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Ab Initio Molecular-Orbital Study of Hydrogen-Bonded Complexes of Carbonyl Aliphatic Compounds and Hydrogen Fluoride

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Ab initio molecular-orbital calculations at the HF/6-31G(d,p) level were used to investigate the hydrogen bonding between open-chain aliphatic carbonyl compounds and hydrogen fluoride. The carbonyl compounds studied are H_2CO, HCOOH, HCOSH, $HCOOCH_3$, $HCONH_2$, $HCONO_2$, HCOCN, HCOF, HCOCl, $HCOCH_3$, $HCOCF_3$, CH_3COOH, CH_3COSH, CH_3COOCH_3, CH_3CONH_2, CH_3CONO_2, CH_3COCN, CH_3COF, CH_3COCl, CH_3COCH_3, and CH_3COCF_3. Geometry optimization and vibrational-frequency and infrared-intensity 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. In agreement with expectations a linear relation ($R = 0.994$) between the energy of hydrogen-bond formation, ΔE, and the H−F stretching frequency shift, $\Delta\nu_{H-F}$, was obtained for the systems studied. A linear dependency was also found between ΔE and the change of H−F bond length, Δr_{H-F} ($R = 0.994$). Effective bond charges of the hydrogen bond, $\delta_{O\cdots H}$, for the series of compounds studied were evaluated from the theoretically derived dipole-moment derivatives. A satisfactory correlation ($R = 0.938$) between $\delta_{O\cdots H}$ and the energy of hydrogen bond formation, ΔE, was obtained. The attempt to explain the differences in hydrogen-bond strength, ΔE, with the variation of the carbonyl oxygen atomic charges in the isolated molecules showed that neither Mulliken nor CHELPG and MK atomic charges can be successfully used for the purpose. However, the molecular electrostatic potential at the carbonyl oxygen in the isolated molecules, Φ_O, correlates in a quite satisfactory manner ($R = 0.979$) with the energy of hydrogen-bond formation for the entire series of compounds. This result appears quite significant in view of its importance for understanding the mechanisms of intermolecular interactions leading to hydrogen bonding.

Introduction

Hydrogen bonding is an important intermolecular phenomenon that determines essential properties of chemical and biological systems. Numerous experimental and theoretical studies aim at quantifying the hydrogen-bond formation in terms of structural and electronic properties of the proton donor and acceptor molecules. The carbonyl group is known as an important proton acceptor. In many organic and biological systems the carbonyl group is a base participating in hydrogen bonding.

The principal aim of this study is to analyze the trends of changes in the energy of hydrogen-bond formation in aliphatic carbonyl derivatives and to explain the results in terms of properties of the isolated molecule or the complex. A representative series of 21 open-chain carbonyl compounds of the type HCOR and CH_3COR (where R = −H, $-CH_3$, $-CF_3$, −OH, −SH, $-OCH_3$, $-NH_2$, $-NO_2$, C≡N, −F, and −Cl) are investigated. Hydrogen fluoride is used as a model proton donor in the respective hydrogen-bonded complexes. Infrared spectra are known to provide rich and easily accessible information on hydrogen-bonded systems. Therefore, an analysis of the link between the energy of hydrogen-bond formation and the variation of infrared spectral parameters induced by the hydrogen bonding is carried out. Since the ability to form hydrogen-bond complexes at the C=O bond is strongly related to the amount of partial charge at the oxygen atom, relations between the energy of hydrogen-bond formation and charge-dependent properties of the isolated molecules are searched for.

