Ab initio calculations of field substituent parameters and evaluation of substituent parameters through substituent effects on stability of ketenimines, isocyanides, and nitriles

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Field substituent parameters of 26 substituents were calculated by *ab initio* calculations at the level of CBS-4M. The field substituent parameters, along with resonance substituent parameter σ_R, group electronegativity ι, and polarizability parameter σ_α, correlate well with stabilization energies (SE) of ketenimines, isocyanides, and nitriles, providing useful information about substituent electronic effects on the stability of ketenimines, isocyanides, and nitriles.

Introduction

The Hammett equation has been one of the most important and popular means to study reaction mechanism.[1] Correlations of substituent electronic effects with the rates and equilibria of organic reactions successfully predict the reaction mechanism of many reactions.[2] Several substituent parameters have been established and are widely used in organic chemistry.[1,3–6] In addition, the substituent parameters have been widely used to predict quantitative structure–activity relationships for interactions of organic compounds with living systems.[1]

At the beginning, Hammett introduced one substituent parameter only.[1] Later, the electronic substituent parameter was divided into two substituent parameters (resonance and inductive substituent parameters).[4d] In 1987, the electronic substituent parameter was further divided into four electronic substituent parameters and they are resonance, field, electronegativity, and polarizability substituent parameters.[7]

The resonance and field substituent parameters were established experimentally in several models,[4] but there are many disadvantages for them, such as difficulty in preparation of a model structure with a variety of substituents, solubility of the model compounds in solvents, and experimental errors. Theoretical calculations of the substituent parameters have been done in several models by *ab initio* calculations,[3] but the methods and basis sets they used are too low to be accurate.

Making a database of the substituent parameters is an important task, and accuracy and easy availability of the substituent parameters should be key points for a good database. In this study, we used high-level *ab initio* calculations to obtain field substituent parameters and evaluated them along with three other substituent parameters through substituent effects on the stability of ketenimines, isocyanides, and nitriles. The model structure we used to obtain the field substituent parameters is 4-substituted quinuclidinium ion **1** and the physical property we tried to calculate is their deprotonation energy. There are three reasons why we used the model structure for the field substituent parameters: (1) there are four σ-bonds between the probe and the substituents, so there is very little resonance effect between them; (2) the substituents are far away from the probe, so it is very hard for the substituents to influence the probe by electronegativity; (3) the rigid quinuclidine structure reduces the number of possible conformations.

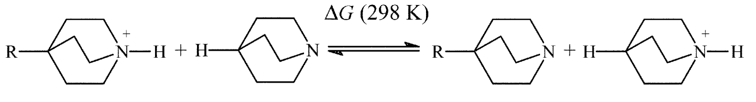
Computational details

All the calculations reported here were performed with the Gaussian98 program.[8] Energies at 0 K and Gibbs free energies at 298 K of 4-substituted quinuclidinium ions **1** and 4-substituted quinuclidines **2** were computed at the level of CBS-4M.[9] The method begins with HF/3-21G* geometry optimization, and zero-point energy and analytical vibration frequencies were computed at the same level to determine the nature of the located stationary points. Thus all the stationary points found were properly characterized by evaluation of the harmonic frequencies. Then it uses a large basis set SCF calculation (6-311+G(3d2f,2df,p)) as a base energy and an MP2/6-31+GD calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31G calculation is used to approximate higher order contributions. The method has a zero-point energy correction, a spin contamination correction, a size-consistent higher order correction, and some additional empirical corrections.[9] The method achieves a mean absolute deviation (MAD) under 2 kcal mol^{-1} with respect to experiment especially for heats of formation, bond dissociation energies, gas phase acidities, and proton affinities.[9]

Results

The calculated deprotonation energy of a neutral acid may have a MAD under 2 kcal mol^{-1} at the level of CBS-4M.[9] If one does calculations of relative acidities among neutral acids as in eqn. (1) at the same level, the MAD should be even smaller because of the cancellation of errors on the two sides of the equilibrium. Therefore, Gibbs free energies (Δ*G*(298 K)) of 4-substituted quinuclidinium ions **1** relative to that of quinuclidinium ion **1** (R = H) were computed at the level of CBS-4M in the gas phase (eqn. (1)), and the results are shown in Table 1.

