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Computational investigation of $CH_{3-n}X_n^+$–NH_3 (n = 0–3; X = F, Cl, and Br) interactions

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Abstract

The $CH_{3-n}X_n^+$—NH_3 (n = 0–3; X = F, Cl, and Br) donor–acceptor complexes were investigated at the G2MP2 level of theory. The G2MP2 results show that the successive fluorine, chlorine, and bromine substitution on the carbon decreases the stability of $CH_{3-n}F_n^+$—NH_3, $CH_{3-n}Cl_n^+$—NH_3, and $CH_{3-n}Br_n^+$—NH_3 complexes. The NBO partitioning scheme shows that elongation of C—F, C—Cl, and C—Br bond lengths upon complexation may be attributed to a decrease in the “s” character of these bonds. It also shows that there is no correlation between charge transfer and the complexation energy.

Keywords: Donor–acceptor; Complexes; G2MP2; Charge transfer; Stability

1. Introduction

Intermolecular forces play a key role in a variety of important phenomena in chemical physics as well as in bio-disciplines [1,2]. Ionic complexes isolated in the gas phase may serve as attractive model systems for studying the ion–ligand interaction potentials from both experimental and theoretical viewpoints. The combination of high-resolution spectroscopic techniques with contemporary quantum-chemical approaches has provided a rather detailed knowledge of the intermolecular potential energy surfaces (PESs) of a variety of small dimers and trimers [3]. Recently, the interaction between fluorinated methyl cations (CF_3^+, CH_2F^+) and alkyl nitrile cluster ions was studied by Alvarez et al. [4]. To the best of our knowledge, there is no comprehensive comparative study of the interaction between halogenated methyl cations (super Lewis acids) and electron donor moieties in the literature. This has motivated us to perform a computational investigation of the ion–molecule donor–acceptor complexes formed between halogenated methyl cations with ammonia in the present study. Very recently we have also reported a computational study of the CH_3^+—$NH_{3-n}X_n$ (n = 0–3; X = F and Cl) interactions [5]. This paper may be regarded as a subsequent part of our previous investigations of the structure and stability of ion–molecule donor–acceptor complexes. In this work, we report the results from our investigation of the $CH_{3-n}X_n^+$—NH_3 (n = 1–3; X = F, Cl, and Br) donor–acceptor complexes at the G2MP2 level of theory. The electronic structure of these complexes was analysed and also the relative stabilities of various molecular species considered were examined.

2. Computational details

All ab initio calculations in the present study were performed using GAUSSIAN98 series of programs [6]. Geometry optimisations were performed at the MP2(full)/6-31G(d) level of theory; the zero-point vibrational energies (ZPE) were obtained from the HF/6-31G(d) harmonic vibrational frequencies (scaled by a factor of 0.893) [7]. G2MP2 [8]

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calculations were subsequently carried out for the optimised geometries at MP2(full)/6-31G(d) level of theory, in order to study the energetics of the systems considered. The charge distribution in the complexes was analysed employing the natural bond orbital (NBO) [9] partitioning scheme at the MP2(full)/6-31G(d) level of theory. Atomic populations obtained from this analysis have been shown to be much less basis set dependent than those obtained from the Mulliken population analysis [10]. On other hand, we did not correct the energies for the basis set superposition errors (BSSE), which are expected to be relatively small at the employed level of theory, since the rather large basis set – 6-311 + G(3df,2p) – was used. Thus, the BSSE is expected to have just a negligible effect on the calculated complexation energies [10,11].

