

References and Notes

- (1) Postdoctoral Research Associate on Grant No. GM 10937 from the National Institutes of Health.
- (2) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 3166 (1961).
- (3) Unpublished research with T. Munekata.
- (4) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).
- (5) K. R. Varma and E. Caspi, *Tetrahedron*, **24**, 6365 (1968).
- (6) H. C. Brown and N. M. Yoon, *Isr. J. Chem.*, in press.
- (7) H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).
- (8) Produced by Aldrich Boranes, Inc., a subsidiary of Aldrich Chemical Co., Inc., Milwaukee, Wis.
- (9) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).
- (10) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962).
- (11) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 1071 (1964).
- (12) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).
- (13) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses, via Boranes", Wiley-Interscience, New York, N.Y., 1975.
- (14) Based on highest rotation of $[\alpha]_D^{+51.1^\circ}$ for (+)- α -pinene reported by F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1031 (1931).

Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy.
Natural-Abundance Nitrogen-15 Chemical Shifts of
Ring-Methylated *N,N*-Dimethylanilines. Effect of
Inhibition of Conjugation

Mukund P. Sibi and Robert L. Lichter*

*Department of Chemistry, Hunter College of the City University of New York,
 New York, New York 10021*

Received February 3, 1977

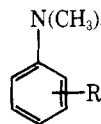
The ¹⁵N chemical shifts of *N*-methylaniline, *N,N*-dimethylaniline, several ring-alkylated *N,N*-dimethylanilines, and their conjugate acids have been measured at the natural abundance level. Relative to aniline, *N*-methylation induces upfield shifts, in contrast to the downfield shifts expected on α -substitution. The influence of ring methyl substitution on the resonance position of dimethylaniline is the same as that reported for aniline, except for ortho substitution. Under these conditions, considerably larger upfield shifts are exhibited. In contrast, the chemical shifts of the conjugate acids of the dimethylanilines all lie within a 2-ppm range. The large diamagnetic shifts induced by ortho methyl substitution are attributed to the torsional distortion of the dimethylamino group from the optimum conformation for nitrogen lone-pair localization. The results correlate with appropriate aniline ¹³C chemical shifts and, especially, with the ionization potentials of the corresponding aniline π orbitals, which are a measure of nitrogen lone-pair π delocalization. The diamagnetic α effects also may be rationalized by this means. The nitrogen shifts of 2,6-diethyl- and 2,6-diisopropyl-*N,N*-dimethylaniline have been used to estimate torsional angles of 77 and 80°, respectively.

Correlations between the behavior of substituted anilines and extent of nitrogen lone-pair delocalization have been explored by investigation of myriad physical and chemical properties. The several relationships between nuclear magnetic resonance (NMR) properties and various functions of electron distribution make NMR spectroscopy eminently suitable for this type of study. Particularly when the NMR behavior of the nitrogen nucleus itself is affected, nitrogen NMR spectroscopy has been a useful probe of these phenomena. The first studies exploiting this possibility using substituted ¹⁵N-enriched anilines,¹ as well as prior work with ¹⁴N NMR,² demonstrated the direct relationship between nitrogen resonance positions and substituent conjugative electronic properties. Subsequently, the nonconjugative methyl group was shown also to influence aniline nitrogen chemical shifts³ in a systematic, additive manner which could be related to polarization in the σ framework.⁴ Because nitrogen lone-pair delocalization is possible with both types of substituents, it is of interest to determine the behavior of the nitrogen resonances when delocalization is in fact inhibited. Several lines of evidence⁵⁻⁹ indicate that this is the case with ortho-methyl-substituted *N,N*-dimethylanilines. Consequently, we have determined the natural-abundance ¹⁵N chemical shifts of a selected group of these compounds, represented in 1a-5, in order to assess the influence of sterically inhibited conjugation on the resonance positions.

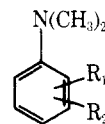
Experimental Section

Compounds 1-5 were either commercially available or were prepared by methylation of the primary amine with trimethyl phos-

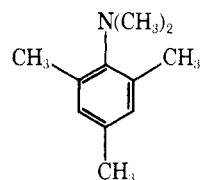
phate.¹⁰ Infrared and ¹H NMR spectra were consistent with the structures, and boiling points agreed with reported values.¹¹



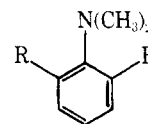
- 1a, R = H
 b, R = 2-CH₃
 c, R = 3-CH₃
 d, R = 4-CH₃



- 2a, R₁ = 2-CH₃; R₂ = 3-CH₃
 b, R₁ = 2-CH₃; R₂ = 6-CH₃



3



- 4, R = C₂H₅
 5, R = *i*-C₃H₇

Spectra were determined on a JEOL PS/PFT-100 spectrometer as described elsewhere.¹² Initially, the free bases were run using 10-15% deuteriobenzene as internal lock in solution, and were referenced to an external capillary of 2.9 M enriched ammonium chloride in 1 M HCl. Subsequently, we noted that the resonance positions were somewhat solvent sensitive. For example, the resonance position of 1a as a pure liquid (see below) differs by 1.5 ppm from that arising from a 25 vol % solution in cyclohexane. On the other hand, 3 remains unaffected upon dilution of the pure liquid to 25% in cyclohexane, yet moves 4 ppm downfield when 15% deuteriobenzene is used as internal

