A Scale of Directional Substituent Polarizability Parameters from ab Initio Calculations of Polarizability Potentials[1]

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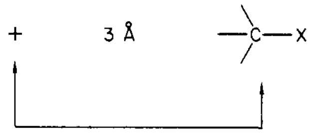
The relative gas-phase acidities and basicities of alkyl-substituted amines,[2] mercaptans,[3] alcohols,[2] and phenols[4] have been shown to be strongly dominated by the charge-induced dipole stabilization of the ion formed by protonation or deprotonation (the substituent polarizability effect[2]). When the alkyl substituent is nonconjugated, the observed acidities or basicities relative to the unsubstituted (H) compound can be attributed approximately quantitatively to the polarizability effect since recent experimental[5] and theoretical[6] evidence indicates that no significant inductive effects are involved. For poorly solvated ions, the substituent polarizability effect can contribute to basicities and acidities in solution.[7] Some success has been reported[8] in correlations of substituent polarizability effects on gas-phase acidities using bulk substituent polarizabilities.

We report here that the directional electrostatic polarization potentials (PP),[9] calculated at the 3-21G//3-21G level[10a,b] set[9] for extended series of CH_3X and HX molecules, provide a definition of a substituent polarizability parameter scale (symbolized as σ_α). The PP values have been obtained by using the following linear arrangement:



Values of $\Delta PP = \sigma_\alpha$ are given in Table I ($\Delta PP = PP_{CH_3X} - PP_{CH_3H}$). Values of PP have also been calculated for H–X molecules (in the same orientation) with the positive charge 2.0, 3.0, and 4.0 Å from the H.[11] The polarization potentials clearly reflect the total number of electrons of the substituent, their proximity to the charge, and the effective nuclear charges that act upon them.

Table I. Polarization Potentials (PP) Calculated for CH_3X Relative to CH_3H from ab Initio 3-21G//3-21G Calculations[a]

X	$\sigma_\alpha \equiv PP(CH_3X) - PP(CH_3H)$[b]	X	$\sigma_\alpha \equiv PP(CH_3X) - PP(CH_3H)$[b]
F	+0.13	N_3	–0.49
H	0.00[d]	C_2H_5	–0.49
OH	–0.03	C_3H_7	–0.54
NH_2	–0.16	$CH{=}CH_2$	–0.50
OCH_3	–0.17	SH	–0.55
CF_3	–0.25	$COCH_3$	–0.55
NO_2	–0.26	$C{\equiv}CH$	–0.60
NC	–0.33	i-C_3H_7	–0.62
CH_3	–0.35	SO_2CH_3	–0.62
CO_2H	–0.42	SCH_3	–0.68
Cl	–0.43	CCl_3	–0.70[c]
$N(CH_3)_2$	–0.44	$Si(CH_3)_3$	–0.72
CN	–0.46	t-C_4H_9	–0.75
CHO	–0.46	C_6H_5	–0.81

[a] Positive charge is on line with CH_3X and CH_3X bonds at 3.0 Å from C. [b] In kcal/mol. [c] From HX calculations. [d] PP of CH_3H is –0.98 kcal/mol.

