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THE NATURE OF FIELD EFFECTS AND THEIR FALL-OFF WITH DISTANCE: THE ACIDITY OF SUBSTITUTED QUINUCLIDINIUM AND BICYCLOOCTYLAMMONIUM IONS

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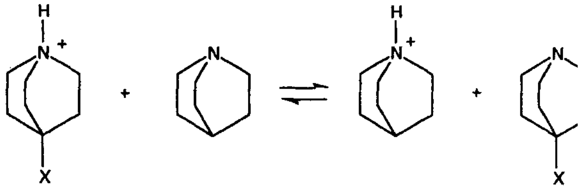
Gas-phase acidities are reported for series of substituted quinuclidinium and bicyclo [2.2.2] octylammonium ions. *Ab initio* calculations are also reported for these equilibria at the STO-3G and 3–21G (for the quinuclidines) bases and can be used to extend the results. pK_a values obtained for the bicyclooctylammonium ions are compared with previously reported results for the quinuclidinium ions. The results, as a whole, are considered together with similar values obtained for other saturated systems, to look at the varying transmission of field effects with distance. The fall-off observed between the two series in the gas phase is considerably less than expected from simple electrostatics. In contradication with a recent claim, it is also shown that field effects, as measured by the parameter σ_F, give a good measure of the effect of the substituents in each series compared with a combination of resonance and electronegativity effects.

INTRODUCTION

In recent years, we have reported gas-phase results on proton-transfer equilibria of various series of organic molecules.[1] The results have intrinsic interest in giving inherent substituent effects in the absence of solvent influences. We have concurrently made *ab initio* molecular orbital calculations of these equilibria both to demonstrate the applicability of such calculations and also to use them to extend our understanding of the processes. We have previously reported such experimental and theoretical results for substituted methylamines,[2] acetic acids,[3] cyanides,[4] phenols,[5,6] pyridines,[7,8] benzoic acids[9] and anilines.[7]

Two additional important series are 4-substituted quinuclidines and bicyclo [2.2.2] octylamines. We report here the experimental $\Delta G^\circ_{(g)}$ values for processes (1) and (2).



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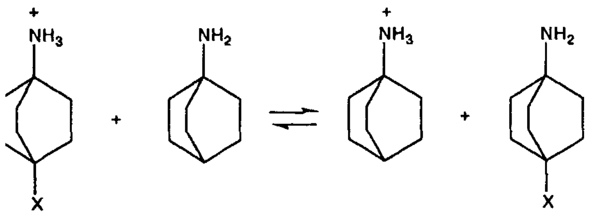


(2)

These systems are sterically well defined and therefore provide clear evidence of the effect of distance on substituent electronic effects in the absence of conjugative interactions that occur in systems such as phenols or pyridines.

Combination of these results with those previously reported for other aliphatic systems allows an analysis of the dependence of substituent effects, both on geometry and also on field effects,[1] as measured by σ_F parameters. This is important in the light of an unusual recent claim[10] that field effect parameters are not a primary measure, but are a derivative of resonance and electronegativity effects.

EXPERIMENTAL

The gas-phase basicities [given as $\Delta G^\circ_{\mathrm{H}^+}$ values in kcal mol^{-1} (1 kcal = 4·184 kJ) at 298 K] for the quinuclidines and bicyclooctylamines were obtained by the ion cyclotron resonance spectroscopic methods given in Ref. 1 or cited therein. Summaries of the results for both series are given in Tables 1 and 2, respectively. The values of $\delta G^\circ_{\mathrm{corr}}$ refer to the results obtained for the proton-transfer equilibria for each of the indicated standard bases ($\Delta G^\circ_{\mathrm{H}^+}$ value given as $\Delta G^\circ_{\mathrm{std}}$) with the given quinuclidines or bicyclooctylamine. The observed δG° values are corrected for any rotational symmetry number entropy effect. The two $\Delta G^\circ_{\mathrm{H}^+}$ columns in Tables 1 and 2 are the individual $\Delta G^\circ_{\mathrm{H}^+}$ values ($\Delta G^\circ_{\mathrm{std}}$ and $\delta\Delta G^\circ_{\mathrm{corr}}$) and the best values, $\Delta G^\circ_{\mathrm{H}^+(\mathrm{bv})}$, obtained for them. All values of $\Delta G^\circ_{\mathrm{H}^+}$ are based on $\Delta G^\circ_{\mathrm{H}^+} = 195{\cdot}6$ kcal mol^{-1} for NH_3.[12] The final column gives the substituent effect values $\delta_x\Delta G^\circ = \Delta_x \mp G^\circ - \Delta G^\circ$, for gas-phase basicities relative to the parent unsubstituted base.

