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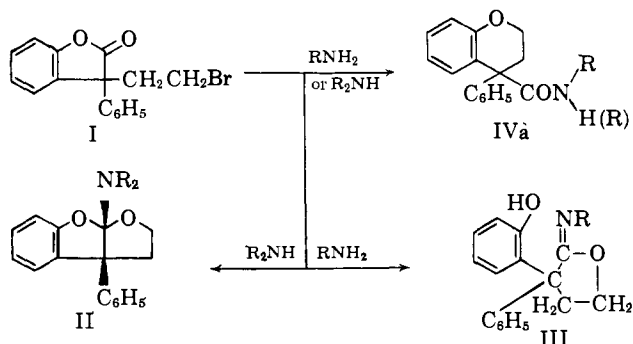
Neighboring Group Reactions. X. A Trapped Tetrahedral Intermediate from the Reaction of a Bromolactone with Ammonia

BY H. E. ZAUGG, V. PAPENDICK, AND R. J. MICHAELS

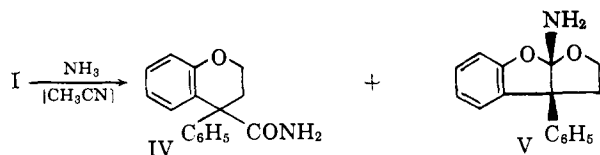
RECEIVED SEPTEMBER 6, 1963

Treatment of 3-(β -bromoethyl)-3-phenyl-2-benzofuranone (I) with ammonia in acetonitrile solution gives a low yield ($\sim 10\%$) of the trapped tetrahedral intermediate V. Unlike the products III obtained from the reaction of I with primary amines, V shows no observable tendency to isomerize to its open-chain tautomer VIII. Treatment with acid or base, however, does cleave the central ring of V. With acid the imidate salt VI (p*K*_a = 4.5) is produced and in basic solution (pH > 10) the anion VII is formed. From these results it can be concluded that the acid-base character of the amino group in V resembles that of a primary amide and is totally unlike that of an aliphatic amine. Thermolytic and solvolytic reactivity of the hydrochloride VI was studied. From the methanolysis reaction, the ortho ester IX was isolated in poor yield.

When 3-(β -bromoethyl)-3-phenyl-2-benzofuranone (I) is treated with primary or secondary amines at room temperature, direct displacement of the halogen atom usually does not occur. Instead, two products resulting from primary nucleophilic attack at the carbonyl carbon atom of I are obtained in varying proportions depending mainly upon the specific amine used. One product, the *N*-substituted 4-phenyl-4-chromancarboxamide IVa, results from intramolecular displacement of the bromine atom by the ring oxygen atom of I.^{1,2} The other derives from similar displacement by the carbonyl oxygen atom. The latter products obtained from secondary amines necessarily have the structure II of a trapped tetrahedral intermediate¹ while those from primary amines prefer the open structure of the cyclic imidate III.²



With ammonia the reaction of the bromolactone I is more nearly unidirectional. Both aqueous and anhydrous ammonia give the rearranged amide IV



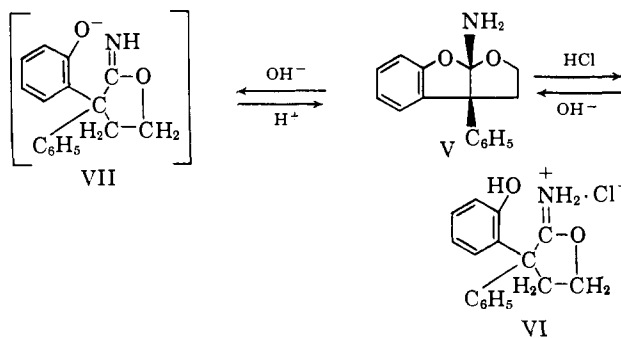
exclusively; and in acetonitrile solution the amide IV still constitutes the bulk (85–90%) of the product.² It is the purpose of the present work to show that the minor component ($\sim 10\%$) of this reaction product is the trapped tetrahedral intermediate V, and to describe some of its properties.³

(1) H. E. Zaugg, F. E. Chadde, and R. J. Michaels, *J. Am. Chem. Soc.*, **84**, 4567 (1962).

