224. Charge Dispersal in the Quinuclidine Radical Cation and in the Quinuclidinium Ion, as Revealed by PE and ICR Spectroscopy

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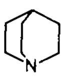
The n_N^{-1} ionization energies I_1^c and the gas-phase basicities GB of CH_3-, Cl-, or CN-substituted quinuclidines have been measured by PE and ICR spectroscopy. The dependence of the shifts ΔI_1^c and Δ GB (relative to the values of the parent molecule) allow conclusions about the charge dispersal accompanying the n_N^{-1} ionization or the protonation of quinuclidine in the gas phase. The agreement with the results of a minimal basis set *ab initio* calculation is excellent. Comparison of the solution pK_a values with either I_1^c or GB reveals that 2-substituted quinuclidines exhibit sizeable solvent-induced proximity effects, *i.e.* that the corresponding quinuclidinium ions are more acidic in solution than expected on the basis of the gas-phase basicities. This agrees with earlier results concerning 2-substituted pyridines.

Introduction. – Substituted quinuclidines, Q, occupy a special place among molecules used for the determination of substituent and reaction constants within LFER treatments [1] of *Hammett* $\rho\sigma$-type [2]. In [3] [4], the substituent constants σ_I^q and the reaction constants ρ_I, obtained from measurements on Q carried out in solution, have been discussed in detail. Whereas the usefulness of the parameters σ_I^q and ρ_I for predictive purposes or for the systematization of equilibrium and rate data in solution is beyond dispute, their rationalization in terms of purely electronic effects within the isolated molecule [4] presents a serious problem, because of the presence of solvent effects [5] of unknown magnitude. To avoid the latter, we present and discuss the results obtained by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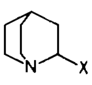
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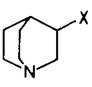
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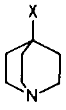
4(X)

PE and ICR spectroscopy for a series of Q, **1** (= quinuclidine = 1-azabicyclo[2.2.2]-octane), **2**(X), **3**(X), and **4**(X) with X = CH_3, Cl, and CN.

The vertical ionization energy corresponding to the ejection of an electron from the N lone-pair orbital of a Q molecule (n_N^{-1} process) and the gas-phase basicity of Q corresponding to the attachment of a proton to its N lone pair in the absence of solvent, provide a safer basis for comparison with theoretical models. From this point of view, the Q molecules are in fact ideal test cases, because of their well defined, rigid structure, and because the position of the completely detached n_N^{-1} N lone-pair band in their PE spectra [6] [7] can be measured with sufficient accuracy. This is in contrast to *e.g.* substituted pyridines which are much more easily accessible, and for which gas-phase basicities are available [8], but which suffer from the defect that the position of their n_N^{-1} bands can not be assessed with any confidence, due to strong overlapping by the equally intense π^{-1} bands in their PE spectra [9].

PE-Spectroscopic Results. – Lone-pair ionization energies $I(n_N^{-1})$ of bridge-head aza- [6] [10] and diaza[h.k.l]bicycloalkanes [10] [11] have been measured previously by PE spectroscopy. In particular, the dependence of $I(n^{-1})$ of **1** on substituents X at C(4), *i.e.* in the series **4**(X) has been studied [7], and the results have been correlated with substituent parameters $\sigma^*(X)$ [1] [2] and $F(X)$ [12], as well as with the pK_a values of the compounds **4**(X) [3].

The PE spectra of **1** and of its derivatives **2**(X), **3**(X), and **4**(X), X = CH$_3$, Cl, CN, *cf. Fig. 1*, exhibit a first band ① in the region from 8.0 to 8.8 eV which is well detached from the overlapping manifold of bands extending from ~ 10 eV towards higher ionization energies [6] [10]. There is no doubt that this band is due to electron ejection from an orbital $\varphi_{HOMO} = \varphi_n$, of symmetry type A_1 within the group C_{3v}, *e.g.* in **1** or **4**(X), and mainly localized in the region of space occupied by the lone-pair of the N-atom. We, therefore, designate this ionization process by n_N^{-1}. Except in the case of 1-azabicyclo[3.3.3]undecane

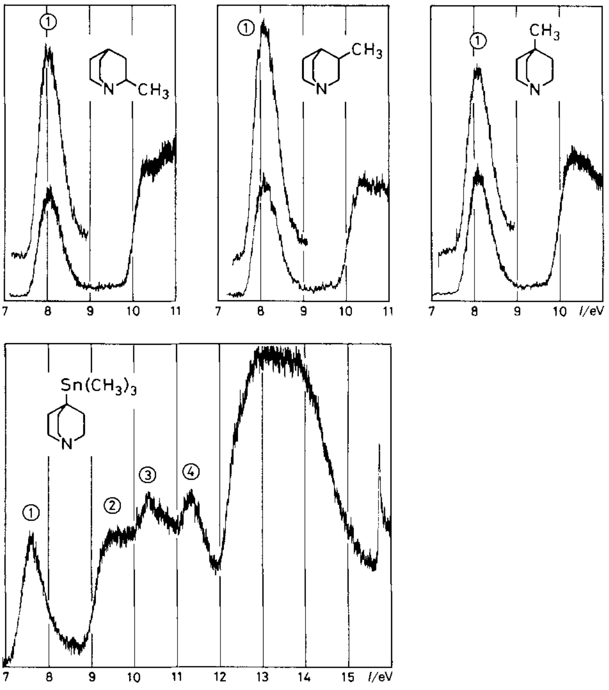

Fig. 1. *He(Iα) PE spectra of* **2**(CH$_3$), **3**(CH$_3$), **4**(CH$_3$), *and* **4** (Sn(CH$_3$)$_3$)

