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PREDICTION OF HYDROGEN BOND BASICITY IN NITRILES FROM DIPOLE MOMENTS, MESOMERIC EFFECTS AND ELECTROSTATIC POTENTIALS

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Measured molecular dipole moments and theoretical percentages of mesomeric zwitterionic forms were used to calculate the attractive electrostatic potentials at short, V(s), medium, V(m), and long, V(l), distances. Values of an attraction power function $\Phi(H) = A + BV(\mathrm{s})V(\mathrm{m})V(\mathrm{l})$ was then deduced for 18 nitriles and cyanamide vinylogues or iminologues along the C≡N direction. The satisfactory agreement observed between $\Phi(H)$ and the hydrogen bond basicity scale pK_{HB} indicates that the method can be a useful tool for the prediction of hydrogen bonding, needing only simple calculations and allowing easy interpretation.

INTRODUCTION

The hydrogen bonding basicity of a large set of ordinary and super-basic nitriles has recently been measured by IR spectroscopy.[1,2] The basicity is expressed in terms of the logarithm of the formation constant, K_{HB}, of the 1:1 complex between 4-fluorophenol and the nitrile XCN in CCl_4 at 298 K:

$$pK_{HB} = \log_{10}[(\text{complex})/(\text{4-fluorophenol})(\text{XCN})] \quad (1)$$

A good correlation was observed between the thermodynamic hydrogen bond basicity scale, pK_{HB}, and a spectroscopic scale $\Delta\nu$(OH) (the IR frequency shift of the OH peak of methanol upon association). Although the latter allows good basicity prediction, it does not give any information on the electrostatic phenomena which are known to be the basis of such specific effects. Electrostatic studies in relation to the basicity scales have emerged from the past three decades,[3–10] in order to interpret and obtain a theoretical prediction of the hydrogen bonding (ability) of molecules.

The method of Gramstad is related to the analysis of experimental dipole moments: comparison between the value of the molecule acceptor (μ_A) and the value of the acceptor–donor complex (μ_{DA}).[4–6] In general, he obtained no smooth correlations between μ and $\Delta\nu_{OH}$ and the detailed analysis is not straightforward. Politzer and co-workers[7–9] used electrostatic potentials in the quantitative description of hydrogen bonding. The local minimum potential (V_{min}) is calculated from an *ab initio* self-consistent field molecular orbital (SCF-MO) wavefunction. He showed that V_{min} within several different families of solvents, treated separately, correlates well with the corresponding β values, linearly connected to pK_{HB}. Recently, Kenny[10] made an advance in this method, particularly by considering the electric field $F(r)$, in addition to the electrostatic potential $V(r)$, at specified distances r from the acceptor atom. He also used quantum mechanical calculations and succeeded in obtaining suitable correlations between $V(r)$, $F(r)$ and the hydrogen bond basicity pK_β (directly related to pK_{HB}) in a set of heterocycles with nitrogen acceptors.

In this paper, we propose a practical way of combining the main advantages of these methods. We consider the attractive electrostatic potential $V(r)$ of the acceptor molecule, following the Politzer and co-workers' and Kenny's general points of view. We perform simple classical $V(r)$ calculations based on the measured dipole moments of the acceptor molecule (μ_A), which is a realistic and suitable basis. In fact, a recent dipolmetric study[11,12] suggested the present work to us.

We present a general calculation method for the vector $\mathbf{\mu}$ of charged mesomeric forms, which allows one to obtain values of the mesomeric form percentages and of the vector $\mathbf{\mu}$ orientations for each molecule. Also, in the study on the basicity of nitriles, mentioned

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previously, we noticed that the more basic nitriles, cyanamides and iminologues, present two resonance structures (or mesomeric forms) which could explain their strong hydrogen-bonding ability.[1] For these reasons, we thought that our improved calculation method of mesomeric effects in dipolmetry[11] could be a useful tool for the prediction of $\mathrm{p}K_{\mathrm{HB}}$ for such molecules. We therefore decided to study in this way seven cyanamides and cyanamide vinylogues or iminologues together with eleven nitriles without resonance effects, to embrace a larger structural field of about 1·6 $\mathrm{p}K_{\mathrm{HB}}$ units from acrylonitrile to a cyanamide iminologue. In the following sections experimental dipole moments are presented, dipole moment calculations are detailed with a preliminary analysis, then our calculations of the molecular attraction power $\Phi(H)$ are described and finally the correlation between $\Phi(H)$ and $\mathrm{p}K_{\mathrm{HB}}$ is discussed.