Calculations

The optimized geometries, vibrational frequencies, and infrared intensities for isolated and hydrogen-bonded molecules of the series were determined at the HF/6-31G(d,p) level using the Gaussian 92W program package.[1] It has been recently shown that HF/6-31G(d,p) ab initio calculations correctly reproduce the trends of changes in vibrational frequency and intensity parameters in carbonyl derivatives.[2]

In determining the energy of hydrogen-bond formation, the zero-point vibrational energy was taken into account. A scaling factor of 0.9135[3] 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 consideration of the electron correlation. The basis-set superposition error (BSSE) was also corrected by recalculating the monomer energies in the basis set of the respective complex.[4]

To connect the ability for hydrogen bonding at the C=O bond with the electric-charge properties of the respective compound, Mulliken,[5] CHELPG,[6] and MK[7] atomic charges were evaluated for isolated and hydrogen-bonded molecules using the Gaussian 92W program package. As a standard output of the program, the molecular electrostatic potentials[8] at each atom of the respective molecule were also obtained. Molecular electrostatic potential is known as an important factor in intermolecular interactions.[9]

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TABLE 1: HF/6-31G(d,p) Ab Initio Calculated Uncorrected Energy of Hydrogen-Bond Formation, ΔE^{SCF}, Zero-Point Vibrational-Energy Correction, ΔE^{ZPE}, BSSE Correction, ΔE^{BSSE}, and Totally Corrected Energy of Hydrogen-Bond Formation, ΔE, for the Molecules Studied

molecule	ΔE^{SCF} kcal/mol	$\Delta E^{ZPE\,a}$ kcal/mol	ΔE^{BSSE} kcal/mol	ΔE kcal/mol
H_2CO	−8.0873	2.3032	1.9942	−3.7899
HCOOH	−8.4068	2.0430	1.9911	−4.3727
HCOSH	−7.7115	1.9776	1.9905	−3.7434
$HCOOCH_3$	−8.8218	2.0012	1.9085	−4.9121
$HCONH_2$	−10.9513	2.4419	2.0043	−6.5051
$HCONO_2$	−5.0358	1.3998	2.1549	−1.4811
HCOCN	−6.2889	1.7856	2.2910	−2.2123
HCOF	−6.6817	1.8326	2.0884	−2.7607
HCOCl	−6.1960	1.7546	2.1097	−2.3317
$HCOCH_3$	−9.0763	2.1204	1.9999	−4.9560
$HCOCF_3$	−6.4809	1.7879	2.1743	−2.5187
CH_3COOH	−9.8268	2.1026	2.1097	−5.6145
CH_3COSH	−8.8975	2.0332	2.2327	−4.6315
CH_3COOCH_3	−10.1657	2.1049	2.0689	−5.9919
CH_3CONH_2	−12.0959	2.3835	2.1825	−7.5299
CH_3CONO_2	−6.0197	1.6716	2.1172	−2.2309
CH_3COCN	−7.2314	1.8601	2.2528	−3.1185
CH_3COF	−8.1193	1.9295	2.1153	−4.0745
CH_3COCl	−7.3224	1.8372	2.1367	−3.3485
CH_3COCH_3	−10.3050	2.1325	2.2703	−5.9022
CH_3COCF_3	−7.7667	1.9089	2.2452	−3.6126

[a] Scaled by 0.9135. See text.

As additional quantities related to the electric properties of molecules, effective bond charges[10] were derived from the respective atomic polar tensors (dipole-moment derivatives with respect to atomic Cartesian displacements). The effective bond charges can be obtained from experimental infrared intensities or ab initio calculated dipole-moment derivatives. The possible contributions to dipole-moment derivatives arising from molecular rotation are subtracted in the process of evaluation of effective bond charges. The heavy-isotope method[11] was used (the mass of the carbonyl group was weighed 10^6 times) in estimating the respective rotational correction contributions. Effective bond charges are molecular quantities that have been shown to reflect, in a generalized way, electric-charge properties of the respective valence bond.[10,12]

Results and Discussion

The uncorrected 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 BSSE corrections, ΔE^{BSSE}, and the totally corrected energies of hydrogen-bond formation, ΔE, for all the molecules studied are given in Table 1. It can be seen that the values of ΔE^{ZPE} and ΔE^{BSSE} are approximately equal for the entire series of molecules. The linear-regression coefficient between the uncorrected energy, ΔE^{SCF}, and the totally corrected energy, ΔE, is 0.997. The absolute magnitude of ZPE and BSSE corrections reaches, however, nearly 40% of ΔE^{SCF}.