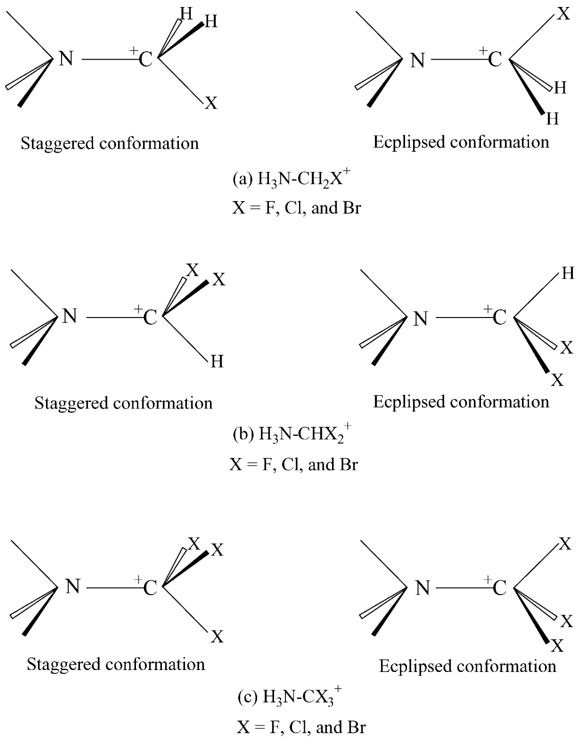

Fig. 1. Definition and numbering schemes of the geometrical parameters of: (a) $H_3C^+{-}NH_2X$, (b) $H_3C^+{-}NHX_2$, and (c) $H_3C^+{-}NX_3$ (X = F, Cl, and Br) complexes in staggered and eclipsed conformations.

3. Results and discussion

First, we have investigated the two possible structures (staggered and eclipsed conformations) for all complexes of the $CH_{3-n}X_n^+{-}NH_3$ type (n = 0–3; X = F, Cl, and Br) at the RHF/6-31G(d) level of theory (Fig. 1). From calculated frequencies for these optimised geometries, the staggered optimised conformations were characterised as minima and the eclipsed ones were characterised as transition structures (first order saddle points on the PESs) in the case of all complexes considered. All the structures corresponding to minima were reinvestigated at the MP2(full)/6-31G(d) level of theory. The fully optimised geometry parameters (within the C_{3v} symmetry for $CX_3^+{-}NH_3$ and C_s symmetry for $CH_2X^+{-}NH_3$ and $CHX_2^+{-}NH_3$ complexes) for all species studied in this work are given in Table 1. In Table 2, the calculated 2s contributions of carbon atoms in the C−F, C−Cl, and C−Br bonds using the NBO partitioning scheme at the MP2(full)/6-31G(d) level of theory are shown. In Table 3, the calculated complexation energies of $CH_{3-n}X_n^+{-}NH_3$ (n = 0–3; X = F, Cl, and Br) complexes at G2MP2 level are given. The NBO-MP2(full)/6-31G(d) charge transfers from

Table 1
Selected optimised bond lengths (Å) and bond angles (deg) of free $CH_{3-n}X_n^+$ (n = 0–3, X = F, Cl, and Br) cations and corresponding complexes with NH_3

Species	C−N	N−H	C−X	C−H	∠H−C−N	∠X−C−X	∠X−C−H	∠H−C−H
NH_3		1.017						
$CH_3{}^+$				1.089				120.0
CH_2F^+			1.242	1.090			116.9	126.1
CHF_2^+			1.243	1.092		118.2	120.9	
CF_3^+			1.245			120.0		
CH_2Cl^+			1.588	1.090			119.3	121.3
$CHCl_2{}^+$			1.621	1.091		124.2	117.9	
CCl_3^+			1.647			120.0		
CH_2Br^+			1.740	1.089			119.2	121.6
$CHBr_2^+$			1.779	1.091		124.3	117.9	
CBr_3^+			1.810			120.0		
$CH_3^+{-}NH_3$	1.509	1.028			108.2			
$CH_2F^+{-}NH_3$	1.513	1.030	1.353	1.089	108.1		111.4	112.8
$CHF_2^+{-}NH_3$	1.517	1.031	1.330	1.090	110.3	111.5	112.2	
$CF_3^+{-}NH_3$	1.517	1.033	1.316			111.0		
$CH_2Cl^+{-}NH_3$	1.512	1.031	1.741	1.089	107.4		111.0	111.1
$CHCl_2^+{-}NH_3$	1.519	1.033	1.741	1.090	106.9	114.7	110.1	
$CCl_3^+{-}NH_3$	1.528	1.033	1.746			112.6		
$CH_2Br^+{-}NH_3$	1.508	1.032	1.916	1.088	108.2		110.2	111.8
$CHBr_2^+{-}NH_3$	1.512	1.033	1.915	1.089	108.1	114.1	110.0	
$CBr_3^+{-}NH_3$	1.519	1.034	1.922			112.4		

