

Structures and Dissociation Energies of the Complexes $\text{CH}_m\text{F}_n\cdots\text{NH}_4^+$ ($n + m = 4$, $n = 1-3$): An *ab Initio* Molecular Orbital Study

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Received: August 25, 1994; In Final Form: October 24, 1994[®]

Intermolecular hydrogen bonding interactions between C–F groups and positively charged N–H groups have been investigated. *Ab initio* molecular orbital calculations were used to determine the structures and dissociation energies of the complexes $\text{CH}_m\text{F}_n\cdots\text{NH}_4^+$ ($n + m = 4$, $n = 1-3$) at the MP2/6-31++G**//MP2/6-31++G** computational level. The value of ΔH°_{298} for the dissociation of the complex $\text{CH}_3\text{F}\cdots\text{NH}_4^+$, in which the orientation of the grouping C–F \cdots H–N is nearly linear, is found to be 13.5 kcal/mol. For $\text{CH}_2\text{F}_2\cdots\text{NH}_4^+$ and $\text{CHF}_3\cdots\text{NH}_4^+$, however, the dissociation energy per H \cdots F interaction drops significantly as the C–F \cdots H–N⁺ geometry becomes progressively less linear. Thus, near-linear interactions (C–F \cdots H–N) between C–F groups and positively charged N–H groups are sufficiently strong to play a role in the alignment of molecules in crystals and complexes, particularly if there are several such interactions per molecule and other stronger interactions are absent.

Introduction

Although intermolecular C–F \cdots H–X (X = C, N, O) interactions are relatively weak, several studies^{1–3} have clearly demonstrated that these interactions can play a significant role in aligning molecules in complexes and crystals, particularly if there are several such interactions per molecule. For example,³ in the crystal structure of the 11-trifluoro derivative of cyclopenta[*a*]phenanthren-17-one there are three C–F \cdots H–C interactions and one C=O \cdots H–C interaction per molecule, while for the corresponding 11-methyl derivative there is only a single C=O \cdots H–C interaction that can serve to orient the molecules. Both of these cyclopentaphenanthrenone compounds pack along the *b* axis. A graph-set analysis^{4–6} of the hydrogen bonds in the 11-trifluoro derivative clearly demonstrates that interactions involving two of the three fluorine atoms and one oxygen atom per molecule result in an infinite two-dimensional hydrogen-bond network throughout the crystal, while interactions with the third fluorine atom serve to connect the various layers of this network. In this way a novel three-dimensional network is created, one which is not found in the 11-methyl derivative that lacks C–F groups. The near linearity of many of these interactions provides further evidence that C–H \cdots O and C–H \cdots F interactions play a weak but significant role in the alignment of such molecules in crystals.³

The interaction of cations with C–F bonds has also been investigated.¹ It has been found that monovalent metal cations gather the fluorine atoms of C–F groups in their coordination spheres in the same way that they gather C=O, C–O[–], and C–OH groups around them.¹ The ammonium (or substituted ammonium) cation interacts in a similar way with C–F groups. It does, however, appear to prefer C–O over C–F groups; this is shown in Figure 1 for the X-ray diffraction study of the complex between (–)-methylbenzylamine and the monoethyl ester of (+)-*erythro*-fluorocitrate.¹ In this crystal structure the N–H group of the substituted ammonium cation forms a three-center hydrogen bond to both the fluorine and oxygen atoms

of the α -fluorocarboxylate group. This hydrogen bonding is unsymmetrical, as shown in Figure 1, in that the hydrogen atom of the N⁺–H group is closer to the oxygen than to the fluorine atom. This implies that the C–O \cdots H–N⁺ hydrogen bond is stronger than the C–F \cdots H–N⁺ hydrogen bond, but that the latter is certainly a valid interaction.

In order to better understand the strength of such weak intermolecular C–F \cdots H–X binding interactions, specifically when X = N⁺, we have carried out *ab initio* molecular orbital calculations on gas phase complexes of the form $\text{CH}_m\text{F}_n\cdots\text{NH}_4^+$ ($n + m = 4$, $n = 1-3$). We report the dissociation energies, atomic charges, and geometries of the C–F \cdots H–N interactions in all three complexes. Only one stable conformer of each of these structures could be found by these calculations, and in each case every available fluorine atom interacted with one of the hydrogen atoms of the ammonium cation. The results of similar calculations on the noncovalent complex $\text{CH}_4\cdots\text{NH}_4^+$ are also reported for comparison.

