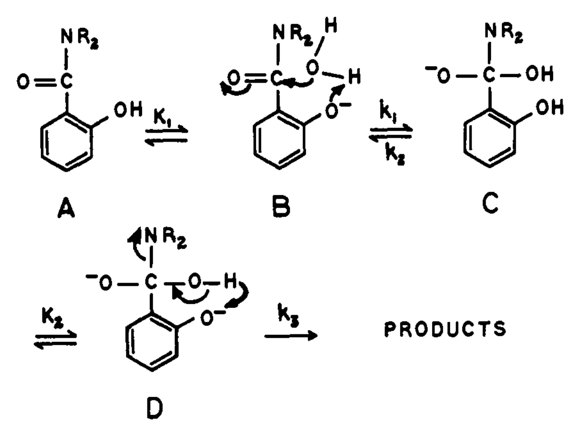

Figure 1. Mechanism of hydrolysis of *N*-salicylylpyrrole (F. M. Menger and J. A. Donohue, *J. Amer. Chem. Soc.*, **95**, 432 (1973)).

The rate law (eq 6) corresponding to the proposed mechanism can be derived (eq 1–5) by application of the steady-state method.

$$-\frac{d[A_T]}{dt} = k_3[D] \qquad (1)$$

$$[A_T] = [A] + [B] \qquad (2)$$

$$\frac{d\{[C] + [D]\}}{dt} = k_1[B] - k_2[C] - k_3[D] = 0 \qquad (3)$$

$$K_1 = [B]/[A][OH^-] \qquad (4)$$

$$K_2 = [D]/[C][OH^-] \qquad (5)$$

$$-\frac{d[A_T]}{dt} = k[A_T] = \frac{k_1k_3K_1K_2[OH^-]^2[A_T]}{\{1 + K_1[OH^-]\}\{k_2 + k_3K_2[OH^-]\}} \qquad (6)$$

$$k = k_1 \text{ for } K_1[OH^-] \gg 1 \text{ and } k_3K_2[OH^-]/k_2 \gg 1 \qquad (7)$$

Menger and Donohue on the basis of an incorrect rate expression indicated that the acid dissociation constant for the tetrahedral intermediate, C, can be obtained. The rate law for the mechanism proposed by Menger and Donohue is given in eq 6 and indicates that the dissociation constant, K_2, cannot be evaluated from their kinetic data apart from k_3K_2/k_2. A value of 3.2×10^{-3} sec^{-1} for the rate constant for the reaction of the *N*-salicylylpyrrole anion, B, with water, can be obtained from the kinetic data[1] as the limiting value of k at high pH (eq 7). Using this value for k_1, a value of 1.1×10^4 for k_3K_2/k_2, and the pK_a value of 8.59 for *N*-salicylylpyrrole reported by Menger and Donohue, a plot of k (theoretical) *vs*. pH is compared with the experimental data in Figure 2.

Although an interpretation in terms of an ionization of a steady-state intermediate is probably correct, it is not required by the kinetics of the reaction. The mechanism may be written as

$$A + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} B + H_2O$$

$$B + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$$C + OH^- \xrightarrow{k_4} \text{products}$$

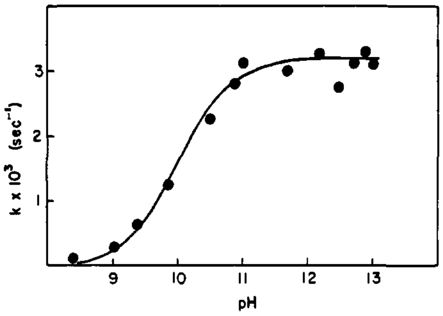

Figure 2. Theoretical variation of observed rate constant, k, with pH. Data points are taken from F. M. Menger and J. A. Donohue, *J. Amer. Chem. Soc.*, **95**, 432 (1973).

The steady-state rate law corresponding to this mechanism is

$$-\frac{d[A_T]}{dt} = \frac{k_1k_4K_1[OH^-]^2[A_T]}{\{1 + K_1[OH^-]\}\{k_2 + k_4[OH^-]\}}$$

Thus, a measurable acidity of a steady-state intermediate is not entirely justifiable by the kinetic data.

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Substituent-Induced ^{13}C Chemical Shifts. A Perturbation Approach

Sir:

It is generally agreed that ^{13}C chemical shifts are proportional to the total electron density at carbon in systems where bond polarization effects and the presence of low-lying energy states are relatively unimportant.[1,2] Accordingly, the recent report[3] that substituent-induced variations in the ^{13}C shifts (SCS) of trans 1-substituted butadienes alternate *in magnitude and sign* along the carbon chain may be interpreted as verification of the alternating induced charge (AIC) effect first noted in the CNDO calculations of Pople and Gordon.[4] Application of first-order perturbation theory to the calculation of substituent-induced chemical shifts indicates (1) that the AIC effect appears to be a general phenomenon, at least for carbon in π systems, and (2) that there should exist a linear correlation between $\Delta\delta_c$ in derivatives and long-range coupling constants in parent hydrocarbons.

