in Table I. Their respective values of −1.385, −0.848, and 0.031 are calculated from the known σ_m and σ_p using the coefficients in Table IV.
(7) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4980 (1958).
(8) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).
(9) For unequivocal assignment of 2- and 8-proton signals in adenine and others, see J. R. Fox, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1965. The current work using 8-deuterated 6-chloro and 6-iodopurine established both of their ^{1}H NMR spectra to be H-2 at lower field than H-8. This is further corroborated by the ^{13}C NMR spectra of the 6-halopurines (ref 2).
(10) R. J. Pugmire, D. M/ Grant, L. B. Townsend, and R. K. Robins, *J. Am. Chem. Soc.*, **95**, 2791 (1973), and pertinent references cited.

Substituent and Medium Effects on Nitrogen-15 Shieldings of Compounds with >C=N Bonds (Imines, Oximes, and Phenylhydrazones)[1a]

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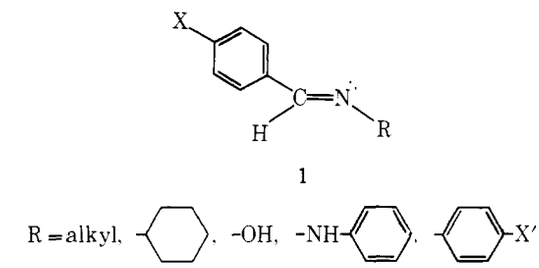
The ^{15}N chemical shifts of 13 *N*-(arylmethylidene)alkanamines, seven *N*-(arylmethylidene)azanols, five 1-(arylmethylidene)-2-phenyldiazanes, and 11 *N*-(arylmethylidene)arenamines have been determined at the natural-abundance level of ^{15}N in several solvents. The shifts of several of the *N*-(phenylmethylidene)alkanamines with different alkane groups have been analyzed in terms of α-, β-, and γ-methyl substituent effects. For those *N*-(arylmethylidene)azanes substituted at the para position, linear correlations with Hammett σ parameters having negative slopes are found for the ^{15}N chemical shifts. However, the ^{15}N shifts of *N*-(phenylmethylidene)arenamines (substituted at the para position of the arenamine moiety) are essentially insensitive to the nature of the substituent. The slopes of the Hammett correlations become more negative with increasing proton-donating power of the solvent for most series of compounds studied. In general, the ^{15}N shifts were found to be 5–12 ppm toward higher fields in methanol compared to chloroform, and except for the alkylidenazanols (oximes), about the same in dimethyl sulfoxide as in chloroform. In contrast, the alkylidenazanol resonances move 13–16 ppm downfield for the change from chloroform to dimethyl sulfoxide.

Systematic nitrogen nuclear magnetic resonance (NMR) studies, which were previously limited by inaccuracies of the ^{14}N NMR data and the expense and difficulties of using ^{15}N-enriched materials,[2] can now be carried out easily with ^{15}N isotope at the natural-abundance level and are expected to lead to a more complete understanding of the factors which contribute to the shieldings of nitrogen nuclei.

Previous studies of structural effects on ^{15}N shifts largely have been confined to systems containing sp^3-hybridized nitrogen atoms.[3–6] Both saturated systems in which inductive and steric effects should dominate and unsaturated systems containing aromatic groups capable of conjugative interaction have been investigated. Thus, the ^{15}N shifts in alkanamines have been found to change with alkyl substituents in much the same manner as ^{13}C shifts in structurally related compounds.[3] Such correlations further substantiate the belief that substituent-induced shielding changes result from external perturbations which are common to several nuclei.[7–9] Investigations of ^{15}N shifts of the amine nitrogens of substituted benzenamines[4–6] have revealed the importance of the inductive and resonance effects of the individual substituents. The basic assumption in all of these correlations is that substituents may be expected to alter the electron density at the nitrogen atom and the C–N bond order, thus causing changes in the paramagnetic part of the Ramsey shift equations.

We report here further evaluation of steric, electronic, and medium effects on ^{15}N chemical shifts for the specific case of imino nitrogens. The bonding in these types of nitrogen can be usefully regarded as involving a C–N σ and a C–N π bond with a lone electron pair on nitrogen which, to the first approximation, is not considered to be involved with the π-bonding orbitals.

In this work, we have chosen to study a number of arylmethylidenamines, azanols, and diazanes with the general structure **1**. These substances, in principle, will allow for conjugation of the unsaturated nitrogen with the *C*-aryl group



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through the C=N π bond and/or of the unshared pair on nitrogen with an *N*-aryl group. The importance of such conjugation was expected to be revealed by the variation of the nitrogen shieldings with the nature of the substituent group (X or X′) on the aryl groups from *p*-N(CH$_3$)$_2$ to *p*-NO$_2$.

