JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 302–306 (1993)

HYDROGEN-BOND BASICITY OF NITRILES

MICHEL BERTHELOT, MARYVONNE HELBERT, CHRISTIAN LAURENCE* AND JEAN-YVES LE QUESTEL

Laboratoire de Spectrochimie, Faculté des Sciences et des Techniques, Université de Nantes, 44072 Nantes, France

A thermodynamic hydrogen-bond basicity scale, pK_{HB}, and a spectroscopic hydrogen-bond basicity scale, $\Delta\nu$(OH), were measured which permitted the construction of the solute hydrogen-bond basicity scale, β_2^H, for 71 nitriles embracing a wide range of structures from trichloroacetonitrile to cyanamides. Field, resonance, and polarizability contributions of the X substituents to the hydrogen-bond basicity of XCN compounds were established. Steric effects do not contribute to the hydrogen-bond basicity of nitriles.

INTRODUCTION

Literature thermodynamic data on the hydrogen-bond basicity of cyanides refer to various solvents, temperatures and hydrogen-bond donors[1–5] and have generally been obtained for a limited number of compounds and on infrared spectrometers of unsatisfactory photometric accuracy.[1–4] These insufficiently homogeneous, numerous and accurate data have not allowed the introduction of a sufficient population of cyanides into the statistical scale of solute hydrogen-bond basicity built by Abraham *et al.*[6] for use in solution chemistry, nor have they permitted a study of hydrogen-bond basicity–structure relationships. The same limitations occur for the solute hydrogen-bond acceptor scale for use in drug design.[7]

The correlational evaluations of polarizability, field, resonance and steric effects on hydrogen-bond basicity are important, however, to achieve a correct understanding of various basicity scales. In the nitrile family, Allerhand and Schleyer[8] have shown only qualitatively the contribution of field and resonance effects. No steric effects are expected if the geometry of dimers XCN···HA is linear (*n* complex),[9] but they are to be considered if the geometry is T-shaped (π complex).[5] Polarizability effects have been indicated[10,11] to influence hydrogen-bond formation in the alcohol series. However, in the nitrile XCN series the hydrogen-bond acceptor atom is further from the X substituent than in the XOH series. This raises the question of whether polarizability effects can be identified.

As in previous papers[11–13] on hydrogen-bond basicity, we chose to measure the hydrogen-bond basicity of nitriles as solutes by pK_{HB}, the logarithm of the formation constant K_{HB} of the 1:1 complex between 4-fluorophenol and XCN in CCl_4 at 298 K, or, for use in linear solvation energy relationships,[14] by its linear transform $\beta_2^H = (pK_{HB} + 1 \cdot 1)/4 \cdot 636$. The β_2^H value permits a quantitative estimate of the value of pK_{HB} for the hydrogen-bonded complex with any hydrogen-bond donor of known hydrogen-bond acidity α_2^H value.[15]

We also measured the lowering of the ν(OH) frequencies of 4-fluorophenol and of methanol, $\Delta\nu_1$(OH) and $\Delta\nu_2$(OH), on going from the free to the hydrogen-bonded OH group. These quantities are generally considered as spectroscopic scales of hydrogen-bond basicity. Within a family of bases, the thermodynamic and spectroscopic scales are often well correlated.[16]

We use the following correlation equation for the effects of substituents X on the hydrogen-bond basicity of XCN compounds:

$$pK_{HB}\ (\text{or } \beta_2{}^H \text{ or } \Delta\nu) = pK^0_{HB}\ (\text{or } \beta_2^{0H} \text{ or } \Delta\nu^0) + \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R\sigma_R^+ \quad (1)$$

where pK^0_{HB} (or β_2^{0H} or $\Delta\nu^0$) refers to HCN, the substituent parameters σ_α, σ_F and σ_R^+ measure the polarizability, field and resonance effects of X substituents, respectively, and the regression coefficients ρ_α, ρ_F and ρ_R measure the sensitivity of hydrogen-bond basicity to these effects.[17]

A valid statistical analysis by equation (1) requires a great number of diversified substituents and low colinearity between the three sets of independent σ variables. In this work we measured pK_{HB} by means of a Fourier transform IR spectrometer of high photometric and wavenumber accuracy for 26 nitriles. If we add our values for six cyanamides and cyanamide vinylogues or

* Author for correspondence.

