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

# Ultraviolet Absorption Spectra of Organic Molecules: The Dependence upon Restricted Rotation and Resonance

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Evidence for the effect of substituent groups upon the ultraviolet absorption of multiple ring compounds has been in the literature for some time. In 1929 Ley[1] reported that studies upon the compounds *trans*-stilbene, *trans*-$\alpha$-methylstilbene and *trans*-$\alpha,\alpha'$-dimethylstilbene showed a progressive shift of the absorption maximum toward the ultraviolet in the order named, and a considerable decrease in absorption intensity. At that time it was not clear perhaps as to the exact reason for the effect of the methyl groups upon the absorption, which was quite beyond anything that had been anticipated. In 1936 Pickett, Walter and France[2] observed a very great decrease in absorption in the case of two biphenyls in which rotation was restricted by substitution in the four *o*-positions. In 1937 Pestemer and Meyer-Pitsch[3] observed a number of changes in absorption of singly substituted biphenyls, which depended both upon the substituent and upon the position; in particular the ortho substituted compounds that they investigated showed considerably reduced absorption at certain wave lengths as compared with biphenyl itself and the meta and para derivatives.

Meanwhile a great deal of progress had been made in the quantum theory of the structure of aromatic molecules by Hückel, Pauling, Mulliken and others.[4] In particular the relation between "conjugation" as the term had been used by organic chemists and "resonance" as defined by quantum mechanics was made clear by the concept of the $\pi$-orbital as an electron orbital of doubly bonded carbon, symmetrical about an axis perpendicular to the plane of the ring. For example, each carbon atom in the benzene ring has one $\pi$-orbital and interaction between any adjacent pair is possible so that a shifting or resonating series of bonds results. It follows from quantum mechanical considerations that the maximum amount of interaction is possible when the $\pi$-orbitals are exactly parallel to each other and perpendicular to the plane of the ring. Hence, the maximum resonance is obtained in a plane ring. For resonance or conjugation to involve two rings as in biphenyl, it is necessary that the $\pi$-orbitals of the adjacent 1,1'-carbons be parallel and this requires the coplanarity of the two rings.

With the development of the quantum mechanical theory of the structure of unsaturated and aromatic molecules it became possible to account for the variations in ultraviolet absorption due to structure, that were noted by workers referred to above. Sklar[5] and Förster were among the first to attempt to calculate the energy levels in the absorption spectra of aromatic molecules. Förster[6] has summarized this work in an excellent review. Mulliken shows that the more probable transitions in ultraviolet absorption by a conjugated molecule are to ionic states and that the lower of these states will be lower in energy relative to the ground state, the greater the extension of the conjugated system. The absorption intensity will be greater the greater the increase in polarity of the molecule in the excited state. It follows from the foregoing that a shift of absorption toward longer wave lengths is to be expected as the number of resonating bonds in a system is increased. Thus, Calvin[7] has pointed out that while a coplanar biphenyl shows an intense absorption band due to the conjugated ring system, a biphenyl with a large degree of hindrance between ortho substituents should show an absorption which approximates the additive absorptions of the single ring structures. He suggested that the spectrum might in some cases be used as a criterion for restricted rotation in place of the difficult and sometimes inconclusive method of optical resolution which has been employed so extensively in the study of restricted rotations in the biphenyls by Adams and his collaborators in this

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(1) H. Ley, "Handbuch der Physik, Vol. XXI, Lichte und Materie," 1929, p. 57.

(2) L. W. Pickett, G. F. Walter and H. France, THIS JOURNAL, **58**, 2182 (1936).

(3) M. Pestemer and I. Meyer-Pitsch, *Monatsh.*, **70**, 104 (1937).

(4) For general references see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939; also E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937), which is a general review of the theory of the electronic structure of unsaturated molecules.

(5) A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); **7**, 984 (1939).

(6) Th. Förster, *Z. Elektrochem.*, **45**, 548 (1939); see also G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

(7) M. Calvin, *J. Org. Chem.*, **4**, 256 (1939).