Experimental Section

The natural-abundance ^{15}N spectra were recorded on a Bruker WH-180 spectrometer operating at 18.25 MHz in the Fourier-transform mode employing quadrature detection and complete noise–proton decoupling. Samples were run as 20 or 36 mol % solutions in chloroform, dimethyl sulfoxide, or methanol contained in 25-mm o.d. precision-ground sample tubes, with 17–22-mL sample volumes. Chemical shifts are reported in parts per million (ppm) upfield with respect to 1.0 M ^{15}N-enriched nitric acid in deuterium oxide contained in a 5-mm o.d. NMR tube. The deuterium oxide was used to produce the field lock signal. The optimum conditions for observation of the imino nitrogen signals of the compounds studied here were found to have a pulse width of 55 μs (70° pulse angle), a repetition rate of 30 s, and gated proton decoupling for which the decoupler was on only during acquisition of data (no NOE). Under these conditions, the sample remained at ambient probe temperature (25 °C), and typical spectra required 200 accumulations to provide an adequate signal-to-noise ratio. Gated proton decoupling during acquisition is preferable to no decoupling to ensure removal of any nitrogen–proton couplings which might broaden the signal and thus reduce the signal-to-noise ratio. For measurement of the shifts of the amino nitrogen signals in the phenyldiazanes, continuous proton decoupling was

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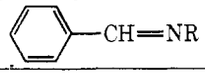
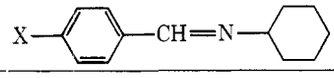
Table I. ^{15}N Chemical Shifts of *N*-(Phenylmethylidene)alkanamines[a]



R	Registry no.	Chemical shift
CH_3	622-29-7	55.9
CH_2CH_3	6852-54-6	40.6
$CH(CH_3)_2$	6852-56-8	28.5
$C(CH_3)_3$	6852-58-0	20.6
$CH_2CH_2CH_3$	6852-55-7	42.9
$CH_2CH(CH_3)_2$	6852-57-9	43.0
$CH_2C(CH_3)_3$	7731-35-3	43.1
$C(CH_3)_2CH_2CH_3$	65815-57-8	21.8

[a] All chemical shifts are given in ppm upfield of external 1.0 M $D^{15}NO_3$. Measured as 36 mol % solutions in chloroform.

Table II. ^{15}N Chemical Shifts of *N*-(Arylmethylidene)cyclohexanamines[a]



X	Registry no.	σ_P[b]	^{15}N chemical shift: Chloroform	Methanol
CH_3O	56644-00-9	−0.268	38.5	50.8
CH_3	65815-58-9	−0.170	33.9	45.0
H	2211-66-7	0.0	30.2	41.0
Cl	24431-14-9	+0.226	28.1	36.6
NO_2[c]	42974-61-8	+0.778	14.7	21.7

[a] All chemical shifts are given in ppm upfield from external $D^{15}NO_3$. Measured in 20 mol % solutions. [b] Taken from ref 41. [c] $\delta_{^{15}N}(NO_2)$ = 6.8 ppm ($CHCl_3$); 5.3 ppm (MeOH).

employed with a pulse width of 25 μs (40° pulse angle) and a 3-s repetition rate.

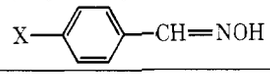
Substituted *N*-(arylmethylidene)arenamines were prepared from the appropriately substituted benzenamines and benzenecarbaldehydes according to the method of Law,[11] or of Roe and Montgomery.[12] Physical and spectral parameters were consistent with reported data.[11-14] The arylmethylidenazanols and diazanes were synthesized from 4-substituted benzenecarbaldehydes and purified by recrystallization from ethanol. Melting points were identical with reported values.[15] *N*-(Phenylmethylidene)alkanamines were prepared by heating the appropriate alkanamines at reflux for 30 min with an equimolar amount of benzenecarbaldehyde in benzene. The solvent was removed under reduced pressure and the crude product purified by distillation. Boiling points were in agreement with those reported.[15-18] *N*-Phenylmethylidenemethanamine was commercially available.

Results

The nuclear Overhauser effect (NOE) resulting from proton decoupling is extremely important in ^{13}C and ^{15}N NMR spectroscopy. The magnetogyric ratio is negative for the ^{15}N nucleus, and thus, when dipole–dipole interactions between the nitrogen and directly bonded protons dominate the relaxation mechanism, irradiation over the range of proton frequencies generally causes inversion of the ^{15}N resonances. A maximum NOE of −3.93[19a] is theoretically possible for the case of pure dipolar relaxation. For nitrogens having no directly bonded protons, dipole–dipole interactions may not dominate the relaxation mechanism, and, consequently, proton irradiation may lead to a decrease in signal intensity or even complete disappearance of the signal.[19b] We have found that, for compounds containing imino nitrogens, continuous proton–noise decoupling does not generally give useful natural-abundance ^{15}N signals.

The ^{15}N chemical shifts of *N*-(phenylmethylidene)alkanamines are given in Table I, and those of *N*-(arylmethylidene)cyclohexanamines in Table II.

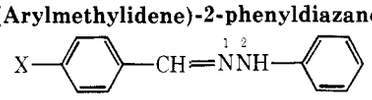
Table III. ^{15}N Chemical Shifts of *N*-(Arylmethylidene)azanols[a]



X	Registry no.	σ_p[b]	^{15}N chemical shift: Chloroform	Dimethyl sulfoxide
$N(CH_3)_2$	2929-84-2	−0.600	32.2	16.9
OCH_3	3235-04-9	−0.268	24.7	11.0
CH_3	3235-02-7	−0.170	23.1	7.0
H	932-90-1	0.0	20.1	4.5
F	459-23-4	+0.062	20.5	5.7
Cl	3848-36-0	+0.226	17.3	2.9
NO_2[c]	1129-37-9	+0.778	*d*	−7.6

[a] All chemical shifts are given in ppm upfield from external $D^{15}NO_3$. Measured in 20 mol % solutions. [b] Taken from ref 41. [c] $\delta_{^{15}N}(NO_2)$ = 6.5 ppm (Me_2SO). [d] Insufficiently soluble to obtain spectrum.