EXPERIMENTAL

Materials. Spectroscopic-grade carbon tetrachloride and benzene were dried over molecular sieves. Cyanamides were purified commercial compounds. The synthesis of $\mathrm{Me_2NCH{=}NC{\equiv}N}$ and $\mathrm{Me_2NC(Me){=}NC{\equiv}N}$ have been described.[11,13]

Dipole moment measurements. Refractive indices, n, were measured on an Abbe refractometer from Zeiss, densities, d, on a DMA 48 densimeter from Anton Paar and dielectric constants, ε, on a DMO1 dipolmeter from WTW. Solutions were made up in benzene and in carbon tetrachloride in the concentration range (weight fraction W) 0·0005–0·01. The experimental dipole moment value was deduced from the classical equations of Guggenheim and Smith (also called Hedestrand's equation)[14] [equation (2)] and of Halverstadt and Kumler[15] [equation (3)].

$$\mu_2^2 = (\varepsilon_0\, 27\; kT\, M_2/N_{\mathrm{A}}(\varepsilon_1 + 2)^2\, d_1)[a(\varepsilon) - a(n^2)] \quad (2)$$

$$\mu_2^2 = (\varepsilon_0\, 27\; kT\, M_2/N_{\mathrm{A}}(\varepsilon_1 + 2)^2\, d_1)[a(\varepsilon) - Y] \quad (3)$$

with

$$Y = [(\varepsilon_1 + 2)/3] \times [N_{\mathrm{A}} d_1(\varepsilon_1 + 2)\bar{\alpha}_2/3\, M_2\varepsilon_0 - (\varepsilon_1 - 1)(1 - a(d)/d_1)]$$

and $a(x) = (\partial x/\partial W)_{W\to 0}$ for $x = \varepsilon$, n^2 or d. The subscript 1 denotes a solvent property and subscript 2 a solute property, the other quantities being related to solutions. M is the molecular weight, T the temperature (in K), k the Boltzmann constant, N_{A} Avogadro's number and ε_0 the permittivity of vacuum. The mean molecular polarizability $\bar{\alpha}_2$ deduced from the additivity of atomic polarizabilities using Vogel's system.[16,17] In all cases we neglected atomic polarizabilities, which is legitimate considering the high measured μ values.[16] Moreover, equations (2) and (3) led to the same μ values, within experimental uncertainties. Measurements and related dipole moments studied in solutions are presented in Table 1, together with literature data.

Table 1. Experimental dipole moments (μ) and related measured slopes $a(\varepsilon)$, $a(n^2)$ and $a(d)$ (g cm^{-3}) at 293 K and 1 atm

		In carbon tetrachloride				In benzene				
No.	Compound	$a(\varepsilon)$	$a(n^2)$	$a(d)$	μ (D)[a]	$a(\varepsilon)$	$a(n^2)$	$a(d)$	μ (D)[a]	(Lit.)[b]
1	Acrylonitrile									3·3
2	Benzonitrile	30·61	−0·55	−0·90	3·98	17·43	0·0	0·12	4·01	4·05
3	Benzylcyanide									3·59
4	*o*-Toluonitrile									3·81
5	Trimethylacetonitrile									3·61
6	Butyronitrile									3·60
7	Acetonitrile	50·75	−0·27	−1·10	3·40	32·97	0·0	−0·10	3·49	3·47
8	Propionitrile									3·69
9	Isobutyronitrile									3·62
10	Cyclopropyl cyanide									3·78
11	4-Dimethylamino benzonitrile	55·83	0·36	−0·78	6·39	33·31	0·40	0·15	6·57	6·60
12	Cyanamide									4·30
13	Dimethylcyanamide	48·96	−0·30	−1·08	4·17	29·92	−0·23	0·04	4·35	4·36
14	1-Piperidine carbonitrile	38·31	0·0	−0·85	4·61	22·47	−0·10	0·12	4·71	
15	Diethylcyanamide	43·30	0·24	−1·27	4·63	22·89	−0·47	0·0	4·52	
16	*trans*-3-Dimethylaminoacrylonitrile					44·85	0·92	0·90	6·12	
17	N^1,N^1-Dimethyl-N^2-cyanoformamidine					50·18	0·32	0·19	6·59	
18	N^1,N^1-Dimethyl-N^2-cyanoacetamidine					49·91	0·0	0·19	7·04	

[a] Our experimental uncertainties $\Delta\mu$ are from 0·03 D (for μ = 3·40 D) to 0·08 D (for μ = 7·04 D).
[b] Lit.: Literature data from Ref. 18.