Thermodynamic pK_a values of 4-substituted quinuclidinium perchlorates in water at 25 °C and their relative acidities (σ_I(Grob) = pK_a^H − pK_a^R) were measured by Grob and



1 **2**

(1)

Table 1 Relative deprotonation Gibbs free energies (ΔG(298 K)) of 4-substituted quinuclidinium ions **1** (eqn. (1)) and the calculated field substituent parameters ($\sigma_F{}^G$) at the level of CBS-4M in the gas phase[a]

R	$-\Delta G$(298 K)/kcal mol^{-1}	σ_F	σ_I(Gr)	ι	α	$\sigma_F{}^G$
H	0.00	0.00	0.00	2.00	0.00	0.00
NO_2	13.16	0.65	3.48	2.75	−0.26	0.75
CH_3	−0.37	0.00	0.11	2.14	−0.35	−0.02
C_2H_5	−0.32	0.00	0.03	2.15	−0.49	−0.02
OH	4.44	0.30	1.68	2.79	−0.03	0.25
OCH_3	3.01	0.25	1.81	2.82	−0.17	0.17
Cl	6.81	0.45	2.51	2.37	−0.43	0.39
CN	11.65	0.60	3.04	2.61	−0.46	0.66
CH_2Cl	3.53	0.23	0.97	2.18		0.20
$CH{=}CH_2$	1.15	0.06	0.56	2.34	−0.50	0.07
Ethynyl	3.05	0.23	1.64	2.52	−0.60	0.17
$C(O)CH_3$	4.30	0.26	1.69	2.39	−0.55	0.25
$C(O)NH_2$	4.21		1.78	2.30		0.24
NH_2	2.01	0.14	0.98	2.47	−0.16	0.11
$NHCH_3$	1.03	0.12	0.80	2.50		0.06
$N(CH_3)_2$	0.21	0.10	0.97	2.48	−0.44	0.01
SCH_3	3.26	0.25	1.66	2.16	−0.68	0.19
F	7.60	0.44	2.57	3.10	0.13	0.43
SH	5.09	0.28		2.17	−0.55	0.29
CF_3	7.88	0.44	0.08	2.47	−0.25	0.45
C(O)H	6.49	0.31		2.39	−0.46	0.37
CO_2H	4.87	0.28		2.36	−0.42	0.28
CH_2F	3.63	0.22		2.24		0.21
CHF_2	6.15	0.36		2.35		0.35
SiH_3	0.95					0.05
PH_2	3.13			1.91		0.18

[a] σ_F: ref. 1; σ_I(Gr): ref. 4*a*; ι: Inamoto's group electronegativity (ref. 6); α: Hehre–Taft–Topsom's polarizability parameter (ref. 5).

Schlageter.[4a] Correlation of ΔG(298 K) with σ_I(Grob) is good with a correlation coefficient of 0.891 and a standard deviation (SD) of 1.32 (eqn. (2)).

$$\Delta G(298\ \text{K}) = (-3.63 \pm 0.32)\ \sigma_I(\text{grob}) + (1.47 \pm 0.56),\ r = 0.891,\ \text{SD} = 1.32 \tag{2}$$

If ΔG(298 K) is correlated with Taft's substituent field parameter σ_F,[1] a better correlation is obtained with a correlation coefficient of 0.962 and an SD of 0.72 (eqn. (3)).

$$\Delta G(298\ \text{K}) = (-19.81 \pm 0.86)\ \sigma_F + (0.85 \pm 0.27),\ r = 0.962,\ \text{SD} = 0.72 \tag{3}$$