Table IV. ^{15}N Chemical Shifts in 1-(Arylmethylidene)-2-phenyldiazanes[a]



X	Registry no.	σ_p[b]	^{15}N chemical shift: N-1	N-2
CH_3O	622-73-1	−0.268	53.8	232.8
CH_3	2829-25-6	−0.170	50.2	231.7
H	588-64-7	0.0	47.8	230.8
Cl	2829-26-7	+0.226	46.6	229.9
NO_2[c]	2829-27-8	+0.778	37.2	224.1

[a] All chemical shifts are given in ppm upfield from external $D^{15}NO_3$. Measured as 20 mol % solution in dimethyl sulfoxide. [b] Taken from ref 41. [c] $\delta_{^{15}N}(NO_2)$ = 5.1 ppm.

Table III and IV give the shifts for para-substituted *N*-(arylmethylidene)azanols and 1-(arylmethylidene)-2-phenyldiazanes, respectively. Both resonance lines of the diazane derivatives were narrow, which indicate that quadrupole relaxation of the adjacent ^{14}N nucleus (I = 1) is rapid.[5] There is no ambiguity in the assignment of the two signals because of the large characteristic shift difference between imine- and amine-like nitrogens. For the nitrogen bonded directly to hydrogen (N-2), continuous proton irradiation gave a strong, inverted ^{15}N signal only after 50–100 transients.

The shifts for the nitro and imino nitrogens of the *p*-nitro derivatives in Tables III and IV are not very far apart, and the assignments were based on ^{14}N data reported for aromatic nitro compounds.[2d]

Chemical shifts for *N*-(arylmethylidene)arenamines in several different solvents are listed in Tables V and VI.

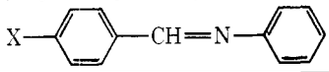
Discussion

Alkyl Substituent Effects. Theoretical considerations of nitrogen chemical shifts[20] have largely focused on the expression for the "paramagnetic" screening contribution which, for second-row elements, appears to dominate the total screening of these nuclei. Contributions from the diamagnetic term appear to be small by comparison.[21] In Pople's LCAO–MO treatment,[22] the paramagnetic term can be approximated by the equation

$$\sigma \frac{\text{para}}{A} = -\frac{e^2h^2}{2m^2c^2}\langle r^{-3}\rangle_{2p}\frac{1}{\Delta E_{av}}\sum_B Q_{AB} \qquad (1)$$

where ΔE_{av} is the average excitation energy for transitions

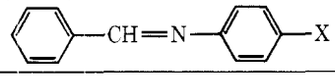
Table V. ^{15}N Chemical Shifts in *N*-(Arylmethylidene)benzenamines[a]



X	Registry no.	σ_p[b]	^{15}N chemical shift: Chloroform	Dimethyl sulfoxide	Methanol
$N(CH_3)_2$	889-37-2	−0.600	66.7[c]	*d*	*d*
OCH_3	836-41-9	−0.268	56.4	55.6	65.6
CH_3	2362-77-8	−0.170	51.9	50.6	*d*
H	538-51-2	0.0	47.9	47.5	53.5
F	5676-81-3	+0.062	49.3	48.8	*d*
Cl	2362-79-0	+0.226	46.6	46.0	51.9
NO_2[e]	785-80-8	+0.778	35.1	36.6	*d*

[a] All chemical shifts are given in ppm upfield from external $D^{15}NO_3$. Measured as 20 mol % solutions. [b] Taken from ref 41. [c] $\delta_{^{15}N}(N(CH_3)_2)$ = 321.9 ppm. [d] Insufficiently soluble to observe signals. [e] $\delta_{^{15}N}(NO_2)$ = 7.1 ($CHCl_3$); 5.7 (Me_2SO).

Table VI. ^{15}N Chemical Shifts in *N*-(Phenylmethylidene)arenamines[a]



X	Registry no.	σ_p[b]	^{15}N chemical shift: Chloroform	Dimethyl sulfoxide
OCH_3	783-08-4	−0.268	51.4	49.9
CH_3	2272-45-9	−0.170	49.0	48.0
H		0.0	47.9	47.5
Cl	780-21-2	+0.226	52.0	51.5
NO_2	785-81-9	+0.778	51.7	*c*

[a] All chemical shifts are given in ppm upfield from external $D^{15}NO_3$. Measured as 20 mol % solutions. [b] Taken from ref 41. [c] $\delta_{^{15}N}(NO_2)$ = 4.4 ppm (Me_2SO); NO_2 signal not observed when chloroform was solvent.

involving σ or nonbonding electrons, $\langle r^{-3}\rangle_{2p}$ is the orbital expansion term, and Q_{AB} are matrix elements which reflect bond orders and charge densities for the LCAO molecular orbitals.

Although an approach focused on the relative importances of the various terms in the paramagnetic expression for screening constants may be theoretically useful to explain large differences in chemical shifts, empirical chemical-shift correlations within series of structurally related molecules are potentially more valuable for structure determinations. One empirical approach, which is especially simple, is correlation of ^{15}N and ^{13}C shifts, because the factors which influence ^{13}C shifts have been extensively investigated, and existence of a correlation implies that the same factors affect both.[3] To this end, the nitrogen shifts in Table I were plotted against the ^{13}C shifts reported for the corresponding carbons of *trans*-2-alkenes[23] (Figure 1). It would have been more appropriate to use the ^{13}C shifts of 1-phenyl-1-alkenes, but too few examples were available. Nonetheless, and despite the rather small number of points, an excellent correlation was observed having a slope of 1.96, an intercept of 300.8, and r = 0.998. This correlation implies that chemical-shift changes induced by the alkyl substituents result from perturbations which act in the same way for each nucleus and, as before,[3] the sensitivity of ^{15}N to these perturbations is about twice that of ^{13}C.

