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ELECTROSTATIC INTERACTION ENERGIES FROM DIPOLE MOMENTS IN NITRILES, AMMONIA AND AMINES. CORRELATIONS WITH HYDROGEN BOND BASICITY

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Experimental molecular dipole moments and related bond and mesomeric moments were used to calculate the energy W_A of the electrostatic attraction between N-containing acceptor molecules and the attracted H atom, the hydrogen bond $N \cdots H$being along the symmetry axis of N. A satisfactory but family-dependent linear relationship is obtained between W_A and the hydrogen-bond basicity scale pK_{HB} in 36 nitriles, ammonia and 11 primary and tertiary amines. The energy W_R of the electrostatic repulsion between the acceptor molecule and the moment of the created $N \leftarrow H$ bond is calculated in a similar way. W_R is strongly family dependent but the total energy $W_A + W_R$ is closely correlated with pK_{HB} in the 48 derivatives studied without a significant family dependence. This analysis clarifies and completes a previous similar study and confirms that dipolmetry and classical electrostatic calculations can be a useful and practicable method for the prediction of the strength of hydrogen bonding. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The hydrogen-bond basicities of a large set of nitriles and of other nitrogen compounds (ammonia, primary and tertiary amines), XN ($X = RC\equiv$, H_3, RH_2 or R_3), have recently been measured by IR spectroscopy.[1–5] 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 XN molecule in CCl_4 solution at 298 K:

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

A good correlation was observed between the pK_{HB} hydrogen-bond basicity scale and a spectroscopic scale, $\Delta\nu$(OH), derived from the IR frequency shift of the OH peak of methanol or 4-fluorophenol, upon association. Nevertheless, this suitable family-dependent relationship does not give any information on the phenomena inducing such specific effects. Several theoretical studies performed in recent years have demonstrated that electrostatic interactions are the basis of the hydrogen-bonding ability of molecules[5–11] and that various correlations can be obtained between electrostatic properties and the basicity pK_{HB} or $\Delta\nu$(OH) scales. The dipole moments analysis of Gramstad is based upon experimental observations but, in general, no smooth correlations are obtained.[6, 7] By quantum mechanical calculations, Politzer and co-workers[8–10] and Kenny[11] succeeded in obtaining suitable correlations between the local minimum electrostatic potential (V_{min}) or the electrostatic potential $V(r)$ and field $E(r)$ at specified distances r from the acceptor atom, and the pK_{HB} and $\Delta\nu$(OH) scales. More recently, the former groups proposed a family-independent relationship between the minimum potential of the molecular surface, $V_{s,\,min}$, and pK_{HB}.[5] In a first related paper on nitriles, we proposed a practical way of combining the advantages of these methods.[12] We consider the electrostatic attraction potential, V, of the acceptor molecule, following Politzer and co-workers point of view, with calculations of V performed from experimental dipole moments μ, as used in Gramstad's method. Our dipole vector $\vec{\mu}$ analysis was based upon the bond-moment $\overrightarrow{\mu_i}$ additivity and a new way of evaluating the $\vec{\mu}$ vector of mesomeric zwitterionic forms in the case of molecules with two resonance structures (the more basic nitriles with strong conjugation effects). The attraction potential was calculated at short distance V(s), medium distance V(m) and long distance V(l) from the attractor atom N along an axially symmetric direction. A good correlation was finally observed between the product $V(\text{s})V(\text{m})V(\text{l})$, noticed as the attraction power Φ(H), and pK_{HB}. In this paper, we present significant improvements on this first study. The dipole

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moment analysis in conjugated systems is simplified by considering a global additional mesomeric moment, instead of the moment of the resonance structures with charged atoms. The expression of the molecular attraction power is clarified by calculating one quantity only, the attraction energy W_A, instead of three different potentials. More and a greater variety of N-containing molecules have been examined (see Table 3): 36 nitriles, ammonia and 11 primary and tertiary amines, instead of only 18 nitriles. Further, the family dependence problem is also studied through an additional electrostatic repulsion term, W_R, leading to the total electrostatic interaction energy W_A+W_R. In the following sections, principles and details of W_A and W_R calculations are presented, then the correlations between pK_{HB} and W_A and between pK_{HB} and W_A+W_R are discussed.