The pK_a measurements were made at 25·0 °C. The samples, 10–20 mg, in 20 ml of 0·6 M KCl solution were titrated with 0·10 M NaOH. The results are given in Table 3. The quinuclidines were available from previous work.

Synthesis of bicyclo[2.2.2]octylamines

The syntheses of bicyclo[2.2.2]octylamine[14] and of its 4-F[15], 4-CH_3[16] and 4-I[17] derivatives have been reported previously.

4-Methoxybicyclo[2.2.2]octylamine. The 4-methoxybicyclo[2.2.2]octylcarboxylic acid[15] was converted to the amide in 84% yield by the method of Boissonnas;[18] m.p. 165–166 °C (from light petroleum–chloroform).

Table 1. Gas-phase acidities (kcal mol^{-1}) of quinuclidine and 4-substituted quinuclidines (X = 4-substituent)

4-X	Standard Base	$\Delta G^\circ_{\mathrm{std}}$	$\delta\Delta G^\circ_{\mathrm{corr}}$	$\Delta G^\circ_{\mathrm{H}^+}$	$\Delta G^\circ_{\mathrm{H}^+(\mathrm{bv})}$	$\delta_x\Delta G^\circ$
$N(CH_3)_2$	$N(C_2H_5)_3$	224·9	0·6	225·5	225·5	0·3
CH3	$N(C_2H_5)_3$	224·9	0·3	225·2	225·2 ± 0·1	0·0
	$N(C_2H_5)_3$	224·9	0·0[a]	224·9		
	$N(C_2H_5)_2C_3H_7$	225·7	−0·4[a]	225·3		
H	$(t\text{-}C_4H_9)_2NH$	225·4	−0·3	225·1	225·2 ± 0·1	(0·0)
	$N(C_2H_5)_3$	224·9	0·3[a]	225·2		
SCH_3	$(C_3H_7)_2NH$	219·7	1·4	221·1	221·2 ± 0·1	−4·0
	$(i\text{-}C_3H_7)_2NH$	222·0	−0·7	221·3		
OH	$(C_3H_7)_2NH$	219·7	0·6	220·3	220·3	−4·9
F	$N(CH_3)_2C_2H_5$	219·7	−1·4	218·3	218·1 ± 0·2	−7·1
	Piperidine	217·9	0·0	217·9		
Cl	Piperidine	217·9	−0·8	217·1	217·5 ± 0·2	−7·8
	4-$CH_3C_5H_4N$	216·7	0·9	217·6		
	$N(CH_3)_3$	217·6	0·1[a]	217·7		
	$(C_2H_5)_2NH$	217·8	−0·1[a]	217·7		
CF_3	Piperidine	217·9	−1·0	216·9	216·9 ± 0	−8·3
	4-$CH_3C_5H_4N$	216·7	0·2	216·9		
CN	cyclo-$C_6H_{11}NH_2$	213·1	0·4	213·5	213·9 ± 0·2	−11·3
	$CH_3(C_2H_5)NH$	215·4	−1·4[a]	214·0		
	t-Amylamine	214·8	−0·7[a]	214·1		
	$OP(CH_3)_2N(CH_3)_2$	214·1	−0·1[a]	214·0		

[a] Ref. 13.