Geometry. The optimized structures of the hydrogen-bonded complexes for some molecules of the series are shown in Figure 1.[14] As can be seen, the C═O···H structure is nonlinear, with the C═O···H angle in the range 100−130°. The O···H−F structure is also nonlinear with the O···H−F angle in the range 130−170°. The O···H hydrogen bond and H−F bond of hydrogen fluoride lay approximately in the plane of the C═O bond. For the entire series of complexes the out-of-plane angles of O···H and H−F bonds are on the order of 10^{-2}−10^{-1} degrees.

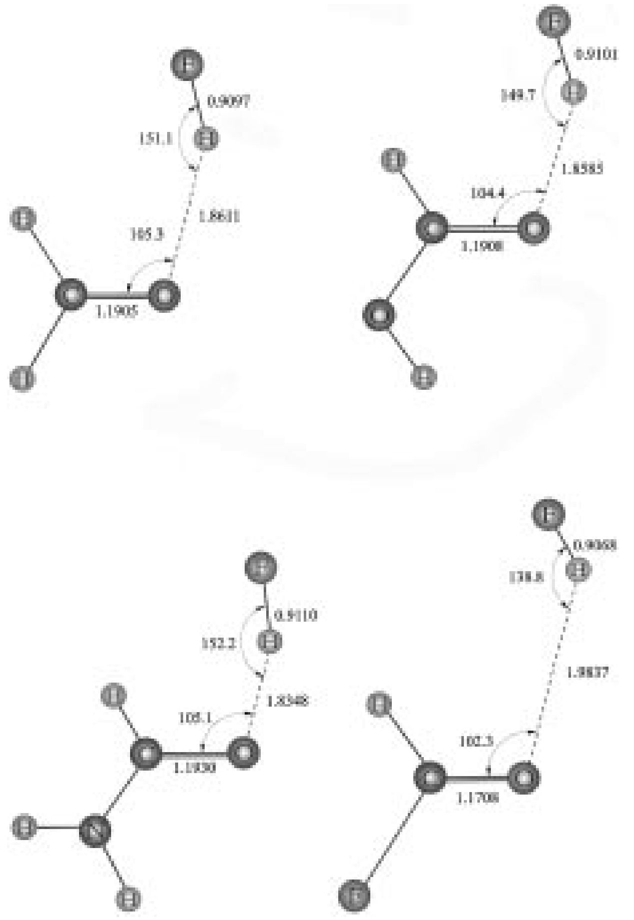

Figure 1. Optimized structures of hydrogen-bonded complexes for some molecules of the series of carbonyl compounds studied.

Experimental geometry data are available from the study of Baiocchi and Klemperer[13] for the H_2CO···HF dimer. The measured C═O···H and O···H−F angles are 115° and 163°, respectively. The respective ab initio calculated values are 105.3° and 151.1° (Figure 1). The experimental O···H and H−F bond lengths (1.7935 and 0.8903 Å) are in reasonable agreement with the theoretically predicted values of 1.8611 and 0.9097 Å, respectively (Figure 1).

Structural features of the complexes studied are presented in Table 2. These are the changes in the carbonyl bond length ($\Delta r_{C=O}$), the changes in the hydrogen fluoride bond length (Δr_{H-F}) with respect to bond lengths in the isolated molecules as well as the hydrogen bond length ($r_{O\cdots H}$). As can be expected, the carbonyl bond length increases with hydrogen-bond formation. The H−F bond length in the complexes is also higher. The variations of Δr_{H-F} can be satisfactorily explained in terms of the different energy of hydrogen-bond formation, ΔE. The dependence is illustrated in Figure 2. A linear relation ($R = 0.994$) is found. As anticipated, a stronger hydrogen bond corresponds to a weaker H−F bond, resulting in an increased bond length.