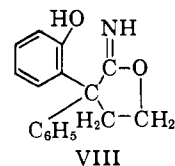
(2) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, **28**, 1795 (1963).

(3) It is interesting to note an even more striking influence of acetonitrile on the course of the reaction of a lactone with ammonia. With aqueous ammonia β -propiolactone gives mostly hydracrylamide (acyl-oxygen cleav-

Compound V is a colorless, thermally stable, crystalline solid, m.p. 94–95°. Its structure follows from its elemental analysis, infrared spectrum (presence of NH₂, absence of C=O or C=N), n.m.r. spectrum (Table IA), and from its amphoteric behavior.



Either ethereal or aqueous hydrochloric acid converts V to the hydrochloride VI, which is poorly soluble in water. Treatment of an aqueous suspension of VI with base regenerates the "ortho amide" V, but when a dilute aqueous solution of the hydrochloride VI is treated with excess base, the initially formed precipitate (presumably V) redissolves. Neutralization of this alkaline solution with acetic acid once again regenerates V. Both infrared and ultraviolet examination of solutions of V in methanolic sodium methoxide point to VII as the structure of the alkali-soluble species. Numerous attempts to isomerize V to its open chain tautomer VIII failed. Infrared evidence clearly indicates that in its uncharged state this compound exists entirely in the "ortho amide" form V whether as a solid or in solution.



The p*K*_a of the hydrochloride VI, determined spectrophotometrically, is 4.5 ± 0.2. Since the measured¹ basicities of the compounds of type II are generally lower than those of the amines from which they are derived by 4 to 5 p*K* units, the low basicity observed

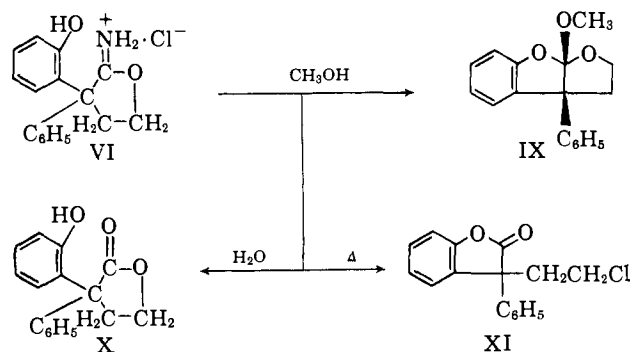
age), but in acetonitrile the main product is β -alanine (alkyl-oxygen cleavage).⁴

(4) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Am. Chem. Soc.*, **73**, 3168 (1951).

for V is thus consistent with its assigned structure (pK_a of ammonium ion = 9.2).

Although examination of its ultraviolet spectrum in alkaline solution clearly showed that conversion of V to VII begins at pH 10, the change is still not complete in 0.1 *N* alkali (pH 12–13). The pK_a of V can therefore only be estimated as being somewhere in the range 11 to 15.

Paralleling previous observations¹ concerning reactivities of the trapped tetrahedral intermediates II, it has been found that V must be converted to its hydrochloride VI in order to impart electrophilic reactivity to it. Thus methanolysis of VI gives the ortho ester IX in poor yield, hydrolysis leads to the lactone X in 85% yield, and heat alone (200°) results in nucleophilic displacement of the ring oxygen atom by chloride ion to give the benzofuranone XI.^{5,6}



Discussion

The most plausible explanation for the difference in prototropic behavior, between the primary amine derivatives III on the one hand and the ammonia derivative V on the other, appears to be a steric one. Because the two five-membered rings in V (and in II) are necessarily *cis*-fused, the substituents (phenyl and amino) attached to the two fusion atoms must lie in a mutually eclipsed configuration. It seems reasonable to suppose, therefore, that substitution of one of the amino hydrogen atoms in V by an alkyl group could produce an increase in intergroup repulsion sufficient to tip the balance in favor of the unstrained open-chain tautomer III.

