removed and the residual amine was distilled at atmospheric pressure; recovery ranged from 87–98%.

Summary

1. The preparation of ten nuclear substituted N,N-dialkylanilines in yields of 53–95% by the use of trialkyl phosphates is described.

2. The procedure is simple, convenient and adaptable to moderately large amounts.

BLOOMINGTON, INDIANA RECEIVED JULY 13, 1944

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

Ultraviolet Absorption Spectra of Organic Molecules. III. Mechanical Interference of Substituent Groups with Resonance Configurations

BY WORTH H. RODEBUSH AND ISAAC FELDMAN

Studies of the ultraviolet absorption of the substituted biphenyls[1,2,3,4] have demonstrated beyond question the effect of mechanical interference between substituent groups in the *ortho* positions of biphenyl. If the group is larger than hydrogen the departure from coplanarity is so great that most of the resonance between the rings is lost and the absorption may not be greatly different from that of two moles of the corresponding benzene derivative.

Recently Brockway[5] has suggested that the coplanar configuration is improbable even in the case of the unsubstituted biphenyls because the accepted van der Waals radius of the hydrogen atom indicates interference between the hydrogens in the *o,o'*-positions. The results obtained from the ultraviolet absorption studies are, of course, not incompatible with Brockway's conclusion. All that can be stated with certainty from the spectrographic studies is that in the unsubstituted biphenyls the configuration is near enough to coplanarity to allow a resonance energy amounting to several large calories.

Likewise, the results of Adams[6] and his coworkers proved that it is impossible to resolve the optically active biphenyls when the *o,o'*-positions are occupied by hydrogen but this does not prove coplanarity or even free rotation since there might be a considerable energy barrier to rotation such as exists in the case of ethane.

The X-ray evidence appears contradictory and inconclusive.[7] Biphenyl and *p*-terphenyl are reported to be coplanar while in 1,3,5-triphenylbenzene the substituent rings are believed to be tilted 25° from the plane of the central ring. However, a number of reservations must be made. The biphenyl configuration was determined a number of years ago. The exact crystal structure of triphenylbenzene has never been determined. The configuration in the crystal may be different from that of the free molecule in solution.

The authors have determined the ultraviolet absorption of symmetrical triphenylbenzene with the hope of obtaining additional evidence upon the question of its structure. The extinction coefficient (Fig. 1) shows a maximum at about the same wave length as biphenyl but the molar extinction is nearly four times that of biphenyl. It must be regarded as a coincidence that the resonance energy of triphenylbenzene, as calculated from thermal data, appears also to be about four times that of biphenyl. One may conclude, therefore, that triphenylbenzene has a considerable amount of resonance energy and that, if the configuration is not planar, the departure from coplanarity has not reduced the resonance to any considerable degree.

Van der Waals Radii.—Any estimate of the interference between the hydrogens in *o,o'*-positions in biphenyl must take account of the accepted values for the van der Waals radius of hydrogen. It must be recognized, of course, that the radii for atoms cannot have such precise values as are assigned, for example, to the covalent radii. The uncertainty is of the order of magnitude of 0.2–0.3 Å.

In ethylene the distance between hydrogens which are on different carbons is 2.4 Å. In ethane the distance between hydrogens similarly placed is 2.3 Å. yet ethane has a potential barrier to rotation of about 3000 calories. This barrier can hardly be due to interference between hydrogens. It may very well be the result of what has been termed hyperconjugation between the methyl groups. It is not known, of course, which configuration has the lower energy.

In biphenyl the distance the hydrogens in *o,o'*-positions is 1.84 Å. and here there must be a good deal of interference. (An estimate based on the calculations of Slater and Kirkwood[8] for helium indicates that the coplanar configuration might be unstable by about 3000 calories.) Since the resonance energy is not more than two or three

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

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

(3) M. T. O'Shaughnessy, Jr., and W. H. Rodebush, THIS JOURNAL, **62**, 2906 (1940).

(4) Barbara Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

(5) I. L. Karle and L. O. Brockway, *ibid.*, **66**, 1974 (1944).

