Computational Investigation of $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) Interactions

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The $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) acceptor−donor complexes have been investigated at the G2MP2 level of theory. The G2MP2 results show that the successive fluorine and chlorine substitution on the nitrogen decreases the stability of $SO_3-NH_{3-n}F_n$ and $SO_3-NH_{3-n}Cl_n$ complexes, in accord with the decreasing basicity of the $NH_{3-n}F_n$ and $NH_{3-n}Cl_n$ ligands. The natural bond orbital (NBO) partitioning schemes show that the shortening of the N−F and N−Cl bond lengths, upon complexation, is due to an increasing “s” character in these bonds.

1. Introduction

It is beyond any doubt that the noncovalent intermolecular interactions are of crucial importance in contemporary chemical physics.[1] The “van der Waals molecules” formed by these interactions are significant in their own right, as they bridge the gap between the free molecular systems and the corresponding condensed phases they form. On the other hand, the noncovalently bonded molecular clusters are of certain practical importance in many areas of applied science, such as atmospheric chemistry, catalysis, and in biochemically relevant processes. It is thus particularly interesting to study such noncovalently bonded clusters in controlled laboratory conditions. Fundamental understanding of the structures and other relevant binding properties of such clusters, however, requires a close cooperation between the most sophisticated experimental and theoretical approaches. In most cases, the experimental detection of the existence of a particular intermolecular interaction is based on indirect spectroscopic data. Thus, besides the more thorough theoretical basis for the interpretation of spectroscopic manifestations of the intermolecular interactions that are crucial for detection of the clusters in question, contemporary theoretical methods may also initiate experimental searches for particular complexes or clusters that have not been previously studied by providing relevant theoretical data for the thermodynamical stability and the various spectroscopic properties of the noncovalent complexes. Previously, we have reported studies of various intermolecular interactions.[2−7] Recently, theoretical studies of noncovalently bonded complexes of SO_3 with HO_2,[6] CH_3X (X = F, Cl, Br),[7] HX (X = F, Cl, Br),[8] CO_2,[9] HCN and CH_3CN,[10] $(H_2O)_n$ ($n = 1-3$),[11−18] NH_3,[19] and C_5H_5N[20] have been reported in the literature. In continuation of our work, we report the results from our investigation of the $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) acceptor−donor complexes at the G2MP2 level of theory. The electronic structure of these complexes was analyzed and the relative stabilities of various molecular species considered were also examined. To the best of our knowledge, the formation of the complexes of sulfur trioxide with $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) ligands has not yet been determined theoretically or experimentally. This has motivated a search for the structure and stability of the title complexes in the present study.

2. Computational Details

Ab initio calculations were performed using the GAUSSIAN98 program.[21] Geometry optimizations were performed for the SO_3-NH_3 complex at the MP2 and B3LYP levels starting from the 6-31G(d) and 6-311++G(d,p) basis sets up to 6-311++G(2df,2pd) and aug-cc-pVTZ basis sets, respectively. The zero point vibrational energies (ZPE) were obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[22] In higher level calculations we computed the energies at the G2(MP2) level of theory.[23] On the other hand, we did not correct for the basis set superposition errors (BSSE), which should be relatively small with a large basis set such as 6-311+G(3df,2p) and have little effect on the calculated complexation energies.[24,25] The NBO[26] method was also used for analysis of the electronic structure of complexes.

3. Results and Discussion

First, we have investigated the two possible structures (staggered and eclipsed conformations) for all $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) complexes at the RHF/6-31G(d) level of theory (Figure 1). From calculated frequencies on the optimized geometries, the staggered optimized conformations were characterized as minima and the eclipsed ones were characterized as transition structures for all complexes. All the minima structures have been reinvestigated at the MP2(full)/6-31G(d) level of theory. To validate

our level of calculation, we report in Table 1 the optimized geometries (C_{3v} symmetry) of the prototypical acceptor−donor complex SO_3-NH_3 at various levels of theory and various basis sets, along with experimental determination. At all levels of theory, the calculated value of the S−N bond length increases in the eclipsed conformation, which represents a local maximum

