Anal. Calcd. as above. Found: C, 49.8; H, 2.5; N, 26.3.

The yield of each solid was about 30%. Orientation of these substances by *ad hoc* syntheses has proved difficult and will be described subsequently. Similarly when 6-imino-3,9-di-*p*-nitrophenyl-1,11-diphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene and the 3,9-di-*m*-nitrophenyl analog were treated with concentrated nitric acid they reacted less vigorously than the 3,9-diphenyl compound, but after refluxing for 1-hour periods both yielded dinitrophenyltetrazoles of m.p. 190°.

(b) 8.86 g. (0.02 mole) of lead tetraacetate dissolved in chloroform was added to a solution of 3.5 g. (0.01 mole) of 6-imino-1,3,9,11-tetraphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene in the same solvent. An immediate fading in color of the formazan solution resulted. The mixture was warmed gently for a few minutes before the chloroform was removed, under reduced pressure. The residue was taken up with 40 ml. absolute ethanol and all the lead precipitated by the passage of hydrochloric acid gas. Filtration, followed by thermal concentration resulted in the deposition of a white feathery material which on purification melted at 101.5–102°. Analysis showed this to be 2,5-diphenyltetrazole.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 70.3; H, 4.5; N, 25.2. Found: C, 70.2; H, 4.6; N, 24.4.

The yield was practically quantitative. The same reaction took place with nitrous oxide in chloroform solution. When 6-imino-3,9-diphenyl-1,11-*o*-nitro-*p*-tolyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene was oxidized by similar methods, 2-*o*-nitro-*p*-tolyl-5-phenyltetrazole of m.p. 101° was obtained.

Anal. Calcd. for $C_{14}H_{11}N_5O_2$: C, 59.7; H, 3.9. Found: C, 59.0; H, 4.4.

(c) 0.005 mole of 6-imino-3-phenyl-1-tetrazolyl-3,6-dicarbaheptaz-1,3-diene was refluxed for 10 minutes with 60 ml. of 5% nitric acid. The resulting straw-yellow solution on filtering from suspended matter was neutralized with 5% sodium hydroxide and allowed to stand at 0° for 12 hours. A slight suspension of a gray material separated, was filtered off and was not further investigated. The remaining solution was thermally concentrated and the resulting organic solid separated from inorganic contaminants by extraction with a chloroform–ethanol mixture. On concentrating, a crystalline solid was precipitated which, after recrystallization from aqueous ethanol melted at 245–246°, yield was *ca.* 20%. The substance has an empirical formula of $C_9H_{10}N_6$.

Anal. Calcd. for $C_9H_{10}N_6$: C, 52.1; H, 4.8; N, 40.5. Found: C, 52.2; H, 4.9; N, 40.3.

A similar experiment using the anisylidene analog resulted in a solid of m.p. 265°. This also corresponds to a similar type empirical formula $C_9H_9N_6{\cdot}OCH_3$. These are being further investigated.

Anal. Calcd. for $C_{10}H_{12}N_6O$: C, 51.6; H, 5.2; N, 36.2. Found: C, 51.8; H, 5.2; N, 36.2.

The use of the dilute acid increased the extent of hydrolysis and thus the evolution of the free aldehyde. This was an undesirable side reaction, but the use of the method was necessitated by the insolubility of the tetrazolylformazans in chloroform. Refluxing a pyridine solution of such formazans with permanganate to effect the oxidation afforded anomalous results.

Cyclization of a Tetrazolylisotetrazene.—On adding a solution of 0.01 mole of 5-tetrazolyldiazonium nitrate to a solution of 0.01 mole of benzohydrazide in aqueous ethanolic solution in the presence of excess sodium acetate solution, a white precipitate of crude 1-benzoyl-4-tetrazolyl-isotetrazene, m.p. 94–98°, 88% yield, separated immediately. As most purification techniques resulted in decomposition of the isotetrazene, it was subjected without purification to the cyclization technique of Dimroth and de Montmollin.[8] Four and one-tenth grams of the well-powdered reaction product was added to 40 ml. of 5 *N* sodium hyroxide solution. An immediate yellow coloration took place. The suspension was agitated while the temperature was raised gently to 70° when ammonia vapor was given off. After filtration and subsequent crystallization from ethanol–water it was obtained as white crystals of m.p. 126°. It was shown to be benzamide by mixed melting point with an authentic sample and by analysis.

Anal. Calcd. for C_7H_7NO: C, 69.3; H, 5.8; N, 11.5. Found: C, 69.1; H, 5.7; N, 11.7.

Neutralization of the filtrate and extraction with ether made possible the recovery of a further yield of benzamide; total yield 20%. This experiment was repeated keeping the temperature of the alkaline suspension of tetrazene at 0° for 24 hours. Again benzamide was the main product recovered. The identification of the tetrazolyl fragment of the tetrazene fission was not pursued.

