2 h. Purification and isolation by the method described above gave 1.411 g (5.95 mmol) of 1,1-diphenyl-3,3-dimethylbutane (89%): mp 33–33.5 °C (lit.[11] mp 33 °C); NMR ($CDCl_3$) δ 7.3 (m, 10 H), 4.1 (t, 1 H), 2.1 (d, 2 H), 0.9 (s, 9 H). Anal. Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.65; H, 9.48.

Synthesis of 1,1,1,2-Tetraphenylethane. The reaction of triphenylmethyllithium (9.0 mmol, in 50 mL of THF) and benzyl fluoride (1.101 g, 10.0 mmol) at 25 °C for 17 min gave 86.3% of 1,1,1,2-tetraphenylethane (2.598 g, 7.77 mmol) having properties identical with those described previously.

Run 2 at −78 °C. Triphenylmethyllithium (4.8 mmol in 20 mL of THF) was stirred with benzyl fluoride (.5286 g, 4.8 mmol) at −78 °C for 2 h. Termination with benzyl chloride (0.7 g, 5.5 mmol), followed by VPC, showed the presence of 72% unreacted benzyl fluoride (0.345 mmol), 1,1,1,2-tetraphenylethane (3.62 mmol, 75.4%), and 12.0% of stilbene (0.289 mmol), together with 3.2% of Ph_3CH (0.152 mmol).

Synthesis of (+)-α-Phenylneopentyl Chloride. (+)-α-Phenylneopentyl alcohol [3.00 g, 0.01827 mol; $[\alpha]^{21}_D$ +30.9° (c 0.03232, acetone)] in 10 mL of CCl_4 was added dropwise during 20 min to thionyl chloride (5.434 g, 0.04570 mol) at −5 °C. CCl_4 and unreacted $SOCl_2$ were distilled in vacuo and (+)-α-phenylneopentyl chloride distilled at 35–36 °C (0.05 mm), yielding 2.495 g (0.01366 mol, 75%) of chloride: $[\alpha]^{21}_D$ +41.1° (c 0.2002, THF); NMR ($CDCl_3$) δ 7.4 (m, 5 H), 4.7 (s, 1 H), 1.0 (s, 9 H).

Reaction of Diphenylmethyllithium with (+)-α-Phenylneopentyl Chloride. (+)-α-Phenylneopentyl chloride [2.000 g, 0.01095 mol; $[\alpha]^{21}_D$ +41.0° (c 0.2000, THF)] in 15 mL of THF was added during 15 min at 25 °C to diphenylmethyllithium (0.01095 mol in 15 mL of THF). This mixture was stirred for 2.5 days, and after workup with aqueous NH_4Cl and ether removal, the residue was triturated with 10 mL of hexane to yield 0.333 g of 1,1,2,2-tetraphenylethane (0.996 mmol, 18.2%). Analysis of the filtrate by VPC (6.0 ft, 10% SE-30/Chrom W, 300/220 °C, 95 mL/min), followed by chromatography over 250 g of alumina using a 95:5 hexane/benzene mixture, gave the results summarized in Table II.

Synthesis of (+)-α-Phenylneopentyl Chlorocarbonate. To a solution of 6.9 g of (R)-(+)-α-phenylneopentyl alcohol (0.0421 mol; $[\alpha]^{21}_D$ +31.1°; 0.0241 g/mL of acetone) in 80 mL of anhydrous ether was added 0.0429 mol of butyllithium in hexane. After stirring overnight at 25 °C, the alkoxide solution was added to a solution of phosgene (9.1 g, 0.091 mol) in 100 mL of dry ether at −60 °C. The mixture was warmed slowly to room temperature, became turbid, and was filtered to separate LiCl. Evaporation of the solvent left 8.8 g of a yellow liquid that was identified as α-phenylneopentyl chlorocarbonate (92% yield): NMR (neat) δ 0.87 (9 H, s), 5.51 (1 H, s), 7.26 (5 H, s); IR $\nu_{C=O}$ 1780 cm^{-1}; $[\alpha]^{21}_D$ +31.6° (0.0474 g/mL, CCl_4). The attempt to distill the crude chlorocarbonate gave a colorless liquid [bp 39–41 °C (0.06 torr) and 47–50 °C (0.2 torr)], which proved to be 46.5% chlorocarbonate and 53.5% (+)-6 by NMR analysis. Warming of this sample of chlorocarbonate at 95 °C completed the decomposition to yield crude (R)-(+)-α-phenylneopentyl chloride (3.7 g, 48%): $[\alpha]^{22}_D$ +67.0° (0.0248 g/mL, THF). The NMR spectrum was identical with that of a racemic sample of α-phenylneopentyl chloride.