Table 2. Gas-phase basicities (kcal mol^{-1} of bicyclooctylamines

4-X	Standard Base	ΔG°_{std}	$\delta\Delta G^{\circ}_{corr}$	$\Delta G^{\circ}_{H^+}$	$\Delta G^{\circ}_{H^+}$ (bv)	$\delta_r\Delta G^{\circ}$
CH_3	*t*-Amylamine	214·8	2·2	217·0	217·0 ± 0·1	0·8
	Pyrrolidine	216·9	0·0	216·9		
H	Pyrrolidine	216·9	−0·8	216·1	216·2 ± 0·1	(0·0)
	t-Amylamine	214·8	1·4	216·2		
OCH_3	2-$OCH_3C_5H_4N$	213·8	1·0	214·8	215·1 ± 0·3	−1·1
	t-Amylamine	214·8	0·3	215·1		
	3-$OCH_3C_5H_4N$	216·2	−0·6	215·6		
CO_2CH_3	2-$OCH_3C_5H_4N$	213·8	0·8	214·6	214·8 ± 0·2	−1·4
	C_5H_5N	213·2	1·8	215·0		
Cl	4-CF_3-piperidine	211·6	−0·7	210·9	210·9	−5·3
F	$C_4H_9NH_2$	210·2	0·9	211·1	210·8 ± 0·3	−5·4
	4-CF_3-piperidine	211·6	−1·3	210·3		
	4-$CO_2CH_3C_5H_4N$	211·1	−0·2	210·9		
	4-$CH_3COC_5H_4N$	209·4	1·5	210·9		

The amine was obtained as an oil in 61% yield by treatment of the carboxamide with iodosobenzene as described.[19] Microanalysis (as the hydrochloride salt, monohydrate m.p. 270–272 °C): found C 51·77, H 9·30, N 6·83; calculated, C 51·52, H 9·62, N 6·68%.

4-Bromobicyclo[*2.2.2*]*octylamine.* The bromocarboxylic acid was prepared from the methoxy acid as described previously;[20] m.p. 261–262 °C (yield 73%) (lit.[20] m.p., 262–265 °C). The acid was converted to the amide (m.p. 230–231 °C) then to the amine (yield 73%), m.p. 73–74 °C. Microanalysis (as the hydrochloride salt, semihydrate, m.p. 285–287 °C): found, C 38·64, H 6·37, N 5·61; Calculated, C 38·55, H 6·47, N 5.62%.

4-Chlorobicyclo[*2.2.2*]*octylamine.* Methyl 4-iodobicyclo[2.2.2]octylcarboxylate was treated with a slight excess of iodine monochloride in carbon tetrachloride in at room temperature for 48 h, as described previously.[20] The chloro ester was obtained as crystals, m.p. 61–63 °C (yield 89%) (lit.[20] m.p. 65–67 °C) The ester was converted to the amide via the acid in 68% yield, m.p. 218–220 °C. Conversion of the amide to the amine was achieved in 77% yield, m.p. 68–70 °C. Microanalysis (as the hydrochloride salt, semihydrate m.p. 274–276 °C): found C 46·16, H 7·90, N 6·74; Calculated, C 46·81, H 7·86, N 6·83%.

Table 3. pK_a of 4-substituted bicyclo[2.2.2]octylamines at 25·0 °C in 0·1 M KCl solution

R	No. of measurements	pK_a	Standard deviation	4-X-Quin pK_a
4-X-BCO				
H	3	10·66	0·01	11·12
CH_3	4	10·66[a]	0·08	11·01
$COOCH_3$	2	9·89	0	9·42
OCH_3	3	9·82	0·06	9·31
I	2	9·61	0·007	8·78
Cl	2	9·56	0·007	8·61
F	2	9·53[a]	0·04	8·55
Br	2	9·55	0·007	8·47
NO_2	2	9·12	0·007	7·64

[a] The end-points tended to drift upwards.

4-Carbomethoxybicyclo[*2.2.2*]*octylamine.* The diethylbicyclo[2.2.2]octylester[21] was converted to the dimethyl ester and then partially hydrolysed with barium hydroxide in 80% methanol to yield the half methyl ester, m.p.[22] 176–178 °C. This was converted to the amide ester, m.p. 158–160 °C (hexane–chloroform) and then in 83% yield to the amine ester, m.p. 35–40 °C. Microanalysis (as the hydrochloride salt, monohydrate m.p. 258–260 °C): found C 50·06, H 8·49, N 5·81; Calculated, C 50·50, H 8·48, N 5·89%.

4-Nitrobicyclo[*2.2.2*]*octylamine.* The compound was prepared from ethyl 4-aminobicyclo[2.2.2]octylcarboxylate by oxidation of the amino group with *m*-chloroperbenzoic acid, followed by conversion of the carboxylate group to the amine in the standard way. Microanalysis (as the hydrochlorate salt, semihydrate m.p. 270–275 °C): found C 45·81, H 7·29, N 13·36; Calculated, C 45·58, H 7·66, N 13·30%.