Experimental μ values of most compounds were taken from Ref. 18. In Table 1, the data on the five last compounds are original, the corresponding μ values not being available in the literature. In order to ensure the validity of the experimental data, we first decided to perform a comparison between our results in carbon tetrachloride and in benzene and the literature data for nine compounds. Except for the three last compounds, no significant deviations occur in the various μ values. For the three last compounds in Table 1, we observed in carbon tetrachloride solutions a strong decrease of the measured μ valuewith concentration, indicating the presence of specific associations (such as dimers). In fact, extrapolation to $W = 0$ gives μ values similar to those in benzene, but the values so extrapolated in carbon tetrachloride are inaccurate and hence are not given in Table 1. We therefore selected the data obtained in benzene for the calculations, because they are homogeneous, and literature data in the other compounds.

CALCULATION OF DIPOLE MOMENT VECTORS

General calculation equation

Our method, described in detail earlier,[11] is a simple combination of the additivity of covalent bond moments and of intramolecular electrostatic calculations. It leads to the following expression for the calculated molecular moment (in chemical notation):

$$\boldsymbol{\mu}_{\text{calc}} = \sum_i \boldsymbol{\mu}_i(0) + 4{\cdot}803 \times \left\{ \mathbf{l} + \sum_j \bar{a}_j [\mathbf{N^-X}_j/(\mathrm{N^-X}_j)^3 - \mathbf{N^+X}_j/(\mathrm{N^+X}_j)^3] \right\} \quad (4)$$

where μ is in D, distances in Å and the mean polarizability, $\bar{a}_j$, of atom X_j in Å^3. $\sum_i \boldsymbol{\mu}_i(0)$ is the sum of covalent bond moments. The three other terms must be considered for molecular forms containing the charged atoms N^+ and N^- (zwitterionic forms denoted 2 in Figure 1); 4·803**l** is the moment of the real charges $+|e|$ and $-|e|$ on N^+ and N^-, respectively ($\mathbf{l} = \mathbf{N^+N^-}$). The third and the fourth terms comprise the sums of the moments induced by the charges $-|e|$ and $+|e|$ on all the other atoms of the molecule.

Details of calculation parameters

Geometric parameters (bond lengths and angles) and structures used in our calculations are reported in Table 2 and Figure 1 (for simplification and consistency reasons we adopted ideal mean values). For the zwitterionic forms (2) all those parameters are needed but for the uncharged forms (1), only the bond angles are necessary because $\boldsymbol{\mu}_{\text{calc}} = \sum \boldsymbol{\mu}_i(0)$. Electro-optic parameters are given in Table 3. As already commented upon,[11,12] we adopted values for charged atoms N^+ and N^- similar to those observed in ions, i.e. $\bar{a}(N^+) = 0{\cdot}494\bar{a}(N)$ and $\bar{a}(N^-) = 1{\cdot}25\bar{a}(N)$ from comparison between the species NH_4^+ and NH_3 and between anions and atoms F, Cl, Br and I.[17] Moreover, because molecular $\bar{a}$ value must be constant, we reported differences $\bar{a}(N) - \bar{a}(N^+) = +\delta$ and $\bar{a}(N) - \bar{a}(N^-) = -\delta$ on bonded atoms (with an equal part for each single bond for $+\delta$).

Results of calculations

The x, y, z components of the vectors $\boldsymbol{\mu}(1)$ and $\boldsymbol{\mu}(2)$ of the two canonical structures calculated through equation (4) are given in Table 4 together with their corresponding percentages p_1, p_2. The experimental values μ_{exp} are also reported in Table 4. $\boldsymbol{\mu}_{\text{exp}}$ can be determined by a statistical averaging of the two limiting forms as follows:

$$100\boldsymbol{\mu}_{\text{exp}} = p_1\boldsymbol{\mu}(1) + p_2\boldsymbol{\mu}(2) \quad (2)$$

Thus, from components $\boldsymbol{\mu}(1)$, $\boldsymbol{\mu}(2)$ and from μ_{exp}, p_1 and p_2 are calculated using the expression

$$(100\mu_{\text{exp}})^2 = [p_1\mu_x(1) + p_2\mu_x(2)]^2 + [p_1\mu_y(1) + p_2\mu_y(2)]^2 + [p_1\mu_z(1) + p_2\mu_z(2)]^2 \quad (5)$$

with $100 = p_1 + p_2$.