Run 2. A comparably sized preparation produced 10.1 g of α-phenylneopentyl chlorocarbonate (90%): $[\alpha]^{20}_D$ +32.3° (0.05965 g/mL, CCl_4). Decomposition by heating in the absence of solvent at 100 °C for 2 h gave 4.7 g of (R)-(+)-α-phenylneopentyl chloride: $[\alpha]^{22}$ +72.0° (0.08943 g/mL, THF); n^{20}_D 1.5130. Anal. Calcd for $C_{11}H_{15}Cl$: C: 72.37; H, 8.28. Found: C, 71.92; H, 8.07.

Acknowledgment. We gratefully acknowledge the support of the City University's Faculty Research Award Program through a PSC-BHE grant (13357).

Registry No. (±)-α-*tert*-Butylphenylacetic acid, 13490-70-5; (−)-α-*tert*-butylphenylacetic acid brucine salt, 71185-51-8; (−)-α-*tert*-butylphenylacetic acid, 13491-16-2; (+)-α-*tert*-butylphenylacetic acid brucine salt, 71185-51-8; (+)-α-*tert*-butylphenylacetic acid, 13490-71-6; (R)-(−)-methyl α-*tert*-butylphenylacetate, 82372-89-2; (R)-(−)-1,1,2-triphenyl-3,3-dimethylbutanol, 82323-53-3; bromobenzene, 108-86-1; (S)-(−)-1,1,2-triphenyl-3,3-dimethylbutanol, 82323-54-4; (±)-1,1,2-triphenyl-3,3-dimethylbutanol, 82372-90-5; (±)-α-phenylneopentyl chloride, 82323-55-5; benzophenone, 119-61-9; 1,1,1-triphenyl-3,3-dimethylbutane, 24523-61-3; neopentyl iodide, 15501-33-4; triphenylmethyllithium, 733-90-4; triphenylethane, 5271-39-6; 1,1-diphenyl-3,3-dimethylbutane, 57123-34-9; diphenylmethyllithium, 881-42-5; neopentyl bromide, 630-17-1; 1,1,1,2-tetraphenylethane, 2294-94-2; benzyl fluoride, 350-50-5; (+)-α-phenylneopentyl chloride, 82323-56-6; (+)-α-phenylneopentyl alcohol, 23439-91-0; (+)-α-phenylneopentyl chlorocarbonate, 82323-57-7; *meso*-$(CH_3)_3CCH(Ph)CH(Ph)C(CH_3)_3$, 62678-51-7; $PhCH(CMe_3)$-$CH(CMe_3)Ph$, 27561-34-8; $PhCH(CMe_3)CHPh_2$, 82323-58-8; Ph_2CH_2, 101-81-5.

Nitrogen-15 Nuclear Magnetic Resonance and Photoelectron Spectroscopy of Substituted *N*-Phenylaziridines†

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^{15}N chemical shifts of ten *N*-arylaziridines were measured at the isotopic natural-abundance level. The values correlate well with ^{15}N and ^{17}O shifts in anilines and anisoles. The range of chemical shifts is consistent with decreased interaction between the lone pair and the benzene ring relative to anilines. Dual-substituent-parameter analysis of the shifts revealed a surprisingly high apparent resonance dependence. The steric effect of 2,6-dimethyl substitution on the ^{15}N resonance line positions was found to be much smaller than in dimethylanilines. Vertical ionization potentials for the three highest occupied orbitals were determined from photoelectron spectra. Attempts to correlate ionization potentials of lone-pair-like orbitals with ^{15}N shifts were unsuccessful; at best, a general trend exists between δ_N and only one of the ionization potentials. The lack of correlation was attributed to direct interactions between the lone-pair-like orbitals and the orbitals of the substituents that are not reflected in the nitrogen shifts.