(6) R. Adams and G. C. Finger, THIS JOURNAL, **61**, 2828 (1939).

(7) Jagattaran Dhar, *Indian J. Phys.*, **7**, 43–60 (1932); L. W. Pickett, *Proc. Roy. Soc.*, **A142**, 333 (1933); C. J. B. Clews and K. Lonsdale, *ibid.*, **A161**, 493 (1937).

(8) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

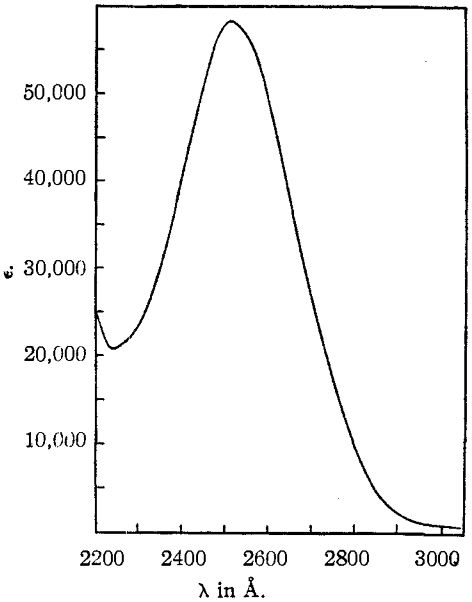


Fig. 1.—1,3,5-Triphenylbenzene.

times this quantity, a non-coplanar configuration might be expected were it not for one other factor. The bending constant for the C–H valence bond is known from infrared data to be small and a rough calculation shows that a small change in the bond angle in the plane of the ring might permit the coplanar positions to be stabilized. In triphenylbenzene, on the other hand, this bending cannot take place since each hydrogen on the central ring is between two substituent rings and the constraint can only be relieved by bending out of the plane of the ring. In this case the twisting of the substituent rings would require the smaller energy. It is possible, therefore, to offer a plausible explanation for the difference in configuration between biphenyl- and triphenylbenzene that the X-ray studies indicate.

Crowding of Substituent Groups in Molecules.—It is evident from the foregoing that the van der Waals radii of atoms in compounds is a highly variable quantity and that if one set out deliberately to do so he might synthesize molecules in which the atoms appeared to be highly compressed with van der Waals radii, much less than would be inferred from the density of crystalline organic compounds. Such an attempt has been successfully carried out by Dr. R. C. Fuson of this Laboratory in a remarkable series of compounds which are essentially substituted vinyl alcohols. Dr. Fuson has kindly made a number of these compounds available to us for spectroscopic study, and since he has discussed their general and chemical properties at length, we shall confine our attention to the deductions as to configuration that can be made by a study of the ultraviolet extinction coefficients.

The valence structure of these molecules has been determined by Dr. Fuson and co-workers but it is not possible to answer from chemical evidence questions of configuration where the change is due to rotation about a bond. When the spectroscopic evidence is combined with the information given by models, it becomes possible to give definite answers to all of these questions.

The central feature of these molecules is the carbon-carbon double bond. The ethylene molecule itself has all six atoms in a plane and according to theory the orbitals of the π electrons which form the second bond are perpendicular to this plane. Hence, if a hydrogen is replaced by an aromatic ring, resonance will be possible between the ring and the ethylenic linkage provided the ring lies in the plane of the hydrogen and carbon atoms. Likewise, the hydroxyl group which makes the molecule a vinyl alcohol will also tend to assume one of two orientations both of which are in the plane determined by the original ethylene configuration. Because of the crowding that must occur when hydrogens are replaced by large groups, departures are inevitable.

Coplanarity.—It is clear that if one or more of the substituent rings can assume a position coplanar with the carbon–carbon double bond, we should expect resonance and enhanced absorption. There will be a strong over-all absorption at wave lengths below λ 2200 because of the presence of unsaturation, but if the resonance of the coplanar configuration is strong enough the absorption due to it will be shifted to longer wave lengths and will show a maximum. Once this maximum is attributed to the coplanar resonance configuration it can be used as a test of coplanarity in other compounds.