If the correlation is made without inclusion of the constant item, then another correlation (eqn. (4)) is obtained with a correlation coefficient of 0.943 and an SD of 0.85 and the coefficient of σ_F is −17.53.

$$\Delta G(298\ \text{K}) = (-17.53 \pm 0.57)\ \sigma_F,\ r = 0.943,\ \text{SD} = 0.85 \tag{4}$$

Therefore, ΔG(298 K) is rescaled by a factor of −1/17.53 to become $\sigma_F{}^G$ (eqn. (5)).

$$(-1/17.53)\ \Delta G(298\ \text{K}) = \sigma_F{}^G \tag{5}$$

On the other hand, correlations of ΔG(298 K) with either group electronegativity (ι)[6] or substituent polarizability parameter (σ_α)[5] are poor with correlation coefficients of 0.230 and 0.007, respectively (eqns. (6) and (7)).

$$\Delta G(298\ \text{K}) = (-6.08 \pm 2.32)\iota + (10.35 \pm 5.60),\ r = 0.230,\ \text{SD} = 3.08 \tag{6}$$

$$\Delta G(298\ \text{K}) = (-1.49 \pm 4.20)\sigma_\alpha + (-4.96 \pm 1.73),\ r = 0.007,\ \text{SD} = 3.94 \tag{7}$$

Previously the homodesmotic reactions (eqns. (8)–(11)) were designed to study substituent effects on the stability of ketenimines, isocyanides, and nitriles, and their corresponding stabilization energies (SE1–4) were correlated with both resonance parameter σ_R and inductive parameter σ_I which is correlated with field parameter σ_F very well.[11]

$$H_2C{=}C{=}NR + H_2C{=}NH \xrightarrow{\Delta E = \text{SE1}} H_2C{=}C{=}NH + H_2C{=}NR \tag{8}$$

$$RHC{=}C{=}NH + H_2C{=}CH_2 \xrightarrow{\Delta E = \text{SE2}} H_2C{=}C{=}NH + RHC{=}CH_2 \tag{9}$$

$$:C{=}NR + H_2C{=}NH \xrightarrow{\Delta E = \text{SE3}} :C{=}NH + H_2C{=}NR \tag{10}$$

$$RC{\equiv}N + HC{\equiv}CH \xrightarrow{\Delta E = \text{SE4}} HC{\equiv}N + RC{\equiv}CH \tag{11}$$

In this study, the stabilization energies (SE1–4) were correlated with four electronic substituent parameters (resonance parameter σ_R, field parameter σ_F, group electronegativity ι, and polarizability parameter σ_α), where field parameter σ_F replaces the previous inductive parameter σ_I. Charton's resonance parameter σ_R,[10] Taft's field parameter σ_F,[1] Inamoto's group electronegativity ι,[6] and Hehre–Taft–Topsom's polarizability parameter σ_α[5] were chosen to do the correlations (eqn. (12)).

$$\text{SE} = (C_R)\sigma_R + (C_F)\sigma_F + (C_\iota)\iota + (C_\alpha)\sigma_\alpha + (C) \tag{12}$$

In order to evaluate $\sigma_F{}^G$, it replaces Taft's field parameter σ_F in the correlations (eqn. (13)), and all the correlation results are shown in Table 2.

$$\text{SE} = (C_R)\sigma_R + (C_F{}^G)\sigma_F{}^G + (C_\iota)\iota + (C_\alpha)\sigma_\alpha + (C) \tag{13}$$

For the π-donating substituents, SE1 has good correlations with the four electronic substituent parameters with correlation coefficients of 0.993 and 0.989 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R, σ_F, and ι are significant while the coefficient of σ_α is not. Regarding the π-accepting substituents, SE1 has good correlations with the four electronic