Laboratory. The experimental results of Pickett, *et al.*, cited above are in agreement with the foregoing consideration, but only a few compounds have been studied whereas there are available a large number of molecules in which the effects of substitution could be studied. It seemed worth while therefore to undertake a general investigation of substituted biphenyls and other molecules in which the various effects of conjugation, coplanarity and restricted rotation might be investigated. About twenty such molecules have been studied and some interesting results have been obtained. In general, the foregoing generalizations have been confirmed completely and it seems that the absorption is possibly an even more sensitive criterion for restricted rotation than was suspected by Calvin.

## Experimental

COMPOUNDS STUDIED

| Number | Name | Source |
|---|---|---|
| I | Biphenyl | 1 |
| II | 2,2′-Dimethylbiphenyl | 2 |
| III | 3,3′-Dimethylbiphenyl | 3 |
| IV | 4,4′-Dimethylbiphenyl | 2 |
| V | 2,2′,4,4′-Tetramethylbiphenyl | 2 |
| VI | Bimesityl | 4 |
| VII | 3,3′-Dimethoxybiphenyl | 3 |
| VIII | 2,2′-Dimethyl-5,5′-dimethoxybiphenyl | 3 |
| IX | 3,3′-(Decamethylenedioxy)-biphenyl | 3 |
| X | 2,2′-Dimethyl-5,5′-(decamethylenedioxy)-biphenyl | 3 |
| XI | 2,2′-Dimethyl-5,5′-(octamethylenedioxy)-biphenyl | 3 |
| XII | Acetophenone | 1 |
| XIII | 2,4-Dimethylacetophenone | 5 |
| XIV | Acetomesitylene | 5 |
| XV | 2,4,6-Triisopropylacetophenone | 6 |
| XVI | Benzophenone | 1 |
| XVII | Benzoylmesitylene | 5 |
| XVIII | Dimesityl ketone | 5 |
| XIX | *cis*-2,4,6,2′,4′,6′-Hexaisopropyl-α,α′-dihydroxystilbene diacetate | 6 |
| XX | *trans*-2,4,6,2′,4′,6′-Hexaisopropyl-α,α′-dihydroxystilbene diacetate | 6 |
| XXI | *cis*-2,4,6,2′,4′,6′-Hexaisopropyl-α,α′-dihydroxystilbene dimethyl ether | 6 |

**Sources:** (1) General chemical stores. (2) Prepared by one of the authors, using the Ullmann coupling of the corresponding substituted iodobenzenes. (3) Prepared by N. Kornblum of the organic division of this Laboratory. (4) From the stocks of organic chemical manufacturers. (5) Prepared by C. H. McKeever of the organic division of this Laboratory. (6) Prepared by E. C. Horning of the organic division of this Laboratory.

**Purification of Compounds.**—Compounds VII, VIII, IX, X, XI, XV, XIX, XX, XXI were analytically pure samples of products prepared in the course of organic research, or were purified carefully for the present work by the men from whom they were obtained.

Compounds I, IV, VI and XVIII were purified by several recrystallizations from ethyl alcohol, followed by recrystallization from the specially purified *n*-hexane used as the spectrographic solvent.

Compounds II, III, V, XII, XIII, XIV, XVI and XVII were purified by several fractional distillations *in vacuo*.

**Solvents.**—For compounds VII to XI Eastman Kodak Co. cyclohexane was used, without further purification, as the spectrographic solvent. For the other compounds commercial *n*-hexane was used, after purification by stirring for successive four-hour periods with one portion of concentrated sulfuric acid, three portions of 15% fuming sulfuric acid, and one portion of 20% sodium hydroxide. The volume of hexane was in each case about four times the volume of the reagent used for purification. The purified solvent was then dried and distilled, and the fraction boiling from 62–68° used. It showed practically complete transparency to the limit of transmission of the spectrograph.