The simplest example of this type of compound is styrene, Fig. 2, which shows a pronounced maxi-

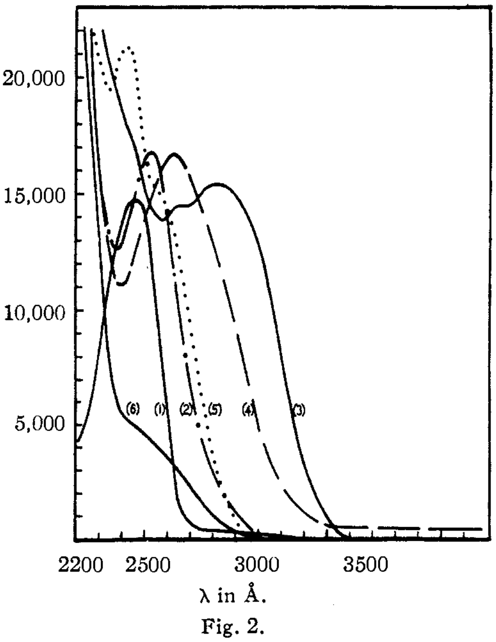


Fig. 2.

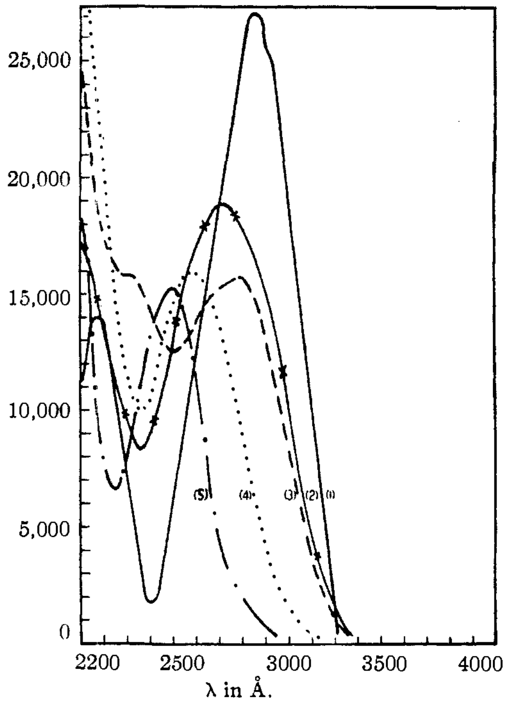


Fig. 3.

mum at λ = 2500 Å. with an extinction coefficient of 14700. *trans*-Stilbene which presumably has both benzene rings coplanar with the ethylenic linkage shows much greater absorption and at longer wave lengths. It seems clear at once that in the compounds whose extinction curves are shown in Figs. 2 and 3 not more than one substituent ring can be coplanar with the carbon-carbon double bond. A study of the models of the molecule shows that this result is to be expected. If two rings, one of which is a mesityl, are on the same carbon then only one ring can assume a position coplanar with the carbon-carbon double bond. If a third group, also mesityl, is in place on the other carbon, it must assume a position perpendicular to the plane of the double bond. The probable configurations are shown in the formulas as written. The coplanar group is assumed in the alcohols to occupy the position *trans* to the hydroxyl. The evidence for this conclusion is obtained partly from infrared studies which will be published elsewhere. In Fig. 4 is drawn a skeleton of the molecule, with the values of the bond angles chosen to give a minimum of interference. The values chosen are, of course, purely guesses but it is believed that the configuration is correctly represented and it is clear that the distances of approach between substituent groups must be much less than the sums of the generally accepted van der Waals radii. For example, the hydrogen of a methyl group must approach within a distance of less than 2.5 Å. of the center of the mesityl ring.

