butanedial was identified as the corresponding 2,4-DNP derivative.

G. Preparation of 2,4-DNP Reagent. Powdered 2,4-DNP (10 g) was suspended in 30 mL of methanol under stirring. To this was added cautiously 20 mL of concentrated H_2SO_4. The solution was filtered while it was warm and the filtrate was cooled.

Reactions under oxygen and air were done similarly.

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Electronic Substituent Effects on Nitrogen-15 Shieldings of *N*-(Arylmethylidene)cyclohexanamine Hydrotrifluoroacetates[1a]

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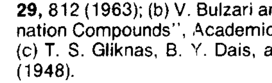
An earlier ^{15}N NMR study[2] of several series of para-substituted *N*-(arylmethylidene)amines 1 and 2 has shown that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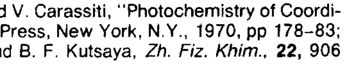
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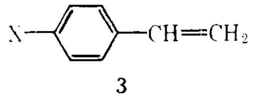
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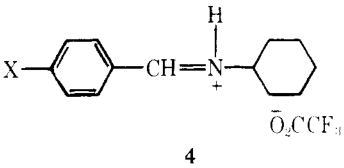
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the nitrogen shifts are sensitive to the electronic influence of the ring substituents (X), as reflected by the Hammett σ substituent parameters. Reasonable linear correlations could also be obtained for the nitrogen shifts of compounds in each series and the β-carbon shieldings of 4-substituted ethenylbenzenes 3, with the changes in the ^{15}N shifts generally being about twice that of the ^{13}C shifts with respect to the substituent effects. To determine whether the greater sensitivity of the nitrogen shifts arises predominantly from a substituent-induced perturbation of the nitrogen unshared pair of electrons, we have measured ^{15}N chemical shifts of a series of para-substituted *N*-(arylmethylidene)cyclohexanamine hydrotrifluoroacetates 4.

The natural abundance ^{15}N spectra were recorded on a Bruker WH-180 spectrometer operating at 18.25 MHz. The optimum conditions for observing imino nitrogens in *N*-(arylmethylidene)cyclohexanamines were a 70° pulse angle, a repetition rate of 30 s, and gated proton decoupling (no NOE). The conditions employed to obtain spectra of their corresponding hydrotrifluoroacetates were a 27° pulse angle, a repetition rate of 2 s, and continuous broad-band proton irradiation. The chemical shifts and one-bond ^{15}N–H coupling constants are summarized in Table I.

Table I. Nitrogen-15 Chemical Shifts of *N*-(Arylmethylidene)cyclohexanamines 2 and Their Hydrotrifluoroacetates 4 [a]

X	4 registry no.	chemical shift: chloroform[b]	chemical shift: trifluoroacetic acid ($^1J_{^{15}N-H}$, Hz)
OCH_3	68051-12-7	38.5	187.7 (91.1)
CH_3	68051-13-8	33.9	181.4 (92.0)
H	68051-14-9	30.2	177.4 (90.3)
Cl	68051-15-9	28.1	175.7 (88.5)
NO_2[c]	68051-16-1	14.7	164.1 (92.0)

[a] All chemical shifts are given in ppm upfield from an external 1.0 M $D^{15}NO_3$ capillary. Measured as 20 mol % solutions in chloroform and trifluoroacetic acid. [b] Data from ref 2. [c] δ $^{15}N(NO_2)$ = 6.8 ppm in chloroform; no signal observed in trifluoroacetic acid.

The ^{15}N shifts of *N*-(arylmethylidene)cyclohexanamines 2 in chloroform cover the range 14.7 to 38.5 ppm. When these compounds are dissolved in trifluoroacetic acid, there is a very large diamagnetic shift (~150 ppm) of the nitrogen resonances as expected for protonation of the nitrogen unshared electron pair, with the ^{15}N shift range becoming 164.1 to 187.7 ppm. Formation of the hydrotrifluoroacetate salts 4 is assured by observation of one-bond ^{15}N–H coupling constants which are of the magnitude expected for hydrogen attached to nitrogens which are sp^2 hybridized.[3] No trends are evident for these couplings with Hammett substituent parameters. No two-bond ^{15}N–C–H couplings were observed, and this is in accord with a previous investigation of structurally similar compounds which suggests that these two-bond couplings should probably be small (<1 Hz).[4]