CALCULATION OF ELECTROSTATIC INTERACTION ENERGIES

Dipole moments used in calculations

Dipole moments $\vec{\mu_i}$ and $\vec{m_i}$ of acceptor molecules are the basic data needed in our calculations. $\vec{\mu_i}$ is the moment of a molecule bond i, deduced through the classical additivity model from the molecular experimental values; it is located at the middle of the bond. $\vec{m}$ is the mesomeric moment, taking account of conjugation effects deduced from the comparison between the experimental molecular value μ_{exp} and the value calculated from additivity $\vec{\mu_l}=\Sigma_i\vec{\mu_i}$,[13, 14] according to the equation

$$\vec{m}=\overrightarrow{\mu_{exp}}-\vec{\mu_l} \qquad (2)$$

The $\overrightarrow{\mu_{exp}}$ direction is obtained, through a method already described,[15, 16] by calculating the moments ($\vec{\mu_1}$, $\vec{\mu_2}$) and the related percentages (p_1, p_2) of the resonance structures according to the equation

$$100\,\overrightarrow{\mu_{exp}}=p_1\vec{\mu_1}+p_2\vec{\mu_2} \qquad (3)$$

For instance, in cyanamide, p_1, $\vec{\mu_1}$ stands for $H_2\bar{N}{-}C{\equiv}N$ (1) and p_2, $\vec{\mu_2}$ for $H_2\overset{+}{N}{=}C{=}N^-$ (2). In the interaction energy calculations, we located $\vec{m}$ at the middle of the distance between the charged atoms of the zwitterionic form (2) (e.g. N^+N^- in cyanamide).

Details of calculation parameters

The geometric parameters (bond lengths and angles) used in our calculations are reported in Table 1 (for reasons of simplification and consistency we adopted only ideal mean values). Other parameters and structural details needed for the $\vec{m}$ calculations (via the zwitterionic forms) in conjugated nitriles have already been considered.[12] For molecules with various conformers (compounds **15**, **16**, **38**, **39**, **40**, **43**, **45** and **48**), we performed calculations for each stable conformers. We then evaluated the conformation energies through a usual molecular mechanics calculation (MM+, Hyperchem) and deduced the related percentages. In these cases, the W values presented in Table 3 are mean values, estimated from W and percentages of various conformers (details are not given for reasons of space).

Electro-optic parameters are given in Table 2. The mean atomic polarizabilities $\bar{\alpha}$ are used for both the $\vec{\mu_2}$ and $\mathbf{w}_R$ (see below) calculations; additional details related to the $\vec{\mu_2}$ calculations (in conjugated nitriles) are given in Ref. 12.

Electrostatic attraction energy, W_A

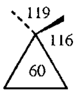
In the classical notation, from usual theoretical expression (see Appendix), the energy due to the electrostatic attraction between the dipole moments $\vec{\mu_i}$ and $\vec{m}$ of the acceptor molecule and a positive charge δ (corresponding to the attracted H-atom) at a given distance is

$$W_A=\left[-\sum_i\frac{\vec{\mu_i}\,\vec{l_i}}{l_i^3}-\frac{\vec{m}\,\vec{l}}{l^3}\right]\frac{\delta}{4\pi\varepsilon} \qquad (4)$$

where $\vec{l_i}$ and $\vec{l}$ are the interaction vectors $\overrightarrow{l_1\delta}$ and $\overrightarrow{l\delta}$, respectively.

The following scheme illustrates the interaction situations with cyanamides ($i=1,4$) and ammonia ($i=1,3$):

Table 1. Structural parameters used in the calculations

(a) Bond lengths (pm)[17, 18]							
H–C (CH_3)	H–C (CH_2)	H–C_{ar}	H–C (=C)	H–C (≡C)	C–C	C–C (cyclopropyl)	C–C (=C)
110	107	108	107	106	154	156	151
C–C (≡N)	C_{ar}–C	C_{ar}–C_{ar}	C=C	C≡C	C–N	C=N	C≡N
146	150	140	133	120	147	134	116
N–H	C_{al}–F	C_{ar}–F	C_{al}–Cl	C_{ar}–Cl	C_{al}–Br	C_{ar}–Br	C_{al}–I
101	133	133	177	170	194	185	214
(b) Bond angles[a] (°)[17, 18]							
X–Y–Z	X=Y–Z	X=Y=Z	X≡Y–Z				
109·46	120	180	180				

[a] X, Y, Z=C, N, H, F, Cl, Br or I.