[11], such n_N^{-1} bands do not exhibit vibrational fine structure. In the present cases, the *Franck-Condon* envelopes of the lone-pair bands ① are slightly skew, *cf. Fig. 1*, so that the position I_1^m of the n_N^{-1} band maximum is found at lower ionization energies (by ~ 0.05 eV) than that of the band centre, I_1^c, which we assume to be close to the vertical ionization energy I_1^v. The width at half height of band ①, $w_{1/2}$, is 0.60 eV to 0.65 eV in all cases, *i.e.* a constant within the limits of error. This indicates that the change in geometry which accompanies the transition from the neutral parent compound to the structurally relaxed radical cation must be about the same for all derivatives studied.

The data I_1^m, I_1^c, and $w_{1/2}$ for the Q **1**, **2**(X), **3**(X), and **4**(X), X = CH_3, Cl, CN, are listed in *Table 1*, together with some previously determined values.

Table 1. *Ionization Energies and Band Width at Half-Height of the n_N^{-1} Band ① in the PE Spectra of* **1**, **2** (X), **3** (X), *and* **4** (X). The standard errors of I_1^c are roughly ± 0.02 eV, those of I_1^m somewhat larger, due to the broadness of the top of the peaks and the noise level. The standard errors of $w_{1/2}$ are ± 0.03 eV.

Compound	X = H (= **1**)			X = CH_3			X = Cl			X = CN		
	$\frac{I_1^m}{eV}$	$\frac{I_1^c}{eV}$	$\frac{w_{1/2}}{eV}$	$\frac{I_1^m}{eV}$	$\frac{I_1^c}{eV}$	$\frac{w_{1/2}}{eV}$	$\frac{I_1^m}{eV}$	$\frac{I_1^c}{eV}$	$\frac{w_{1/2}}{eV}$	$\frac{I_1^m}{eV}$	$\frac{I_1^c}{eV}$	$\frac{w_{1/2}}{eV}$
2 (X)	8.06	8.08	0.62	8.02	8.06	0.58	8.51	8.56	0.62	8.69	8.74	0.60
3 (X)	8.06	8.08	0.62	8.02	8.08	0.60	8.38	8.42	0.62	8.57	8.60	0.63
4 (X)	8.06	8.08	0.62	8.05	8.11	0.60	8.45	8.49	0.59	8.66	8.68	0.62
[a])	8.06	8.09	0.58	8.06	8.09	0.58	8.55	8.57	0.55	8.71	8.74	0.60
[b])	8.06											
[c])	8.02		0.60									

[a]) Values taken from [7]; the discrepancy between the present data for **4** (Cl) and those in [7] may be due to a calibration error in the latter.

[b]) Value obtained from regression I_1^m *vs.* σ* given in [7] for σ* = 0.

[c]) From [6].

The dependence of the n_N^{-1} ionization energies I_1^m and I_1^c of substituted Q on the nature and the position of the substituent X is displayed in *Fig. 2*. We believe that I_1^c is the better approximation to the vertical ionization energy I_1^v, and we shall, therefore, use the former values in the subsequent analysis. However, as is evident from *Fig. 2*, our main conclusions would remain unaffected, if I_1^m had been used instead.

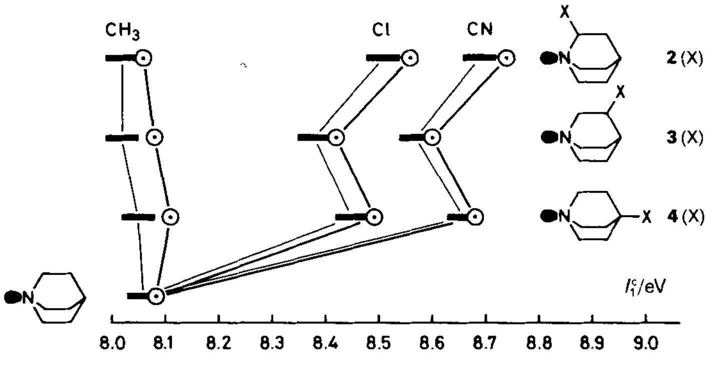

Fig. 2. n_N^{-1} *Ionization energies* I_1^c (circles) *of quinuclidine and its CH_3-, Cl-, and CN-substituted derivatives.* The horizontal bars in front of the circles correspond to I_1^m.

Gas-Phase Basicities. – Gas-phase basicities of the Q molecules were determined by ICR spectrometry under conditions described in [13]. The equilibrium constant K_{eq} for the proton transfer reaction

$$QH^+ + B \rightleftharpoons Q + BH^+ \qquad (1)$$

between the quinuclidinium cation or a substituted quinuclidinium cation, QH^+, and a reference base B, yields the change

$$\Delta_r G_m = -RT \ln K_{eq} \qquad (2)$$

in molar free enthalpy at the temperature $T = 313$ K of the experiment. Using the known gas-phase basicities GB(B) of the reference bases B [13] [14], the measured value $\Delta_r G_m$ (*2*) allows the calculation of the gas-phase basicity GB(Q) of Q according to

$$GB(Q) = GB(B) + \Delta_r G_m \qquad (3)$$

Reaction times up to 1 s were used. At least three independent measurements have been carried out for each pair QH^+, B, with the pressure ratio of Q and B varying by roughly a factor of 5.

