J. Phys. Chem. A **1999,** *103,* 8121−8124

Hydrogen Bond Types, Binding Energies, and ^{1}H NMR Chemical Shifts

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Received: June 21, 1999; In Final Form: August 9, 1999

Ab initio calculations at the MBPT(2)/(qzp,qz2p) level of theory were carried out using the gauge-invariant atomic orbital method to evaluate ^{1}H NMR chemical shifts for the hydrogen-bonded proton in two series of complexes, the first containing Cl−H−N and Cl−H−Cl hydrogen bonds, and the second O−H−O, N−H−O, and N−H−N hydrogen bonds. In both series a correlation exists between increasing hydrogen bond strength and increasing proton chemical shift relative to the corresponding neutral proton donor molecule. However, while this correlation does not hold between the two series, complexes with proton-shared hydrogen bonds have similar chemical shifts of about 20 ppm for the hydrogen-bonded proton in both series, independent of the binding energy of the complex. ^{1}H NMR chemical shifts computed along the proton-transfer coordinate for ClH:NH$_3$ also approach 20 ppm for a proton-shared hydrogen bond.

Introduction

There has been considerable discussion in the recent literature concerning short strong hydrogen bonds (SSHBs), sometimes also referred to as "low-barrier hydrogen bonds" (LBHBs), and their possible role in enzyme catalysis.[1−7] It has been suggested that such hydrogen bonds are characterized by large downfield NMR chemical shifts of about 20 ppm or greater for the hydrogen-bonded proton. In a recent paper, Kumar and McAllister reported the results of computed Hartree−Fock proton NMR chemical shifts and hydrogen bond strengths in two series of closely related anionic model complexes.[8] The model complexes contained formic acid with substituted formate anion and formic acid with enol-substituted enolate anion. They found a linear correlation between computed binding energies and proton NMR chemical shifts, but noted that care must be taken when attempting to compare SSHB proton NMR resonances between different classes of compounds. This comment suggested that it might be very informative to investigate ^{1}H NMR chemical shifts in a variety of hydrogen-bonded complexes, taking account of both binding energy and hydrogen bond type.

In an earlier paper we reported the results of an ab initio study at the MBPT(2)/6-31+G(d,p) level of theory of neutral hydrogen-bonded complexes formed between HCl and a series of 4-substituted pyridines.[9] The hydrogen bonds in these complexes span the range of hydrogen bond types as a function of the proton affinity of the substituted pyridine. Complexes formed with the weaker bases have traditional hydrogen bonds which are structurally characterized as having "normal" Cl−N distances, which range from 3.00 to 3.11 Å, and Cl−H distances ranging from 1.31 to 1.34 Å, slightly elongated relative to the HCl monomer distance of 1.27 Å. As the proton affinity of the substituted pyridine increases in this series, two complexes stabilized by proton-shared hydrogen bonds are formed. These have dramatically shortened intermolecular Cl−N distances of 2.91 and 2.83 Å, and long Cl−H distances of 1.63 and 1.67 Å. A further increase of the proton affinity of the substituted pyridine leads to proton transfer from Cl to N in complexes containing hydrogen-bonded ion pairs. These complexes have long Cl−H distances of 1.89 and 1.94 Å, and Cl−N distances of 2.96 and 3.00 Å, which are longer relative to Cl−N distances in complexes with proton-shared hydrogen bonds. The ion-pair complexes are stabilized by $Cl^-\cdots{}^+H-N$ hydrogen bonds.

For the present study we have selected neutral and positively charged hydrogen-bonded complexes which contain Cl−H−N, Cl−H−Cl, O−H−O, N−H−O, and N−H−N traditional and proton-shared hydrogen bonds. It is the purpose of this paper to report the computed relative NMR chemical shifts for the hydrogen-bonded proton in these complexes, and to relate these shifts to binding energies and hydrogen bond type. Many of these complexes should be amenable to experimental study.