Table 2
2s MP2-NBO contributions of carbon atoms in the C—F, C—Cl, and C—Br bonds (%)

Species	$2s_{(C-F)}$	Species	$2s_{(C-Cl)}$	Species	$2s_{(C-Br)}$
CH_2F^+	26.27	CH_2Cl^+	29.58	CH_2Br^+	28.62
CHF_2^+	28.94	$CHCl_2{}^+$	31.36	$CHBr_2{}^+$	30.88
CF_3^+	33.29	$CCl_3{}^+$	33.27	$CBr_3{}^+$	33.29
CH_2F^+—NH_3	21.13	CH_2Cl^+—NH_3	22.60	CH_2Br^+—NH_3	22.97
CHF_2^+—NH_3	22.84	$CHCl_2^+$—NH_3	24.13	$CHBr_2^+$—NH_3	20.80
CF_3^+—NH_3	25.32	CCl_3^+—NH_3	25.86	CBr_3^+—NH_3	25.36

the NH_3 Lewis base to $CH_{3-n}X_n^+$ (n = 0–3; X = F, Cl, and Br) Lewis acids (Q_t) are presented in Table 3. The complexation energies are calculated as energy differences between the donor–acceptor complexes and the respective monomeric species.

As it may be concluded From Table 1, there is a small distortion of the N–H and C–H bond lengths upon complexation. Moreover, the present calculations also predict a lengthening of the C–X bonds. This is in agreement with the natural bond orbital analysis-derived results for these bonds (Table 2). Indeed, the NBO-MP2(full)/6-31G(d) calculations show that in the case of isolated $CH_{3-n}X_n^+$ (n = 1–3; X = F, Cl, and Br) moieties the acceptor “C” atom has a larger “s” character in comparison to the situation in the complexes. Hence, we can deduce from these results that this change alone would imply a lengthening of the bond length due to the decrease “s” character of these bonds. Table 2 shows that the 2s atomic orbital (AO) contributions of C in the C–X bond lengths are more important in $CH_{3-n}X_n^+$ (n = 1–3; X = F, Cl, and Br) moieties than $CH_{3-n}X_n^+$–NH_3 complexes. So, one can straightforwardly understand why there is an elongation of the C–X bond length upon complexation in all of the presently studied cases. On the other hand, we can observe from Table 1 that the C–X bond length of $CH_{3-n}F_n^+$–NH_3 series decreases as n goes from 1 to 3. This irregular trend is due to C^-–F^+ electrostatic attraction which increase as n goes from 1 to 3. Indeed, the NBO analysis shows that the electrostatic attraction increases since the net atomic charge increases on going from CFH_2^+–NH_3 ($d_{C\text{–}F}$ = 1.353 Å, q_C = 0.21 e, and q_F = −0.33 e) to CHF_2^+–NH_3 ($d_{C\text{–}F}$ = 1.330 Å, q_C = 0.793 e, and q_F = −0.33 e), and to CF_3^+–NH_3 ($d_{C\text{–}F}$ = 1.316 Å, q_C = 0.1.302 e, and q_F = 0.31 e)

Regarding the ∠X(H)–C–X(H) bond angles, it is worth noting that there is no notable deviation of these parameters going from isolated $CH_{3-n}X_n^+$ species to the $CH_{3-n}X_n^+$–NH_3 complexes. This bond angle in fact decreases only slightly (∼ 7–10 degrees) in going from the isolated $CH_{3-n}X_n^+$ (n = 1–3; X = F, Cl, and Br) ligands to the complex adducts of the $CH_{3-n}X_n^+$–NH_3 type.