CORK, IRELAND

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Steric Hindrance to Coplanarity in *o*-Fluorobenzidines[1a,b]

BY ANDREW J. BILBO AND GEORGE M. WYMAN

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2,2′-Difluoro-, 2,2′,6,6′-tetrafluoro-, 2,2′-dichloro- and 3,3′-dichlorobenzidine were synthesized by standard methods and their ultraviolet absorption spectra measured. The spectra indicate that there is an appreciable inhibition of resonance in the *o*-halogenated benzidines, probably resulting from displacement of the molecule from a coplanar configuration. The bromine water tests observed for these molecules further support this theory.

Introduction

In conjunction with some work on conjugated polyphenyls, it was considered desirable to ascertain the steric interference with coplanarity caused by the introduction of fluorine atoms in the *o*-positions in the biphenyl structure. In contrast with the corresponding alkyl and chlorine compounds, the *o*-tetrafluorinated derivatives of biphenyl have not been successfully resolved,[2] although a schematic drawing of the spatial arrangement of atoms in such a molecule indicates the existence of considerable steric interference between the fluorine atoms on adjacent rings, as shown in Fig. 1. In order to accommodate these "overlapping" fluorine atoms in the limited space available between the two benzene rings, it is necessary for the phenyl groups to take up noncoplanar positions by twisting about the connecting 1,1′-bond until the steric interference is removed. Since the distance of closest approach in space between two adjacent fluorine atoms in organic molecules has been reported to be 2.70 Å.,[3] the angle of torsion of the benzene rings can be calcu-

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(1) (a) The research reported in this paper was performed in part under the sponsorship of the Ordnance Corps, Department of the Army; (b) presented before the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(2) E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4219 (1933).

(3) H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950).

lated from the normal bond distances and bond angles shown in Fig. 1. On the basis of this calculation it appears that the angle between the planes of the benzene rings in these compounds should be close to 60°.

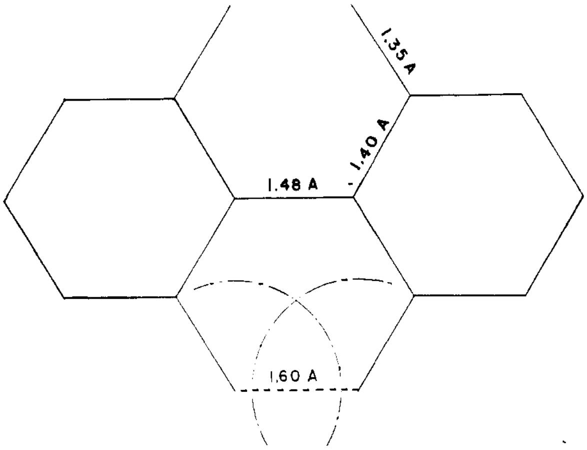

Fig. 1.—The coplanar configuration of 2,2′,6,6′-tetrafluorobenzidine, drawn to scale. Circles (-·-·-·-) indicate the effective size of the fluorine atoms.

In order to determine the existence and, perhaps, the extent of such steric hindrance in molecules of this type, the synthesis of some fluoro- and chlorobenzidines was undertaken and their ultraviolet absorption spectra studied. A similar study had been made previously on the steric effect of methyl groups on the 2-position on the 4-amino-4′-nitrobiphenyl and 4,4′-dinitrobiphenyl molecules by Sherwood and Calvin.[4] The present work supplements their results and it is hoped that together they provide a better understanding of the steric inhibition of resonance in 2-substituted biphenyl derivatives.

In addition, the effect of halogen substituents on the bromine water test[5] for benzidine was determined and these results were found to be consistent with the conclusions from the spectrophotometric measurements.

Experimental

(A) **Syntheses.**—2,2′-Difluorobenzidine, 2,2′,6,6′-tetrafluorobenzidine, 2,2′-dichlorobenzidine and 3,3′-dichlorobenzidine were prepared by the standard synthetic method involving alkaline reduction of the appropriate halogenated nitrobenzene followed by treatment with tin and hydrochloric acid.[6] The crude products were recrystallized from boiling water. The physical properties of the compounds are listed in Table I.

(B) **Measurement of the Absorption Spectra.**—The ultraviolet absorption spectra of the various compounds were determined in approximately 10^{-4} *M* solutions in 95% ethanol by means of a Cary recording spectrophotometer with the solvent as reference, using 2-cm. matched fused quartz absorption cells. The spectral absorption curves are shown in Figs. 2 and 3.