**Absorption Measurements.**—A Bausch and Lomb medium quartz spectrograph, with sectorphotometer attached, and the condensed spark between tungsten–steel electrodes, were used in all the measurements. The absorption cells were of fused quartz, 5 cm. in length, of accurately matched length and optical properties. The solutions were made up by dissolving 0.00005 mole, weighed out to an accuracy well within 0.5%, in 50 cc. of solvent to form a 0.001 $M$ solution, and then preparing 0.0001 and 0.00001 $M$ solutions by volume dilution. Extinction coefficients in most cases were measured throughout the entire wave length range from 2330 A. 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, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, . . . , 1.0, on the sector scale, and values of the extinction coefficient determined from the extinction values for lines of matched intensity by means of the equation

$$\epsilon = \frac{1}{cd} E$$

where $E = \log_{10}$ (ratio of sector opening in solution light path to sector opening in solvent light path). $C$ is molar concentration and $d$ is the cell thickness in centimeters.

**Method of Plotting Results.**—The extinction coefficients themselves, rather than their logarithms, have been plotted as a function of wave length. This procedure has been followed because the chief interest in the present work has been in the correlation of intensity of absorption with structure and the method of plotting chosen illustrates differences in intensity much better than the alternative method. The compounds have been grouped on the plots for convenience in comparison and discussion.

## Discussion of Results

Before the absorption of molecules such as biphenyls with various substituent groups can be compared, it is necessary to consider what the immediate effect of the entering group may be upon the absorption of the ring into which it is

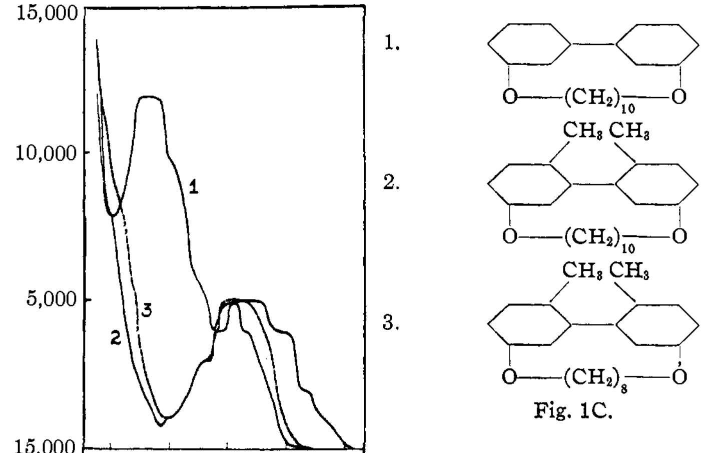

Fig. 1C.

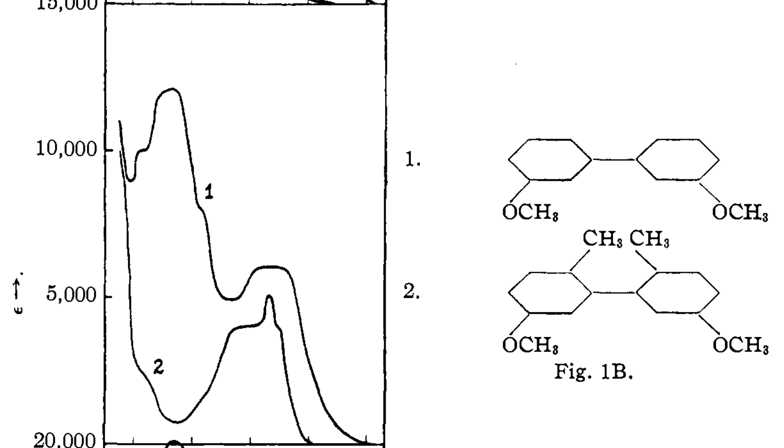

Fig. 1B.

