

An Investigation of the Acidic Properties of the Methyl Cation and Its Possible Role as a Hydrogen Bond Donor. Characterization of Complexes of the Type $[H_2C-H^+ \cdots B]$ ($B = NH_3, H_2O, \text{ and } HF$)[†]

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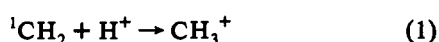
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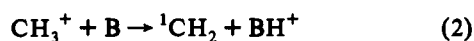
Abstract: Results of quantum chemical calculations of the title complexes show that they are strongly bonded. The bond dissociation enthalpies (298 K) of the $H_2C-H^+ \cdots B$ bonds were calculated to be 85–88, 71–74 and 44–47 kJ mol⁻¹ for $B = NH_3, H_2O, \text{ and } HF$, respectively. The periodic trend in the bond dissociation enthalpies, C–H vibrational frequencies, and C–H bond lengths is found to be in accord with a model of the interaction which in addition to the normal ion/dipole terms incorporates a variable amount of hydrogen bonding. The hydrogen bond character is most pronounced in the complex with ammonia and practically absent in the complex with hydrogen fluoride. The complex with water represents an intermediate situation. The role of this general type of complexes in gas-phase and condensed-phase reactions is discussed.

Introduction

The methyl cation is a key species in both gas-phase and solution chemistry.¹ The fact that this molecule is a potential acid toward strong bases appears to have been overseen by most workers in the field. Using available thermochemical data,² the proton affinity of the corresponding base, singlet methylene, is easily calculated from the heat of the reaction of

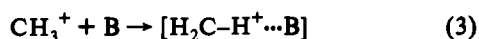


to be $PA[{}^1CH_2] = 867 \text{ kJ mol}^{-1}$. This simple finding has the important consequence that the methyl cation should transfer a proton to bases of higher proton affinity than singlet methylene (bases with $PA[B] > 867 \text{ kJ mol}^{-1}$):



This group of bases includes all organic amines and various other compounds.

Being a potential proton donor, the methyl cation may also act as a hydrogen bond donor toward bases weaker than singlet methylene (bases with $PA[B] < 867 \text{ kJ mol}^{-1}$):



One motivation of the present work is that recent experimental and quantum chemical data point toward a hydrogen-bonded

methyl species as an intermediate during loss of methane from the trimethyloxonium ion.³

It was expected that the degree of hydrogen bonding in such complexes would be more pronounced the more closely the proton affinity of B resembles that of singlet methylene (see below). The purpose of this paper is to investigate this possibility by a quantum chemical investigation of species of the type $[H_2C-H^+ \cdots B]$ ($B = NH_3, H_2O, \text{ and } HF$). In all three cases isomerization to the more stable covalent form CH_3B^+ should be a facile process. For this reason it has been necessary to investigate the complexes and other relevant parts of the three potential energy surfaces computationally.

Ion-neutral complexes of the type $[R^+X]$ are known to exist during unimolecular dissociation of ions in the gas phase⁴ as well as in solution:⁵



In the gas phase, ion-neutral complexes are formed when a sufficient amount of energy is transferred to the reactant molecule RX^+ . Ion-neutral complexes are also formed as intermediates in ion-molecule reactions of the type

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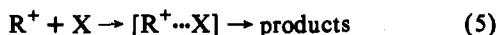
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[†] Dedicated to Professor Johannes Dale on the occasion of his 70th birthday.

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In condensed phases many solvolytic reactions (nucleophilic substitution and/or elimination) are believed to proceed *via* intermediates of this type.

For many years there was a discussion about the intrinsic nature of ion-neutral complexes. A problem was the lack of a comprehensive definition of an ion-neutral complex. It was therefore highly welcome when Morton introduced the so-called reorientation criterion some years ago.⁶ Briefly explained, the reorientation criterion is met when one of the two partners (R^+ or X) is free to flip relative to the other during the transient lifetime of the complex. During this period of time the structures of R^+ and X may rearrange before further reactions take place.

In most simple models for interaction between an ion and a neutral molecule, the ion is considered to be a point charge (or a charged hard sphere). The potential energy function will therefore include ion-dipole and ion-induced-dipole attraction terms and in addition an attraction/repulsion Lennard-Jones 12/6 term. Although often applicable, this description has its limitations. Examples of this are found for ion-neutral complexes which are held together by a proton bridge. Well-known examples include $(H_2O)_2H^+$ and $(NH_3)_2H^+$. These complexes are unusually strongly bonded, and a significant part of the interaction can be described in the framework of an extreme type of hydrogen bonding. One of the objectives of this work has been to investigate to what degree a hydrogen bond model also is relevant for $[H_2C-H^+ \cdots B]$ complexes. Upon the basis of the found topography of each potential energy surface, it will be demonstrated that a distinction can be made between the covalently bonded species RX^+ , the hydrogen-bonded ion-neutral complex $[R^+ \cdots X]$, freely rotating ion-neutral complexes $[R^+X]$, and completely dissociated products $R^+ + X$.

Method of Calculation

The calculations were performed using standard procedures of the program suite GAUSSIAN 92.⁷ All critical points of the potential energy surface were characterized at the MP2/6-31G(d,p) level by complete optimization of the molecular geometries and consideration of the calculated harmonic vibrational frequencies. Harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix, calculated from analytical second derivatives of the total energy. Harmonic frequencies obtained in this manner were used to calculate the zero point vibrational energies as described below. For the most important molecular species, geometry optimizations were also performed at the MP4/6-311G(d,p) level. Single point MP4/6-311+G(2df,2pd) energy calculations were finally performed at the MP2/6-31G(d,p) and MP4/6-311G(d,p) optimized geometries. In addition calculations were also performed to estimate the basis set superposition error (*vide infra*) at these highest levels of theory. All relative enthalpies were calculated by including the MP2/6-31G(d,p) zero point vibrational energies scaled by a factor of 0.94 and by explicit consideration of rotational and translational contributions. The thermal contributions to the vibrational enthalpies were found to be negligible and were therefore not included.