Methods

All complexes containing N−H−N, N−H−O, and O−H−O hydrogen bonds were optimized with correlation at second-order many-body Møller/Plesset perturbation theory[10−13] [MBPT(2)] with the 6-31+G(d,p) basis set.[14−17] Because the aug′-cc-pVDZ basis set[18−20] (aug′-cc-pVDZ is Dunning's aug-cc-pVDZ basis without diffuse functions on hydrogen atoms) appears to give a better description of the vibrational spectral properties of hydrogen-bonded complexes containing HCl, complexes with Cl−H−Cl and Cl−H−N hydrogen bonds were optimized at both MBPT(2)/6-31+G(d,p) and MBPT(2)/aug′-cc-pVDZ, except for HCl:pyridine. The geometry used for this complex is the MBPT(2)/6-31+G(d,p) geometry from ref 9. Vibrational frequencies were computed for all complexes to ensure that they correspond to equilibrium structures on their respective potential energy surfaces. It is important to note that in all systems, only a single equilibrium structure exists along the proton-transfer coordinate, that is, none of these systems have double-minima potential wells for proton transfer.

The ^{1}H chemical shifts were computed at MBPT(2) using the gauge-invariant atomic orbital (GIAO) method.[21] The basis

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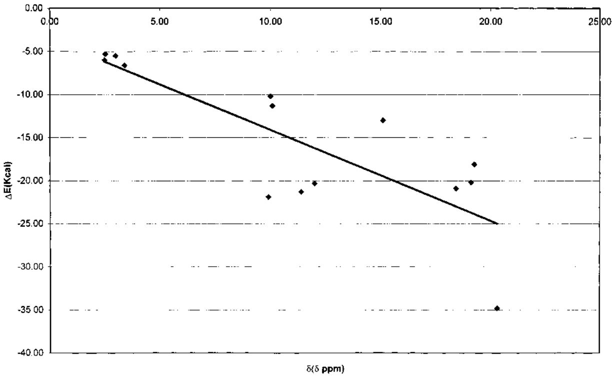

Figure 1. MBPT(2)/(qzp,qz2p) binding energies versus MBPT(2)/(qzp,qz2p) NMR proton chemical shifts for all complexes.

TABLE 1: Neutral and Positively Charged Complexes with Cl−H−N and Cl−H−Cl Hydrogen Bonds[a]

complex	type[b]	*R* (Cl−H, Å)[c]	*R* (Cl−Y, Å)	ΔE_e (kcal)	$\delta(\delta_{ppm})$[d]
ClH:NCH	T	1.299	3.350	−5.3	2.5
ClH:NC(CH$_3$)	T	1.303	3.281	−6.6	3.4
ClH:NH$_3$	T	1.341	3.080	−10.2	10.0
ClH:pyridine	T	1.323	3.044	−11.3	10.1
ClH:NH$_2$(CH$_3$)	PS[e]	1.401	2.923	−13.0	15.1
ClH:NH(CH$_3$)$_2$	PS	1.630	2.814	−18.1	19.3
Cl$_2$H$_3$$^+$	PS	1.573	3.144	−20.2	19.1
ClH:N(CH$_3$)$_3$	PS	1.657	2.825	−20.9	18.4

[a] All complexes have a single minimum along the proton-transfer coordinate. [b] T = traditional hydrogen bond; PS = proton-shared hydrogen bond. [c] Monomer HCl distance = 1.270 Å at MBPT(2)/6-31+G(d,p); 1.288 Å at MBPT(2)/aug′-cc-pVDZ. [d] $\delta(\delta_{ppm})$ is the computed chemical shift for the hydrogen-bonded proton relative to HCl. [e] The hydrogen bond in ClH:NH$_2$(CH$_3$) has been classified as PS. See text.

set used is Ahlrich's polarized quadruple-split (qzp,qz2p) basis,[22] which has been shown to be appropriate for NMR chemical shift calculations.[23] Least-squares correlations were obtained between computed MBPT(2)/(qzp,qz2p) proton chemical shifts and MBPT(2)/(qzp,qz2p) binding energies and between MBPT-(2)/(qzp,qz2p) chemical shifts and binding energies computed for the optimized complex at the level at which optimization was done. Binding energies (D_e) were computed as the energy of the complex minus the sum of the energies of the isolated monomers. The chemical shifts were computed relative to the appropriate neutral proton donor (H$_2$O, NH$_3$, pyrrole, or HCl). While differences in absolute binding energies using the different basis sets were found, similar correlations between binding energies and chemical shifts were observed. Moreover, a slightly better correlation was found between binding energies and chemical shifts relative to the corresponding neutral proton donor than for binding energies and chemical shifts for the proton donor molecule in neutral complexes and the proton-donor ion in the positively charged complexes. Therefore, the data and plots presented in this paper are based on MBPT(2)/(qzp,qz2p) binding energies and MBPT(2)/(qzp,qz2p) ^{1}H NMR chemical shifts relative to the corresponding neutral proton donor. The ^{1}H NMR chemical shift calculations were done using the ACES-II program.[24]