Calculations

All calculations were performed at the *ab initio* STO-3G and 3–21G bases, using the Guassian 82[23] and Gaussian 86[24] series of programs. The geometry of quinuclidine was optimized (with CH as 1·09 Å) and then used throughout that series with standard geometries for substituents, the NH bond in the cations being

Table 4. *Ab Initio* molecular orbital calculations (STO-3G) on 4-X-substituted quinuclidines

	−*E*(hartrees)			
	STO-3G		3–21G	
X	4-X-Quin	4-X-QuinH$^+$	4-X-Quin	4-X-QuinH$^+$
H	323·21421	323·66473	325·27112	325·67330
CH_3	361·79494	362·24686	364·09402	364·49728
NH_2[a]	377·51052	377·96160	379·98304	380·38641
NMe_2	454·65764	455·10932		
OH	397·04418	397·48911	399·71032	400·10562
OMe	435·61209	436·05778		
CHO	434·43166	434·87689	437·35592	437·74857
COMe	473·00886	473·45529		
CO_2Me	546·86885	547·31418		
CF_3	654·17790	654·61924		
F	420·66826	421·11022	423·59833	423·98807
CN	413·76029	414·19410	416·48853	416·87143
NO2	523·90551	524·33377	527·56336	527·93981
Cl			781·99657	782·38424

[a] Planar NH_2.

Table 5. *Ab Initio* molecular orbital calculations (STO-3G) on 4-X-bicyclo[2.2.2]octylamines

	−*E*(hartrees)	
X	4-X-$C_8H_{12}NH_2$	4-X-$C_8H_{12}NH_3^+$
H	361·78956	362·23174
CH_3	400·36239	400·80543
NH_2	416·08593	416·53543
OH	435·61645	436·05441
OMe	474·18598	474·62477
CHO	473·00670	473·44492
COMe	511·59205	512·03082
CO_2Me	585·44377	585·88253
CF_3	692·74456	693·18056
F	459·24313	459·67933
CN	452·33535	452·76565
NO_2	562·48058	562·90669

taken as 1·0 Å. The calculations on the bicyclooctanes were performed at standard geometries. The energies of the 4-substituted quinuclidines and quinuclidinium cations are given in Table 4 and those for the 4-substituted bicyclo[2.2.2]octylamines and bicyclo[2.2.2]octylammonium ions in Table 5.

RESULTS AND DISCUSSION

We obtained experimental pK_a results in aqueous solution for 4-substituted bicyclooctylamines having a reasonable range of substituents. Corresponding results obtained previously[25] for 4-substituted quinuclidines under identical conditions are also given in Table 3. A plot of one series against the other is shown in Figure 1. The linearity is excellent ($r = 0·998$), with a slope of 0·44 for the bicyclooctylamine results versus the corresponding quinuclidines.

This fall-off facor is in broad agreement with calculations based on geometry and an expected decrease in the field effect of $1/r^2$ as the distance increases (the distribution of the pole to the CX bond is co-linear in both cases). Thus, assuming the mean distance from the C-4 atom of the bicyclic system to the mid-point of the CX dipole is 0·7 Å, calculations suggest a fall-off factor of *ca* 0·5.

Fewer results are available in the gas phase (Table 6) for the bicyclooctylamines. Unfortunately, the 4-nitro derivative decomposed under the measurement conditions. However, the results for the 4-fluoro and 4-chloro compounds suggest a fall-off factor of only about 0·75, and this result is supported by calculations as described below.

A fuller analysis[1] can be done against field, resonance and polarizability parameters (electronegativity proves to be of no consequence if this term is included) using the equation

$$\Delta G^\circ = \rho_F\sigma_F + \rho_R\sigma_R + \rho_\alpha\sigma_\alpha + C \tag{3}$$

The results for the aqueous solution are as follows:

$$\text{Quin:}\quad \Delta G^\circ = 7·0(\pm 0·5)\sigma_F - 1·3(\pm 0·6)\sigma_R - 0·01 \quad (r = 0·986) \tag{4}$$

$$\text{BCONH}_2\text{:}\quad \Delta G^\circ = 3·2(\pm 0·3)\sigma_F + 0·11 \quad (r = 0·984) \tag{5}$$

