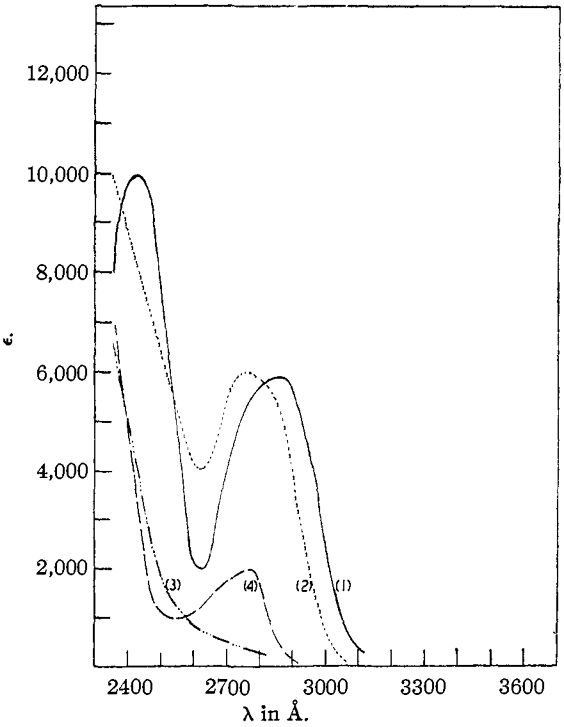

Fig. 2.—Absorption spectra: (1) 2,2′-dihydroxybiphenyl; (2) 2,2′-dimethoxybiphenyl; (3) 2,2′-dichlorobiphenyl; (4) diphenyl-2,2′-disulfonic acid (disodium salt).

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[8] C. F. H. Allen, C. G. Eliot and A. Bell, *Can. J. Research*, **17B**, 75 (1939).

the interference of groups in the ortho position is a predictable phenomenon, there remained several points to be cleared up by further study. In Figs. 1 and 2 are curves for various *o*-substituted biphenyls. In every case there is evidence for interference and departure from coplanarity. If we assume that the interference is purely mechanical, their departure from coplanarity should be proportional to the size of the group. According to the best estimates of the van der Waals radii, the interference of the groups in the ortho position should be in decreasing order $SO_3Na > NO_2 > Cl > CH_3 > COOH > NH_2 > OH > OCH_3$. Some assumptions about free rotations have been made in the case of certain of the above groups. In addition to the simple steric hindrance between groups, some interaction of dipole moments and even van der Waals attractions may exist but these effects are likely to be small.

Any attempt at correlation involves an estimate of the amount of observed deviation and this estimate is by no means easy. There are two methods of comparison that may be adopted. The first involves a comparison of the extinction curve for the biphenyl with the extinction curve for the corresponding benzene derivative, the values of the extinction coefficient for the latter being multiplied by two. This involves the assumption that with complete interference a biphenyl with two rings at right angles would behave as two separate benzene molecules. In Figs. 3 and 4 we have such comparisons. It is easily seen that the extinction curve for *o,o'*-diphenic acid does not differ greatly from the doubled extinction curve for benzoic acid. Similar agreements are observed for the 2,2'-dinitrobiphenyl and even in the case of 2,2'-diaminobiphenyl the deviation is not great. This would indicate that the interference of these groups is large and that there is a great departure from coplanarity. In the case of the smaller substituents the deviation is large, the absorption being always much greater for the biphenyl, which indicates that resonance throughout involves both rings and hence that there is little departure from coplanarity. Quantitative comparisons, however, are difficult and complicating effects exist which have been neglected in formulating the simple hypothesis above.