Table I. Nitrogen-15 Chemical Shifts of *N,N*-Dimethylanilines^a

Registry no.		δ_N^b	$\Delta\delta_N^c$	$\Delta\delta_N'^d$	$\delta_{NH+}^{b,e}$	$\Delta\delta_{NH+}^f$	pK_a^g	$IP_{\pi_4}^h$	$IP_{\pi_2}^h$
62-53-3	Aniline	31.5 ⁱ	0	11.9	26.1	-5.4	4.26	8.05	10.81
100-61-8	<i>N</i> -Methylaniline	27.8	-3.7	8.2	19.6	-8.2	4.29	7.65	10.20
121-69-7	1a	19.6	-11.9	0	22.6	3.0	4.39	7.37	9.80
609-72-3	1b	8.9 (-20.3) ^k	-22.6	-10.7	21.1	12.2	5.15	7.92	9.51
121-72-2	1c	18.7 (-12.0)	-12.8	-0.9	22.6	3.9	4.66	7.24	9.61
99-97-8	1d	17.0 (-12.0)	-14.5	-2.6	21.7	4.7	4.94	7.27	9.55
24226-35-5	2a	8.4 (-19.5)	-23.1	-11.2	20.8	12.4	5.25		
769-06-2	2b	-7.9 (-33.9)	-39.4	-27.5	21.4	29.3	4.81	7.85	8.85
13021-15-3	3	-9.6 (-32.2) ^l	-41.1	-29.2	20.7	30.3	5.15 ^m		
2909-78-6	4	-11.9 (-35.1) ⁿ	-43.4	-31.5	20.8	32.7			
2909-77-5	5	-14.6 (-37.0) ⁿ	-46.1	-34.2	19.2	33.8			

^a Chemical shifts and differences in parts per million. ^b With respect to ¹⁵NH₄Cl; see Experimental Section. Positive values denote downfield shifts. ^c $\Delta\delta_N = \delta_i - \delta_{aniline}$. ^d $\Delta\delta'_N = \delta_i - \delta_{1a}$. ^e Chemical shifts of anilinium ions. ^f $\Delta\delta_{NH+} = \delta_{ion} - \delta_{amine}$ = change in chemical shift on protonation. ^g Reference 6b, in 50% ethanol. ^h Vertical ionization potentials (eV), ref 9a,c. ⁱ Reference 4a. ^j Reference 4b. ^k Parenthesized values are differences between the substituted *N,N*-dimethylanilines and the corresponding anilines, ref 3. ^l $\delta_{mesidine}$ = 22.6 ppm. ^m Reference 13. ⁿ The chemical shifts of 2,6-diethyl- and 2,6-diisopropylaniline are 23.2 and 22.4 ppm, respectively.

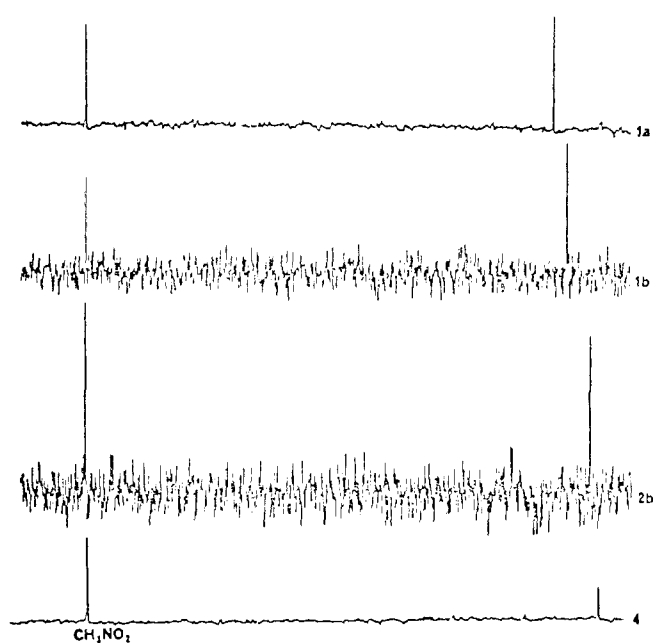


Figure 1. Natural-abundance ¹⁵N spectra of *N,N*-dimethylanilines. The spectra were obtained at 1-s repetition rates for total accumulations ranging from 8800 (**1b**) to 61 800 (**1a**). The numbers on the spectra correspond to compound numbers in Table I.

lock. Hence, to circumvent this uncertainty, all free bases were run as pure liquids containing 10–20 mg of chromium tris(acetylacetonate) to shorten T_1 values, and a reference signal was derived from a concentric capillary of ca. 20% enriched nitromethane in deuteriobenzene, which provided the field frequency lock. Under these conditions the resonance of 2.9 M ammonium chloride lies 351.85 ppm to higher field. The experimental measurement uncertainty is estimated to be ± 0.2 ppm or better.

The amine trifluoroacetates were prepared by dissolving the amines in 2 equiv of trifluoroacetic acid in deuteriobenzene. Final concentrations were 1–2 M, but the effect of concentration on the resonance positions was not determined.

Results and Discussion

The chemical shifts of 1–5 and their protonated forms are given in Table I, which also includes literature values for the pK_a s of some of the bases^{6,13} and photoelectron vertical ionization potentials.^{9a,c} Table I also includes various chemical shift differences which will be useful in the ensuing discussion.