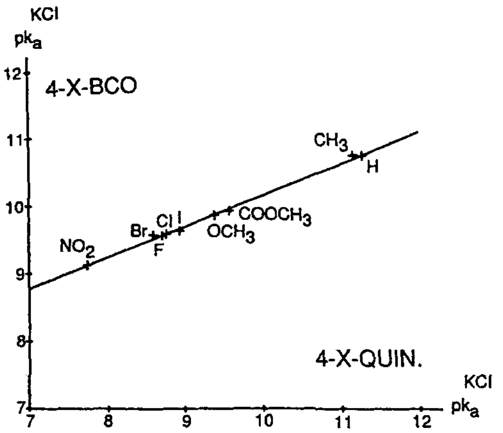


Figure 1. Plot of aqueous pK_a values for 4-substituted bicyclooctylamines (4-X-BCO) versus those for 4-substituted quinuclidine (4-X-QUIN)

Table 6. Acidities of 4-X-substituted quinuclidinium ions (Quin) and 4-X-bicyclo[2.2.2]octylammonium ions (BCO) (ΔG° and ΔE° in kcal mol^{-1})

	Quin			BCO		
X	$-\Delta G^\circ_{(g)}$	$-E^\circ$	$-\Delta G^\circ_{(aq)}$[a]	$-\Delta G^\circ_{(g)}$	$-\Delta E^\circ$	$-\Delta G^\circ_{(aq)}$
H	0·00	0·00	0·00	0·0	0·00	0·00
CH_3	0·0	−0·88(−0·06)[b]	0·15	−0·8	−0·54	0·00
NH_2		−0·35(−0·75)	−1·45		1·02	
NMe_2	−0·3	−0·73	−1·43			
OH	4·9	3·51(4·32)	1·74		2·65	
OMe		3·02	2·47	1·1	2·13	1·15
CHO		3·37(5·98)			2·48	
COMe		2·56	2·31		2·14	
CO_2Me		3·26	2·32	1·4	2·15	1·05
CF_3	8·3	5·74			3·87	
F	7·1	5·37(7·81)	3·51	5·4	3·75	1·54
CN	11·3[a]	10·48(12·10)	4·15		7·45	
NO_2		13·90(16·15)	4·75		10·08	2·10
Cl	7·8[a]	(9·11)	3·42	5·3		1·50

[a] From Ref. 25.

[b] Values in parentheses are 3–21G.

and for the gas phase:

$$\text{Quin:}\quad \Delta G^\circ = 18\cdot4(\pm 0\cdot5)\sigma_F - 3\cdot3(\pm 0\cdot5)\sigma_R + 0\cdot2 \quad (r = 0\cdot998) \tag{6}$$

$$\text{BCONH}_2\text{:}\quad \Delta G^\circ = 12\cdot8(\pm 1\cdot4)\sigma_F + 0\cdot6 \quad (r = 0\cdot975) \tag{7}$$

The $\rho_{F(g)}/\rho_{F(aq)}$ ratios found are 2·6 for the quinuclidines and 4·0 for the bicyclooctylamines, showing markedly different solvent attenuation effects (see below). The apparent dependence of the gas-phase acidities of the quinuclidines on a significant resonance term is also discussed below.

Other results for similar analyses against substituent parameters are recorded in Table 7. For comparison, the results are also expressed as the ratio of the ρ_F values to those for the $XCH_2NH_3^+$ taken as standard. This gives the fall-off factor for each system compared with the substituted methylammonium ions. In the last column in Table 7, the approximate fall-off factors calculated from the geometry of the various systems are listed, assuming that the effect is proportional to $\cos\theta/r^2$, where r is the mean distance of the C—X bond to the charged site and θ the angle that the CX bond makes to a line going its mid-point to the charged centre. It is clear that whilst the fall-off factors found in aqueous solution are in approximate agreement with calculation, there is a much smaller than expected fall-off in the gas phase. This is shown most clearly in the fall-off from the quinuclidines to the 4-substituted bicyclooctylamines, systems of well defined geometry. Here, a fall-off of about 50% is expected, based on electrostatic calculations (see above), and indeed this is approximately observed in the aqueous results. However, the fall-off observed in the gas phase is only about half of this, thus leading to the observed difference in the solvent attenuation factors noted above.