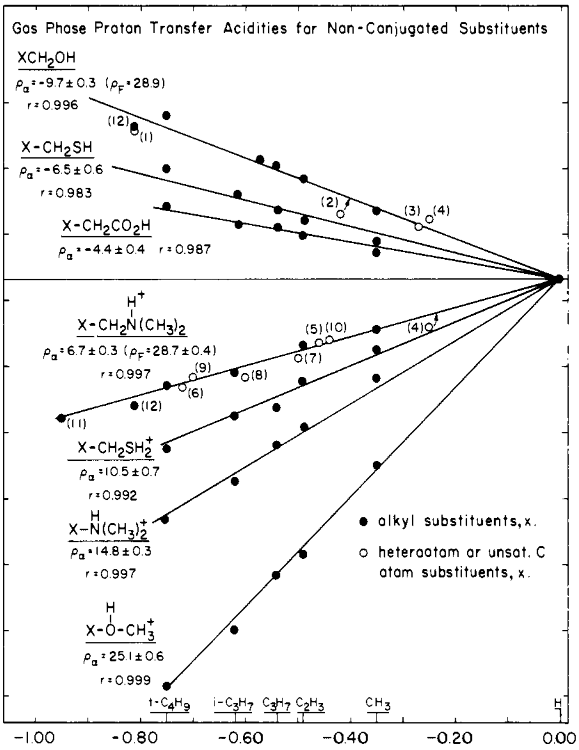


Figure 1. Correlation of the effects on gas-phase acidities of unconjugated substituents with the σ_α substituent directional polarizability parameter obtained from calculations of the relative polarization potentials, $PP_{CH_3X} - PP_{CH_3H}$. Ordinate: $-\delta\Delta G^\circ{}_g$, kcal/mol (for alkyl substituents); for others $-\delta\Delta G^\circ{}_g - \sigma_F\rho_F$. Abscissa: $PP_{CH_3X} - PP_{CH_3H}$ (at 3 Å) $= \sigma_\alpha$, kcal/mol. Open circle numbers denote the substituents: (1) C_6H_5; (2) CH_3OCH_2; (3) HCF_2; (4) CF_3; (5) CN; (6) $Si(CH_3)_3$; (7) $H_2C{=}CH$; (8) $HC{\equiv}C$; (9) CCl_3; (10) $N(CH_3)_2$; (11) c-C_6H_{11}; (12) 1-adamantyl.

Figure 1 shows the excellent linear relations obtained for *nonconjugated* alkyl substituents between the relative gas-phase acidities plotted vs. corresponding σ_α values. The correlation equation is $-\delta\Delta G^\circ = c + \rho_\alpha\sigma_\alpha$, where ρ_α is a reaction constant (slope of the regression line in Figure 1). Both the standard deviations of the correlations and the residual intercepts (c) are 0.1–0.4 kcal/mol for all series, which are approximately equal to the experimental errors in the data. Further, since $-\delta\Delta G^\circ$ is

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(11) The latter PP values give linear correlations (R^2 = 0.945 or greater) with the corresponding PP values for CH_3X.

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the alkyl substituent effect (relative to X = H) on the acidity of either HA or of BH^+, the ρ_α values are negative for neutral acids but positive for BH^+ acids.[2,7]

Unconjugated heteroatom or unsaturated carbon atom substituents give rise to substituent field/inductive effects (F).[7b] The F effects can be removed through the use of the dual parameter relationship: $-\delta\Delta G^\circ = c + \sigma_\alpha\rho_\alpha + \sigma_F\rho_F$, where ρ_α and ρ_F are the corresponding reaction constants. Values of the required σ_F parameters have been independently evaluated under conditions appropriate to the gas phase.[4b,5d,12] The use of this equation is shown for two typical gas-phase acidity series in Figure 1 (open circle points). The applicability and precision of fit of σ_α values for heteroatom and unsaturated carbon substituents are illustrated for these by the linear relationships which result from plotting $-\delta\Delta G^\circ{}_g - \sigma_F\rho_F$ vs. corresponding σ_α values.[15,16]

The ρ_F and ρ_α values given in Figure 1 show the expected trends resulting from increased distances of separation. In full papers the widespread utility of this approach will be reported.

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(12) Values of σ_F used are zero for all alkyl substituents and for others: C_6H_5, 0.10; CH_3OCH_2, 0.12; HCF_2, 0.34; CF_3, 0.44; CN, 0.60, $Si(CH_3)_3$, −0.02; $H_2C{=}CH$, 0.06; $HC{\equiv}C$, 0.23; CCl_3, 0.44; $N(CH_3)_2$, 0.10. Values of σ_α for CH_3OCH_2, HCF_2, $c\text{-}C_6H_{11}$, and 1-adamantyl have been estimated.

(13) The result shown in Figure 1 that $1.00 \neq \rho_\alpha(XCH_2SH_2^+)/\rho_\alpha(XCH_2SH) = 1.6$ does not support the previous attempt[14] to evaluate P and F effects of alkyl substituents.

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(15) Deviations of the open circle points from the regression lines, of course, include errors in the $\sigma_F\rho_F$ as well as $\sigma_\alpha\rho_\alpha$ relationships.

(16) Values of $-\Delta G^\circ{}_g$ for HA acidities which are not given in ref 3, 4, or 18 have been obtained as described in ref 4b.

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Creutz-Taube Ion: A Model for the EPR *g* Tensor Which Includes the Bridging Ligand

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The Creutz-Taube ion, a pyrazine-bridged mixed-valence dimer of ruthenium, $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$, has been the center of controversy for the last 17 years.[1-9] One important piece of its puzzle which must be accounted for is the observed anisotropy of the EPR g tensor.[1-8] Here we report the first model to predict successfully the components of the *g* tensor which also includes essential features of the pyrazine bridging ligand.