The effect of a substituent on the electron distribution within a π system can be assessed in terms of perturbational molecular orbital (PMO) theory.[5] Assuming the substituent not to interact mesomerically with the π system, its primary effect will be to alter the effective electronegativity of the atom to which it is bound. Within the Hückel approximation, this case

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[1] J. E. Bloor and E. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

[2] T. Tokuhiro and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).

[3] O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972).

[4] J. A. Pople and M Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

[5] M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapter 6, and references therein.

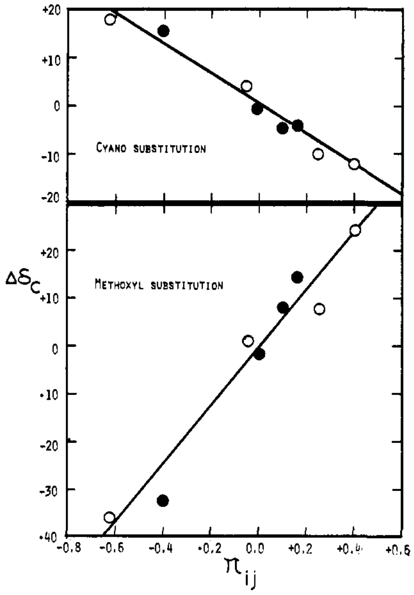

Figure 1. ^{13}C SCS plotted against atom–atom polarizibilities in benzene (filled circles) and butadiene (open circles).

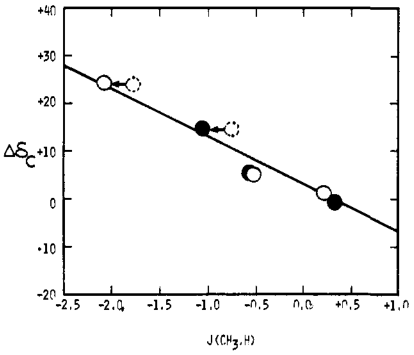

Figure 2. Alkoxyl SCS plotted against $J(CH_3,H)$ in toluene (filled circles) and 1,3-pentadiene (open circles). Arrows indicate −0.3 Hz correction for σ-electron contribution to allylic couplings.

can be accommodated by a change in the Coulomb integral at carbon.

If a substituent attached to C_i produces a change ($\Delta\alpha_i$) in the Coulomb integral of that carbon, the first-order correction to the electron density at some other position (C_j) is

$$\Delta q_j = 4\Delta\alpha_i\pi_{ij} \tag{1}$$

The atom–atom polarizibility, π_{ij}, is defined by

$$\pi_{ij} = \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{unocc}} \frac{a_{i\mu}a_{i\nu}a_{j\mu}a_{j\nu}}{E_\mu - E_\nu} \tag{2}$$

where the a's are atomic orbital coefficients in the molecular orbitals μ (unoccupied) and ν (unoccupied), and the E's are orbital energies. Since ^{13}C chemical shifts are proportional to electron density, we can write

$$\Delta\delta_{cj} = \kappa\Delta\alpha_i\pi_{ij} \tag{3}$$

implying that, for a given substituent ($\Delta\alpha_i$ fixed), both the magnitude and sign of $\Delta\delta_j$ are controlled by π_{ij}. In agreement with this interpretation, plots of $\Delta\delta_j$ against π_{ij} for a given substituent are linear (Figure 1).[6]

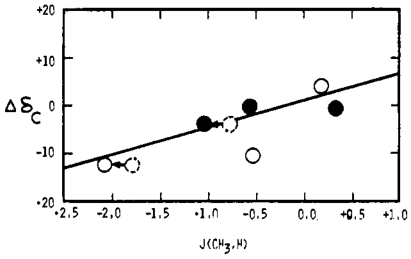

Figure 3. Cyano SCS plotted against $J(CH_3,H)$ in toluene (filled circles) and 1,3-pentadiene (open circles). Arrows indicated −0.3 Hz correction for σ electrons contribution to allylic couplings.

Interestingly, there also exists a connection between the AIC's and long-range coupling constants. The theoretical expression for the coupling constant between two nuclei, i and j, in a π system can be written, with a number of simplifications, as[7]

$$J_{ij} = \kappa'\pi_{ij} \tag{4}$$

where κ' is a collection of constants, leading to the expectation that

$$\Delta\delta_{cj} = \kappa''\Delta\alpha_i J_{ij} \tag{5}$$

Hence the substituent-induced chemical shifts should exhibit a linear correlation with the π-electron contribution to the coupling constant between C_i and C_j.