0894–3230/93/050302–05$07.50

Received 9 July 1992
Revised 7 January 1993

iminologues, published previously,[18] and four carefully selected literature values for benzonitriles[19] and trimethylsily cyanide,[5] we have at hand a set of 36 primary pK_{HB} (or β_2^H) values. Because of the ease and accuracy of $\Delta\nu$(OH) measurements, and the need for a very large set of β_2^H values in linear solvation energy relationships, we measured $\Delta\nu_2$(OH) for 35 new nitriles (mainly ring-substituted benzonitriles and phenylacetonitriles), and established a correlation between the thermodynamic and spectroscopic scales which allowed the calculation of secondary β_2^H values. The final set of 71 primary and secondary β_2^H values embraces a large structural field of 2·5 pK_{HB} units from CCl_3CN to a cyanamide iminologue.

EXPERIMENTAL

Materials. Spectroscopic-grade carbon tetrachloride and methanol were dried over 4 and 3 Å molecular sieves, respectively. 4-Fluorophenol was sublimed over P_2O_5. Cyanoacetylene was prepared by dehydration of $HC{\equiv}CCONH_2$. Commercially available cyanides were purified by fractional distillation or recrystallizations from solvents.

Infrared measurements. These were carried out with a Bruker IFS 45 WHR spectrometer with 1 cm^{-1} resolution and 256 scans. The photometric accuracy was ±0·005 absorbance unit. The temperature of the quartz cell was maintained at 25 ± 0·1 °C by a thermoelectric device. The 1 cm path length permitted the 4-fluorophenol concentration (*ca* 4×10^{-3} M) to be kept under the limit of self-association. The solutions were prepared and the cell was filled inside a dry-box.

The equilibrium constant is defined by $K_{HB} = C_c/(C_aC_b) = (C_a^0 - C_a)/[C_a(C_b^0 - C_a^0 + C_a)]$ where C_c, C_b and C_a are the equilibrium concentrations of complex, nitrile (base) and 4-fluorophenol (acid), respectively, and C_a^0 and C_b^0 are the initial concentrations. C_a^0 and C_b^0 are known by weighing and C_a is determined from the absorbance of the free OH band of 4-fluorophenol at 3614 cm^{-1} (molar absorptivity = 235 l mol^{-1} cm^{-1}). The equilibrium constants are taken as the mean of five values obtained from five nitrile concentrations. These concentrations range from 0·1–1 M (CCl_3CN) to 0·003–0·03 M (cyanamides). K_{HB} is estimated to be accurate to within 5–10% and consequently pK_{HB} to within ±0·02–0·05 unit.

The frequency shifts of the OH bands of methanol at 3644 cm^{-1} and 4-fluorophenol at 3614 cm^{-1} are defined as $\Delta\nu_2 \equiv 3644 - \nu_2(OH\cdots)$ and $\Delta\nu_1 \equiv 3614 - \nu_1(OH\cdots)$, respectively. They are strongly dependent on nitrile concentration and correspond to the very low nitrile concentrations attained by spectra accumulation. They are believed to be accurate to within ±1–5 cm^{-1}.

RESULTS

The pK_{HB} and frequency shifts are reported for the pimary set in Table 1. The calculation of secondary pK_{HB} or β_2^H values from spectroscopic shifts needs a relationship of high precision between pK_{HB} and $\Delta\nu$(OH) and accurate values of spectroscopic shifts $\Delta\nu$(OH).

