

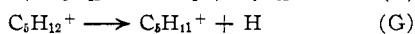
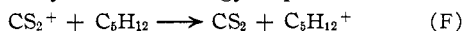
from $m/e = 73$ to 78 was $0.14 i_{72}$ and $0.52 i_{72}$ respectively. For comparison, in mixtures with C_2H_6 and C_4H_{10} the values were $0.23 i_{72}$ and $0.45 i_{72}$. Also, such a hypothesis would not explain the dependence of Q upon E_e^{-1} .

TABLE VII
ENERGY DEPENDENCE FOR REACTION CROSS SECTIONS

| Primary ion | Secondary ion | $\frac{\sigma_1}{\text{cm.}^2 \times 10^{16}} \times 10^{16}$ e.v. ^{1/2} | $\frac{\sigma_0}{\text{cm.}^2 \times 10^{16}}$ $\times 10^{16}$ | $\frac{QE_e}{\text{cm.}^2 \times 10^{16}}$ e.v. |
|--------------------------|-----------------------------|--|--|--|
| CS_2^+ | $C_5H_{12}^+ + C_5H_{11}^+$ | 5.3 | 3.1 | |
| $C_3H_5^{+a}$ | $C_5H_{11}^+$ | 30 | 15 | |
| $C_2H_4^{+b}$ | $C_5H_{11}^+$ | 7 | 4 | |
| $C_2D_4^{+c}$ | $C_5H_{12}^+$ | | | 1.5 |
| $C_2H_4^+ + C_3H_6^{-d}$ | $C_5H_{12}^+$ | | | 1.5 |
| $C_2H_4^{+e}$ | $C_5H_{12}^+$ | | | 1.0 |
| CS_2^+ | $C_5H_{12}^+$ | | | 5.3 |

^a For pure neopentane or added propylene. ^b Combined average for $C_2H_4^+$ and $C_2D_4^+$ from runs with C_2H_6 or with C_2D_6 . ^c From C_2D_6 . ^d Combined average for $C_2H_4^+$ and $C_3H_6^+$ from C_3H_8 , assuming equal efficiencies. ^e From C_2H_6 .

The combined current, $\Delta i_{72} + \Delta i_{71}$, should be a measure of the primary process F, provided decomposition does not proceed beyond $C_5H_{11}^+$. In fact equation 8 describes the results very well on this basis, and it would be expected that the primary process F obey such an energy dependence.



The results appear in Table VII. On the other hand, the net Δi_{72} obeys equation 11. Considering all the evidence, we conclude that Δi_{72} also obeys the particular law, 10. If one accepts this interpretation, the critical energy for the decomposition

reaction G can be obtained from the measured values of the parameters in equations 8 and 10 if we assume that $\sigma_K = 0$. We have $QE_e = 2\sigma_1 E_e^{1/2} - \sigma_0 E_e = 5.3 \times 10^{-16} \text{ cm.}^2 \text{ e.v.}$ and $2\sigma_1 = 10.6 \times 10^{-16} \text{ cm.}^2 \text{ e.v.}^{1/2}$; $-\sigma_{K0} = \sigma_0 = 3.1 \times 10^{-16} \text{ cm.}^2$. One obtains $E_c = 0.39 \text{ e.v.}$ for $C_5H_{12}^+$. Finally, using the same parameters we find $E_t = (5.3/1.3)^2 = 2.9 \text{ e.v.}$ for $C_5H_{11}^+$ and $C_5H_{12}^+$ combined which places an approximate upper limit on the range of validity of the measurements suitable for testing the preceding equation.

The preceding data in Table VI also support the crude description by collision theory mentioned above, *viz.* $\sigma_1/\sigma_0 = \sigma_L/\sigma_K$, assuming that reaction P-factors cancel. For the first three entries in Table VII we find ratios of 1.7, 2.0 and 1.8. The corresponding calculated ratios of σ_L/σ_K are 1.5, 1.1 and 1.0.

Neopentane.—It appears that no single ionic species is responsible for the enhanced 71-ion formation, either in mixtures or in neopentane alone. Comparison of the results in Table I with the mass spectral patterns suggests that CH_3^+ , $C_2H_5^+$ and $C_2H_4^+$ are effective. The parameters σ_1 and σ_0 for the more efficient reactions appear in Table VII. It is significant that every additive which enhances i_{72} also enhances i_{71} , while the converse appears not to hold. This suggests that, in addition to the mechanism previously proposed by Lampe and Field,¹⁰ there is also a spontaneous decomposition following charge transfer. The effect is most pronounced for carbon disulfide for which we postulate, as suggested by the data of Table II, the consecutive reactions F and G.

Acknowledgment.—We are grateful to Dr. D. P. Stevenson for critical comment.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The Ultraviolet Spectra of N-Phenyl-substituted Cyclic Imines¹

BY ALBERT T. BOTTINI AND CHARLES P. NASH

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The ultraviolet spectra of *N*-phenyl-substituted cyclic imines ranging in ring size from 3 to 6 have been examined. From comparisons of the ultraviolet spectra, base strengths and molar refractions it can be concluded that the resonance energy due to phenyl ring-nitrogen interaction increases as the ring size of the imine is varied in the order $3 < 6 < 4 < 5$. Comparison of the spectra of these imines with that of *N,N*-dimethylaniline (I) indicates that the configuration about nitrogen in I and the great majority of aromatic amines approaches the pyramidal configuration much more closely than the trigonal configuration and that π - sp^3 -conjugation between a phenyl ring and an amine nitrogen is as effective as π - π -conjugation in lowering the energy of the system. The effects of polar and hydrogen-bonding solvents on the spectra of the amines studied are discussed.