Results and Discussion

Figure 1 presents a plot of computed binding energies for the 14 complexes investigated in this study, which are listed in Tables 1 and 2. This figure suggests a general trend of increasing binding energy (increasing stability) with increasing relative proton NMR chemical shift. However, the correlation coefficient obtained from the least-squares fit is only 0.66. Closer examination of Figure 1 shows that for binding energies greater than 5 kcal/mol, data points for all complexes involving HCl lie above the least-squares line, while those for the nitrogen and oxygen complexes lie below this line. We will therefore consider the two sets of complexes separately.

TABLE 2: Neutral and Positively Charged Complexes with N−H−N, N−H−O, and O-H-O Hydrogen Bonds[a]

complex	type[b]	*R* (X−H, Å)[c]	*R* (X−Y, Å)	ΔE_e (kcal)	$\delta(\delta_{ppm})$[d]
(H$_2$O)$_2$	T	0.970	2.914	−5.5	3.0
pyrrole:OH$_2$	T	1.013	2.977	−6.0	2.5
NH$_4$$^+$:OCH$_2$	T	1.045	2.731	−20.3	12.0
NH$_4$$^+$:OH$_2$	T	1.051	2.725	−21.3	11.4
NH$_4$$^+$:NCH	T	1.049	2.829	−21.9	9.9
O$_2$H$_5$$^+$	PS	1.190	2.385	−34.8	20.3

[a] All complexes have a single minimum along the proton-transfer coordinate. [b] T = traditional hydrogen bond; PS = proton-shared hydrogen bond. [c] X−H distances (Å) in monomers: H$_2$O = 0.963; H$_3$O$^+$ = 0.980; pyrrole = 1.007; NH$_4$$^+$ = 1.023. [d] $\delta(\delta_{ppm})$ is the computed chemical shift for the hydrogen-bonded proton relative to the neutral proton-donor monomer (H$_2$O, NH$_3$, pyrrole).

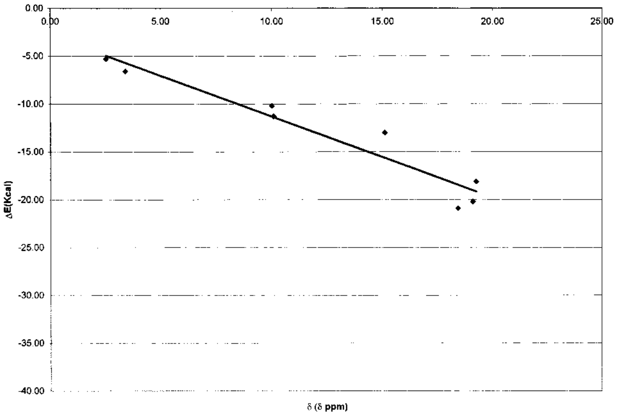

Figure 2. MBPT(2)/(qzp,qz2p) binding energies versus MBPT(2)/(qzp,qz2p) NMR proton chemical shifts for complexes with Cl−H−N and Cl−H−Cl hydrogen bonds.

