Molecular Electrostatic Potential as Reactivity Index in Hydrogen Bonding: Ab Initio Molecular Orbital Study of Complexes of Nitrile and Carbonyl Compounds with Hydrogen Fluoride†

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Ab initio molecular orbital calculations at the HF/6-31+G(d,p) level were used to investigate the hydrogen bonding between hydrogen fluoride and two series of molecules, nitrile and carbonyl compounds of the type R−CN and R−CHO, respectively, where R= −H, −OH, −SH, $-OCH_3$, $-NH_2$, $-NO_2$, −C≡N, −F, −Cl, $-CH_3$, and $-CF_3$. Geometry optimization and vibrational frequency calculations at the optimized geometry were performed for isolated and hydrogen-bonded systems. The estimated energies of hydrogen-bond formation were corrected for zero-point vibrational energy and basis set superposition error (including the relaxation correction). Linear relations between the energy of hydrogen-bond formation (ΔE) and the H−F stretching frequency shift ($\Delta\nu_{HF}$) are obtained for the two series studied. Linear dependencies are also found between ΔE and the change of H−F bond length (Δr_{HF}). An excellent linear dependence is found between ΔE^{R-CN} and the ab initio calculated molecular electrostatic potential at the nitrile nitrogen (V_N) in isolated nitrile molecules. A linear dependence is also found between E^{R-CHO} and the ab initio calculated molecular electrostatic potential at the carbonyl oxygen (V_O) in isolated carbonyl molecules. These relations show that the molecular electrostatic potential can be successfully used to predict the reactivity of the molecules studied with respect to hydrogen bonding. Significantly, a dependence that unifies the two series of proton-acceptor molecules was also found. It can be used with confidence in predicting the energy of hydrogen-bond formation when different substituents are added to the simplest member of a series.

Introduction

In view of the known importance of the electrostatic forces in intermolecular interactions and in particular hydrogen-bond formation,[1−17] it is not surprising that the molecular electrostatic potential has been used to provide some useful guidelines concerning hydrogen bonding. The positions of the minima of the molecular electrostatic potential associated with the electron-donating center in isolated molecules have been used successfully in predicting the sites and directionality of hydrogen bonds in a variety of systems.[18−21] A satisfactory correlation has been found between the calculated energies of hydrogen-bond formation and the magnitude of the molecular electrostatic potential at a fixed distance from the proton-accepting molecule in a series of complexes between hydrogen fluoride and various acceptors.[18] More recently, it has been shown that the calculated electrostatic potential minima in the vicinities of the hydrogen-bond-accepting atoms correlate well with the solvatochromic hydrogen bond acceptor parameter, β, for a variety of molecules.[22] In a recent study from this laboratory[23] a series of over 20 hydrogen-bonded complexes between carbonyl compounds and hydrogen fluoride was investigated using ab initio molecular orbital calculations at the HF/6-31G(d,p) level. We have examined the variation the molecular electrostatic potential *at* the carbonyl oxygen rather than the potential *in the vicinity* of the carbonyl group and demonstrated that the so-defined electrostatic potential correlates excellently with the energy of hydrogen-bond formation.

The principal aim of the present study is to further investigate these dependencies in another class of proton-acceptor molecules, a series of simple nitrile compounds. Eleven molecules of the type R−CN, where R= −H, −OH, −SH, $-OCH_3$, $-NH_2$, $-NO_2$, −C≡N, −F, −Cl, $-CH_3$, and $-CF_3$, are studied by quantum mechanical calculations at the HF/6-31+G(d,p) level of theory. To compare nitrile and carbonyl compounds, 11 carbonyl molecules of the type R−CHO, where again R= −H, −OH, −SH, $-OCH_3$, $-NH_2$, $-NO_2$, −C≡N, −F, −Cl, $-CH_3$, and $-CF_3$, are recalculated using the same basis set. For both series of molecules hydrogen fluoride is used as a model proton donor in the respective hydrogen-bonded complexes. The trends of changes in the energy of hydrogen-bond formation in the two classes of molecules are analyzed. The results are explained in terms of the variation of the molecular electrostatic potential at the nitrile nitrogen for the series of nitrile compounds, and the molecular electrostatic potential at the carbonyl oxygen for the series of carbonyl compounds, respectively. It was also of interest to seek a dependence between the calculated molecular electrostatic potential and interaction energy that can unify the two series studied.