Introduction

Wepster² has pointed out that the stereochemistry of nitrogen in aromatic amines is complicated, among other reasons, because the optimum configuration is a compromise between the intrinsic tendency of trivalent nitrogen to be pyramidal and the expected tendency in conjugated systems to assume the trigonal configuration in order to maximize the resonance interaction with the benzene ring. Thus, the lone pair of electrons on the

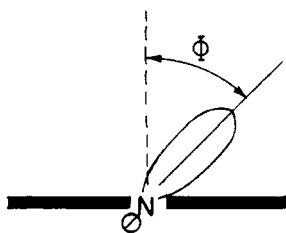
nitrogen atom in an aromatic amine may have sp^3 -character, p -character or some intermediate character, depending upon how the various factors affecting the potential energy of the molecule vary with the valency angles about nitrogen. For example, in aromatic amines in which rotation about the aromatic carbon-nitrogen bond can occur, the valency angles of nitrogen would be expected to increase toward 120° as the "angle of twist" ϕ^3 approaches 0° , provided that the resonance energy

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) B. M. Wepster, *Rec. trav. chim.*, **72**, 661 (1953).

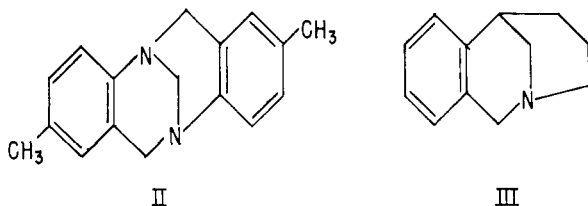
(3) The angle of twist ϕ is defined by the plane through the aromatic carbon-nitrogen bond perpendicular to the benzene ring and the plane through the aromatic carbon-nitrogen bond and the axis of symmetry of the lone pair of the nitrogen atom.

of the molecule is greater when the configuration about nitrogen is trigonal rather than tetrahedral.



Studies of the ultraviolet spectra of aromatic amines have yielded considerable information concerning the effect of steric factors on the resonance interaction between the aromatic ring and the amino nitrogen.⁴ In a series of *ortho*-substituted dimethylanilines, the oscillator strengths and, to a good first approximation, the molar absorptivities of the three principal bands in the ultraviolet spectrum have been found to vary as the \cos^2 of the estimated value of ϕ .⁵ Since that part of the resonance energy of aromatic amines due to the phenyl ring-nitrogen interaction also varies as $\cos^2 \phi$,⁶ the molar absorptivities (more properly, the oscillator strengths) of the principal ultraviolet bands should serve as a good measure of the phenyl ring-nitrogen resonance. The band at about $250 \text{ m}\mu$ ⁷ is most conveniently studied and the effect of *ortho*-substitution on steric inhibition of resonance has been correlated with the intensity of the $250 \text{ m}\mu$ band for a large number of aromatic amines.⁴

Steric inhibition of resonance in a number of dialkylanilines brought about by factors other than *ortho*-substitution also have been investigated by means of ultraviolet spectroscopy. Of particular interest is the comparison of the spectrum of dimethylaniline (I) with the spectra of amines such as Troeger's base (II)² and 1,5-methano-2,3,4,5-tetrahydrobenzo[*b*]azepin (III),⁸ in which the



nitrogen atoms are definitely pyramidal because they are incorporated in rigid, bicyclic systems. The bands of I, II and III near $250 \text{ m}\mu$ in isoöctane have essentially the same λ_{max} ($249 \pm 2 \text{ m}\mu$) and the molar absorptivities are 15,500, 8490 and 2750, respectively. These results have been interpreted⁴

(4) See B. M. Wepster in "Progress in Stereochemistry," Vol. II, Edited by W. Klyne and P. B. D. de la Mare, Academic Press, Inc., New York, N. Y., 1958, Chapt. 4.

(5) H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).

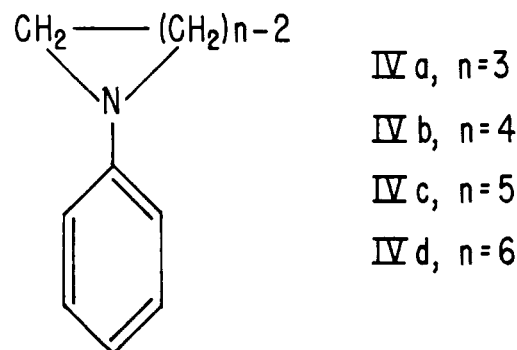
(6) (a) M. J. S. Dewar, *ibid.*, **74**, 3345 (1952); (b) see also L. L. Ingraham in "Steric Effects in Organic Chemistry," Edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 11.