Results and Discussion

The results of the quantum chemical calculations are given in Table 1, and the most relevant optimized geometries are depicted in Figures 1, 2, and 3. Geometries not shown here are available as supplementary material.

1. Proton Affinities and Evaluation of the Quantum Chemical Method Used. In order to evaluate the performance of the various wave functions, proton affinities were calculated for each of the seven bases relevant to the discussion and compared to the well-known corresponding experimental figures. The data are presented in Table 2. The MP2/6-31G(d,p) method gives qualitatively correct results for the proton affinity. It is clear from the data of column 2 of Table 2 that at this level of theory

Table 1. Energies Obtained from the Quantum Chemical Calculations

molecule	MP2/6-31G(d,p) (hartrees)	MP4/6-311G(d,p) (hartrees)	MP4/6-311+G(2df,2pd)// MP2/6-31G(d,p)		Ezpv at MP2/6-31G(d,p) ^a (kJ mol ⁻¹)	BSSE ^b (kJ mol ⁻¹)
			(hartrees)	(hartrees)		
CH ₃ ⁺ (1)	-39.346 63	-39.379 77	-39.401 90	-39.401 88	80.6	
¹ CH ₂ (2)	-38.987 20	-39.030 64	-39.056 67	-39.056 61	42.8	
NH ₄ ⁺	-56.733 68	-56.775 82	-56.812 87	-56.812 82	125.6	
NH ₃ (4)	-56.383 22	-56.428 07	-56.474 28	-56.474 24	87.5	
H ₃ O ⁺ (5)	-76.506 11	-76.562 27	-76.607 68	-76.607 73	87.1	
H ₂ O (6)	-76.219 79	-76.276 34	-76.334 00	-76.333 94	54.0	
H ₂ F ⁺ (7)	-100.402 12	-100.477 87	-100.531 92	-100.531 96	48.1	
HF (8)	-100.194 64	-100.274 21	-100.337 29	-100.337 28	23.6	
CH ₃ ⁺ ...NH ₃ (9)	-95.770 00	-95.847 43	-95.910 19	-95.910 11	175.4	
CH ₃ ⁺ ...OH ₂ (10)	-115.599 57	-115.689 30	-115.764 13	-115.764 08	141.5	3.4
CH ₃ ⁺ ...FH (11)	-139.563 29		-139.756 61		108.9	
H ₂ C...H ₄ N ⁺ (12)	-95.766 11		-95.908 26		176.1	
CH ₃ NH ₃ ⁺ (13)	-95.916 46		-96.052 47		201.4	
CH ₂ NH ₂ ⁺ (14)	-94.691 64		-94.814 09		137.5	
CH ₃ OH ₂ ⁺ (15)	-115.689 43		-115.848 67		163.1	
CH ₂ OH ⁺ (16)	-114.469 75		-114.615 63		103.1	
CH ₃ FH ⁺ (17)	-139.605 13		-139.791 42		124.6	
CH ₂ F ⁺ (18)	-138.383 21		-138.557 00		69.2	
H ₂ (19)	-1.157 66		-1.170 22		25.9	
CH ₃ NH ₂ (20)	-95.550 28		-95.696 03		163.5	
CH ₃ OH (21)	-115.382 01		-115.549 90		130.7	
CH ₃ F (22)	-139.360 10		-139.554 27		100.4	
H ₃ N...CH ₃ (23)	-95.759 00		-95.900 87		174.3	
H ₂ O...CH ₃ ⁺ (24)	-115.593 06		-115.758 84		140.2	
HF...CH ₃ ⁺ (25)	-139.562 20		-139.756 51		108.2	
TS1 (9 → 13)	-95.768 84		-95.903 53		174.7	
TS2 (10 → 15)	-115.599 31		-115.763 71		141.7	
TS3 (11 → 17)	-139.563 27		-139.756 76		108.4	
TS4 (13 → 16 + 19)	-95.768 39		-95.911 89		178.7	
TS5 (15 → 17 + 19)	-115.575 43		-115.741 30		146.2	
TS6 (17 → 18 + 19)	-139.521 11		-139.711 70		114.1	
TS7 (9 → 12)	-95.764 87		-95.905 35		167.4	

^a Zero point vibrational energies (MP2/6-31G(d,p)), scaled by a factor of 0.94. This factor was chosen to give the best agreement between calculated and experimental frequencies for NH₃, H₂O, HF, and H₂. ^b The basis set superposition error was estimated using the counterpoise method (see text).