Calculations

Ab initio calculations at the HF/6-31+G(d,p) level were carried out to obtain the structures of isolated and hydrogen-bonded molecules of the two series studied. Harmonic vibrational frequencies (at the same level of theory) confirmed that the located structures correspond to minima having no imaginary frequencies. In determining the energy of hydrogen-bond formation, the zero-point vibrational energy was taken into

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account. A scaling factor of 0.9135[24] was used to approximately correct for vibrational anharmonicity as well as for overestimation of the force constants at the SCF level due to lack of proper consideration of the electron correlation. The obtained interaction energies were also corrected for the basis set superposition error (BSSE), which is known to be appreciable in estimating the energy of hydrogen-bond formation.[14] The counterpoise method (CP)[25] was used. Its applicability in calculations on van der Waals complexes has been recently reviewed.[26] Fragment relaxation energy terms were also taken into account to estimate BSSE.[27] All calculations were carried out with the Gaussian 92W program package.[28]

As a standard output of the program, the molecular electrostatic potential at the nitrile nitrogen for the series of isolated nitrile molecules and at the carbonyl oxygen for the series of isolated carbonyl molecules was also obtained. The molecular electrostatic potential at an atomic site can be defined as follows:[29]

$$V_{\mathrm{Y}} = V(\mathbf{R}_{\mathrm{Y}}) = \sum_{\mathrm{A}\neq \mathrm{Y}} \frac{Z_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{Y}} - \mathbf{R}_{\mathrm{A}}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{R}_{\mathrm{Y}} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}' \qquad (1)$$

where Z_A is the charge on nucleus A located at $\mathbf{R}_A$, Y represents the nitrile nitrogen for the series of nitrile compounds and the carbonyl oxygen for the series of carbonyl compounds, respectively, $\rho(\mathbf{r})$ is the electronic density function of the respective molecule as obtained from ab initio molecular orbital calculations, and $\mathbf{r}'$ is a dummy integration variable. Equation 1 is written in atomic units and contains a summation over the atomic nuclei treated as positive point charges and an integration over the "continuous" negative charge distribution of the electrons.

Results and Discussion

Interaction Energy. The noncorrected energies of hydrogen-bond formation calculated as a difference between the respective SCF energies of the complex and the monomers (ΔE^{SCF}), the zero-point vibrational energy corrections (ΔE^{ZPE}), the counterpoise corrections (ΔE^{CP}), the relaxation corrections (ΔE^{REL}), and the totally corrected energies of hydrogen-bond formation (ΔE) for the two series of hydrogen bonded complexes studied are given in Table 1. The molecules of each series are listed in order of descending absolute value of the energy of hydrogen-bond formation. In most cases, the influence of the same substituent on the interaction energy is similar for the carbonyl and nitrile compounds. For example, in both series the $-NH_2$ substituent corresponds to the highest energy of hydrogen-bond formation in the respective series, whereas the $-NO_2$ substituent corresponds to the lowest interaction energy. For a number of substituents, however, such regularities are not found. For example, ΔE_{FCHO} is 0.1691 kcal/mol higher than $\Delta E_{\mathrm{ClCHO}}$ for the carbonyl series, whereas ΔE_{FCN} is 0.1634 kcal/mol smaller than ΔE_{ClCN} for the nitrile series. These differences in the influence of different substituents on the energy of hydrogen-bond formation can be explained in terms of molecular electrostatic potential, as will be seen later in the text.

The values of ΔE^{CP} and ΔE^{REL} are the same order of magnitude. This is further evidence that the omission of the fragment relaxation energy terms in estimating the BSSE corrections can introduce significant errors.[27] The BSSE correction is greater for the series of carbonyl molecules. It is between 3 and 6% for the series of nitrile compounds and reaches 10% for the carbonyl compounds. It is worth mentioning that the magnitudes of ΔE^{CP} estimated at the HF/6-31+G(d,p) level of theory are approximately 10 times smaller than the respective values at the HF/6-31G(d,p) level previously estimated in studying carbonyl derivatives. [23]

TABLE 1: HF/6-31+G(d,p) ab Initio Calculated Noncorrected Energy of Hydrogen Bond Formation (ΔE^{SCF}), Zero-Point Vibrational Energy Correction (ΔE^{ZPE}), Counterpoise Correction (ΔE^{CP}), Relaxation Correction (ΔE^{REL}), and Totally Corrected Energy of Hydrogen-Bond Formation (ΔE) for the Two Series of Molecules Studied[a]

molecule	ΔE^{SCF}	$\Delta E^{\mathrm{ZPE}\ b}$	ΔE^{CP}	ΔE^{REL}	ΔE
		Nitrile Derivatives			
NH_2CN	−8.2417	1.6377	0.1255	0.1443	−6.3342
CH_3OCN	−8.1357	1.6824	0.1450	0.1450	−6.1633
CH_3CN	−7.7761	1.6905	0.1776	0.0878	−5.8202
HOCN	−7.4680	1.6452	0.1971	0.0602	−5.5655
HSCN	−6.6930	1.5861	0.2378	0.0182	−4.8509
HCN	−6.3240	1.7048	0.1726	0.0532	−4.3934
ClCN	−5.9513	1.5185	0.1826	0.0527	−4.1975
FCN	−5.8220	1.5420	0.1738	0.0723	−4.0341
CF_3CN	−4.5752	1.4090	0.1243	0.0634	−2.9785
NCCN	−3.8849	1.3431	0.2397	0.0201	−2.2820
NO_2CN	−3.3076	1.2393	0.1688	0.0364	−1.8631
		Carbonyl Derivatives			
NH_2CHO	−10.1945	2.2230	0.1067	0.3746	−7.4902
CH_3CHO	−8.4971	1.9564	0.2748	0.1902	−6.0757
CH_3OCHO	−8.4124	1.8940	0.1995	0.2887	−6.0302
HOCHO	−7.7523	1.8831	0.2397	0.2309	−5.3986
HCHO	−7.4969	2.0843	0.3508	0.1343	−4.9275
HSCHO	−7.1028	1.8177	0.2824	0.1945	−4.8082
FCHO	−5.5648	1.6561	0.2366	0.1462	−3.5259
ClCHO	−5.2912	1.5976	0.2812	0.1556	−3.2568
CF_3CHO	−5.1657	1.6028	0.2880	0.0960	−3.1789
CNCHO	−4.8243	1.6113	0.3056	0.0823	−2.8251
NO_2CHO	−3.3616	1.2932	0.2742	0.0647	−1.7295