Table 7. Fall-off in substituent effect in various systems

System	$\rho_{F(g)}$[a]	$\rho_{F(aq)}$[a]	Calc. rel. values
$X\text{-}CH_2NH_3^+$	33·1(1·0)	12·0(1·0)	1·0
$X\text{-}CH_2NMe_2H^+$	28·6(0·86)	13·7(1·1)	1·0
$X\text{-}CH_2CO_2H$	24·6(0·75)	5·2(0·43)	0·52
$4\text{-}X\text{-}QuinH^+$	18·4(0·56)	7·2(0·60)	0·47
$4\text{-}X\text{-}C_8H_{12}NH_3^+$	12·8(0·39)	3·17(0·26)	0·24
$4\text{-}X\text{-}C_8H_{12}CO_2H$	12·9(0·39)	1·29(0·11)	0·19

[a] Values in parentheses are values relative to the substituted methylamines taken as unity.

Comparison of experimental ΔG° values with calculated ΔE° values

Table 6 also lists the calculated ΔE° values for processes (1) and (2). The agreement between experiment and results calculated at the STO-3G basis are generally good, as found in similar calculations for other proton-transfer reactions. This gives confidence in the general trends of such results which is particularly useful for equilibrium (2), where experimental gas-phase results are limited.

The substituent parameters analyses for the quinuclidines give

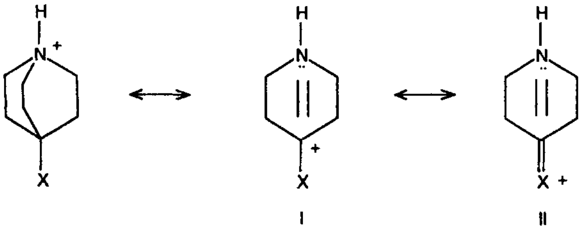
$$\Delta E^\circ_{(\text{STO-3G})} = 18\cdot9(\pm 2\cdot4)\sigma_F + 3\cdot9(\pm 2\cdot6)\sigma_R - 0\cdot6 \quad (r = 0\cdot971) \tag{8}$$

$$\Delta E^{\circ}_{(3\text{-}21G)} = 21\cdot5(\pm1\cdot5)\sigma_F + 6\cdot1(\pm1\cdot8)\sigma_R + 0\cdot1 \quad (r = 0\cdot995) \tag{9}$$

and for the bicyclooctylamines

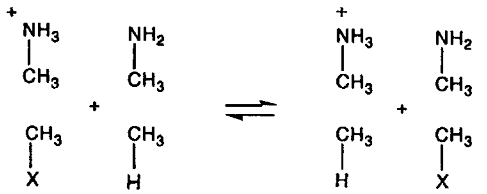
$$\Delta E^{\circ}_{(STO\text{-}3G)} = 14\cdot0(\pm1\cdot6)\sigma_F - 1\cdot28 \quad (r = 0\cdot939) \tag{10}$$

The calculated results for the quinuclidines also show an apparent dependence on resonance effects as found with the experimental values above; this term is not important in either the calculated or experimental results for the bicyclooctylamines. Equation (8) for the STO-3G calculations is also remarkably similar to equation (6), which results from the experimental gas-phase results. The most pressing evidence for a resonance contribution is the analysis of the gas-phase data given in equation (6), where the error in the resonance term is low. Such a resonance effect could arise from the contribution of σ resonance forms I and II in structure (11).



(11)

We also calculate results for process (12):



(12)

where the substituents and NH_3^+ or NH_2 groups were kept at the same geometry to each other, as in the bicyclooctylamines. The results are shown in Table 8. Clearly the removal of the framework between systems (2) and (12) makes very little difference to the derived ΔE° values. This is understandable in terms of a simple electrostatic field effect, dependent only on geometry. At the same time, it is convincing evidence against the involvement of any through-bond (electronegativity) effects.

These effects at the bicyclooctylamine distance are also in accord[26] with electrostatic calculations for a point charge at a similar distance from the substituent dipole. Hence it seems that the results for the bicyclooctylamines should be used as the standard. This would mean that in aqueous solution the 4-substituted quinuclidines behave roughly as expected (see above) from electrostatic calculations, but in the gas phase they act as if the charge was more dispersed. Certainly the calculations show that a considerable amount of the positive charge is located on the hydrogens attached to the carbons adjacent to the nitrogen and the differing effective angles to the dipole would lower the effect.