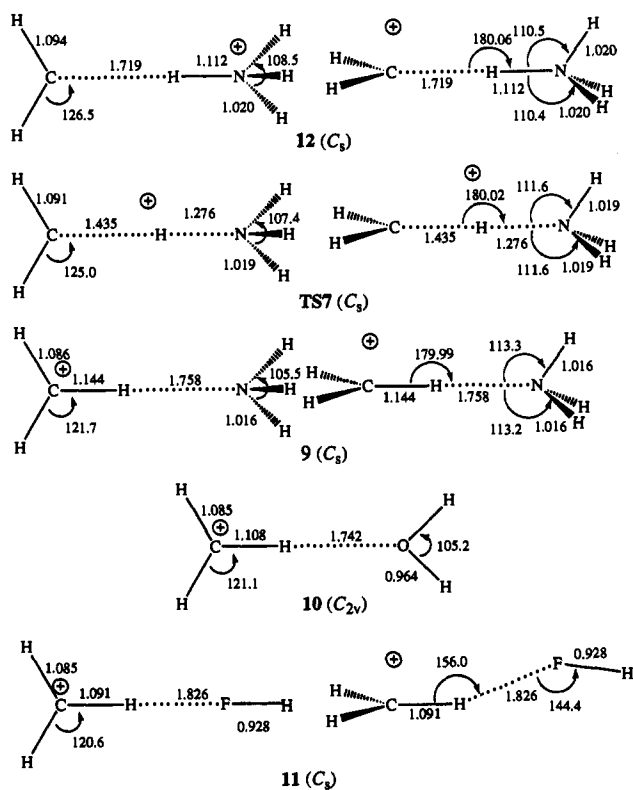


Figure 1. Geometry-optimized structures (MP2/6-31G(d,p)) of the complexes. Bond distances are given in angstroms and angles in degrees.

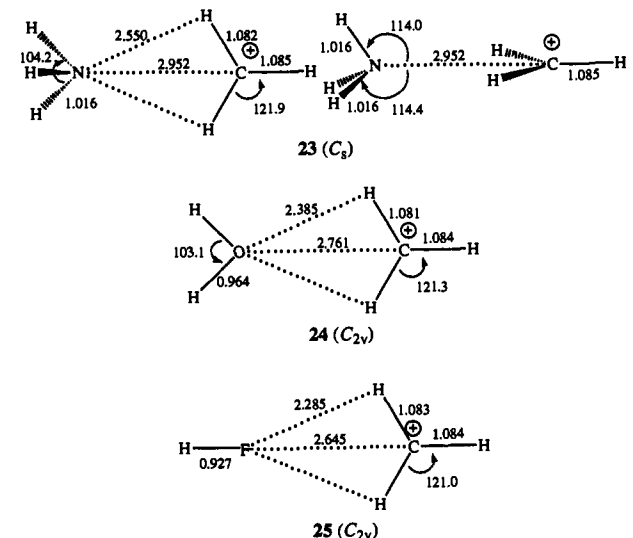


Figure 2. Geometry-optimized structures (MP2/6-31G(d,p)) of complexes where the base has been displaced by an equatorial rotation of 60° (compared to the corresponding structures of Figure 1) and frozen in that position. All structures correspond to higher order saddle points, and there are no signs of hydrogen bonding (see text).

absolute proton affinities are systematically overestimated by approximately 30 kJ mol⁻¹ but that relative proton affinities are within experimental accuracy. A slight improvement is obtained by performing geometry optimizations at the higher, but more time consuming, MP4/6-311G(d,p) level as can be seen from Table 2. Optimum electron structures and thereby near quantitative agreement with experiment are obtained by performing MP4 with a large basis set including both diffuse functions and an improved set of polarization functions. The MP4/6-311+G-(2df,2pd) data are presented in column 3 of Table 2. It is interesting to notice that the proton affinities are calculated to be equal within ±0.2 kJ mol⁻¹ irrespective of whether the calculations are performed using the MP2/6-31G(d,p) or MP4/

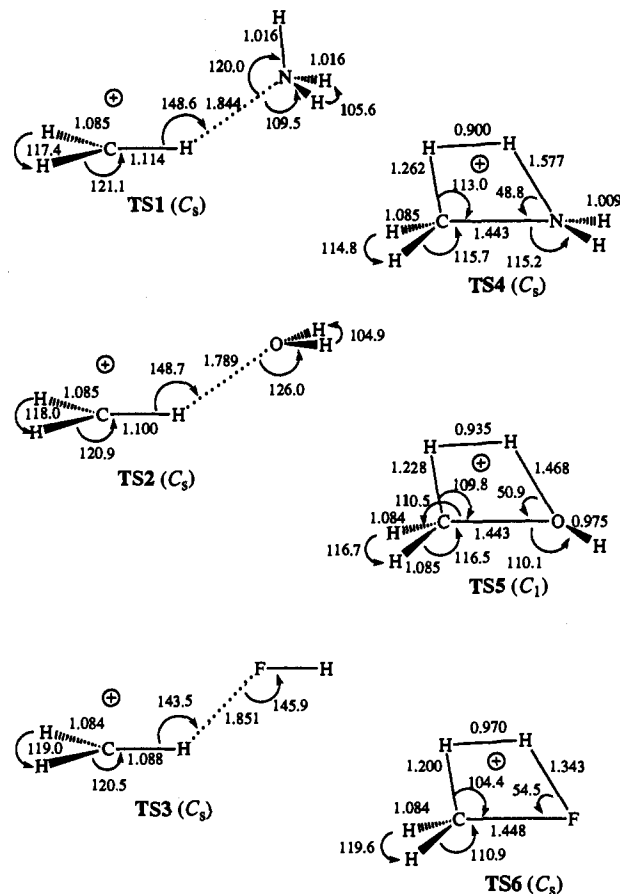


Figure 3. Geometry-optimized transition structures (MP2/6-31G(d,p)).