The GB(Q) values so obtained are collected in *Table 2*. For convenience, they have been converted into eV. The values are in agreement within ±0.015 eV with the GB(Q) values reported in [14] [15]: GB(**1**) = 9.696 eV, GB(**3**(CH_3)) = 9.709 eV, GB(**3**(Cl)) = 9.445 eV. Note that no symmetry changes occur on protonation of the Q molecules, so that the corresponding enthalpy changes, *i.e.* the proton affinities PA(Q), can be deduced from the GB(Q) values by adding a constant $T\Delta S$ term of 0.356 eV.

Table 2. *Gas-Phase Basicities (GB) from Equilibrium Proton-Transfer Reactions between Quinuclidinium Cation* $\mathbf{1}H^+$ *or Substituted Quinuclidinium Cations* $\mathbf{2}H^+$(X), $\mathbf{3}H^+$(X), $\mathbf{4}H^+$(X), *and Reference Bases B.* Defining reaction: *e.g.* $\mathbf{1}H^+ + B \rightleftharpoons \mathbf{1} + BH^+$. GB values of reference bases from [14], based on GB (NH_3) = 8.52 eV.

Quinuclidinium Cation QH^+	Reference Base	$\frac{GB(B)}{eV} \pm 0.002$	$\frac{\Delta_r G}{eV} \pm 0.002$	$\frac{GB(Q)}{eV} \pm 0.01$	$\frac{\Delta GB(Q)}{eV} \pm 0.01$
$\mathbf{1}H^+$	Et_3N	9.688	+ 0.013	9.70	–
$\mathbf{2}H^+$ (Me)	Et_2PrN	9.722	+ 0.039	9.77	+ 0.07
	Pr_3N	9.783	– 0.004		
$\mathbf{3}H^+$ (Me)	Et_2PrN	9.731	– 0.013	9.71	+ 0.01
	Pr_3N	9.783	– 0.061		
$\mathbf{4}H^+$ (Me)	Et_3N	9.688	0.000	9.70	0.00
	Et_2PrN	9.722	– 0.017		
$\mathbf{2}H^+$ (Cl)	Piperidine	9.419	– 0.013	9.40	– 0.30
	Indoline	9.454	– 0.061		
$\mathbf{3}H^+$ (Cl)	Piperidine	9.419	+ 0.013	9.43	– 0.27
	Indoline	9.454	– 0.026		
$\mathbf{4}H^+$ (Cl)	Et_2NH	9.406	– 0.004	9.40	– 0.30
	Me_3N	9.389	+ 0.004		
$\mathbf{2}H^+$ (CN)	Cyclohexylamine	9.232	– 0.039	9.19	– 0.51
	Pyridine	9.219	– 0.026		
$\mathbf{3}H^+$ (CN)	(*tert*-Pentyl)amine	9.276	– 0.004	9.28	– 0.42
	EtMeNH	9.315	– 0.030		
$\mathbf{4}H^+$ (CN)	OP (Me_2) NMe_2	9.263[a]	– 0.004	9.25	– 0.45
	(*tert*-Pentyl)amine	9.276	– 0.030		
	EtMeNH	9.315	– 0.061		

From the GB(Q) values, the difference

$$\Delta \mathrm{GB(Q)} = \mathrm{GB(Q)} - \mathrm{GB}(\mathbf{1}) \tag{4}$$

i.e. the shifts in gas-phase basicity due to the substituent X, have been obtained, where Q now stands for **2**(X), **3**(X), or **4**(X). The ΔGB(Q) are also given in *Table 2* and displayed in *Fig. 3.* Positive (negative) ΔGB(Q) values correspond to an increase (decrease) in gas-phase basicity of **1** as a consequence of substitution.

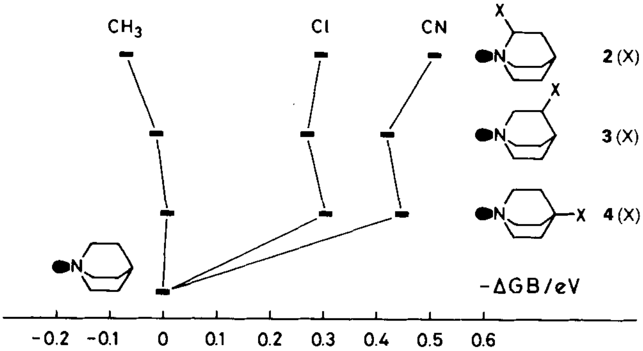

Fig. 3. *Shifts ΔGB of the gas-phase basicities GB(X) of* **2**(X), **3**(X), *and* **4**(X) *relative to the gas-phase basicity GB* (**1**) *(cf. Table 2)*

Discussion of the Results. – The observed trends in the I_1^c and ΔGB values, as depicted in *Figs. 2* and *3* are unexpected, if this expectation is based on the pK_a values of the corresponding quinuclidinium ions. Applying a least-squares treatment to the pK_a values (at 25° in 0.1M aq. KCl solution) of 12 triples **2**(X), **3**(X), **4**(X), which differ in the substituents X, *Grob* [4] has derived relative $\rho_I(\mu)$ values (μ = 2, 3, 4 = positions in the quinuclidine system), named inductivities in [4], arbitrarily defining $\rho_I(4) = 1.00$:

$$\rho_I(4):\rho_I(3):\rho_I(2) = 1.00:1.00:1.74 \tag{5}$$

If p$K_a(\mu,$X) is the pK_a of QH$^+$ carrying a substituent X in position μ, and if Δp$K_a(\mu,$X) = p$K_a(\mu,$X) – pK_a(**1**), then the $\rho_I(\mu)$ values given in (*5*) are essentially those of a *Hammett* equation Δp$K_a(\mu,$X) = $\rho_I(\mu)\sigma_I^q$(X) with σ_I^q(X) = ΔpK_a(4,X).