Table 2 Coefficients, correlation coefficients (r), and standard deviations (SD) of the correlations of stabilization energies (SE) with four electronic substituent parameters (eqns. (12) and (13))

Substituent type[a]	SE	C_R	C_F or $C_F{}^G$	C_ι	C_α	C	r	SD
D	SE1[b]	6.6 ± 1.1	−8.4 ± 2.1	−6.9 ± 1.3	−1.1 ± 1.1	13.6 ± 2.8	0.993	0.65
D	SE1[c]	6.9 ± 1.5	−8.8 ± 3.1	−6.9 ± 1.7	−0.7 ± 1.4	13.7 ± 3.8	0.989	0.84
A	SE1[b]	9.4 ± 1.3	8.3 ± 1.5	−20.7 ± 1.4	−2.8 ± 0.4	41.4 ± 2.8	1.000	0.10
A	SE1[c]	7.0 ± 5.4	4.4 ± 5.8	−17.4 ± 6.4	−3.1 ± 2.0	34.8 ± 12.8	0.995	0.47
D	SE2[b]	12.5 ± 1.8	−9.8 ± 3.4	−2.9 ± 2.1	−2.8 ± 1.8	5.2 ± 4.6	0.986	1.04
D	SE2[c]	12.8 ± 2.0	−10.6 ± 4.2	−2.8 ± 2.4	−2.3 ± 1.9	5.1 ± 5.2	0.982	1.16
A	SE2[b]	−5.8 ± 0.0	−17.9 ± 0.1	9.0 ± 0.1	−8.2 ± 0.0	−17.9 ± 0.1	1.000	0.00
A	SE2[c]	−0.5 ± 9.5	−10.5 ± 10.0	3.3 ± 10.9	−7.0 ± 3.4	−6.8 ± 22.0	0.960	0.80
D	SE3[b]	5.1 ± 4.0	−44.7 ± 7.6	−11.8 ± 4.6	−17.4 ± 4.0	22.7 ± 10.3	0.989	2.35
D	SE3[c]	6.8 ± 2.8	−51.3 ± 5.8	−10.0 ± 3.3	−15.1 ± 2.7	19.1 ± 7.2	0.994	1.61
A	SE3[b]	9.8 ± 2.9	67.5 ± 3.3	−104.1 ± 3.2	−24.4 ± 1.0	208.2 ± 6.4	1.000	0.22
A	SE3[c]	−9.2 ± 38.1	39.1 ± 41.1	−81.5 ± 44.8	−27.8 ± 13.8	163.6 ± 90.3	0.972	3.28
D	SE4[b]	−5.7 ± 2.6	−8.1 ± 4.5	−1.2 ± 3.1	−2.4 ± 2.8	2.9 ± 6.8	0.861	1.35
D	SE4[c]	−5.0 ± 2.3	−10.2 ± 4.4	−0.2 ± 2.8	−2.5 ± 2.4	0.7 ± 6.2	0.900	1.15
A	SE4[b]	3.5 ± 1.4	−8.2 ± 1.6	−4.3 ± 1.5	1.8 ± 0.5	8.6 ± 3.1	1.000	0.11
A	SE4[c]	6.5 ± 5.0	−3.7 ± 5.4	−8.0 ± 5.9	2.6 ± 1.8	15.8 ± 11.8	0.996	0.43

[a] D: π-donor substituents (F, Cl, OH, NH_2, vinyl, ethynyl, CH_3, H); A: π-acceptor substituents (CO_2H, CN, C(O)H, NO_2, CF_3, H). [b] Eqn. (12), C_F, and σ_F were used. [c] Eqn. (13), $C_F{}^G$, and $\sigma_F{}^G$ were used.

substituent parameters with correlation coefficients of 1.000 and 0.995 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. All the coefficients are significant for the correlation involving σ_F.