The correlation coefficient r and the standard deviation s show excellent correlations between pK_{HB} and $\Delta\nu_1$ or $\Delta\nu_2$:

$$pK_{HB} = 0{\cdot}0167\ \Delta\nu_2(OH) - 0{\cdot}42$$
$$n = 35; \quad r = 0{\cdot}9951; \quad s = 0{\cdot}046 \qquad (2)$$

$$pK_{HB} = 0{\cdot}0102\ \Delta\nu_1(OH) - 0{\cdot}79$$
$$n = 35; \quad r = 0{\cdot}9953; \quad s = 0{\cdot}045 \qquad (3)$$

CCl_3CN was excluded from these correlations because it deviates by about three times the standard deviation. This deviation probably originates from the high concentrations of this weakly basic and polar compound (the dielectric constant is 7·74) necessary to displace the equilibrium towards complex formation. We are then too far removed of the conditions of determination of thermodynamic equilibrium constants.

In the excellent correlation between the frequency shifts $\Delta\nu_2$ of methanol–nitrile complexes and $\Delta\nu_1$ of *p*-fluorophenol–nitrile complexes:

$$\Delta\nu_1(OH) = 1{\cdot}634\ \Delta\nu_2(OH) + 35$$
$$n = 36; \quad r = 0{\cdot}9986; \quad s = 2{\cdot}5\ cm^{-1} \qquad (4)$$

$\Delta\nu_1$ and $\Delta\nu_2$ mutually support themselves as good candidates for the calculation of secondary pK_{HB} (or β_2^H) values. We preferred to select $\Delta\nu_2$(OH) for technical reasons.

Hence equation 2 can be safely used for calculating secondary pK_{HB} (or β_2^H) values for those nitriles for which only $\Delta\nu_2$ has been measured. The experimental $\Delta\nu_2$ and calculated pK_{HB} and β_2^H values are reported in Table 2.

DISCUSSION

Hydrogen bonding site

A number of cyanides involved in this work possess, in addition to the N(sp) atom of the nitrile group, various heteroatoms available for hydrogen-bond formation (e.g. sulphur in MeSCN, oxygen in PhOCN or nitrogen in Me_2NCN). Vibrational spectroscopy allows one to establish precisely that the interaction site is the nitrile group. When 4-fluorophenol is hydrogen bonded to cyanides in Tables 1 and 2, one new enlarged ν(OH) band is observed at lower frequencies [the shifts vary from 70 cm^{-1} for CCl_3CN to 300 cm^{-1} for $Me_2NC(Me){=}NCN$] and one new $\nu(C{\equiv}N)$ band is observed at higher frequencies (upwards shifts of about

Table 1. Frequency shifts (cm^{-1}) $\Delta\nu_1$(OH) of *p*-fluorophenol and $\Delta\nu_2$(OH) of methanol, and primary pK_{HB} and β_2^H values for nitriles

Compound	$\Delta\nu_2$	$\Delta\nu_1$	pK_{HB}	β_2^H
Trichloroacetonitrile	23	71	−0·26	0·18
Dibromoacetonitrile	39	98	0·19	0·28
Cyanogen bromide	44	103	0·19	0·28
Chloroacetonitrile	48·5	118	0·39	0·32
α,α,α-Trifluoro-*p*-tolunitrile	59	133	0·54	0·35
α,α,α-Trifluoro-*m*-tolunitrile	60	133	0·53	0·35
2-Fluorobenzonitrile	62	141	0·64	0·38
α-Bromo-*o*-tolunitrile	64	145	0·69	0·39
2-Bromobenzonitrile	65	143	0·71	0·39
2-Chlorobenzonitrile	66	143	0·67	0·38
Acrylonitrile	67	146	0·70	0·39
Methyl thiocyanate	69	148	0·73	0·39
4-Fluorobenzonitrile	70	149	0·72	0·39
Phenyl cyanate	70	150	0·77	0·40
Benzonitrile[a]	72·5	157	0·80	0·41
Benzyl cyanide	73	152	0·81	0·41
o-Tolunitrile	75	162	0·83	0·42
Acetonitrile	75·5	157	0·91	0·43
Acetonitrile-d_3	75·5	157	0·87	0·42
Propionitrile	79	164	0·96	0·44
Butyronitrile	79	166	0·89	0·43
Trimethylsilyl cyanide[b]	80	165	0·93	0·44
Isobutyronitrile	81	169	1·00	0·45
2-Methoxybenzonitrile	82	173	1·06	0·47
Hexanenitrile	83	168	0·89	0·43
Trimethylacetonitrile	83	172	0·89	0·43
4-Methoxybenzonitrile[a]	83·5	176	0·97	0·45
Cyclopropyl cyanide	86	171	1·03	0·46
1-Adamantanecarbonitrile	87	180	1·00	0·45
4-(Dimethylamino)benzonitrile[a]	100	203	1·23	0·50
Dimethylcyanamide[c]	117·5	226	1·56	0·57
1-Piperidinecarbonitrile[c]	122	234	1·58	0·58
Diethylcyanamide[c]	124	238	1·63	0·59
trans-3-Dimethylaminoacrylonitrile[c]	129	246	1·70	0·60
N^1,N^1-Dimethyl-N^2-cyanoformamidine[c]	149·5	280	2·09	0·69
N^1,N^1-Dimethyl-N^2-cyanoacetamidine[c]	161	298·5	2·24	0·72