Table 2. Proton Affinities at 298 K (kJ mol⁻¹)^a

base (B)	MP2/6-31G(d,p)//	MP4/6-311G(d,p)//	MP4/6-311+G-(2df,2pd)//	exptl ^c
	MP2/6-31G(d,p)	MP4/6-311G(d,p)	MP2/6-31G(d,p) ^b	
CH ₂ (2)	913	885	875	867
NH ₃ (4)	889	882	857	852
H ₂ O (6)	725	724	692	691
HF (8)	525	515	492	490
CH ₃ NH ₂ (20)	930		903	902
CH ₃ OH (21)	781		759	761
CH ₃ F (22)	626		605	605

^a Calculated taking differences in *E*_{zpv} plus rotational and translational components of the enthalpy into account as explained under Method of Calculation. ^b Same results as these with MP4/6-311+G(2df,2pd)//MP4/6-311G(d,p), see text. ^c Experimental results from ref 2.

6-311G(d,p) optimized geometries. It therefore turns out that second-order electron correlation seems to be the most important factor in determining the relative molecular structures and that higher order corrections approximately cancel out. No significant improvement in relative geometries appears to be obtained by performing geometry optimization using one extra valence basis function for each angular quantum number (*s* and *p*).

A recent paper by Smith and Radom gives a convincing demonstration of the ability of the G2 procedure in predicting proton affinities generally within state-of-the-art experimental errors.⁸ However, as shown here, the less expensive and far less cumbersome MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p) method is equally successful.

2. Structures and Properties of the Complexes. As is clear from Table 1 and Figure 1, the anticipated hydrogen-bonded complexes with structures (H₂C-H)⁺...NH₃ (9), (H₂C-H)⁺...OH₂ (10), and (H₂C-H)⁺...FH (11) were located as local minima of their respective HF/3-21G (data not shown here) as well as MP2/6-31G(d,p) potential energy surfaces. While the C-H...B bonds

Table 3. Comparison of Some Physical Properties for the Complexes

base (B)	bond diss. enthalpy (BDE, 298 K), calcd ^a (kJ mol ⁻¹)	proton affinity (PA(B), 298 K), calcd (exptl) ^b (kJ mol ⁻¹)	distance C...B in complex (R), calcd ^c (Å)	elongation of C-H bond (ΔR), calcd ^d (Å)	shift in C-H str. freq. (Δν), calcd ^e (cm ⁻¹)	shift in H pop. (Δρ), calcd ^f (e)	permanent dipole moment (μ), exptl ^g (C m)	polarizability (α), exptl ^h (J ⁻¹ C ² m ²)
NH ₃ (4)	85-88	857 (852)	2.902	+0.059	-777	+0.164	4.9 × 10 ⁻³⁰	2.5 × 10 ⁻⁴⁰
H ₂ O (6)	71-74	692 (691)	2.850	+0.023	-268	+0.147	6.2 × 10 ⁻³⁰	1.7 × 10 ⁻⁴⁰
HF (8)	44-47	493 (490)	2.857	+0.006	-37	+0.047	6.4 × 10 ⁻³⁰	5.7 × 10 ⁻⁴¹

^a Calculated from MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p) taking differences in Ezpv and BSSE into account. ^b Calculated from MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p) taking differences in Ezpv into account. Experimental values are given in parentheses. ^c MP2/6-31G(d,p) distance between the carbon and the "heavy" atom of B. ^d Difference between the C-H bond distances in the complex and in the free methyl cation calculated at the MP2/6-31(d,p) level. The C-H bond distance in free methyl is 1.085 Å. ^e Difference between the C-H bond stretch harmonic vibrational frequencies (unscaled) in the complex and in the free methyl cation calculated at the MP2/6-31G(d,p) level. The C-H bond stretch harmonic vibrational frequency in free methyl is 3153 cm⁻¹. ^f Difference between the H atom Mulliken populations in the complex and in the free methyl cation calculated at the HF/6-31G(d,p) level at the MP2/6-31G(d,p) geometry. The H atom Mulliken population in free methyl is +0.119. ^g Data from the following: Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: Oxford, U.K., 1992. Thermochemical data reported in this table are taken from the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, 17 (Suppl. 1).

in the ammonia and water complexes are linear, a deviation from linearity is noticed for the hydrogen fluoride complex as seen from Figure 1. The weak directional properties of the C-H...F bond in 11 cast doubt about whether this complex is hydrogen bonded at all and will be the subject of more detailed discussions in subchapter 3. For the rest of the discussion in this subchapter, it is not relevant whether (H₂C-H)⁺...FH (11) really represents a hydrogen-bonded species or not.

The bond dissociation enthalpies (BDE) at 298 K (dissociation into CH₃⁺ and B) were calculated at the highest level of theory applied to be 88, 74, and 47 kJ mol⁻¹, which are quite substantial. The corresponding quantity for the hydrogen bond of the neutral water dimer is known⁹ to be 20 kJ mol⁻¹. It must, however, be realized that in neither of the three methyl cation complexes a hydrogen bond is likely to be the dominating interaction and that electrostatic forces are largely responsible for the bond. This will be discussed below.

The reliability of ab initio calculated energies of intermolecular bonds (including hydrogen bonds) is known to be strongly dependent on the basis set used because of the basis set superposition error (BSSE). Although an extended basis set of the kind used here (6-311+G(2df,2pd)) would be anticipated to be nearly free from this defect, it was important to verify that this is the case. We decided to employ the traditional counterpoise method,¹⁰ which is simple but has been criticized for overestimating the BSSE.¹¹ A counterpoise calculation was performed for the methyl/water complex (10) at the MP4/6-311+G(2df,2pd)/MP2/6-31G(d,p) level of theory, and the result from this calculation was considered to be applicable to the two other complexes. Not surprisingly, the BSSE estimated by this procedure was found to be small, only 3.2 kJ mol⁻¹. It can also be mentioned that the MP2/6-31G(d,p) BSSE was calculated to be 6.4 kJ mol⁻¹. Because the counterpoise method may perhaps at best only provide an approximate upper limit to the BSSE, a range of values of the BDEs including approximate upper and lower limits is given in Table 3.