[a] The molecules of each series are listed in order of descending absolute value of the corrected energy of hydrogen-bond formation. All values are in kcal/mol. [b] Scaled by 0.9135. See text.

Structural and Infrared Spectral Parameters. The optimized structures of the hydrogen-bonded complexes for some molecules of the series of nitrile and carbonyl compounds are shown in Figure 1.[30] For most substituents the hydrogen fluoride molecule binds at the nonsubstituted side of the R−CHO molecule. For complexes of the type R−CHO···HF where R = −OH, −SH, and $-NH_2$, however, the most stable structures are with the hydrogen fluoride molecule bound at the substituted side of HOCHO, HSCHO, and NH_2CHO, respectively. Alternative local minima are found at the nonsubstituted side of R−CHO molecules. The differences in the energies of the two types of complexes are very small: 0.6884, 0.0577, and 0.3357 kcal/mol, respectively. It should be emphasized that for systems where a hydrogen fluoride molecule binds at the side of substituents containing a polarized X−H bond (−OH, −SH, $-NH_2$), a possibility for interaction between the fluorine atom of hydrogen fluoride and the hydrogen atom of the substituent exists. Indeed, the estimated F···H distances are 2.1057 Å (F···H−O), 2.5323 Å (F···H−S), and 2.4145 Å (F···H−N), respectively. These distances are rather small and suggest the formation of a secondary hydrogen bond or, at least, increased nonbonded interaction. The optimized structure of the HOCHO···HF complex, for example, with HF bound at the side of −OH substituent, is illustrated in Figure 2. The formation of a secondary hydrogen bond has been also suggested in an experimental argon matrix infrared spectroscopic study of the complex between NH_2CHO and HF.[31] As in our previous study,[23] in order to avoid such secondary effects, we considered the complexes where the hydrogen fluoride molecule binds at the nonsubstituted side of the R−CHO molecule for all carbonyl