Since the steric requirement of an hydroxyl group is no greater than that of a primary amino group, the fact⁷ that the lactone X shows little if any tendency to equilibrate with its "ortho acid" tautomer merely reflects the lower electrophilic reactivity of the carbonyl

(5) It should be noted that methanolysis of the hydrochloride of II ($\text{NR}_2 = \text{morpholino}$) gave¹ a 33% yield of 3-(β -methoxyethyl)-3-phenyl-2-benzofuranone resulting from nucleophilic displacement of the ring oxygen atom (*cf.* VI). In contrast, the ortho ester IX must arise from nucleophilic attack by methanol at the imidate carbon atom in VI. However, the low yield of isolated products obtained in the two cases does not preclude the likely possibility that both types of attack may actually occur in both methanolysis reactions.

Previous work⁶ revealed that when the bromide I was refluxed for 2 weeks in methanol under strictly neutral conditions, three solvolysis products could be detected by v.p.c. in yields ranging from 0.8 to 3.9%. The two minor components of the product mixture were identifiable by comparing their retention times with those of authentic samples. Although it was suggested that the third component (3.9% yield) might be the ortho ester IX, the absence of an authentic specimen prevented proof. The availability of such a sample has now made possible the demonstration that the unknown methanolysis product is indeed the ortho ester IX.

(6) H. E. Zaugg and R. J. Michaels, *Tetrahedron*, **18**, 893 (1962).

(7) H. E. Zaugg, R. W. DeNet, R. J. Michaels, W. H. Washburn, and F. E. Chadde, *J. Org. Chem.*, **26**, 4753 (1961).

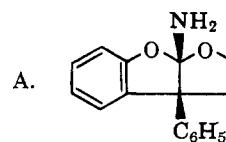
carbon atom in X as compared to the imidate carbon atom in VIII.

It is generally agreed that tetrahedral intermediates are involved in the aminolysis reactions of many esters and acids as well as in the reverse processes, the solvolyses of amides.⁸ The present work is therefore of interest in connection with these important reactions.

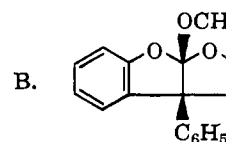
In line with previous findings,¹ the present work shows that in a tetrahedral intermediate of type V, much of the basicity generally associated with simple amines is lost. At the same time, the relative acidity is greatly increased (the theoretically calculated pK_a of ammonia and of simple amines is of the order 33 to 35⁹ compared to the estimated pK_a 11 to 15 for V). This behavior clearly arises from the fact that in acid and in base ring opening of V occurs to give the conjugate acid VI and conjugate base VII, respectively, of the tautomer VIII. Consequently, V exhibits

TABLE I

Chemical shift, ^b c.p.s.	N.m.r. spectra ^a assignment	Relative area ^c
80–130	NH_2	1.9 ^d
130–200	C- CH_2 -C	1.9
200–270	O- CH_2 -C	2.1
403–460	Aromatic H	9.0 ^c

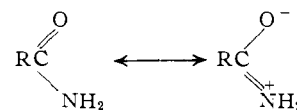


144–167	C- CH_2 -C	1.5
203	O- CH_3	2.8
210–268	O- CH_2 -C	1.5
405–452	Aromatic H	9.0 ^c



^a 60 Mc. ^b $(\text{CH}_3)_4\text{Si}$ as internal standard in CDCl_3 solution. Numbers denote range of frequencies of complex absorption. A single frequency notation represents a singlet. ^c Assuming 9 aromatic protons. ^d Band disappears when D_2O is added.

the acid–base strength that one would expect from its uncharged tautomer VIII, *i.e.*, acidity closer to that of a phenol and basicity analogous to that of an imino nitrogen atom. In short, the amphoteric behavior of V parallels that of an amide group.¹⁰