Infrared Spectral Parameters. The theoretically predicted changes in the vibrational frequencies associated with the C═O and H−F stretching modes with respect to the quantities in isolated molecules are given in Table 2. Carbonyl and H−F stretching modes are shifted to lower energies because of weakening of the bonds. Carbonyl frequencies of the complexes are lower by 1−3% compared with the respective quantities in isolated molecules. H−F stretching frequencies of the complexes are 2.5−8.5% smaller than the respective H−F frequency

TABLE 2: HF/6-31G(d,p) Ab Initio Calculated Changes in Structural and Spectral Parameters of Hydrogen Bonded to Hydrogen Fluoride Carbonyl Compounds with Respect to the Isolated Molecules, Calculated at the Same Level of Theory

molecule	$\Delta r_{C=O}$ Å	Δr_{H-F} Å	$r_{O\cdots H}$ Å	$\Delta\nu_{C=O}$ cm^{-1}	$\Delta A_{C=O}$ km/mol	$\Delta\nu_{H-F}$ cm^{-1}	ΔA_{H-F} km/mol	$\delta_{O\cdots H}$ electrons
H_2CO	0.0061	0.0092	1.8610	−27	10.1	−209	335.6	0.942
HCOOH	0.0089	0.0096	1.8585	−43	61.5	−216	339.9	0.965
HCOSH	0.0073	0.0089	1.8788	−34	48.2	−198	379.7	0.991
$HCOOCH_3$	0.0095	0.0105	1.8348	−46	74.8	−240	447.9	1.008
$HCONH_2$	0.0109	0.0144	1.7707	−45	89.5	−339	572.3	1.056
$HCONO_2$	0.0042	0.0036	2.2184	−19	8.1	−60	27.9	0.880
HCOCN	0.0056	0.0058	2.0104	−23	26.4	−115	143.3	0.899
HCOF	0.0067	0.0063	1.9835	−35	26.0	−128	155.5	0.880
HCOCl	0.0074	0.0058	1.9989	−35	19.2	−117	162.6	0.912
$HCOCH_3$	0.0071	0.011	1.8219	−30	34.1	−256	468.4	0.997
$HCOCF_3$	0.0053	0.0063	1.9670	−21	6.1	−131	172.4	0.891
CH_3COOH	0.0097	0.0118	1.8100	−48	93.3	−271	478.2	0.989
CH_3COSH	0.0093	0.0104	1.8427	−45	83.0	−236	547.7	1.010
CH_3COOCH_3	0.0099	0.0125	1.7961	−51	89.1	−290	582.5	1.017
CH_3CONH_2	0.0113	0.0163	1.7451	−51	127.7	−384	704.0	1.065
CH_3CONO_2	0.0061	0.0055	2.0045	−30	52.5	−108	187.1	0.880
CH_3COCN	0.0062	0.0075	1.9193	−27	66.4	−162	336.1	0.939
CH_3COF	0.0078	0.0085	1.8884	−42	61.8	−185	306.7	0.924
CH_3COCl	0.0087	0.0075	1.9177	−45	69.3	−162	343.9	0.951
CH_3COCH_3	0.0075	0.0128	1.7993	−33	68.8	−299	612.8	1.018
CH_3COCF_3	0.0058	0.0083	1.8943	−24	38.1	−183	347.5	0.932

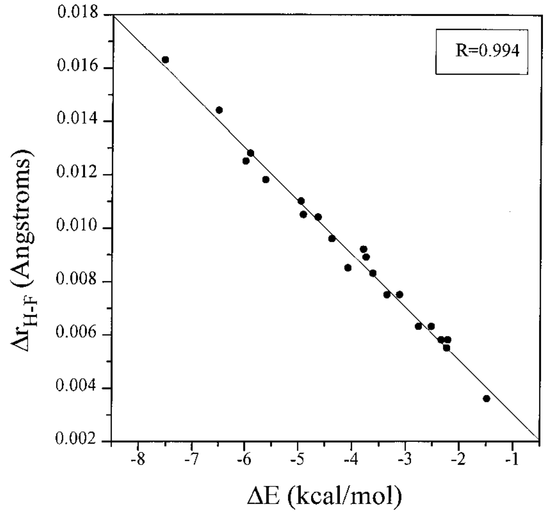

Figure 2. Dependence between energy of hydrogen-bond formation, ΔE, and the changes in hydrogen fluoride bond length, Δr_{H-F}, for hydrogen bonded to HF complexes of carbonyl compounds.