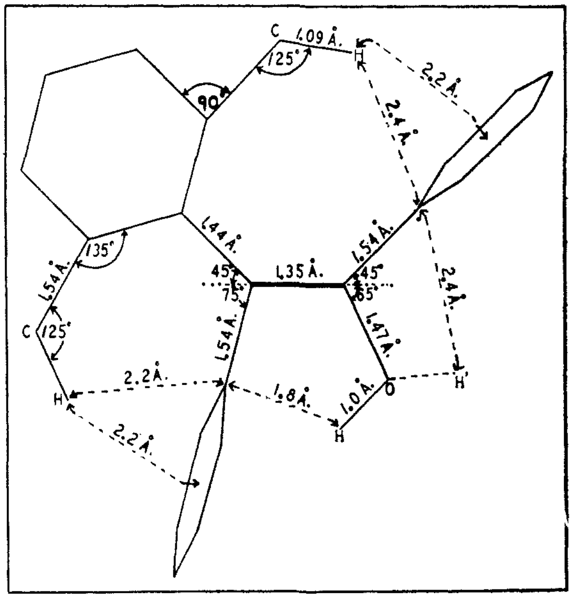


Fig. 4.—Trimesityl vinyl alcohol.

Dependence of Extinction Coefficient and Wave Length of Maximum on Molecular Structure.—The extinction coefficient is remarkably insensitive to changes in the substituent groups. This would indicate that the polar forms of the excited state which contribute to the dipole strength of the transition are essentially the same in all cases.

On the other hand the energies of these excited states vary considerably as is evidenced by the shift in wave length. The situation of an aromatic group on the α-carbon clearly favors the polar structures in the excited state presumably by some sort of an inductive effect.

Experimental

The instrument used was a Beckman Quartz Spectrophotometer Model DU. Measurements were made from 220 to 400 mμ.

Samples were weighed in duplicate to four significant figures and were dissolved and diluted to 40 ml. with normal hexane which had been purified by the method of O'Shaugnessy and Rodebush[3] and which had been tested for transparency to ultraviolet light.

Dilutions were made from these solutions to give the concentrations necessary for obtaining optical density readings within the range 0.3 to 0.63 at the absorption maxima. Measurements at maximum absorption were within ±3% of the values indicated by the graphs.

The values of the molar extinction coefficient ε were calculated from the density readings 'd' ($= \log_{10} I_0/I$) by means of the equation: $\epsilon = d/cl$ were c = molar concentration and l = length of cell in centimeters, this distance being one centimeter for the cell used.

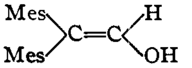
The list of compounds follows with references to articles by Fuson and his co-workers describing their preparation and properties. They are grouped according to the figures in which the extinction curves are shown and the number designates the curve for each particular compound.

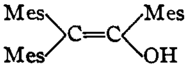
Symmetrical Triphenylbenzene.—An impure sample obtained from Organic Stores was purified by Mr. H. Porter. The compound was recrystallized four times from glacial acetic acid, including one decolorization with charcoal, and once finally from 95% ethyl alcohol. The purified compound melted at 173–173.5°.

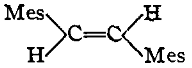
LIST OF COMPOUNDS STUDIED

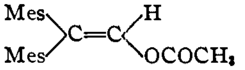
FIGURE 2

(1) $C_6H_5—C=CH_2$ styrene[9]

(2)

2,2-Dimesitilvinyl alcohol[10]

(3)

Trimesitylvinyl alcohol[11]

(4)

1,2-Dimesitylethylene[12]

(5)

2,2-Dimesitylvinyl acetate[13]

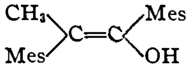
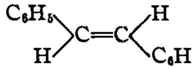
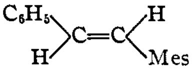
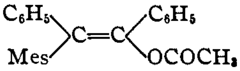
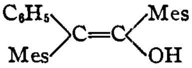
(6)

1,2-Dimesityl-1-propen-1-ol[14]

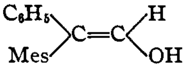
FIGURE 3

(1)

trans-Stilbene[15]

(2)

1-Mesityl-2-phenylethylene[16]

(3)

2-Mesityl-1,2-diphenylvinyl acetate[17]

(4)

1,2-Dimesityl-2-phenylvinyl alcohol[18]

(5)

2-Mesityl-2-phenylvinyl alcohol[19]

Summary

1. The ultraviolet extinction coefficient of symmetrical triphenylbenzene indicates that the molecule possesses a large amount of resonance energy. An explanation is offered for the non-coplanarity of triphenylbenzene (indicated by the X-ray evidence) as contrasted with biphenyl.