Table 2. Electro-optic parameters used in the calculations

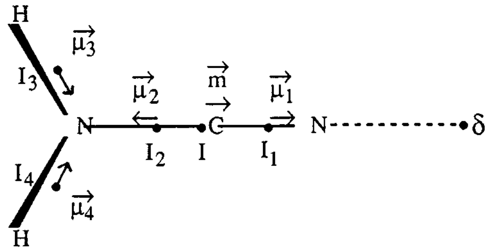
(a) Atomic mean polarizabilities $\overline{\alpha_j}$[a] (in 10^6 pm^3)[19]									
H	C sp^3	C sp^2	C sp	C_{ar}	N sp^3	N sp^2	N sp		
0·408	1·027	1·329	1·419	1·322	1·088	1·400	1·529		
F	Cl	Br	I	$>\overset{+}{N}=$		$\overset{-}{N}=$			
0·321	2·317	3·465	5·530	0·537 (from N sp) 0·692 (from N sp^2)		1·750 (from N sp) 1·911 (from N sp^2)			
(b) Bond moments μ_i (in 10^{-30} C m)[b 13, 14, 20, 21]									
H–C_{ar}	H–C sp	H–C sp^2	H–C sp^3	C–N	C=N	C≡N	H–N	C–F	
0	0	0	1·001	1·501	6·005	10·64	4·370	4·670	
C_{ar}–F	C–Cl	C_{ar}–Cl	C–Br	C_{ar}–Br	C–I				
4·904	5·671	5·338	5·671	5·238	5·238				
(c) Mesomeric moments $\vec{m}$ (in 10^{-30} C m)[c]									
Molecule[d]	**5**	**6**	**7**	**8**	**10, 13, 18**	**11, 12**	**15**	**16**	**19, 20**
m_x	3·136	2·736	3·503	1·902	1·902	2·736	2·202	2·802	3·503
m_y	0	0·200	0	0·033	0·033	0·200	0·033	0·167	0
Molecule[d]	**21**	**22**	**23**	**24**	**25**				
m_x	3·269	2·736	2·502	2·869	3·036				
m_y	0	0	0·033	0·167	0				

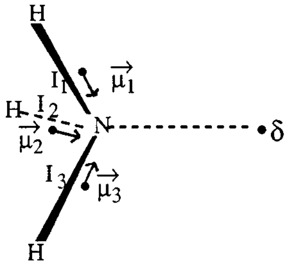
[a] 1 $pm^3 = 10^{-6}$ $Å^3 = 1{\cdot}1127 \times 10^{-46}$ SI (C^2 m^2 J^{-1}).

[b] 1 C m $= 2{\cdot}998 \times 10^{29}$ D.

[c] $\vec{m}$ is deduced from comparison between μ_{exp} values[12, 22] and $\overrightarrow{\mu_1}$, $\overrightarrow{\mu_2}$ calculations on canonical structures (see text). m_α is the component along the α axis. Axes x, y are along C≡N and perpendicular to C≡N, in the aromatic ring plane, respectively.

[d] The molecule numbers are those in Table 3.





As in our previous study on the potential at short distance $V(s)$, $\overrightarrow{N\delta}$ is along the symmetry axis of the acceptor N atom with $N\delta$, the Van der Waals radius, being 1·5 Å. The changes and improvements implied by the use of W_A with respect to our previous analysis are the following. In our first study,[12] the attraction potentials at three different distances were considered in order to take into account the total attraction from the distance $r=\infty$ to $r=1{\cdot}5$ Å. The rigorous approach to this procedure is an integral including all the configurations and in fact W_A is more adapted. Indeed, in the basic case of the attraction between two charges $+q$ and $-q$, the integral $\int_{r_0}^{\infty} dW = 1/4\pi\varepsilon \int_{r_0}^{\infty} (qq'/r^2)\, dr$ gives $W = -qq'/4\pi\varepsilon r_0$, which is consistent with the value at short distance (r_0 for $N\delta = 1{\cdot}5$ Å). In fact, this logical point was not evident in our first analysis because we considered a too rough interaction scheme at short distances: only the $\overrightarrow{\mu_i}$ value of the bond close to the N acceptor. In contrast, in this work all the molecule's bonds (and $\vec{m}$) are included in the W_A calculations [equation (4)]. Calculated W_A values are reported in Table 3. We assumed the constant $4\pi\varepsilon = 1$ (without units) for simplification and adopted $\delta = 3{\cdot}75$ D $Å^{-1}$ for the constant charge of the attracted H atom, this value being obtained by fitting the final correlation with pK_{HB}.

Electrostatic repulsion energy, W_R

After its attraction by the acceptor molecule, the H atom is bonded to the N atom and a hydrogen bond dipole moment $\overrightarrow{\mu_{(H)}}$ appears between N and H. This dipole moment, intermediate between zero and the dipole moment of a covalent NH bond, is logically along $\overrightarrow{HN}$ on the symmetry axis, in accordance with the W_A calculation, and $\overrightarrow{\mu_{(H)}} = p\,\vec{\mu}_{(HN)}$, with $p \leq 1$ and $\vec{\mu}_{(HN)} = 1{\cdot}31$ D (Table 2). As indicated in the following scheme (cyanamide and ammonia), the interaction between $\overrightarrow{\mu_{(H)}}$ and the acceptor's moments $\overrightarrow{\mu_i}$ (and $\vec{m}$) leads to a repulsive (positive) term W_R for the electrostatic energy. Indeed, $\overrightarrow{\mu_{(H)}}$ is an antagonist with the closer $\overrightarrow{\mu_i}$ (and $\vec{m}$) vectors.