Several trends may be noted at the outset. First, successive

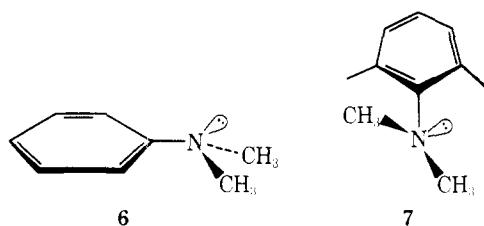
methylation at nitrogen (aniline \rightarrow *N*-methylaniline \rightarrow **1a**) displaces the nitrogen resonance positions *upfield* by 5.3 and 11.9 ppm, respectively. While the direction of the change persists in going from anilinium to *N*-methylanilinium ion, protonated **1a** reverses the pattern. These changes stand in marked contrast to the effects of α -substitution on the ¹³C chemical shifts of structurally analogous alkylbenzenes, where downfield shifts of ~ 9 ppm arise.¹⁴ Similarly, α -substitution of aliphatic amines is reported to deshield nitrogen nuclei, although the magnitude of the shift (~ 9 ppm) was derived by multiple regression analysis of primary amine data rather than by direct measurements.¹⁵ Isolated examples of upfield α effects have been reported. Thus, the nitrogen resonance of 1,1,3,3-tetramethylurea lies 14.2 ppm upfield from that of urea,^{15b} and the resonances of several *N*-methyldecahydroquinolines lie ~ 5 ppm upfield of those of the unsubstituted compounds.¹⁶ In a related manner, the nitrogen chemical shift of *N*-methylpiperidine is only 0.3 ppm downfield from that of piperidine. Similarly, an upfield shift on methylation of an aminoglycoside was reported very recently.¹⁷ Because of the disparate nature and paucity of examples, a general rationalization of this behavior is not apparent.

Second, as in the anilines, ring methyl substitution of *N,N*-dimethylaniline shifts the nitrogen resonances to higher fields. Indeed, the effect of 3- and 4-methyl substitution (**1c** and **1d**, respectively) compares with that found in the anilines.³ However, 2-methyl substitution (**1b** and **2a**) induces an additional 7–8 ppm change over that found in **1c** and **1d**. This is apparent from the parenthesized values in column 2 of Table I, which are expected to partially correct for effects of the methyl group common to both the anilines and the *N,N*-dimethylanilines. Further substitution at the ortho position (**2b** and **3**) augments the change. Thus, the nitrogen shift of **2b**, 34 ppm higher than that of 2,6-xylylidine, is almost 40 ppm higher field than that of aniline itself, lying in a range characteristic of aliphatic amines.¹⁵ As demonstrated by **4** and **5**, the upfield displacement is enhanced by increasing the size of the 2,6-dialkyl groups. These trends may be discerned easily in Figure 1.

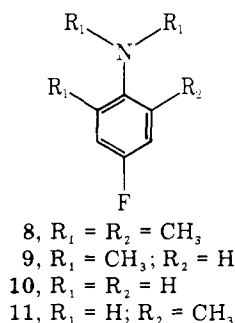
Third, while changes of the aniline nitrogen positions on protonation are consistently upfield,^{4b} those displayed by 1–5 are all downfield. Indeed, with the exception of **5**, the chemical shifts of the ions in this series differ by amounts, just outside experimental error, averaging 21.5 ppm with a standard deviation of 0.8 ppm. While effects of solvent, concentration, and nature of the anion are likely to influence the shifts of the cations,¹⁸ nonetheless the relative constancy of the values probably reflects structural factors to a large extent. It is in-

interesting that, with the exception of **2b**, all the resonances lie at higher field than those of the corresponding primary anilinium ions.^{4b} This appears to be another example of an upfield α effect, although the absence of detailed concentration studies makes such an observation speculative. The resonance positions of the first three cations in Table I (column 5) do not parallel those of the carbons of the isoelectronic toluene, ethylbenzene, and cumene, respectively.¹⁴

The upfield displacements induced by ortho alkyl substitution are most readily interpreted in terms of the well-established distortion of the dimethylamino group from the optimum conformation (**6**) for nitrogen lone-pair interaction with the benzene π system. In this case, the pyramidal nitrogen is still oriented such that the axis of the lone-pair orbital makes a dihedral angle of 90° with respect to the plane of the



ring. Distortions from this geometry have been correlated with changes in basicity,^{5,6} UV absorption intensities,⁶ pK_a s of substituted benzoic acids,⁸ chemical shifts of ¹³C^{7a} and ¹⁹F,^{7b} and changes in ¹³C-H coupling constants.²⁰ Thus, the increased basicity of **1b**, **2a**, and **3** relative to **1a**, **1c**, and **1d**, is attributable *in part* to greater localization of electron density at nitrogen in a twisted conformation (**7**). Similarly the lower field ¹⁹F shift of **8** relative to that of **9** is attributable to reduced nitrogen delocalization, hence greater fluorine delocalization in the former, so that the fluorine is deshielded.^{7b} Qualitatively, the change in the ¹⁹F chemical shifts in the series **8**–**11**



parallels that displayed by **2b**, **1a**, aniline, and 2,6-xylidine, respectively, but there is no direct correlation. Similarly, if the ¹⁹F and ¹⁵N chemical shift differences between corresponding nonmethylated and dimethylanilines are compared, a qualitative but not quantitative parallelism exists. The absence of a direct correlation probably reflects the different degrees to which inductive and mesomeric effects contribute to the shifts in the disubstituted compounds compared to the monosubstituted.^{7b}