The ^{15}N chemical shifts of *N*-(phenylmethylidene)alkanamines fall between 20.6 and 55.9 ppm. Thus, there is approximately a 250-ppm shift to lower field associated with the structural change, $C_6H_5CH_2{}^*NHR$ to $C_6H_5CH{=}{}^*NR$,[5] and the corresponding change for analogous carbon compounds produces a ^{13}C shift change only about half as large. The very substantially greater downfield shift of ^{15}N over ^{13}C for this kind of structural change is best understood as arising from the ΔE_{av} term in eq 1. Mixing into the ground-state wave function in a magnetic field of an electronic configuration corresponding to a n → π^* transition of one of the nitrogen electrons is expected to lead to a paramagnetic circulation of electrons around the nitrogen and thus decrease the shielding of the nitrogen nucleus. Because there is no unshared pair on the β carbon of ethenylbenzenes, the ΔE_{av} term corresponding to this effect will not be important. In fact, when *N*-(arylmethylidene)alkanamines are protonated[24] and become isoelectronic with phenylethenes as the result of bond formation to the nitrogen unshared electron pair, there is a very large diamagnetic shift (~150 ppm) of the nitrogen resonances.

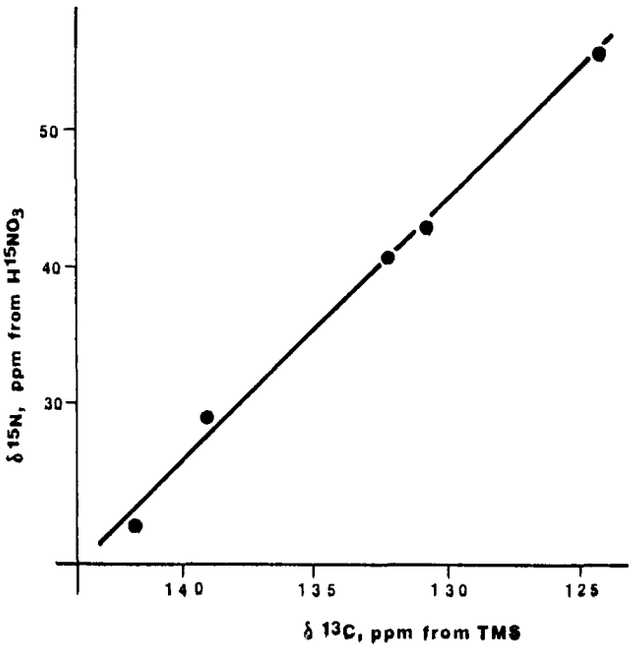


Figure 1. Correlation of the C-2 chemical shifts of *trans*-2-alkenes with the ^{15}N chemical shifts of *N*-(phenylmethylidene)alkanamines.

The α, β, and γ shifts found for *N*-(phenylmethylidene)alkanamines closely parallel those previously found for primary amines. The α shift derived from the reported ^{14}N resonance position for *N*-(phenylmethylidene)amine[2d] is approximately −8 ppm, which can be compared with the reported α shifts for primary amines of −8.7[3a] and −7.8 ppm.[25] The α effects all produce downfield shifts which seem to increase with increasing substituent electronegativity: α_{CH_3} = −8.1, α_{NHPh} = −16.1, and α_{OH} = −43.9 ppm. These parallel in a remarkable way α effects in the ^{13}C spectroscopy of alkanes, where an α-methyl group generally causes a 9-ppm downfield shift, and a hydroxyl −40 to −50 ppm shifts.[9]

The β_N shift for the imines in Table I is similar to those found for other nitrogen-containing systems, although somewhat smaller than for primary amines. Thus, a single β-methyl group causes a 15.3-ppm downfield shift for the imino nitrogen resonance, with smaller β shifts of −12.1 and −7.9 ppm, respectively, for a second and a third β-methyl substituent. Introduction of methyl groups α to the unsaturated nitrogen atom may be accompanied by increases in steric interactions that could lead to upfield shifts which would oppose the fundamental downfield shift. As the steric bulk at the α carbon increases with additional methyl substituents, the β effect of that substituent decreases in absolute value.

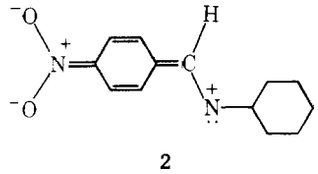
Although the directions of the β shifts parallel those observed in ^{13}C spectroscopy, the magnitude of β_N is more than

twice β_C (−6.0 ppm).[26] It has been suggested for ^{13}C that the β-alkyl substituent parameter arises partly by way of an inductive mechanism and partly through substituent-induced distortion of the α–β bond.[27] For the nitrogen atoms, a substituent-induced polarization of the lone-pair electrons might play an additional role.[3]

As for primary amines, the γ shift was found to be shielding for the imines studied. However, the size of the γ-shift influences is smaller than for amines and, in fact, introduction of a second and a third γ-methyl group has almost no effect. By analogy with alkenes and alkanes,[28] imines could well have rotational conformer populations different from those expected for saturated systems. Thus, interactions between a γ substituent and an imine nitrogen may be quite different from a γ-gauche interaction in a primary amine. Furthermore, the pattern of steric perturbations affects the shifts of unsaturated nitrogens in the same way as saturated nitrogens. Indeed, there are indications that steric interactions of methyl substituents with the nitrogen unshared pair of oximes lead to deshielding of the imino nitrogens.[29]