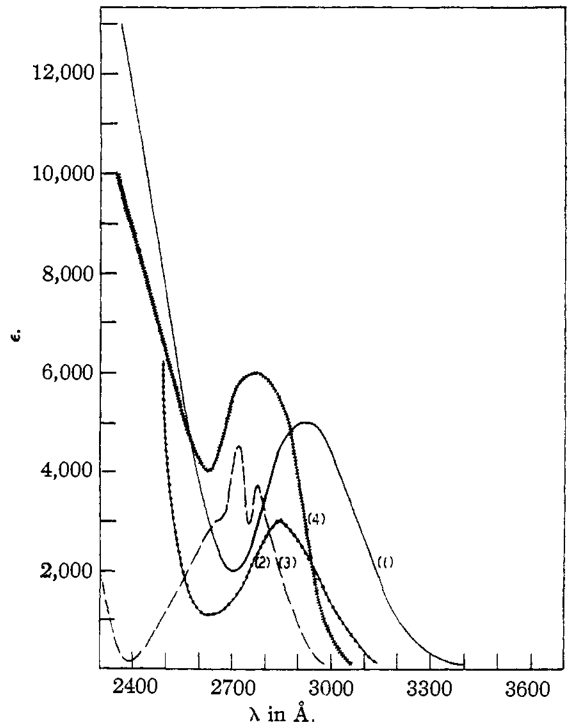

Fig. 3.—Absorption spectra: (1) 2,2'-diaminobiphenyl; (2) 2 × aniline[9]; (3) 2 × anisole[9]; (4) 2,2'-dimethoxybiphenyl.

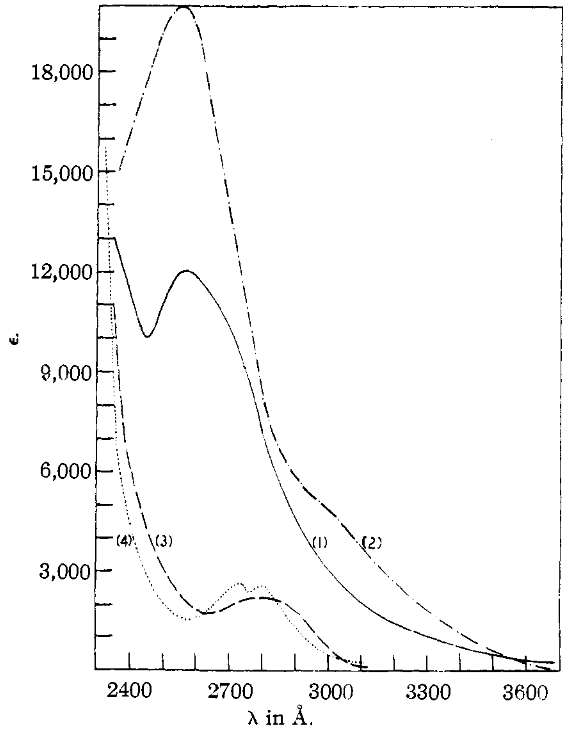

Fig. 4.—Absorption spectra: (1) 2,2'-dinitrobiphenyl; (2) 2 × nitrobenzene[9]; (3) 2,2'-dicarboxybiphenyl; (4) 2 × benzoic acid.[10]

There is one other method of drawing conclusions, which is shown in Figs. 5 and 6. In Fig. 5

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(9) K. L. Wolf and W. Herold, *Z. physik. Chem.*, **13B**, 201 (1931).

(10) H. Mohler and J. Polya, *Helv. Chim. Acta*, **20**, 96 (1937).

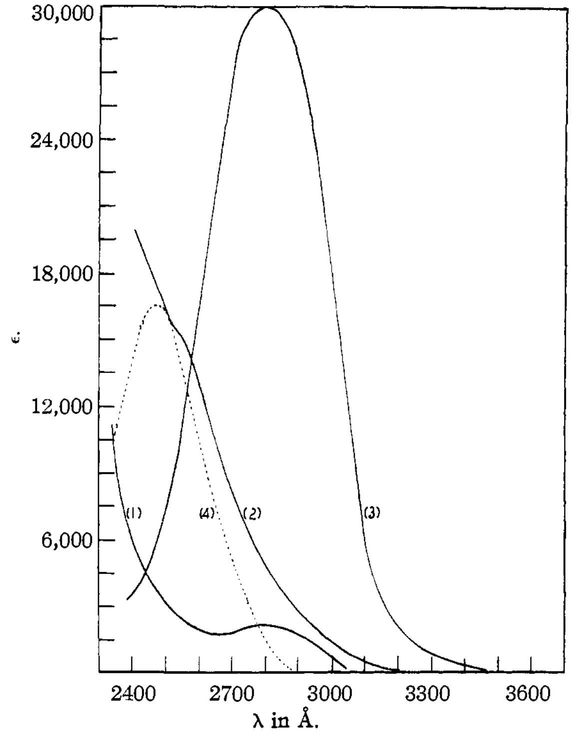

Fig. 5.—Absorption spectra: (1) 2,2′-dicarboxybiphenyl; (2) 3,3′-dicarboxybiphenyl; (3) 4,4′-dicarboxybiphenyl, dimethyl ester; (4) biphenyl.[1]