(7) For a discussion of the nature of the transitions that are observed in the ultraviolet spectra of aromatic amines, see J. N. Murrell, *J. Chem. Soc.*, 3779 (1956).

(8) Unpublished work of ten Bruggen Cate and Wepster cited in ref. 4, pp. 121-122.

to mean that π - sp^3 -conjugation in aromatic amines can be appreciable and that the configuration about nitrogen in most simple aromatic amines is more nearly pyramidal than trigonal.

In an effort to evaluate the effect on the resonance interaction between nitrogen and the phenyl ring brought about by incorporating the nitrogen in a saturated ring system, we have prepared the N-phenyl-substituted cyclic imines IVa-d and examined their ultraviolet spectra. In these imines, any tendency of the nitrogen atom to assume the trigonal conformation will be opposed by the concomitant strain added to the heterocyclic ring.



Experimental

Melting points are corrected. Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. The nuclear magnetic resonance spectra were obtained at 60 mc. with a Varian Associates high resolution spectrometer (HR-60) system using samples contained in 5-mm. o.d. tubes. Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, California, and Drs. Weiler and Strauss, Oxford, England.

Preparation of Cyclic Imines.—Following the procedure of Heine, Kapur and Mitch,⁹ 105 g. (0.373 mole) of 2-anilinoethyl bromide hydrobromide,¹⁰ m.p. 135.5-137.5°, was converted in 56% yield to 1-phenylaziridine (IVa), b.p. 37-38° (1 mm.), n_D^{25} 1.5009, d_4^{25} 1.0047; lit.¹¹ b.p. 73-74° (18 mm.), n_D^{25} 1.5118.

1-Phenylpyrrolidine (IVc) was prepared in 55% yield from 96 g. (1.35 moles) of dry, redistilled pyrrolidine, 25 g. (0.64 mole) of sodium amide (Roberts Chemidals, Inc.) and 40 g. (0.255 mole) of bromobenzene by the general procedure described by Bunnett and Brotherton¹² for the preparation of dialkylanilines. The product had b.p. 100-102° (6 mm.), n_D^{25} 1.4796, d_4^{25} 1.0132; lit.¹³ b.p. 107° (6 mm.), n_D^{20} 1.581, d_4^{20} 1.0178.

1-Phenylpiperidine (IVd) was prepared in 65% yield from 100 g. (1.18 moles) of dry piperidine, 40 g. (0.255 mole) of bromobenzene and 2.0 g. (0.29 mole) of lithium by the procedure described by Horning and Bergstrom.¹⁴ The product had b.p. 104-106° (6 mm.), n_D^{25} 1.5590, d_4^{25} 0.9954; lit.¹⁴ b.p. 93-97° (3-4 mm.), n_D^{25} 1.5593.

Examination of the infrared and n.m.r. spectra of IVa, IVc and IVd, and gas-liquid partition chromatography of the compounds on a 2-m. column packed with silicone #550 on firebrick at 235° failed to reveal the presence of any impurity.

3-Anilinopropanol.—A mixture of 105 g. (0.76 mole) of 3-bromopropanol and 200 g. (2.15 moles) of aniline was heated on a steam bath for 3 hr. After 30 min., solid aniline

(9) H. W. Heine, B. L. Kapur and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).

(10) W. J. Pearlman, *ibid.*, **70**, 871 (1948).

(11) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(12) J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **22**, 832 (1957).

(13) Ya. K. Yur'ev and G. A. Minkina, *J. Gen. Chem. (U.S.S.R.)*, **7**, 2945 (1937); *Chem. Abstr.*, **32**, 5399 (1938).

(14) C. H. Horning and F. W. Bergstrom, *J. Am. Chem. Soc.*, **67**, 2110 (1945).

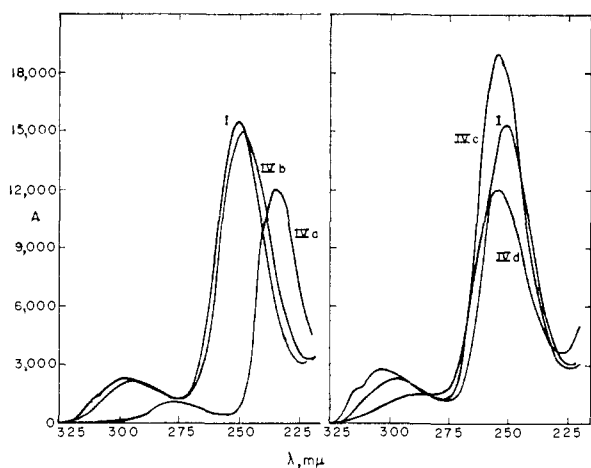


Fig. 1.—Ultraviolet spectra of N,N-dimethylaniline (I), 1-phenylaziridine (IVa), 1-phenylazetidine (IVb), 1-phenylpyrrolidine (IVc) and 1-phenylpiperidine (IVd) in isoöctane. Spectra were taken of solutions $0.5 - 4.0 \times 10^{-4} M$ in amine in 1.00 cm. silica cells using a Beckman DU spectrophotometer.

hydrobromide began to separate. The reaction mixture was diluted with 300 ml. of ether, shaken, and the precipitated salts (118 g. after air drying, 89% if all aniline hydrobromide) were collected by suction filtration and washed twice with 25-ml. portions of dry ether. The ether was removed by distillation and the residue was distilled through an 8×600 -mm. Podbielniak-type column.¹⁴ Aniline (46 g.) was collected at 55° (2 mm.). 3-Anilinopropanol (57 g., 50%) had b.p. $145-147^\circ$ (6 mm.), $134-137^\circ$ (2 mm.) n_D^{20} 1.5664. The residue weighed 39 g.