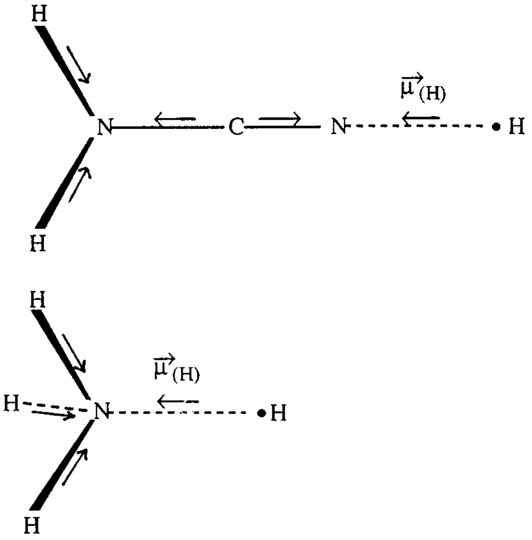
We adopted a simplified form for the electrostatic interdipolar interaction energy (see Appendix) and the final

Table 3. Electrostatic interaction energies W (W_A = attraction, W_R = repulsion, $W_T = W_A + W_R$) and comparison with pK_{HB}[a]

Compounds	W_A	W_R	W_T	pK_{HB}
Nitriles:				
1 Trichloroacetonitrile	−2·299	2·186	−0·113	−0·26
2 Dibromoacetonitrile	−2·471	2·194	−0·277	0·19
3 2-Chloroacrylonitrile	−2·580	2·212	−0·368	0·36
4 Chloroacetonitrile	−2·663	2·225	−0·438	0·39
5 3,5-Dichlorobenzonitrile	−2·783	2·253	−0·530	0·52
6 3-(Trifluoromethyl)benzonitrile	−2·865	2·253	−0·612	0·53
7 4-(Trifluoromethyl)benzonitrile	−2·921	2·252	−0·669	0·54
8 2-(Trifluoromethyl)benzonitrile	−2·925	2·277	−0·648	0·57
9 Bromoacetonitrile	−2·659	2·211	−0·448	0·57
10 2-Fluorobenzonitrile	−2·918	2·264	−0·654	0·64
11 3-Bromobenzonitrile	−2·850	2·255	−0·595	0·65
12 3-Chlorobenzonitrile	−2·846	2·253	−0·593	0·65
13 2-Chlorobenzonitrile	−2·914	2·267	−0·647	0·67
14 Iodoacetonitrile	−2·670	2·213	−0·457	0·67
15 2-(Bromomethyl)benzonitrile	−2·876	2·260	−0·616	0·69
16 3-(Bromomethyl)benzonitrile	−2·895	2·258	−0·637	0·70
17 Acrylonitrile	−2·813	2·274	−0·539	0·70
18 2-Bromobenzonitrile	−2·910	2·265	−0·645	0·71
19 4-Chlorobenzonitrile	−2·888	2·261	−0·627	0·72
20 4-Fluorobenzonitrile	−2·891	2·259	−0·632	0·72
21 4-(Bromomethyl)benzonitrile	−2·910	2·258	−0·652	0·75
22 Benzonitrile	−2·936	2·254	−0·682	0·80
23 2-Methylbenzonitrile	−2·921	2·252	−0·669	0·83
24 3-Methylbenzonitrile	−2·966	2·262	−0·704	0·85
25 4-Methylbenzonitrile	−2·974	2·263	−0·711	0·88
26 Trimethylacetonitrile	−2·858	2·232	−0·626	0·89
27 Acetonitrile	−2·843	2·242	−0·601	0·91
28 Propanenitrile	−2·846	2·240	−0·606	0·96
29 Cyclopropanecarbonitrile	−2·846	2·236	−0·610	1·03
30 4-(Dimethylamino)benzonitrile	−3·259	2·294	−0·965	1·23
31 Cyanamide	−3·120	2·329	−0·791	1·49[b]
32 *N*,*N*-Dimethylcyanamide	−3·259	2·394	−0·865	1·56
33 *N*,*N*-Diethylcyanamide	−3·368	2·358	−1·010	1·63
34 *trans*-3-(dimethylamino)acrylonitrile	−3·484	2·368	−1·116	1·70
35 N^1,N^1-Dimethyl-N^2-cyanoformamidine	−3·608	2·365	−1·243	2·09
36 N^1,N^1-Dimethyl-N^2-cyanoacetamidine	−3·776	2·391	−1·385	2·24
37 Ammonia	−2·813	1·993	−0·820	1·68
Primary amines:				
38 (2,2,2-Trifluoro)ethylamine	−1·924	1·458	−0·466	0·72
39 Propargylamine	−2·303	1·550	−0·753	1·48
40 Benzylamine	−2·306	1·433	−0·873	1·75
41 Methylamine	−2·389	1·447	−0·942	2·15
42 *n*-Butylamine	−2·363	1·436	−0·927	2·17
Tertiary amines:				
43 Diethyl-(2,2,2-trifluoroethyl)amine	−1·140	0·485	−0·655	0·23
44 Tris(propargyl)amine	−1·339	0·429	−0·910	0·70
45 Benzyldimethylamine	−1·448	0·413	−1·035	1·56
46 Triethylamine	−1·613	0·428	−1·185	1·93
47 Dimethyl(*n*-propyl)amine	−1·500	0·390	−1·110	1·98
48 Cyclohexyldimethylamine	−1·429	0·387	−1·042	2·08