The van der Waals radii of N, O, and F are 1.60, 1.54, and 1.35 Å, respectively.¹² The C...B distances in the corresponding

complexes were calculated to be 2.90, 2.85, and 2.86 Å (Table 3 and Figure 1), which implies that the "effective" radii of the methyl groups in the complexes are 1.30, 1.31, and 1.51 Å, respectively. The experimental gas-phase bond dissociation enthalpies (BDE) for alkali metal ion complexes of the types M⁺...OH₂ and M⁺...NH₃ are well-known. Within each of the two series, the BDEs have been found to correlate linearly with the inverse of the ionic radius of the alkali metal ion.¹³ Each BDE in the ammonia series is 15-22% higher than that in the corresponding figure in the water series, probably as a result of the higher polarizability of ammonia. The experimental BDEs for the K⁺ complexes are practically identical to the BDEs for the corresponding CH₃⁺ complexes calculated here. From the literature, K⁺...O and K⁺...N distances are known to be around 2.87 and 2.79 Å, respectively.¹⁴ Subtracting the van der Waal radii of N and O from these values leads to effective ionic radii of K⁺ in these complexes of 1.27 Å (for N) and 1.25 Å (for O). This suggests that the potassium ion is slightly smaller than the methyl cation. Because the methyl cation forms an intramolecular bond of the same strength as that of the smaller K⁺ ion, the extra stabilization in complexes of the former is most likely due to a greater displacement of the positive charge toward the neutral molecule. As a consequence, a fraction of the positive charge will be located on the hydrogens (of particular interest here is the hydrogen atom closest to the base B). This simple qualitative argument is therefore seen to be in accord with an interaction which incorporates some degree of hydrogen bonding (A-H(δ⁺)...B) in the cases where B = NH₃ and H₂O.

Another qualitative indication of the interaction is also obtained from the Mulliken population analysis. Although the exact figures should not be taken too literally, it is clear that the hydrogen atoms of the free methyl cation (1) carry a substantial part of the positive charge. The population of each hydrogen was calculated (6-311+G(2df,2pd) basis set) to be ρ = +0.119. Populational analysis of the complexes 9-11 shows that the C-H bond which points toward the base in all three cases is more strongly positively polarized than in the free methyl cation (Table 3). This extra polarization is seen to increase with increasing bond dissociation energy and is therefore largest for B = NH₃. In all three complexes, the populations of the two other hydrogens remain virtually unaltered. At the same time, only a negligible net charge transfer from the base to the methyl cation is observed.

Another indication of the hydrogen bond character can be inferred from the bond distances calculated for the interconnecting C-H bond in the three complexes (Figure 1 and Table 3). This distance becomes larger the stronger the interaction is, and the C-H bond is most extended in the ammonia complex. Parallel to this bond elongation, a significant decrease in the harmonic

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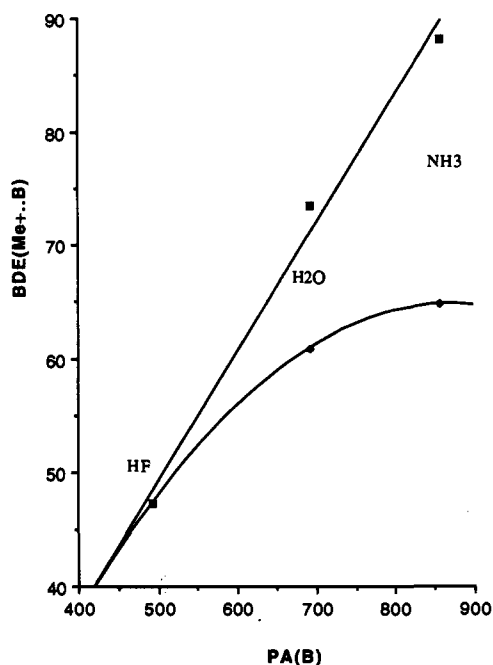


Figure 4. Plot of the bond dissociation enthalpies (kJ mol^{-1}) of the complexes 9–11 versus the proton affinities of the bases (upper curve) and of the complexes 23–25 (lower curve). The difference between the two curves gives an approximate measure of the contribution of hydrogen bonding in the complexes 9–11 as explained in the text.

stretching frequency of the C–H bond is observed (Table 3). Both bond elongation and a decrease in vibrational frequency are characteristic features of a hydrogen bond.¹⁵

Proton-bound dimers of water and ammonia have been studied extensively both experimentally and theoretically. The hydrogen bond character in these species has been noticed and is very pronounced. For example, in the $(\text{H}_2\text{O})_2\text{H}^+$ dimer, the interconnecting proton is situated midway between the two oxygen atoms, showing that the bridging proton in this extreme case is shared equally between the two bases.¹⁶ Proton-bound dimers which consist of two different monomers have been demonstrated to have bond dissociation enthalpies that are linearly correlated to the difference in their proton affinities.¹⁷ The upper part of Figure 4 shows that a plot of the bond dissociation energies of the methyl cation complexes versus the proton affinities of the corresponding bases also gives an approximately straight line.

The interaction between a base and CH_3^+ can roughly be divided into two contributions, one coming from the interaction with the partial positive charge on the bridging H (hydrogen bonding) and the other from an interaction with the positive charge on C (as in the K^+ complexes already discussed). An inherent weakness of correlations of the type depicted in the upper part of Figure 4 is that they do not provide the information which can help in distinguishing between the two contributions. This becomes even clearer when we also observe a linear correlation between the BDEs and the polarizabilities of the bases (Table 3).

