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Investigation of hydrogen bonding between nitrosamine and sulfuric acid using Density Functional Theory

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Abstract DFT calculations were performed to analyze those interactions; B3LYP and B3PW91 methods were applied and the following basis sets were used: 6-311++G(2d, 2p), 6-311++G(3df, 3pd) and aug-cc-pVDZ. The natural bond orbital (NBO) analysis and atom in molecules (AIM) theory were applied to understand the nature of the interactions. The most stable complex NS1 with an eight-membered cyclic structure contains two O–H···O and N–H···O hydrogen bonding interactions. From the values of ρ(r) at O···H critical points, it can be concluded that the H-boding in eight-membered cyclic NS1 is stronger than other. The elongation of the O–H bond length is caused by the electron-density transfer to the O–H antibonding orbital.

Keywords: DFT, H-bonding, AIM, NBO, nitrosamine, sulfuric acid

1. Introduction

Aerosols play an important role in the atmospheric chemistry of both the stratosphere and the troposphere. New particle formation involving sulfuric acid as a principal atmospheric nucleating agent represents an important contributor to nucleation mode aerosols [1]. Although nucleation phenomena have been intensively studied in the past, there are still major uncertainties concerning nucleation mechanisms and species involved in the atmospheric nucleation. Atmospherically relevant hydrogen-bonding complexes have been the subject of numerous theoretical studies in recent years [2-3].

A hydrogen bond is weaker than a common chemical bond, and can be encountered in solid, liquid and gas phases. It is commonly represented as X–H···Y, where X and Y are atoms having electronegativity higher than that of hydrogen (e.g., O, N, F, Cl, S). The X–H group is termed ‘‘electron acceptor’’ or ‘‘hydrogen bond donor’’, whilst Y is the ‘‘electron donor’’ or ‘‘hydrogen bond acceptor’’.

The interactions of NH_2NO (isomers and dimer isomers) [4] with formic acid and formamide [5], H_2O_2 [6], were studied. The nitrosamines constitute a family of potent carcinogenic compounds, which are formed readily from various nitrogen compounds such as nitrite and their various derivatives [7-8]. In this work, the hydrogen bonded complexes formed between sulfuric acid and nitrosamine have been completely investigated by a DFT study.

2. Theory and Method

All the structures studied in this work were optimized by using B3LYP [9-11] and B3PW91 [12-14] methods with 6-311++G(2d,2p) [15-16], 6-311++G (3df,3pd) and (aug-cc-pVDZ) [17-18] basis sets. A set of vibrational frequency calculations was further carried out on the all complexes at the B3LYP/6-311++G(3df,3pd) and B3PW91/6-311++G(3df,3pd) levels to include the zero point- energy (ZPE). For all the complexes, the basis set superposition error (BSSE) [19] was evaluated using the counterpoise method. In addition, fragment relaxation energy (E_{rel}) correction to counterpoise method was incorporated employing $E_{rel}(A) = E_{AB}(A) - E_A(A)$, with $E_{AB}(A)$ the energy of monomer A in dimer geometry. The NBO analysis was carried out with version 3.1 [20] included in Gaussian-03 [21] (on a Pentium 4 Computer with a single processor) program at the B3LYP/6-311++G(3df,3pd) level. The topological analysis was performed by using the quantum theory of atoms in molecules (QTAIM) of

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Bader [22-23] with the AIM2000 package [24] at the B3LYP/6-311++G(3df,3pd) and B3PW91/6-311++G(3df,3pd) levels to investigate the nature of hydrogen-bonded complexes.