Anal. Calcd. for $C_9H_{12}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.58; H, 8.78; N, 9.17.

3-Anilinopropyl Bromide Hydrobromide.—The procedure is a modification of that used by Pearlman¹⁰ for the preparation of 2-anilinopropyl bromide. A mixture prepared by the addition of 310 ml. of cold, constant boiling hydrobromic acid to 99.3 g. (0.66 mole) of 3-anilinopropanol was heated at reflux for 2 hr. and then distilled through a 25×250 -mm. column packed with glass helices until the head temperature reached 125° . On cooling, the residue solidified. The solid was taken up in 350 ml. of hot 90% ethanol, treated with Norite and filtered. The solution was cooled and white flakes of 3-anilinopropyl bromide hydrobromide separated. The product weighed 128 g. (66%) and had m.p. $130.5-132.5^\circ$. The mother liquor was concentrated and a second crop of 40.5 g. (21%), m.p. $129.5-131.5^\circ$, was taken. A portion of the first crop was recrystallized from ethanol-water, m.p. $132.3-133.3^\circ$.

Anal. Calcd. for $C_9H_{12}NBr_2$: C, 36.64; H, 4.44; N, 4.75. Found: C, 36.72; H, 4.54; N, 4.92.

1-Phenylazetidine (IVb).—The procedure is a modification of that used by Heine, Kapur and Mitch⁹ for the preparation of IVa. A solution of 50 g. of sodium hydroxide, 200 ml. of water and 525 ml. of ethanol was heated at 50° in a water bath and treated dropwise with stirring with a warm solution of 125 g. (0.42 mole) of 3-anilinopropyl bromide hydrobromide in 450 ml. of water and 170 ml. of ethanol. The stirred mixture was heated at reflux for 5 hr., cooled to 40° , saturated with sodium chloride, cooled to 10° and extracted 3 times with 300-ml. portions of ether. The extracts were combined and concentrated to 250 ml. when 2 phases separated. The heavy, aqueous phase was extracted 3 times with 50-ml. portions of ether. The ether extracts and the organic phase were combined, dried over sodium hydroxide and concentrated until a separation of phases occurred. The organic phase was dried over sodium hydroxide and distilled through the Podbielniak column. The fraction with b.p. $88-90^\circ$ (8 mm.), n_D^{20} 1.5674, weighed 7.4 g. (13%) and contained about 60% IVb and 40% N-

(15) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, pp. 237-243.

allylaniline as determined by gas-liquid partition chromatography¹⁶ and n.m.r. spectroscopy.

Anal. Calcd. for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.64; H, 8.39; N, 10.85.

Another fraction with b.p. $139-140^\circ$ (7 mm.), n_D^{20} 1.5259, had an infrared spectrum consistent with the 1-ethoxy-3-anilinopropane structure. It weighed 16.2 g. (22%).

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.20; H, 9.88; N, 7.32.

An intermediate fraction of 2.5 g., b.p. $88-139^\circ$ (7 mm.), n_D^{20} 1.5427, and the residue, 12.6 g., were discarded.¹⁷

The mixture of IVb and N-allylaniline was dissolved in 30 ml. of dry pentane and cooled to -50° in a Dry Ice-acetone bath. Crystals of IVb formed and the mother liquor was withdrawn by suction through a fritted-glass disk. The crystals were allowed to melt, taken up in 30 ml. of dry pentane and recrystallized as before. The crystalline material was allowed to melt and distilled through a semimicro distillation column to yield 0.96 g. of 1-phenylazetidine, b.p. $76-80^\circ$ (4 mm.), n_D^{20} 1.5701, d_4^{25} 1.0015.

Anal. Calcd. for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.02; H, 8.47; N, 10.61.

Examination of the infrared and n.m.r. spectra of the product indicated that it contained less than 2% of N-allylaniline. In addition to the aromatic-hydrogen bands at $\tau = 2.2-3.3$,¹⁸ the n.m.r. spectrum of IVb possessed the triplet at $\tau = 6.1$ and the quintet at $\tau = 7.7$, $J = 7.3$ c.p.s., characteristic of azetidines.¹¹ The fine structure of the aromatic hydrogen bands in the n.m.r. spectrum of IVb was virtually identical with the fine structure of the aromatic hydrogen bands of IVc.

Other Materials.—The N,N-dimethylaniline (I) was reagent grade material that had been freed from methylaniline. It was redistilled before use, b.p. $89-91^\circ$ (21 mm.), n_D^{20} 1.5557, d_4^{25} 0.9522; lit.¹⁹ n_D^{20} 1.5578, d_4^{25} 0.9571. The acetonitrile, isoöctane and methanol were Spectro grade. All other materials were reagent grade.