Table 8. *Ab initio* molecular orbital calculations (STO-3G) on the acidity of $CH_3NH_3^+/CH_3X$ pairs conforming to the geometries of 4-X-substituted bicyclo[2.2.2]octylammonium ions

	$-\Delta E^{\circ}$ (kcal mol^{-1})	
X	Pairs	4-X-$C_8H_{12}NH_3^+$
H	0·00	0·00
CH_3	−0·46	−0·54
NH_2	1·59	1·02
OH	2·80	2·65
CHO	2·31	2·48
CF_3	3·93	3·87
F	4·12	3·75
CN	7·15	7·45
NO_2	9·76	10·08

Are field effects a primary substituent measure?

It has, surprisingly, recently been suggested[10] that field effects are not a primary effect, but rather are constitutionally dependent on a combination of resonance and electronegativity effects (and in some cases also of polarizability). The authors reached this conclusion by a statistical analysis on a wide range of σ_F, σ_R and various electronegativity parameters. The fits obtained were generally not very good, r values of 0·56–0·88 being obtained, for example, for an analysis of σ_X parameters versus σ_F and σ_R. This was improved to a range of 0·74–0·95 if the substituents were restricted to those having a first-row element as the first atom.

The claim is surprising for several reasons. First, the field effect parameters σ_F or σ_I (older terminology) have proved remarkably effective in describing a wide variety of aliphatic reactivities and, in combination with σ_R, also of aromatic reactivities. Second, little evidence exists[1,27] for the transmission of electronegativity effects past the first atom to which the substituent is attached. Further, although resonance effects have been observed[27,28] in some properties of XCH_2Y systems, it is likely that any such effect would alter even from one aliphatic system to another as the substituent was attached to primary, secondary or tertiary carbon atoms.

The primary test is, of course, against experimental data. Table 9 lists the gas-phase experimental data for the acidities of substituted acetic acids[3] and 4-substituted bicyclo[2.2.2]octylcarboxylic acids.[9] Together with the data for the quinuclidines and

Table 9. Relative gas-phase acidities of substituted acetic acids and 4-substituted bicyclooctylcarboxylic acids

X	X-CH_2CO_2H	4-X-$C_8H_{12}CO_2H$
H	0·0	0·0
NH_2	5·9	
OMe	6·0	2·7
CH_3	1·2	0·9
F	9·6	5·6
Cl	12·0	6·2
CF_3	13·1	6·3
CN		8·4
CO_2Me		3·2
NO_2		8·7

bicyclooctylamines, they provide a most useful test-bed. If the earlier claim is true that the two parameter equation

$$\Delta G^\circ_{(g)} = \rho_X\sigma_X + \rho_R\sigma_R = c \qquad (13)$$

must give a better fit than the one-parameter equation

$$\Delta G^\circ_{(g)} = \rho_F\sigma_F + c' \qquad (14)$$

The results of these tests show quite the opposite, as shown in Table 10. In each case, the single-parameter equation (14) gives a much better fit than equation (13).

We also checked the dependence of the σ_F values for thirteen common substituents (NMe_2, NH_2, OMe, OH, Me, F, Cl, CF_3, CN, CO_2Me, COMe, NO_2CHO) against σ_R and σ_X. The equation obtained:

$$\sigma_F = 0{\cdot}60\sigma_R + 0{\cdot}67\sigma_X + 0{\cdot}2 \qquad (15)$$

had a correlation coefficient of only 0·781. The correlation only improved to 0·83 when a term in σ_α was included, leading to the equation

$$\sigma_F = 0{\cdot}58\sigma_R + 0{\cdot}82\sigma_X + 0{\cdot}33\sigma_\alpha + 0{\cdot}07 \qquad (16)$$

The poor correlation for a range of substituent types is hidden in a statistical analysis of a large number of data when the correlation is not precise.

We conclude that field effects are indeed a primary substituent measure.

Table 10. Analyses of gas-phase experimental acidity data versus dual substituent equation in σ_X and σ_R versus analyses using a single parameter equation in σ_F

	Eqn (σ_X, σ_R)			Eqn (σ_F)	
System	r	ρ_R	ρ_X	r	ρ_F
X-CH_2CO_2H	0·369	9·0	9·2	0·965	24·0
X-$C_8H_{12}CO_2H$	0·727	10·5	8·8	0·990	13·1
X-QuinH$^+$	0·582	12·4	10·7	0·975	18·9
X-$C_8H_{12}NH_3^+$	0·625	4·5	7·3	0·975	12·8

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