To begin with, the ρ_I ratios (*5*) have to be compared to the analogous ratios of $\rho_{PE}(\mu)$ and $\rho_{ICR}(\mu)$ values derived from the I_1^c(Q) and ΔGB(Q) values given in *Tables 1* and *2* for **2**(X), **3**(X), and **4**(X) with X = Cl and CN. The corresponding values for X = CH$_3$ can not be used, because the ΔI_1^c(Q) and ΔGB(Q) values for **2**(CH$_3$), **3**(CH$_3$), and **4**(CH$_3$) are of the same order (or smaller) than the errors of the measurements *(cf. Figs. 2* and *3)*. As before, $\rho_{PE}(4)$ and $\rho_{ICR}(4)$ have arbitrarily been set equal to 1.00, which yields the following ratios:

Ionization energies:

$$\Delta I_1^c = \rho_{PE}(\mu)\sigma_{PE}(\mathrm{X}) \tag{6}$$

$$\rho_{PE}(4):\rho_{PE}(3):\rho_{PE}(2) = 1.00:(0.86 \pm 0.03):(1.12 \pm 0.04) \tag{7}$$

Gas-phase basicities:

$$\Delta \mathrm{GB} = \rho_{\mathrm{ICR}}(\mu)\, \sigma_{\mathrm{ICR}}(\mathrm{X}) \tag{8}$$

$$\rho_{\mathrm{ICR}}(4):\rho_{\mathrm{ICR}}(3):\rho_{\mathrm{ICR}}(2) = 1.00:(0.92 \pm 0.02):(1.06 \pm 0.06) \tag{9}$$

Note that the 'errors' indicated are in fact the *ranges* of the values obtained for X = Cl and CN.

There is a significant and striking difference between the ρ_{I}-value set (*5*) and either of the two sets (*7*) and (*9*). Whereas in (*5*), we have $\rho_{\mathrm{I}}(4) = \rho_{\mathrm{I}}(3) \ll \rho_{\mathrm{I}}(2)$, the ρ values in (*7*) and (*9*) show only small absolute differences. However, these differences are significant and lead to the ordering $\rho_{\mathrm{M}}(3) < \rho_{\mathrm{M}}(4) < \rho_{\mathrm{M}}(2)$ for both methods, PE or ICR. We note in passing that in the case of the ionization energies the different order (*7*) as compared to (*5*) can not be attributed to the fact that we compare the vertical quantity I_1^{c} to an equilibrium constant pK_{a}, because the adiabatic ionization energies I_1^{a} of the Q molecules investigated are consistently shifted by the same constant decrement $w_{1/2}/2 = 0.3_0$ eV towards lower energies in all cases. Consequently, the same difference between (*5*) and (*7*) would have been observed, if I_1^{a} values had been used instead of I_1^{c}.

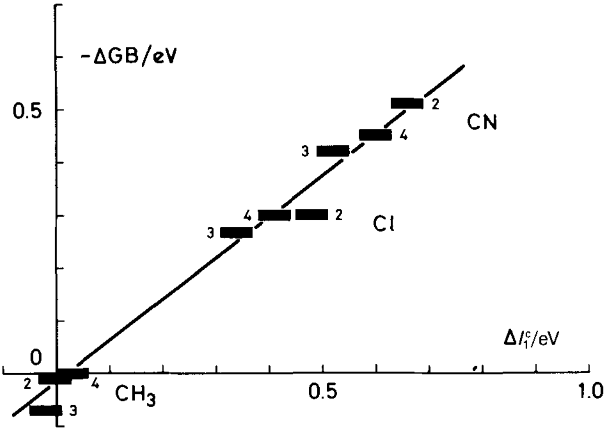

Fig. 4. *Correlation of the gas-phase basicity shifts ΔGB with the differences* ΔI_j^{c} *of the* n_N^{-1} *ionization energies of substituted quinuclidines*. The regression line is defined in (*10*).

As shown in *Fig. 4*, the substituent-induced shifts in ionization energy, $\Delta I_1^{\mathrm{c}}(\mathrm{Q})$, correlate satisfactorily with the changes ΔGB(Q) of the gas-phase basicities for the ten Q molecules investigated in this work:

$$-\left(\frac{\Delta \mathrm{GB(Q)}}{\mathrm{eV}}\right) = -(0.22 \pm 0.014) + (0.792 \pm 0.035)\left(\frac{\Delta I_1^{\mathrm{c}}(\mathrm{Q})}{\mathrm{eV}}\right) \tag{10}$$

