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LONE-PAIR CHARGES AND STRUCTURAL EFFECTS

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The lone-pair charge, Q_{lpf}, of a base B is a (theoretically calculated) measure of the amount of charge on the lone pair of B that binds to an acid A^{ν} ($\nu = 0, 1$) in an acid–base reaction. It is shown how they can be used for the quantitative study of structural effects on gas-phase proton affinities, vertical ionization potentials and hydrogen-bonding basicities.

INTRODUCTION

The systematic development of experimental and theoretical gas-phase ion chemistry[1–8] in the last 10 years has led to a rapid accumulation of information and it is now possible to analyse *a posteriori* a substantial body of different experimental data relating to the Lewis concept of basicity.

Special attention has been paid to the study of substituent effects.[5] *Ab initio* SCF calculations provide useful information on the role played by substituents on the structure and reactivity of a given system.[6,7] A considerable number of linear relationships between gas-phase proton affinities [defined as PA = $-\Delta H^0$ for the process

$$B(g) + H^+ \underset{}{\overset{\Delta H^0}{\rightleftharpoons}} BH^+ \text{ (g)},$$

where B is a base] and some theoretical indices have been proposed.[6] Energy-charge correlations have been especially useful in reactivity studies.

It is usually accepted that some characteristics of a basic centre are correlated with its gas-phase PA. One of these characteristics is the charge on the lone pair involved in the formation of the corresponding cation on protonation. It has been shown[9] that the electronic population of the basic centre bears only a rough relationship with the energy variation of the corresponding proton-transfer equilibrium.

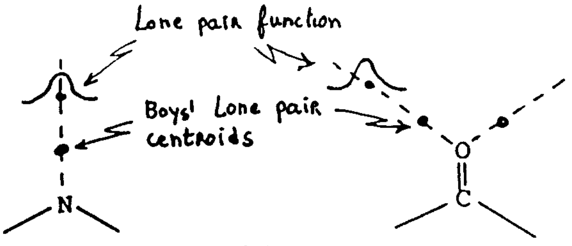
In previous work an economical way to evaluate the lone-pair charge in an SCF procedure was proposed.[8–11] The lone-pair-charge (Q_{lpf}) concept reflects the interest in finding theoretical methods that allow the prediction of structural effects on basicity. It has been shown[8–11] that the gas-phase proton affinities of a wide variety of organic bases are linear functions of the Q_{lpf} values of their protonation sites.

We report here that a series of compounds exists for which this simple linear relationship breaks down, and show how this failure provides a new and powerful tool for the analysis of molecular properties.

COMPUTATIONAL DETAILS

For compatibility with our previous studies[8–11] we carried out *ab initio* calculations at the minimal basis set level following the model employed previously based on fully optimized INDO geometries, where the CH, NH and OH bond lengths were conveniently scaled to account for the fact that the INDO method overestimates them. The scaling factors for CH (0·974), NH (0·935) and OH (0·924) bond lengths are the ratios of the experimental CH bond lengths in naphthalene, NH bond lengths in pyrrole and OH bond lengths in phenol, respectively, to the INDO optimized values.

The lone-pair charge is evaluated using a lone-pair function (LPF) formed by one s-type and three p-type (x, y, z) Gaussian-type orbitals (GTOs) with identical exponents and centred at the same point in space. This basis (to be added to the STO-3G[12] minimal basis set) is located on the line that joins the basic centre (either N or O) to the centroid of charge of the corresponding Boys' localized[13] lone-pair orbital (see Scheme 1) from a previous STO-3G calculation. The charge on the LPF is evaluated using the well known Mulliken population method.



Scheme 1

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The previously reported[8] values of exponents (0·10) and position (0·85 Å away from the N atom) are used in this work, when N is the basic centre. Following the same methodology as given in Ref. 8 and taking benzaldehyde as a probe, we obtained for compounds in which O is the basic centre exponent = 0·133 and position 0·773 Å away from the O atom.

We have proved[8] that the basis set STO-3G + LPF does not present any abnormal behaviour.

All the calculations were performed at UAM/IBM Scientific Centre and CC/UAM Centre in Madrid using the programs GEOMO[14] and our version of GAUSSIAN 80[15] (IBM MVS version by E. M. Fluder and L. R. Kahn, modified by us to run under VM/CMS).