Experimental

Reaction of 3-(β -Bromoethyl)-3-phenyl-2-benzofuranone (I) with Ammonia in Acetonitrile. Preparation of 6a-Amino-3a-phenyl-2,3,3a,6a-tetrahydro-4,5-benzofuro[2,3-*b*]furan (V) and 4-Phenyl-4-chromancarboxamide (IV).—To a stirred solution of 31.7 g. (0.1 mole) of the bromide I in 250 ml. of acetonitrile cooled to 20° was added about 30 g. of liquid ammonia in a steady stream. A precipitate formed almost immediately and the mix-

(8) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

(9) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 136.

(10) The pK_a of acetamide is about 15 and it is generally recognized that simple amides protonate at the oxygen atom.

ture was stirred for 2 days at room temperature. Then 30 g. more ammonia was added and the mixture was allowed to stand for a week. The precipitated solid (23.3 g.) was collected at the filter, suspended in water (200 ml.), and collected again. Drying gave 14.9 g. of the rearranged amide IV, m.p. 178–181°, identical (mixture m.p. and infrared spectrum) with an authentic sample.¹¹ The acetonitrile filtrate was concentrated to dryness under reduced pressure at room temperature using a rotating evaporator. The residual oil was taken up in chloroform and extracted with two portions of ice-cold dilute (1:4) hydrochloric acid. From the neutral chloroform layer a further quantity (6.9 g.) of amide IV was obtained, bringing the total yield of this rearrangement product IV to 21.8 g. (86%). The combined aqueous acid extracts (containing some insoluble hydrochloride) were made strongly alkaline with cold 50% sodium hydroxide solution and the liberated base was taken up in chloroform. Removal of the chloroform at or below room temperature (under reduced pressure) gave a viscous glass (3.8 g.) which crystallized on trituration with pentane. Recrystallization from 95% ethanol gave 2.2 g. (9%) of a mixture of V and IV, m.p. 90–93°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 2.93, 2.99 (NH₂), 5.95 (CONH₂). From the intensity of the 5.95 μ band it could be estimated that IV constituted roughly 15% of the mixture.

Anal. Calcd. for C₁₆H₁₅NO₂: C, 75.86; H, 5.97; N, 5.54. Found: C, 76.09; H, 6.22; N, 5.74.

In three other runs carried out in essentially the foregoing manner, similar mixtures of V and IV were obtained in yields ranging from 8 to 12%. In one run the much lower intensity of the 5.95 μ absorption indicated that IV constituted less than 5% of the total yield.

Preparation of Pure V. A. By Recrystallization.—Recrystallization three times from 95% ethanol of a sample of the mixture rich in V (<5% of IV) gave pure V, m.p. 94–95°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 1.47, 1.51, 2.00, 2.93, 2.99 (five peaks characteristic of –NH₂), no significant absorption between 3.6 and 6.2 (no C=N or C=O); $\lambda_{\text{max}}^{\text{Nujol}}$ (μ) 2.93, 2.99, no significant absorption between 3.6 and 6.2; see Table IA for the n.m.r. spectrum.

Anal. Calcd. for C₁₆H₁₅NO₂: C, 75.86; H, 5.97; N, 5.54. Found: C, 75.57; H, 5.70; N, 5.55.

B. By Conversion to and Recovery from the Hydrochloride VI.—The 2.2 g. of the mixture of V and VI (m.p. 90–93°) was dissolved in 200 ml. of ether and extracted with two portions of dilute (1:4) hydrochloric acid. The resulting hydrochloride was insoluble in both ether and water and was removed by filtration.¹² Drying gave pure hydrochloride VI, m.p. 165–191°¹³; $\lambda_{\text{max}}^{\text{Nujol}}$ (μ) 2.81 (OH), 6.01–6.09 (C=N–H₂).