Table 1 presents selected data for complexes formed with HCl, including ClH:NCH, ClH:NC(CH$_3$), ClH:NH$_3$, ClH:pyridine, ClH:NH$_2$(CH$_3$), ClH:NH(CH$_3$)$_2$, Cl$_2$H$_3$$^+$, and ClH:N(CH$_3$)$_3$. The complexes are listed in order of increasing stability. The data in Table 1 include a designation of hydrogen bond type (T for traditional and PS for proton-shared), Cl−H distances, intermolecular Cl−N and Cl−Cl distances, and MBPT(2)/(qzp,qz2p) binding energies and proton NMR chemical shifts. Figure 2 shows graphically a linear correlation between computed binding energies and chemical shifts, with a correlation coefficient of 0.93. The first two complexes in this series, ClH:NCH and ClH:NC(CH$_3$), have traditional hydrogen bonds. The intermolecular distances are long at 3.350 and 3.281 Å, the Cl−H distances are slightly elongated relative to the HCl monomer, the hydrogen bonds are relatively weak at −5.3 and −6.6 kcal/mol, and the corresponding chemical shifts are only 2.5 and 3.4 ppm, respectively. The complexes of HCl with NH$_3$ and pyridine also have traditional hydrogen bonds, but these complexes are more strongly bound, with binding energies of −10.2 and −11.3 kcal/mol, respectively. The Cl−N distances in ClH:NH$_3$ and ClH:pyridine are 3.080 and 3.044 Å, and the proton chemical shifts are 10.0 and 10.1 ppm, respectively. It is interesting that although these two complexes differ in stability by 1.1 kcal/mol, their chemical shifts are essentially identical. The lack of differentiation in the computed chemical shifts means that these two properties may be sensitive to some different factors, or that relative weightings of the same factors are different in these two cases.

There are three complexes in Table 1 which have characteristic proton-shared hydrogen bonds, namely, ClH:NH$(CH_3)_2$, $Cl_2H_3^+$, and ClH:N$(CH_3)_3$. The two complexes with the methyl-substituted amines have short Cl−N distances of 2.814 and 2.825 Å, long Cl−H distances of 1.630 and 1.657 Å, and binding energies of −18.1 and −20.9 kcal/mol, respectively. However, although ClH:N$(CH_3)_3$ is 2.8 kcal/mol more stable than ClH:NH$(CH_3)_2$, the chemical shift in the former is about 1 ppm less. These two complexes are structurally very similar, although the hydrogen bond in the dimethylamine complex is slightly nonlinear. (The angle between the Cl−H bond and the Cl−N axis is 3°.) These comparisons again suggest that different factors or different weightings of the same factors may be important in determining binding energies and NMR chemical shifts. The complex $Cl_2H_3^+$ also has a proton-shared hydrogen bond, but in this complex the proton is symmetrically bonded to the two Cl atoms, at a Cl−H distance of 1.573 Å. The binding energy of $Cl_2H_3^+$ is −20.2 kcal/mol, and the computed chemical shift is 19.1 ppm relative to HCl. The Cl−H distance, binding energy, and relative proton NMR chemical shift of $Cl_2H_3^+$ are consistent with the values of these properties for the two other complexes with proton-shared Cl···H···N hydrogen bonds.

It is not obvious how the hydrogen bond in the complex ClH:$NH_2(CH_3)$ should be classified, although it has been designated in Table 1 as belonging to the proton-shared group. As evident from the data of Table 1, the Cl−N and Cl−H distances are intermediate between those for traditional and proton-shared hydrogen bonds. Obviously, the transition in hydrogen bond type from traditional to proton-shared is a continuous one, and attempting to place all hydrogen bonds into one of these two categories is an oversimplification. Even within the proton-shared category, the degree of proton-sharing may differ, with the proton being more closely associated with Cl than N, or vice versa. Nevertheless, the binding energy and NMR proton chemical shift for this complex are consistent with the data for the other complexes in which HCl is the proton donor, as evident from Figure 2.

To what extent does the type of hydrogen bond influence the relative NMR chemical shift of the hydrogen-bonded proton? This is a difficult question to answer on the basis of the data from Table 1, since as the binding energy of these complexes increases, the hydrogen bond type changes from traditional to proton-shared. However, there is another approach, which is to examine the binding energy and the computed chemical shift for a particular complex as a function of proton position. For this purpose we have used the normal coordinate displacement vector for the harmonic proton-stretching mode in ClH:NH_3 to generate structures which move the proton away from its equilibrium position in a systematic way.[25] In the harmonic approximation, this motion is essentially pure proton motion. At each point we have computed the binding energy and the relative proton NMR chemical shift. The curves shown in Figure 3 illustrate how these two properties vary with proton position. The curve through the triangles is the potential energy curve, which shows that the stability of the complex decreases as the proton moves in either direction away from its equilibrium position. The shoulder in the curve for larger HCl distances is associated with the proton-shared region of the potential surface. The curve through the squares depicts the variation of chemical shift with proton position. As the proton moves away from equilibrium toward N, the relative chemical shift increases to a maximum of about 19 ppm in the region associated with a proton-shared hydrogen-bonded complex, and then decreases as the proton moves closer to the nitrogen. The fact that the curves in Figure 3 do not correlate with each other provides strong evidence that not only the binding energy but also the hydrogen bond type plays an important role in determining the proton chemical shift in a complex.