Although the CC coupling constant data necessary to test eq 5 are not readily accessible, the relation can be verified using long-range proton–proton coupling constants.

Long-range HH coupling constants and the factors affecting their magnitudes and signs have been extensively investigated,[8] and it has been concluded that: (1) their magnitudes are dominated almost entirely by the π contribution; (2) their signs are negative if the protons are separated by an even number of bonds and positive if separated by an odd number.

This, in conjunction with eq 5, immediately leads to the predictions of both the AIC effect and the observed alternation of ^{13}C SCS.

The relationship is quantitatively applicable. Figures 2 and 3 are graphs of $\Delta\delta_j$ in trans 1-substituted butadienes[3] and monosubstituted benzenes[9] (for methoxyl and cyano substitution, respectively) *vs.* $J(CH_3,H)$ in toluene[10] and *trans*-1,3-pentadiene,[11] and as expected, very good linear correlations result.

The significance of these observations is twofold. First, some light is shed on the basic mechanism of the AIC effect, and these results provide the basis for a semiempirical theory of substituent-induced ^{13}C chemical shifts which is currently under investigation and will be developed in future papers in this series. Secondly, since the slopes of the correlation lines for individual substituents are a measure of the magnitude of the perturbation, hence of the degree of admixture of different symmetry characteristics in the highest oc-

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(6) Atom–atom polarizabilities taken from: C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965.

(7) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(8) (a) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); (b) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 767 (1969); (c) D. J. Sardella and G. Vogel, *J. Phys. Chem.*, **74**, 4532 (1970).

(9) W. B. Smith and D. L. Deavenport, *J. Magn. Resonance*, **7**, 364 (1972).

(10) K. L. Williamson, D. Kostelnik, and S. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968).

(11) A. L. Segre, L. Zetta, and A. Di Corato, *J. Mol. Spectrosc.*, **32**, 296 (1969).

cupied molecular orbital, it may be that studies of ^{13}C SCS will provide a set of reactivity parameters measuring the ability of a substituent to alter the magnitudes of symmetry-imposed activation barriers.[12-14]

[12] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

[13] J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, 5, 402 (1972).

[14] The explanation proposed by J. E. Baldwin and A. H. Andrist (*J. Amer. Chem. Soc.*, 93, 3289 (1971)) for the existence of a linear correlation between electronic transition energies of a series of cyclic olefins and the activation energies for their thermal isomerizations can be viewed as perturbation of a parent olefin (π_{ii} remains constant) by various alkyl substituents ($\Delta\alpha_j$ is allowed to vary). It seems consistent with the approach proposed here, except for the specific probe chosen to monitor the magnitude of the perturbation imposed on the system.

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Received February 14, 1973

Regarding Heats of Solution of Gaseous Anilinium and Pyridinium Ions in Water and Intrinsic Basicities in Aqueous Solution[1]

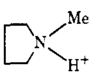
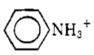
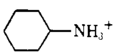
Sir:

Accurate evaluation of the (relative) heats of solution ($-\Delta H_S°_{(BH^+)}$, kcal/mol) of NH_4^+ and of 20 aliphatic ammonium ions from the gas phase to dilute aqueous solution has recently shown[2] that there exist four nonoverlapping ranges, according to classical categories: NH_4^+, 84.0; primary ammonium, 75.0–78.0; secondary ammonium, 70.0–73.0; and tertiary ammonium, 62.0–65.0. The remarkably distinct increase in $-\Delta H_s°_{(BH^+)}$ values with increasing number of N-H protons in BH$^+$ was ascribed to predominant $NH^+\cdots OH_2$ hydrogen bonding contributions of about 6–7 kcal.

We wish to report here that the results of a similar evaluation of the heats of solution of aromatic cations, *e.g.*, pyridinium and anilinium ions, follow the same scheme. Values of $-\Delta H_s°_{(BH^+)}$ are[3] (primary) $C_6H_5NH_3^+$, 76.0; (tertiary) $C_5H_5NH^+$, 64.0; and 4-CH_3-$C_5H_4NH^+$, 62.0. These results are of profound significance with respect to the extents of proton transfer equilibria in gas, aqueous, and other phases. Thus, the 20 kcal more exothermic heat of solution of $NH_4^+{}_{(g)}$ than $C_5H_5NH^+{}_{(g)}$ (due largely to the cationic hydrogen bonding) is the leading term accounting for the pronounced inversion in base strengths between the gas and aqueous phases;[4] C_5H_5N is about 11 powers of ten (in pK_A units) *more* basic than NH_3 toward $H^+{}_{(g)}$ but is about four powers of ten *less* basic than NH_3 toward $H^+{}_{(aq)}$.