3. Results and Discussions

Regarding complex formed, we have found four structures, two of them (NS1 and NS2) have cyclic structure, two (NS3 and NS4) have open structure whereas remaining. All complexes were identified for real minimum energy structures without any imaginary frequency. The optimized structures are show in **Fig.1.**

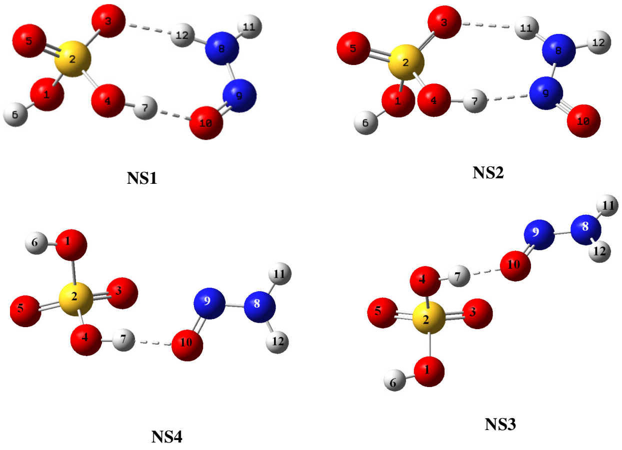


Fig. 1. Structures of $NH_2NO\cdots H_2SO_4$ complexes.

The most stable complex NS1 with an eight-membered cyclic structure contains two O–H···O and N–H···O hydrogen bonding interactions. In this structure, the O4–H7 group of H_2SO_4 acts as a proton donor and its O3 atom as a proton acceptor.

The eight-membered cyclic structure of NS2 has two O–H···O and N–H···O hydrogen bonding interactions. As can be seen in **Table 1**, BSSE and ZPE corrections affect the binding energies.

The best levels of our theoretical treatments are B3PW91/6-311++G(3df,3pd), and B3LYP /6-311++G(3df, 3pd), ones. The BE of complexes decreases in the order of NS1 >NS2 > NS3 > NS4 at all levels. Hence, at all levels of theory, NS1 is the most stable complex. Bond formation energy corrected with ZPE and BSSE (D_0^{BSSE}) for NS1 complex have -10.49 kcal/mol at B3PW91/6-311++G(2d, 2p), -10.92Kcal/mol at B3LYP/6-311++G(2d, 2p), -11.29 kcal/mol at B3PW91/6-311++G(3df, 3pd), -11.69 kcal/mol at B3LYP/6-311++G(3df, 3pd), -10.77 kcal/mol at B3PW91/aug-cc-pVDZ and -11.18 kcal/mol at B3LYP/aug-cc-pVDZ.

Geometric characteristics and vibrational frequencies of the complexes are summarized in **Table 2.** Two complexes NS1 and NS2 have cyclic configuration. From Table 2, the H···O distance for complex NS1 at B3LYP/6-311++G(3df, 3pd) and B3PW91/6-311++G(3df, 3pd) levels of theory are 1.618 and 1.578 Å respectively, which is the shortest. The hydrogen bond distance in hetronuclear nitrogen in NS2 complex (N8–H11···O3) is 1.979Å at B3PW91/6-311++G(3df,3pd). In absence of experimental data, it is a hard task to distinguish between blue shift and red shift because it has been noted that contrasting results can be obtained from B3LYP and MP2 calculations [25].

Table 1. Binding energies (kcal/mol) of $H_2SO_4{\cdot}NH_2NO$ complexes. $D_0 = D_e$ (electronic binding energy) + DZPE, $D_0^{BSSE} = D_0 + BSSE$.

	D_0			BSSE			D_0^{BSSE}		
Complex	**a**	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**
PW91									
1	-11.36	-12.29	-11.62	0.87	1.00	0.85	-10.49	-11.29	-10.77
2	-10.32	-10.83	-10.33	0.87	0.76	0.83	-9.45	-10.06	-9.50
3	-7.73	-8.07	-7.85	0.62	0.69	0.63	-7.10	-7.38	-7.22
4	-7.62	-7.96							
B3LYP									
1	-11.67	-12.52	-11.97	0.74	0.83	0.79	-10.92	-11.69	-11.18
2	-10.43	-10.91	-10.51	0.74	0.63	0.78	-9.69	-10.28	-9.73
3	-8.11	-8.45	-8.13	0.54	0.58	0.46	-7.58	-7.87	-7.67
4	-8.02	-8.35							