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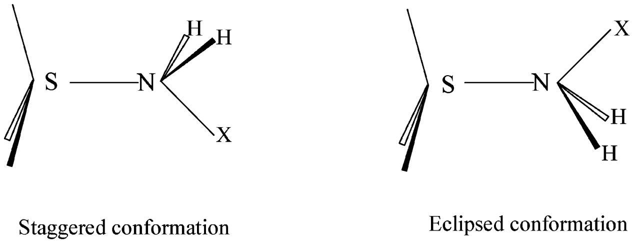
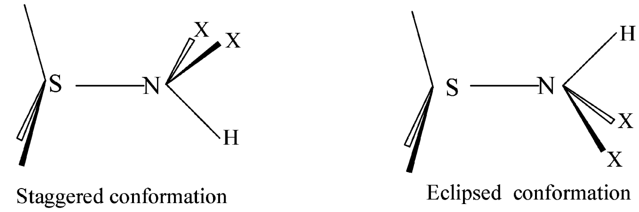
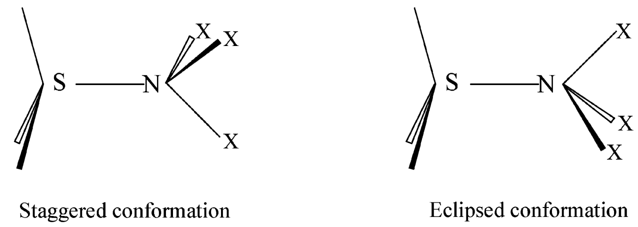


(a) SO_3-NH_2X
X = F, Cl



(b) SO_3-NHX_2
X = F, Cl



(c) SO_3-NX_3
X = F, Cl

Figure 1. Schemes of the geometrical structures of $SO_3-NH_{3-n}X_n$ (X = F, Cl) complexes in staggered and eclipsed conformations.

TABLE 1: Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of the NH_3-SO_3 Complex at Various Level of Theory

method	S−N	S−O[a]	N−H	−O−S−N
MP2(full)/6-31G(d)	2.081	1.457	1.021	96.21
	2.121	1.457	1.020	96.22
MP2(full)/6-311++G(d,p)	2.120	1.448	1.017	96.39
	2.179	1.447	1.017	95.94
MP2/6-311++G(2df,2pd)	2.008	1.437	1.014	96.92
	2.042	1.437	1.014	96.89
B3LYP/6-311++G(d,p)	2.131	1.453	1.017	96.60
	2.170	1.452	1.017	96.45
B3LYP/6-311++G(3df,3pd)	2.047	1.432	1.015	97.04
	2.080	1.432	1.014	97.01
B3LYP/aug-cc-pVTZ	2.088	1.446	1.014	96.85
	2.116	1.443	1.014	96.86
experimental[b]	1.957			97.6

[a] Second value corresponds to the eclipsed conformation. [b] Microwave spectroscopy from Larson et al.[13]

on the torsional potential. Thus, the MP2(full)/6-31G(d) optimized structures are reliable to study the present acceptor−donor complexes. Completely optimized geometries (C_{3v} symmetry for the SO_3-NH_3 and SO_3-NX_3 complexes and C_s symmetry for the SO_3-NH_2X and SO_3-NHX_2 complexes) for all species studied in this work are given in Table 2. In Table 3, we give the calculated complexation energies of the $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) complexes at the G2MP2 level. The complexation energies are calculated as the energy difference between the acceptor−donor complex and the respective moieties. In Table 3, we also give the proton affinities of $NH_{3-n}X_n$ moieties and the NBO-MP2(full)/6-31G(d) transferred charge from $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) Lewis bases to an SO_3 Lewis acid (Q_t). The proton affinities (PA) are taken as the energy difference between the neutral and protonated $NH_{3-n}X_n$ Lewis bases. In Table 4, we have reported the 2s calculated contributions of nitrogen atoms in the N−H, N−F, and N−Cl bonds using the NBO partitioning scheme at the MP2(full)/6-31G(d) level of theory.

From Table 2, it is relevant that small changes in the N−H and N−X bond distances result from halogen substitution in NH_3. Upon complexation, the MP2 calculation shows a small distortion for the N−H and N−X bond lengths. Moreover, this calculation predicts a shortening of the N−X bond length upon complexation (Table 2). To explain the bonding situation in the sulfur trioxide complexes, we applied the NBO analysis on these bonds (Table 4). The NBO-MP2(full)/6-31G(d) analysis shows that in isolated $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) moieties the lone pair on the donor atom “N” has lower “s” character than in the complexes. Hence, we can deduce from these results that this change alone would imply a shortening of the bond length due to the increased “s” character in these bonds. Table 4 shows that the 2s atomic orbital (AO) contributions of N in the N−X bond lengths are more important in $SO_3-NH_{3-n}X_n$ complexes than $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) moieties. Then, we can understand why we had a shortening of the N−X bond length.

In addition to the shortening of the N−X bond upon complexation, we can observe from Table 2 that the S−N bond length of the SO_3-NH_2X complex series increases as X goes from F to Cl, but the S−N bond length of SO_3-NX_2H and the SO_3-NX_3 complexes series decreases as X goes from F to Cl. This irregular trend is due to $S^{+}-N^{+}$ electrostatic repulsion in the SO_3-NF_2H and SO_3-NF_3 complexes and to $S^{+}-N^{-}$ electrostatic attraction in the SO_3-NCl_2H and SO_3-NCl_3 complexes. Indeed, the NBO analysis shows that the net atomic charge of S and X (X = F, Cl) are $q_S = 2.369$ e and $q_N = 0.107$ e for the SO_3-NF_2H complex, $q_S = 2.390$ e and $q_N = -0.725$ e for the SO_3-NCl_2H complex, $q_S = 2.343$ e and $q_N = 0.649$ e for the SO_3-NF_3 complex, and $q_S = 2.366$ e and $q_N = -0.565$ e for SO_3-NCl_3 complex.