The chemistry and bonding of small-ring organic molecules are of considerable interest to organic chemists. Numerous spectroscopic methods have been applied in this area, and nuclear magnetic resonance (NMR) spectroscopy has played an important role in these investigations. For nitrogen-containing compounds, ^{15}N NMR spectroscopy can be a particularly valuable experimental tool. For this purpose, it is important to establish the relationships between ^{15}N NMR parameters (chemical shifts, coupling

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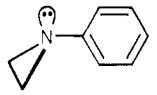
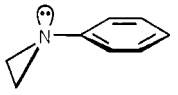
constants, relaxation behavior) and molecular structure, especially in molecules which may have peculiar structural properties. In this context, we have been investigating ^{15}N chemical shifts of aziridines and azetidines, in which effects of *N*- and ring-alkyl substitution have been elucidated.[1] Continuing these studies, we report here ^{15}N chemical shifts of *N*-arylaziridines. Part of our goal was to determine if the nitrogen shifts of these molecules reflect any changes in the way in which the aniline-type nitrogen interacts with the aromatic ring.

Also of interest in connection with the ^{15}N shifts of *N*-arylaziridines is the fact that, in many instances, ^{15}N chemical shifts correlate with photoelectron spectroscopic ionization potentials. Requirements for existence of a correlation are not yet clear. For example, the ^{15}N shifts of methyl-substituted formamides and acetamides correlate separately with the ionization potentials of the nitrogen lone pair.[2] However, in ureas[3] an "average ΔIP" for the two lone-pair-like orbitals does not correlate with δ_N; rather, only a general trend is displayed. ^{15}N chemical shifts of 2,6-dialkyl-*N*,*N*-dimethylanilines[2] correlate well with the difference in IP between π_2 and π_4, the orbitals arising by interaction between the nitrogen lone pair and the appropriate benzene π orbital. However, only a moderate correlation is exhibited with π_2, the orbital considered to have the greater lone-pair contribution. While δ_N of 4-substituted *N*,*N*-dimethylanilines does not correlate with either π_2 or π_4,[3b] the shifts for a series of 4-substituted benzamides[4] display a good correlation with the IP of the nitrogen lone pair.

In the parent molecule, *N*-phenylaziridine, two minimum-energy conformations are likely: the bisected conformation, in which the axis of the nitrogen lone pair orbital is in the plane of the ring (**1B**), and the perpendicular



1B

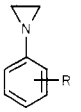


1P

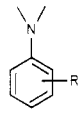
conformation, in which the lone pair is effectively perpendicular to the benzene plane (**1P**). The bisected conformation, which allows overlap of the small-ring Walsh orbitals with the benzene π system, is preferred in phenylcyclopropane and 2-phenylaziridine.[1] However, in *N*-phenylaziridine, electron-diffraction studies in the gas phase[5] and dipole moment and Kerr constant measurements in solution[6] all point exclusively to the perpendicular conformation **1P**, which optimizes lone-pair delocalization.

Previous work has shown the extent of conjugation in *N*-phenylaziridines to be less than that in anilines. Results from ^{19}F chemical shifts[7] and infrared intensities[8] suggest that the 1-aziridinyl group is not as conjugatively electron-donating as either the amino or the dimethylamino group. Investigations by means of ^{13}C NMR,[9] infrared intensities,[8] and UV spectroscopy,[10] all suggest that *N*-phenylaziridine is the least conjugated of the series of *N*-phenyl cyclic amines.

Table I. ^{15}N Chemical Shifts of *N*-Arylaziridines[a]



A



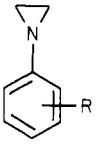
B

compd	R	δ_N	$\Delta\delta_N$[b]	δ_N[c]	$\Delta\delta_N$[b]
1	H	39.8	0.0	44.9	0.0
2	4-$N(CH_3)_2$	35.0[d]	−4.8	42.6	−2.3
3	4-OCH_3	36.1	−3.7	40.8	−4.1
4	4-CH_3	38.0	−1.8	42.8	−2.1
5	4-F	37.4	−2.4	40.5	−4.4
6	4-Cl	39.6	−0.2	49.1	4.2
7	4-CN	45.7[e]	5.9	59.6	14.8
8	4-NO_2	47.3[f]	7.5	68.6	23.7
9	2-CH_3	37.9	−1.9	33.8[g]	−11.1
10	2,6-$(CH_3)_2$	37.8	−2.0	16.8[g]	−28.1