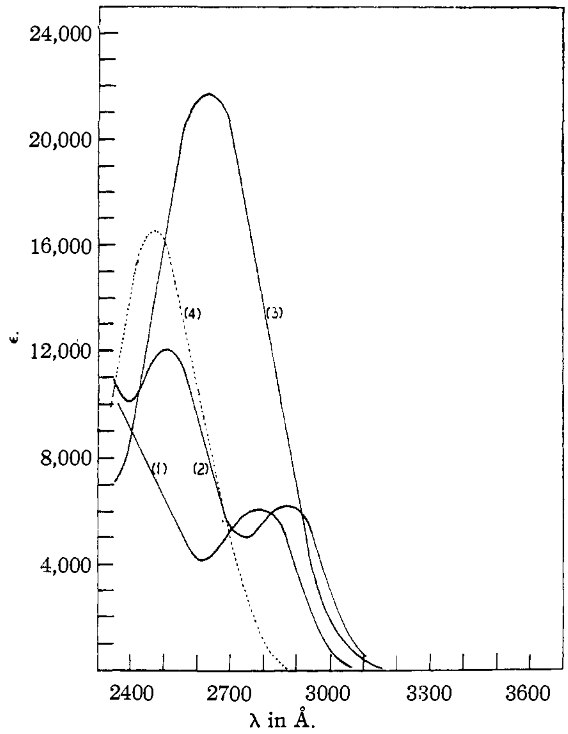

Fig. 6.—Absorption spectra: (1) 2,2′-dimethoxybiphenyl; (2) 3,3′-dimethoxybiphenyl[1]; (3) 4,4′-dimethoxybiphenyl; (4) biphenyl.[1]

the extinction curves for 2,2′- and 4,4′-diphenic acids are compared. In the absence of steric interference between the ortho substituents, the two molecules might be expected to show the same amount of resonance and as a first approximation the same absorption. The enormous difference in the case of the two diphenic acids confirms the assumption of a nearly complete departure from coplanarity. When this test is applied to the dimethyl biphenyls,[1] however, it indicates almost as much interference for methyl as for carboxyl so that one suspects that the postulate of the same absorption for the coplanar ortho and para derivatives is not valid. It is evident that neither of the above criteria can be regarded as having more than qualitative significance. It is clear, of course, that the absorption of the *o,o′*-substituted biphenyls is modified by factors other than that of the simple departure from coplanarity and one of the more important of these factors will be discussed in a later paragraph.

If one allows for these complicating effects it seems clear that the departure from coplanarity is greater the larger the size of the interfering group. With the smaller groups one may assume that a molecule is part of the time in a coplanar configuration. The case of 2,2′-dihydroxybiphenyl, Fig. 2, is especially interesting in that we observe the biphenyl absorption considerably reduced in intensity ($E = 10{,}000$ as compared to 16,500) and at the same time an absorption maximum characteristic of phenol. The hydroxyl group is one of the smallest of the interfering groups and we do not find the two absorption maxima characteristic of the coplanar and non-coplanar configurations for any other derivative. With other substituents an absorption at longer wave lengths characteristic of the non-coplanar form acting as two benzene derivatives is observed but the absorption characteristic of biphenyl has disappeared—at least in the range studied.

Comparison of Ortho, Meta and Para Substitution.—In Figs. 5 and 6 are shown some representative extinction curves for ortho, meta and para substituents. The different diphenic acids are striking in their behavior. The *o,o′*-derivative shows very little absorption because of the non-coplanar configuration. The *p,p′*-derivative shows a great increase in extinction coefficient and a shift in wave length as compared to biphenyl because of the resonance between the carboxyl group and the biphenyl nucleus. The *m,m′*-derivative shows an absorption that is far less than that of the p,p'-derivative since there can be no resonance between the biphenyl nucleus and substituents in the meta position. The situation is even clearer in the case of the dimethoxybiphenyls where not only the o,o'- but even the m,m'-derivatives show absorption that is characteristic of anisole. The behavior of the latter molecule cannot be accounted for by interference of groups.