Electronic Substituent Effects. (a) *N*-(Arylmethylidene)cyclohexanamines. The range of chemical shifts for the 4-substituted *N*-(arylmethylidene)cyclohexanamines in chloroform is 23.8 ppm. The nitrogen shifts depend on the polar characteristics of the individual substituents located on the benzene ring; electron-withdrawing substituents cause downfield shifts, whereas electron-donating substituents cause upfield shifts. The range of ^{15}N shifts in the corresponding para-substituted benzenamines is nearly the same (25.5 ppm),[4] although this is best regarded as coincidence because the type of interaction between the aromatic π system and the nitrogen is rather different for the two series. A good linear correlation is obtained of the ^{15}N shifts of 4-substituted *N*-(arylmethylidene)cyclohexanamines in methanol and chloroform (Table II) with Hammett σ constants (Figure 2). A least-squares treatment gave a line of best fit with a slope of −21.3, an intercept of 31.5, and r = 0.989 for the chloroform values, and for methanol, −26.3, 42.0, and 0.993, respectively.

The substituent-induced shift changes are so large as to be due clearly to the paramagnetic term in the expression for the screening constant. Even if this is so, there are several ways that the shifts can be rationalized. For example, the paramagnetic term depends, in part, on total electron density about the nitrogen nucleus, so any conjugative interaction which might influence electronic distributions at the nitrogen should have an important influence on its chemical shift. Indeed, the downfield shift of benzenamine compared to that of ammonia, and the shifts of amides compared to amines, have been attributed to a decrease in shielding arising from lone-pair delocalization over the aromatic system in the former[30a] and into the carbonyl group in the latter.[30b] The observed downfield nitrogen shifts produced by 4-nitro group substituents might arise from an increase in the contribution of forms such as **2** to the ground state because of the conjugative electron-attracting power of the substituent. The imines are somewhat different from benzenamines and amides because their unshared pairs are in n orbitals essentially orthogonal to the π bonds. Nonetheless, contributions to the ground state of the imines of high-energy states corresponding to n → π^* (or other π^*) optical transitions could be expected to lead to a paramagnetic electron circulation around the nitrogen. Because the nitro group should decrease the energy of the higher state, it could, in consequence, also decrease the sheilding at the nitrogen, as is observed.



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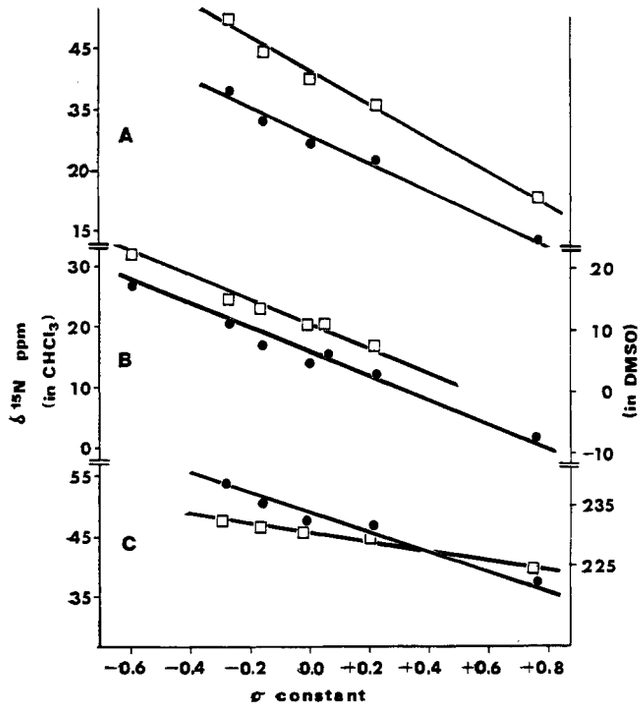


Figure 2. Correlation of ^{15}N chemical shifts with Hammett substituent constants: (A) para-substituted *N*-(arylmethylidene)cycloalkanamines in chloroform (●) and methanol, (□); (B) para-substituted *N*-(arylmethylidene)azanols in chloroform (□) and dimethyl sulfoxide (●); and (C) para-substituted 1-(arylmethylidene)-2-phenyldiazanes, where the scale for the N-1 shifts (●) is shown to the left of the graph, and for the N-2 values (□) to the right.

There is a complication with this interpretation, because we have found the ρ value for the Hammett correlation for *N*-(arylmethylidene)cyclohexanamine hydrotrifluoroacetates[24] to be nearly the same as the one for the unprotonated derivatives reported here. Clearly, if this similarity is as good as it seems to be, there can be no compelling reason to invoke significant shift effects produced by substituents in the 4 position of the phenyl ring as the result of changing the degree of mixing in states corresponding to n → π^* (or other) optical transitions involving π orbitals, because there is no unshared pair on the nitrogen in the protonated imines.

(b) *N*-(Arylmethylidene)azanols. Plots of the ^{15}N chemical shifts of several *N*-(arylmethylidene)azanols in chloroform and in dimethyl sulfoxide against Hammett σ constants are also shown in Figure 2. Least-squares analysis of the data for chloroform gave a slope of −17.7, intercept of 20.8, and r = 0.988. For dimethyl sulfoxide, the respective values were −17.3, 5.8, and 0.989. The analysis of the shifts of the *N*-(arylmethylidene)cyclohexanamines considered above also applies here.

However, additional insight can be gained from a plot of the nitrogen shieldings of the azanols in dimethyl sulfoxide (Table III) against the β-carbon shieldings of 4-substituted ethenylbenzenes.[10] The least-squares fit (Figure 3) has a slope of −2.3, an intercept of 271.0, and r = 0.985. This apparently linear ^{15}N–^{13}C shift correlation indicates that both nuclei respond similarly to polar substituents on the aromatic ring, although, as for the correlation of Figure 1, the ^{15}N shifts appear to be about twice as sensitive as ^{13}C shifts to substituent effects.