Ultraviolet spectra were taken of I and IVa-d in acetonitrile, isoöctane and methanol using 0.1, 1.0 and 2.0-cm. silica cells with a Beckman DU spectrophotometer. The data given in Table I and shown in Fig. 1 were obtained using the same set of matched 1.0-cm. cells and solutions $0.5-4.0 \times 10^{-4} M$ in amine. The methanol solutions were made approximately $0.01 M$ in sodium hydroxide. Spectra of the methanol solutions were taken within 2 hr. after their preparation.

pK-Measurements.—A $9.82 \times 10^{-3} M$ solution of IVb in 50% ethanol (by volume) was neutralized with 0.0248 N hydrochloric acid in the same solvent. The reading, at the point of half-neutralization, on the pH-scale of a Beckman pH-meter calibrated against aqueous buffer solutions using glass and saturated potassium chloride-calomel electrodes without correction for liquid junction potentials, was 4.04 ± 0.05 . A duplicate determination yielded a value of 4.11 ± 0.05 . The average value, 4.08, was taken as the apparent pK_A of IVb. The apparent pK_A of IVc, determined in the same manner, was 3.45 ± 0.05 ; lit.²⁰ pK_A 3.52. Attempts to determine the apparent pK_A of IVa by this method failed because of the rapid polymerization of IVa in hydroxylic solvents containing a trace of acid.

Discussion

1-Phenylazetidine (IVb), which is the first N-arylazetidine prepared,²¹ was prepared in 8% yield by treatment of 3-anilinopropyl bromide with sodium hydroxide in aqueous ethanol.²² 1-Phenyl-

(16) The retention times of IVb and N-allylaniline (Aldrich Chemical Co., Inc.) on a 2-m. column packed with Silicone No. 550 on firebrick with a flow rate of 110 cc./min. of helium at 235° were 190 sec. and 155 sec., respectively.

(17) 3-Anilinopropanol, which was probably the major product, was not isolated because of the workup procedure used.

(18) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(19) A. I. Vogel, *J. Chem. Soc.*, 1925 (1948).

(20) Ref. 4, p. 129.

(21) See A. Fischer, R. D. Topsom and J. Vaughan, *J. Org. Chem.*, **25**, 463 (1960).

(22) W. R. Vaughan, R. S. Klonowski, R. S. McElhinney and B. B. Millward, *ibid.*, **26**, 138 (1961), have prepared a number of azetidines

TABLE I
ULTRAVIOLET SPECTRA OF DIMETHYLANILINE AND N-PHENYL-SUBSTITUTED CYCLIC IMINES IN VARIOUS SOLVENTS

| Compound | Solvent | λ_{\max} , m μ | A^b | f^c |
|----------|--------------|----------------------------|--------|-------------------|
| I | Isooctane | 250.0 | 15,500 | 0.30 |
| | Isooctane | 297.5 | 2250 | .034 |
| | Acetonitrile | 253.5 | 13,200 | .29 |
| | Acetonitrile | 300.0 | 2160 | .033 |
| | Methanol | 251.0 | 13,250 | .27 |
| | Methanol | 298.0 | 1840 | .030 |
| IVa | Isooctane | 235.0 | 11,900 | .18 |
| | Isooctane | 277.5 | 1160 | .017 |
| | Acetonitrile | 235.3 | 11,350 | .17 |
| | Acetonitrile | 278.0 | 1120 | .017 |
| | Methanol | 229.0 | 9840 | >.14 |
| | Methanol | 272.0 | 720 | .011 |
| IVb | Isooctane | 248.5 | 15,000 | .30 |
| | Isooctane | 294.0 | 2090 | .033 |
| | Acetonitrile | 250.1 | 14,420 | .30 |
| | Acetonitrile | 295.0 | 2080 | .033 |
| | Methanol | 246.3 | 12,040 | .27 |
| | Methanol | 291.0 | 1830 | .028 |
| IVc | Isooctane | 253.5 | 19,100 | .33 |
| | Isooctane | 302.0 | 2750 | .039 |
| | Acetonitrile | 255.7 | 18,050 | .33 |
| | Acetonitrile | 305.5 | 2560 | .039 |
| | Methanol | 254.5 | 17,650 | .33 |
| | Methanol | 304.0 | 2520 | .038 |
| IVd | Isooctane | 254.0 | 12,000 | .24 ^d |
| | Isooctane | (287.0) ^a | (1580) | .021 ^d |
| | Acetonitrile | 255.5 | 11,700 | .24 ^f |
| | Acetonitrile | (287.0) ^a | (1520) | .021 ^g |
| | Methanol | 251.0 | 8950 | >.22 ^h |
| | Methanol | (285.0) ^a | 1200 | .017 ^e |