[a] Ref. 19.
[b] Ref. 5.
[c] Ref. 18.

$10\ cm^{-1}$). The presence of one OH hydrogen-bonded band suggests that one complex is formed and the shift of ν(C≡N) to higher frequencies indicates[1] that this is a nitrile complex.

Another piece of evidence is the relationship between pK_{HB} and $\Delta\nu$(OH) [equations (2) and (3)]. It shows that there is no marked difference between the hetero-substituted nitriles and the others. This strongly suggests that the preferred hydrogen-bonding site is the same in all cases.

Steric effects of substituents on the hydrogen-bond basicity of nitriles

Steric effects can be analysed in the RC≡N series where R are alkyl groups of various steric sizes, and in the series of *ortho*-substituted benzonitriles.

In the RC≡N series one observes that both the lengthening and the branching of the alkyl R chain increases the spectroscopic shifts of nitriles. We observe the regular sequences *n*-Pen > *n*-Bu > *n*-Pr > Et > Me for lengthening and 1-Adam > *t*-Bu > *i*-Pr > Et > Me for branching. If steric effects had operated, the reverse sequences would have been observed. The sequences of pK_{HB} values are less regular. This may arise from greater uncertainty in thermodynamic than in spectroscopic determinations, but nevertheless the greatest pK_{HB} is also found for adamantyl, the most voluminous substituent.

In the series of *ortho*-substituted benzonitriles, we

Table 2. Experimental frequency shifts (cm^{-1}) $\Delta\nu_2$(OH), of methanol and secondary calculated pK_{HB} and β_2^H values for nitriles

Compound	$\Delta\nu_2$	pK_{HB}	β_2^H
Ethynyl cyanide	43	0·30	0·30
4-Nitrobenzonitrile	46	0·35	0·31
2-Chloroacrylonitrile	47	0·36	0·32
1,2-Dicyanobenzene	48	0·38	0·32
3-Nitrobenzonitrile	51	0·43	0·33
1,3-Dicyanobenzene	54	0·48	0·34
3,5-Dichlorobenzonitrile	56	0·52	0·35
α,α,α-Trifluoro-*o*-tolunitrile	59	0·57	0·36
Bromoacetonitrile	59	0·57	0·36
3-Chlorobenzonitrile	64	0·65	0·38
3-Bromobenzonitrile	64	0·65	0·38
Iodoacetonitrile	65	0·67	0·38
α-Bromo-*m*-tolunitrile	67	0·70	0·39
3-(Trifluoromethyl)phenylacetonitrile	67	0·70	0·39
4-Chlorobenzonitrile	68	0·72	0·39
4-Bromophenylacetonitrile	68	0·72	0·39
3-Chloropropionitrile	69	0·73	0·40
4-Bromobenzonitrile	69	0·73	0·40
3-Chlorophenylacetonitrile	69·5	0·74	0·40
α-Bromo-*p*-tolunitrile	70	0·75	0·40
(Methylthio)acetonitrile	71	0·77	0·40
4-Fluorophenylacetonitrile	71	0·77	0·40
3,5-Dimethoxybenzonitrile	72	0·78	0·41
3-Methoxybenzonitrile	73	0·80	0·41
4-Chlorophenylacetonitrile	74	0·82	0·41
4-Chlorobutyronitrile	75	0·83	0·42
4-Biphenylcarbonitrile	75	0·83	0·42
4-Methylbenzyl cyanide	75·5	0·84	0·42
m-Tolunitrile	76	0·85	0·42
5-Chlorovaleronitrile	77	0·87	0·42
3-Methylbenzyl cyanide	77	0·87	0·42
(4-Methoxyphenyl)acetonitrile	77	0·87	0·42
p-Tolunitrile	78	0·88	0·43
Valeronitrile	80·5	0·92	0·44
Cyclohexyl cyanide	83	0·97	0·45