On the other hand, the bond angle ∠O−S−N varies slightly in going from the SO_3 free moiety to the $SO_3-NH_{3-n}X_n$ complexes. This has a consequence for the S geometrical environment, which passes from D_{3h} (flat) in free SO_3 to slightly pyramidal in the complexes. For the bond angles ∠X(H)−N−X(H), we note that no notable deviation is observed in going from isolated $NH_{3-n}X_n$ to $SO_3-NH_{3-n}X_n$ complexes. One can see that this bond angle increases slightly in going from the isolated $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) ligands to the complex adducts $SO_3-NH_{3-n}X_n$.

The G2MP2 calculated complexation energies of $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl), reported in Table 3, show that the successive fluorine and chlorine substitution on NH_3 decreases the basicity, which is reflected by their calculated G2MP2 stability of the corresponding complexes. Indeed, by halogen substitution on the central atom (N) of the donor fragment, the complexation energy decreases. This effect is more pronounced upon fluorine substitution. Indeed, the fluorine substitution destabilizes the complex by ~6, ~11, and ~14 kcal/mol for SO_3-NH_2F, SO_3-NHF_2, and SO_3-NF_3 complexes, respectively, and the chlorine substitution destabilizes the complex only by ~3, ~6, and ~8 kcal/mol for the SO_3-NH_2Cl, SO_3-NHCl_2, and SO_3-NCl_3 complexes, respectively. The reported values in Table 3 of ΔE_0 (electronic energy including the scaled zero point energy), ΔH_0 (electronic energy including

TABLE 2: MP2(full)/6-31G(d) Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of Free $NH_{3-n}X_n$ (n = 0−3, X = F, Cl) Ligands and Complexes with SO_3

species	S−N	S−O[a]	N−X[b]	N−H	−O−S−N[c]	−X−N−X	−X−N−H	−H−N−H
SO_3-NH_3	2.081	1.457		1.021	96.2			109.5
SO_3-NH_2F	2.159	1.460 1.455	1.402	1.025	91.3 96.3		104.7	109.6
SO_3-NHF_2	2.524	1.455 1.457	1.392	1.029	90.9 91.9	104.4	101.6	
SO_3-NF_3	2.760	1.457	1.376		90.2	102.4		
SO_3-NH_2Cl	2.166	1.460 1.455	1.732	1.025	91.2 96.8		107.0	108.6
SO_3-NHCl_2	2.307	1.455 1.458	1.741	1.028	96.1 92.2	112.2	105.5	
SO_3-NCl_3	2.423	1.457	1.756		92.4	109.2		
SO_3		1.458						
NH_3				1.017				106.3
NH_2F			1.433	1.028			100.9	105.0
NHF_2			1.406	1.028		103.2	99.6	
NF_3			1.383			101.6		
NH_2Cl			1.754	1.022			104.4	105.8
$NHCl_2$			1.759	1.027		110.4	102.3	
NCl_3			1.773			107.6		

[a] Second value corresponds to equivalent oxygen atoms. [b] X is the halogen atom. [c] Second value corresponds to equivalent O−S−N angles.

TABLE 3: G2(MP2) Thermodynamic (Kcal/Mol) of the Complexation PA (kcal/mol) of $NH_{3-n}X_n$ Ligands and MP2(full)/6-31G(d) NBO Transferred Charge Q_t (e)

complex	ΔE_0[a]	ΔH_0[b]	ΔG_{298}[c]	PA[d]	Q_t[e]
SO_3-NH_3	−17.52	−18.58	−8.30	202.5	0.22
SO_3-NH_2F	−11.59	−12.07	−1.91	181.15	0.16
SO_3-NHF_2	−6.08	−5.65	1.86	158.15	0.04
SO_3-NF_3	−3.04	−2.30	4.08	132.18	0.01
SO_3-NH_2Cl	−14.21	−14.55	−4.57	189.42	0.17
SO_3-NHCl_2	−11.30	−11.00	−2.14	178.86	0.10
SO_3-NCl_3	−9.79	−9.25	−0.49	170.43	0.07

[a] ΔE_0 is the energy of the complexation including zero point correction (ZPE) and without thermal corrections. [b] ΔH_0 is the energy of the complexation processes including the internal thermal energy. [c] ΔG_{298} is the Gibbs free energy of the complexation processes (at room temperature). [d] PA is the proton affinities of the $NH_{3-n}X_n$ (n = 0−3; X = F, Cl) Lewis bases. [e] Q_t is the transferred charge from $NH_{3-n}X_n$ (n = 0−3; X = F, Cl) Lewis bases to SO_3 Lewis acid.