The Effect of Ortho-Para- and Meta-Directing Groups.—The generalizations in the preceding paragraph are true in a broad sense but closer observation shows that the behavior is greatly dependent upon the nature of the substituent group. This is perhaps most easily seen when we compare the behavior of the m-substituted derivatives in Fig. 7. Here we see that while the dimethoxy derivative behaves essentially as though the biphenyl molecule were split in half, the dicarboxy derivative shows indication of an increased absorption over that of biphenyl itself. These substituent groups belong, respectively, to the two classes characterized as ortho–para- and meta-directing. In terms of resonance theory, the ortho–para-directing groups are those which may contribute additional electrons to the benzene nucleus, while the meta-directing groups are those which tend to remove electrons from the benzene nucleus. In the resonance structures that may be written for these benzene derivatives the carbons ortho and para to the substituent group tend to become negatively charged in the case of the ortho–para-directing groups, while the carbons in the meta position tend to become positively charged. With the meta-directing substituents the situation is reversed, the carbons in the meta positions now becoming negative. Now in a m,m'-substituted biphenyl no resonance structure involving the whole molecule can be written in orthodox fashion but with a meta-directing substituent, the piling up of the electron charge in the bond between the rings favors the existence of some sort of ionic structure and this, one believes, accounts for the increased absorption observed in these cases over the absorption of biphenyl alone. On the other hand, with ortho–para-directing substituents the removal of electrons from the bond between the rings actually interferes with the normal biphenyl conjugation.

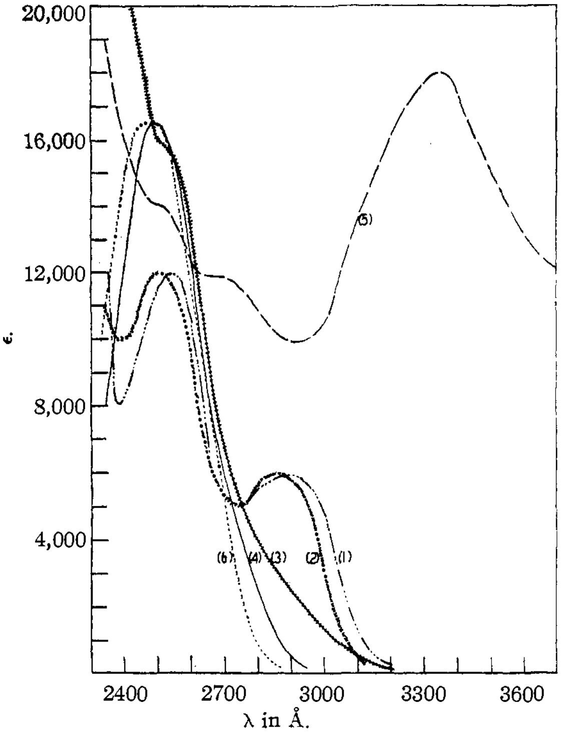

Fig. 7.—Absorption spectra: (1) 3,3′-dihydroxybiphenyl; (2) 3,3′-dimethoxybiphenyl[1]; (3) 3,3′-dicarboxybiphenyl; (4) 3,3′-dimethylbiphenyl[1]; (5) 3,3′-dinitrobiphenyl; (6) biphenyl.[1]

In the case of o,o'-substituted biphenyls the most important effect is the interference of the groups with the resultant departure from coplanarity. In the discussion of this effect in a previous section, it was noted that the correlation between size of group and extinction curves was not good and it was assumed that other effects must be taken into account. Undoubtedly one of the most important of these effects is the one discussed in the paragraph above. While conjugation involving the whole molecule is interfered with seriously by the departure from coplanarity, we see that now ortho–para-directing groups will tend to concentrate electrons in the bond between the rings and thus favor the ionic structures even when the two rings are not in the same plane. This would account for the increased absorption of the o,o'-biphenyls as compared to the benzene derivatives as in the case of Cl-, CH_3-, SO_3-, NH_2- and other substituents which are ortho–para-directing.

The case of the sodium salt of diphenyl-2,2′-disulfonic acid requires special consideration. The SO_3- group is so large that the coplanar position must be impossible. The SO_3- group, however, behaves as a saturated group and does not resonate with the benzene nucleus. As a result the absorption both of benzene sulfonate and the biphenyl derivative is very small compared to the nitro derivates, for example. However, the extinction coefficient of the biphenyl derivative is considerably more than twice that of the corresponding benzene derivative so that one must assume that the charges on the SO_3-ions polarize the biphenyl nucleus and favor an ionic form in the ionic state. The net result so far as absorption is concerned is the same as if the SO_3-group were an ortho-para-directing group. However, this behavior has little to do with chemical reactivity.