[a] Measured with respect to external CH_3NO_2 and reported with respect to anhydrous liquid ammonia by using the relationship $\delta_{NH_3} = \delta_{CH_3NO_2} + 380.2$ (see ref 21). [b] $\Delta\delta_{N_R} = \delta_{N_R} - \delta_{N_H}$. [c] Reference 3b, Me_2SO solutions. [d] $\delta_{N(CH_3)_2}$ 41.5. [e] δ_{CN} 254.4. [f] δ_{NO_2} 370.1. [g] Reference 2.

Magnitudes of ^{15}N chemical shifts can be useful in estimating the degree of n–π interaction, which may be influenced by 4-substituents[3b,11] and by steric hindrance[3a] to conjugation in anilines. Shielding of the nitrogen in *N*,*N*-dimethylanilines upon 2,6-dimethyl substitution or upon 4-substitution by electron-donating groups is attributable to decreased electron delocalization. This is evidenced by correlation of substituent chemical shifts in 4-substituted anilines and *N*,*N*-dimethylanilines with σ_I and σ_R^- values in a dual-substituent-parameter (DSP) analysis.[3b,12]

The goal of this study was to measure the ^{15}N chemical shifts and photoelectron vertical ionization potentials of a series of *N*-arylaziridines (**1**–**10**) and, assisted by corre-



1, R = H
2, R = 4-$N(CH_3)_2$
3, R = 4-OCH_3
4, R = 4-CH_3
5, R = 4-F
6, R = 4-Cl
7, R = 4-CN
8, R = 4-NO_2
9, R = 2-CH_3
10, R = 2,6-$(CH_3)_2$

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Table II. Vertical Ionization Potentials (in eV) of *N*-Arylaziridines

R in A	E_2	E_3	E_4	$E_2 - E_4$ ($E_{2,4}$)
H	10.3	9.1	8.1	2.2
4-N(CH_3)$_2$	10.4	9.0	7.1	3.3
4-OCH_3	9.7	9.1	7.6	2.1
4-CH_3	10.1	9.2	8.0	2.1
4-F	10.4	9.5	8.2	2.2
4-Cl	10.3	9.6	8.3	2.0
4-CN	10.5	9.7	8.5	2.0
4-NO_2	11.0	10.0	8.9	2.1
2,6-(CH_3)$_2$	10.1	8.6	7.9	2.2

lations with DSP parameters and with IPs, to describe the n–π interaction. In fact, the shifts do not correlate well with the IPs, and possible reasons are discussed below.

Results

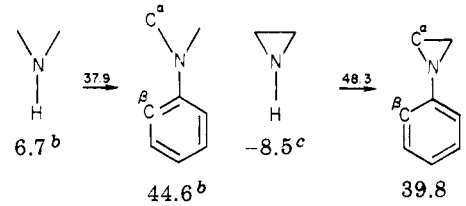
Two new compounds, *N*-(2,6-dimethylphenyl)aziridine and *N*-[4-(dimethylamino)phenyl]aziridine, have been synthesized by using procedures from the literature (see Experimental Section). All other compounds were prepared by published methods. ^{15}N chemical shifts of *N*-arylaziridines **1–10** along with the values for the corresponding *N,N*-dimethylanilines (from ref 3b) are listed in Table I. The vertical ionization potentials of the three highest occupied orbitals are listed in Table II. Chemical shift assignments were straightforward, and IP assignments were based on those of the corresponding anilines.