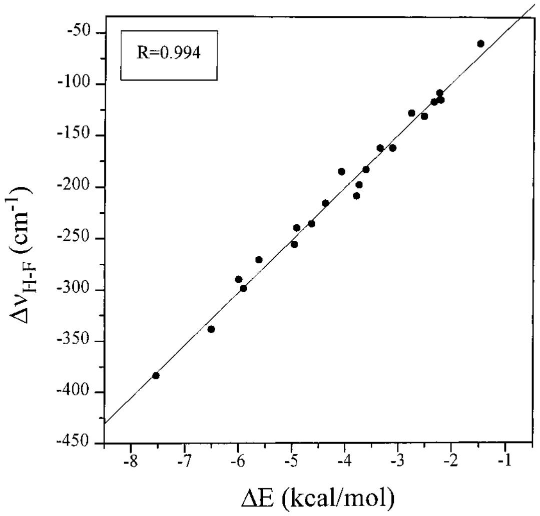

Figure 3. Dependence between energy of hydrogen-bond formation, ΔE, and H−F stretching frequency shift, $\Delta\nu_{H-F}$, for hydrogen bonded to HF complexes of carbonyl compounds.

of hydrogen fluoride. In agreement with expectations an excellent linear relation ($R = 0.994$) between the shift in the H−F stretching mode frequency ($\Delta\nu_{H-F}$) and the energy of hydrogen-bond formation, ΔE, is found. The dependence is shown in Figure 3.

The variations of C=O and H−F stretching band intensities are also given in Table 2. Carbonyl stretching band intensities of the complexes are greater by 4−30% with respect to C=O band intensities of the isolated molecules. The H−F stretching mode intensities are highly sensitive to hydrogen-bond formation. For the series studied the H−F stretching mode band is quite intensive; the calculated intensities of this mode are 2−7 times greater than the respective quantity for hydrogen fluoride.

Another quantity derived from infrared spectra is the effective charge of the hydrogen bond, $\delta_{O\cdots H}$. The hydrogen-bond effective charges, as presented in Table 2, were evaluated from the sets of dipole-moment derivatives with respect to Cartesian coordinates following the formulation put forward by Galabov et al.[10] The relation between $\delta_{O\cdots H}$ and the energy of hydrogen-bond strength, ΔE, is characterized by a linear-regression coefficient $R = 0.938$. In view of the generalized character of $\delta_{O\cdots H}$, which is a quantity determined by the intensities of all vibrational modes involving the O···H bond, the relationship found may be considered satisfactory. ΔE and $\delta_{O\cdots H}$ change in a similar way, though the dependence found is far from a perfect linear match.

Properties Depending on the Electric-Charge Distribution. The calculated molecular parameters related to the electric-charge distribution for the isolated carbonyl compounds studied are presented in Table 3. These are the partial oxygen atomic charge in isolated molecules, Q_O, derived via different procedures (Mulliken, CHELPG, MK) and the molecular electrostatic potential at the carbonyl oxygen in the isolated molecules, Φ_O.

It is notable that the energy of hydrogen-bond formation, ΔE (Table 1), is greater in the CH_3COR series than in the HCOR series. This can be explained by the positive inductive and resonance effect of the methyl group. As a result, the negative charge at the carbonyl oxygen is increased, thus facilitating the hydrogen-bond formation. These charge shifts are qualitatively well represented by the estimated charges associated with the carbonyl oxygen atom derived via all schemes applied (Table 3). In quantitative terms the effect of the methyl group in CH_3-

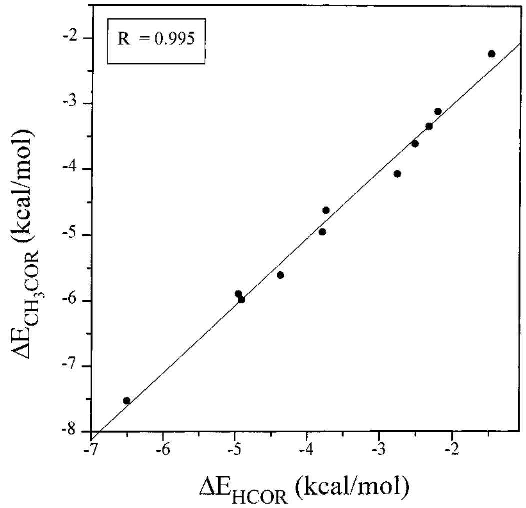

Figure 4. Dependence between energy of hydrogen-bond formation for the HCOR series, ΔE_{HCOR}, and energy of hydrogen-bond formation for the CH_3COR series, ΔE_{CH_3COR}, for hydrogen bonded to HF complexes of carbonyl compounds.