In the case of the 4,4′-substituents we might expect to observe similar differences between the different types of substituents but now the resonance involving the whole ring is perfect and so strong that the slight hindrance of the charge distribution that would exist with a meta-directing group in the para position can scarcely have a noticeable effect. One case in a somewhat different molecule has already been noted, however. Hydroxydiphenylmethane does not show absorption much different from that of diphenylmethane. The resonance structure here is one in which the carbon para to the hydroxyl must be positive.

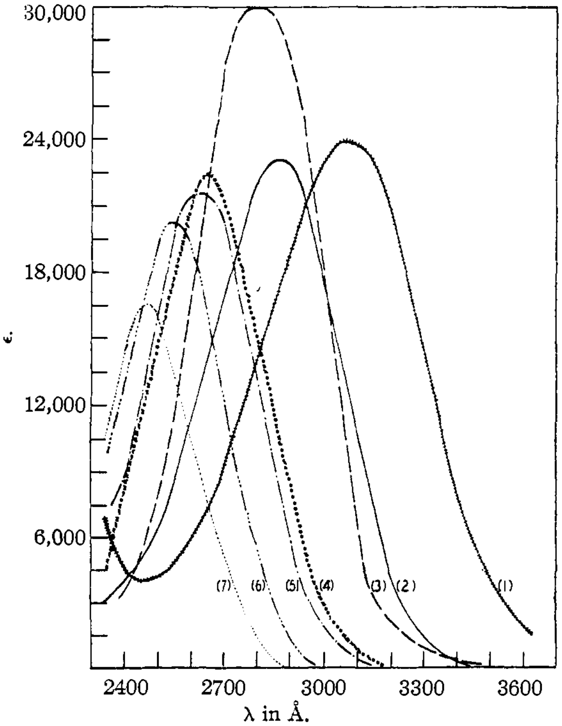

Fig. 8.—Absorption spectra: (1) 4,4′-dinitrobiphenyl; (2) 4,4′-diaminobiphenyl; (3) 4,4′-dicarboxydiphenyl, dimethyl ester; (4) 4,4′-dihydroxybiphenyl; (5) 4,4′-dimethoxybiphenyl; (6) 4,4′-dimethylbiphenyl[2]; (7) biphenyl.[1]

Correlation of Wave Length Shift with Character of Substituent.—The *wave length* of maximum absorption will be shifted toward longer wave lengths as the energy of the ionic form is lowered and the energy of the ionic form will be lowered as the number and extent of resonance forms is increased. Thus we will expect that in biphenyl derivatives in which resonance involves the whole molecule as a unit the maximum will be shifted to markedly longer wave lengths. For purposes of comparison the extinction curves of the 4,4′-substituted biphenyls are shown in Figs. 6 and 7. Here in every case the resonance involves the whole molecule. The maximum farthest to the right is given by the dinitro derivative which undoubtedly has the largest number of resonance forms. In the case of the diamino derivative we have fewer resonance forms but still a low energy because of the readiness with which the nitrogen acts as a donor of electrons to the carbon. The methoxy and dihydroxy derivatives are less stable because the oxygen is not as good a donor as the nitrogen. The dicarboxy derivative acts like the nitro group, not as a donor but as an acceptor, but there is only one resonance structure possible so that the shift is small. In the case of the di-