have nine substituents (in order of increasing steric size H, F, OMe, CN, Me, Cl, CH_2Br, Br and CF_3) which may alter the hydrogen-bond basicity by electrical and/or steric effects. However, the correlations of $\Delta\nu_2$(OH) and of pK_{HB} with the steric substituent parameter υ[20] and the electrical substituent parameters σ_α, σ_F and σ_R^+[21] do not show any dependence on the steric parameter. In fact, the field substituent parameter σ_F and the resonance parameter σ_R^+ are sufficient to explain 92% of the variances of $\Delta\nu_2$(OH) and of pK_{HB}. The correlations are

$$\Delta\nu_2(\text{OH}) = 72 - 36\cdot3\sigma_F - 42\cdot4\sigma_R^+$$
$$n = 9; \quad r = 0\cdot9614; \quad s = 3\ \text{cm}^{-1} \qquad (5)$$
$$pK_{HB} = 0\cdot79 - 0\cdot630\sigma_F - 0\cdot910\sigma_R^+$$
$$n = 9; \quad r = 0\cdot9598; \quad s = 0\cdot06 \qquad (6)$$

This absence of steric effects of *ortho* substituents in hydrogen-bonded benzonitriles and of bulky alkyl substituents in hydrogen-bonded aliphatic nitriles is not in favour of π T-shaped *p*-fluorophenol–nitrile complexes suggested in a dipole moment study.[5] They rather support the rotational spectroscopic results[9] on the dimers XC≡N···HA and the *ab initio* calculations on the dimers MeC≡N···HOH[22] and MeC≡N···HOMe[23] which show that the hydrogen bond occurs quasi-linearly at the sp lone pair of the nitrogen.

Electrical effects of substituents on the hydrogen-bond basicity of nitriles

Equation (1) was applied to analyse $\Delta\nu_2$(OH) and pK_{HB} of 20 XC≡N compounds of Tables 1 and 2. The X substituents are, CCl_3, Br, $ClCH_2$, MeS, $ClCH_2CH_2$, $PhCH_2$, $Cl(CH_2)_3$, Me, Et, *n*-Pr, *n*-Bu, $SiMe_3$, *i*-Pr, *n*-Pen, *c*-Hex, *t*-Bu, *c*-Pr, 1-Adam, NMe_2 and NEt_2. The value of pK_{HB} (but not of $\Delta\nu_2$) for CCl_3 in Table 1 was excluded owing to the larger uncertainty for this weak base (see above). The data set does not include X = Ph, OPh or $CH{=}CH_2$. The σ_R^+ values for these latter conjugated substituents seem to be appropriate only for proton transfer or similar reactions.[24] The colinearity of the independent parameters for this data set is very weak: $r(\sigma_\alpha \text{ vs } \sigma_F) = 0\cdot01$, $r(\sigma_\alpha \text{ vs } \sigma_R^+) = 0\cdot31$ and $r(\sigma_F \text{ vs } \sigma_R^+) = 0\cdot10$. Making use of this data set, the following equations are obtained:

$$\Delta\nu_2(\text{OH}) = 64 - 18\cdot2\sigma_\alpha - 112\cdot2\sigma_F - 89\cdot8\sigma_R^+$$
$$n = 20; \quad r = 0\cdot9934; \quad s = 2\cdot7\ \text{cm}^{-1} \qquad (7)$$
$$pK_{HB} = 0\cdot37 - 0\cdot170\sigma_\alpha - 1\cdot978\sigma_F - 1\cdot467\sigma_R^+$$
$$n = 19; \quad r = 0\cdot9940; \quad s = 0\cdot04 \qquad (8)$$

Equations (7) and (8) have excellent statistics and allow the prediction of the hydrogen-bond basicity of numerous nitriles and, particularly, of the parent HCN, a gaseous cyanide difficult to handle. The predicted $\Delta\nu_2^0$(OH) value is 64 cm^{-1}. The value of 64 cm^{-1} agrees fairly well with a value of 52 cm^{-1} calculated from a linear correlation [equation (9)] between $\Delta\nu_2$(OH) in the XCN and XCOOEt series:

$$\Delta\nu_2(\text{XCN}) = 1\cdot03\ \Delta\nu_2(\text{XCOOEt}) - 7\cdot3$$
$$n = 15; \quad r = 0\cdot9880; \quad s = 3\ \text{cm}^{-1} \qquad (9)$$

and from $\Delta\nu_2$ (HCOOEt) = 58 cm^{-1}. It is noteworthy that if we do not take into account the σ_α term in equation (7), the intercept $\Delta\nu_2^0$(OH) increases to 75 cm^{-1}, a seemingly worse value.

For CCl_3CN ($\sigma_\alpha = -0\cdot70$, $\sigma_F = 0\cdot44$ and $\sigma_R^+ = 0\cdot00$), the above equations give $pK_{HB} = -0\cdot02$, in excellent agreement with the value ($-0\cdot04$) that is calculated from $\Delta\nu_2$(OH) [equation (2)].

Examination of the sensitivity coefficients ρ_α, ρ_F and

ρ_R in equations (7) and (8) shows that resonance effects are important but that field effects play the leading part [$\rho_R/\rho_F = 0{\cdot}80$ for equation (7) and $0{\cdot}74$ for equation (8)]. The polarizability effects are much less important [$\rho_\alpha/\rho_F = 0{\cdot}16$ for equation (7) and $0{\cdot}09$ for equation (8)], than generally found for gas-phase basicities.[17] This is expected for proton sharing (instead of proton transfer) in solution (instead of the gas phase). Nevertheless, the ρ_α regression coefficients seem significant: the probabilities that ρ_α does not differ significantly from zero are only $0{\cdot}3\%$ for equation (7) and 3% for equation (9).

In ring-substituted benzonitriles, the larger distances between the substituent and the hydrogen-bonding centre indicate that polarizability effects are not significant. The dual substituent parameter equation gives excellent correlations [equations (10)–(13)]:

meta-substituted benzonitriles:

$$\Delta\nu_2(\mathrm{OH}) = 73{\cdot}5 - 32{\cdot}0\sigma_F - 21{\cdot}0\sigma_R^+$$
$$n = 9; \quad r = 0{\cdot}9901; \quad s = 1{\cdot}4\ \mathrm{cm}^{-1} \qquad (10)$$
$$\mathrm{p}K_{HB} = 0{\cdot}81 - 0{\cdot}554\sigma_F - 0{\cdot}377\sigma_R^+$$
$$n = 9; \quad r = 0{\cdot}9875; \quad s = 0{\cdot}03 \qquad (11)$$

para-substituted benzonitriles:

$$\Delta\nu_2(\mathrm{OH}) = 73{\cdot}1 - 35{\cdot}8\sigma_F - 46{\cdot}9\sigma_R^+$$
$$n = 10; \quad r = 0{\cdot}9833; \quad s = 2{\cdot}9\ \mathrm{cm}^{-1} \qquad (12)$$
$$\mathrm{p}K_{HB} = 0{\cdot}81 - 0{\cdot}617\sigma_F - 0{\cdot}754\sigma_R^+$$
$$n = 10; \quad r = 0{\cdot}9839; \quad s = 0{\cdot}05 \qquad (13)$$