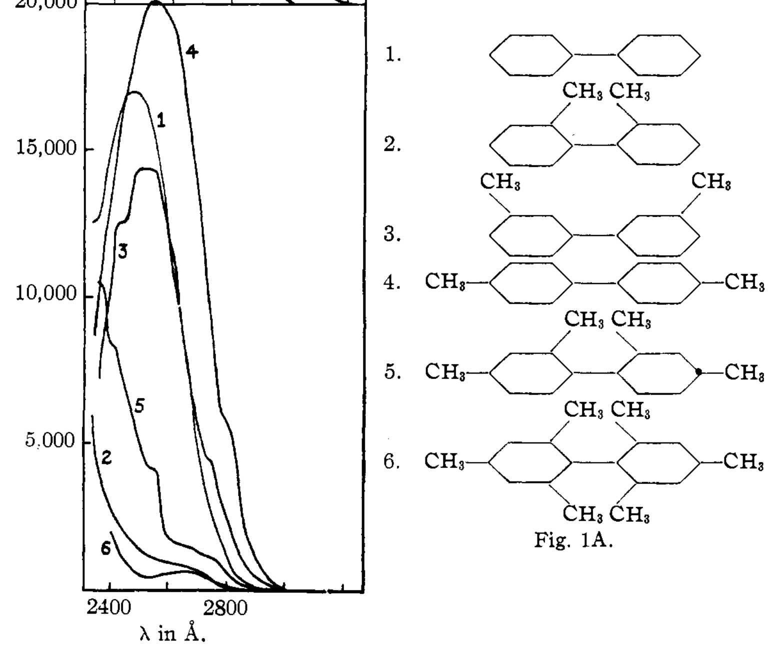

Fig. 1A.

introduced. Both theoretical consideration and experimental results show that substituents such as halogen, methyl or $NH_3^+$ exhibit very little electronic interaction with an aromatic ring, while hydroxyl, methoxyl and amino groups show somewhat more, and unsaturated groups show a great deal of interaction. The degree of interaction is registered by the absorption spectrum. Thus the first mentioned substituents modify the absorption spectrum of benzene very slightly, the intermediate group enhances the absorption five- or ten-fold without destroying all vibrational structure, while unsaturated substituents produce a great increase in absorption and destroy all vibrational structure. These results are in agreement with the theoretical conclusions of Mulliken,[8] who considers that the excited state in absorption is of ionic character and that unsaturated substituent groups may lower the energy of this form very considerably. Thus, in biphenyls two unsaturated para substituents may have the effect of adding two more double bonds to the conjugated system and favoring the formation of ionic structures. On the other hand, meta substituents cannot contribute to the polarity of the molecule as a whole because a conjugated structure requires a double bond between the carbon atoms linking the rings and there is no possibility for conjugation of meta substituents with this configuration. A much greater effect is to be anticipated from ortho substituents which interfere with the rotation of the two rings. If the interference is slight the two rings may still maintain coplanarity since this gives a state of lowest energy, but any considerable interference must turn the rings out of co-

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[8] R. S. Mulliken, *J. Chem. Phys.*, **7**, 14, 20, 121, 339, 353, 364, 570 (1939).

planarity and prevent conjugation between the two rings, and thus greatly reduce the absorption.

Reference to Fig. 1, shows that these conclusions are well substantiated. Curve 1, Fig. 1A, shows the absorption curve for biphenyl: this curve is included for comparison purposes and agrees fairly well with the results of previous investigators. Curve 2 shows the absorption of 2,2′-dimethylbiphenyl. The absorption of this molecule has not been reported previously. It shows a very surprising drop in the amount of absorption, although it would be desirable to obtain results at shorter wave length. The only adequate explanation that suggests itself is that the methyl group interferes with the hydrogen to such an extent as to turn the two rings well out of plane and destroy all resonance between them. This result is not entirely surprising as reference to Fig. 4 shows, where a plot of van der Waals radii for the ortho group shows considerable overlap when the two benzene rings are coplanar. It is not certain of course that rotation of the methyl groups about the carbon–carbon bond might not permit rotation of the rings and render optical resolution difficult, but there can be little doubt that the average configuration is not coplanar. Curves 3 and 4 show the augmentation and diminution of absorption that might be expected for para and meta substituents, respectively. The effect here is thought to be entirely due to the contribution or interference with the ionic form of the molecule considered as a whole. In Fig. 1A, Curve 5 shows the absorption of 2,2′,4,4′-tetramethylbiphenyl. The increase in absorption over that of dimethylbiphenyl is perhaps to be attributed to the effect of the para substituents in promoting the ionic state and the coplanar configuration. The bimesityl spectrum has been reported previously but the curve has been redetermined with our present technique for comparison purposes. The reduction in absorption is seen to be greater than in the 2,2′-dimethylbiphenyl: a minimum and a maximum are noted. The latter corresponds closely to the absorption of mesitylene itself. The molecule is evidently non-coplanar.