Computational Methods

All calculations were carried out on the CRAY computer at the National Cancer Institute using the GAUSSIAN 92 series of programs.⁷ Preliminary optimizations were performed at the restricted Hartree–Fock (RHF) level using the 6-31++G** basis set,^{8–10} which includes both polarization and diffuse functions on all the atoms. The need to use diffuse functions to predict dimer binding energies with accuracy for structures that include fluorine atoms is well-documented.¹¹ Final optimizations were all performed using second-order Møller–Plesset perturbation theory¹² at the MP2(FC)/6-31++G** level in order to include the effects of electron correlation. For the complexes $\text{CH}_4\cdots\text{NH}_4^+$ and $\text{CH}_3\text{F}\cdots\text{NH}_4^+$, vibrational frequencies were obtained from analytical second derivatives at the MP2(FC)/6-31++G**//MP2(FC)/6-31++G** level in order to verify that the computed structures were stable states and not transition states, as well as to calculate the thermal and entropy contributions to the dissociation energies.^{13–15} For the more computationally demanding complexes, $\text{CH}_2\text{F}_2\cdots\text{NH}_4^+$ and $\text{CHF}_3\cdots\text{NH}_4^+$, vibrational frequencies from analytical second derivatives could be obtained only at the RHF/6-31++G**//

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[®] Abstract published in *Advance ACS Abstracts*, December 15, 1994.

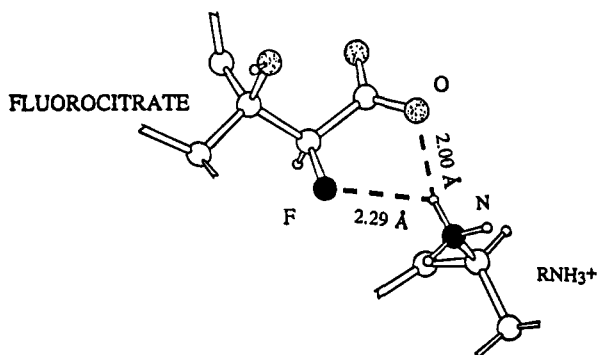


Figure 1. Interaction of a substituted ammonium (RNH_3^+ = methylbenzylammonium) ion with a fluorocitrate anion in the crystal structure of a salt.¹ The N–H group appears shared between the fluorine atom of the C–F and a C=O group in the α -fluorocarboxylate group, but the sharing is unequal, favoring N–H \cdots O over N–H \cdots F, as shown by the distances. F and N atoms are filled and O atoms stippled.

RHF/6-31++G** level. In several instances, fourth-order Møller–Plesset perturbation calculations at the MP4SDTQ(FC)/6-311++G**//MP2(FC)/6-31++G** level, and configuration interaction calculations including single and double substitutions with a triples contribution added to the energy at the QCISD(T)/6-311++G**//MP2(FC)/6-31++G** level were also performed to determine the extent to which higher level calculations alter the dissociation energies of these complexes.¹⁶ Corrections for basis set superposition errors (BSSE) have not been included in the calculations, since MP2 calculations without BSSE corrections often more closely reproduce experimental energy differences than do calculations with them.^{17–21} The reason for this is that the increase in binding energy due to BSSE may be comparable to that which would result from physical reasons (e.g., an improved description of the dispersion interaction), as the basis set becomes more complete.¹⁷

Results

The MP2(FC)/6-31++G** optimized geometries of CH_mF_n ($n + m = 4$, $n = 0–3$) and NH_4^+ are shown in Figure 2, and the corresponding geometries of the complexes $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 0–3$) are shown in Figure 3; complete details of the geometries can be found in the form of x , y , and z coordinates in Table 1S of the supplementary material. The total molecular energies, thermal corrections, and entropies of all the molecules shown in Figures 2 and 3 are listed in Table 1; the dissociation energies of the various complexes are presented in Table 2. Atomic charges from the MP2(FC)/6-31++G** generalized density based on the \mathbf{Z} vector,²² as well as charges fit to the electrostatic potential at points selected according to the CHELPG scheme of Breneman and Wiberg,²³ are also given in Figures 2 and 3. The computed vibrational frequencies are listed in Table 2S of the supplementary material.