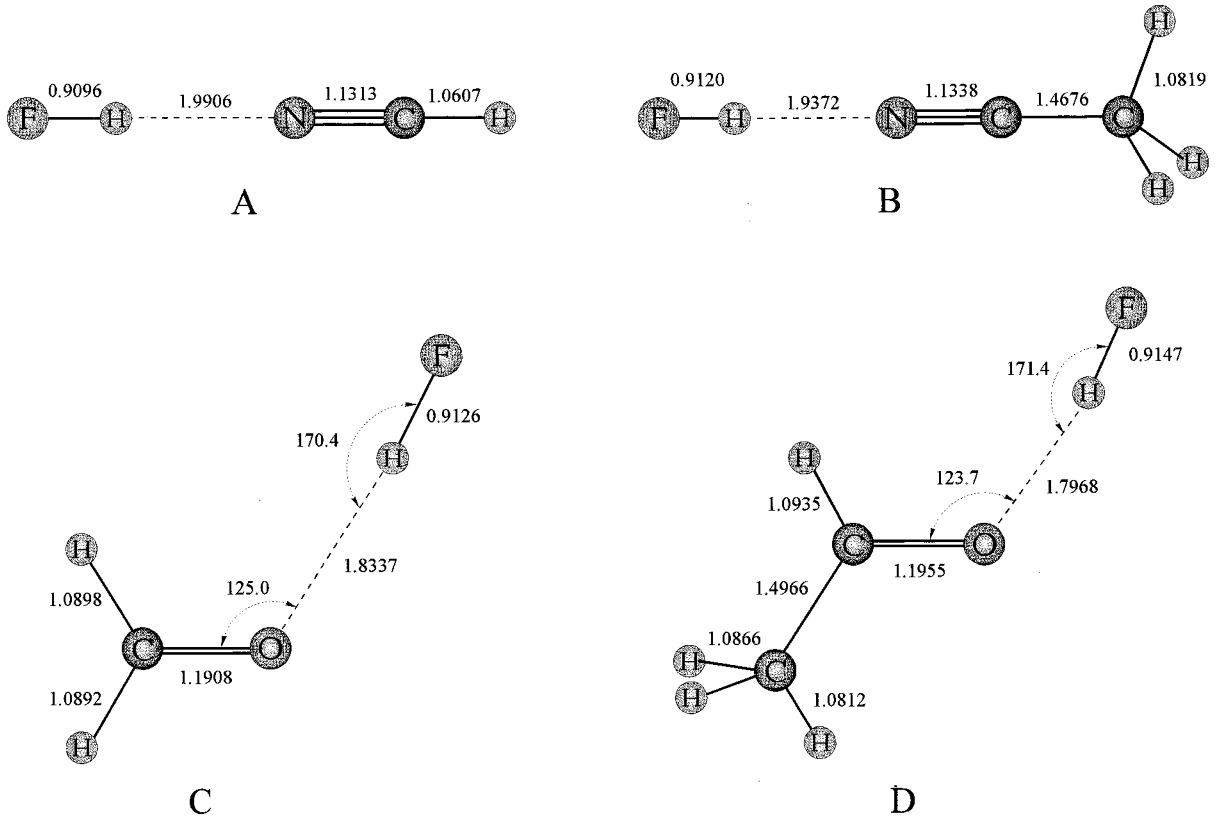

Figure 1. Optimized structures of hydrogen-bonded complexes for some molecules of the series of nitrile and carbonyl compounds studied: valence bond lengths in angstroms, angles in degrees.

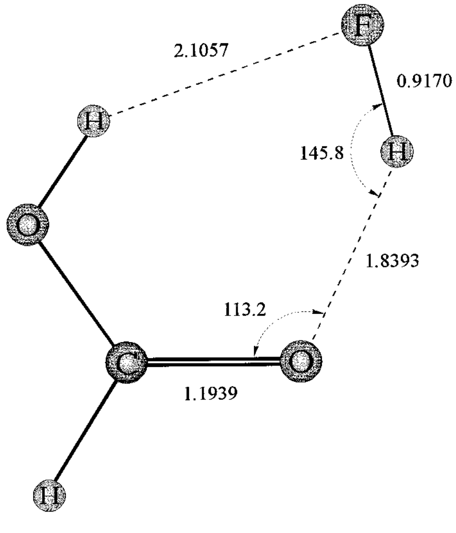

Figure 2. Optimized structure of HOCHO···HF complex with HF bound at the side of −OH substituent: valence bond lengths in angstroms, angles in degrees.

complexes studied (Figure 1). It should, of course, always be remembered that such secondary interactions can often be found in actual complexes and need careful consideration.

In the case of the nitrile complexes studied, both the $C\equiv N\cdots H$ and $N\cdots H-F$ structures are linear. In the case of carbonyl complexes the $C=O\cdots H$ structure is nonlinear, with the $C=O\cdots H$ angle in the range 109°−128°. The $O\cdots H-F$ structure is also nonlinear with the $O\cdots H-F$ angle in the range 135°−174°. The $O\cdots H$ hydrogen bond and H−F bond of hydrogen fluoride lay in the plane of the C=O bond; i.e., all complexes of carbonyl compounds have C_s symmetry. The theoretically determined structures of the complexes are in good agreement with the experiment where available. Experimental geometry data are available for the following complexes.

HCN···HF.[32] The experimentally measured $N\cdots F$ length is 2.795 Å, which is in reasonable agreement with the calculated value of 2.9002 Å (Figure 1A).

CH_3CN···HF.[33] The experimentally measured $N\cdots F$ length (2.76 Å) is in accord with the calculated value of 2.8492 Å (Figure 1B).

NCCN···HF.[34] The experimentally measured $N\cdots F$ length is 2.862 Å, which is again in reasonable conformity with the calculated value of 2.9983 Å.

It is worth mentioning that there is very good correspondence between the variations of the experimentally measured and HF/6-31+G(d,p) ab initio calculated values of the $N\cdots F$ length for these three complexes.

HCHO···HF.[35] The experimentally measured value for the $C=O\cdots H$ angle is 115°. The respective ab initio calculated value is 125.0° (Figure 1C). The authors of the experimental study[35] indicate that the hydrogen bond is nonlinear and deviates from linearity by approximately 10°. This statement is in very good agreement with the ab initio calculated deviation of 9.6°. The experimental $O\cdots H$ and $O\cdots F$ lengths (1.794 and 2.659 Å) are in reasonable agreement with the theoretically predicted values of 1.8337 and 2.7376 Å, respectively (Figure 1C).

The calculated hydrogen bond lengths ($r_{Y\cdots H}$) for the complexes of nitrile (Y=N) and carbonyl (Y=O) molecules are given in Table 2. In most cases, for the same substituent the hydrogen bond length is higher for the series of nitrile compounds than the respective value for the series of carbonyl compounds. This is in conformity with the fact that the energies of hydrogen-bond formation are higher for the series of carbonyl compounds (Table 1). The changes in the nitrile and carbonyl bond length (Δr_{CY}) and the changes in the hydrogen fluoride