RESULTS AND DISCUSSION

Table 1 shows the relative proton affinities, δPA [i.e. the standard enthalpy changes, for reaction (1) in the gas phase] for *para*-substituted benzaldehydes (Data from Ref. 16 except for 4-NH_2 value, kindly communicated by Prof. R. W. Taft) (Y = H, series I) and acetophenones[17] (Y = CH_3, series II). Also given are calculated Q_{lpf} values for the lone pairs of their carbonyl oxygens.

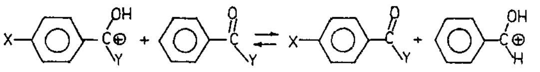
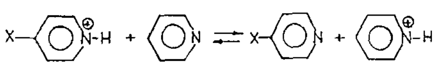

(1)

Figure 1 shows plots of δPA vs Q_{lpf} for series I and II. The Q_{lpf} calculated for 4-substituted pyridines taken from Ref. 9 are shown for comparison purposes (series III in Figure 2). δPAs for these compounds were taken from Ref. 5 and are defined according to reaction (2).


(2)

It appears that in all three cases, +R (electron-acceptor) and −R (electron-donor) substituents define two different lines, the ratios $\xi = S_{-\mathrm{R}}/S_{+\mathrm{R}}$ of their slopes (S) being $\xi_{\mathrm{I}} = 2{\cdot}42 \pm 0{\cdot}27$, $\xi_{\mathrm{II}} = 2{\cdot}19 \pm 0{\cdot}73$ and $\xi_{\mathrm{III}} = 1{\cdot}29 \pm 0{\cdot}35$ (excluding the 4-F value, $\xi_{\mathrm{III}} = 1{\cdot}16 \pm 0{\cdot}29$).

The same applies to vertical ionization potentials (VIP).[18] In Figure 3 the VIPs for the n_0 orbitals of the carbonyl oxygen (for some compounds experimental values were estimated from the excellent linear relationships between experimental VIPs and the STO-3G energies of the n_0 orbitals; see Table 2) are plotted against Q_{lpf}. The linear relationships are excellent (r^2 and standard deviations in the ranges 0·974–0·992 and

Table 1. Relative gas-phase proton affinities (δPA), vertical ionization potentials (VIP) and lone-pair charges (Q_{lpf} and Q'_{lpf}) for 4-X-substituted benzaldehydes and acetophenones

X	Y	δPA (kcal mol^{-1})[16,17]	VIP (kcal mol^{-1})[18]	Q_{lpf} (electron units)	Q'_{lpf} (electron units)
$N(CH_3)_2$	H	21·1	216·8	0·3732	0·3804
NH_2	H	14·9	219·7[b]	0·3689	0·3736
OCH_3	H	10·2	224·9	0·3629	0·3675
OH	H	6·9	223·7[b]	0·3628	0·3643
CH_3	H	4.5	225·6	0·3578	0·3593
F	H	−0·6	227·2	0·3563	0·3556
H	H	(0)	228·1	0·3554	0·355
Cl	H	−0·5	231·8	0·3494	—
CHO	H	−4·5[a]	232·0[b]	0·3493	0·3503
CF_3	H	−5·9	235·3[b]	0·3442	0·3472
CN	H	−8·0	238·7	0·3436	0·3448
NO_2	H	−8·7	239·2	0·3382[c]	0·3430
$N(CH_3)_2$	CH_3	18·1	208·4[b]	0·3938	0·4013
NH_2	CH_3	11·4	209·4	0·3924	0·3957
OCH_3	CH_3	8·1	212·2	0·3869	0·3900
OH	CH_3	5·4	213·3[b]	0·3865	0·3874
CH_3	CH_3	3·9	216·3	0·3834	0·3835
F	CH_3	−0·6	217·4[b]	0·3805	0·3797
H	CH_3	(0)	219·3	0·3797	0·380
Cl	CH_3	−0·7	219·6	—	—
CHO	CH_3	−4·5	221·8	0.3731	0·3747
CN	CH_3	−8·2	226·5	0·3682	0·3689
NO_2	CH_3	−8·8	230·2	0·3624	0·3675

[a] Calculated from the excellent linear relationship between $(\delta PA)_{\mathrm{I}}$ and $(\delta PA)_{\mathrm{II}}$ given in Ref. 17.

[b] Calculated from the excellent linear relationship found between the experimental VIPs and the STO-3G calculated energies of the n_0 orbitals (see Table 2).

[c] Q_{lpf} for the 3-NO_3 derivative is 0·3385 electrons.