$\text{CH}_4 \cdots \text{NH}_4^+$. The MP2(FC)/6-31++G** optimized structure of the complex $\text{CH}_4 \cdots \text{NH}_4^+$, **6**, is shown in Figure 3 and involves an interaction between a single hydrogen atom from the ammonium ion and two hydrogen atoms from methane. It should be noted that no symmetry constraints were employed during this optimization and that repeated attempts to find other stable conformers of $\text{CH}_4 \cdots \text{NH}_4^+$ using a variety of computational levels and symmetry constraints were not successful.²⁴ Both H \cdots H distances are computed to be relatively long, 2.010 Å, and a comparison of the geometrical parameters of this complex with those of the isolated molecule CH_4 , **1**, and ion NH_4^+ , **5**, shows relatively little perturbation of either molecule, suggesting a very weak interaction. An examination of the atomic charges based on the generalized MP2(FC)/6-31++G**

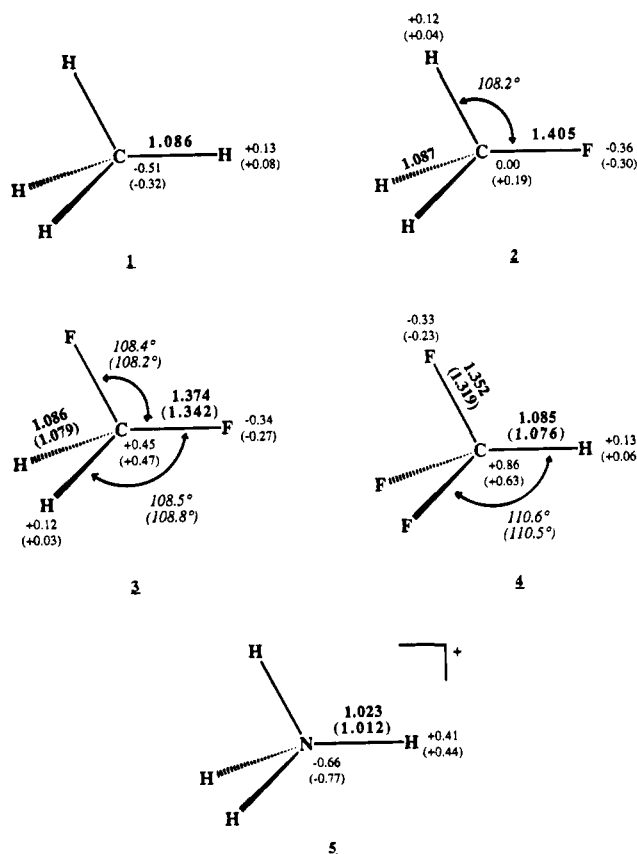


Figure 2. MP2(FC)/6-31++G**//MP2(FC)/6-31++G** optimized structures of CH_mF_n ($n + m = 4$, $n = 0–3$) and NH_4^+ . For several of the structures RHF/6-31++G**//RHF/6-31++G** geometrical parameters are also given in parentheses. Charges from the MP2(FC)/6-31++G** generalized density based on the \mathbf{Z} vector²² and, in parentheses, from a fit to the electrostatic potential using points selected by the CHELPG scheme of Breneman and Wiberg²³ are also shown.

electron density for $\text{CH}_4 \cdots \text{NH}_4^+$ shows a transfer of less than 0.1e to the ammonium cation, and the overlap population for each H \cdots H interaction is less than 0.05. As shown in Table 2, the value of ΔH°_{298} for the dissociation of the complex is only 1.9 kcal/mol at the MP2(FC)/6-31++G**//MP2(FC)/6-31++G** computational level, confirming that this is indeed a very weak complex. Higher level MP4SDTQ/6-311++G** and QCISD(T)/6-311++G** single point calculations at the MP2(FC)/6-31++G** optimized geometries only raise the dissociation energy of **6** by a few tenths of a kcal/mol, see Table 2. The value of ΔG°_{298} for dissociation of the complex is calculated to be positive, but only to the extent of +0.2 kcal/mol, and the experimental identification and characterization of this complex will present some interesting challenges. The shifts in the vibrational frequencies from the isolated species to those of the complex may help in the identification; calculated values are given in Table 2S of the supplementary material.