A more fruitful comparison arises with the ¹³C shifts of the anilines.^{7a} To the extent that the same factors influence both sets of resonances, the differences between δ_{C4} of the dialkyl-*N,N*-dimethylanilines relative to the primary anilines are expected to reflect largely the electronic effect of the nitrogen. Hence literature values^{7a} for the carbon shifts of the series, supplemented by new measurements for **2b**, **4**, and **5**, were plotted against the nitrogen shifts (Figure 2). The scatter exhibited by these points may arise from two sources. First, steric and electronic factors are likely to influence the nitrogen shifts in the less hindered primary amines to a different extent than in the tertiary compounds, and this difference may be

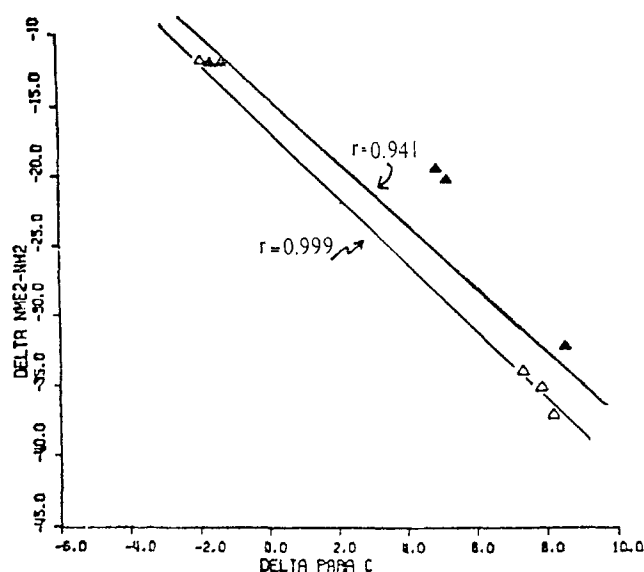


Figure 2. Plot of nitrogen shifts of dialkylanilines vs. carbon shifts of C₄. The upper line represents the least-squares correlation of all points, while the lower line (open triangles) represents the correlation within the 2,6-dialkyl-substituted series **1a**, **2b**, **4**, and **5**.

compensated only partially by taking the chemical shift differences (parenthesized values in column 2, Table I). Second, the positional influence of the ring alkyl substituents on the ¹³C and ¹⁵N resonances is likely to be different. Thus, in **2a**, the methyl group at C-3 is ortho to C-4, but meta to C-1, which bears the amino group; nothing requires that the responses of the two positionally different nuclei to the same substituent parallel each other exactly. Given these several possibilities, the moderate correlation displayed in Figure 2 ($r = 0.941$, slope = -2.3 ppm N/ppm C) is encouraging. To limit the number of variables influencing the shifts, the series **1a**, **2b**, **4**, and **5** may be examined, where only the nature of the alkyl substituents at C-2 and C-6 is changed. Here, electronic perturbations at C-4 and the nitrogen are expected to vary little throughout the series, and the correlation, admittedly with a smaller number of points, is much improved ($r = 0.999$, slope = -2.4 ppm N/ppm C). Hence it is reasonable to suggest that both the nitrogen and the C-4 resonance positions are primarily influenced by common factors, of which the torsional distortion of the dimethylamino group is likely to be dominant.^{21,22}

That the nitrogen resonance positions move upfield as delocalization is inhibited is consistent with an increase in electron density as well as a decrease in the C₁-N π bond character. Within the qualitative Karplus-Pople treatment of chemical shifts an increase in the latter parameter is expected to increase the paramagnetic part of the chemical shift and deshield the nitrogen.²³ An approach of this type has been used to rationalize the nitrogen shifts of conjugatively substituted anilines.¹⁻³ A measure of the validity of this argument may be obtained by examination of vertical ionization potentials of the anilines, obtained from photoelectron spectroscopy.⁹ Delocalization of the nitrogen lone pair results in splitting of one of the degenerate highest occupied molecular orbitals (HOMO) of benzene with the correct symmetry (b_1). The other is shifted only slightly, presumably because of an inductive effect. These interactions are indicated schematically in Figure 3. Calculations²⁴ indicate that the first and third ionization bands, labeled π_4 and π_2 , respectively,^{9a} may be assigned to those arising by interaction with the nitrogen lone pair; furthermore, from overlap populations²⁴ π_2 has a considerably higher degree of lone-pair character. Hence the difference between the π_4 and π_2 ionization potentials, ΔIP ,