The $\boldsymbol{\mu}$ components are

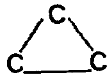
$$\mu_x = p_1\mu_x(1) + p_2\mu_x(2); \quad \mu_y = p_1\mu_y(1) + p_2\mu_y(2); \quad \mu_z = p_1\mu_z(1) + p_2\mu_z(2) \quad (6)$$

pK_{HB} values[1,2] are also reported in Table 4 for the following preliminary analysis. Comparison of μ_{exp} and p_2 with pK_{HB} shows a global consistency between the two electrostatic properties and the basicity. High values of μ_{exp} and p_2 are generally related to a strong basicity but the correlation is not smooth. For instance, in spite of a higher μ_{exp} value, benzonitrile is less basic than acetonitrile. For 4-dimethylamino benzonitrile a strong value of μ_{exp} and a medium value of p_2 correspond to a relatively low value of pK_{HB}. This inadequate correlation in the details corroborates previous observations[4–6] and is not surprising. Indeed, μ_{exp} and p_2 describe well the electrostatic state of a molecule but not its ability to attract protons along specific directions and at various distances. The effective attraction criterion is evidently the electrostatic potential V, as claimed by Politzer and co-workers[7–9] and detailed in the next section. In fact, the theoretical expressions for V at a distance r from the molecular acceptor are as follows: for a dipole,

$$V = \mu \cos \theta / 4\pi\varepsilon r^2 \quad (7)$$

Table 2. Structural parameters used in the calculations

(a) Bond lengths (Å)[19,20]

C–H(CH$_3$)	C–H(CH$_2$)	C$_{ar}$–H	C–C	C$_{ar}$–C$_{ar}$	C$_{ar}$–C	C–C(=C)
1·10	1·07	1·08	1·54	1·40	1·50	1·51
	C–C(≡N)	C=C	C≡N	C=N	C–N	N–H
1·56	1·46	1·33	1·16	1·34	1·47	1·01

(b) Bond angles (°)[19,20]

X–Y–Z	X=Y–Z	X=Y=Z	X≡Y–Z
109·46	120	180	180

X, Y, Z = C, N or H

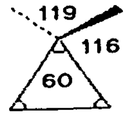


Table 3. Electro-optic parameters used in the calculations

(a) Atomic mean polarizabilities $\bar{\alpha}_j$ (Å^3)[17]

H	C	C$_{ar}$	⩾N	–N=	$\overset{+}{\text{N}}$	=$\bar{\text{N}}$
0·408	1·027	1·322	1·088	1·400	0·692	1·750

(b) Bond moments μ_i (D)[16,21–23]

H–C$_{sp_2}$	H–C$_{sp_3}$	C–N	C=N	C≡N	H–N	*m* (ar/C≡N)[a]
0	0·30	0·45	1·80	3·19	1·31	0·82

[a] The mesomeric moment *m* (along C≡N) is deduced from comparison between benzonitrile and acetonitrile μ_{exp} values. This *m* value is adopted in benzonitrile, *o*-toluonitrile and 4-(dimethylamino)benzonitrile.

Table 4. Calculated dipole moment components [μ(1) for uncharged form, μ(2) for zwitterionic form], experimental values μ_{exp} and percentages p_1 and p_2 of mesomeric forms (μ in D)