[a]6-311++(2d,2p) [b]6-311++g(3df,3pd) [c]aug-cc-pVDZ

Table 2. Characteristics of H_2SO_4-NH_2NO complexes at the B3LYP and B3PW91 Levels and 6-311++G(3df,3pd) Basis Set

Method	Δr (O-H)	Δν (O-H)	Δr (N-H)	Δν (N-H) symmetric	Δν (N-H) asymmetric	r (O-H...O(N))	r (N-H...O)
B3LYP/ 6-311++g(3df,3pd)							
1	0.043	846	0.013	186	41	1.618	1.865
2	0.036	729	0.008	21	90	1.767	2.009
3	0.030	608				1.672	
4	0.029	596				1.675	
PW91/ 6-311++g(3df,3pd)							
1	0.051	958	0.015	213	23	1.578	1.827
2	0.044	831	0.010	14	79	1.719	1.979
3	0.033	638				1.648	
4	0.033	630				1.652	

Table 3. The selected results of AIM at B3LYP/6-311++G(3df,3pd) level for NH_2NO-H_2SO_4 complexes

	ρBCP	∇^2ρBCP	ρBCP	∇^2ρBCP	ρBCP	BCP
B3LYP/6-311++g(3df,3pd)						
	NA	H_2SO_4	1		2	
O3…H12			0.030	0.096	0.021	0.081
O10 (N9)…H7			0.057	0.097	0.048	0.070
O4-H7			0.313	-2.419	0.321	-2.496
N8-H12(11)			0.332	-1.932	0.346	-2.079
			3		4	
O10…H7			0.050	0.100	0.049	0.100
O4-H7			0.328	-2.582	0.328	-2.593

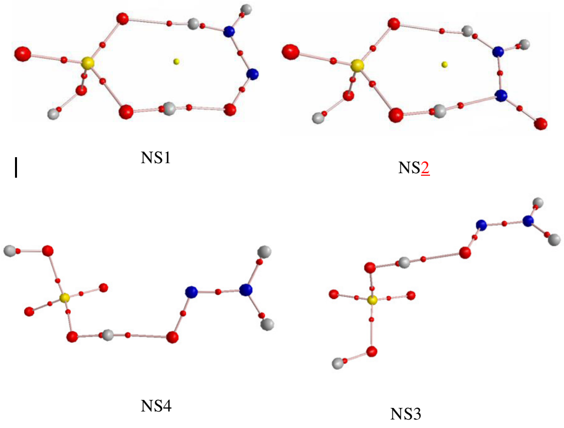
In accord with the elongation of O–H bonds upon complex formation, both B3LYP/6-311++G (3df, 3pd) and B3PW91/6-311++G(3df, 3pd) computations predict that the vibrational frequencies of O4–OH7 bond of H_2SO_4 moiety in all complexes are red-shifted.

The amount of red-shift in the complexes NS1, NS2, NS3 and NS4 is -846, -729, -608 and -596cm at B3LYP/6- 311++G(3df,3pd) level and -958, -831, -638 and -630cm^{-1} at B3PW91/6-311++G(3df,3pd) level, respectively. Bond lengths of O–H and N–H increase during bond formation (see table 2). This shows red shifts in frequencies.

3.1. Atoms in molecules (AIM)

Bader's theory of atoms in molecules (AIM) [22] is one of the widely used theoretical tools to understand the H-bonding interaction. Critical points (CPs) of the electron density, rc, are points where the gradient of ρ(r) vanishes. According to the AIM theory, the essential condition to detect an AH···B hydrogen bond is the existence of a (3, -1) BCP at the H···B path and some of its properties have been proposed to set the criteria to characterize Hydrogen bonding [26-28].

The values of ρ (*r*c) and ∇^2ρ *r*c) for the hydrogen bonds present in complexes are listed in **Table 3.** The molecular graphs (including the critical points and bond paths) for the studied complexes are shown in **Figs. 2.** Besides all of the expected BCPs, the electron density reveals two additional BCP in H···O and H···N distances.



NS1 NS2

NS4 NS3

Fig. 2. Topological parameters at BCPs of the hydrogen bonds of the complexes (in a.u.)