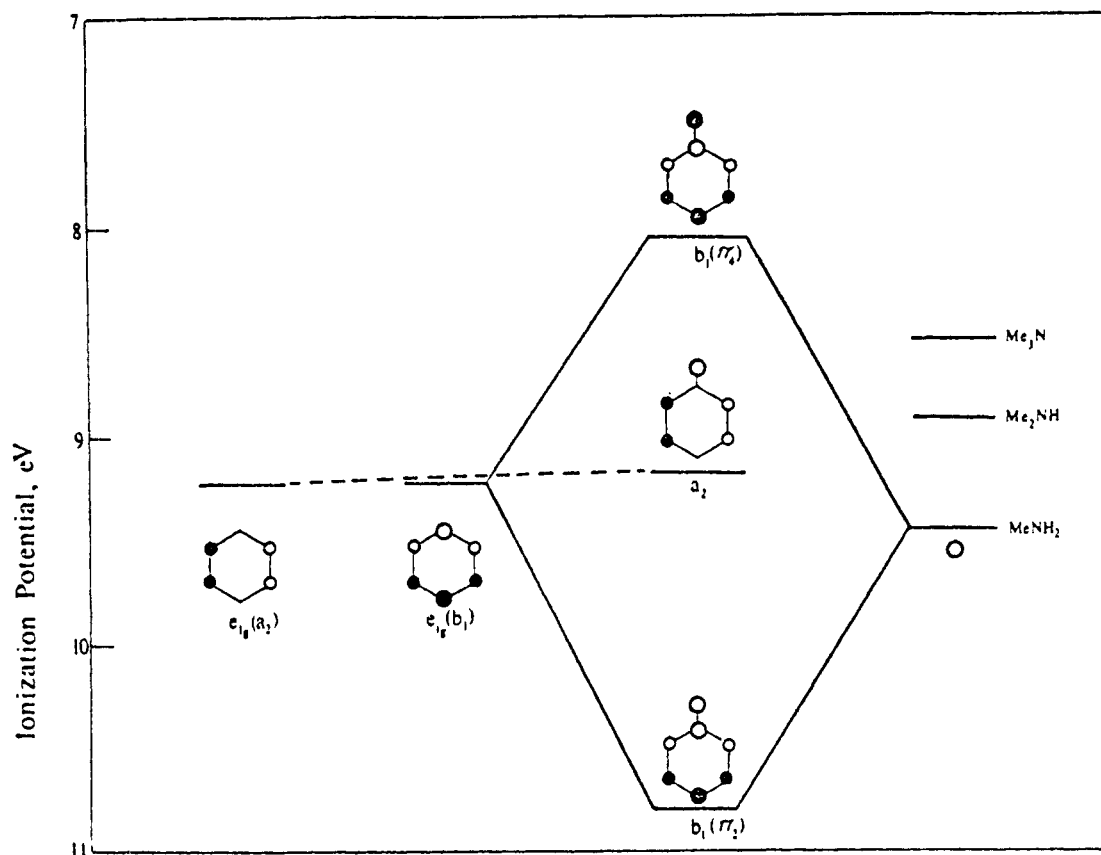


Figure 3. Schematic representation of the interaction between the 2p orbital of an amine nitrogen and the HOMOs of benzene.

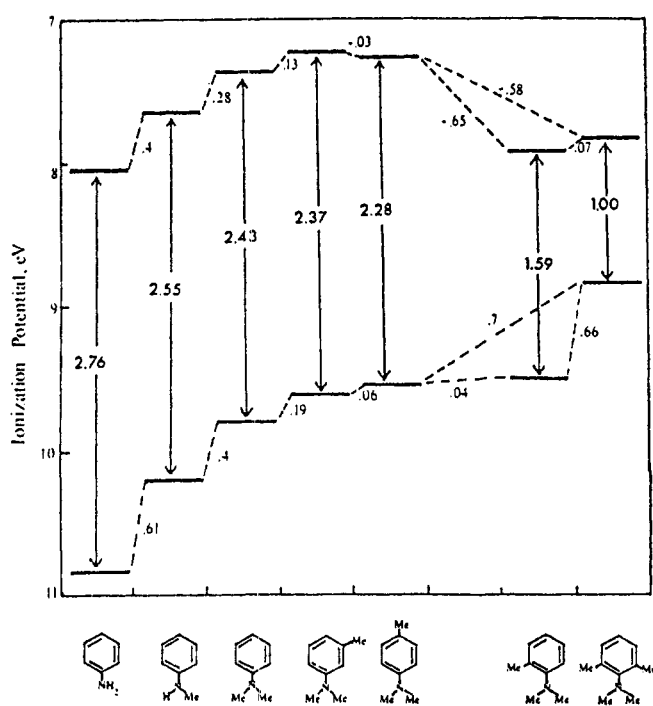


Figure 4. Schematic representation of the benzene orbital splitting by an amino group, obtained from photoelectron spectroscopy (ref 9c).

reflects the extent of lone-pair delocalization; this is represented in Figure 4, where it is apparent that both ionization bands undergo similar changes in all compounds which do not bear ortho methyl groups. Indeed, the changes are comparable to those displayed in the series ammonia \rightarrow methylamine \rightarrow dimethylamine. On the other hand, substitution in the ortho

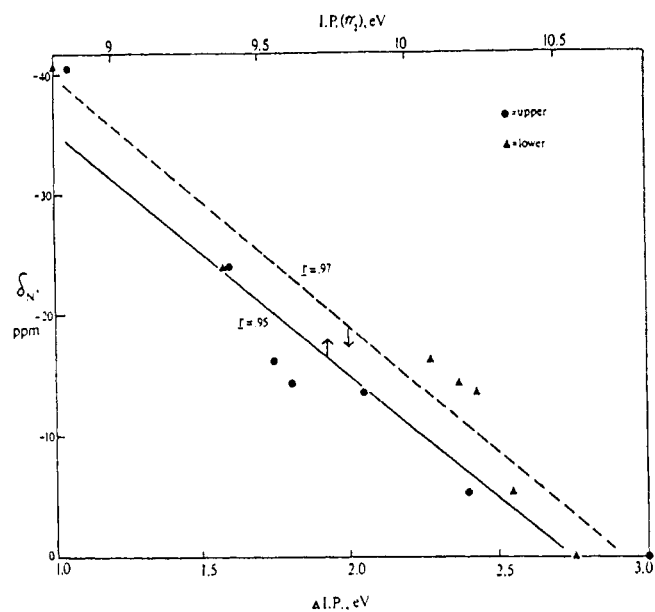


Figure 5. Plot of nitrogen chemical shifts of dimethylanilines vs. photoelectron ionization potentials and differences. The upper scale represents the π_2 ionization potential, while the lower gives the difference between the π_2 and π_4 ionization potentials.