Compound	$\mu_x(1)$	$\mu_y(1)$	$\mu_z(1)$	$\mu_x(2)$	$\mu_y(2)$	$\mu_z(2)$	μ_{exp}	p_1	p_2	pK_{HB}[1,2]
1	3·19	0·0	0·0				3·30	100	0	0·70
2	4·01	0·0	0·0				4·01	100	0	0·80
3	3·39	–0·28	0·0				3·59	100	0	0·83
4	3·86	0·26	0·0				3·81	100	0	0·83
5	3·49	0·0	0·0				3·61	100	0	0·89
6	3·49	0·0	0·0				3·60	100	0	0·89
7	3·49	0·0	0·0				3·49	100	0	0·91
8	3·49	0·0	0·0				3·69	100	0	0·96
9	3·49	0·0	0·0				3·62	100	0	1·00
10	3·63	0·26	0·0				3·78	100	0	1·03
11	4·07	0·0	–0·71	22·45	0·0	0·0	6·57	87	13	1·23
12	3·62	0·0	–1·23	9·28	0·0	0·0	4·30	91	9	1·49[1]
13	3·25	0·0	–0·71	8·83	0·0	0·0	4·35	81	19	1·56
14	3·47	0·0	–0·60	10·50	0·0	–0·99	4·71	83	17	1·58
15 a	3·25	0·0	–0·71	7·40	0·0	0·0	4·52	70	30	1·63
b				8·86	0·21	0·0		78	22	
16	3·25	0·0	–0·71	17·94	–5·28	0·0	6·12	81	19	1·70
17 a	3·70	–1·56	–0·71	16·09	–5·51	0·0	6·59	80	20	2·09
b				12·18	1·37	–1·19		67	33	
18 a	3·55	–1·82	–0·71	14·79	–5·94	0·0	7·04	75	25	2·24
b				12·81	0·56	–1·19		64	36	

[1] Roughly estimated from compounds **13** and **15**: pK_{HB}(**13**) – pK_{HB}(**12**) = pK_{HB}(**15**) – pK_{HB}(**13**).

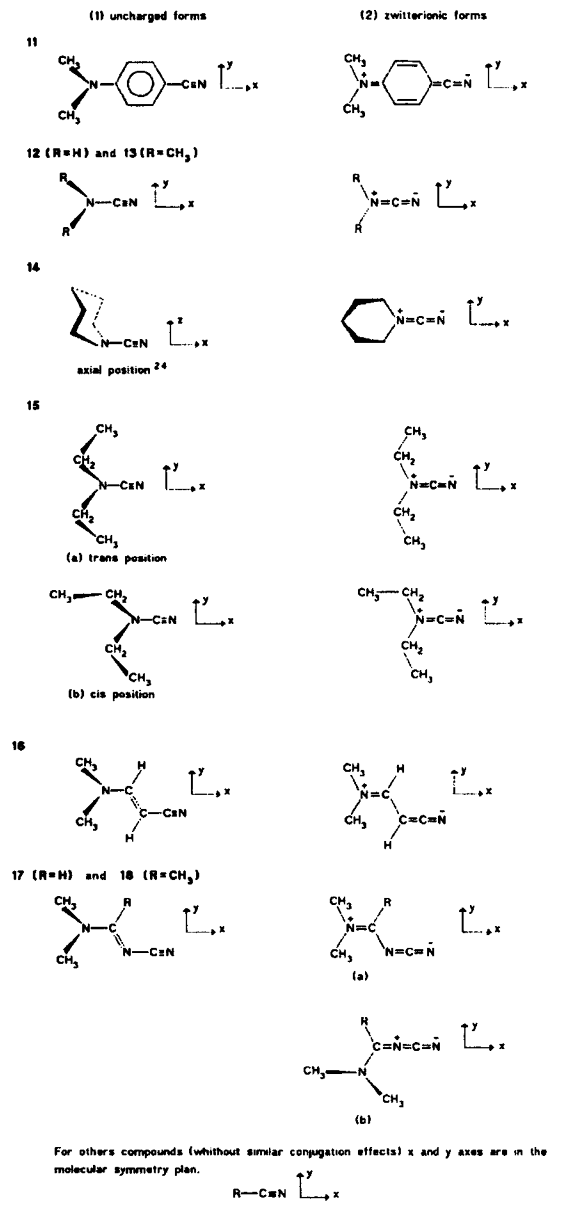


Figure 1. Molecular geometries and structures (only information complementary to Table 2 is given; x, y and z are the Cartesian axes of reference

and for a real charge,

$$V = q/4\pi\varepsilon r \qquad (8)$$

where θ is the angle $\mathbf{\mu}$, $\mathbf{r}$ and ε, the permittivity, can be considered as a constant for the studied series. Hence it is clear that in addition to μ and p_2, the factors $\cos\theta/r^2$ and $1/r$ must be analysed. Examination of $\cos\theta/r^2$ in Table 5 (detailed in the next section) gives a consistent interpretation of the two discrepancy examples already mentioned. The lower pK_{HB} of benzonitrile is due to a lower $\cos\theta/r^2$ value, $2{\cdot}85 \times 10^{-2}$ instead of $6{\cdot}19 \times 10^{-2}$ for acetonitrile. The relatively low pK_{HB} of 4-dimethylamino benzonitrile is due to a very low $\cos\theta/r^2$ value: $1{\cdot}98 \times 10^{-2}$ (arbitrary units).