This regression is characterized by a standard error SE(ΔGB(Q)) = 0.029 eV and a correlation coefficient r = 0.9923. Note that (*10*) includes the pair of values ΔGB(1) = $\Delta I_1^{\mathrm{c}}(1) = 0$. On the other hand, the correlation of either $\Delta I_1^{\mathrm{c}}(\mathrm{Q})$ or ΔGB(Q) with the pK_{a}(Q) values [4] of the same ten Q molecules as independent variable is rather poor, as is already obvious from a comparison of the ρ_I values given in *(5)*, with ρ_{PE} *(7)* or ρ_{ICR} *(9)*. In the first case, the standard error is SE(ΔGB(Q)) = 0.75 eV, *i.e.* larger by a factor of 26 than for *(10)* (r = 0.936), and in the second case SE(ΔI_1^c(Q)) = 0.62 eV (r = 0.957). At first sight, this lack of a satisfactory correlation between pK_a(Q) and ΔI_1^c(Q) seems to be in contrast to what has been observed previously [7], namely an excellent regression of the n^{-1} ionization energies *vs.* pK_a values. However, the latter investigation refers to a set of 15 differently substituted Q **4**(X), all of which carry the substituent X in the *same* position, *i.e.* at C(4), which, in addition, is far removed from the N-atom. A closer look at this regression (labeled *(9)* in [7]) reveals that for a given I_1^v the observed pK_a values of the cation **4H**$^+$(X) tend to get smaller than the values *on* the regression line, with increasing size of the substituent X. An extreme case is that of **4**($Sn(CH_3)_3$) (= 4-(trimethylstannyl)quinuclidine) [15], the PE spectrum of which is shown in *Fig. 1*. This molecule exhibits the lowest n^{-1} ionization energy of the series **4**(X), I_1^v = 7.59 eV, and should, therefore, possess a very high pK_a = 12.83, according to regression *(9)* of [7]. In fact, a much smaller pK_a = 11.38 is found experimentally [3]. A possible rationalization of these systematic discrepancies is to assume that the acid-base equilibrium in condensed phase is strongly influenced by solvation, which is absent in the gas phase. If this effect is assumed to be significant, then it should also show up especially in the pK_a of **2H**$^+$(X), compared to the expected values based on either ΔI_1^c or ΔGB of these molecules. Because of the change in distance between the substituent X and the acidic centre NH^+, going from **4**(X) or **3**(X) to **2**(X), we expect in the latter an increased perturbation of solvation at the protonation site, and accordingly smaller pK_a values than predicted on the basis of their ionization energies. This is indeed the case.

The regression of the pK_a of **1** and of **4**(X), with X = CH_3, CH_2OH, OH, $OCOCH_3$, Cl, CN [4], on the I_1^c values yields

$$\mathrm{p}K_a = (11.191 \pm 0.138) - (4.694 \pm 0.367)\left(\frac{\Delta I_1^c}{\mathrm{eV}}\right) \qquad (11)$$

$$N = 7,\ \mathrm{SE(pK_a)} = 0.230;\ r = 0.985$$

which differs slightly but not significantly from the regression given in [7], because the pK_a values have been determined in a different medium, because I_1^c rather than I_1^m values have been used, and because the number of data points is now only N = 7 instead of 15 in [7]. Using regression *(11)*, we can now calculate confidence limits for the expected pK_a values of **3**(X) and **2**(X), X = CN, Cl, on the basis of the measured ionization energies I_1^c of these compounds. Such 90% confidence limits are presented in *Fig. 5*, where it has been assumed that regression *(11)* describes only the correlation of pK_a *vs.* I_1^c, and that it is not an estimate of a true functional dependence. Thus, the range of the limits is wider than it would have been, if a functional dependence had been assumed. It is immediately apparent that for **2**(Cl) and **2**(CN), the pK_a (expected), *i.e.* expected on the basis of the lone-pair ionization energies I_1^c, deviate considerably from the experimentally observed pK_a (observed). Indeed, I_1^c = 8.56 eV for **2**(Cl) and I_1^c = 8.74 eV for **2**(CN) yield according to *(11)* pK_a (expected) = 8.9 for **2H**$^+$(Cl) and pK_a (expected) = 8.1 for **2H**$^+$(CN) instead of the pK_a(observed) = 7.0 and 5.9, respectively. As in the case of **4H**$^+$($Sn(CH_3)_3$), the cations **2H**$^+$(Cl) and **2H**$^+$(CN) are more acidic than expected on the basis of the ionization energies I_1^c of **2**(Cl) and **2**(CN). The same trend is observed for **3H**$^+$(Cl) and **3H**$^+$(CN),

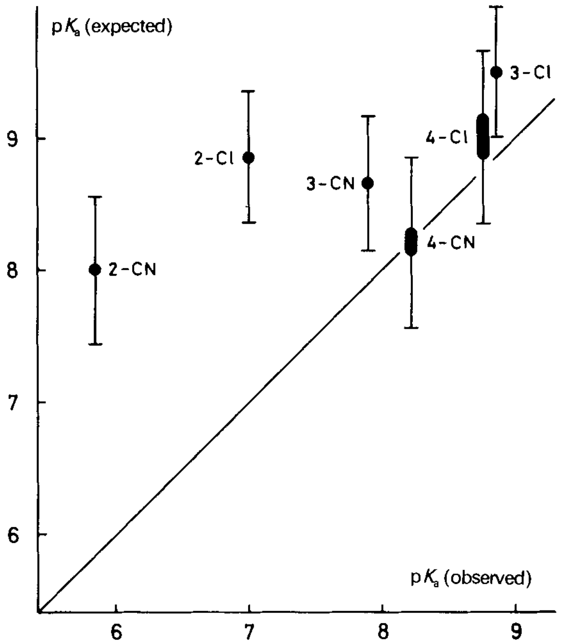

Fig. 5. *Correlation of the* pK_a *values expected on the basis of the* ΔI_l^c *values for* **2**(X), **3**(X), *and* **4**(X), *X* = *Cl and CN, with the corresponding experimental values* pK_a *(observed)*. The pK_a (expected) are obtained from (*11*). The vertical bars delimit the 90% confidence range for the expected values.

although to a lesser but still significant degree *(cf. Fig. 5)*. Because of the close correlation between ΔI_1^c and ΔGB shown in *Fig. 4*, exactly the same discrepancies would have been observed if the latter values had been used as independent variables.