position decreases $\Delta I.P.$ progressively, and a plot of δ_N vs. $\Delta I.P.$ yields a straight line with a least-squares correlation coefficient of 0.97 and a slope of 20.6 ppm/eV (Figure 5, lower scale, dotted line). Similarly, δ_N correlates⁹ moderately well with the π_2 ionization potential, correlation coefficient = 0.95, slope = 20.2 ppm/eV.²⁵ While the correlations displayed in Figure 5 suggest that both the $\Delta I.P.$ s and the nitrogen shifts reflect the same changes in nitrogen lone-pair delocalization, it may not be immediately apparent why the correlation should be nearly

linear. This derives, however, from the relationship between the nitrogen 2p- π interaction and the C=N π bond order, whose role in influencing the nitrogen shifts was summarized above. Hence, preponderance of these factors may account for the high linearity exhibited.

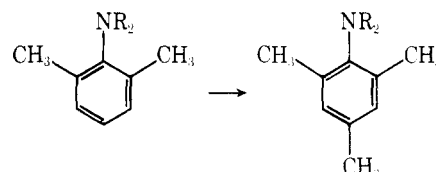
The progression of IPs also rationalizes the upfield shifts in the series aniline \rightarrow **1a**. Evidently, increasing methyl substitution reduces lone pair interaction with the ring. The influence is larger on π_2 , which has the higher lone pair character. This may reflect an increase in the energy difference between the hypothetical nitrogen lone pair and the benzene b_1 orbitals as a function of methyl substitution. The change in δ_N parallels both Δ IP as well as the IP of π_2 . It is likely that an effect of this type may also account for the nitrogen chemical shift difference between urea and tetramethylurea, cited above. It should also be noted that the change in Δ IP displayed by **1b** reflects a much larger change in π_4 ; only with the second methyl substitution is π_2 affected. Possibly, more extensive geometrical changes arise in the dimethylamino group itself in **2b** than in **1b**.

The decrease in Δ IP has been correlated with the torsional angle about the C₁-N bond, with values (55 and 69° for **1b** and **2b**, respectively) in good agreement with those estimated from UV data^{6b} and from p*K*_a values of substituted benzoic acids.⁸ Changes in photoelectron ionization potentials have been applied to geometrical studies of nitrobenzenes,^{9c} phenols,^{9a} anisoles,^{9c} and disulfides.²⁶ In all cases the splitting between orbitals of appropriate symmetry is reduced when the geometry is perturbed from that which optimizes orbital overlap. Because the ionization potentials have been related to the cosine of the dimethylamino torsional angle,^{9a,b} it is possible to use the chemical shifts to estimate these angles for other related compounds. Indeed, values of δ_N (Table I) for **1a**, **1b**, and **2b** correlate ($r = 0.95$) with $\cos \theta$, giving a slope of -0.022 ppm^{-1} and an intercept of 0.929. Applying these results to δ_N of **4** and **5**, values of 77 and 80° for the torsional angles are obtained. If the parenthesized δ_N values (column 2 of Table I) are used instead, in order to partially compensate for steric interactions in the primary amines themselves, values of 74 and 77° are obtained for **4** and **5**, respectively. Since the experimental θ values for **1a**, **1b**, and **2b** are estimated to have an uncertainty of $\pm 5^\circ$, both sets of calculated torsional angles are in reasonable agreement with each other. It should be noted that geometrical changes other than in the torsional angle may be anticipated. The C-N-C bond angles are particularly susceptible to sterically induced distortion, and this would be expected to influence the shifts. However, the correlation of the nitrogen shifts with other data which are interpretable in terms of torsional angle distortion makes this structural factor highly likely to exert the major influence. Clearly, further studies on the effects of changes in bond angles on the nitrogen shifts would be welcome.

The other points deserve additional comment. In general, to the extent that the lone pair exerts a major paramagnetic influence on nitrogen resonance positions, its removal by protonation is expected to result in an upfield displacement of the nitrogen resonance position. This may be seen in the protonation-induced changes of pyridine (-110 ppm) and azobenzene (-150 ppm).²⁷ Thus the -5.4-ppm change exhibited by aniline may be attributed to the compensating influence of removal of the nitrogen lone pair (upfield shift) and generation of a positive charge. The effect of the latter is seen in the 24-ppm downfield shift of the ammonium ion relative to ammonia,²⁷ which has been shown²⁸ to arise from a change in the diamagnetic part of the chemical shift associated with the presence of the positive charge. That *N*-methylaniline also moves to higher field would seem to suggest that its lone pair is comparably delocalized, while the downfield shift exhibited by **1a** suggests that delocalization is partially reduced. The

larger protonation shifts displayed by the remainder of the series are all consistent with successive attenuation of nitrogen lone-pair delocalization. The apparent anomalous behavior of *N*-methylaniline, in view of the correlation with the ionization potential data, must remain without explanation.