CALCULATION OF THE MOLECULAR ATTRACTION POWER $\Phi(H)$

Electrostatic attraction potentials V at characteristic distances

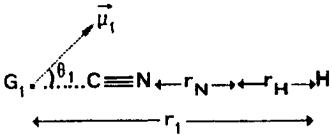
The calculation of the attraction potential V in each point of the space around the molecule is complicated and not practical for easy interpretation. Consequently, we decided to calculate V in the direction of the C≡N bond and at three significant distances. The choice of the C≡N direction is logical because pK_{HB} values correspond to the related N atom and to the more statistically probable orientation for the hydrogen bonding.[1,2] Moreover, Kenny[10] already adopted an equivalent orientation in heterocycles with nitrogen as bond acceptor, along the lone pair axis of N. We adopted the centre of mass G for the interacting site of the molecule at medium and long distances because it is the mean position of both the positive and negative total electric charges centres.[26] At short distance we considered only the end part of the molecule acceptor (C≡N or C=N$^-$), which induces almost the whole potential. For the medium and short positions we adopted a point at 2·7 Å and a point at 1·5 Å from the N atom along the C≡N direction, respectively. These distances are characteristic of the Van der Waals radii of the atoms N (1·5 Å) and H (1·2 Å)[20] implied in the hydrogen bond, 2·7 Å being the sum. In his study, Kenny noticed that similar distances, 1·4 and 2·5 Å, led to optimal fits for electrostatic potential and field, respectively.[10] This coincidence can be considered as an independent justification. Below we detail our V expressions, based on equations (7) and (8) applied to the two canonical forms. These V expressions are relative, particularly because we assumed that $4\pi\varepsilon$ is constant in the whole series. Unspecified arbitrary units for V are used, our aim being a comparative study.

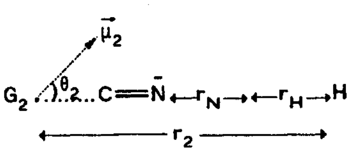
Electrostatic potential V(s) at short distance

$$100V(\mathrm{s}) = p_1 \frac{\mu(\mathrm{C{\equiv}N})}{l_1^2} + p_2\left[\frac{\mu(\mathrm{C{=}N})}{l_2^2} + \frac{q(\mathrm{N^-})}{r_\mathrm{N}}\right] \quad (9)$$

μ(C≡N) and μ(C=N) are the moments of the C≡N and C=N bonds; l_1 and l_2, the interacting distances of bond moments, are the sum of the Van der Waals radius of N, r_N, and of the half bond length; $q(\mathrm{N^-})$ is the electrostatic charge, $|e|$, on atom N in the zwitterionic form 2. In practical calculations, p_1 and p_2 are expressed in %, μ in D, l_1 and l_2 in Å, $r_\mathrm{N} = 1{\cdot}5$ Å and $q = 4{\cdot}803$ D Å^{-1}. From the parameters in Tables 2–4 we deduced the $V(s)$ values reported in Table 5.

Electrostatic potential V(m) at medium distance





G$_1$ and G$_2$ are the molecule centres of mass and H the attracted atom.

$$100V(\mathrm{m}) = p_1 \frac{\mu(1)}{r_1^2}\cos\theta_1 + p_2 \frac{\mu(2)}{r_2^2}\cos\theta_2 \quad (10)$$

where $\mu(1)$ and $\mu(2)$ are the molecular dipole vector intensities of forms 1 and 2; $\mathbf{r}_i$ is the interacting vector $\mathbf{G}_i\mathbf{H} = \mathbf{G}_i\mathbf{N} + \mathbf{NH}$, with NH = 2·5 Å along C≡N or C=N; θ_i is the angle $\boldsymbol{\mu}_i$, $\mathbf{r}_i$. With the units already noted and from parameters in Tables 2–4 and Figure 1, we deduced the V(m) values reported in Table 5. It may be noted that the scheme of global molecular moments is an approximation, suitable for simple calculations.