Equally important is the comparison of base strengths for BH$^+$'s of the same or nearly the same $\Delta H°_{s(BH^+)}$. Simplification results from consideration of the effects of "degree of saturation" of carbon chains on base strength. Table I shows typical results for three representative pairs of nitrogen bases in the gas and aqueous phases. It is clearly evident that pairs of the same type, *i.e.*, with the same NH$^+$ and carbon numbers and similar frameworks, have very similar values of $\Delta H_s°_{(BH^+)}$, and, in turn, base strengths prevail in aqueous solution which are remarkably similar to those in the gas phase. The paired $\delta_R\Delta G_i°$ values for the relatively large effects of changing degrees of saturation are quantitatively only 10–20% smaller in water than in the gas phase. This result clearly indicates that there *are not* unusual (polarization or other) interactions associated with the different degrees of saturation of the carbon chain which are uniquely manifest in the gas phase. Instead, the large polarization and inductive effects which are frequently evident in the gas phase[2,5] may be masked almost completely in aqueous solution

Table I. Heats of Solution and Relative Gas- and Aqueous-Phase Acidities for Appropriate Pairs of Nitrogen Conjugate Acids Showing the Effects of Degree of Saturation[a]

Pair no.[b,c]	BH$^+$	$-\Delta H_s°_{(BH^+)}$[d]	$\delta_R\cdot\Delta G_i°_{(g)}$	$\delta_R\cdot\Delta G_i°_{(w)}$	$\delta_R\cdot\Delta H_i°_{(w)}$
1		73.0	−4.3	−3.88	−2.98
	$Me_2NH_2^+$	73.0	(0.0)	(0.00)	(0.00)
2		64.0	−8.3	−7.16	−4.25
		62.0	(0.0)	(0.00)	(0.00)
3		76.0	−9.6	−8.16	−7.19
		76.0	(0.0)	(0.00)	(0.00)

[a] Symbolism is as previously used except $\delta_R\Delta P$ refers to the standard thermodynamic property for ionization of the unsaturated BH$^+$ relative to the saturated member. Units are kcal/mol. [b] For pair 2, the "unsaturation effect" may be ascribed to effects of hybridization changes at N and C, *cf.* ref 8. [c] For pair 3, the "unsaturation effect" may be ascribed to a combination of inductive and resonance effects. According to an analysis of $\delta_R\Delta G_i°_{(w)}$ by Wepster, these effects contribute almost equally (1/2 each) to the total: B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 71, 1171 (1952). [d] $-\Delta H_s°_{(BH^+)} = 84.0 - [\delta_R\Delta H_i°_{(g)} + \delta_R\Delta H_s°_{(B)} - \delta_R\Delta H_i°_{(w)}]$, which is eq 7 of ref 2a (with NH_3 the reference base). Values of $\delta_R\Delta H_i°_{(g)}$ have been obtained by us from the $\delta_R\Delta G_i°_{(g)}$ results from pulsed icr measurements in a trapped ion cell as described in ref 2a except values for ethylenimine and *N*-methylpyrrolidine are from ref 8. Values of $\delta_R\Delta H_s°_{(B)}$ and $\delta_R\Delta H_i°_{(w)}$ (as well as $\delta\Delta_R G_i°_{(w)}$ for aliphatic amines were taken from a recent tabulation by F. M. Jones III (Ph.D. Thesis, University of Pittsburgh, 1970). For pyridines, these values were obtained from L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 82, 3828, 3831 (1960); for aniline $\delta_R P_i°$ values are from J. W. Larson and L. G. Hepler in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie Ed., Marcel Dekker, New York, N. Y., 1969, p 14; $\delta_R\Delta H_{s(B)}$ is from the heat of vaporization listed by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 283, and the heat of solution of liquid aniline in water obtained by Dr. J. F. Wolf; for cyclohexylamine $\delta_R\Delta H_{s(B)}$ is from the heat of vaporization estimated by the equation of Jones (*loc. cit.*, p 270) and the heat of solution of the liquid amine also obtained by Dr. Wolf.

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[1] This work was supported by the National Science Foundation.

[2] (a) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 94, 4724 (1972); (b) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, 94, 4726 (1972).

[3] For basis and references *cf.* footnote *d* of Table I.

[4] M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 94, 1369 (1972); J. P. Briggs, R. Yamdagni, and P. Kebarle, *ibid.*, 94, 5128 (1972).

[5] (a) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, 94, 4728 (1972); (b) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, 93, 3914 (1971).