[a] W values are in arbitrary units (D^2 Å^{-3}) with μ ion D, q in D Å^{-1} and distance in Å (see text and footnotes to Table 2 for units conversion).

[b] Assumed value.[12]



expression used for our calculations is

$$W_R = \left[\sum_i \frac{\vec{\mu}_i}{l_i^3} + \frac{\vec{m}}{l^3} + \sum_j \frac{\vec{m}_i}{l_j^3} \right] \frac{p\overrightarrow{\mu_{(H)}}}{4\pi\varepsilon} \tag{5}$$

As for other dipoles, we located $\overrightarrow{\mu_{(H)}}$ at the middle of the (N · · · H)bond and l_i, l and l_j are the distances between the interaction centers. For the N · · · Hbond length we adopted 1·25 Å, a value intermediate between a covalent bond length, 1·0 Å, and the attraction distance, 1·5 Å. This arbitrary low value is discussed in the following sections. For simplification and coherence with the previous W_A calculations, we assumed $p=1$ and $4\pi\varepsilon=1$ (without units).

The third term of equation (5) is related to the moments induced by $\overrightarrow{\mu_{(H)}}$ in all the atoms j of the acceptor molecule (except the bonded N atom). These moments are calculated through the usual formula $\overrightarrow{m_j} = \alpha_j T_{jH} \overrightarrow{\mu_{(H)}}$, where α_j is the polarizability tensor of atom j, assumed in practice to be the mean value $\bar{\alpha}_j$ (Table 2); T_{jH} is the interaction tensor (see Appendix). In fact, the last term is minor but allows a more rigorous expression. Calculated W_R values, from equation (4) and parameters in Tables 1 and 2, are reported in Table 3.

CORRELATION BETWEEN ATTRACTION ENERGY W_A AND pK_{HB}

From the Maxwell–Boltzmann statistical distribution,[23] the number of $H^{\delta+}$ atoms (of the donor molecule) attracted is proportional to $\exp(-W_A/kT)$, where k is the Boltzmann constant and T the absolute temperature. Consequently, from equation (1), $-W_A$ must be proportional to pK_{HB}. The W_A values calculated by equation (4) are compared with pK_{HB} in Table 3 and the correlations are presented in Figure 1. As expected, the agreement between the W_A variations and the pK_{HB} scale is satisfactory in a given family; the linear correlation in the more significant series (nitriles) is good. In nitriles, $n=36$, $r=0{\cdot}95$ and $s=0{\cdot}16$, with p$K_{HB} = -1{\cdot}64W_A - 3{\cdot}96$. The mesomeric moments related to conjugation between the aromatic cycle and the C≡N bond are probably too high, particularly because the delocalized electrons are mainly located in the aromatic part (the values in Table 3 correspond to medium repartitioning between the two parts) and because the vector direction is not along the C≡N direction in the general case. If these $\vec{m}$ vectors are not considered, the correlation is improved: $n=36$, $r=0{\cdot}97$ and $s=0{\cdot}12$ with p$K_{HB} = -1{\cdot}49W_A - 3{\cdot}55$ (the fitted constant $\delta=3{\cdot}9$ D Å^{-1}). The last correlation is similar to that in our first study[12] ($r=0{\cdot}98$, $s=0{\cdot}08$) and corresponds to a significant improvement in several respects. More compounds have been studied, 36 instead of 18; the pK_{HB} scale is larger, from $-0{\cdot}26$ to $+2{\cdot}24$, instead of only $+0{\cdot}70$ to $+2{\cdot}24$; the electrostatic model is simpler and more coherent, only one quantity being used (W_A) instead of a combination of three, V(s), V(m) and V(l). More detailed considerations can probably improve the actual correlation, but more serious points have to be examined. The more immediate problem is the strong family dependence of pK_{HB} versus W_A as visible in Fig. 1, similar to that observed for pK_{HB} versus $\Delta\nu$(OH).[1–5] This discrepancy between families shows that the attraction energy, W_A, alone is not sufficient to explain completely the hydrogen-bond acceptor ability of a molecule. Other interaction phenomena must also be considered in order to explain that, in spite of lower electrostatic attractions (in relation to low molecular dipole moments), amines and ammonia present pK_{HB} values similar to those of nitriles.