Thus, the evaluation of the experimental data lead to the following conclusions which must be considered as preliminary because of the relatively small size of the sample:

a) Substituent-induced changes ΔGB(Q) and ΔI_1^c(Q) yield a satisfactory correlation *(Eqn. 10; cf. Fig. 4)*.

b) The regression (*11*) does not miss the origin significantly, so that for all practical purposes one has

$$\Delta \mathrm{GB(Q)} \approx 0.79\, \Delta I_1^c\mathrm{(Q)} \tag{12}$$

Accordingly, the substituent-induced shifts ΔGB(Q) are about 20% smaller than ΔI_1^c(Q).

c) Although it is known from previous experience that in many cases ΔpK_a(Q) and ΔI_1^c(Q) correlate well (*cf.* regressions (*9*) in [7], (*9*) in [9], and for aliphatic amines [16]), especially if the substituent of Q is well removed from the centre of protonation and not too large (*cf.* **4**($Sn(CH_3)_3$) as an exception), it is found that the pK_a values of **2H**$^+$(X), X = Cl, CN, are much smaller than expected on the basis of either their ΔI_1^c or ΔGB values. This enhanced acidity is due to the perturbation of solvation by the substituents in close proximity to the centre of protonation, which is more effective for the charged species **2H**$^+$(X) than the neutral base **2**(X). Note, however, that this effect is not observed for the **2H**$^+$ (CH_3), **2**(CH_3) pair, at least not within the limits of our measurements, which might suggest that the polar effect dominates, *cf.* last section of this work.

Comparison with Theory. – Closed- or open-shell *ab initio* SCF calculations have been carried out for the parent molecule **1**, its radical cation $\mathbf{1}^{+}$, and the protonated cation $\mathbf{1H}^{+}$ using a minimal basis set (STO-3G [17]) and standard bond length [18] under strict C_{3v} symmetry. The atomic charges q_{μ} and the changes δq_{μ} which accompany the following processes are collected in *Table 3*.

$$\delta q^{I}_{\mu}\text{: Ionization } n^{-1}\text{: } \mathbf{1} \rightarrow \mathbf{1}^{+} + e^{-} \tag{13}$$

$$\delta q^{P}_{\mu}\text{: Protonation: } \mathbf{1} + H^{+} \rightarrow \mathbf{1H}^{+} \tag{14}$$

Table 3. *Atomic Charges q_{μ} from an* ab initio *STO-3G Calculation of* **1**, $\mathbf{1}^{+}$, and $\mathbf{1H}^{+}$, *and Atomic Charge Changes δq_{μ} which Accompany Ionization (13) and Protonation (14) of* **1**. Note that all δq_{μ} values have been rounded *after* the difference having been computed from the original q_{μ}. Units are e/100, e = elementary charge unit = $1.602 \cdot 10^{-19}$ C.

μ	$\frac{q_{\mu}}{e \cdot 10^{-2}}$			$\frac{\delta q_{\mu}}{e \cdot 10^{-2}}$	
	1	$\mathbf{1}^{+}$	$\mathbf{1H}^{+}$	*(13)*	*(14)*
N	– 26.68	– 0.56	– 21.26	+ 26.12	+ 5.42
C(2)	– 2.91	– 3.23	– 1.74	– 0.32	+ 1.17
C(3)	– 11.66	– 10.86	– 11.32	+ 0.81	+ 0.34
C(4)	– 3.07	– 3.25	– 3.08	– 0.18	0.00
H–C(2)	+ 6.11	+ 12.46	+ 11.36	+ 6.36	+ 5.25
H–C(3)	+ 5.23	+ 10.09	+ 9.29	+ 4.86	+ 4.07
H–C(4)	+ 5.51	+ 10.78	+ 10.12	+ 5.27	+ 4.62
H–N			+ 29.47		

For the process *(13)*, the by far largest change δq^{I}_{μ} occurs on the N-atom, which is consistent with the interpretation that the electron is removed from a HOMO of essentially lone-pair type (n^{-1}). However, only a quarter of the positive hole created by electron ejection resides on the N-atom, the remaining three quarters being delocalized over the rest of the molecule. Note, however, from the q_{μ} values of $\mathbf{1}^{+}$, that the N-atom has become almost neutral in $\mathbf{1}^{+}$, having carried a negative excess charge in **1**, and that the positive charge of $\mathbf{1}^{+}$ resides on the H-atoms, the C-atoms being still negative.

In contrast, protonation according to *(14)* changes the charges q_{μ} on the N-atom and the H-atoms by roughly the same positive amount δq_{μ}, whereas the charge on the C-atoms remains largely unaffected. Again, the excess positive charge is found on the H-atoms, the N-atom and the C-atoms still carrying a negative charge.

The above results suffer from the defect that they have been computed under the assumption of zero change in geometry both on ionization (which may be acceptable) and on protonation, and that a minimal basis set underestimates by necessity effects of polarization. Notwithstanding these obvious shortcomings, the trends in relative charge changes δq_{μ} are most probably correct.