The curve for 3,3′-dimethoxybiphenyl (Fig. 1B) illustrates the general effects to be expected in substitution. Meta substituents reduce the general biphenyl absorption but a maximum appears corresponding to the absorption of the two halves of the molecule (anisole nuclei). When two methyl groups are introduced in the ortho position the general biphenyl absorption is markedly de-

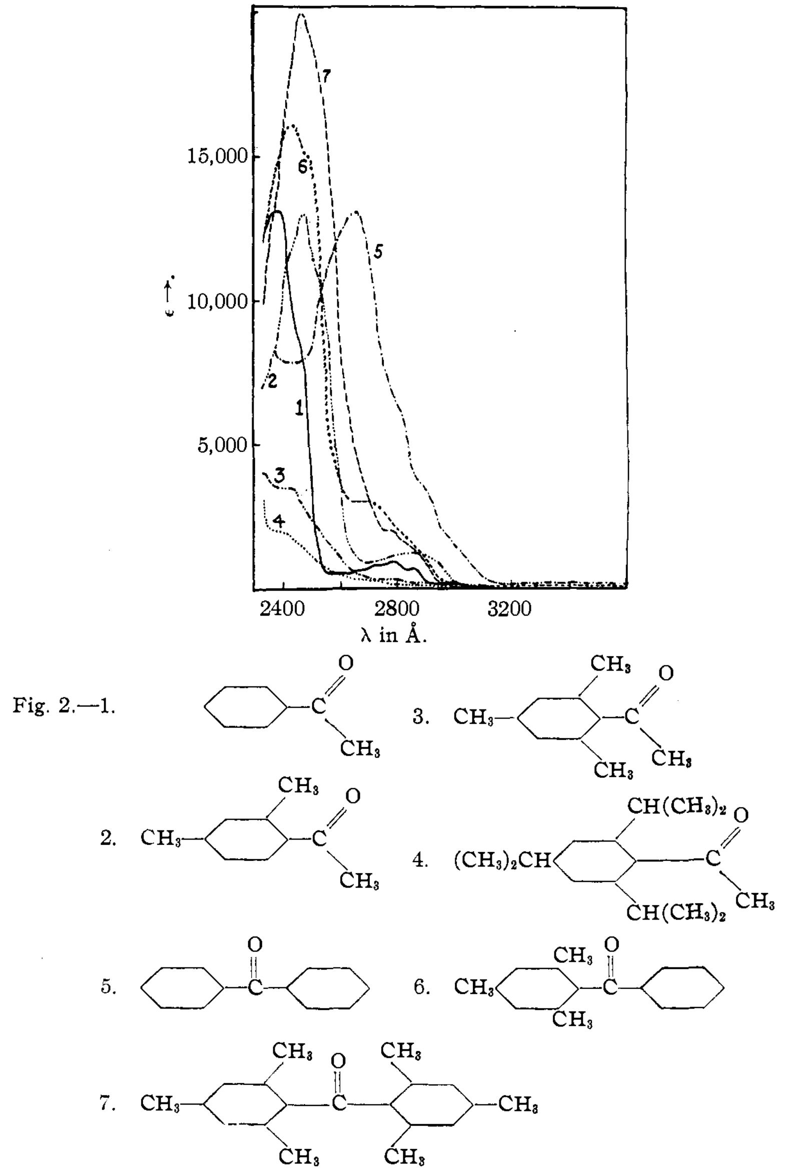


Fig. 2.—1.

creased while little or no effect is observed on the maximum characteristic of the anisole absorption.