Discussion

^{15}N Chemical Shifts. The range of ^{15}N shifts spanned by aziridines **1–10** (Table I) is substantially less than that (51.8 ppm) for the corresponding *N,N*-dimethylanilines. Exclusion of anilines with ring substitution corresponding to **9** and **10** and in which conjugation is known to be sterically hindered still affords a larger chemical shift range (28.1 ppm) than for the aziridines. Thus, consistent with earlier studies, the aziridine nitrogen appears to interact less extensively with the benzene ring than other aniline nitrogens. Nonetheless, the manner in which the phenylaziridine and aniline nitrogen nuclei respond to substituents seems to be parallel. The aziridine values correlate well (r = 0.988, standard deviation = 0.69 ppm) and moderately well (r = 0.957, standard deviation = 1.3 ppm) with those for primary anilines and *N,N*-dimethylanilines, respectively. The slope of the latter correlation line, 0.414 ppm (aziridine)/ppm (aniline), also points to attenuated interaction with the benzene ring; indeed, the behavior more nearly resembles that of 4-substituted *N,N*,2,6-tetramethylanilines.[3b] Interestingly, the aziridine values in Table I correlate well (r = 0.988, standard deviation = 0.63 ppm) with the ^{17}O shifts of corresponding anisoles[13] and yield a slope similiar to that of the aniline plot, 0.422 ppm (N)/ppm (O).

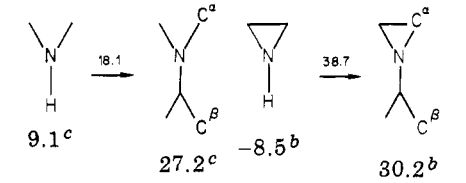
The discussion so far supports the idea that *N*-phenylaziridine nitrogens interact less effectively with a benzene ring than do aniline nitrogens. This inference seems at variance with the phenyl substituent effect shown in Scheme I. The larger deshielding for aziridine would appear to imply greater conjugative interaction in this system. However, even alkyl groups have a greater influence on aziridine resonance positions than on amines (see Scheme II). In the acyclic molecules, deshielding expected upon additional α and β substitution may be partly attenuated by a shielding "$\alpha\beta$" effect.[15] The contribution from this effect, which varies with geometry, might be expected to be smaller in the aziridines because the ring α-carbons are constrained to be further away from β-carbons (see below). Operation of the same effect in *N*-phenylaziridine would account for the larger deshielding (smaller shielding) induced by the phenyl group.

Scheme I[a]



[a] Chemical shifts in parts per million. [b] Pure liquid.[14] [c] In $CDCl_3$.[1]

Scheme II[a]



[a] Chemical shifts in parts per million. [b] In $CDCl_3$.[1] [c] In C_6H_{12}.[14]

The influence of 2-methyl substitution on the *N*-phenylaziridine resonance position (cf. **9** and **10**) is an order of magnitude smaller than that in the *N,N*-dimethylanilines.[3a] If n–π interaction in the aziridines is attenuated, then the effect of any steric perturbations would be expected to be smaller. Molecular models indicate that the larger exocyclic bond angles of the aziridine ring cause the methylene ring carbons to be bent further away from the aryl ring plane than the *N*-methyl carbons of *N,N*-dimethylanilines. Furthermore, adoption of the bisected conformation induces severe steric interactions with 2-substituents on the aryl ring. Thus, it is likely that there is little conformational change on 2-methyl substitution and that the corresponding changes in nitrogen chemical shift are largely inductive.

While the nitrogen shifts are consistent with reduced interactions between aziridine and benzene rings, they do not alone reflect the nature of the interaction, especially in terms of the classical separation into inductive and conjugative effects. To assess the latter possibility, the 4-substituted *N*-arylaziridine chemical shifts have been subjected to a DSP analysis using values of σ_I and σ_R^-. The latter parameter is considered to be most appropriate for electron-rich aniline-type systems.[12] The eight compounds under consideration fit the requirements for a minimum basis set of substituents as suggested by Taft.[12]

Values of ρ_I and ρ_R were derived from a multiple regression analysis of the experimental data fitted to eq 1.

$$\Delta\delta_N = \rho_I\sigma_I + \rho_R\sigma_R^- \quad (1)$$

Values of ρ_I = 4.31 and ρ_R = 10.98 were obtained from this treatment, with a correlation coefficient r = 0.993 and a Taft f value of 0.13. Correlations are considered reasonable if $f < 0.2$. Attempted correlations of the data with either

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σ_I or σ_R^- separately or with σ_P gave much lower correlation coefficients. The ratio $\lambda = \rho_R/\rho_I = 2.55$ is higher than is obtained from any other set of data for aniline systems, including ^{15}N shifts of 4-substituted anilines, ionization constants of anilinium salts, and reaction rates of anilines as nucleophiles.[12] This would appear to suggest that conjugative interactions are relatively more important than inductive interactions in the aziridines than in the anilines. At the same time the ρ values themselves are smaller than those derived for the same aniline chemical shifts, again consistent with the suggestion that the extent of total substituent interaction is considerably smaller than that in the anilines.