Anal. Calcd. for C₁₆H₁₆ClNO₂: C, 66.31; H, 5.56; N, 4.83. Found: C, 66.23; H, 5.74; N, 4.66.

This salt was suspended in 75 ml. of ice-water and treated dropwise with excess cold 50% sodium hydroxide solution. The solid material was then taken up in ether (in which it was now soluble) and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave 1.2 g. of the base V, m.p. 92–93°, identical (infrared spectrum) with the material obtained from procedure A. Treatment of a sample of it with a mixture of ether and dilute hydrochloric acid reconverted it to VI, identical with the product obtained from the mixture of IV and V. Repetition of procedure B with a different mixture of IV and V gave similar results. In this case the final basic product was triturated with pentane to give pure V, m.p. 92–94°. Concentration of the pentane filtrate gave a residue, m.p. 91–94°, which, judging from its infrared spectrum, was of a purity comparable to that of the first crop. Identical results were obtained when a chloroform suspension of VI was treated with excess 50% sodium hydroxide solution. Hence, treatment of pure VI with base leads exclusively to V.

(11) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, **26**, 4821 (1961).

(12) Only 0.2 g. of an impure material, not further characterized, was obtained by treating the aqueous acid layer with excess alkali. For the work-up of the neutral ether layer, see the end of procedure B.

(13) The wide melting range of this salt undoubtedly stems from the fact that it undergoes conversion to other products at elevated temperatures. Thus, when a sample was heated at 210° for several hours, the infrared spectrum of the resulting material lost all characteristics of VI and a strong peak developed at 5.54 μ , typical of the 2-benzofuranone carbonyl group. Furthermore, when a sample of VI was prepared in the absence of water by treating a mixture of IV and V with ethereal hydrogen chloride, a neutral ether-soluble by-product, m.p. 65–66°, could be isolated. It proved to be identical (infrared spectrum and mixture m.p.) with an authentic specimen¹¹ of β -chloroethyl-3-phenyl-2-benzofuranone (XI).

The original neutral ether layer¹² was dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residue (0.5 g.) solidified, m.p. 173–177°. It proved to be identical (infrared spectrum and mixture m.p.) with an authentic specimen¹¹ of the rearranged amide IV. In a separate run, treating an ether suspension of pure V (0.796 g.) with dilute (1:4) hydrochloric acid gave, in addition to VI (0.873 g.), 0.015 g. of neutral product whose infrared spectrum showed peaks at 5.54 (benzofuranone XI) and at 5.95 μ (rearranged amide IV). This suggests that the phenolic oxygen atom in VI can compete intramolecularly with chloride ion¹³ to effect nucleophilic displacement of the ring oxygen atom.

Hydrolysis of the Hydrochloride VI.—A suspension of 120 mg. (0.414 mmole) of VI in 5 ml. of water was refluxed for 3 hr. A clear solution formed at first followed by the separation of a solid. Filtration and drying gave 90 mg. (85%) of 2-(*o*-hydroxyphenyl)-2-phenyl-4-hydroxybutyric acid γ -lactone (X), m.p. 158–160°, identical (infrared spectrum and mixture m.p.) with the known⁷ material.

Methanolysis of the Hydrochloride VI.—A solution of 223 mg. (0.77 mmole) of VI in 10 ml. of dry methanol was refluxed for 18 hr. The clear solution was concentrated to dryness under reduced pressure and the residue was taken up in 50 ml. of dry ether. Insoluble ammonium chloride (32 mg.) was removed by filtration and the ether was removed from the filtrate by distillation. The oily residue (205 mg.) contained halogen (Beilstein test) and its infrared spectrum showed the absence of OH or NH and the presence of a benzofuranone carbonyl group (5.54 μ). Hence, it probably contained some of the chloroethyl derivative XI. However, on standing, it set to a semisolid mass from which, by two recrystallizations from 95% ethanol, a poor yield of a crystalline solid, m.p. 105–106°, could be obtained. No OH, NH, or carbonyl absorption was evident in its infrared spectrum and its n.m.r. spectrum (Table IB) was consistent with the ortho ester structure of **6a-methoxy-3a-phenyl-2,3,3a,6a-tetrahydro-4,5-benzofuro[2,3-b]furan (IX)**.