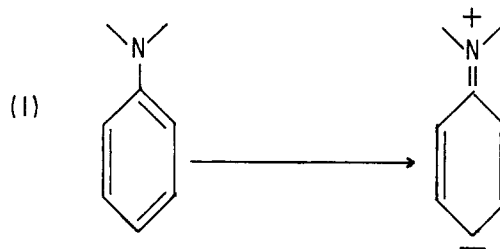
^a A diffuse band with no maximum. ^b $\pm 2\%$. ^c f , the oscillator strength = $4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} A d\nu$ where ν_1 is the low frequency minimum and ν_2 is the high frequency minimum of the absorption band; $\pm 4\%$. ^d $\lambda_1 = 278\text{m}\mu$, $\lambda_2 = 226\text{m}\mu$. ^e $\lambda_1 = 235\text{m}\mu$, $\lambda_2 = 278\text{m}\mu$. ^f $\lambda_1 = 282\text{m}\mu$, $\lambda_2 = 225\text{m}\mu$. ^g $\lambda_1 = 330\text{m}\mu$, $\lambda_2 = 282\text{m}\mu$. ^h $\lambda_1 = 278\text{m}\mu$, $\lambda_2 = 225\text{m}\mu$.

aziridine⁹ (IVa), 1-phenylpyrrolidine¹³ (IVc) and 1-phenylpiperidine¹⁴ (IVd) have been described by others. Examination of the spectra of I and IVa-d in isoctane, which are shown in Fig. 1, reveals that (1) the position of the band in the spectrum of IVa corresponding to the "250 m μ " (electron transfer⁷) band of the other amines is shifted about 15 m μ to the blue; (2) the spectra of I and IVb are strikingly similar; (3) the "250 m μ " band of IVc is over 1.5 times as intense as the "250 m μ " band of IVd; and (4) the wave lengths and molar absorptivities of the "290 m μ " bands increase as the imine ring size is varied in the order $3 < 6 < 4 < 5$.

The positions of the λ_{\max} 's of I and IVa-d show that incorporation of the nitrogen atom in a four-, five- or six-membered ring has relatively little effect on the energy of the "250 m μ " transition, but incorporation of the nitrogen in a three-membered ring raises the transition energy by about 7 kcal./mole. Excitation of aniline or an N-alkyl derivative of aniline is expected to result in a migration

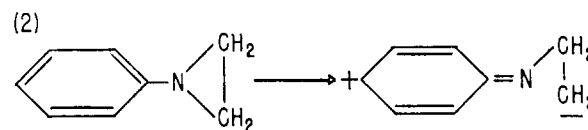
in good yields by cyclization of the O-tosylates of 3-alkylaminopropyls. An adaptation of their method might prove a better source of IVb than the procedure reported here.

of charge from the nitrogen and an increase in the bond order of the aromatic carbon-nitrogen bond as represented by 1.²³ Although the excitation energy



of IVa is considerably larger than that of other tertiary aromatic amines, the spectrum of this compound is sufficiently similar to that of aniline and its various ring-alkylated and N-alkylated derivatives²⁴ to make it appear most probable that the transitions observed in IVa are analogous to those observed in other aromatic amines.

Another explanation for the differences in the spectra of IVa and the other amines studied is that the band at 235 m μ is due to a transition altogether different from that of other aromatic amines. A charge transfer from the phenyl ring to the imine ring (2) seemed plausible and is analogous to the transition proposed by Matsen and co-workers²⁵



to explain the differences in the spectra of cyclopropylbenzene and other alkyl benzenes. However, when the solvent is changed from isoctane to methanol the λ_{\max} is shifted to the blue by 6 m μ . IVa is hydrogen-bonded in methanol,¹¹ and a transition that results in an increase in charge density at a center adjacent to nitrogen should tend to strengthen the hydrogen bond to nitrogen and lower, not raise, the transition energy.

The energy of transition 1 appears to be more sensitive to factors which stabilize the positive charge on nitrogen in the excited state than it is to factors which affect the ease of formation of the carbon-nitrogen double bond. Whereas I, II and III have λ_{\max} 's near 250 m μ which differ by only 3 m μ , λ_{\max} for I exceeds λ_{\max} for aniline by 16 m μ .²⁴ This latter large difference can be attributed to charge stabilization by the two methyl groups. Thus, it follows that the α -methylene group of the three-membered-ring imine is far less able to stabilize a positive charge on nitrogen than the α -methylene group of a larger ring imine.

The contribution to the increase in excitation energy of IVa due to the increase in ring strain caused by the increase in double-bond character of the aromatic carbon-nitrogen bond is difficult to assess, but the small difference in the excitation

(23) See C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, 1963 (1949).

(24) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser and B. M. Wepster, *Rec. trav. chim.*, **77**, 491 (1958).

(25) J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950); W. W. Robertson, J. F. Music and F. A. Matsen, *ibid.*, **72**, 5260 (1950).

energies of I and IVb, in which the increase in ring strain should also be appreciable, indicates that it is not the major factor.

Another possible explanation for part of the increased excitation energy observed for IVa is that the angle α defined by the aromatic carbon-nitrogen bond and the axis of the lone-pair orbital may be larger than the corresponding angle in the other imines. It is to be expected that an increase in α would make interaction between the phenyl ring and nitrogen more difficult and raise the energy of the transition. Unfortunately, α in IVa-IVd, and other amines, is unknown, but if one allows that the value of the H-C-H angle in a cycloalkane²⁶ is a good first approximation to α in a cyclic imine of comparable ring size, then α should be very close to the tetrahedral angle in IVc and IVd, whereas α in IVa should be nearly 118°. The value of α in IVb can be estimated as 112-114° from the reported values of the H-C-H angles in cyclobutane (114 ± 8°)²⁶ and oxetane (112°).²⁷ The slight increase in excitation energy observed for IVb as compared with IVc and IVd then could be due to a slightly greater value of α .