TABLE 4: 2s MP2−NBO Contributions of Nitrogen Atoms in the N−H, N−F, and N−Cl Bonds (%)

	$ns_{(N-H)}$	$ns_{(N-F)}$		$ns_{(N-H)}$	$ns_{(N-Cl)}$
NH_3	25.17		NH_3	25.17	
NH_2F	24.43	12.73	NH_2Cl	25.78	14.44
NHF_2	23.90	12.59	$NHCl_2$	26.22	14.22
NF_3		12.36	NCl_3		13.54
SO_3-NH_3	27.07		SO_3-NH_3	27.07	
SO_3-NH_2F	25.01	14.38	SO_3-NH_2Cl	26.07	15.98
SO_3-NHF_2	24.93	13.71	SO_3-NHCl_2	27.09	16.13
SO_3-NF_3		13.25	SO_3-NCl_3		15.73

the internal thermal energy), and ΔG_{298} (Gibbs free energy, at room temperature) for the association process

$$SO_3 + NH_{3-n}X_n \rightarrow SO_3{-}NH_{3-n}X_n$$

indicate that all complexes except SO_3-NHF_2 and SO_3-NF_3 are expected to be experimentally observable in the gas phase at room temperature. We expect from the result that the complexes SO_3-NHF_2 and SO_3-NF_3 may be observed at temperatures lower than room temperature.

On the other hand, we have established a good linear relationship between complexation energy and proton affinity of the Lewis base. In parts a−b of Figure 2, we present the linear correlation between the G2(MP2) proton affinities of the Lewis bases, $NH_{3-n}X_n$ (n = 0−3) (X = F, Cl), and the G2(MP2) complexation energies of $SO_3-NH_{3-n}X_n$ complexes. This correlation reflects that the stability of the complex depends on the nature of the ligand, which increases when the basicity of the Lewis bases increases.

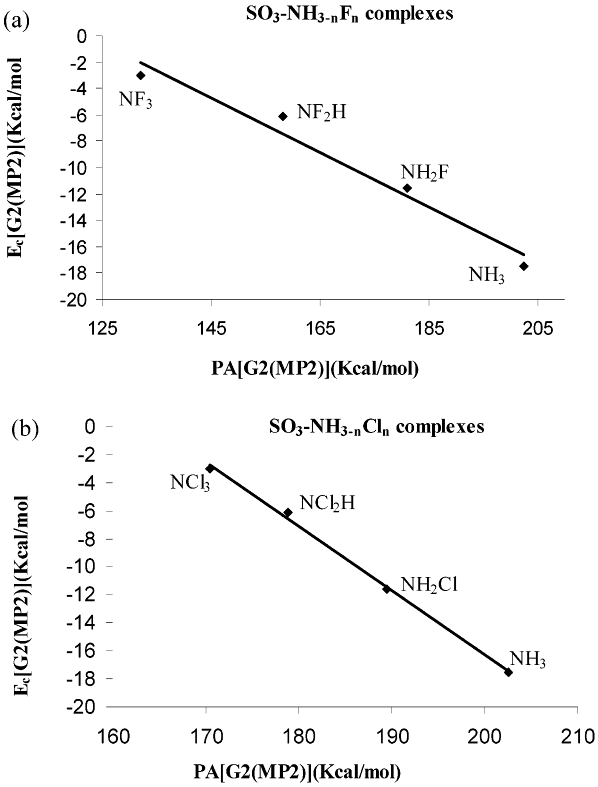


Figure 2. Linear correlation between the G2(MP2) proton affinities and the G2(MP2) complexation energies of (a) $SO_3-NH_{3-n}F_n$ and (b) $SO_3-NH_{3-n}Cl_n$.

4. Conclusion

The substitution effect on ammonia complexes was investigated at the G2MP2 level of theory. The G2MP2 results show that the stability of the $SO_3-NH_{3-n}X_n$ (n = 0−3; X = F, Cl) complexes decreases with the degree of halide substitution at the nitrogen atom. These substitutions also decrease the basicity of the $NH_{3-n}X_n$ Lewis bases. Indeed, the complexation energy varies linearly with the G2(MP2) proton affinity of the corresponding Lewis bases. Upon complexation, the MP2(full)/6-31G(d) calculated structural parameters of $SO_3-NH_{3-n}X_n$ complexes show shortening of the N−X (X = F, Cl) bonds. The analysis of the electronic structure using the NBO partitioning scheme shows that this change was related to the contribution of the "s" character in these bonds.

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