The G2MP2 calculated complexation energies of CH_3^+–$NH_{3-n}X_n$ (n = 0–3; X = F, Cl, and Br) reported in Table 3, show that the successive fluorine, chlorine, and bromine substitution in the CH_3^+ moiety leads to a decrease in the acidity, which is indeed reflected in the stability of the corresponding complexes. Upon halogen substitution on central atom (C) of the acceptor fragment, the complexation energy decreases. This effect is slightly more important when substitution with bromine occurs. Indeed, the bromine substitution destabilises the complexes by ∼38, ∼55, and ∼65 kcal/mol in the case of CH_2Br^+–NH_3, $CHBr_2^+$–NH_3, and $CHBr_3^+$–NH_3, respectively. The chlorine substitution destabilises the complexes by ∼36, ∼52, and ∼62 kcal/mol in the case of CH_2Cl^+–NH_3, $CHCl_2^+$–NH_3, and $CHCl_3^+$–NH_3, respectively. The fluorine substitution destabilises the complex by ∼24, ∼34, and ∼29 kcal/mol for CH_2F^+–NH_3, CHF_2^+–NH_3, and CHF_3^+–NH_3, respectively. To summarize, in the series with the fluorine substitution there is a general trend of decreasing complexation energies upon substitution, but in this case the trend is broken since CF_3–NH_3 has larger complexation energy than its congenial CHF_2^+–NH_3 species. We suggest that the unusual destabilisation of the CHF_2^+–NH_3 complex is due to F–F repulsion, since the F–F bond becomes shorter and the net atomic charge increases on going from CF_3–NH_3 ($d_{F\text{–}F}$ = 2.181 Å, q_F = −0.31 e) to CHF_2^+–NH_3 ($d_{F\text{–}F}$ = 2.013 Å, q_F = −0.33 e). The same trend has been recently observed in the $H_3BPH_{3-n}F_n$ type (n = 0–3) complexes [12] as well.

On the other hand, one can see, from the NBO-MP2(full)/6-31G(d) analysis (Table 3), that there is no correlation between charge transfer and the complexation energy. For all the complexes, the charge transferred is about 0.66 e, while the complexation energy decreases when descending

Table 3
G2MP2 complexation energies (E_c) (kcal/mol) of $CH_{3-n}X_n^+$—NH_3 (n = 0–3; X = F, Cl, and Br) complexes, and NBO charge transferred Q_t (electron) from NH_3 to $CH_{3-n}X_n^+$

Complexes	E_c	Q_t	Complexes	E_c	Q_t	Complexes	E_c	Q_t
CH_3^+—NH_3	−102.50	0.66	CH_3^+—NH_3	−102.50	0.66	CH_3^+—NH_3	−102.50	0.66
CH_2F^+–NH_3	−78.65	0.63	CH_2Cl^+–NH_3	−66.70	0.66	CH_2Br^+–NH_3	−64.40	0.66
CHF_2^+—NH_3	−68.47	0.63	$CHCl_2^+$—NH_3	−50.46	0.66	$CHBr_2^+$—NH_3	−47.82	0.66
CF_3^+—NH_3	−73.77	0.64	CCl_3^+—NH_3	−40.91	0.66	CBr_3^+—NH_3	−37.08	0.66

in the corresponding periodic table column, from fluorine to bromine atoms, and with the degree of halide substitution at the carbon atom.

4. Conclusion

The substitution effects on complexation of ammonia with halogenated methyl cations were investigated at the G2MP2 level of theory. The G2MP2 results show that the stability of the $NH_3–CH_{3-n}X_n^+$ (n = 0–3; X = F, Cl, and Br) complexes decreases with the degree of halide substitution at the carbon atom. Upon complexation, the MP2(full)/6-31G(d) calculated structural parameters of $NH_3–CH_{3-n}X_n^+$ complexes show elongation of C–X (X = F, Cl, and Br) bonds. The analysis of the electronic densities using the NBO partitioning scheme shows that this change is related to the “s” character in these bonds.

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