Table 5. Electrostatic attraction potentials V of molecules (l = at long distance, m = at medium distance, s = at short distance), proton attraction power $\Phi(H)$ [= 0·52 + 0·929V(s)V(m)V(l)] and comparison with pK_HB[1]

Compound	$\frac{\cos\theta_1}{r_1^2}\times 10^2$	$\frac{\cos\theta_2}{r_2^2}\times 10^2$	V(l)	V(m)	V(s)	V(l)V(m)V(s)	$\Phi(H)$	pK_HB
1	4·86		3·30	0·160	0·737	0·38	0·87	0·70
2	2·85		4·01	0·112	0·737	0·33	0·83	0·80
3	2·83		3·59	0·101	0·737	0·27	0·77	0·81
4	2·94		3·81	0·112	0·737	0·32	0·82	0·83
5	4·07		3·61	0·147	0·737	0·39	0·88	0·89
6	3·79		3·60	0·136	0·737	0·36	0·85	0·89
7	6·19		3·49	0·222	0·737	0·57	1·05	0·91
8	4·80		3·69	0·177	0·737	0·48	0·97	0·96
9	4·39		3·62	0·159	0·737	0·42	0·91	1·00
10	4·61		3·78	0·174	0·737	0·49	0·98	1·03
11	1·98	1·96	6·54	0·130	1·107	0·94	1·40	1·23
12	6·10	5·89	4·15	0·250	0·993	1·03	1·50	1·49[2]
13	4·36	4·23	4·31	0·190	1·278	1·05	1·50	1·56
14	3·62	3·35	4·66	0·171	1·221	0·97	1·42	1·58
15 a	4·16	4·05	4·49	0·187	1·592	1·16	1·60	1·63
b	3·85	3·75	4·49	0·162	1·364			
16	2·61	2·55	6·01	0·160	1·278	1·23	1·65	1·70
17 a	2·62	2·48	6·14	0·170	1·307	1·63	2·03	2·09
b		2·53	6·51	0·174	1·677			
18 a	2·65	2·59	6·36	0·183	1·449	1·96	2·34	2·24
b		2·40	6·92	0·181	1·763			

[1] All values are in arbitrary units with μ in D, q in D Å^{-1} and r in Å (see text). For compounds **15**, **17** and **18**, V(s)V(m)V(l) and $\Phi(H)$ values are the mean values of a and b. For compounds **1**, **3–6** and **8–10**, we adopted the μ_exp values, more realistic than the calculated $\mu(1)$ values.

Electrostatic potential $V(\mathrm{l})$ at long distance

When the interacting distance r is large in relation to the molecular size, r is the same for all molecules and must be regarded as constant. Then equation (10) becomes

$$100V(\mathrm{l}) = p_1\,\mu(1)\cos\,\theta_1 + p_2\,\mu(2)\cos\,\theta_2 \qquad (11)$$

The $V(\mathrm{l})$ values so obtained are reported in Table 5.

The comparison of $V(\mathrm{l})$, $V(\mathrm{m})$ and $V(\mathrm{s})$ with $\mathrm{p}K_{\mathrm{HB}}$ indicates a regulate qualitative correlation: low values of the three potentials always correspond to low $\mathrm{p}K_{\mathrm{HB}}$ values and high values lead to high $\mathrm{p}K_{\mathrm{HB}}$ values. Hence the qualitative consistency of the method seems unambiguous.

MOLECULAR ATTRACTION POWER $\Phi(H)$ AND CORRELATION WITH $\mathrm{p}K_{\mathrm{HB}}$

From the Maxwell–Boltzmann statistical distribution,[25] the number of $\mathrm{H}^{+\delta}$ (of the molecule donor) attracted at short, medium and long distances are

$$N(i) = b(i)\exp[a(i)V\,(i)/kT]$$

where $i =$ s (short), m (medium) or l (long). $b(i)$ is assumed to be constant in the homogeneous series studied and $a(i)$ is a factor related to the attraction energy. Then, from the general probability rules, the total number of attracted $\mathrm{H}^{+\delta}$ can be expressed as the product $N = N(\mathrm{s})N(\mathrm{m})N(\mathrm{l})$. We expressed the molecular attraction power with the function

$$\Phi(H) = \log N \qquad (12)$$

$$\Phi(H) = A + \sum a'(i)V(i) \qquad (13)$$

where $i =$ s, m or l and $a'(i) = a(i)/kT$; $A = \log[b(\mathrm{s})b(m)b(\mathrm{l})]$ is a constant. Indeed, $b(i) = N(i)$ for $V(i) = 0$ in the statistical distribution; this indicates that A depends mainly on the concentration and on the solvent properties, which must not vary for similar compounds studied under the same conditions.