If we compare *ortho- meta-* and *para*-substituent effects [equations (6), (11) and (13)], we find that $\rho_R^0/\rho_F^0 (= 1{\cdot}44) > \rho_R^p/\rho_F^p (= 1{\cdot}22) \gg \rho_R^m/\rho_F^m (= 0{\cdot}68)$. The latter inequality is a generalized behaviour for proton-transfer equilibria.[17]

ACKNOWLEDGEMENTS

We are grateful to Professor R. W. Taft for numerous discussions on this paper. We gratefully thank Professor Duguay (Nantes) for the gift of a sample of phenyl cyanate.

REFERENCES

1. S. C. White and H. W. Thompson, *Proc. R. Soc. (London), Ser A 291*, 460 (1966).
2. M. C. Sousa-Lopes and H. W. Thompson, *Spectrochim. Acta, Part A*, **24**, 1367 (1968).
3. T. Gramstad and J. Sandström, *Spectrochim. Acta, Part A*, **25**, 31 (1969).
4. I. Jawed, *Bull. Chem. Soc. Jpn.* **50**, 2602 (1977).
5. A. Austerheim and T. Gramstad, *Acta Chem. Scand. Ser. B*, **39**, 583 (1985).
6. M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 521 (1990).
7. M. H. Abraham, P. P. Duce, D. V. Prior, D. G. Baratt, J. J. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1355 (1989).
8. A. Allerhand and P. V. R. Schleyer, *J. Am. Chem. Soc.* **85**, 866 (1963).
9. A. C. Legon and D. J. Millen, *Acc. Chem. Res.* **20**, 39 (1987).
10. J. L. Abboud, K. Sraïdi, G. Guihéneuf, A. Negro, M. Kamlet and R. W. Taft, *J. Org. Chem.* **50**, 2870 (1985).
11. C. Laurence, M. Berthelot, M. Helbert and K. Sraïdi, *J. Phys. Chem.* **93**, 3799 (1989).
12. D. Gurka and R. W. Taft, *J. Am. Chem. Soc.* **91**, 4794 (1969).
13. R. W. Taft, D. Gurka, L. Joris, P. V. R. Schleyer and J. W. Rakshys, *J. Am. Chem. Soc.* **91**, 4801 (1969).
14. R. W. Taft, J. L. Abboud, M. J. Kamlet and M. H. Abraham, *J. Solution Chem.* **14**, 153 (1985).
15. M. H. Abraham, P. L. Grellier, D. V. Prior, R. W. Taft, J. J. Morris, P. J. Taylor, C. Laurence, M. Berthelot, R. M. Doherty, M. J. Kamlet, J. L. Abboud, K. Sraïdi and G. Guihéneuf, *J. Am. Chem. Soc.* **110**, 8534.
16. T. Gramstad, *Spectrochim. Acta*, **19**, 497.
17. R. W. Taft and R. D. Topsom, *Prog. Phys. Chem.* **16**, 1 (1987).
18. M. Berthelot, M. Helbert, C. Laurence, J. Y. Le Questel and R. W. Taft, *J. Chem. Soc. Perkin Trans. 2*, in press.
19. L. Joris, J. Mitsky and R. W. Taft, *J. Am. Chem. Soc.* **94**, 3438 (1972).
20. M. Charton, in *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*, edited by R. I. Zalewski, T. M. Krygowski and J. Shorter, p. 629, Elsevier, Amsterdam (1991).
21. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **91**, 165 (1991).
22. J. R. Damewood and R. A. Kumpf, *J. Phys. Chem.* **91**, 3449 (1987).
23. T. H. Tang, X. Y. Fu, *Int. J. Quantum Chem.* **24**, 317 (1983).
24. R. W. Taft, personal communication.