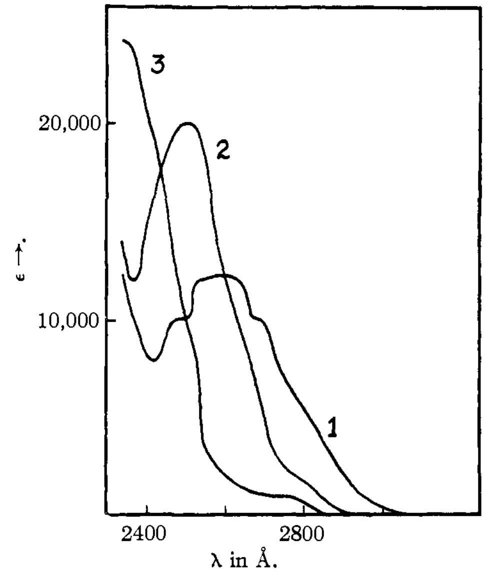
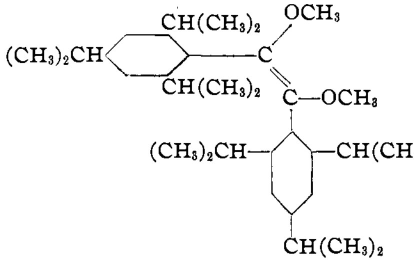


Fig. 3.—1.



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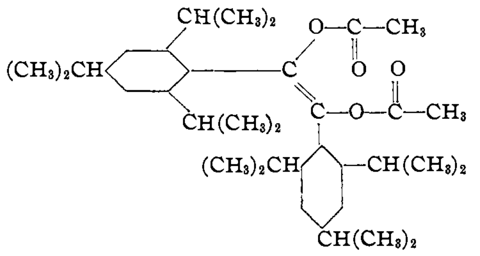

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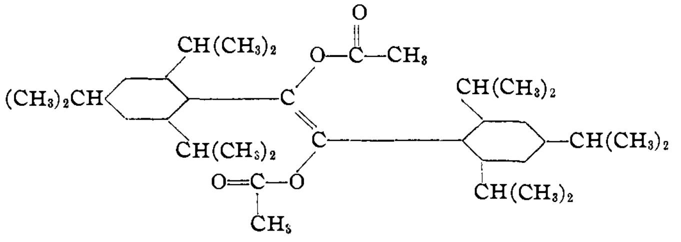


In Fig. 1C are shown absorption curves for some compounds which have been prepared by Mr. N. Kornblum of this Laboratory. The properties of these compounds will be discussed by Mr. Kornblum elsewhere. It is sufficient here to note that Curve 1 indicates a coplanar structure as in simple biphenyl while 2 and 3 show evidence in the reduced absorption that there is interference between the methyl groups and the hydrogens in the ortho position.

**Hindrance in Other Types of Ring Compounds.**—Since there is clear indication of interaction (conjugation, resonance) between unsaturated groups and an aromatic ring it is of course an elementary consideration to apply the principle of coplanarity to these compounds. In Fig. 2 are shown the curves for acetophenone and substituted acetophenones. The effect of para substitution is shown in Curve 2 where a shift to longer wave length is produced. There is no appreciable decrease in intensity so that it would appear that no interference occurs between the *o*-methyl group and the oxygen of the carbonyl. When both ortho positions are substituted, however (Curves 3 and 4) a striking decrease in absorption, at least at longer wave lengths, occurs. Figure 4 shows a diagram of the van der Waals radii for 2,4,6-trimethylacetophenone which indicates great interference between the adjacent methyl groups. Much less hindrance is indicated between the methyl of the aceto group and hydrogen, and between an ortho methyl group and the carbonyl oxygen. This interference, it is assumed, is not strong enough to prevent a coplanar configuration. The hindered benzophenones show an interesting behavior. Benzophenone itself shows absorption at a sufficiently long wave length to indicate conjugation of the carbonyl with both rings and this is to be expected, though perhaps not without some interference. In the case of the substituted benzophenones greater interference is to be expected. A completely coplanar structure is not possible.