If values of ρc at the two bond paths of A–H···O indicate that the electron redistribution decreases ρ(r) in the covalent bond A-H and increases it in the hydrogen bond H···O as A···O intermolecular distance shortens, the Laplacian of ρ(r) tells how this redistribution affects the bond environment locally. Let us recall that in the AIM theory, strong sharedshell interatomic interactions (such as covalent bonding) are characterized by local concentration of charge ($\nabla^2\rho(r) < 0$) and thus the BCPs of covalent bonds have negative $\nabla^2\rho$ (r), whereas weak closed-shell interactions (such as hydrogen bonding) exhibit local depletion of charge ($\nabla^2\rho$ (r) (r)> 0) and the BCPs of H-bonds have positive $\nabla^2\rho$ (r)(r) [29]. For O–H···O hydrogen bonds for O–H BCPs, the Laplacian values are negative, while for H···O contacts, they are positive indicating that these interactions are covalent and noncovalent, In complexes NS1, NS3 and NS4, the values of ρ(r) at H7···O10 BCP are 0.057, 0.050 and 0.049 a.u. and of $\nabla^2\rho$ r) (*r*) are 0.097, 0.093 and 0.090 a.u., respectively.

From the values of ρ (*r*) at O…H critical points, it can be concluded that the H-boding in eight-membered cyclic NS1 is stronger than NS3 and NS4. The comparison between ρ(*r*) of the N···H and O···H hydrogen bonds shows that the O···H hydrogen bond in complexes NS1, NS3 and NS4 are stronger than that of the N…H one in complex NS 2.

The comparison between ρ(r) of the O–H···O and N–H···O hydrogen bonds shows that the homonuclear O–H···O hydrogen bond is stronger than heteronuclear N–H···O.

The comparison of (atoms in molecules) AIM data of O–H bond of complexes NS1–NS4 with H_2SO_4 monomer shows that the ρ (r) for O–H BCPs decreases upon H-bonding, in agreement with the increase of the corresponding O–H distances. This shows a red shift. The frequency changes in O–H bond versus changes in O–H bond length are shown in **Fig 3.** As can be seen, there is a linear relationship between them. The correlation coefficient is equal to 0.996 at the B3LYP/6-311++G(3df, 3pd) level of theory.

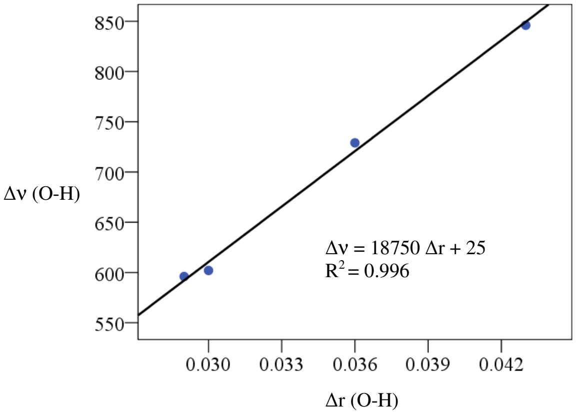


Fig. 3. Correlation between the frequency shifts in O-H bond and the elongation of O-H bond at B3LYP/6-311++G(3df,3pd) level of theory.

3.2. Natural bond orbital analyses (NBO)

The NBO analysis has been a reliable tool for the rationalization of H-bonds, which correlate well with changes in bond length in accordance with the basic chemical concepts. It is also used to derive information on the changes of charge densities in proton donor and proton acceptor as well as in the bonding and antibonding orbitals. As we know, H-bonds are formed due to charge transfer from the proton acceptor to proton donor, and hence the amount of charge transfer plays a significant role in the elongation and contraction of the H-Y bond. For each donor and acceptor, the stabilization energy *E* associated with *i-j* delocalization is given by the following Eq. (1) (NBO).

$$E^2 = -n_\sigma \frac{\langle\sigma|F|\sigma^*\rangle}{\epsilon_{\sigma^*}-\epsilon_\sigma} = -n_\sigma \frac{F_{ij}{}^2}{\Delta\epsilon} \qquad (1)$$

where Fij is the Fock matrix element between the NBO i and j, ε_σ and ε_{σ^*} are the energies of σ and σ^* NBOs, and nσ is the population (it is a lone pair in the HB complex) [30].