$\text{CH}_3\text{F} \cdots \text{NH}_4^+$. The MP2(FC)/6-31++G** optimized structure of the complex $\text{CH}_3\text{F} \cdots \text{NH}_4^+$, **7**, is shown in Figure 3 and involves the fluorine atom of methyl fluoride interacting with one hydrogen atom of the ammonium cation. No symmetry constraints were employed during the optimization. The C–F and H–N bonds are in a nearly linear arrangement in which the angles C–F \cdots H and F \cdots H–N are 156.3° and 166.0°, respectively; see Table 3. As shown in Figure 3, the H \cdots F distance in **7** is only 1.695 Å, significantly shorter than that found in the X-ray study of the complex between (–)-methylbenzylamine and the monoethyl ester of (+)-erythro-fluorocitrate,¹ 2.29 Å, suggesting a significant interaction. Furthermore, a comparison of the geometrical parameters of

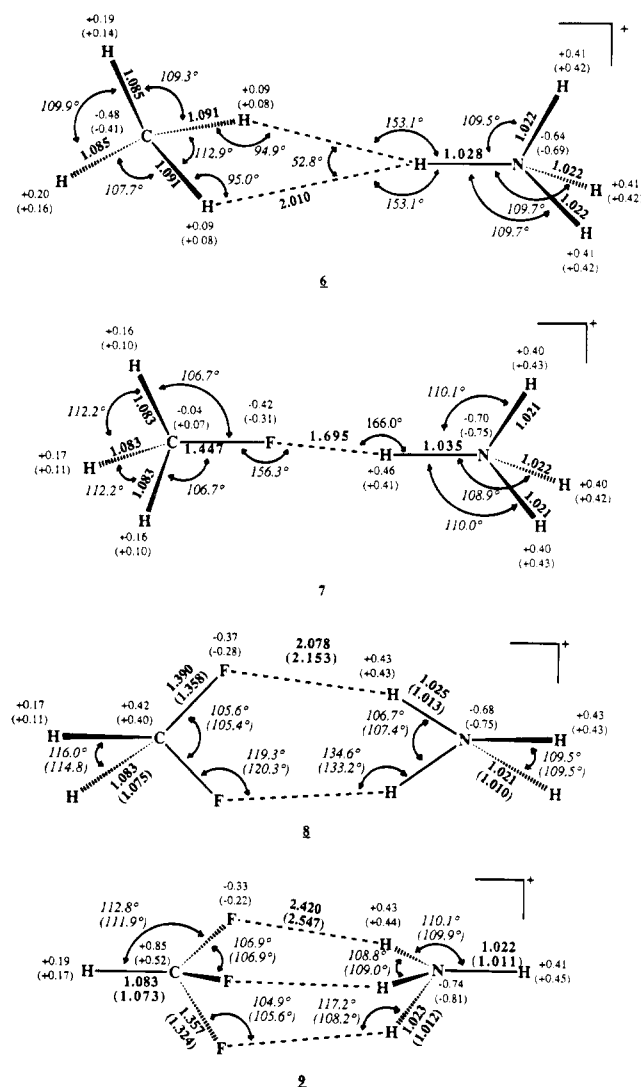


Figure 3. MP2(FC)/6-31++G**//MP2(FC)/6-31++G** optimized structures of $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 0-3$). For several of the structures RHF/6-31++G**//RHF/6-31++G** geometrical parameters are also given in parentheses. Charges from the MP2(FC)/6-31++G** generalized density based on the \mathbf{Z} vector²² and, in parentheses, from a fit to the electrostatic potential using points selected by the CHELPG scheme of Breneman and Wiberg²³ are also shown.

$\text{CH}_3\text{F} \cdots \text{NH}_4^+$ with those of the isolated molecule CH_3F , **2**, and the ion NH_4^+ , **5**, shows substantial changes to both; see Table 4. Of particular interest is the C-F bond, which increases in length by more than 0.04 Å in the formation of the complex; the increase in the N-H bond length is much less, only 0.012 Å. The value of ΔH°_{298} for the dissociation of the complex is calculated to be 13.5 kcal/mol at the MP2(FC)/6-31++G**//MP2(FC)/6-31++G** computational level, and higher level MP4SDTQ/6-311++G** and QCISD(T)/6-311++G** single point calculations at the MP2(FC)/6-31++G** optimized geometries only lower the computed dissociation energy by a few tenths of a kcal/mol, see Table 2. The computed charges show a transfer of less than 0.1e to NH_4^+ , but the H \cdots F overlap population is nearly 0.08.