We adopt a three-site, purely electronic model Hamiltonian given by

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{cov}} + \sum_k(\hat{H}_{\text{tet}}{}^k + \hat{H}_\rho{}^k + \hat{H}_{\text{SO}}{}^k) \qquad (1)$$

$$\hat{H}_{\text{cov}} = \sum_\mu \alpha|\pi^{*u}\rangle\langle\pi^{*\mu}| + \sum_k\sum_\mu J\{|xz_k{}^\mu\rangle\langle\pi^{*\mu}| + |\pi^{*\mu}\rangle\langle xz_k{}^\mu|\} \qquad (2)$$

$$\hat{H}_{\text{tet}}{}^k = (D/3)(\hat{L}_z{}^2 - {}^1\!/_3L(L+1))_k \qquad (3)$$

$$\hat{H}_\rho{}^k = (E/12)(\hat{L}_+{}^2 + \hat{L}_-{}^2)_k \qquad (4)$$

$$\hat{H}_{\text{SO}}{}^k = \xi(\hat{L}_z\hat{S}_z + {}^1\!/_2\hat{L}_+\hat{S}_- + {}^1\!/_2\hat{L}_-\hat{S}_+)_k \qquad (5)$$

where $\hat{H}_{\text{cov}}$ contains the strong coupling between one π^* state on the bridging ligand and the $4d_{xz}$ orbitals on the two Ru ions. J is the coupling constant for this interaction and α is the energy gap between the parent π^* state and the parent $4d_{xz}$ orbitals. μ is the spin index (+ or −) and k (=L or R) labels the left and right Ru ion orbitals. D is the tetragonal splitting, E the rhombic splitting, and ξ the spin-orbit coupling.[10]

Spin-orbit coupling on the bridge is neglected and the π^* state is assumed to be orthogonal to all of the Ru 4d orbitals. $\hat{H}_{\text{cov}}$ is taken to be of the one-electron type, and only $|xz_L\rangle$ and $|xz_R\rangle$ are assumed to be coupled via the bridging ligand.

Of the five Hamiltonian parameters α, J, D, E, and ξ, we calculate four of these—α, J, D, and E—from a first-principles MO calculation by the HFS-DVM method.[11] The values for the parameters correspond to a delocalized (D_{2h}) ground state.[9] Since this is a spin-polarized calculation, different values for the parameters are obtained for spin up ↑ and spin down ↓ electrons. Each parameter was obtained by averaging the values found for L↑, L↓, R↑, and R↓ Ru electrons in the converged ground state. The results are given in the last column of Table I. The nonrelativistic HFS-DVM does not give the spin-orbit coupling ξ. This we take as our one fit parameter.

The MO calculations[11,12] have shown that the basis orbitals $|xz_L\rangle$, $|\pi^*\rangle$, and $|xz_R\rangle$ form linear combinations resembling the bonding, nonbonding, and antibonding MO's of the Hückel allyl radical, and we label them $|B\rangle$, $|N\rangle$, and $|A\rangle$. In the mixed-valence species, the $|N\rangle$ state is half-occupied. We diagonalize eq 2 and write expressions for the three energy gaps ($E_A - E_N$), ($E_N - E_B$), and ($E_A - E_B$) in terms of the two parameters α and J. Using the numerical values for these energy gaps obtained from the converged ground state in our MO calculation, we solve for α and J with two of them and the third provides a check.

From standard methods,[10] we obtain the components of the *g* tensor as matrix elements of the ground-state Kramers doublet states. Values for the spin-orbit coupling in the range ξ = 600–750 cm^{-1} give qualitatively reasonable *g* values. Our best fit was obtained for ξ = 690 cm^{-1}. Table I compares the experimental *g* values with those obtained from the present and previous models.

We caution that our tetragonal splitting, albeit reasonable, should not be taken too seriously. It is of the order of the error in the HFS-DVM procedure. We have tried a series of values for the tetragonal splitting in the range $|D|$ = 0–800 cm^{-1}. For D = −800 cm^{-1}, the corresponding g values are qualitatively reasonable (g_x and g_y change by 10–15%, while g_z stays the same).

The best fit value for the spin-orbit coupling, 690 cm^{-1}, is smaller than that calculated earlier for the Ru^{3+} ion (1200 cm^{-1})[13] and somewhat smaller than the value of 1000 cm^{-1} used in previous models of this type. In part, this can be accounted for by the

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