(C) **Bromine Water Test.**—A few crystals of the compound to be tested are dissolved in about 5 cc. of carbon disulfide, 5 drops of bromine water added and the mixture shaken vigorously. A heavy blue-green precipitate is a positive test for benzidine.

TABLE I

PHYSICAL PROPERTIES OF HALOGENATED BENZIDINES

Substituents	M.p., °C. Obs.	M.p., °C. Lit.[a]	F Analyses, % Calcd.	F Analyses, % Found
2,2′-Difluoro-	115–116	[b]	17.25	17.4
2,2′,6,6′-Tetrafluoro-	165–166	[b]	29.66	29.3
2,2′-Dichloro-	165–166	167		
3,3′-Dichloro-	132–133	132		

[a] "Beilstein," Fourth Edition, Vol. 13. [b] New compound. *m*-Fluoronitrobenzene was made according to Roe[7] and 3,5-difluoronitrobenzene was prepared according to the procedure described by Finger.[8] The two chloronitrobenzenes used were obtained commercially. *m*-Fluoroaniline was prepared by the reduction of *m*-fluoronitrobenzene with iron and acetic acid. 3,5-Difluoroaniline was obtained through the kindness of Dr. G. C. Finger.

Discussion of Results

The normal effect of halogen substitution upon the ultraviolet absorption spectrum of benzidine may be readily evaluated by comparing it with that of 3,3′-dichlorobenzidine. The introduction of chlorine in those positions where there is no possibility for steric hindrance gives rise to a slight shift toward longer wave lengths (*bathochromic shift*), accompanied by a similar increase in the intensity of absorption. This *bathochromic shift* is similar to that observed when chlorine is introduced in the

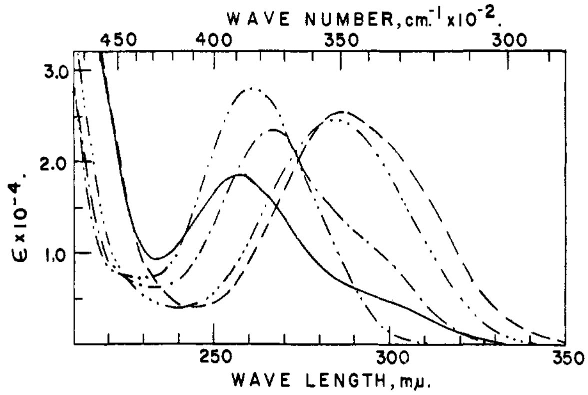

Fig. 2.—Absorption spectra of benzidines in 95% ethanol: (·······) benzidine; (- - - -), 3,3′-dichlorobenzidine; (——) 2,2′-dichlorobenzidine; (-·-·-·-) 2,2′-difluorobenzidine; (-·-·····) 2,2′,6,6′-tetrafluorobenzidine.

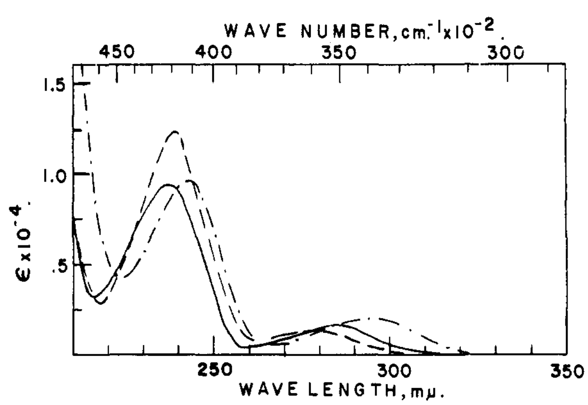

Fig. 3.—Absorption spectra of halogenated anilines in 95% ethanol: (-·-·-) *m*-chloroaniline [this curve obtained for solution in absolute ethanol by Dr. J. M. Vandenbelt]; (——) *m*-fluoroaniline; (- - - -) 3,5-difluoroaniline.

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(4) D. W. Sherwood and M. Calvin, THIS JOURNAL, **64**, 1350 (1942).

(5) "Beilstein," Fourth Edition, Vol. 13, p. 218.

(6) H. Schmidt, *Ann.*, **207**, 330 (1881).

(7) "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York N. Y., 1949, p. 203.

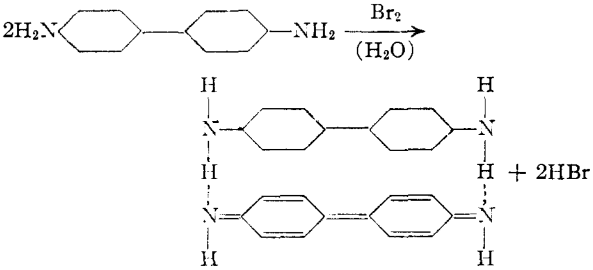
(8) G. C. Finger, F. H. Reed and J. L. Finnerty, THIS JOURNAL, **73**, 153 (1951).