Conjugation of the carbonyl with only one ring would account for the absorption maximum at shorter wave lengths. The substitution in para position may account for some increase in extinction coefficient, but one could hardly predict so great an increase, and some other effect may be involved. There is need to study a variety of these compounds.

In Fig. 3 are shown absorption curves for some "ene-diols." These molecules have the stilbene configuration but have a high degree of hindrance due to substitution, so that they are certainly not coplanar. Both forms show great reduction in the absorption intensity as compared with *cis*- and *trans*-stilbene. The *trans* form (Curve 1) seems to show less conjugation than the *cis* forms since the absorption maximum is shifted to shorter wave lengths. These results are to be compared with those of Ley on the methylstilbenes referred to earlier in this paper. Further study is necessary for generalization about such complicated molecules.

It should be emphasized in connection with the foregoing studies that in most cases it would be highly desirable to extend the observations to shorter wave lengths, *i. e.*, beyond the range of the medium quartz spectrograph. Unless a maximum in the absorption curve is obtained, it becomes difficult to distinguish between a shift in wave length and a change in intensity of absorption. Mulliken has emphasized the significance of the extinction coefficient itself as a quantitative check on the theories of molecular structure.

It should be also remembered that the spectroscopic test for restricted rotation will not necessarily agree with the results of optical resolution in every case. A heat of activation of rotation of about 20 large calories is required for optical resolution. A much smaller degree of interference might serve to maintain an average non-coplanar position for the rings. Of course some additional stabilization is to be expected in the coplanar configuration but this will perhaps be greater in the excited state of the molecule than in the ground state.

The authors wish to acknowledge their indebtedness to Dr. Roger Adams and his students for helpful discussions and material assistance in this work, and to Dr. R. S. Mulliken for suggestions regarding the application of his theories to the problem.

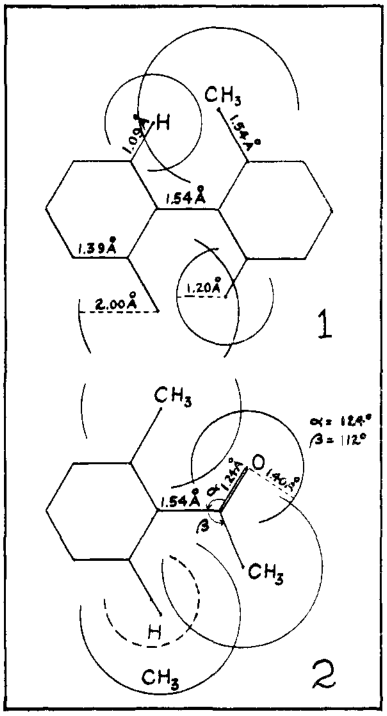
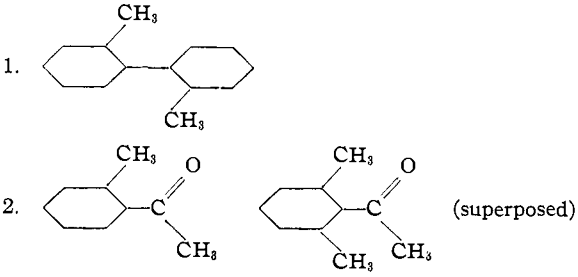


Fig. 4.—



Ring–ring distance in biphenyl and phenyl–carbonyl distance in acetomesitylene have been given the single bond values of 1.54 Å., though in a compound in which the coplanar orientation predominates they would be less because of partial double bond character. The interferences shown are in this sense minimal interferences.

## Summary

A study of the ultraviolet absorption spectra of some twenty molecules containing aromatic rings indicates that certain generalizations can be made which are in agreement with current theory. In particular the ultraviolet absorption promises to serve as a test for restricted rotation in the biphenyls and similar molecules where coplanarity is necessary for resonance.

Urbana, Illinois Received June 21, 1940