To overcome this dilemma, calculations were performed for the complexes 23–25 shown in Figure 2. Each of these “backside” complexes differs from the corresponding “frontside” complexes 9–11 of Figure 1 in that the base has been rotated 60° equatorially

with respect to the methyl cation. In these positions it was assumed that hydrogen bonding would be relatively unimportant. During optimization, the geometries were forced to keep the symmetries indicated in Figure 2. In the case of the ammonia/methyl system 23, the additional constraint of an N–C–H angle of 180° was introduced. Otherwise, each molecular systems would collapse to the respective covalent isomer. This leads to the final MP2/6-31G(d,p) geometries of Figure 2. Analysis of the force constant matrices showed that the structures 23 and 25 correspond to second-order saddle points, while structure 24 is a third order saddle point. For all three saddle points, motion along two internal coordinates leads to lower potential energies. These internal coordinates correspond to (i) equatorial rotation, leading to the “frontside” complex, and (ii) out-of-plane bending, leading to the covalent isomer. In the case of 24, the third internal coordinate which leads to lower potential energy is rotation of the water molecule around the O–C axis, giving a perpendicular arrangement of water relative to the plane of the methyl cation. The potential energy of this 90° rotated form is 3.5 kJ mol^{-1} lower than 24 at the MP2/6-31G(d,p) level of theory (zpe included) and corresponds to a second-order saddle point with the same characteristics as structures 23 and 25.

From the calculated geometries of the “backside” complexes 23–25 of Figure 2, it appears that hydrogen bonding is relatively unimportant. For this reason the enthalpy difference between the “frontside” complex and the “backside” complex should give an approximate measure of the contribution of hydrogen bonding in the former. Using the data of Table 1, these enthalpy differences are 23, 13, and 0 kJ mol^{-1} for the NH_3 , H_2O , and HF complexes, respectively (MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p)). The bond dissociation enthalpies calculated for the complexes 23–25 are plotted as the lower curve of Figure 4. The enthalpy difference and therefore the contribution from hydrogen bonding in the “frontside” complex are obtained by subtracting the lower from the upper curve.

Although numerous studies of both neutral–neutral and ionic–neutral hydrogen-bonded complexes exist,^{16,18} previous studies of complexes between alkyl cations and different bases are quite sparse in the literature. One relevant paper is devoted to a quite detailed study of the isopropyl cation/ammonia system.¹⁹ SCF calculations show that there are two noncovalent isomers. The more stable isomer corresponds to an arrangement where the central methine hydrogen points toward the lone pair of the ammonia nitrogen. The interaction in this complex is, however, not dominated by H-bonding because the intermolecular distances are far too large and because the C–H bond is only slightly affected. The two methyl groups clearly stabilize the carbocation relative to the deprotonated carbene (for which the PA is probably far above 900 kJ mol^{-1}), and the acidity of the central H atom is therefore much smaller than that of the methyl cation. The acidity of the methyl hydrogens in the isopropyl cation is much higher, and they are able to form a hydrogen bond, which is the interaction responsible for the other isomer. Deprotonation via this mechanism leads to the stable propene molecule whose PA is only 751 kJ mol^{-1} . This shows that acidity is the key factor which governs the ability to form H-bonds.

3. Potential Energy Surfaces and the Role of the Complexes in the Chemistry of the CH_3B^+ Species. The complexes treated here are higher in potential energy than their covalently bonded

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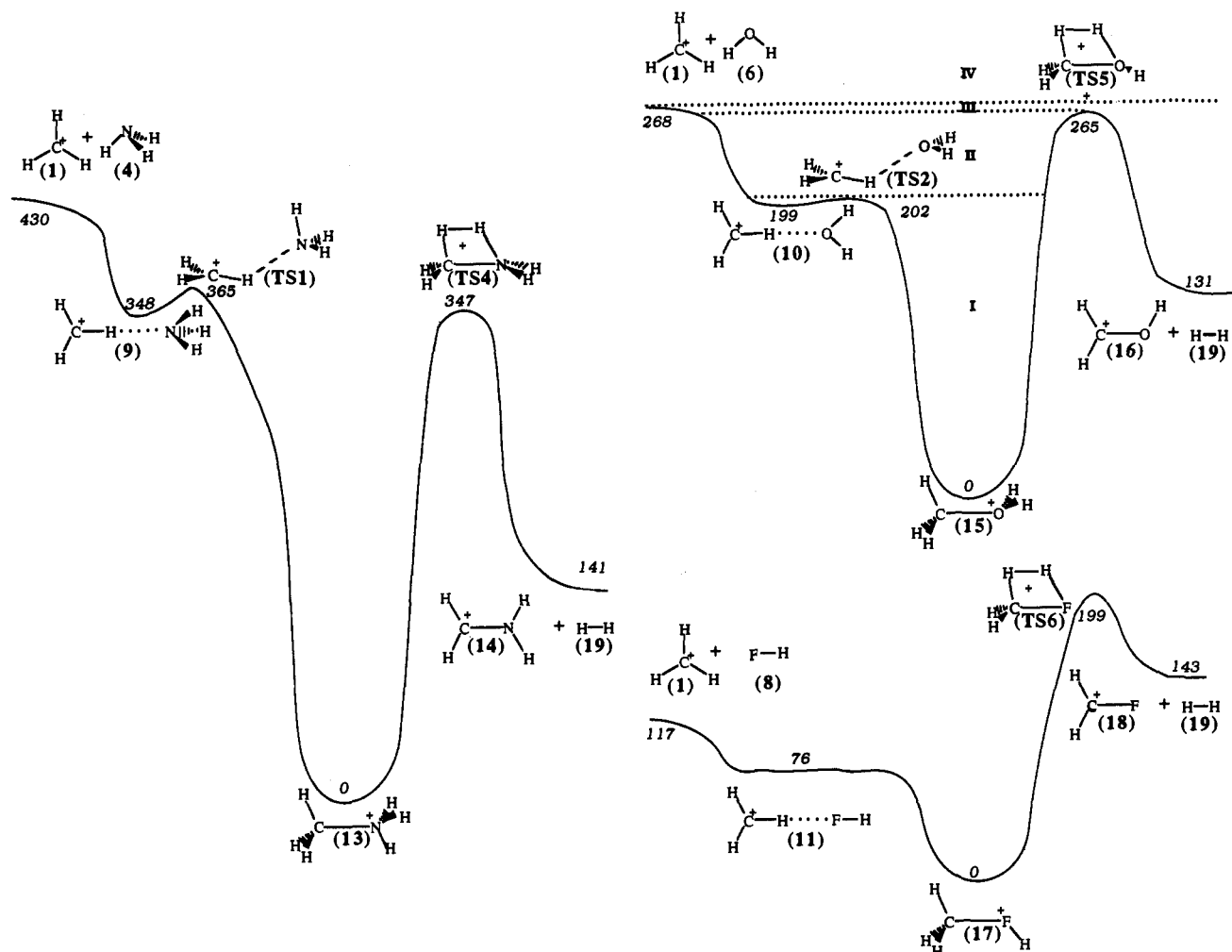
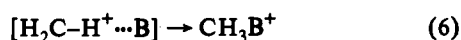