With the possible (but unlikely) exception of IVa, there is no doubt that the transition leading to the "250 m μ " band of these amines is similar to that assigned to this band in *ortho*-substituted dimethylanilines, for which an approximately linear relationship between oscillator strength and phenyl ring-nitrogen resonance has been observed. Thus, it may be concluded that the resonance energy due to interaction between nitrogen and the phenyl ring increases in the same order as the oscillator strengths of the "250 m μ " band, namely IVa < IVd < I \approx IVb < IVc.

It is striking that the resonance interaction in IVb is comparable to that in I. The configuration about nitrogen in IVb is definitely not trigonal because the nitrogen atom is incorporated in a four-membered ring. The steric interactions between the α - and *ortho*-hydrogens of IVb, which could be reduced if the α -carbons became coplanar with the benzene ring, are expected to be less than the comparable interactions in I. The nitrogen atom of I is therefore much freer to assume the trigonal conformation than the nitrogen atom of IVb. If π - π -conjugation between the phenyl ring and the amine nitrogen were more effective than π - sp^3 -conjugation in lowering the energy of the system, the valency angles about nitrogen in I would be distorted toward 120°, and the resulting difference in the hybridization of nitrogen would surely result in a significant difference in the spectra of the two compounds. Yet, the spectra of I and IVb are remarkably similar. This strongly indicates that the configuration about nitrogen in I, as well as in practically all other aromatic amines, is essentially tetrahedral.

The nitrogen-phenyl ring interaction in IVc is notably greater than that in IVb (and I), which, in turn, is notably greater than the nitrogen-phenyl

ring interaction in IVd. Rotation about the aromatic carbon-nitrogen bond is restricted not only by the variation of the phenyl ring-nitrogen resonance with ϕ but also by the steric interaction between the α - and *ortho*-hydrogens. These steric interactions are more important in IVc and IVd than in the other compounds studied. Inspection of molecular models of IVc and IVd in which the configurations about nitrogen are tetrahedral indicates that the α -*ortho*-interactions in IVc are less when $\phi = 0^\circ$ than when $\phi = 20^\circ$. Thus, the average value of ϕ (ϕ_a) for IVd should be greater than ϕ_a for IVc and the average value for the resonance energy due to phenyl-ring nitrogen interaction should be greater for IVc than for IVd.²³

The exaltation of molar refraction, ΔR_D and base strength have been used as qualitative measures of resonance energy.^{4,6b} The ΔR_D of a series of aromatic amines has been observed to increase with increasing phenyl ring-nitrogen resonance.⁴ Inhibition of resonance lowers the stability of an aromatic amine relative to its conjugate acid and, all other factors being equal, results in an increase in the base strength.²⁹ In Table II, we see that the ΔR_D 's due to phenyl ring-nitrogen resonance increase in the order IVa < IVd < I < IVb \leq IVc, and the base strengths decrease in the order IVd < I < IVb < IVc.³⁰ These orders are in good agreement with the order of increasing oscillator strengths.

TABLE II

MOLAR REFRACTIONS AND APPARENT pK_A 'S IN 50% AQUEOUS ETHANOL OF N,N-DIMETHYLANILINE AND N-PHENYL-SUBSTITUTED CYCLIC IMINES AT 25°

| Compound | R_D , calcd. ^a | R_D , expt. | ΔR_D | pK_A |
|---------------------------|--------------------------------|--------------------|--------------|-------------------|
| N,N-Dimethylaniline (I) | 39.40 | 40.89 ^c | 1.49 | 4.39 ^e |
| 1-Phenylaziridine (IVa) | 37.39 ^b | 37.82 | 0.43 | ... |
| 1-Phenylazetidine (IVb) | 42.04 ^b | 43.64 | 1.60 | 4.08 |
| 1-Phenylpyrrolidine (IVc) | 46.69 | 48.33 ^d | 1.64 | 3.45 |
| 1-Phenylpiperidine (IVd) | 51.34 | 52.30 | 0.96 | 5.22 ^f |

^a Calculated assuming no phenyl ring-nitrogen resonance and using the group constants given by A. I. Vogel, "Practical Organic Chemistry," 3rd Edition, Longmans, Green and Co., New York, N. Y., 1956, p. 1035. ^b No exaltation of molar refraction was observed for a number of N-alkylaziridines and N-alkylazetidines (unpublished results of A. T. Bottini, R. L. Van Etten and C. P. Nash). ^c Lit.¹⁹ R_D 40.81 at 20°. ^d Lit.¹³ R_D 48.17 at 20°. ^e Ref. 24. ^f Ref. 20.

It is noteworthy that the oscillator strength and wave length of the local excitation band⁷ (ca. 290 m μ) also increase with increasing phenyl ring-nitrogen resonance.