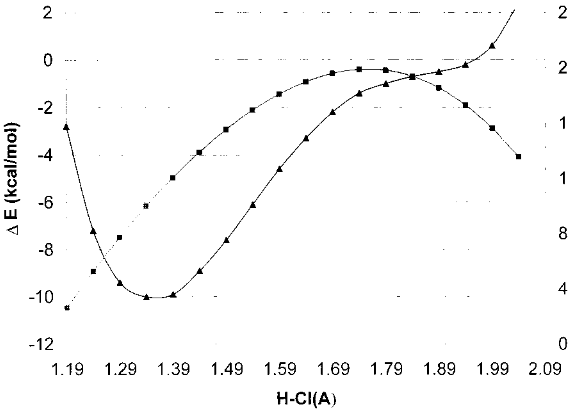

Figure 3. Binding energies for ClH:NH_3 (▲) and NMR chemical shifts (■) for the hydrogen-bonded proton along the normal coordinate displacment vector for the harmonic proton-stretching mode in ClH:NH_3, parametrized in the HCl distance.

Further insight into relationships among binding energies, structure type, and relative proton NMR chemical shifts may be obtained by examing the second set of complexes which have N and O as the hydrogen-bonded atoms. From the point of view of this study, it is unfortunate that neutral hydrogen-bonded complexes with N−H and O−H as the proton donor groups tend to be weakly bound by traditional hydrogen bonds. To expand the range of binding energies, it was necessary to include positively charged complexes with NH_4^+ as the proton donor and the protonated water dimer, $O_2H_5^+$. The complexes included in this group are listed in Table 2 in order of increasing binding energy and include $(H_2O)_2$, pyrrole:OH_2, NH_4^+:OCH_2, NH_4^+:OH_2, NH_4^+:NCH, and $O_2H_5^+$. All of these complexes have essentially linear hydrogen bonds, and all have only a single minimum along the proton-transfer coordinate. It should be noted however, that the structures of complexes with NH_4^+ indicate that an ion−dipole interaction is a significant factor in stabilizing these complexes.

Table 2 reports selected data for complexes with N−H−N, N−H−O, and O−H−O hydrogen bonds, and Figure 4 presents a plot of binding energy versus ^{1}H NMR chemical shift for these complexes. The correlation coefficient obtained from the least-squares fit is 0.97. As is evident from Table 2, the two neutral complexes, water dimer and pyrrole−water, are stabilized by traditional hydrogen bonds, have binding energies of −5.5 and −6.0 kcal/mol, and have correspondingly small chemical shifts of 3.0 and 2.5 ppm, respectively. In these complexes the hydrogen-bonded O−H and N−H bond lengths are only slightly elongated relative to the monomers. The binding energies and chemical shifts for these complexes are comparable to those of the weakly bound ClH:NCH and ClH:NC(CH_3) complexes, which also have traditional hydrogen bonds. When NH_4^+ is the proton donor, the complexes NH_4^+:OCH_2, NH_4^+:OH_2, and NH_4^+:NCH exhibit traditional hydrogen bonds, but have increased binding energies which range from −20.3 to −21.9 kcal/mol. The chemical shifts (computed relative to NH_3) also increase and range from 9.9 to 12.0 ppm. (If the shifts had been computed relative to NH_4^+, they would be reduced by 4.9 ppm.