(c) 1-(Arylmethylidene)-2-phenyldiazanes. Unfortunately, because of poor solubility, it was not possible to record the spectra of the 1-(arylmethylidene)-2-phenyldiazanes

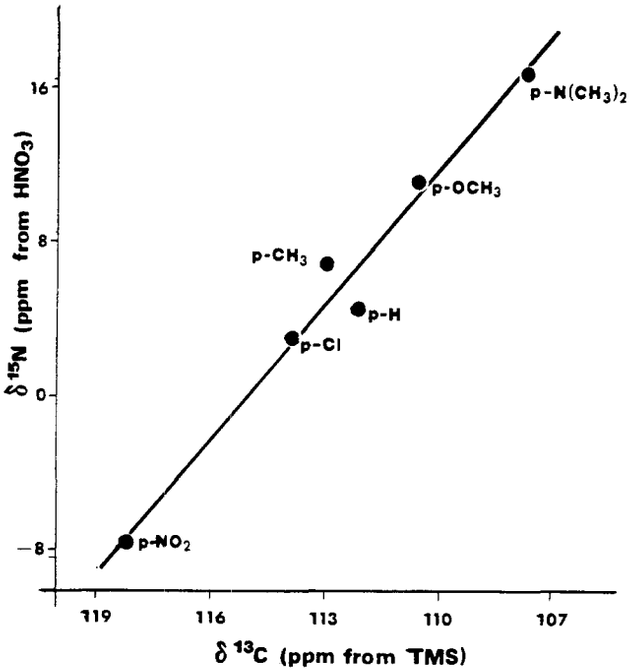
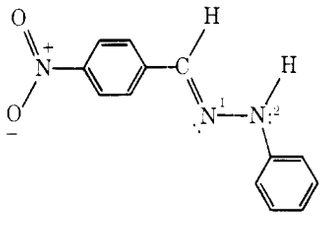
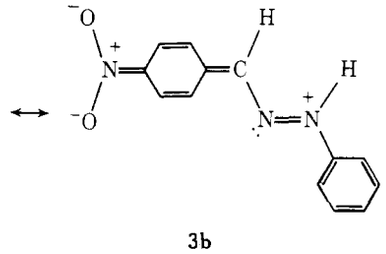


Figure 3. Correlation of β-alkenic carbon shieldings of para-substituted phenylethenes with ^{15}N shieldings of para-substituted *N*-(arylmethylidene)azanols.

(phenylhydrazones) in solvents other than dimethyl sulfoxide. A Hammett-type plot of the imino nitrogen shifts for the series of para-substituted derivatives is nonetheless shown in Figure 2. The line of best fit has a slope of −14.9, an intercept of 48.8, and a correlation coefficient of 0.984. The trends found for the ^{15}N shifts of oximes are evident in the data for the corresponding diazanes, and the imino nitrogen shifts of the diazanes are upfield by 25–30 ppm of the shifts in similarly substituted oximes. Interestingly, the N-2 chemical shifts are quite sensitive to para substituents on the benzene ring. The Hammett correlation of these shifts, also shown in Figure 2, has a slope of −8.0, intercept of 230.8, and r = 0.986. This pattern of sensitivity of N-2 shifts to substituent changes suggests that contributions of resonance structures, such as **3b,** with a 4-nitro group, are important to the N-2 chemical shifts. Contributions of forms such as **3b** also provide a qualitative explanation for the decreased sensitivity of the N-1 shifts of these diazanes to substituent changes compared to the other compounds studied here. This is because in the



3a



3b

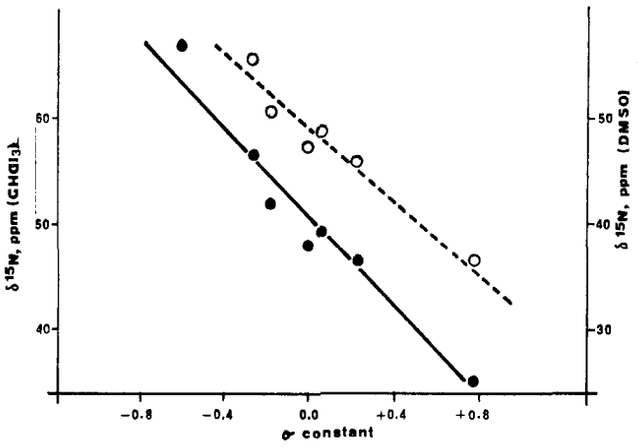
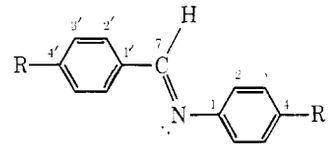


Figure 4. Correlation of ^{15}N chemical shifts of para-substituted *N*-(arylmethylidene)benzenamines with Hammett substituent constants. Separate ^{15}N shift scales are indicated for the two solvents, chloroform (●) and dimethyl sulfoxide (○), to the left and right of the figure, respectively. The methanol line is not shown because of the small number of points.

electron-pairing schemes **3a** and **3b,** N-2 has a greater difference of charge distribution and bonding than N-1.