TABLE 2: HF/6-31+G(d,p) ab Initio Calculated Changes in Structural Parameters of Hydrogen Bonded to Hydrogen Fluoride Nitrile and Carbonyl Derivatives with Respect to the Isolated Molecules[a]

molecule	$r_{Y\cdots H}$[b]	Δr_{CY}	Δr_{HF}
	Nitrile Derivatives		
HCN	1.9906	−0.0021	0.0074
HOCN	1.9468	−0.0018	0.0091
HSCN	1.9767	−0.0016	0.0080
CH_3OCN	1.9231	−0.0017	0.0103
NH_2CN	1.9202	−0.0014	0.0105
NO_2CN	2.1224	−0.0017	0.0036
NCCN	2.0919	−0.0017	0.0042
FCN	2.0067	−0.0020	0.0066
ClCN	2.0020	−0.0016	0.0069
CH_3CN	1.9372	−0.0017	0.0098
CF_3CN	2.0593	−0.0017	0.0052
	Carbonyl Derivatives		
HCHO	1.8337	0.0047	0.0104
HOCHO	1.8201	0.0075	0.0107
HSCHO	1.8399	0.0078	0.0099
CH_3OCHO	1.7973	0.0081	0.0120
NH_2CHO	1.7460	0.0094	0.0160
NO_2CHO	2.1285	0.0042	0.0038
CNCHO	1.9393	0.0049	0.0065
FCHO	1.9108	0.0057	0.0068
ClCHO	1.9205	0.0070	0.0066
CH_3CHO	1.7968	0.0059	0.0125
CF_3CHO	1.9173	0.0043	0.0068

[a] All values are in angstroms. [b] Y = N, O.

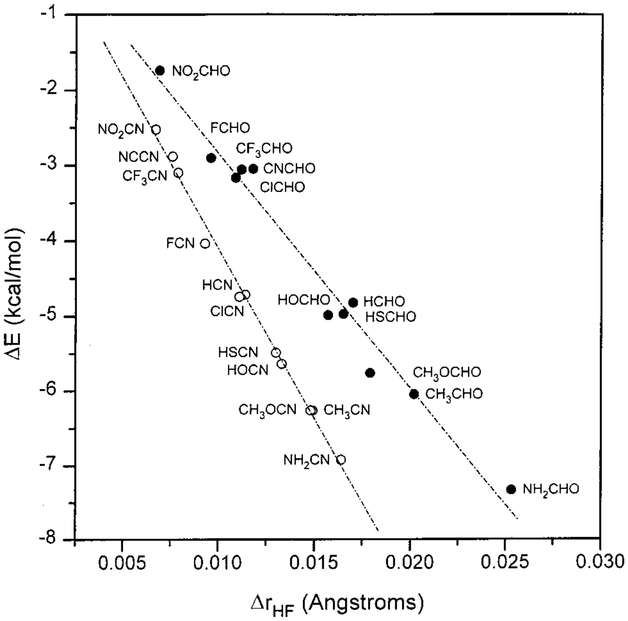

Figure 3. Dependence between the energy of hydrogen-bond formation (ΔE) and the changes in hydrogen fluoride bond length (Δr_{HF}) for hydrogen bonded to hydrogen fluoride complexes of nitrile and carbonyl derivatives.

TABLE 3: HF/6-31+G(d,p) ab Initio Calculated and Experimentally Determined Changes in Spectral Parameters of Hydrogen Bonded to Hydrogen Fluoride Nitrile and Carbonyl Derivatives with Respect to the Isolated Molecules[a]

	$\Delta\nu_{CY}$[b]			$\Delta\nu_{HF}$		
molecule	calcd	exptl[c]	exptl[d]	calcd	exptl[c]	exptl[d]
			Nitrile Derivatives			
HCN	17	24[36]	26[37]	−175	−245[36]	−293[37]
HOCN	19			−214		
HSCN	13			−190		
CH_3OCN	16			−245		
NH_2CN	14		42[38]	−251		−461[38]
NO_2CN	14			−82		
NCCN	9		11[39]	−96	−154[42]	−162[39]
FCN	21		37[39]	−154		−257[39]
ClCN	13		37[39]	−162		−322[39]
CH_3CN	14		32[40]	−233	−334[43]	−436[40]
CF_3CN	13			−118		
			Carbonyl Derivatives			
HCHO	−16		−10[44]	−252		−346[44]
HOCHO	−32			−258		
HSCHO	−33			−239		
CH_3OCHO	−35			−290		
NH_2CHO	−33		−18[31]	−392		−677[31]
NO_2CHO	−17			−78		
CNCHO	−16			−152		
FCHO	−25			−157		
ClCHO	−30			−153		
CH_3CHO	−21		−6[45]	−308	−321[46]	−503[45]
CF_3CHO	−13			−160		

[a] All values are in cm^{-1}. [b] Y = N, O. [c] Gas-phase data. [d] Matrix-isolation data.

bond length (Δr_{HF}) with respect to the respective bond length in isolated molecules are also given in Table 2. As can be seen, the H−F bond length in both series of complexes increases with respect to its value in isolated hydrogen fluoride. The values of Δr_{HF} can be satisfactorily explained in terms of the different energies of hydrogen-bond formation (ΔE). The dependencies between ΔE and Δr_{HF} for the two series studied are illustrated in Figure 3. Linear relations are found with linear regression coefficients, respectively, 0.998 for the nitrile series and 0.994 for the carbonyl complexes. As anticipated, a stronger hydrogen bond corresponds to a weaker H−F bond, resulting in an increased bond length. The carbonyl bond length also increases with hydrogen-bond formation, as can be expected. However, the nitrile bond length decreases upon hydrogen bonding. This corresponds to strengthening of the C≡N with hydrogen-bond formation, which is at a first sight surprising. However, this finding is in accord with infrared spectral data[36−40] and previous ab initio calculations[41] as is discussed further in the text.