Finally, the previously reported substituent effects on the chemical shifts of the anilines themselves¹⁻³ assume that nitrogen lone-pair delocalization is influenced only by the degree of electronic interaction involving the substituent. It is reasonable to expect that these effects will differ if the nitrogen is sterically inhibited from conjugation. The nitrogen shift of **3** relative to **2b** supports this expectation. The 1.7-ppm upfield shift arising in the change **2b** \rightarrow **3** is only half that characterizing the change 2,6-xylylidine \rightarrow mesidine. Preliminary results



$$R = \text{CH}_3; \Delta\delta = -1.7 \text{ ppm}$$

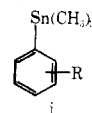
$$R = \text{H}; \Delta\delta = -3.4 \text{ ppm}$$

with 4-substituted 2,6,*N,N*-tetramethylanilines reveal similar differences.²⁹ Further studies are in progress to characterize this behavior.

Acknowledgments. This work was supported by the U.S. Public Health Service, Grant GM-21148 from the Division of General Medical Sciences, by the CUNY Faculty Research Award Program, the Research Corporation, and Eli Lilly and Co. Funds for the spectrometer were provided in part by National Science Foundation Instrument Grant GP-37025.

References and Notes

- (1) T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley, and G. W. A. Milne, *J. Am. Chem. Soc.*, **93**, 6536 (1971).
- (2) P. Hampson, A. Mathias, and R. Whitehead, *J. Chem. Soc. B*, 397 (1971).
- (3) R. L. Lichter and J. D. Roberts, *Org. Magn. Reson.*, **6**, 636 (1974).
- (4) (a) G. Adler and R. L. Lichter, *J. Org. Chem.* **39**, 3547 (1974); (b) L. Psota, M. Franzen-Sievekling, J. Turnier, and R. L. Lichter, *Org. Magn. Reson.*, submitted for publication.
- (5) H. C. Brown and A. Cahn, *J. Am. Chem. Soc.*, **72**, 2939 (1950).
- (6) (a) B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **71**, 1159 (1952); (b) *ibid.*, **76**, 357 (1957); (c) A. J. Hoefnagel, M. A. Hoefnagel, and B. M. Wepster, *J. Am. Chem. Soc.*, **98**, 6194 (1976).
- (7) (a) P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1415 (1963); (b) M. J. S. Dewar and Y. Takeuchi, *J. Am. Chem. Soc.*, **89**, 390 (1967).
- (8) J. P. Schaefer and T. J. Miraglia, *J. Am. Chem. Soc.*, **86**, 64 (1964).
- (9) (a) J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 521 (1973); (b) S. A. Cowling and R. A. W. Johnstone, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 161 (1973); (c) T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **47**, 2563 (1974).
- (10) W. A. Sheppard, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 1085.
- (11) A. W. Hoffmann, *Ber.*, **5**, 704 (1872); (b) C. E. Ingham and G. C. Hampson, *J. Chem. Soc.*, 981 (1939); (c) H. Ley and G. Pfeiffer, *Ber.*, **54**, 363 (1921); (d) M. Fedtke and M. Gernhardt, *J. Prakt. Chem.*, **29**, 259 (1965).
- (12) S. N. Y. Fanso-Free, R. L. Lichter, R. B. Nelson, G. W. Gribble, G. T. Furst, and P. R. Srinivasan, *J. Am. Chem. Soc.*, submitted for publication.
- (13) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).
- (14) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 98.
- (15) (a) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 2495 (1972); (b) J. P. Warren and J. D. Roberts, *J. Phys. Chem.*, **78**, 2507 (1974).
- (16) S. N. Y. Fanso-Free, G. T. Furst, and R. L. Lichter, unpublished results.
- (17) D. E. Dorman, J. W. Paschal, and K. E. Merkel, *J. Am. Chem. Soc.*, **98**, 6885 (1976).
- (18) J. M. Briggs and E. W. Randall, *Mol. Phys.*, **26**, 699 (1973).
- (19) L. V. Vilkov and T. P. Tinasheva, *Dokl. Akad. Nauk SSSR*, **161**, 351 (1965).
- (20) (a) C. H. Yoder, B. A. Kaduk, and R. E. Hess, *Tetrahedron Lett.*, 3711 (1970); (b) C. H. Yoder, F. K. Sheffy, R. Howell, R. E. Hess, L. Pacala, C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Org. Chem.*, **41**, 1511 (1976).
- (21) The nitrogen shifts of **1a**, **1b**, **2b**, and **3** also correlate well ($r = 0.971$) with the ¹¹⁹Sn shifts of substituted phenyltrimethyltin compounds (i): H.-J. Kroth, H. Schumann, H. G. Kuivala, C. D. Schaeffer, Jr., and J. J. Zuckerman, *J.*



- Am. Chem. Soc.*, **97**, 1754 (1975).
- (22) After this work was completed, Westerman and Roberts reported effects of steric inhibition of conjugation on the nitrogen shifts of enamines: P. Westerman and J. D. Roberts, *J. Org. Chem.*, **42**, 2249 (1977). Their trends agree with our observations.
- (23) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
- (24) D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.*, **17**, 90 (1972).
- (25) The correlation coefficient is improved ($r = 0.97$) if aniline is excluded arbitrarily from the data.
- (26) A. D. Baker, M. Brisk, and M. Gellender, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 227 (1974).
- (27) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **51**, 735 (1964).
- (28) W. M. Litchman, *J. Magn. Reson.*, **12**, 182 (1973).
- (29) M. P. Sibi and R. L. Lichter, unpublished results.