The possibility that the unexpectedly large λ value arises from inappropriate use of σ_R^- for the weakly interacting aziridinyl group suggested that correlation of the data with σ_R^0 might be appropriate. This parameter has been applied successfully to chemical shifts of the weakly donating ^{19}F substituent. Thus, multiple regression fitting of $\Delta\delta_N$ to eq 1 by using σ_R^0 in place of σ_R^- affords values of $\rho_I = 7.0$ and $\rho_R = 12.8$, with $r = 0.981$ and $f = 0.22$. Although the ratio $\lambda = 1.83$ is now lower, it is still larger than that for nitrogen chemical shifts of 4-substituted anilines. In addition, the f value indicates at best a marginal correlation, casting doubt on the significance of the ρ and λ values obtained.

In order to determine whether the results obtained by using σ_R^- could be artifacts of a particular data set, we correlated several partial sets of substituent chemical shifts (SCS) with σ_I and σ_R^-. Omission of the shift of the 4-N-$(CH_3)_2$ compound, which displayed the largest deviation from the calculated shift, results in values of $\rho_I = 4.39$ and $\rho_R = 10.41$, with $f = 0.054$. This much-improved fit of the data gives $\lambda = 2.37$, which is only slightly lower than that for the whole data set, and eliminates the possibility that insufficiently good fitting of the data produced the high λ value. Use of data sets lacking NO_2, CN and $N(CH_3)_2$, or OCH_3 and $N(CH_3)_2$, produces values of $f < 0.1$ and $\lambda > 2$. The high λ value consequently is a real result from this set of data, not merely an artifact.

The unusually high λ value for the phenylaziridines accords with the observation that DSP analyses of nonproton NMR shifts generally give high λ values;[12] e.g., $\lambda = 4.35$ for ^{19}F shifts of aryl fluorides. Probably these values merely serve to confirm the stronger dependence of shifts of second-row nuclei on π-electron distribution, reflected in the resonance term, rather than on σ-electron density. Even so, this does not explain why the λ value for the aziridine SCS is so much higher than that of the aniline SCS. Fitting of inversion barriers in *N*-aryl-2,2-dimethylaziridines[16] to eq 1 also produces a high λ value (2.02), with $f = 0.105$. Since these inversion barriers are dependent on n–π overlap, it is possible that λ can be characteristic of the property measured rather than of the system, as with ^{19}F shifts. Alternatively, the geometry of the *N*-phenylaziridine molecule, which discourages twisting of the lone pair from the perpendicular conformation, maximizes n–π interaction and thereby the ratio of resonance to inductive contributions. A relevant example given by Taft[12] is the saponification of phthalide esters, which are constrained to coplanarity. The λ value of 1.10 is higher than values for benzoate ester, $\lambda < 1.0$, even though the ρ values for the phthalide esters are lower. Thus, a system with less total substituent interaction can have a higher contribution from conjugative interactions if the geometry consistent with maximum overlap is highly favored. While this picture seems to be consistent with the data for the *N*-arylaziridines, confidence in it is lessened by the possibility that σ_I and σ_R^- values derived for other systems may not accurately reflect substituent interaction in this system.