$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$. The RHF/6-31++G** and MP2(FC)/6-31++G** optimized structures of the complex $\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$, **8**, constrained to have C_{2v} symmetry are shown in Figure 3. A frequency analysis at the RHF/6-31++G**//RHF/6-31++G** level found this C_{2v} form to be stable. An attempt at the MP2(FC)/6-31++G** level to find a second stable form of $\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$ starting with the near linear geometry of C-F \cdots H-N in $\text{CH}_3\text{F} \cdots \text{NH}_4^+$, **7**, and replacing one hydrogen

TABLE 1: Total Molecular Energies (hartrees), Sum of Thermal Corrections (hartrees), and Entropies (cal/(mol K)) for CH_mF_n ($n + m = 4$, $n = 0-3$), NH_4^+ , and $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 0-3$)

molecule	total energy ^a	Σ (thermal corrections)	entropy
CH_4 (1)	-40.366 113 -40.405 352 ^c -40.406 207 ^d	0.049 057	44.432
CH_3F (2)	-139.377 362 -139.475 997 ^c -139.475 243 ^d	0.049 057	53.226
CH_2F_2 (3)	-238.406 609	0.038 613 ^b	58.689 ^b
CHF_3 (4)	-337.444 946	0.031 096 ^b	61.632 ^b
NH_4^+ (5)	-56.734 618 -56.776 422 ^c -56.777 073 ^d	0.050 813 0.055 840 ^b	44.392 44.315 ^b
$\text{CH}_4 \cdots \text{NH}_4^+$ (6)	-97.106 940 -97.188 393 -97.189 847	0.103 977	82.969
$\text{CH}_3\text{F} \cdots \text{NH}_4^+$ (7)	-196.138 569 -196.278 488 -196.278 271	0.097 253	83.670
$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$ (8)	-295.164 375	0.097 379 ^b	83.841 ^b
$\text{CHF}_3 \cdots \text{NH}_4^+$ (9)	-394.194 385	0.089 752 ^b	95.772 ^b

^a Energy in hartrees computed at the MP2(FC)/6-31++G**//MP2(FC)/6-31++G** level. ^b Computed at the RHF/6-31++G**//RHF/6-31++G** level. ^c Energy in hartrees computed at the MP4SDTQ/6-311++G**//MP2(FC)/6-31++G** level. ^d Energy in hartrees computed at the QCISD(T)/6-311++G**//MP2(FC)/6-31++G** level.

TABLE 2: Dissociation Energies (kcal/mol) and Rate Constants (s^{-1}) of the Complexes $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 0-3$) Computed at the MP2(FC)/6-31++G//MP2(FC)/6-31++G** Level**

reaction	ΔE	ΔH°_{298}	ΔG°_{298}	k_{298}
$\text{CH}_4 \cdots \text{NH}_4^+ \rightarrow \text{CH}_4 + \text{NH}_4^+$	3.9 4.2 ^b 4.1 ^c	1.9	0.2	3.8×10^{11}
$\text{CH}_3\text{F} \cdots \text{NH}_4^+ \rightarrow \text{CH}_3\text{F} + \text{NH}_4^+$	16.7 16.4 ^b 16.3 ^c	13.5	9.4	7.2×10^4
$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+ \rightarrow \text{CH}_2\text{F}_2 + \text{NH}_4^+$	14.5	13.3 ^a	7.6 ^a	1.4×10^6
$\text{CHF}_3 \cdots \text{NH}_4^+ \rightarrow \text{CHF}_3 + \text{NH}_4^+$	9.3	8.1 ^a	5.1 ^a	3.0×10^6

^a Thermal corrections and entropies computed at the RHF/6-31++G**//RHF/6-31++G** level. ^b Computed at the MP4SDTQ/6-311++G**//MP2(FC)/6-31++G** level. ^c Computed at the QCISD(T)/6-311++G**//MP2(FC)/6-31++G** level.