From first-order perturbation arguments, one predicts that in a first approximation the perturbations of I^{c}_{1} and GB of **1**, resulting from the replacement of a H-atom at C(2), C(3), or C(4) by a substituent (*e.g.* X = Cl or CN), parallel the δq_{μ} values at these H-atoms which accompany the processes in *(13)* and *(14)*. A comparison of *Fig. 6*, where these δq_{μ} *(cf. Table 3)* are displayed graphically, with *Figs. 2* and *3* shows that this is indeed the case. In fact, the agreement is much better than one might have expected, in

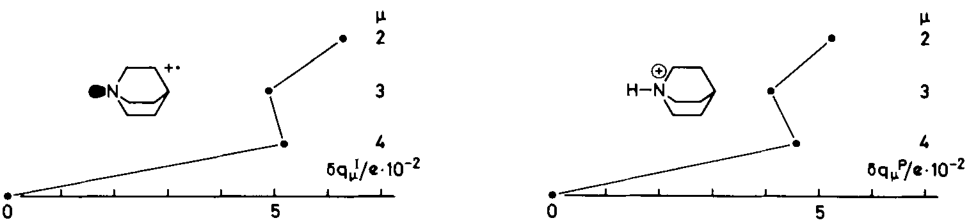

Fig. 6. *Predictions of the change in charge, δq_μ, at the C-atoms μ of the quinuclidine frame on ionization* (δq^I_μ: n_N^{-1} process (*13*) *and on protonation* (δq^P_μ: (*14*)). The abscissae are calibrated in hundredth of an elementary charge unit e.

view of the crudeness of the argument. Not only is the trend of the ΔI_1^c and of the ΔGB values well reproduced, but it is found that the absolute perturbation of GB should be *smaller* than that of I_1^c by a factor of 0.85, which is practically the same as the slope 0.79 of regression (*10*) (*cf.* (*12*) and *Fig. 4*).

With all due caution, we conclude that the changes ΔI_1^c and ΔGB are valid probes for the changes δq_μ, which occur in the ionization and the protonation processes (*13*) and (*14*), and, thus, of the charge dispersal in $\mathbf{1}^+$ and $\mathbf{1H}^+$. On the other hand, the changes ΔpK_a obtained from measurements in condensed phases do not allow conclusions about purely electronic effects which accompany the protonation of **1**, because of important differences in the solvation energetics between different isomeric pairs **2**(X)/**2H**$^+$(X), **3**(X)/**3H**$^+$(X), and **4**(X)/**4H**$^+$(X).

Solvent-Induced Proximity Effect. – One of the interesting results is that the inductivities ρ_I for position 2 of Q [3] [4] are smaller than expected, if compared to the ΔGB(**2**(X)) and ΔI_1^c(**2**(X)) values for X = Cl and CN, or – in other words – if we assume that the ρ_I values reflect only the changes in positive-charge distribution on protonation (charge dispersal) of the isolated molecule. As mentioned before, this suggests that the solvent plays an important role, when the substituent X is close to the centre of protonation. However, it is obvious that this is not a purely steric effect, *i.e.* that the enhanced acidity of the quinuclidinium ions **2H**$^+$(X) is not due only to the extrusion of solvent molecules from the region of space between the substituent X and the protonation site, but must also be due to changes of charge distribution induced within the molecular framework by the surrounding solvent molecules. One could even think of other mechanisms responsible for the lack of correlation between gas-phase and solution basicities of **2**(Cl) and **2**(CN). (For a review of the complex nature of the problem, *cf.* [19] [20]. As has been pointed out [21], the present sample is certainly too small to allow straightforward conclusions.)

On the other hand, it is not without interest to compare our results with those obtained for substituted pyridines, the only example for which the pK_a values [22] and the gas-phase basicities GB [8] are known for a wider range of substituents X (including X = CH_3, Cl, and CN) at C(2), C(3), or C(4). Unfortunately, it is not possible to measure the position of the n_N^{-1} lone-pair band in the PE spectra of substituted pyridines with sufficient precision for our purposes, because of the strong overlap of this band by the π^{-1} bands of the pyridine π-system.

The data, taken from [8] and [22] have been transformed into changes of free enthalpy (ΔG/eV) as explained in the legend to *Table 4*, in which they are listed. From these, we can draw the following conclusions:

1) In analogy to *Fig. 3*, the ΔGB values of X-substituted pyridines, X = CH_3, Cl, CN, are shown in *Fig. 7*. As in the case of the quinuclidines, ΔGB does not vary substantially with position μ for a given X. The range of shifts, from X = CH_3 to X = CN is ~ 0.7 eV for the pyridines, as compared to ~ 0.6 eV for the quinuclidines, *i.e.* practically the same, notwithstanding the fact that the former range refers to an aromatic and the latter to a saturated system. Note, however, that the CH_3-induced shifts are significantly larger for the pyridines than for the quinuclidines.

