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NEW EMPIRICAL MODELS OF SUBSTITUENT POLARISABILITY AND THEIR APPLICATION TO STABILISATION EFFECTS IN POSITIVELY CHARGED SPECIES

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Two simple new models of substituent polarisability have been devised to take into account attenuation of substituent influence, and have been used to quantify electron relaxation effects in core-ionised chlorine and nitrogen compounds, and relative stabilisation of protonated alkylamines.

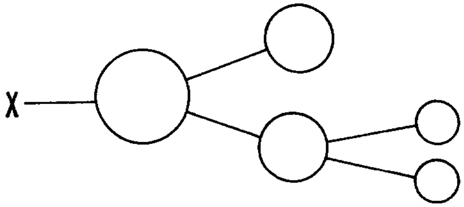
It has been realised that polarisability has a fundamental influence on chemical reactivity especially in the gas phase, as is well established,[1] but also in solution as demonstrated by more recent work.[2] Polarisability data are determined experimentally from physical measurements on bulk systems, and therefore reflect a *mean* molecular property. However, in describing chemical reactivity one has to consider the *local*, site-specific effect of polarisability on electronic changes induced by reagents. For charge development, stabilisation deriving from a remote atom is less than when the same atom is close to the charged centre. Progress toward quantifying the effect has foundered on the absence of any model which takes into account this attenuation of influence, as well as the different contributions to polarisability of the different elements. We now describe two new models of substituent polarisability which allow for these observations, and their application to three systems where polarisability is known to be of importance in stabilising positive charge in the gas phase.

A formula has recently been published[3] for the calculation of mean molecular polarisabilities α (eqn. 1), dependent on the parameters τ_i, a polarisability contribution for each atom i, characteristic of the atom type and its hybridisation state, and N, the total number of electrons in the molecule. In order to ensure an attenuated polarisability contribution for more remote atoms, we have modified this formula by a damping factor, d^{n_i-1}, to give the substituent polarisability, α_d (eqn. 2) where n_i is the smallest number of bonds between the reaction centre and i, and d is given a value of 0.75 (determined empirically from the study of several systems). The polarisability-induced stabilisation of charge can then be taken as proportional to α_d. Figure 1 attempts to demonstrate the model pictorially.

$$\alpha = 4(\sum_i \tau_i)^2/N \qquad (1)$$

$$\alpha_d = 4(\sum_i d^{n_i-1}\tau_i)^2/N \qquad (2)$$

Figure 1

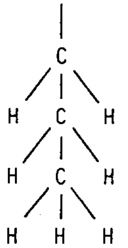


polarisability contribution τ_i $0.75\ \tau_i$ $(0.75)^2\tau_i$

attenuated as atoms are further away from the reaction centre X

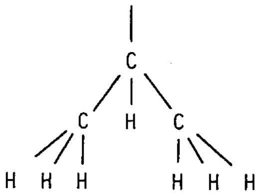
For unsubstituted alkyl groups, an even simpler model has been devised which accounts for the attenuation of polarisability-induced charge stabilisation. This is based on a bond-counting *ansatz* which leads to a connectivity number, N_c. Figure 2 shows for ^{n}Pr and ^{i}Pr how the number of bonds per level, b_n, are summed to give N_c, while allowing for an attenuation by a factor of one half for each level further from the reaction centre.

Figure 2



No. of bonds in n'th level, b_n	Contribution to N_c = $b_n(0.5)^{n-1}$
1	$1(0.5)^0$ +
3	$3(0.5)^1$ +
3	$3(0.5)^2$ +
3	$3(0.5)^3$

$N_c(^n\text{Pr}) = 3.625$



$1(0.5)^0$ + $3(0.5)^1$ + $6(0.5)^2$

$N_c(^i\text{Pr}) = 4.000$

$$\text{In general: } N_c = \sum_n b_n(0.5)^{n-1} \qquad (3)$$

For a series of non-heteroatom substituted alkyl groups, N_c correlates with the α_d values of equation 2 (n 49, r 0.9965, s 0.35 N_c units). As a comparison, the α_d (and N_c) values of ^{n}Bu and ^{t}Bu are 3.53 (3.81) and 4.72 (4.75) respectively, reflecting the greater effective substituent polarisability of the more branched alkyl group.

The value of any model can only be demonstrated by its ability to reproduce experimental data, and accordingly we now exemplify the effectiveness of these two models with respect to three experimental data sets. The systems have been analysed by linear regression techniques.