The large upfield protonation shifts for the change 2 to 4 are best accounted for by changes in the paramagnetic screening contribution (σ_A^{para}), which appears to dominate the total screening of nitrogen nuclei.[5] The paramagnetic expression depends, in part, on contributions from the average electronic excitation energy, ΔE_{av}.[6] Thus, for the specific case of a nitrogen atom in a C–N double bond as in 1, mixing into the ground-state wave function in an external field of an electronic configuration corresponding to a low lying $n \rightarrow \pi^*$ transition is expected to lead to a paramagnetic circulation of electrons around the nitrogen and thereby decrease the shielding of the nitrogen nucleus. Because there is no unshared electron pair in the protonated imines, the ΔE_{av} term corresponding to this effect will be much less important. The extent of this paramagnetic contribution to the shielding of nitrogen nuclei in compounds containing C–N double bonds can be seen by comparing changes in ^{15}N and ^{13}C shieldings for the structural change $C_6H_5CH_2Y^*(H)_nR \rightarrow C_6H_5CH{=}Y^*(H)_{n-1}R$, where * denotes the nucleus undergoing the NMR transition. The shift to lower field (~250 ppm) for Y = ^{15}N for this change is about twice that for Y = ^{13}C.[7] However, when the imines are protonated and become isoelectronic with the corresponding phenylethenes, the downfield shifts of ^{15}N and ^{13}C nuclei associated with this change are then quite similar.

As we have said, the ^{15}N shieldings of *N*-(arylmethylidene)cyclohexanamines 2 correlate quite well with Hammett σ parameters, yet the ^{15}N shifts appear to be twice as sensitive

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as ^{13}C shifts in analogous carbon compounds to the electronic substituent effects.[2] The magnitudes of these ^{15}N and ^{13}C shift differences (up to 25 ppm) associated with changing the ring substituents are so large as to be clearly due to changes in the paramagnetic contribution for the screening constant. The basic assumption in these Hammett shift correlations is that, because the paramagnetic term depends on the π-electron density at the nucleus undergoing the transition, any inductive or conjugative interactions of the substituents which might affect the electronic distributions about that nucleus should have an important influence on its chemical shift. Even if this assumption is correct, then the substantially greater sensitivity of ^{15}N over ^{13}C shifts in these correlations might arise from additional shift effects produced by substituents as a result of changing the degree of mixing in states corresponding to $n \rightarrow \pi^*$ or other optical transitions involving π orbitals of the imines.

However, when the ^{15}N chemical shifts of our series of para-substituted *N*-(arylmethylidene)cyclohexanamines **2** are plotted against the corresponding shifts of the N-protonated hydrotrifluoroacetates **4**, it is found that there is a good overall linear correlation with a slope of 0.963 and a correlation coefficient of 0.994. The near unit slope indicates clearly that the effect of 4 substituents in the phenyl ring on the shifts is nearly the same for series **2** and **4**. We can only conclude on the basis of these results that the $n \rightarrow \pi^*$ contribution to the ^{15}N shifts in the **2** series is essentially constant and is *not* substantially influenced by substituent groups in the 4 position of the phenyl ring. This seems to be the only way to rationalize the fact that there is essentially no change in the effects of 4 substituents when the $n \rightarrow \pi^*$ contribution is cut off on conversion to the salt series **4**. Substituent influences on the unshared nitrogen electrons through interactions with the substituent groups involving the n and π orbitals should not be very large because the n orbital is essentially orthogonal to the p orbitals of the double bond system. It is much more likely that the substituents would influence the energy of mixing in of the π^* state (or other appropriate excited states), but this does not seem to be important.

Overlying the influence of the nitrogen unshared pair on the shifts is a considerable substituent effect which is associated with the conjugated π system made up of the phenyl and $-CH{=}N-$ (or $-CH{=}^+NH-$) groups and which responds in a rather simple way to 4 substituents, probably through changes in the π-electron densities and/or bond orders of the imine and immonium nitrogen. The fact that the ^{15}N shifts for *both* the **2** and **4** series seem to be inherently more sensitive to substituent effects than analogously situated carbons[8] is not easy to explain. Possible contributors are differences in bond lengths, polarizability, and nuclear charge.