TABLE 3: HF/6-31G(d,p) Ab Initio Calculated Electric-Charge Distribution-Dependent Properties of Carbonyl Compounds: Partial Oxygen Atomic Charge in Isolated Molecules, Q_O, Derived via Different Procedures (Mulliken, CHELPG, MK) and Molecular Electrostatic Potential at the Carbonyl Oxygen in the Isolated Molecules, Φ_O

molecule	Q_O (Mulliken) electrons	Q_O (CHELPG) electrons	Q_O (MK) electrons	Φ_O au
H_2CO	−0.4314	−0.4773	−0.4579	−22.2987
HCOOH	−0.5206	−0.5997	−0.5821	−22.3132
HCOSH	−0.4549	−0.4830	−0.4451	−22.2935
$HCOOCH_3$	−0.5324	−0.5968	−0.5871	−22.3212
$HCONH_2$	−0.5618	−0.61865	−0.5967	−22.3498
$HCONO_2$	−0.3598	−0.3823	−0.3693	−22.2217
HCOCN	−0.4558	−0.4284	−0.4065	−22.2493
HCOF	−0.4399	−0.5028	−0.4886	−22.2801
HCOCl	−0.3849	−0.4250	−0.3947	−22.2626
$HCOCH_3$	−0.4749	−0.5392	−0.5303	−22.3160
$HCOCF_3$	−0.4206	−0.4319	−0.4122	−22.2610
CH_3COOH	−0.5536	−0.6380	−0.6234	−22.3283
CH_3COSH	−0.4839	−0.5021	−0.4743	−22.3058
CH_3COOCH_3	−0.5658	−0.6426	−0.6342	−22.3346
CH_3CONH_2	−0.5910	−0.6674	−0.6460	−22.3606
CH_3CONO_2	−0.4016	−0.4479	−0.4370	−22.2458
CH_3COCN	−0.4488	−0.4908	−0.4802	−22.2690
CH_3COF	−0.4757	−0.5591	−0.5483	−22.2987
CH_3COCl	−0.4218	−0.4696	−0.4510	−22.2778
CH_3COCH_3	−0.5157	−0.5890	−0.5813	−22.3303
CH_3COCF_3	−0.4839	−0.5021	−0.4743	−22.2812

COR on the hydrogen-bond formation can be estimated from the slope of the dependency between ΔE_{CH_3COR} and ΔE_{HCOR} (Figure 4):

$$\Delta E_{CH_3COR} = 1.0258(\pm 0.0355)\Delta E_{HCOR} - 0.9462(\pm 0.1374)$$

where $n = 11$, $R = 0.995$, and SD = 0.1686.

The result shows that the hydrogen bond in CH_3COR compounds is about 1 kcal/mol stronger than in HCOR compounds throughout the respective series.

The attempt to explain the differences in hydrogen-bond strength, ΔE (Table 1), with the variations in electric charge associated with the carbonyl oxygen in isolated molecules showed that Mulliken, CHELPG, and MK atomic charges cannot be successfully used to rationalize the energy of hydrogen-bond formation. The respective regression coefficients, 0.931 for Mulliken charges, 0.931 for CHELPG, and 0.915 for MK charges, show that no satisfactory linear relations exist.