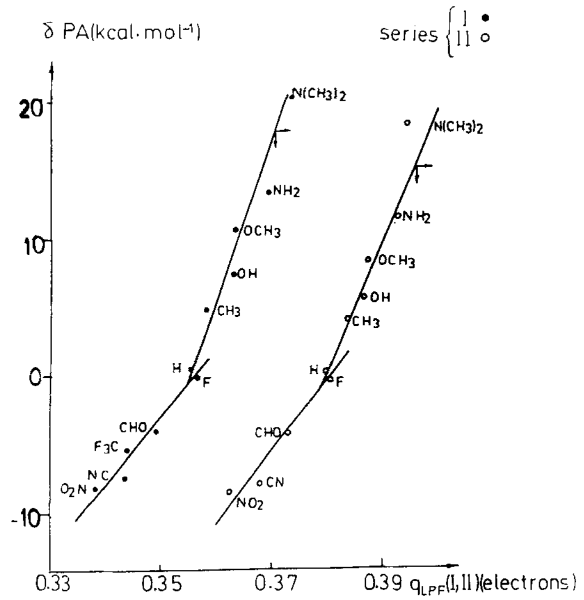


Figure 1. Relative proton affinities (δPA) for series I and II (benzaldehydes and acetophenones) vs. calculated lone-pair charges (Q_{lpf})

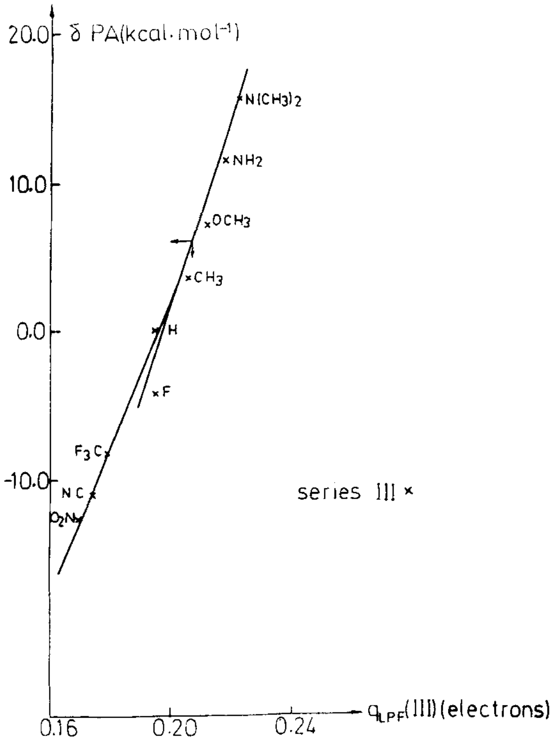


Figure 2. Relative proton affinities (δPA) for series III (pyridines) vs. calculated lone-pair charges (Q_{lpf})

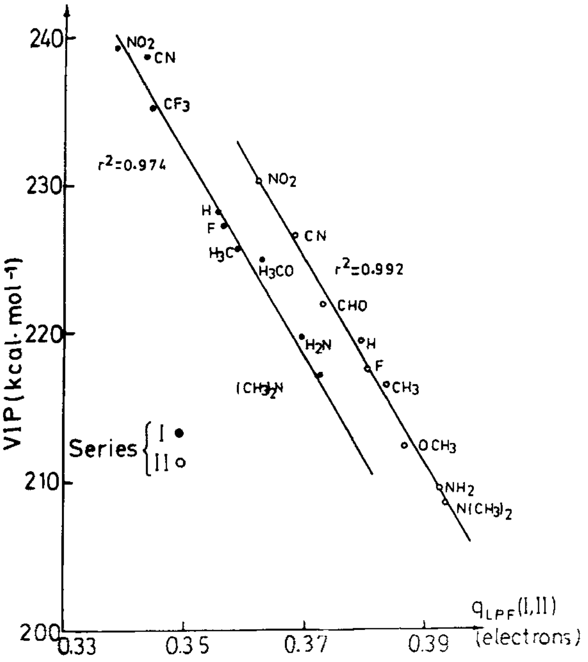
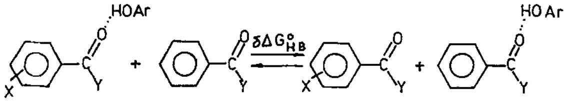


Figure 3. Vertical ionization potentials (VIP) for series I and II (benzaldehydes and acetophenones) vs. calculated Q_{lpf} values

0·5–1·0 kcal mol^{-1}, respectively). As expected, the plots of δPA vs VIP are bilinear. This is to be compared with the highly precise linear relationships that exist between PAs and adiabatic ionization potentials.[19]