Anal. Calcd. for C₁₇H₁₆O₃: C, 76.10; H, 6.01; O, 17.89. Found: C, 75.81; H, 6.14; O, 17.85.

Treatment of the Hydrochloride VI with Alkali in Dilute Aqueous Solution.—When 389 mg. of analytically pure hydrochloride VI was treated with 50 ml. of water at room temperature, all but 59 mg. dissolved. The filtered, ice-cold solution was treated with excess 50% sodium hydroxide solution. The first drop of alkali produced a turbidity (formation of V), but further addition of base caused a clear solution to form (conversion of V to VII). When this solution was neutralized with acetic acid an oil precipitated (reconversion of VII to V) and was taken up in ether and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave an oil (270 mg.) which crystallized, m.p. 82–90°. Its infrared spectrum was identical with that of pure V (no C=N absorption).

Unsuccessful Attempts to Induce Tautomerization of the Trapped Tetrahedral Intermediate V to the Cyclic Imidate VIII.

A. By Acid Catalysis.—To a solution of 10 mg. of pure V in 1 ml. of chloroform was added an equivalent amount (0.25 ml. of 0.161 *N*) of hydrogen chloride in chloroform. The infrared spectrum of this solution did not change on standing and resembled that of pure V with the superposition of slight absorption at 5.94 μ due to the presence of some VI. When a chloroform solution of V in excess hydrogen chloride (20 mg. of V in 2 ml. of 0.161 *N* HCl–CHCl₃) was examined, absorption at 5.94 μ became proportionately larger and a broad band between 3 and 4 μ (ammonium salt formation) appeared. After standing 3 hr., a precipitate formed. It was collected and dried. Its infrared spectrum (Nujol mull) was qualitatively the same as that of the imidate salt VI, and the infrared spectrum of the solution from which it came was identical with that of the base V. Thus, the 5.94 μ absorption appearing in chloroform–hydrogen chloride must be due to the salt VI and not to any VIII. A 20% solution of V in 0.447 *N* methanolic hydrogen chloride showed a peak in the infrared (BaF₂ cell) at 5.89 μ which did not change on standing. In methanol alone there was no peak at 5.89 μ and none appeared on standing for 24 hr. The solid material which crystallized slowly from this was pure V (determined by its infrared spectrum in chloroform).

B. By Basic Catalysis.—To a 20% solution of V in methanol were added five increments of sodium methoxide resulting in final methoxide concentrations ranging from 2.8 to 36.7 mg./ml. The intensity of the absorption observed at 5.95 μ increased regularly with the concentration of base and was invariant with

time. This behavior is consistent with the ultraviolet spectral observations noted below. Apparently the only effect of the base is to convert V to the anion VII which has the carbon-nitrogen double bond producing the absorption at 5.95 μ .

Spectrophotometric Variation with pH of the System VII \rightleftharpoons VI \rightleftharpoons V and Determination of the pK_a of the Hydrochloride VI.—Spectrophotometric pK_a determination was carried out by the method of Brown and Mihm¹⁴ using the change in absorbance with pH of the 275 $m\mu$ maximum in water containing 28.5% (v./v.) ethanol. Absorbances were measured with a Beckman DU spectrophotometer and the reversibility of the acid-base equilibrium was checked with a Cary recording spectrophotometer. pH's of the buffer solutions were determined with a Beckman Zeromatic pH meter. Preliminary experiments with buffers revealed that below pH 3 no further decrease in absorbance at 275 $m\mu$ was detectable. Hence, protonation of V must be complete below this pH. Likewise, between pH 7 and 9 there was no change in absorbance, indicating the presence of the free base V