Spectra were taken of I and IVa-IVd in acetonitrile and methanol as well as in isoöctane. The λ_{max} , A_{max} (molar absorptivity) and oscillator strength of the bands in the various spectra are given in Table I.

In acetonitrile, a highly polar but non-hydrogen bonding solvent having refractive index and dielec-

(28) L. H. Klemm, H. Ziffer, J. W. Sprague and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955).

(29) For a pertinent discussion of factors that complicate interpretation of the base strength of an aromatic amine as a function of phenyl ring-nitrogen resonance, see ref. 4.

(30) Experiments based on the thermochromic method of S. Soloway and P. Roscn, *Science*, **121**, 99 (1955), indicate that the base strength of IVa is comparable with that of IVd.

(26) Bond angles in cycloalkanes are included in the compilation in G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 695-799.

(27) J. Fernandez, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **23**, 758 (1955).

tric constant close to those of methanol, we observe a slight red shift of the bands of I and IVa-IVd. If the "250 $m\mu$ " band arises from the electron-transfer transition (1),⁷ the observed red shift in the polar solvent is in accord with the predictions by Bayliss and McRae.³¹ The enhancement of the dipole moment accompanying excitation leads to a greater solvent-stabilization of the excited state than the ground state and hence to a shift of the "250 $m\mu$ " band to longer wave lengths.

Although the A_{\max} 's are slightly diminished by transfer from the hydrocarbon to the polar solvent, the oscillator strengths are unchanged. The first implication is that the spectra have become more diffuse, again in agreement with Bayliss and McRae.³¹ Further, it suggests that there are no specific interactions between solute and solvent which would decrease the resonance stabilization of the ground state and hence the oscillator strength of the electron-transfer band.

In methanol, the bands of I and IVc are shifted slightly to the red, though the shift is not as pronounced as in acetonitrile. The bands of IVb and IVd are shifted slightly to the blue, and the bands of IVa are shifted substantially to the blue. With the exception of the bands of IVc, the oscillator strengths also are diminished.

The experiments in acetonitrile presumably measure the spectral effects to be attributed to generalized polar solvation of these amines. The fact that all the bands in methanol are shifted to the blue relative to their positions in acetonitrile may be interpreted on the basis of hydrogen bonding to the lone pair on nitrogen. Pimentel³² has discussed the effects of hydrogen bonding on electronic spectra and has predicted a blue shift of bands of I in "acidic" solvents. In this connection

(31) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(32) G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).

it may be noted that Bayliss and McRae³¹ have evidently misinterpreted the spectral results of Ungnade,³³ who found a progressive blue shift of the bands of dimethylaniline in the solvent-order cyclohexane, ethanol, water.

If, as Bayliss and McRae³¹ assert, refractive index dependent polarization shifts are the only ones to be expected for I, the peaks should shift to the blue in the solvent-order isoöctane, acetonitrile, methanol. In addition, the maxima in methanol (251 $m\mu$) and water (244 $m\mu$)³³ should coincide. The experimental facts are quite different. The actual blue shift solvent-order can be rationalized, however, on the basis of dipole-dipole interactions, with hydrogen bonding stabilization of the ground state superimposed in the cases of methanol and water.

Two other points deserve comment. The order of increasing blue shift in methanol (relative to acetonitrile) is the same as the order of increasing base strength. Evidently the differences in the base strengths of these amines are smaller in the excited states than in the ground states. Also, the oscillator strengths of the bands of all the compounds except IVc are decreased in methanol. Since hydrogen bonding to the nitrogen doubtless decreases its resonance interaction with the aromatic ring, a decreased intensity is to be expected. The anomaly of IVc may be rationalized on the grounds of relative basicities. Since IVc is the weakest base of all, the specific hydrogen bonding effects might be expected to be proportionately less important; purely polar effects might indeed dominate, and we already have shown that polar effects do not diminish the spectral intensities.

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(33) H. E. Ungnade, *ibid.*, **75**, 432 (1953).

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LCAO MO Theory of an Organic Biradical with a Probable Triplet Ground State^{1a}

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The triphenylmethyl derivative biradical recently prepared by Yang and Castro^{1c} is predicted by LCAO MO calculations to have a triplet ground state. Preliminary measurements of the paramagnetic susceptibility (3.1×10^{-3} cm.³/mole) and the observation, following the theoretical prediction, of a long wave length absorption peak (beyond 1μ) seem to support this conclusion.

Introduction

Yang and Castro^{1c} recently reported the synthesis of a molecule whose structure is shown in Fig. 1. A number of classical resonance structures may be written for this molecule, but, neglecting ionic structures, there are always at least two carbon or oxygen atoms which must have a de-

fiency of valence bonds. Potentially interesting properties are suggested for this molecule as a result of this deficiency. In this paper we detail a number of these properties and give the results of our approximate theoretical calculations in comparison with some recently obtained experimental results.

Longuet-Higgins² has given a proof based on LCAO MO theory for alternant hydrocarbons which states that a molecule will have at least as

(1) (a) This work was partially supported by the AF Office of Scientific Research of the Air Research and Development Command under contract No. AF49(638)-923. (b) Laboratory of Molecular Structure and Spectra. (c) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

(2) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).