Little electron demand is involved in hydrogen-bonding processes in which proton transfer is not a significant contributor.[20] The charge involved in hydrogen-bonding processes is much lower than in protonation processes. We may expect a better description using Q_{lpf}. Some relative standard free energies, $\delta\Delta G^0_{\mathrm{HB}}$, for the formation of 1 : 1 complexes between substituted benzaldehydes or acetophenones and phenol (ArOH) in CCl_4 or C_2Cl_4 solutions at 25·0 °C [reaction (3)] are available. (δG^0_{HB} is calculated from equilibrium constants at 298 K in the concentration scale, taken from Ref. 21. For related compounds, the $\delta\Delta G^0_{\mathrm{HB}}$s closely follow the ranking of $\delta\Delta H^0_{\mathrm{HB}}$ values.[22]) We have represented this in Figure 4, which shows that $\delta\Delta G^0_{\mathrm{HB}}$ values are indeed linear, with $r^2 = 0{\cdot}971$ for series I (*para*-substituted benzaldehydes) and $r^2 = 0{\cdot}0{\cdot}988$ for series II (*para*-substituted acetophenones). Q_{lpf} is thus a means of describing hydrogen-bonding free energies.



(3)

Table 2. STO-3G oxygen lone-pair energies (ε_{n_0}) and experimental vertical ionization potentials (VIP)[18] in kcal mol^{-1} for *para*-substituted benzaldehydes and acetophenones[a,b]

Benzaldehydes	Exp.	STO-3G	Acetophenones	Exp.	STO-3G
$N(CH_3)_2$	216·8	205·1	NH_2	209·4	201·0
$O(CH_3)$	224·9	210·3	$O(CH_3)$	212·2	204·9
CH_3	225·6	211·4	CH_3	216·3	206·0
F	227·2	214·9	H	219·3	207·6
H	228·1	213·3	CHO	221·6	214·0
Cl	231·8	220·5	CN	226·5	219·2
CN	238·7	225·2	NO_2	230·2	222·9
NO_2	239·2	229·2			

[a] Benzaldehydes: VIP (kcal mol^{-1}) = 0·8981 ($-\varepsilon_{n_0}$) + 34·83; $r = 0·9785$
Acetophenones: VIP (kcal mol^{-1}) = 0·9300 ($-\varepsilon_{n_0}$) + 22·83; $r = 0·992$.
[b] Calculated oxygen lone-pair energies at STO-3G level:
benzaldehydes: NH_2 205·0, OH 210·2, CHO 219·5, CF_3 223·2 kcal mol^{-1};
acetophenones: $N(CH_3)_2$ 199·5, OH 209·2, F 204·8 kcal mol^{-1}.

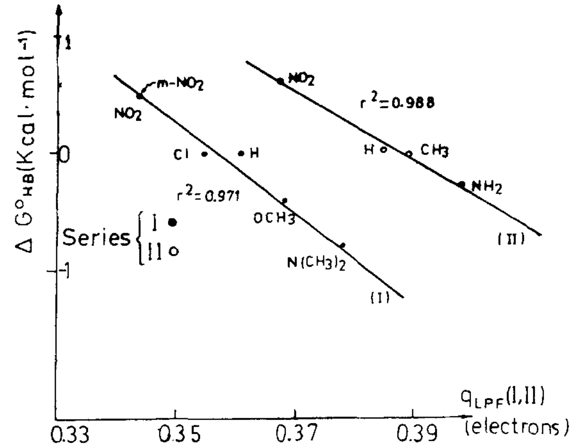


Figure 4. Relative standard free energies ($\delta\Delta G^0_{HB}$) [reaction (3)] for series I and II (benzaldehydes and acetophenones) vs. calculated Q_{lpf} values

The substituent effects on the PAs may be separated[5] into three contributions:

$$\delta\Delta G = R + P + F = \rho_R\sigma_R + \rho_P\sigma_P + \rho_F\sigma_F$$

where R, P and F are the contributions of the resonance, polarizability and field effects, respectively. A quantitative analysis of substituent effects on the δPAs of series I, II and III[5] shows that the importance of the resonance effect increases in the order III < II < I (see Table 3). This is also the order of increasing electron demand on the corresponding protonated systems.

A similar analysis of Q_{lpf} will indicate how substituents contribute to this value and also how substituents transmit their effect (ρ). For this analysis we employ the corresponding σ_R for neutral molecules, which we define as the arithmetic mean of the corresponding values for acid–base equilibria in cationic and anionic systems. Data are taken from Ref. 5.