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Micellar Catalysis of Proton-Transfer Reactions. 2.[1] Hydrolysis of Covalent *p*-Tolylsulfonylmethyl Perchlorate Catalyzed by Arenesulfinate Anions in the Presence of CTAB. Irrelevance of the Hydrophobicity of the Arene Moiety of the Sulfinate

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During the last decade, studies of catalysis and inhibition of chemical processes by micellar aggregates of surfactant molecules have developed beyond the qualitative stage and many of the recent results have now been summarized in pleasing reviews.[2] Nevertheless, there is still only limited insight into the factors which determine the catalytic efficiency of a particular surfactant aggregate. Recent work from these laboratories[1] has shown that the rates of arenesulfinate, formate, and hydroxide-catalyzed hydrolysis of covalent arylsulfonylmethyl perchlorates[3,4] (Scheme I) are greatly enhanced (by factors of 10^3–10^4) in the presence of micelles of cetyltrimethylammonium bromide (CTAB). Since electronic effects of substituents on the pK_A values of para-substituted benzenesulfinic acids are relatively small,[5] it could be anticipated that dynamic basicities within a series of $p\text{-}XC_6H_4SO_2^-$ ions (**2a**, X = CH_3; **2b**, X = H; **2c**, X = Br; **2d**, X = NO_2) solubilized by CTAB will be rather insensitive to electronic effects of X but might instead respond to the hydrophobicity of the substituent. The present study reports an attempt to find such a relationship. Hydrophobic fragmental constants as defined by Rekker[6] (f_X; X = CH_3, H, Br, NO_2) for the system octanol–water were employed to quantify relative hydrophobicities of the sulfinate anions **2a–d**.

Results and Discussion

Binding of Arenesulfinate Ions to CTAB. Since the efficiency of micellar CTAB catalysis will be directly affected by the strength of sulfinate–micelle interaction as well as by the location of the sulfinate ion in the micelles, we will first discuss these factors.

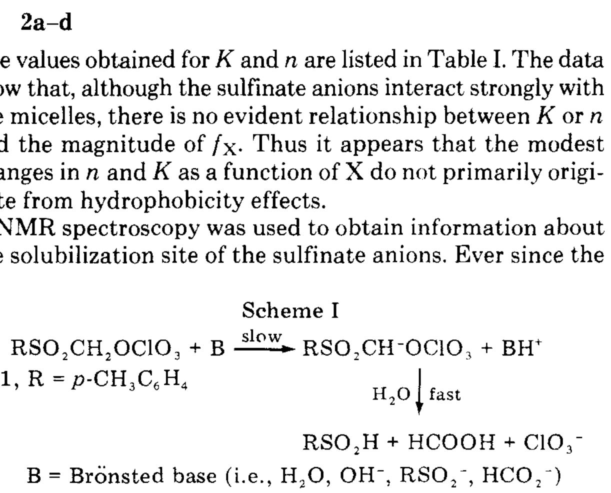
The binding between the sodium sulfinates **2a–d** and CTAB micelles was investigated by measuring the change in absorbance of **2a–d** in the presence of varying concentrations of CTAB according to the method of Riegelmann et al.[7] The plots were analyzed by using a Langmuir-type model as delineated by Sepulveda[8] (eq 1). Herein $(CTAB)_n$ is a portion of a micel consisting of *n* detergent molecules necessary for sorbing one sulfinate anion.

$$\underset{\mathbf{2a\text{–}d}}{p\text{-}XC_6H_4SO_2^-} + (CTAB)_n \overset{K}{\rightleftarrows} [(CTAB)_n \cdot p\text{-}XC_6H_4SO_2^-]$$

The values obtained for *K* and *n* are listed in Table I. The data show that, although the sulfinate anions interact strongly with the micelles, there is no evident relationship between *K* or *n* and the magnitude of f_X. Thus it appears that the modest changes in *n* and *K* as a function of X do not primarily originate from hydrophobicity effects.

NMR spectroscopy was used to obtain information about the solubilization site of the sulfinate anions. Ever since the

Scheme I



$$RSO_2CH_2OClO_3 + B \xrightarrow{slow} RSO_2CH^-OClO_3 + BH^+$$

1, R = $p\text{-}CH_3C_6H_4$

$$\xrightarrow[H_2O]{fast} RSO_2H + HCOOH + ClO_3^-$$

B = Brönsted base (i.e., H_2O, OH^-, RSO_2^-, HCO_2^-)

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