In fact, because $V(\mathrm{s})$, $V(\mathrm{m})$ and $V(\mathrm{l})$ are three values of the same molecular attraction potential, the limiting conditions lead to $a'(\mathrm{s})V(\mathrm{s}) = a'(\mathrm{m})V(\mathrm{m}) = a'(\mathrm{l})V(\mathrm{l})$. The general solutions of these equalities are $a'(\mathrm{s}) = (B/3)V(\mathrm{m})V(\mathrm{l})$, $a'(\mathrm{m}) = (B/3)V(\mathrm{s})V(\mathrm{l})$ and $a'(\mathrm{l}) = (B/3)V(\mathrm{s})V(\mathrm{m})$. Finally, we obtain

$$\Phi(H) = A + BV(\mathrm{s})V(\mathrm{m})V(\mathrm{l}) \qquad (14)$$

In the general case, B is a function of $a'(i)$ and $V(i)$. Because it is not possible to obtain this function precisely from our simple model and in order to simplify our analysis, we arbitrarily decided to take B as a constant in the studied series.

The values of the characteristic product $V(\mathrm{s})V(\mathrm{m})V(\mathrm{l})$ are given in Table 5. The agreement between its variation for the studied nitriles and the $\mathrm{p}K_{\mathrm{HB}}$ scale is satisfactory, as expected from two properties representing the logarithm of the complex (or associated protons) number. The $V(\mathrm{s})V(\mathrm{m})V(\mathrm{l})$ values are systematically lower, which indicates that the constants A and B are theoretically consistent and must be taken into account for a suitable practical analysis. Because our measurements in benzene (see Table 1) gave a homogeneous system, we fitted the results on benzonitrile (**2**), acetonitrile (**7**) and seven cyanamides (**11**, **13–18**) and obtained $A = 0{\cdot}485$ and $B = 0{\cdot}953$ with the correlation $n = 9$, $r = 0{\cdot}97$ and $s = 0{\cdot}11$. The correlation parameters obtained in the whole series were $A = 0{\cdot}52$, $B = 0{\cdot}929$ with $n = 18$, $r = 0{\cdot}98$ and $s = 0{\cdot}08$. The values of $\Phi(H) = 0{\cdot}929V(\mathrm{l})V(\mathrm{m})V(\mathrm{s}) + 0{\cdot}52$ thus deduced are given in Table 5. With regard to the uncertainty in the $\Phi(H)$ values, which is not easy to evaluate and which is of the same order of magnitude as the mean quadratic deviation, the agreement is good. Most of the remaining deviations between $\Phi(H)$ and $\mathrm{p}K_{\mathrm{HB}}$ can be explained either by doubtful μ_{exp} values for the compounds not measured in this work, by the use of assumed geometries or by the lack of knowledge of the exact conformation percentages (see compound **18**).

Finally, by means of a simple practical method we succeeded in obtaining reasonable agreement between observed and calculated values of the basicity parameters $\mathrm{p}K_{\mathrm{HB}}$ in a homogeneous series of nitriles. Our model is more elaborate than that based on dipole moment analysis only,[4–6] but is more empirical than those from quantum mechanical calculations[7–10] in its basic principle. Nevertheless, the starting point of the calculations, the observed dipole moments, offers the advantage of being a realistic representation of the molecular electrostatic state. Our method of taking into account conjugation effects allows us to introduce crucial improvements into the dipole vector model. In spite of the necessary assumptions and simplifications, our derivation of the electrostatic attraction power $\Phi(H)$ is consistent with accepted electrostatic and statistical theoretical expressions. In conclusion, these first results are very encouraging for the elaboration of a more general method allowing basicity predictions, the model being easily perfectable because of its relative simplicity. Indeed, we envisage an extension to other series together with various improvements, such as taking into account more than three representative potentials, more than one attraction direction and also by considering more carefully the short distance state, introducing, for instance, induced effects on polarizable atoms.

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