Using multivariate regression analysis the following were obtained:

Benzaldehydes:

$$Q_{lpf} = 0·3537 - 0·040\sigma_R - 0·020\sigma_F - 0·004\sigma_P \quad (4)$$
$$(n = 11, r = 0·993)$$

Acetophenones:

$$Q_{lpf} = 0·3801 - 0·035\sigma_R - 0·020\sigma_F - 0·002\sigma_P \quad (5)$$
$$(n = 10, r = 0·994)$$

Pyridines:

$$Q_{lpf} = 0·1953 - 0·060\sigma_R - 0·0347\sigma_F - 0·008\sigma_P \quad (6)$$
$$(n = 9, r = 0·997)$$

After establishing the transmittance factors of these effects (ρ_R, ρ_F and ρ_P), we can find the values of Q_{lpf} that will correspond to our studied series of compounds if they showed cationic behaviour, i.e. the calculated lone-pair charge (Q'_{lpf}) corresponding to the use in equa-

Table 3. Comparison between ρ_R and ρ_F taken from Ref. 5 and the calculated ratio $\xi = S_{-R}/S_{+R}$

Series	Compounds	ρ_R	ρ_F	ρ_R/ρ_F	$\xi = S_{-R}/S_{+R}$
I	Benzaldehydes	31·6 ± 0·7	16·6 ± 0·6	1·90	2·42
II	Acetophenones	27·4 ± 0·5	16·1 ± 0·5	1·70	2·19
III	Pyridines	25·7 ± 0·6	21·8 ± 0·6	1·18	1·29

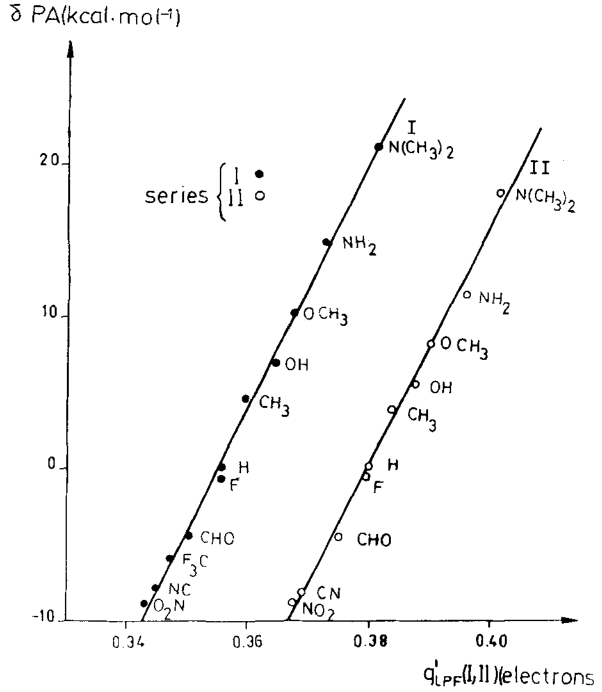
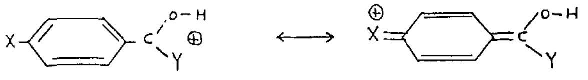


Figure 5. Relative proton affinities (δPA) for series I and II (benzaldehydes and acetophenones) vs. calculated A'_{lpf} values

tions (4) and (5) of the σ_R values reported in Ref. 5 for cationic systems.

Following this procedure, we obtained the values of Q'_{lpf} shown in the last column in Table 1. Figure 5 shows a plot of Q'_{lpf} vs δPA in the gas phase. There is an excellent agreement and the plot is linear ($r = 0{\cdot}997, r = 0{\cdot}996$).

As Q_{lpf} is calculated on neutral molecules, it is not able to reproduce completely π-donor effects in the positively charged protonated form[23] and it may explain the ranking of the ξ values, namely $\xi_{\mathrm{I}} < \xi_{\mathrm{II}} < \xi_{\mathrm{III}}$. Our multivariate analysis of Q_{lpf} shows that Q'_{lpf} will reproduce this effect.



CONCLUSIONS

There is a proportionality between basicity (proton affinity) and the electronic charge density that the system is able to place on the basic centre (Q_{lpf}). Also the amount of this charge can change depending on the electron demand of the attacking acid (gas-phase basicity H^+; hydrogen-bonding basicity $RH^{\delta+}$, etc.).

The present findings confirm that the lone-pair charge formalism is a reliable tool for the study of substituent effects, and can be used for the quantitative study of structural effects on δPA, vertical ionization potentials and hydrogen-bonding basicities as shown Figures 1–5.

ACKNOWLEDGEMENT

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