The results of NBO analyses including charge transfer energy, natural charge, and the occupancy of NBOs at B3LYP/6-311++G (3df, 3pd) level of theory are given in **Tables 4.**

The charge transfer energy associated with lp(N6) →σ*(N9=O10) interaction is 72.9 kcal/mol in NH_2NO which increases to 97.29, 87.67, 80.81 and 80.28 kcal/mol in complexes from NS1 to NS4, respectively.

The greater charge transfer energy obtained for NS1 complex. From NBO analysis, the red-shift of v (O–H) is related to the electron density in the σ*(O-H). The electron density in the σ *(O-H) increases with decreasing r(H7…O10) from 2.009 to 1.618 Å, which strengthens the red-shift degrees of v (O–H). The greater charge transfer energy is in consistent with the greater population of acceptor orbital (σ *). The population of σ *(O4–H7) (0.0892 a.u.) in NS1 is greater than other complexes.

4. Conclusions

The B3LYP and B3PW91 methods are used to optimize all of the plausible conformers by using the most popular basis set. The nature of interactions has been characterized by NBO and AIM analyses. The optimized structures are illustrated in Figure 1. NS1-NS2 and NS3- NS4 complexes have cyclic and linear configurations, respectively. The greater stability of NS1- NS2 with respect to the NS3-NS4 can be attributed to the formation of double H bonding between NH_2NO and H_2SO_4. The comparison of (atoms in molecules) AIM data of O–H bond of complexes NS1– NS4 with H_2SO_4 monomer shows that the ρ(r) for O–H BCPs decreases upon H-bonding, in agreement with the

Table 4. The selected results of NBO at B3LYP/6-311++G(3df, 3pd) level for NH_2NO-H_2SO_4 complexes.

	H_2SO_4	NA	1	2	3	4
B3LYP/6-311++g(3df,3pd)						
S2^{a}	2.5678		2.5971	2.5917	2.5800	2.5800
O3^{a}	-0.9111		-0.9692	-0.9672	-0.9290	-0.9290
O4^{a}	-0.8821		-0.9094	-0.9078	-0.9115	-0.8910
H7^{a}	0.5093		0.5125	0.5048	0.5177	0.5050
N8^{a}		-0.5663	-0.5143	-0.5254	-0.5142	-0.5149
N9^{a}		0.2145	0.2429	0.1701	0.2475	0.2440
O10^{a}		-0.3967	-0.4654	-0.3747	-0.4430	-0.4400
H11^{a}		0.3843	0.3891	0.3728	0.3990	0.3990
H12^{a}		0.3643	0.4057	0.4244	0.3790	0.3790
NA→H_2SO_4^{b}			0.0579	0.0672	0.0615	0.0606
LPO3 → σ*S2-O4^{c}	30.65		24.95	25.46	28.24	28.26
LPO 5 →σ S2-O3^{c}	23.04		23.59	23.55	22.86	22.86
LPO4 → σ*S2-O3^{c}	5.04		7.12	6.47	6.65	2.59
LPO3 → σ*N8-H12^{c}			14.32			
LPO3 → σ*N8-H11^{c}				6.38		
LPO10→ σ*O4-H7^{c}			36.72		27.21	26.49
LPN9→ σ*O4-H7^{c}			0.49			
LPN8 → σ*N9-O10^{c}		72.9	97.29	87.67	80.81	80.28
BD*(1) N 8 - H 11^{d}		0.0109		0.0204		
BD*(1) N 8 - H 12^{d}		0.0333	0.0523			
BD*(1) O 4 - H 7^{d}			0.0892	0.0856	0.0635	0.0061

aNatural charge(e),   bCharge transfer(e),   cE(2)/kJ mol^{-1},   dOccupancy increase of the corresponding O–H distances. This shows a red shift. According to NBO the greater charge transfer energy obtained for NS1 complex.

5. References

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