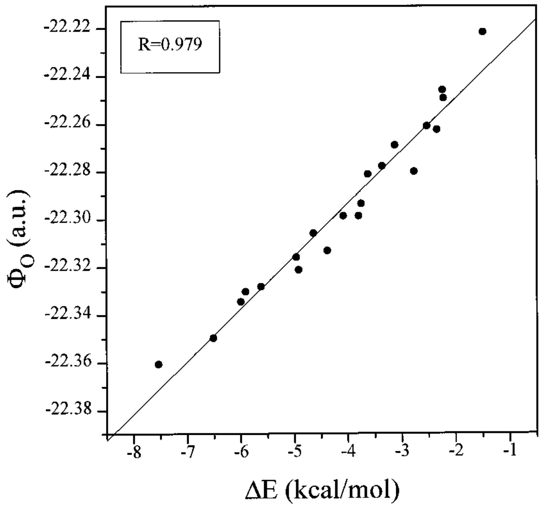

Figure 5. Dependence between energy of hydrogen-bond formation, ΔE, and the molecular electrostatic potential at carbonyl oxygen in isolated carbonyl compounds, Φ_O.

In the last column of Table 3 the molecular electrostatic potential at the carbonyl oxygen atom in the isolated molecules, Φ_O, as obtained from the ab initio calculations, is given. The dependence between Φ_O and ΔE is presented in Figure 5. As can be seen, a very good linear relation exists ($R = 0.979$). It is quite significant that a property of the isolated molecules that can explain the differences in the energy of hydrogen-bond formation for the entire series of carbonyl compounds studied was eventually found. The dependency, as established for a representative series of carbonyl compounds and their hydrogen-bonded complexes with HF, appears quite significant. In general, the results obtained show that localized electric charges at atomic sites of the isolated molecules do not correctly characterize their ability to participate in hydrogen bonding. On the other hand, the theoretically estimated molecular electrostatic potentials of the end atom of the C═O group in the series correlate excellently with the energy of hydrogen-bond formation. Further studies on other hydrogen-bonded systems are needed to confirm and verify this result in view of its significance in understanding the mechanism of hydrogen bonding.

Conclusions

The ab initio study of the hydrogen bonding between aliphatic carbonyl compounds and hydrogen fluoride confirms the known linear relations between the energy of hydrogen-bond formation (ΔE) and the following: (a) the change of H−F bond length (Δr_{H-F}); (b) the characteristic vibrational frequency shift ($\Delta\nu_{H-F}$). A satisfactory correlation is also found between ΔE and the effective bond charges of the hydrogen bond ($\delta_{O\cdots H}$).

The differences in the energy of hydrogen-bond formation (ΔE) is interpreted in terms of properties of the isolated molecules. The theoretical results show that there is no clear dependence between ΔE and the carbonyl oxygen atomic charge (Q_O) evaluated via different schemes (Mulliken, CHELPG, and MK). However, an excellent linear dependence between ΔE and the theoretically estimated molecular electrostatic potential at the carbonyl oxygen (Φ_O) is found. This relation shows that the molecular electrostatic potential at the carbonyl oxygen of isolated carbonyl compounds can be successfully used to predict their ability for hydrogen bonding. Further studies of the dependence established for other hydrogen-bonded systems are of considerable interest.

References and Notes

(1) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1992.

(2) Galabov, B.; Bobadova-Parvanova, P.; Dudev, T. *J. Mol. Struct*. **1997**, *406*, 119.

(3) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(4) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev. (Washington, D.C.)* **1994**, *94*, 1873.

(5) Mulliken, R. S. *J. Chem. Phys*. **1955**, *23*, 1833.

(6) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(7) Besler, B. H.; Merz, K. M.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431.

(8) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1993**, *206*, 239.

(9) Politzer, P., Truhlar, D. G., Eds. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press: New York, 1981.

(10) Galabov, B.; Dudev, T.; Ilieva, S. *Spectrochim. Acta* **1993**, *49A*, 373.

(11) van Straten, A. J.; Smit, W. M. A. *J. Mol. Spectrosc*. **1975**, *56*, 484.

(12) Galabov, B.; Dudev, T. In *Vibrational Intensities*; Durig, J. R., Ed.; Vibrational Spectra and Structure 22; Elsevier: Amsterdam, 1996.

(13) Baiocchi, F. A.; Klemperer, W. *J. Chem. Phys*. **1983**, *78*, 3509.

(14) The optimized geometry parameters for the entire series of molecules and complexes are available from the authors upon request.