4,4'-positions in the biphenyl molecule[9] and is generally observed upon introducing halogen atoms into aromatic rings.[10]

It is immediately apparent that the effect of introducing fluorine atoms in the 2,2'-positions in the benzidine molecule is considerably different. There is a large shift in the position of the absorption band toward shorter wave lengths (*hypsochromic shift*), accompanied by a slight decrease in the intensity of absorption. This behavior is similar to that reported for a number of *o*-substituted biphenyls,[11,12] and it is, in all likelihood, attributable to a departure from coplanarity, brought about by the introduction of the bulky fluorine atoms in the *o*-positions.[13] This *hypsochromic shift* is more pronounced in 2,2',6,6'-tetrafluorobenzidine and stronger yet in 2,2'-dichlorobenzidine (*cf.* Fig. 2). Thus, it appears that steric hindrance and the resulting displacement from coplanarity increases in this order. This is in accordance with expectations, since the sum of the van der Waals radii for hydrogen and chlorine (1.2 and 1.8 Å., respectively) is greater than twice the van der Waals radius for fluorine (1.35 Å.).[14] The increased absorption intensity of the tetrafluoro compound might at first glance tend to contradict the idea of increased resonance inhibition. This is probably, however, only another demonstration of the tendency of fluorine atoms attached to aromatic systems to increase markedly the intensity of absorption, "more nearly resembling methoxyl and amino groups than chlorine."[10] Such an increase in the intensity of absorption may well occur in such a highly fluorinated aromatic molecule, even though there be complete insulation of the two rings due to steric hindrance.

A comparison of the spectra of the sterically hindered benzidines with those of the corresponding half-molecule anilines (*cf.* Figs. 2 and 3) shows that the former are intermediate between the spectra of benzidine and the various substituted anilines. This suggests that, albeit there is a considerable barrier to resonance, insulation of the two rings is not by any means complete. It is accordingly to be expected that *o*-tetrafluoro-substituted biphenyl derivatives could not be resolved into optical antipodes, because the fluorine atoms are not large enough to cause a sufficient energy barrier to racemization.[15]

These conclusions are supported by the results obtained with the bromine water test for benzidines. This test depends on the oxidation of a conjugated aromatic *p*-diamine to a quinoneimine, followed by the formation of a deeply colored quinhydrone by addition to a molecule of starting material[16] as shown in this equation



Displacement of the molecule from a coplanar structure because of bulky substituents in the *o*-positions would be expected to make the formation of the quinoneimine (which requires a coplanar structure) difficult and, perhaps, impossible. Naturally, in the absence of the formation of the quinoneimine, no quinhydrone could be formed and the test would be negative for such sterically hindered benzidines. Table II summarizes the results of such tests with the five benzidines studied and also lists the wave lengths of the principal absorption band. It is immediately apparent from Table II that there is a close parallelism between the test results and the absorption data. Benzidines having the main absorption band at wave lengths longer than 267 mμ give positive tests while the others fail to give the deep blue-green precipitate under these conditions; 2,2'-difluorobenzidine is apparently on the borderline and gives only a faint green precipitate. Thus the test provides additional independent evidence for the existence of steric hindrance to coplanarity in these benzidines and confirms the order of increasing non-coplanarity obtained from spectroscopic data.

TABLE II

RESULTS OF THE BROMINE WATER TEST FOR BENZIDINES

Substituent	λ_{max}, mμ	Test result
None	284	Positive
3,3'-Dichloro-	286	Positive
2,2'-Difluoro-	267	Weakly positive
2,2',6,6'-Tetrafluoro-	261	Negative
2,2'-Dichloro-	257	Negative

Acknowledgment.—The authors express their appreciation to Dr. G. C. Finger for the sample of 3,5-difluoroaniline and to Dr. J. M. Vandenbelt for the absorption curve of *m*-chloroaniline. They are also indebted to Drs. C. W. Beckett and Max Hellmann for many helpful discussions.

WASHINGTON, D. C.

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(9) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, curves No. 161 and 183.

(10) F. Smith and L. M. Turton, *J. Chem. Soc.*, 701 (1951).

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

(12) L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).

(13) For discussions of the relation between ultraviolet absorption spectra and coplanarity of biphenyl derivatives, *cf.* reference (11), or R. N. Jones, THIS JOURNAL, **65**, 1820 (1943).

14) L. Pauling, "Nature of the Chemical Bond," Second Ed., Cornell University Press, Ithaca, N. Y., 1942, p. 189.

(15) The minimum energy barrier necessary to permit resolution has been estimated at 20 kcal. (ref. 11).

(16) J. Piccard, *Ber.*, **46**, 1843 (1913).