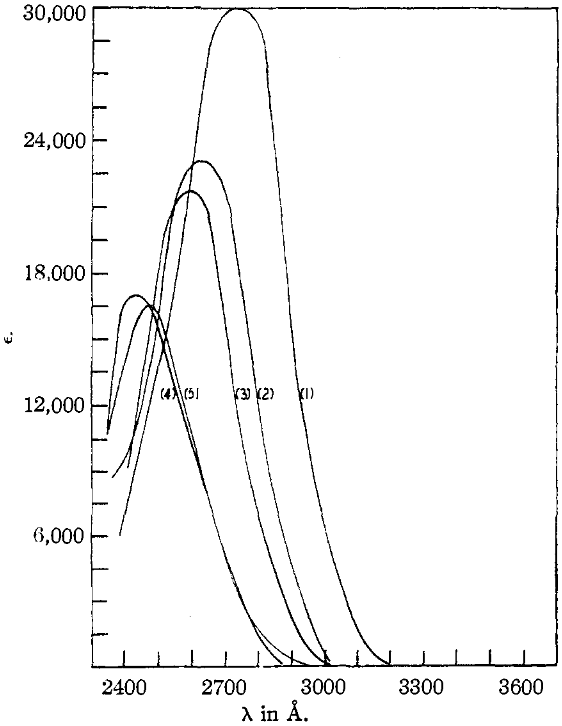

Fig. 9.—Absorption spectra: (1) 4,4′-diiodobiphenyl; (2) 4,4′-dibromobiphenyl; (3) 4,4′-dichlorobiphenyl; (4) 4,4′-difluorobiphenyl; (5) biphenyl.

methyl the resonance state involves hyperconjugation[11] with a correspondingly high energy for the ionic state of biphenyl itself. In the case of the dihalogen derivatives, Fig. 9, the number of resonance states is the same for all derivatives, and the different energy of the ionic state and the wave length shift are solely due to the differences in the polarizability of the halogens.

The Correlation of Extinction Coefficient with Polarizability.—In the introduction it was stated that the extinction coefficient depends somewhat indirectly upon the polarizability and that, in general, changes in extinction coefficient and wave length of maximum absorption should parallel each other. The polarizability of a substituent group is directly proportional to the molecular refraction which may be calculated for the group with which we are concerned. We have prepared Table II in which molecular refraction and extinction coefficient are compared. It will be noted that the correlation is good with two or three exceptions. It is probable that these exceptions are due to the appearance of resonance forms in biphenyl which will increase the polarizability to a larger value than is observed in the non-resonating molecule. It should be noted that the extinction coefficient of molecules such as a 4,4′-substituted biphenyl does not depend upon the polarity of the substituent group but upon the polarizability, that is, the change in polarity when the molecule is excited to the ionic state.

TABLE II

Group	Mol. refr.	Max., ϵ(p,p'-biphenyl)
F	0.881	17,000
H	1.051	16,500
OH	2.572	22,400
NH_2	5.312	23,200
CH_3	5.654	21,100
Cl	5.998	21,700
NO_2	7.30	24,000
OCH_3	7.337	21,700
Br	8.927	23,300
$COOCH_3$	12.125	30,000
I	14.12	30,000

The authors wish to acknowledge their indebtedness to Professor Roger Adams and other members of the organic division for their helpful discussions and advice on the preparation of some of the compounds studied. For the preparation and purification of some of the samples we are indebted to Mr. E. C. Dunlop of the State Water Survey and Dr. G. C. Finger of the State Geological Survey.

Summary

The effect of type and position of substituent in the biphenyls upon their ultraviolet absorption has been investigated in a number of cases. Excellent correlation has been obtained in most cases between the possible resonance structures and values for extinction coefficient and wave length of maximum absorption. Evidence has been obtained for increasing departure from coplanarity with increasing size of group in the ortho positions. The difference in the behavior of ortho-para- and meta-directing groups is particularly interesting.

URBANA, ILL. RECEIVED AUGUST 4, 1941

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[11] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXIV. The Photochemical Decomposition of Benzene

BY JOSEPH E. WILSON[1] AND W. ALBERT NOYES, JR.

The photochemical decomposition of benzene vapor, both direct[2,3] and sensitized by mercury vapor,[4] has been reported. In the direct decomposition radiation from the aluminum spark, presumably lying below 2000 Å., was found to be particularly effective. Hydrogen was identified as a product, and biphenyl was assumed to be formed. Definite proof was not given, however, for the formation of biphenyl. The products of the sensitized reaction were not completely analyzed, but hydrogen and methane were reported. Bates and Taylor[4] also mention a strong odor of biphenyl and state that the formation of such large amounts of hydrocarbon (40% of the gaseous products) must mean that excited mercury atoms can bring about a complete rupture of the benzene ring.

In a recent article Forbes and Cline[5] found that benzene vapor is decomposed by mercury atoms

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[1] Holder, during 1939–1940, of the Eastman Kodak Company Fellowship in Photochemistry at the University of Rochester.

[2] Krassina, *Acta physicochim. U. R. S. S.*, **10**, 189 (1939).

[3] Prilezhaeva, *ibid.*, **10**, 193 (1939).

[4] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[5] Forbes and Cline, *ibid.*, **63**, 1713 (1941).