For the π-donating substituents, SE2 has good correlations with the four electronic substituent parameters with correlation coefficients of 0.986 and 0.982 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R and σ_F are significant while coefficients of ι and σ_α are not. Regarding the π-accepting substituents, SE2 has a good correlation with the four electronic substituent parameters involving σ_F with a correlation coefficient of 1.000, which is better than the correlation involving $\sigma_F{}^G$, and coefficients of σ_R, σ_F, ι, and σ_α are all significant.

For the π-donating substituents, SE3 has good correlations with the four electronic substituent parameters with correlation coefficients of 0.989 and 0.994 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R, σ_F, ι, and σ_α are all significant for the correlation involving $\sigma_F{}^G$. Regarding the π-accepting substituents, SE3 has good correlations with the four electronic substituent parameters with correlation coefficients of 1.000 and 0.972 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R, σ_F, ι, and σ_α are all significant for the correlation involving σ_F.

For the π-donating substituents, SE4 has good correlations with the four electronic substituent parameters with correlation coefficients of 0.861 and 0.900 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R and σ_F are significant while coefficients of ι and σ_α are not. Regarding the π-accepting substituents, SE4 has good correlations with the four electronic substituent parameters with correlation coefficients of 1.000 and 0.996 for the correlations involving σ_F and $\sigma_F{}^G$, respectively. Coefficients of σ_R, σ_F, ι, and σ_α are all significant for the correlation involving σ_F.

Discussion

It is reasonable that the correlation coefficient for the correlation between $\sigma_F{}^G$ and σ_I(Grob) is 0.891 (eqn. (2)), because σ_I(Grob) was measured in an aqueous system but $\sigma_F{}^G$ was calculated in the gas phase. A better correlation (r = 0.962) was achieved when $\sigma_F{}^G$ was correlated with Taft's σ_F (eqn. (3)), but very poor correlations were obtained when $\sigma_F{}^G$ was correlated with either group electronegativity (ι)[6] or substituent polarizability parameter (σ_α)[5] (eqns. (6) and (7)), indicating $\sigma_F{}^G$ is a field substituent parameter.

In general, the correlations of the SE1–4 with the four substituent parameters give similar results to the correlations of the SE1–4 with the dual substituent parameters,[11] except for the correlations involving the SE2 and SE4 with the π-accepting substituents (Table 2). Both the correlations involving the SE2 and SE4 with the π-accepting substituents show better correlation with the four substituent parameters than with the dual substituent parameters,[11] so the correlations involving the four substituent parameters are more reliable. The correlations involving $\sigma_F{}^G$ sometimes are better than or similar to the correlations involving σ_F, indicating field substituent parameters $\sigma_F{}^G$ obtained by eqn. (1) and *ab initio* calculations at the level of CBS-4M are useful.

The field effect in this study involves dipole–charge interactions (eqn. (1)) and dipole–dipole interactions (eqns. (8)–(11)) between the substituents and the probes. It is a long-range electrostatic interaction without transfer of charge and it has a pronounced angular dependence.[7,12] Either stabilizing or destabilizing effects caused by the field effect depend on sign of charge and dipole orientation.[7,12] Based on a chemist's point of view, a dipole moment vector points from the positive to the negative charge. To be clear about the dipole orientation, in this study a pulling dipole means the one which has electron density pulled away from the probe, while a pushing dipole means the one which has electron density pushed toward the probe.

In eqns. (8)–(11), substituents stabilize reactants if the corresponding stabilization energies (SE) become more positive. When the SE correlates with the four electronic substituent parameters, the coefficient for each of the electronic substituent parameters is meaningful and it indicates how electronic properties of the substituents stabilize or destabilize the probes of reactants in eqns. (8)–(11). Since the substituents are directly attached to the probes for the reactants in eqns. (8)–(11), π-effects of both the substituents and the probes may work on each other directly, and that causes the dipole magnitude and the orientation of both the substituents and the probes to be changed. Therefore, the substituents were divided into two groups (π-donors and π-acceptors), and substituent effects on the probes were studied in each of the two groups.