2. Ultraviolet extinction curves have been obtained for a number of substituted vinyl alcohols, where the crowding is so great as to permit only one aromatic ring to assume a position coplanar with the carbon–carbon double bond.

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[9] Prepared in this laboratory. Similar results were obtained by A. Smakula, *Z. angew. Chem.*, **47**, 777 (1934).

[10] R. C. Fuson and S. P. Rowland, THIS JOURNAL, **65**, 992 (1943).

[11] R. C. Fuson, D. H. Chadwick and M. L. Ward, unpublished work.

[12] R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland and J. L. Marsh, THIS JOURNAL, **64**, 30 (1942).

[13] R. C. Fuson, P. L. Southwick and S. P. Rowland, *ibid.*, **66**, 1109 (1944).

[14] R. C. Fuson, J. Corse and C. H. McKeever, *ibid.*, **62**, 3250 (1940).

[15] A. Smakula, *Z. physik Chem.*, **155A**, 356 (1931).

[16] R. C. Fuson, J. J. Denton and C. Best, *J. Org. Chem.*, **8**, 64 (1943).

[17] R. C. Fuson, L. J. Armstrong, D. H. Chadwick, J. W. Kneisley, S. P. Rowland, W. J. Shenk and Q. F. Soper, THIS JOURNAL, **67**, 386 (1945).

[18] R. C. Fuson, L. J. Armstrong, J. W. Kneisley and W. J. Shenk, *ibid.*, **66**, 1464 (1944).

[19] R. C. Fuson, N. Rabjohn and D. J. Byers, *ibid.*, **66**, 1272 (1944).

URBANA, ILLINOIS RECEIVED NOVEMBER 8, 1945

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Salts and Esters of Hydroxylamine-O-sulfonic Acid[1]

BY R. N. KELLER AND PETER A. S. SMITH[2,3]

In a previous communication[4] the amination of aromatic nuclei by means of hydroxylamine-O-sulfonic acid in the presence of aluminum chloride was reported

$$R—H + H_2N—O—SO_3H \xrightarrow{AlCl_3} R—NH_3^+HSO_4^-$$

At that time no attempt was made to explain the role of the aluminum chloride in the reaction. It was felt that the intermediate formation of the aluminum salt of hydroxylamine-O-sulfonic acid might be involved, since a recorded attempt[5] to prepare salts of this acid indicates that they are extremely unstable and reactive. We have therefore prepared a series of hydroxylamine-O-sulfonates and, although the aluminum salt could not be isolated, the properties of the sodium, silver, lead, ammonium, hydroxylamine, guanidine, pyridine and trimethylamine salts are recorded in this paper. Several of these salts were obtained in two forms, one which was relatively stable and one which deflagrated violently in a matter of minutes after preparation. Among the decomposition products of the salts were hydrazoic acid, hydroxylamine, and, in the case of ammonium hydroxylamine-O-sulfonate, hydrazine. These observations confirm and extend the original findings of Sommer, Schulz and Nassau[5] and support their explanation that NH (or NH_2^+) is an intermediate in the decomposition reaction. A discussion of the bearing of the chemical behavior of these salts on the mechanism of the amination reaction follows the experimental part.

In our original investigation[4] it was suggested that the low yields of aromatic amine obtained by amination with hydroxylamine-O-sulfonic acid might be improved by using a derivative of this

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[1] Presented in part at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April, 1944.

[2] From a thesis submitted to the Horace H. Rackham School of Graduate Studies in 1944 by Peter A. S. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Allied Chemical and Dye Fellow, 1943-1944.

[4] R. N. Keller and Peter A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

[5] F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).