The N-2 chemical shift of 1-(phenylmethylidene)-2-phenyldiazane is approximately 57 ppm downfield of the phenyl-substituted nitrogen shift of phenylhydrazine.[4] Part of this shift difference can be ascribed to the second-order paramagnetic effect brought about by the interaction of the nitrogen lone pair with the extended π system. Thus, there is a 14-ppm downfield shift in the nitrogen resonances associated with the change $C_6H_{11}\ddot{N}H_2 \rightarrow C_6H_5\ddot{N}H_2$, which can be attributed mainly to the interaction of the aromatic ring with the nitrogen unshared electrons. The other 40 ppm, or more, of the shift difference remains unexplained, especially because the corresponding shift change for a carbon attached to a double bond compared to a saturated carbon is only downfield by a few parts per million. Unlike diazanes whose conformations have been rather well studied,[31] little is known about the conformations about the =N—N< single bond of phenyldiazanes, and it is conceivable that stereoelectronic effects that depend on the disposition of adjacent lone-pair electrons in these systems would account for the additional shielding difference.

(d) *N*-(Arylmethylidene)arenamines. Early NMR studies[14] of various para-substituted *N*-(arylmethylidene)-benzenamines have shown that the H-7 proton chemical shifts correlate with Hammett σ constants for para substituents on the benzenecarbaldehyde moiety, but not for para substituents on the benzenamine, where, in fact, they have only a small



influence. This was reasonably attributed to lack of planarity of the benzenamine aromatic ring and CH=N bond in solution, as is indicated by x-ray data for the crystalline state.[32-34] However, Inamoto and co-workers[35] have demonstrated a Hammett correlation with ρ = −4.4 between the C-7 chemical shifts of the same derivatives and para substituents on the benzenamine ring. These researchers rationalized the apparently anomalous behavior of the H-7 chemical shifts as the result of substituent–field effects.[36]

The ^{15}N chemical shifts of seven para-substituted *N*-(arylmethylidene)benzenamines follow a Hammett relationship, as can be seen from Figure 4. The least-squares lines

have slopes of −16.5, −21.8, and −28.3, intercepts of 49.2, 50.6 and 56.6, and correlation coefficients of 0.976, 0.977, and 0.933 in dimethyl sulfoxide, chloroform, and methanol, respectively. The large negative ρ values have the same sign as the Hammett plots for the ^{13}C shifts of C-1, C-4, and C-7 for the same compounds.[35] The signs of the ρ values (except for that of C-7) accord with the earlier observation[35] that ρ values for each atom in a particular series of compounds appear to alternate in sign and decrease in magnitude as one progresses from the substituted atom along the conjugated framework. It is not possible to compare the absolute magnitudes of ρ for ^{15}N and ^{13}C nuclei because of the generally different sensitivities of the two nuclei to electronic effects.

The ^{15}N shifts of five para-substituted *N*-(phenylmethylidene)arenamines are generally small and do not appear to correlate with Hammett σ constants even though the scatter in the nitrogen shieldings is significantly larger than the experimental error of the measurements (see Table VI).

Similar behavior of the α-carbon shieldings of 4-substituted phenylethenes[10] suggests that the shielding of an α nucleus in an unsaturated group is insensitive to conjugation effects of substituents on the adjoining aryl ring. This could be because little difference in charge distribution and bonding at the α nucleus is expected as the result of electron delocalization in the π system. While the good correlation for the ^{13}C shifts of C-7 with changes in para substituents on the benzenamine ring indicates that there is a reasonable amount of conjugative interaction between the arenamine π system and the orbitals of the C=N bond, the ^{15}N results for these compounds suggest that there is little or no interaction of the aromatic ring with the nitrogen lone-pair electrons.

Solvent Effects. To this point, we largely have confined the discussion to the effects of various substituents within a particular series of structurally related molecules in a particular solvent. Substantial solvent effects have been observed for these compounds, but, unfortunately, limitations on solubility have prevented complete analysis of any of the series in more than two different solvents.

The ^{15}N chemical shifts of the *N*-(arylmethylidene)cyclohexanamines in methanol are 7.0–12.3 ppm upfield of the values for the same derivatives determined in chloroform. The corresponding shift differences for *N*-(arylmethylidene)-benzenamines are from 5.3 to 9.2 ppm. For comparison, the ^{14}N shift of pyridine moved 9-ppm upfield on dilution with methanol[37] and that of quinoline in methanol is 12.3-ppm upfield of its shift in chloroform.[38] The direction of the solvent shifts has general analogy in the ^{15}N shift changes produced on protonation of azine-type nitrogens.[38] This behavior suggests that hydrogen bonding is a major source of the shift changes found for strongly hydrogen-bonding solvents such as methanol. The smaller solvent effects observed for the *N*-phenyl series may be rationalized in terms of the inductive and electron-delocalizing influences of the phenyl group compared to cyclohexyl, thus limiting the extent of solvent interaction with the nitrogen unshared pair of electrons. There are only slight, downfield ^{15}N chemical shifts for these Schiff bases (see Tables V and VI) on changing solvent from chloroform to dimethyl sulfoxide despite the fact that hydrogen-bond association of chloroform with the carbonyl groups of amides is well established, as evidenced by ^{1}H as well as ^{15}N NMR spectroscopy.[38,39] However, chloroform is not really a strong hydrogen-bonding solvent and differences between methanol and dimethyl sulfoxide are not as large as with some other types of =N– compounds.