TABLE 3: H \cdots F Distances (Å) and C-F \cdots H and N-H \cdots F Angles (deg) for the Complexes $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 1-3$) Calculated at the the MP2(FC)/6-31++G//MP2(FC)/6-31++G** Computational Level**

complex	H \cdots F	C-F \cdots H	N-H \cdots F
$\text{CH}_3\text{F} \cdots \text{NH}_4^+$	1.695	156.3	166.0
$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$	2.078	119.3	134.6
$\text{CHF}_3 \cdots \text{NH}_4^+$	2.420	104.9	117.2

atom attached to the carbon atom with a fluorine atom was not successful. The optimization again produced the structure **8**, in which both fluorine atoms interact with hydrogens on the ammonium cation. At the MP2(FC)/6-31++G** computational level, the H \cdots F distance in **8**, 2.078 Å, is nearly 0.4 Å longer in the monofluoro complex, **7** (see Table 3), but some 0.2 Å shorter than that observed in the complex between (-)-methylbenzylamine and the monoethyl ester of (+)-erythro-fluorocitrate shown in Figure 1.¹ The N-H bonds directly involved in the interactions are approximately 0.01 Å shorter than the corresponding N-H length in **7**. Furthermore, the C-F bond lengths in **7** have increased less than 0.02 Å compared to the corresponding bond lengths in the isolated molecule CH_2F_2 , **3**, significantly less than the corresponding increase observed in $\text{CH}_3\text{F} \cdots \text{NH}_4^+$. The computed C-F \cdots H and F \cdots H-N angles

TABLE 4: N-H and C-F Bond Lengths (Å) in the Complexes $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 1-3$) Compared to the Corresponding Bond Lengths in the Isolated Molecules CH_mF_n and Ion NH_4^+

complex	N-H distance in NH_4^+	N-H distance in complex ^a	C-F distance in CH_mF_n	C-F distance in complex ^a
$\text{CH}_3\text{F} \cdots \text{NH}_4^+$	1.023	1.035 (1.2)	1.405	1.447 (3.0)
$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$	1.023	1.025 (0.2)	1.374	1.390 (1.2)
$\text{CHF}_3 \cdots \text{NH}_4^+$	1.023	1.023 (0.0)	1.352	1.357 (0.4)

^a The percent increase in the N-H and C-F bond distances in the various complexes compared to their values in the isolated molecules or ions are given in parentheses.

are 119.3° and 134.6° , respectively, 37.0° and 31.4° less than the corresponding values found in 7.

These geometrical changes all suggest that each $\text{H} \cdots \text{F}$ interaction in the difluoro complex is significantly weaker than the corresponding interaction in the monofluoro complex. The value of ΔH°_{298} for the dissociation of $\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$, with two $\text{H} \cdots \text{F}$ interactions, is calculated to be 13.3 kcal/mol, 0.2 kcal/mol less than for $\text{CH}_3\text{F} \cdots \text{NH}_4^+$. Thus, each $\text{H} \cdots \text{F}$ interaction in the difluoro complex is approximately half the strength of the corresponding interaction in the monofluoro complex. Again, the computed charges show that relatively little charge is transferred to the ammonium cation (see Figure 5), and each $\text{H} \cdots \text{F}$ overlap population has dropped to approximately 0.03. Interestingly, if the two hydrogen atoms bonded to the carbon atom in $\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$ are replaced by fluorine atoms, and the $\text{CF}_4 \cdots \text{NH}_4^+$ complex is reoptimized at the RHF/6-31++G** level within a C_{2v} symmetry constraint, a frequency analysis shows that the resulting structure is not stable, but a first-order transition state. The computed $\text{H} \cdots \text{F}$ distances are 2.418 Å, approximately 0.26 Å longer than the corresponding distances in the difluoro complex, suggesting a much weaker $\text{H} \cdots \text{F}$ interaction in $\text{CF}_4 \cdots \text{NH}_4^+$.

$\text{CHF}_3 \cdots \text{NH}_4^+$. The RHF/6-31++G** and MP2(FC)/6-31++G** optimized structures of the complex $\text{CHF}_3 \cdots \text{NH}_4^+$, 9, constrained to have C_{3v} symmetry are shown in Figure 3. A frequency analysis at the RHF/6-31++G**//RHF/6-31++G** level found this C_{3v} form to be stable. No attempts to look for other stable conformations of this complex were made. At the MP2(FC)/6-31++G** level, the calculated $\text{H} \cdots \text{F}$ distances are 2.420 Å, more than 0.3 Å longer than the calculated $\text{H} \cdots \text{F}$ distances in the difluoro complex and over 0.7 Å longer than that calculated in the monofluoro complex; see Table 3. In fact, this $\text{H} \cdots \text{F}$ distance is 0.13 Å longer than the corresponding distance in the complex between (–)-methylbenzylamine and the monoethyl ester of (+)-erythro-fluorocitrate, in which there is a competing $\text{H} \cdots \text{O}$ interaction.¹ The calculated N-H and C-F bond lengths are less than 0.001 Å and 0.007 Å greater than their values in the isolated molecule CHF_3 , 4, and ion NH_4^+ , 5; see Table 4. The calculated C-F \cdots H and N-H \cdots F angles are only 104.9° and 117.2° , respectively, 14.4° and 17.4° smaller than the corresponding values in the difluoro complex.