in this range. At pH 10 two new peaks appeared at 240 and at 296 $m\mu$, clearly demonstrating the formation of phenoxide ion, *i.e.*, species VII (this is consistent with the infrared spectrum of V in methanolic sodium methoxide). However, even in 0.1 N sodium hydroxide solution, absorbances of these new peaks were not stabilized, indicating incomplete conversion to VII in this medium. The following molar extinction coefficients at 275 $m\mu$ were observed: 2360 (0.1 N HCl), 2595 (acetate buffer, pH 4.75), and 2724 (phosphate buffer, pH 7.53). Appropriate calculations¹⁴ led to a value of 4.5 ± 0.2 for the pK_a of VI, *i.e.*, VI \rightleftharpoons V. Because the conversion to VII was not complete even in 0.1 N sodium hydroxide, the pK_a of V (V \rightleftharpoons VII) could not be determined. However, it must be greater than 12 (pH of 0.1 N NaOH is 12–13).

Acknowledgments.—We wish to thank Mr. Orville Kolsto, Mr. William Washburn, and Dr. Richard Mattoon and their associates, respectively, for the microanalyses, infrared spectra, and n.m.r. spectra, and Mrs. Taimi Anderson for the v.p.c. analyses.

(14) H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Intramolecular Interactions between Nonbonded Chromophores. The Spectra of Some Phenylsilanes and Siloxanes

BY JOHN F. BROWN, JR., AND PAUL I. PRESCOTT

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The ultraviolet spectra of the polyphenylated silanes and siloxanes, like those of the polyphenylated paraffins and the paracyclophanes, show considerable variations in the appearance of the 250–270 $m\mu$ band, particularly as regards the absolute and relative intensities of the different peaks in the vibrational structure. These variations were studied in detail, with particular emphasis on those in the spectra of the polycyclic phenylsilsesquioxanes, where the relative orientations of the benzenoid chromophores could be specified quite precisely. It was found that all the observed variations in peak heights could be related to variations in the absolute and relative intensities of the two overlapping systems which make up the observable 1L_b absorption. In the polyphenylsilsesquioxanes, these intensity variations in turn could be accounted for quantitatively in terms of two types of intramolecular electrostatic interactions, namely, induced dipole-dipole (or polarizability) interactions, which affect both the vibrationally induced and the substituent-induced components of intensity, and static dipole-induced dipole interactions (field effects), which affect only the substituent-induced component. The spectra of the diphenylsiloxanes were found to differ somewhat from those silanes and siloxanes carrying only one phenyl group per silicon, apparently as a result of weak bonding interactions between the two phenyls attached to the same silicon. Within the series of diphenylsiloxanes, however, the intensity variations were similar to those in the phenylsilsesquioxanes and could be related qualitatively to the same two types of intramolecular interactions between nonbonded phenyl chromophores.

Introduction

The near-ultraviolet spectra of the polyphenylated silanes and siloxanes show noticeable variations from each other and from the analogous monophenylated species, particularly as regards the absolute and relative intensities of the vibrational peaks in the 250–270 $m\mu$ region.^{1–5} Similar variations have long been known in the spectra of polyphenylated paraffins,^{6–8} polyphenylated ethers,⁸ and the higher paracyclophanes^{8,9} and have usually been ascribed qualitatively to the existence of weak bonding interactions between the phenyl rings.^{8,10}

The present study was undertaken in order to obtain more detailed characterization of these spectral variations, and to attempt their interpretation.

At the outset, we recognized that part of the spectral variations must arise from induced dipole-dipole, or polarizability, interactions between proximate but nonbonded chromophores in the same molecule. These are the interactions that may cause wave length shifts (bathochromism or hypsochromism) in dye aggregates and molecular crystals^{11,12} and intensity changes (hypochromism or hyperchromism) in these species, in double chain polynucleotides,¹³ and in helical polypeptides.¹⁴ Detailed expressions for calculating these interactions have recently been reported.¹³ Accordingly, we decided to carry out such calculations on our polyphenylated species in order to find out what portion of the observed spectral variations they could account for.

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