The theoretically predicted changes in the vibrational frequencies associated with the C≡N, C=O, and H−F stretching modes with respect to the quantities in isolated molecules are given in Table 3. Experimentally determined values are also given for comparison where available. For the two series of complexes, the H−F stretching mode frequency is shifted to lower values with respect to the isolated hydrogen fluoride. This is in conformity with the elongation of r_{HF} upon hydrogen bonding and reflects the weakening of the bond. The available experimental spectral data are in reasonable conformity with the ab initio estimated shifts. The trends of changes of $\Delta\nu_{HF}$ for both series studied are very well predicted by the calculations. In agreement with expectations, linear relations between the shift in the H−F stretching mode frequency ($\Delta\nu_{HF}$) and the energy of hydrogen-bond formation (ΔE) are found for both series studied. The dependencies are shown in Figure 4. The linear regression coefficients are, respectively, 0.998 for the nitrile and 0.993 for the carbonyl complexes.

The carbonyl stretching frequencies are also red-shifted upon hydrogen-bond formation, which is in agreement with the elongation of that bond discussed earlier. The available experimentally measured values of $\Delta\nu_{C=O}$ are in reasonable accord with the theoretically predicted shifts. The nitrile stretching frequencies are, however, blue-shifted upon hydrogen-bond formation for the entire series of nitrile complexes studied. This corresponds to shortening of the C≡N bond as pointed out earlier. The theoretically calculated increase of the nitrile stretching frequency is in agreement with the experimental

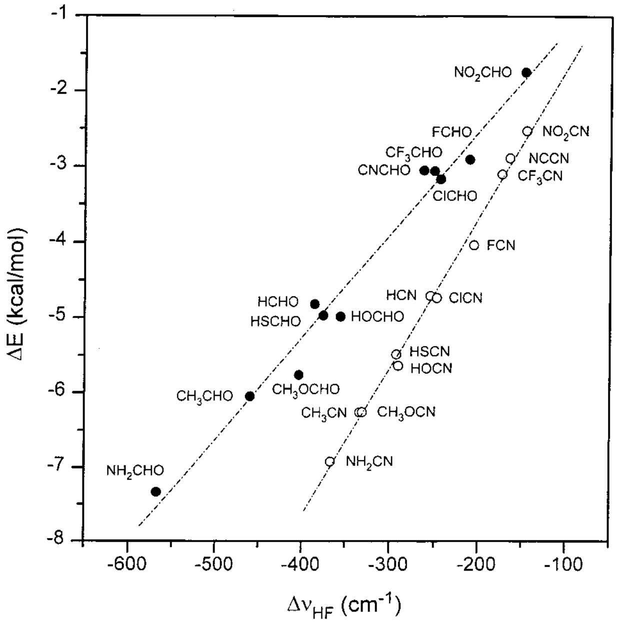

Figure 4. Dependence between the energy of hydrogen-bond formation (ΔE) and H−F stretching frequency shift ($\Delta\nu_{HF}$) for hydrogen bonded to hydrogen fluoride complexes of nitrile and carbonyl derivatives.

measurement[36−40] as well as with previously performed ab initio calculations.[41] The experimentally measured values for $\Delta\nu_{C\equiv N}$ are all positive and in reasonable conformity with the theoretically predicted shifts. Both experimental results and ab initio calculations show that the nitrile bond is reinforced upon hydrogen-bonding with hydrogen fluoride.

Molecular Electrostatic Potential and Hydrogen Bonding. The ab initio calculated molecular electrostatic potentials in the isolated molecules calculated at the nitrile nitrogen for the series of nitrile derivatives and at the carbonyl oxygen for the series of carbonyl derivatives (eq 1) are presented in Table 4. The molecules of each series are listed in order of descending absolute value of the respective molecular electrostatic potential. The dependence between V_N and the interaction energy for the nitrile compounds, ΔE^{R-CN}, and the dependence between V_O and the energy of hydrogen-bond formation for the carbonyl compounds, ΔE^{R-CHO}, are shown in parts A and B of Figure 5, respectively. As can be seen, excellent linear relations are found for both series of molecules. The respective linear regression results are

$$\Delta E^{R-CN} = 46.7828(\pm 1.3273)V_N + 852.5494(\pm 24.3137),\quad n = 11, R = 0.996, \mathrm{SD} = 0.1372 \tag{2}$$

for the series of nitrile derivatives and

$$\Delta E^{R-HCO} = 47.6889(\pm 2.0321)V_O + 1057.8491(\pm 45.2679),\quad n = 11, R = 0.992, \mathrm{SD} = 0.2298 \tag{3}$$

for the series of carbonyl derivatives.