These geometrical features suggest each $\text{H} \cdots \text{F}$ interaction is relatively weak. The value of ΔH°_{298} for the dissociation of $\text{CHF}_3 \cdots \text{NH}_4^+$, 9, is calculated to be 8.1 kcal/mol. Thus, each $\text{H} \cdots \text{F}$ interaction contributes only 2.7 kcal/mol to the overall binding energy of the complex, which is only 20% of the strength of the $\text{H} \cdots \text{F}$ interaction in $\text{CH}_3\text{F} \cdots \text{NH}_4^+$, 7. The charge transferred to the NH_4^+ is less than 0.04e, and each $\text{H} \cdots \text{F}$ overlap population is less than 0.01. If the hydrogen atom bonded to the carbon atom in $\text{CHF}_3 \cdots \text{NH}_4^+$ is replaced by a fluorine atom and the $\text{CF}_4 \cdots \text{NH}_4^+$ complex is reoptimized at the RHF/6-31++G** level with a C_{3v} symmetry constraint, a

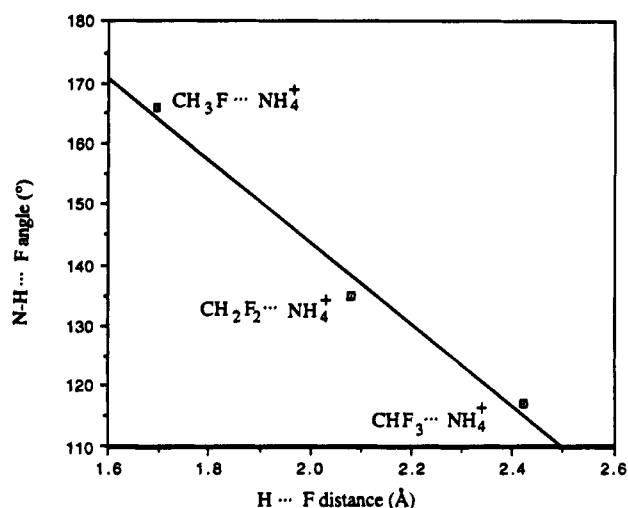


Figure 4. Graph showing the nearly linear relationship between the N-H \cdots F angles (deg) and the H \cdots F distances (Å) in the complexes $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 1-3$). The equation of the line is $Y = 279.4 - 67.852X$, where Y is the N-H \cdots F angle and X is the H \cdots F distance.

frequency analysis shows that the resulting structure is not stable, but a second-order transition state. The computed $\text{H} \cdots \text{F}$ distance is 2.816 Å, significantly longer than the corresponding value in $\text{CHF}_3 \cdots \text{NH}_4^+$, 2.547 Å, suggesting a much weaker interaction. It thus seems quite likely that the structures of complexes of the form $\text{CX}_n\text{F}_m \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 1-3$) can depend dramatically on the specific substituent X. In Figure 4 the value of the N-H \cdots F angle is plotted as a function of the H \cdots F distance for the mono-, di-, and trifluoro complexes. The relationship is nearly linear over the range of H \cdots F distances from ~ 1.7 to 2.4 Å, and the slope is approximately $68^\circ/\text{Å}$.

Discussion

Complexes of the ammonium ion with CH_4 , CH_3F , CH_2F_2 , and CHF_3 are weak, but stable, at room temperature with ΔG°_{298} values of +0.2, +9.4, +7.6, and +5.1 kcal/mol, respectively. The complex of NH_4^+ with CH_4 is certainly much weaker than that with any of the fluorocarbons. Although there is only a rather limited transfer of electrons to the ammonium ion in any of the fluorocarbon complexes, there is clear evidence of an $\text{H} \cdots \text{F}$ interaction in the lengthening of the C-F and N-H bonds in these complexes, compared with the corresponding lengths in the isolated molecules; see Table 4. This is particularly evident in the monofluoro complex, $\text{CH}_3\text{F} \cdots \text{NH}_4^+$, in which the N-H bond directly involved in the interaction is lengthened by 1.2% and the C-F bond by 3.0%.