Photoelectron Spectroscopy. The photoelectron spectra of aniline systems are characterized by three low-energy bands. The first (lowest IP, π_4) and third (π_2) energy levels arise from interaction of the nitrogen lone pair with the degenerate highest occupied benzene π orbitals. Furthermore, analysis of overlap populations suggests that π_2 has somewhat greater lone-pair character than π_4.[17] The second (π_3) level is localized on the benzene ring and has no lone-pair character. The IP difference $E_{2,4} = E_2 - E_4$ decreases with reduced delocalization of the lone pair.[3a,18] In *N*,*N*-dimethylanilines this difference is 2.4 eV, less than the 2.8 eV value for aniline, in which delocalization is more extensive. The $E_{2,4}$ difference in *N*-phenylaziridine is 2.2 eV (Table II), confirming the decrease in n–π interaction inferred from the ^{15}N shifts and other studies. The probable reason for this small interaction is the lower lone-pair energy of aziridine[19] relative to $(CH_3)_2NH$. However, $E_{2,4}$ remains very close to this value throughout much of the series, despite the variable lone-pair delocalization which is manifested in the chemical shifts. These data closely parallel those for *N*,*N*-dimethylanilines[20] with the sole exception of the 2,6-dimethyl compound. This substitution seems to have much less effect on delocalization in *N*-arylaziridines (see the ^{15}N NMR discussion) than in dimethylanilines, so it is not surprising that $E_{2,4}$ is nearly the same as for the unsubstituted *N*-phenylaziridine.

Attempts to correlate δ_N with the IP of the orbitals resulting from lone-pair π interaction were fruitless. A general trend in which a lower IP coresponds to an increase in ^{15}N shielding is indicated in the E_4 vs. δ_N comparison, but this is not statistically significant ($r = 0.883$). Moreover, E_2, the energy of the orbital considered to have greater lone-pair character, shows not even a trend with δ_N values.

The constancy of $E_{2,4}$ and the lack of correlation of the ^{15}N shifts with E_2 or E_4 separately result from direct interaction of the 4-substituent with π_2 and π_4. The correlations are good in the case of 2,6-dialkyl-*N*,*N*-dimethylanilines where inductive effects of differing alkyl substituents on E_2 and E_4 are fairly constant. Thus, sterically induced reduction in delocalization dominates both $E_{2,4}$ and the ^{15}N shifts. However, with a variety of functional groups as substituents, the situation is more complicated. The strong resonance donors OCH_3 and $N(CH_3)_2$ interact with π_4 to decrease its IP, thereby increasing $E_{2,4}$. This overcomes any decrease associated with lessened lone-pair delocalization. On the other hand, the electron-withdrawing CN and NO_2 lower all orbital IPs. This lowering is likely to be greater for π_4 than for π_2 because of the close proximity of the former to the NO_2 antibonding orbitals.[18] Thus, $E_{2,4}$ will decrease and in this way compensate for any increase owing to enhanced n–P interaction. These direct substituent effects on π_2 and π_4 are not likely to affect ^{15}N resonance positions in the same way and will thereby make a correlation between δ_N and $E_{2,4}$ less likely.

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In several series of disubstituted benzenes, the IP of the highest occupied orbital has been correlated with the corresponding ionization from the monosubstituted benzene.[4] When benzene is substituted with an electron-donating group and a series of 4-substituents, the slope of the correlation line is less than unity. This slope decreases with an increase in $E_{3,4} = E_3 - E_4$, the displacement energy of the highest occupied orbital, π_4, from the relatively unperturbed π_3. The quantity $E_{3,4}$ is not strictly a measure of electron donation to the phenyl group by the substituents. For *N*-phenylaziridines $E_{3,4}$ = 1.0 eV, which falls between the values of 0.83 and 1.16 observed for anisole and aniline, respectively. The slope of 0.678 (r = 0.978, standard deviation = 0.11 eV) for 4-substituted *N*-phenylaziridines is similar to the values of 0.7 and 0.67 found for substituted anisoles and anilines. Thus, the slope of this plot is a rough measure of the interaction between 4-substituents and π_4 and so may be useful in confirming assignments of PES bands in similar systems.[4]