CORRELATION BETWEEN THE TOTAL INTERACTION ENERGY $W_A + W_R$ AND pK_{HB}

Examination of Table 3 shows that the W_R values present low variations in the same family and strong deviations from one family to another: $W_R = 2{\cdot}29 \pm 0{\cdot}11$ for nitriles, 1·99 for ammonia, $1{\cdot}41 \pm 0{\cdot}06$ for primary amines and $0{\cdot}46 \pm 0{\cdot}07$ (D^2 Å^{-3}) for tertiary amines. This family dependence is easy to understand: W_R mainly depends on the close intramolecular surrounding of the acceptor atom N (see the previous interaction scheme) because it strongly decreases with the distance [see equation (5)] and the families studied are characterized by this surrounding. It may be noticed that $\Delta\nu$(OH), variations of which strongly depend on the family, is related to interactions between donor and acceptor and thus is probably also mainly related to interactions between the donor and the close surrounding of the acceptor. The following qualitative interpretation of W_A and W_R can be proposed: $-W_A$ corresponds to the

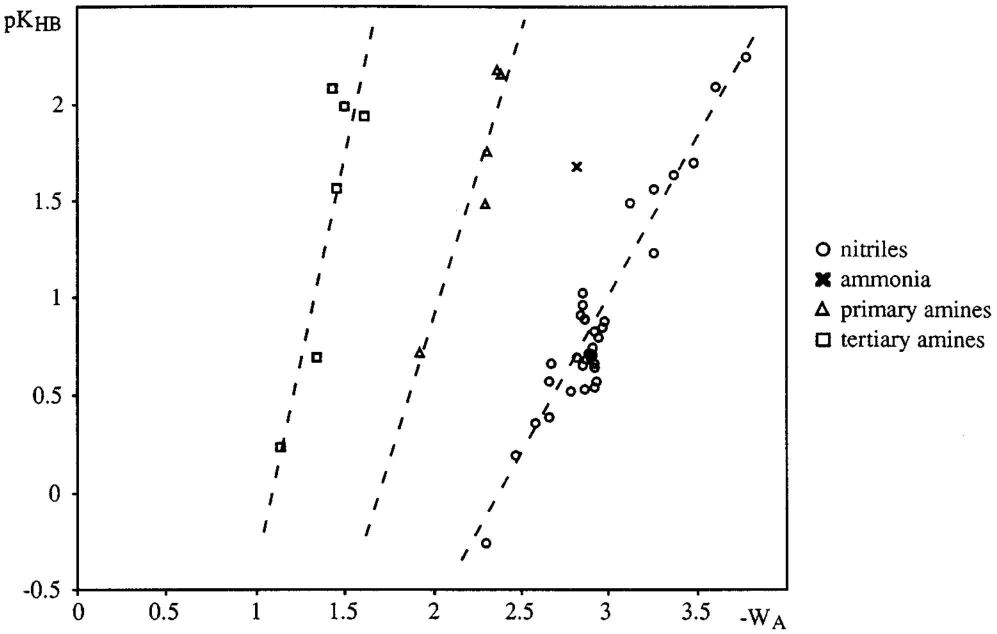


Figure 1. Correlation between pK_{HB} and attraction energy W_A (in arbitrary units, D^2 Å^{-3})