Molecular Orbital Theory of the Electronic Structure of Molecules. 36. A Theoretical Study of Several α -Substituted Vinyl Cations^{1a}

Y. Apeloig,^{1b} P. v. R. Schleyer,^{*1c} and J. A. Pople^{1d}

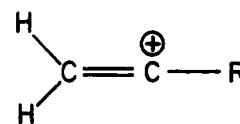
Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and the Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany

Received March 18, 1977

The α -ethynylvinyl (4), α -ethenylvinyl (5), α -cyclopropylvinyl (6), and α -phenylvinyl (7) cations have been investigated by SCF-MO ab initio methods, using both the STO-3G and the 4-31G basis sets. The cations 5, 6, and 7 are more stable in perpendicular conformations (5a, 6a, and 7a, respectively) where the interaction between the "empty" cationic orbital and the HOMO of the substituent is maximized. The calculated rotation barriers around the C⁺-substituent bonds are 22.2, 15.8, and 24.7 kcal/mol for 5, 6, and 7, respectively, approximately half the barrier in the corresponding primary alkyl cations. The efficiency of the α substituent in stabilizing the vinyl cation follows the order $C_6H_5 > c-C_3H_5 \approx HC=CH_2 \gg C\equiv CH \approx CH_3 \gg H$. The ability of the substituents to donate electrons to the empty cationic orbital follows the order $C_6H_5 > CH=CH_2 > C\equiv CH > c-C_3H_5 > CH_3 > H$. No correlation is found between the total charge at the cationic center or the corresponding populations of the formally empty p orbital and the stability of the cation. The cations vinyl (2), α -methylvinyl (3), and 6 have stabilities which are intermediate between those of the corresponding primary and secondary alkyl cations. However, the π -stabilized cations 4, 5, and 7 are of comparable stability to the corresponding primary alkyl cations. Corresponding substituted ethyl cations are 12–17 kcal/mol more stable than the vinyl cations, suggesting that, for the groups examined here, substituent effects are inherently similar for alkenyl and for alkyl cations. The proton affinities of substituted acetylenes and olefins are comparable, with the olefins being 1–5 kcal/mol more basic.

Vinyl cations are by now well-established reaction intermediates in solvolytic reactions.² Despite active research in the field over the last 10 years, very little is known about their inherent stabilities, their structures, or their charge distributions. The use of solvolysis rates to deduce the relative stability of resulting cations is complicated by ground state and solvation effects.² Observation of stable vinyl cations in superacid media has been claimed but not fully substantiated.^{3a,b} Related experimental data in the gas phase are rare, although some heats of formation are known. These are for the parent vinyl cation (2),^{3c} the propenyl cation (3),^{3c-e} and $C_4H_3^+$ and $C_4H_5^+$ cations of unknown structure.^{3b}

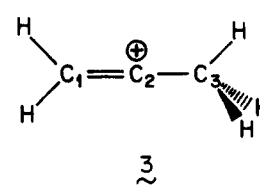
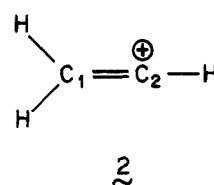
Extensive research has established that ab initio molecular orbital calculations even with minimal basis sets are a powerful, accurate, and inexpensive tool for the study of organic molecules.⁴ Many theoretical studies of carbocations have been made,⁵ but the vinylic cation family has received only little attention, with most of the emphasis devoted to the structure of the parent, 2.^{5a,6} The only other α -substituted vinylic cation which has been investigated in detail by ab initio methods is the 2-propenyl cation 3.^{7a} The energies of several other alkyl-substituted vinyl cations (1, R = Et, *i*-Pr, *t*-Bu) have been reported but not discussed in detail.^{7b} We reported recently a systematic study of α -substituted vinyl cations 1 where R is varied along the whole series of first short period substituents, Li, BeH, BH₂, CH₃, NH₂, OH, and F.⁸ In the present paper we use standard MO-SCF ab initio procedures to study the effect of substituents which are frequently used in solvolysis reactions (i.e., 1, R = ethynyl, vinyl, phenyl, and cyclopropyl).²



- | | |
|------------------------|--------------------------------------------------------------|
| 2, R = H | 5, R = CH=CH ₂ |
| 3, R = CH ₃ | 6, R = <i>c</i> -C ₃ H ₅ (cyclopropyl) |
| 4, R = C≡CH | 7, R = C ₆ H ₅ |

Method, Geometrical Models, and Results

Calculations were carried out at the restricted Hartree-Fock (RHF) level using the ab initio SCF-MO Gaussian 70 series of programs.⁹ The structures were fully or partially optimized using the minimal basis RHF/STO-3G method,^{10a} followed by single-point calculations at the split-valence basis RHF/4-31G level.^{10b} This procedure has been used previously for 2^{6d} and 3.^{7a}



The structure of 4 was fully optimized (Figure 1). In the