All the stable conformers of the NH_4^+ complexes with CH_3F , CH_2F_2 , and CHF_3 we found in this study involved every available fluorine atom interacting with one of the hydrogen atoms of the ammonium cation, with no $\text{H} \cdots \text{H}$ interactions. This results in a structure for $\text{CH}_3\text{F} \cdots \text{NH}_4^+$ in which the C-F \cdots H-N grouping is nearly linear, whereas the structures for $\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$ and $\text{CHF}_3 \cdots \text{NH}_4^+$ necessarily involve progressively larger deviations of the angles C-F \cdots H and N-H \cdots F from 180.0° . At the MP2(FC)/6-31++G**//MP2(FC)/6-31++G** computational level, the dissociation energy per $\text{H} \cdots \text{F}$ interaction is calculated to be the largest, $\Delta H^\circ_{298} = 13.5$ kcal/mol, and the $\text{H} \cdots \text{F}$ distance is calculated to be the smallest, 1.695 Å, for the near-linear arrangement of the C-F and N-H bonds in the monofluoro complex, $\text{CH}_3\text{F} \cdots \text{NH}_4^+$. As the number of fluorine acceptors increases in the complexes

$\text{CH}_2\text{F}_2 \cdots \text{NH}_4^+$ and $\text{CHF}_3 \cdots \text{NH}_4^+$, however, the $\text{H} \cdots \text{F}$ distances increase dramatically to 2.078 Å and 2.420 Å, respectively, while the dissociation energy per $\text{H} \cdots \text{F}$ interaction drops substantially to 6.7 and 2.7 kcal/mol, respectively.

Thus, it has been found in the *ab initio* molecular orbital calculation that when the C–F and $\text{N}^+ \cdots \text{H}$ bonds in $\text{C}-\text{F} \cdots \text{H}-\text{N}^+$ are nearly collinear, the $\text{H} \cdots \text{F}$ interaction is near its optimal value with respect to geometry and energy. Such interactions may play a significant role in the alignment of molecules in complexes and crystals, particularly if there are several such interactions per molecule and no other stronger interactions are available that can distort this relatively weak binding. This is in line with X-ray diffraction results involving the related $\text{C}-\text{F} \cdots \text{H}-\text{C}$ interactions in the 11-trifluoro derivative of cyclopenta[*a*]phenanthren-17-one,³ in which the C–F group forms nearly linear interactions with a C–H group.

Finally, in order to compare the strengths of the $\text{C}-\text{F} \cdots \text{H}$ and $\text{C}-\text{Cl} \cdots \text{H}$ interactions, the Cambridge Structural Database (CSD)²⁵ was searched for compounds involving either $-\text{CCl}_3 \cdots \text{H}$ or $-\text{CF}_3 \cdots \text{H}$ interactions. For the chlorine compounds the mean $\text{H} \cdots \text{Cl}$ bond distance was found to be 2.3(1) Å, while for the fluorine structures the mean $\text{H} \cdots \text{F}$ bond distance was much longer, 2.6(1) Å, despite the fact that a chlorine atom is significantly larger than a fluorine atom. Clearly, $\text{C}-\text{F} \cdots \text{H}$ interactions are generally much much weaker than $\text{C}-\text{Cl} \cdots \text{H}$ interactions.

Acknowledgment. We thank the Advanced Scientific Computing Laboratory, NCI-FCRF, for providing time on the Cray Y-MP supercomputer. This work was supported by grants CA-10925 (to J.P.G.) and CA-06927 (to I.C.R.) from the National Institutes of Health and by an appropriation from the Commonwealth of Pennsylvania.

Supplementary Material Available: Two tables listing *x*, *y*, and *z* coordinates and frequencies and symmetry assignments of CH_mF_n ($n + m = 4$, $n = 0-3$), NH_4^+ , and $\text{CH}_m\text{F}_n \cdots \text{NH}_4^+$ ($n + m = 4$, $n = 0-3$) (3 pages). Ordering information is given on any current masthead page.

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JP942289A