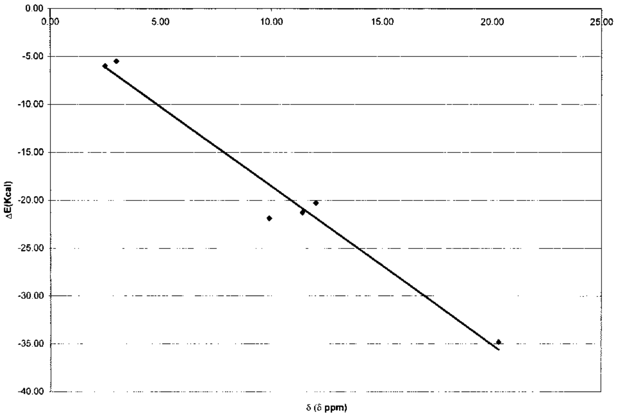

Figure 4. MBPT(2)/(qzp,qz2p) binding energies versus MBPT(2)/(qzp,qz2p) NMR proton chemical shifts for complexes with N−H−N, N−H−O and O−H−O hydrogen bonds.

Using NH_3 as the reference for these complexes and H_2O for $O_2H_5^+$ permits a comparison between neutral and charged complexes stabilized by traditional hydrogen bonds with N−H and O−H as proton donors.) It is important to note, however, that although the binding energies of the complexes with NH_4^+ with traditional hydrogen bonds are comparable to the binding energies of the HCl complexes with proton-shared hydrogen bonds, the chemical shifts for the NH_4^+ complexes are significantly smaller.

This situation changes for $O_2H_5^+$, a complex stabilized by a proton-shared hydrogen bond, in which the proton is symmetrically hydrogen-bonded to the two oxygens. This complex has a very short O−O distance of 2.385 Å, a long hydrogen-bonded O−H distance of 1.190 Å, a very large binding energy of −34.8 kcal/mol, and a proton NMR chemical shift of 20.3 ppm. It is striking that although the binding energy of this complex is 14 kcal/mol greater than that of the most stable proton-shared complex with HCl, the proton NMR chemical shift is very similar to the chemical shifts computed for the proton-shared complexes with HCl, and to the maximum chemical shift computed along the normal coordinate displacement vector for $ClH:NH_3$. This again provides supporting evidence that neutral and positively charged complexes stabilized by proton-shared hydrogen bonds have large relative proton NMR chemical shifts of around 20 ppm. While this shift correlates with binding energy within a closely related series of complexes, it appears to be related to the X−H−Y hydrogen bond type across the series, independent of the nature of X and Y and the absolute binding energy of the complex.

Conclusions

Second-order MBPT(2) calculations with the (qzp,qz2p) basis set employing the gauge-invariant atomic orbitals method have been performed to determine the relative ^1H NMR chemical shifts of the hydrogen-bonded proton in two series of complexes. The first consists of complexes with Cl−H−N and Cl−H−Cl hydrogen bonds, while the second has complexes with O−H−O, N−H−O, and N−H−N hydrogen bonds. Complexes which are neutral or positively charged and which have traditional or proton-shared hydrogen bonds, are included in both series. In all complexes, there is only a single minimum along the proton-transfer coordinate.

In each series, the ^1H NMR chemical shift relative to the corresponding neutral proton donor molecule [$\delta(\delta_{ppm})$] tends to increase with increasing binding energy. Since within a series increasing binding energy is also associated with a change of hydrogen bond type from traditional to proton shared, the effect of binding energy and hydrogen bond type on the proton chemical shift cannot be independently determined. However, MBPT(2)/(qzp,qz2p) calculations along the normal coordinate displacement vector for the proton stretch in $ClH:NH_3$ show that the maximum in the chemical shift curve occurs in the region of the proton-shared hydrogen bond, with $\delta(\delta_{ppm})$ approaching 20 ppm. Since the structure with the proton-shared hydrogen bond is not the equilibrium structure for this complex, hydrogen-bond type must also be a factor in determining the proton chemical shift. Although binding energies and ^1H NMR chemical shifts do not correlate across the two series of complexes investigated in this study, the chemical shifts for complexes with proton-shared hydrogen bonds are near 20 ppm in both series, independent of binding energy.

Acknowledgment. This work was supported by the National Science Foundation CHE-9873815 (J.E.D.B.) and the Air Force Office of Scientific Research AFOSR F49620-98-0116 (R.J.B.). The NMR calculations were carried out at the Ohio Supercomputer Center on the Cray T94 computer.

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