Experimental Section

NMR Spectra. With the exceptions of solutions of the 4-NO_2 and 4-CN compounds, which were 2.2 M, natural-abundance ^{13}C and ^{15}N spectra of 4 M solutions of the compounds in $CDCl_3$ were determined at 25.03 and 10.09 MHz, respectively, by the pulsed Fourier transform method with a JEOL PS/PFT-100 spectrometer equipped with the JEOL EC-100 data system. For ^{13}C spectra, a spectral width of 5 kHz over 4K or 8K data points was used, with pulse angles of ~20° and a repetition time of 2 s. Chemical shifts were measured with respect to internal $(CH_3)_4Si$ (0.0 ppm) or $CDCl_3$ (76.9 ppm). ^{15}N spectra were obtained with a 5-kHz spectral width, 4K or 8K data points, and ~20° pulse angles. All compounds were run with 10–20 mg of chromium tris(acetylacetonate), $Cr(acac)_3$, to shorten T_1 values. This allowed a repetition time of 3–4 s to be used. Chemical shifts were measured with respect to partially enriched $CH_3{}^{15}NO_2$ is a concentric capillary and are reported on the anhydrous ammonia scale.[21]

^1H NMR spectra were obtained in $CDCl_3$ at 60 MHz on a Varian A-60A spectrometer. Shifts are measured with respect to internal $(CH_3)_4Si$.

Photoelectron Spectra. PES ionization potentials of vaporized samples were determined by using a modified[22] Perkin-Elmer PS-16 photoelectron spectrometer. Solid compounds and liquids boiling above 250 °C (760 mm) were placed in the probe and heated to 40–65 °C, while more volatile samples were introduced from a flask connected via a glass stopcock to the probe inlet. The argon (15.75 eV) or nitrogen (15.58 eV) ionization was used for calibration.

Materials. ***N*-(2,6-Dimethylphenyl)aziridine** was synthesized by the literature procedure[23] for *N*-(4-methylphenyl)-aziridine. It has the following physical properties: bp 105–106 °C (11 mm); ^1H NMR ($CDCl_3$) δ 6.9 (3 H, s, aromatic CH), 2.35 (6 H, s, CH_3), 2.1 (4 H, s, CH_2); ^{13}C NMR ($CDCl_3$) 150.9, 128.8, 128.7, 121.8, 29.8, 18.6 ppm.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84; N, 9.52. Found: C, 81.74; H, 9.03; N, 9.55.

***N*-[4-(Dimethylamino)phenyl]aziridine** was obtained by the literature procedure[24] for *N*-phenylaziridine from the corresponding amino alcohol. This in turn was produced by alcoholic base hydrolysis of the crude hydrochloride salt formed by reaction of *N*,*N*-dimethyl-*p*-phenylenediamine with 2-chloroethyl chloroformate.[25] The product had the following physical properties: bp 63 °C (0.05 mm); ^{13}C NMR ($CDCl_3$) 146.5, 145.7, 121.3, 113.6, 41.0, 27.4 ppm.

Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64; N, 17.28. Found: C, 73.78; H, 8.48; N, 17.09.

All other compounds are known and were synthesized by literature procedures.[24-26] Structures were confirmed by boiling point or melting point comparisons and ^{13}C NMR. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories.

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Note Added in Proof: Very recent photoelectron spectroscopic results on *N*-phenyl cyclic amines, including **9** and **10**, support our suggestion that these compounds are not conformationally twisted: Rozeboom, M. D.; Houk, K. N.; Searles, S.; Seyedrezai, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3448–3453.

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Micellar Effects upon the Reaction of Hydroxide Ion with *N*-Alkyl-2-bromopyridinium Ion

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The reactivity of *N*-alkyl-2-bromopyridinium ions (alkyl = Me, Et, n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, n-$C_{16}H_{33}$) toward OH^- is affected by cationic micelles of alkyltrimethylammonium chloride or bromide (alkyl = n-$C_{14}H_{29}$, n-$C_{16}H_{33}$) which inhibit reactions of the methyl and ethyl substrates and catalyze reactions of the more hydrophobic derivatives. These results are understandable, qualitatively, in terms of the distribution of both reactants between the aqueous and micellar pseudophases. The distribution of OH^- between aqueous and micellar pseudophase is governed by an ion-exchange equilibrium. The rate enhancements can be treated quantitatively, and second-order rate constants in the micellar pseudophases are essentially independent of substrate hydrophobicity and are slightly smaller than those in water. The rate differences are understandable in terms of the high electrolyte concentration at the micellar surface.

Rate enhancements of many bimolecular reactions by aqueous micelles have been treated quantitatively by estimating the concentrations of both reactants in the aqueous and micellar pseudophases.[2-4] In some cases, e.g.,

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