ability to attract H$^{\delta+}$ and thus to the probability of creating an N · · · H bond; in addition, $-W_R$ corresponds to the stability (or strength) of this created bond (if repulsion is strong, the stability is low) and thus to the probability of maintaining the previous created bond. The mutual compensating effects of W_A and W_R clearly explain the family dependence of the relationship between W_A and pK_{HB} (Fig. 1): the lower attraction ($-W_A$) of ammonia and amines than nitriles is compensated by the higher stability (or lower repulsion W_R). Finally, the ability both to create and maintain hydrogen bonding must be well represented by the total electrostatic interaction $W_T = W_A + W_R$. The W_T values are reported in Table 3 and compared with pK_{HB}; the correlation is presented in Figure 2. As expected, the family dependence is drastically reduced and an acceptable linear correlation is observed with regard to the various approximations of our model. For the 48 molecules studied, $r = 0{\cdot}89$ and $s = 0{\cdot}28$ with p$K_{HB} = -2{\cdot}17W_T - 0{\cdot}55$ (Figure 2). If the vector $\vec{m}$ of aromatic nitriles is not considered (see previous comments on W_A), we obtain $r = 0{\cdot}92$ and $s = 0{\cdot}24$. The quality of our correlation is similar to that obtained by Politzer and co-workers between $V_{s,\min}$ and pK_{HB} for 33 compounds with more different families ($r = 0{\cdot}90$, $s = 0{\cdot}39$). Two other similarities, indicating a mutual consistency, can be noticed: the attraction distances in both the models correspond to Van der Waals radii of the acceptor molecules; these distances are surely too short (because the geometry of attracted atoms must also be considered), which explains, in our model, the arbitrary δ and $\mu_{(H)}$ values and also the too short hydrogen bond, 1·25 instead of about 1·8 Å, the average value in the literature.[24] the electrostatic energy differences are very close: from p$K_{HB} = -0{\cdot}2$ to p$K_{HB} = +2{\cdot}2$, Politzer and coworkers calculated a deviation of about -18 kcal mol^{-1} and in our work the W_T deviation (by using $4\pi\varepsilon_0$, where ε_0 the permittivity of vacuum) is also about -18 kcal mol^{-1}.

CONCLUSION

We have significantly improved our electrostatic dipolmetric model for the prediction of hydrogen bonds in several respects: a simplification and a better coherence of our attraction scheme (W_A) as well as the logical introduction of a repulsion term (W_R). The total interaction energy $W_A + W_R$ allowed us to obtain an acceptable correlation with the basicity pK_{HB} scale for 48 molecules, including four different families with a nitrogen atom acceptor. The objective of our electrostatic method and of the quantum mechanical methods is the same: a better understanding of intermolecular interactions and association phenomena together with the elaboration of prediction equations. The prediction aspect is useful, particularly when suitable measurements cannot be obtained. At first sight, because we are in the elaboration step of the method, all necessary parameters seem to lead to laborious calculations. In further steps, most of the basical data will be included in a calculation program, as in the various semi-empirical or *ab initio* programs. In fact, our method is simpler than the quantum mechanical methods because the included parame-

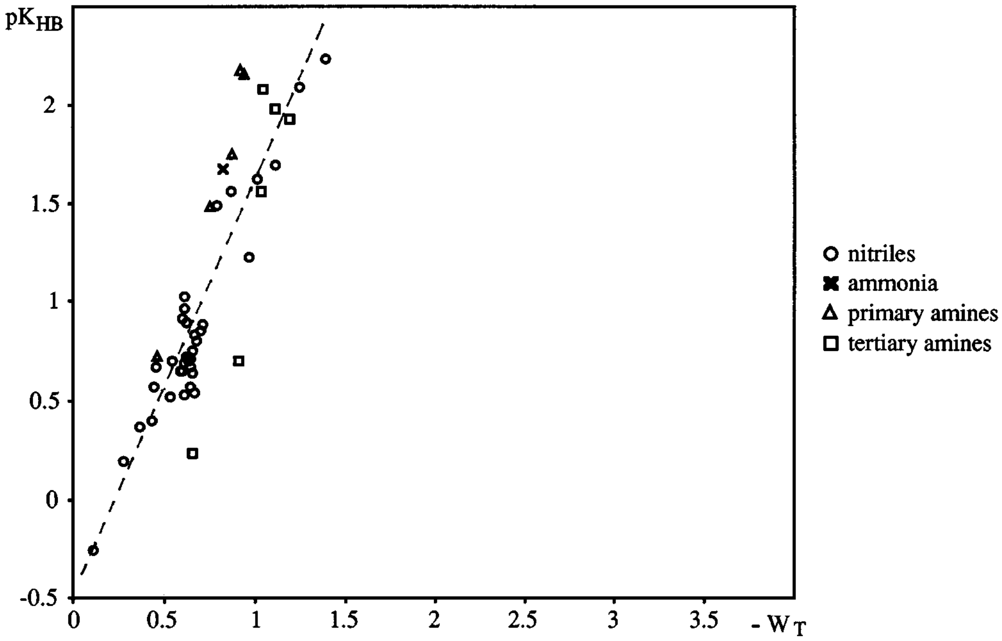


Figure 2. Correlation between pK_{HB} and the total interaction energy W_T (in arbitrary units, D^2 $Å^{-3}$)