Solvent effects for the azanol derivatives are at first sight remarkably different from those for Schiff bases. There are large downfield shifts in dimethyl sulfoxide compared to chloroform. The solvent shift $\Delta\delta_{^{15}N}(CHCl_3\text{–}Me_2SO)$ ranges from 13.7 to 16.1 ppm. Formation of hydrogen bonds between the oxygen of dimethyl sulfoxide and the oxime group would account for a large portion of the solvent shift. Previous concentration studies[28] on the ^{15}N shift of cyclohexanone oxime in benzene have established intermolecular association of oxime molecules in that solvent. However, in a strong hydrogen-bond acceptor solvent, such as dimethyl sulfoxide, solute–solute interactions should be minimized and hydrogen bonding to the nitrogen unshared pair should become much less important, thus causing the observed downfield shift.

The nitrogen chemical shifts for the compounds studied here are generally linear with the Hammett σ constants which measure the electronic properties of substituents on the aromatic ring. It is interesting that the absolute magnitude of the ρ constants of these correlations becomes larger as the hydrogen-bonding ability of the solvent increases. Thus, ρ for the correlation of the *N*-(arylmethylidene)benzenamines is −16.5 in dimethyl sulfoxide, −21.8 in chloroform, and −28.3 in methanol. This holds true for correlations of the *N*-(arylmethylidene)cyclohexanamine shifts, where ρ is −21.3 and −26.3 in chloroform and methanol, respectively. Clearly, in addition to electron density and π-bond order changes at the nitrogen atom, electronic perturbations brought about by the influence of ring substituents affect hydrogen-bond interactions which can influence nitrogen shifts as well. The Hammett correlations in dimethyl sulfoxide should be useful to estimate shift changes without complications from hyrogen-bonding effects. Although the chloroform–dimethyl sulfoxide chemical-shift differences are relatively small, the Hammett correlations in the two solvents do suggest association of the chloroform with the nitrogen unshared pairs. Indeed, if one supposes a linear relationship of hydrogen-bond energies with the ρ for the ^{15}N chemical-shift changes,[40] then the energy of the chloroform interaction is about 40% of that of methanol.

Although the observed shift differences for oxime derivatives in chloroform and dimethyl sulfoxide are quite large, the ρ values of the Hammett correlations in these solvents are nearly the same. This is not expected from the results with the other compounds, but the oxime shifts in chloroform are clearly complicated by self-association, and, in the absence of data for ρ, where this type of intermolecular hydrogen bonding is not important, it seems unwise to speculate on the reasons for the lack of ρ changes with these solvents.

Registry No.—Methylamine, 74-89-5; ethylamine, 75-04-7; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; propylamine, 107-10-8; isobutylamine, 78-81-9; neopentylamine, 5813-64-9; 2-methyl-2-butylamine, 594-39-8; *p*-(dimethylamino)benzaldehyde, 100-10-7; *p*-anisaldehyde, 123-11-5; *p*-tolualdehyde, 104-87-0; benzaldehyde, 100-52-7; *p*-fluorobenzaldehyde, 459-57-4; *p*-chlorobenzaldehyde, 104-88-1; *p*-nitrobenzaldehyde, 555-16-8.

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Stabilities of Trivalent Carbon Species. 4. Electrochemical Reduction of Carbocations in Sulfuric Acid[1]

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The reduction of 11 stable carbocations in aqueous sulfuric acid was studied by rapid-scan triangular-wave cyclic voltammetry. For most cations, two one-electron waves are seen, corresponding to reduction to the radical followed by reduction to the hydrocarbon. The reduction potential of the first wave becomes more negative with increasing sulfuric acid concentration, but the second wave is independent of solvent composition. Differences between reduction potentials for different cations are constant in various solvents, implying similar solvation energies for the cations. The potential of the first reduction is used in an analysis of the ionization of alcohols. The analysis divides the ionization reaction into a bond dissociation and an electron-transfer reaction. The C–O bond dissociation energies increase in the order planar < triarylmethyl < cyclopropenyl alcohols. For planar or triarylmethyl alcohols, the free energy of ionization is independent of dissociation energy within each group and varies directly with the ionization potential of the corresponding free radical. Free energies of ionization of cyclopropenyl alcohols vary with both bond dissociation energies and radical ionization potentials. The second reduction potential measures the radical-anion energy difference and pK_a values of hydrocarbons may be estimated thereby.

The stabilities of very reactive trivalent carbon species, such as aliphatic anions,[4] antiaromatic[5,6] and antihomoaromatic,[7] ions and radicals, have been determined uniquely by electrochemical measurements. Breslow and his co-workers have measured reduction potentials of several carbocations using the techniques of rapid scan triangular wave cyclic voltammetry[5] and second harmonic alternating current voltammetry.[4,8] The reduction potentials for the conversions of cations to radicals ϵ_1 and radicals to anions ϵ_2 were used in a thermodynamic cycle to obtain pK_a values for hydrocarbons (e.g., cyclopropenes) whose corresponding anions are very unstable.

$$ROH \rightleftharpoons R^+ \rightleftharpoons R\cdot \rightleftharpoons R^- \rightleftharpoons RH$$

ΔG related to: pK_{R^+} ϵ_1 ϵ_2 pK_a

Two assumptions are implicit in this calculation: (1) the free energy change for conversion of carbinols to their corresponding hydrocarbons is constant for the series of compounds studied; (2) the medium effect which arises from measuring ionization equilibria and reduction potentials in different solvents is the same for all compounds studied.

We present results of a study of reductions of carbocations in aqueous sulfuric acid, the solvent used for the determination of pK_{R^+} values, which support the validity of the second assumption. Patterns of stabilities of trivalent carbon species of different structural types are also reported.

Aqueous sulfuric acid is a useful solvent for polarography,[9] and studies on the electrochemical behavior of a few carbocations in this medium have been reported previously.[6,7,10,11] In general, the choice of aqueous sulfuric acid as solvent pre-

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