These linear relations clearly show that the energy of hydrogen-bond formation between proton-acceptor molecules and a constant proton donor can be rationalized in terms of a property of the isolated proton-acceptor molecule. This is the molecular electrostatic potential at the atom participating in hydrogen-bond formation: the nitrile nitrogen for the series of compounds containing a nitrile group and the carbonyl oxygen for the series of carbonyl derivatives.

TABLE 4: HF/6-31+G(d,p) ab Initio Calculated Molecular Electrostatic Potential at the Nitrile Nitrogen and at the Carbonyl Oxygen in the Isolated Molecules (V_Y, Where Y = N, O) and the Variations of Molecular Electrostatic Potential (ΔV, Eq 4) and Energy of Hydrogen-Bond Formation ($\Delta E'$, Eq 5)[a]

molecule	V_Y (au)	ΔV (au)	$\Delta E'$ (kcal/mol)
	Nitrile Derivatives		
NH_2CN	−18.3557	−0.0329	−1.9408
CH_3OCN	−18.3519	−0.0291	−1.7699
CH_3CN	−18.3504	−0.0276	−1.4268
HOCN	−18.3408	−0.0180	−1.1721
HSCN	−18.3273	−0.0045	−0.4575
HCN	−18.3228	0	0
ClCN	−18.3144	0.0084	0.1959
FCN	−18.3121	0.0107	0.3593
CF3CN	−18.2881	0.0347	1.4149
NCCN	−18.2717	0.0511	2.1114
NO_2CN	−18.2602	0.0626	2.5303
	Carbonyl Derivatives		
NH_2CHO	−22.3343	−0.0468	−2.5627
CH_3OCHO	−22.3096	−0.0221	−1.1027
CH_3CHO	−22.3048	−0.0173	−1.1482
HOCHO	−22.2994	−0.0119	−0.4711
HCHO	−22.2875	0	0
HSCHO	−22.2827	0.0048	0.1193
FCHO	−22.2656	0.0219	1.4016
ClCHO	−22.2540	0.0335	1.6707
CF_3CHO	−22.2477	0.0398	1.7486
CNCHO	−22.2394	0.0481	2.1024
NO_2CHO	−22.2128	0.0747	3.1980

[a] The molecules of each series are listed in order of descending absolute value of the corrected energy of hydrogen-bond formation.

It is seen from eqs 2 and 3 that the slopes of the dependencies between V_N and ΔE^{R-CN} and between V_O and ΔE^{R-CHO} are approximately the same. This finding has allowed us to unify the two series studied. Two new quantities are introduced:

$$\Delta V = V_N^{R-CN} - V_N^{H-CN} \quad \text{for the series of nitrile derivatives}$$
$$= V_O^{R-CHO} - V_O^{H-CHO} \quad \text{for the series of carbonyl derivatives} \tag{4}$$

and

$$\Delta E' = \Delta E^{R-CN} - \Delta E^{H-CN} \quad \text{for the series of nitrile derivatives}$$
$$= \Delta E^{R-HCO} - \Delta E^{H-CHO} \quad \text{for the series of carbonyl derivatives} \tag{5}$$

The values of ΔV and $\Delta E'$ are given in Table 4. ΔV and $\Delta E'$ are the shifts of the molecular electrostatic potential and the energy of hydrogen-bond formation with respect to the values for the simplest member of the respective series (R = −H). The dependence between $\Delta E'$ and ΔV is presented in Figure 6. The linear regression result is

$$\Delta E' = 47.5099(\pm 1.2978)\Delta V - 0.1707(\pm 0.0439),\quad n = 22, R = 0.992, \mathrm{SD} = 0.1998 \tag{6}$$

The linear regression coefficient of 0.992 shows that a very good linear relation is found. The dependence appears quite significant because it unifies two different series of proton-acceptor molecules. Needless to say, eq 6 can be used with confidence in predicting the energy of hydrogen-bond formation when different substituents are added to the simplest member of a series. In view of the complex nature of intra- and intermolecular factors influencing hydrogen bonding,[1−17] it is still to be