ters are less numerous and, above all, the calculation equations are more easy to apply (applications can be performed by using ordinary calculators). With regard to quantum mechanical methods, our calculations are empirical, mainly because of the level considered for the practical approximations: the global scheme of bond moments instead of the electronic density functions. Nevertheless, the bond moments scheme is directly connected to the measured values of molecular dipole moments, which ensures an empirical but realistic basis for the analysis of electrostatic effects, the undisputable origin of the examined phenomena. Our calculations yield quantities suitable for easy detailed interpretations: the attraction between H atom and acceptor for W_A and the stability of the created hydrogen bond for W_R. If W_A or W_R is separately considered, a strong family dependence is observed, and this strong dependence vanishes for the total energy $W_A + W_R$. Finally, such a method, complementary to quantum mechanical methods, must be continued and extended. In particular, we envisage the examination of a more complete and rigorous interaction scheme by considering the whole O–H bond of the donor together with more general dipolar interaction equations (see Appendix), instead of the H atom only and of an ideal dipolar formula.

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APPENDIX

Details of electrostatic potential *V* and energy *W* expressions

The basic expression is the potential due to a charge q, at a distance l:$V(q)=q/l$ (the constant multiplying factor $1/4\pi\varepsilon$ being omitted for simplification; ε is the permittivity of the medium). From this expression, the potential due to a dipole $\vec{\mu}$ at a distance l is[23] $V(\vec{\mu})=-\vec{\mu}\,\vec{l}/l^3$ (chemical notation).

For energy, because we used for W_{A} the expression $W_{\mathrm{A}}=qV(\vec{\mu})$, we also used for reasons of coherence (see figure below) $W_{\mathrm{R}}=-|q|V_-(\vec{\mu}_1)+|q|V_+(\overrightarrow{\mu_1})$ for the interaction energy between $\overrightarrow{\mu_1}$ and $\overrightarrow{\mu_2}=(\overrightarrow{l_-}-\overrightarrow{l_+})|q|$ ($\overrightarrow{\mu_1}$ concerns a bond dipole of the acceptor molecule, $\overrightarrow{\mu_2}$ is the N · · · Hbond moment). Then,

$$W_{\mathrm{R}}=-|q|\left(\frac{\overrightarrow{l_+}}{l_+^3}-\frac{\overrightarrow{l_-}}{l_-^3}\right)\overrightarrow{\mu_1}$$

and

$$\frac{\overrightarrow{l_+}}{l_+^3}-\frac{\overrightarrow{l_-}}{l_-^3}=\frac{1}{l_+\overrightarrow{l_+}}-\frac{1}{l_-\overrightarrow{l_-}}=\frac{l_-\overrightarrow{l_-}-l_+\overrightarrow{l_+}}{l_+\overrightarrow{l_+}\,l_-\overrightarrow{l_-}}.$$

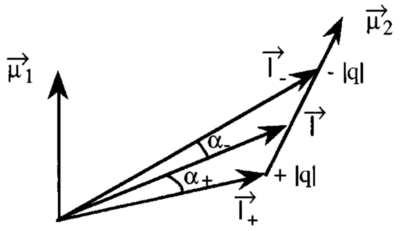
We consider ideal dipoles, for reasons of simplification, and $l_+\approx l_-\approx l$, $\overrightarrow{l_+}\;\overrightarrow{l_-}\approx l_+l_-\cos(\alpha_++\alpha_-)\approx l^2$ if $\alpha_++\alpha_-\rightarrow 0$.
Finally, we obtain

$$W_{\mathrm{R}}=-|q|\frac{\overrightarrow{l_-}-\overrightarrow{l_+}}{l^3}\overrightarrow{\mu_1}=\frac{-\overrightarrow{\mu_1}\,\overrightarrow{\mu_2}}{l^3}$$

In fact, the more general expression, based upon $W=-\overrightarrow{\mu_1}\,\overrightarrow{E_2}$ (where $\overrightarrow{E_2}$ the field due to $\overrightarrow{\mu_2}$) for dipolar interactions, is $W=-\overrightarrow{\mu_1}\,T_{12}\overrightarrow{\mu_2}$ with the interaction tensor:[23]

$$T_{12}=(1/r^5)\begin{bmatrix} 3x^2-r^2 & 3xy & 3xz \\ 3xy & 3y^2-r^2 & 3yz \\ 3xz & 3yz & 3z^2-r^2 \end{bmatrix}$$

where x, y and z are the components of $\vec{l}$.



Our W_{R} expression is valid only for ideal dipoles but it is simpler and, overall, coherent with our W_{A} expression.