Figure 5. Schematic potential energy diagrams of (a) $[\text{CH}_5\text{N}]^+$, (b) $[\text{CH}_5\text{O}]^+$, and (c) $[\text{CH}_5\text{F}]^+$. Relative enthalpies (in italics) are from the MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p) calculations and are given in kJ mol^{-1} .

isomers CH_3B^+ (Figure 5). A necessary criterion for possible experimental observation of the complexes must be that there are sufficiently high barriers toward the rearrangements:



On this basis, the stability of the hydrogen fluoride complex **11** may be questioned. The bent geometry of the $\text{C}-\text{H}\cdots\text{F}-\text{H}$ moiety is an indication of the absence of a H-bond. Weak directionality is typical for weak H-bond acceptors as has been demonstrated repeatedly in the literature.²⁰ Likewise, the linear geometries of the NH_3 and H_2O complexes indicate stronger directionalities, which is seen to be directly related to the contribution of hydrogen bonding. To obtain more quantitative information about the stabilities, a search for the transition structures for rearrangement according to eq 6 was conducted. At the MP2/6-31G(d,p) level, transition structures with one negative eigenvalue of the Hessian corresponding to the reaction coordinate were located in all three systems. The MP2/6-31G(d,p) TS structures are depicted in Figure 3. The existence of these TS structures was anticipated from the fact that both reactants and products are stable structures with all positive eigenvalues at this level of theory. Calculation of the relative energies at the MP4/6-311+G(2df,2pd)//MP2/6-31G(d,p) level revealed that the stability of the HF complex **11** may seriously be questioned because the transition structure **TS3** separating **11** and **17** is found to have lower energy than **11**. In order to investigate this matter further, all three complex

structures were reoptimized at the MP4/6-311(d,p) level. At this level of theory, both **9** and **10** are local minima (all positive eigenvalues of the Hessian). However, structure **11** is no longer a local minimum and attempts to optimize the geometry starting with the MP2/6-31G(d,p) geometry and leads to the covalent structure **17**. An MP4/6-311G(d,p) optimized structure of **11** with forced C_{2v} symmetry (linear arrangement) has two negative eigenvalues, indicating a second-order saddle point. The conclusion to be drawn from these calculations is that the hydrogen fluoride complex **11** probably does not exist in a potential energy well but that the ammonia **9** and water complexes **10** do.

Figure 5 shows the potential energy diagrams for the three systems investigated. The unimolecular chemistry of protonated methylamine, methanol, and methyl fluoride has been the subject of previous experimental and theoretical studies.²¹ From these studies, it is known that the only unimolecular reaction observed in addition to dissociation into CH_3^+ and B is loss of H_2 . In the latter case, the translational energy release associated with H_2 loss was found to increase with an increasing barrier of the reverse reaction.

As already noted, the complex with hydrogen fluoride does not correspond to a proper minimum of the potential surface and its existence can only be transient. For the complex with water, a minimum energy structure is found at all levels of theory but the transition structure for rearrangement into the covalent protonated methanol structure is only slightly higher in energy. The

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vibrational frequency analysis reveals that the complex is quite "floppy". A harmonic frequency of vibration of 96 cm^{-1} (uncorrected) was calculated (MP2/6-31G(d,p)) for the hindered rotation of water (torsional motion) relative to methyl around the C-H...O bond axis. The bending motion of the water molecule relative to the methyl cation (which leads to the covalent structure **15** via **TS2**) was calculated to have a harmonic frequency of vibration of 164 cm^{-1} . The shallow potential energy well of the complex and the low barrier for the rearrangement make the chances for direct experimental observation of this species rather small.