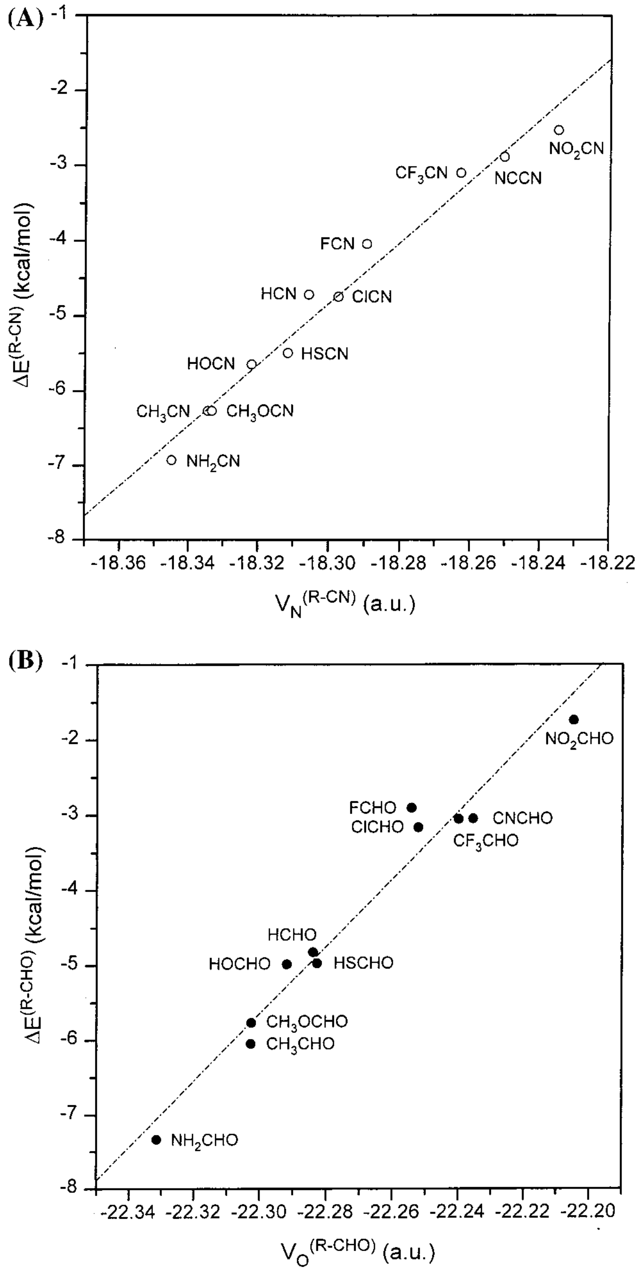

Figure 5. Dependence between the energy of hydrogen-bond formation (ΔE) and the molecular electrostatic potential at the proton-accepting atom in isolated molecules: (A) for the series of nitrile derivatives; (B) for the series of carbonyl derivatives studied.

understood why such perfect linear dependencies between the variations in the electrostatic potential at the reaction site and the energy of hydrogen-bond formation were found. Nevertheless, it is gratifying to discover that the ability of these molecules to form hydrogen bonds can be quantified in terms of easily obtainable, accurately defined, and simple molecular quantity. In can be stated, at least for the series of complexes studied, that the molecular electrostatic potential at atomic sites can be used as a reactivity index for the process of hydrogen bonding.

Conclusions

The ab initio study of the hydrogen bonding between nitrile and carbonyl compounds and hydrogen fluoride confirms the known linear relations between the energy of hydrogen-bond formation (ΔE) and the change of H−F bond length (Δr_{HF}), as well as between ΔE and the characteristic vibrational frequency shift ($\Delta \nu_{HF}$). Moreover, an excellent linear dependence is found between ΔE^{R-CN} and the ab initio calculated molecular electrostatic potential at the nitrile nitrogen (V_N) in isolated nitrile molecules. A linear dependence is also found between ΔE^{R-CHO} and the ab initio calculated molecular electrostatic potential at the carbonyl oxygen (V_O) in isolated carbonyl molecules. These relations show that the molecular electrostatic potential can be successfully used to predict the ability of molecules for hydrogen-bond formation.

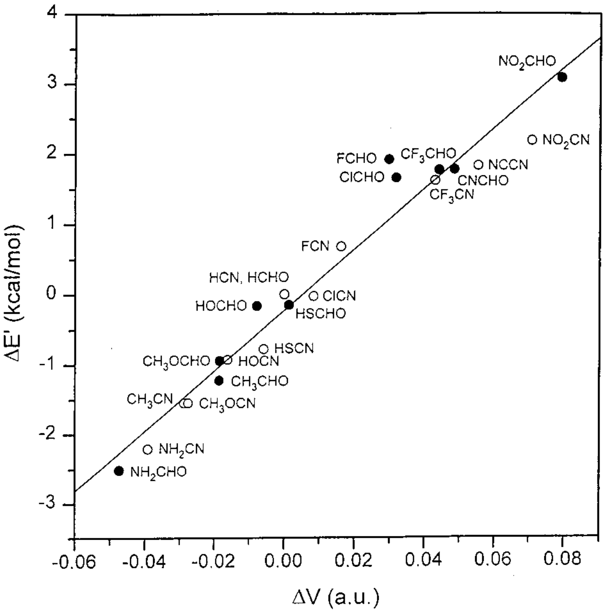

Figure 6. Dependence between variations of energy of hydrogen-bond formation ($\Delta E'$) and molecular electrostatic potential (ΔV).

An excellent linear dependence that unifies the two series of proton-acceptor molecules is also found. The established relation between the shifts of the energy of hydrogen-bond formation ($\Delta E'$) and the shifts of the molecular electrostatic potential at the atomic site of the proton-acceptor atoms (ΔV) can be used with confidence in predicting the energy of hydrogen-bond formation when different substituents are added to the simplest member of a series. The results obtained indicate that the molecular electrostatic potential at atomic sites can be used as a reactivity index, reflecting the ability of molecules from the series studied to participate in hydrogen bonding.

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