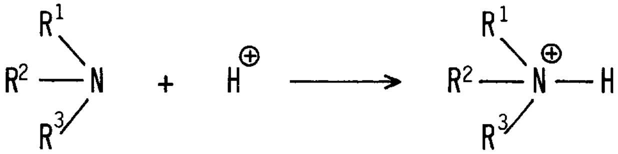
On X-ray-induced core ionisation of an atom in a molecule, the remaining electrons in the molecule relax so as to maximise stabilisation of the developed positive charge. This relaxation has been taken to be dependent on the relative polarisability of the substituents.

$$RCl + h\nu \xrightarrow[\text{ESCA}]{-e^-} RCl^{+} \xrightarrow[\text{AUGER}]{-e^-} RCl^{++} \qquad (4)$$

Combined ESCA-Auger *X*-ray photoelectron spectral data on a series of organochlorine compounds (eqn. 4) have been used to derive quantitative measures of the relaxation energy of the ligands around the ionised chlorine atom.[4] Substituent polarisability values calculated from equation 2 for the molecules in question correlate directly with these data (n 14, r 0.955, s 0.13 eV) demonstrating the significance of the model of equation 2.

We have extended this study, and our earlier one of C-1s ESCA data,[5] to the N-1s ESCA data of a series of nitrogen derivatives ranging from $(Me_3Si)_2NH$ to NF_3. As before,[5] we find that the overall trend of ESCA shifts correlates well with the charge on the nitrogen atom, with the notable exception of the alkylamines. These molecules define a trend perpendicular to that of the broad range of molecules. This deviation is due to a failure to make allowance for the different electron relaxation effects of the various alkyl groups. When the latter are accounted for by either of the polarisability models described above (equations 2 and 3), the alkylamine trend is brought into correspondence with that of the other molecules of the series (n 32, r 0.995, s 0.32 eV).

The third system can be regarded as a prototype of an ionic bond-forming reaction. Thus, a charge can also be introduced into a molecule by protonation (eqn. 5).



(5)

$$PA = -\Delta H_r \quad (5)$$

R^1, R^2, R^3 = H, alkyl

If other polarity effects are minimised by restricting attention to simple alkylamines, relative substituent polarisability should parallel the stabilisation of the charge. In fact, it is found that the proton affinities (PA) of these molecules[1,7] correlate well with values derived from equations 2 and 3. Thus alkylamine PA, covering a range of 100 kJ/mole, is quantitatively reproduced by a single parameter equation (Figure 3).

Mean molecular polarisabilities (*i.e.* no attenuation of effect, as calculated by equation 1) are totally unsatisfactory in all three of these systems, and lead to no correlation.

Thus, we believe that the two models introduced here can be used to quantify local polarisability effects. Accordingly, we are using them, with success, in analysing reactivity data in diverse systems. One important example is discussed in the accompanying Letter.

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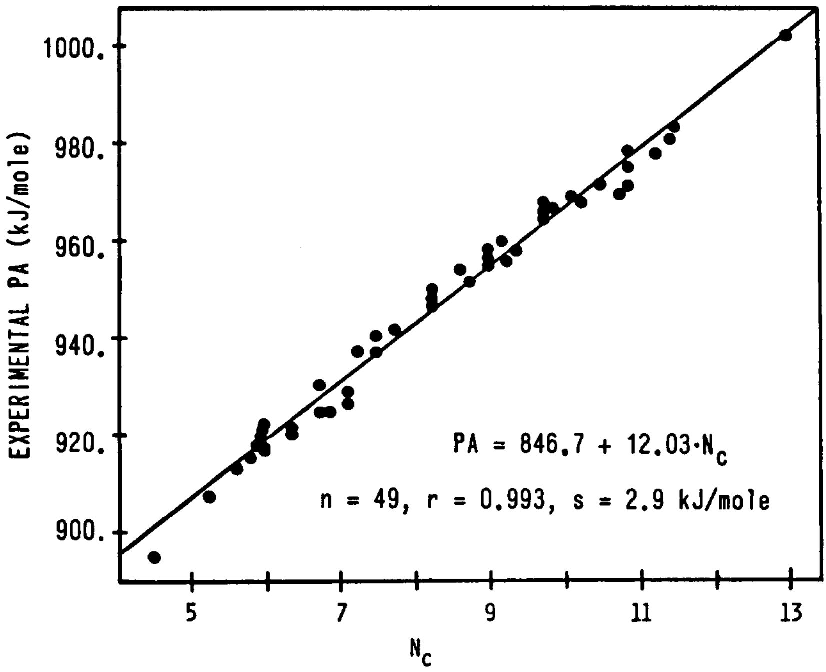

Figure 3: Proton affinity of unsubstituted alkylamines (primary,secondary,tertiary)

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