In eqns. (8)–(11), interactions between the substituents and the probes are dipole–dipole and dipole-induced dipole interactions. Both field and polarizability effects are electrostatic interactions without transfer of charge, and their magnitudes depend on the distance between the two dipoles.[7,12] The field effect is proportional to $1/r^3$, while the polarizability effect is proportional to $1/r^6$.[7,12] Therefore, the field effect is long-range and much more significant, but the polarizability effect is short-range and much less significant. In Table 2, the coefficient for the field substituent parameter σ_F is always much more significant than that for the polarizability substituent parameter σ_α in each correlation of eqns. (12) and (13). Therefore, the polarizability effect is neglected in the following discussion regarding substituent effects on the stability of ketenimines, isocyanides, and nitriles.

In the case of the N-substituent effect on the stability of ketenimines with π-donor substituents (eqn. (8) and Table 2), a positive coefficient of σ_R indicates that π-donors destabilize ketenimines; a negative coefficient of ι indicates that σ-acceptors destabilize them; a negative coefficient of σ_F implies that pulling dipoles destabilize them. As far as the N-substituent effect on the stability of ketenimines with π-acceptor substituents is concerned (eqn. (8) and Table 2), a positive coefficient of σ_R indicates that π-acceptors stabilize ketenimines; a negative coefficient of ι indicates that σ-acceptors destabilize them; a positive coefficient of σ_F implies that pulling dipoles stabilize them.

In the case of the C_β-substituent effect on the stability of ketenimines with π-donor substituents (eqn. (9) and Table 2), a positive coefficient of σ_R indicates that π-donors destabilize ketenimines; a negative coefficient of σ_F implies that pulling dipoles destabilize them. As far as the C_β-substituent effect on the stability of ketenimines with π-acceptor substituents is concerned (eqn. (9) and Table 2), a negative coefficient of σ_R indicates that π-acceptors destabilize ketenimines; a positive coefficient of ι indicates that σ-acceptors stabilize them; a negative coefficient of σ_F implies that pulling dipoles destabilize them.

In the case of the substituent effect on the stability of isocyanides with π-donor substituents (eqn. (10) and Table 2), a positive coefficient of σ_R indicates that π-donors destabilize isocyanides; a negative coefficient of ι indicates that σ-acceptors destabilize them; a negative coefficient of σ_F implies that pulling dipoles destabilize them. As far as the substituent effect on the stability of isocyanides with π-acceptor substituents is concerned (eqn. (10) and Table 2), a positive coefficient of σ_R indicates that π-acceptors stabilize isocyanides; a negative coefficient of ι indicates that σ-acceptors destabilize them; a positive coefficient of σ_F implies that pulling dipoles stabilize them.

In the case of the substituent effect on the stability of nitriles with π-donor substituents (eqn. (11) and Table 2), a negative coefficient of σ_R indicates that π-donors stabilize nitriles; a negative coefficient of σ_F implies that pulling dipoles destabilize them. As far as the substituent effect on the stability of nitriles with π-acceptor substituents is concerned (eqn. (11) and Table 2), a positive coefficient of σ_R indicates that π-acceptors stabilize nitriles; a negative coefficient of σ_F implies that pulling dipoles destabilize them; a negative coefficient of ι indicates that σ-acceptors destabilize them.

Conclusion

We successfully developed 26 field substituent parameters by using high-level *ab initio* calculations (CBS-4M). The field substituent parameters, along with resonance substituent parameter σ_R, group electronegativity ι, and polarizability parameter σ_α, correlate well with stabilization energies (SE) of ketenimines, isocyanides, and nitriles, indicating that the field substituent parameters $\sigma_F{}^G$ are useful. By means of the correlations of the SE1–4 with the four electronic substituent parameters, useful information about electronic substituent effects on the stability of ketenimines, isocyanides, and nitriles was obtained.

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