In the case of ammonia, the complex is separated from the covalent structure with a relatively low barrier, as can be seen from Figure 5a. The specificity of the H-bond interaction is reflected in the finding of a bending vibrational frequency of 293 cm^{-1} and that rotation of ammonia around the C-H...N bond axis is practically free (the analysis shows that the corresponding vibrational frequency is 12 cm^{-1}). Of the three complexes studied here, the ammonia complex is therefore seen to be the most likely candidate for direct observation. One feature of the potential energy surface should, however, be noted. Molecules prepared by protonation of methylamine and with internal energy in the region of the complex are more likely to lose H_2 than to rearrange into the complex structure because the barrier for the former process is slightly lower. For this reason a better alternative for preparation of the complex is probably to start with free CH_3^+ and NH_3 . Formation of the complex could then be achieved in an ion-molecule association reaction. In order for the complex to be trapped inside its well, the extra internal energy has to be taken out in collisions with third body molecules present.

Despite the small odds for direct observation, the calculations show that these species may still be of chemical relevance. Taking the protonated methanol molecule as an example, it is clear that a certain portion of the potential energy surface can only be described as belonging to the complex structure. Protonated methanol molecules with sufficient internal energy (above 202 kJ mol^{-1}) will occasionally transverse into the region of the complex and, after a short period of time, slip out again.

The potential energy diagram of Figure 5b has been divided into four energy regimes (I-IV) to illustrate how the structure of protonated methanol depends on the available total energy. In regime I ($E < 202\text{ kJ mol}^{-1}$), only the covalently bonded structure **1** can be realized. In regime II ($202\text{ kJ mol}^{-1} < E < 265\text{ kJ mol}^{-1}$), the molecule is free to isomerize between the covalent structure and the ion-neutral complex. Reorientation between CH_3^+ and H_2O is therefore possible for $E > 199\text{ kJ mol}^{-1}$ as explained above. In the regimes III and IV reactions may take place. For $E > 265\text{ kJ mol}^{-1}$, the passage into the product region of CH_2OH^+ plus H_2 is open. For $E > 268\text{ kJ mol}^{-1}$, the passage into the product region of CH_3^+ plus H_2O is also open.

Midland and Morton have elegantly shown how the intramolecular dynamics within the $\text{NH}_4^+\cdots\text{FH}$ complex are affected by the energy available.²² The minimum energy configuration of this complex is quite similar to that of the $\text{CH}_3^+\cdots\text{FH}$ complex in that hydrogen bonding is relatively unimportant. The $\text{NH}_4^+\cdots\text{FH}$ complex is very "floppy". Reorientation of the FH moiety is described as a hindered rotation (low-frequency bending vibration). However, detailed analysis shows that already at 13 kJ mol^{-1} above the ground vibrational state the two partners are free to rotate relative to each other. The analogy to the hindered rotation in ethane was pointed out by the authors. The situation is apparently quite similar to that of the $\text{CH}_3^+\cdots\text{FH}$ complex,

although we have not made any attempts to investigate this interesting possibility further.

4. Proton Transfer from the Methyl Cation to Ammonia. The difference in proton affinity between $^1\text{CH}_2$ and NH_3 is only $12\text{--}15\text{ kJ mol}^{-1}$, the latter being the most basic. It is therefore not surprising that in addition to $\text{CH}_3^+\cdots\text{NH}_3$ (**9**) we also find that the complex $\text{CH}_2^+\cdots\text{NH}_4^+$ (**12**) is a stable species. Quite surprisingly, the latter complex is calculated to be 4.3 kJ mol^{-1} higher in energy than the former despite the fact that NH_3 is more basic. The potential energy function for proton transfer from CH_3^+ to NH_3 therefore has the form of a double-well potential. The transition structure **TS7** separating the two minima **9** and **12** was also located, and this structure is found to be 4.7 kJ mol^{-1} higher in energy than **9**. The molecular structures of these species are depicted in Figure 1. In **TS7** the proton is seen to be closer to N than to C. Although the significance of the small energy differences calculated may be questioned, it is clear that there exists a very efficient route for proton transfer and that this may act as a mechanism for reversible proton exchange between the two partners within the complex.

5. Further Chemical Consequences of Hydrogen Bonding from the Methyl Cation. Not discussed here are calculations of a methyl cation where all three hydrogens are bridged to one water molecule each. The stabilization of the methyl cation obtained in this manner is substantial (on the order of 2-3 times the interaction energy of methyl and one water). For this reason, hydrogen bonding to surrounding solvent molecules must be considered important during many reactions where methyl cations are involved. One obvious example is nucleophilic displacement reactions of substrates where the central carbon atom belongs to a methyl group. These reactions are known to proceed either via transition structures where the central carbon atom transiently obtains local planarity ($\text{S}_{\text{N}}2$) or via intermediate carbocations ($\text{S}_{\text{N}}1$). The indicated interaction will stabilize these intermediates and transition structures relative to reactants and products. Such specific stabilization has previously been suggested to be important during nucleophilic substitution reactions in a crown ether environment.²³

If the oxygen atoms of the structure of Figure 3 instead of being parts of water molecules are parts of a rigid supramolecular framework (e.g., in zeolites), hydrogen-bonded methyl cations may even be the subject of direct observation. When the hydrogen bond acceptor sites are sufficiently basic (as they are known to be in zeolites²⁴), proton transfer from the methyl cation would lead to free singlet methylene molecules. Singlet methylene is known to insert directly into C-H bonds without activation energy.²⁵ This could provide a mechanism for the critical C-C bond formation step in Mobil's methanol-to-gasoline process.²⁶

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Supplementary Material Available: Figure showing the geometry-optimized structures (MP2/6-31G(d,p)) of the other minimum energy structures discussed (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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