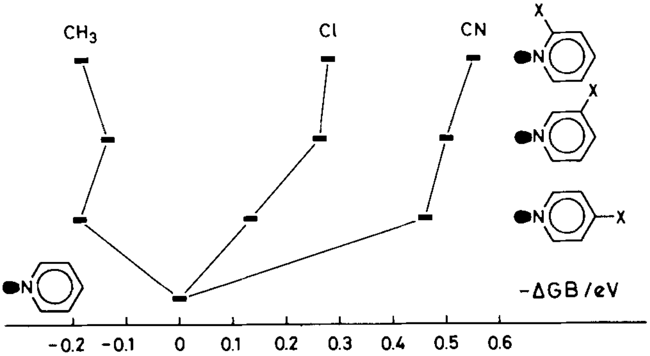

Fig. 7. *Shifts ΔGB of the gas-phase basicities GB of substituted pyridines* (X = CH_3, Cl, CN; *cf. Table 4*) *relative to GB (pyridine)*

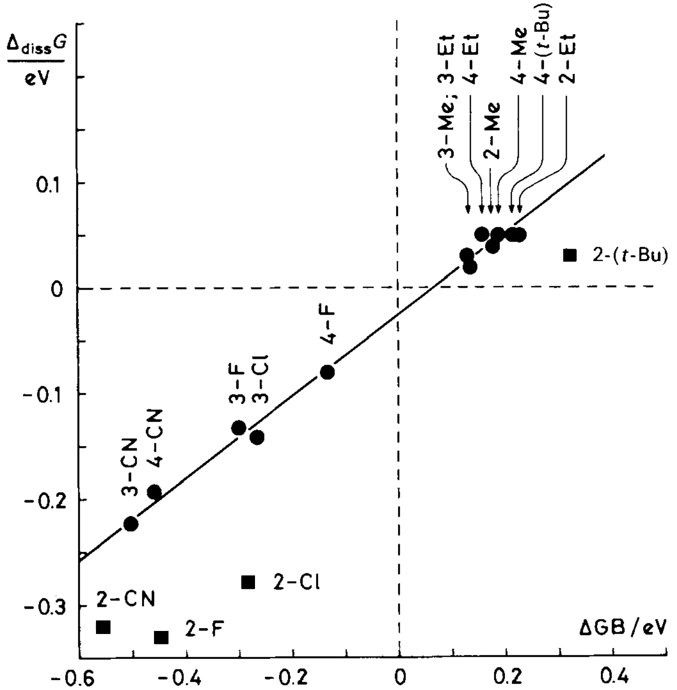

Fig. 8. *Correlation of Δ_{diss}G and ΔGB* (as defined in the legend to *Table 4*) *of substituted pyridines*. The regression line (*cf.* (*15*)) is defined by the black, round dots. The squares correspond to those four pyridines for which large *ortho*-effects are expected.

Table 4. *Gas-phase-Basicity Differences ΔGB and pK_a Differences ΔpK_a for Substituted Pyridines: ΔGB = GB (substituted pyridine) – GB (pyridine), ΔpK_a = pK_a (substituted pyridine) – pK_a (pyridine).* For the sake of comparison, the ΔpK_a values have been converted into $\Delta_{diss}G$ values using the conversion factor $\Delta_{diss}G/\Delta$pK_a = 0.059 eV. The Δ values refer to GB (pyridine) = 9.241 eV and pK_a (pyridine) = 5.20.

Substituent	Position	ΔGB/eV	ΔpK_a	$\Delta_{diss}G$/eV
Me	2	0.178	0.7_5	0.04
	3	0.134	0.3_5	0.02
	4	0.186	0.8_5	0.05
Et	2	0.230	0.8_0	0.05
	3	0.130	0.5_0	0.03
	4	0.160	0.8_0	0.05
t-Bu	2	0.321	0.5_5	0.03
	4	0.217	0.8_0	0.05
F	2	– 0.447	-5.6_5	– 0.33
	3	– 0.299	-2.2_0	– 0.13
Cl	2	– 0.282	-4.6_5	– 0.27
	3	– 0.265	-2.3_3	– 0.14
	4	– 0.134	-1.3_5	– 0.08
CN	2	– 0.555	-5.4_5	– 0.32
	3	– 0.503	– 3.8	– 0.22
	4	– 0.460	– 3.3	– 0.19

2) *Fig. 8* shows the correlation between the $\Delta_{diss}G$ values (obtained from the ΔpK_a; *cf. Tab. 4*) and the ΔGB values for 12 substituted pyridines with X in the positions indicated above the regression line

$$\frac{\Delta_{diss}G(\mathrm{X})}{\mathrm{eV}} = -(0.026 \pm 0.003) + (0.376 \pm 0.010)\frac{\Delta \mathrm{GB(X)}}{\mathrm{eV}} \qquad (15)$$

which is characterized by a residual error of s = 0.009 and a correlation coefficient r = 0.996. Thus, for a given X in a given position μ, the ΔGB values are 2.7 times larger than the $\Delta_{diss}G$ values in the case of the pyridines, as compared to the corresponding ratio of 2.3 for the quinuclidines. In view of the next remark, attention is drawn to the fact that the points for X = CH_3 and CH_3CH_2 in position 2 do not deviate significantly from the regression line (*15*).

3) As shown by the square dots included in *Fig. 8*, the pyridinium cations carrying a polar group (X = F, Cl, CN) or a very bulky group (X = *t*-Bu) at C(2) are again more acid in solution than expected on the basis of their ΔGB(X) values. It is noteworthy that this effect is larger for the polar groups, notwithstanding the fact that *t*-Bu is much more bulky. This confirms that the origin of the additional acidifying influence of the solvent on 2-substituted pyridinium and quinuclidinium ions can not be reduced to a simple space-filling effect of the substituent close to the protonation site [19] [21] (*cf.* also last remark in the previous section).

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