



DFT study of the interaction between 3-nitro-1,2,4-triazole-5-one and hydrogen fluoride

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ABSTRACT

Three fully optimized geometries of 3-nitro-1,2,4-triazole-5-one–hydrogen fluoride (NTO–HF) complexes have been obtained with density functional theory (DFT) method at the B3LYP/6–311++G** level. The intermolecular interaction energy is calculated with zero point energy (ZPE) correction and basis set superposition error (BSSE) correction. The greatest corrected intermolecular interaction of the NTO–HF complexes is -34.155 kJ/mol. Electrons in complex systems transfer from NTO to HF. Natural bond orbital (NBO) analysis is performed to reveal the origin of the interaction. The strong hydrogen bonds contribute to the interaction energies dominantly. Frequency calculations are carried out on each optimized structure, and their IR spectra are discussed. Vibrational analysis show that there are large red-shifts for H–X (X = N and F) stretching vibrational frequencies in the NTO and hydrogen fluoride complexes. The changes of thermodynamic properties from the monomer to complexes with the temperature ranging from 200 K to 1500 K have been obtained using the statistical thermodynamic method. It is found that two of three NTO–HF complexes can be produced spontaneously from NTO and HF at room temperature.

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1. Introduction

3-Nitro-1,2,4-triazole-5-one (NTO), developed at Los Alamos National Laboratory in 1983, was found to possess desirable and attractive characteristics such as high energy release on decomposition, high detonation velocity, good thermal stability (decompose only above 200°C [1]), relatively insensitive to impact and shock, and autocatalytic behavior during thermal decomposition [2–9]. NTO has the lower shock sensitivity than that of trinitrotoluene (TNT) and high explosive performance as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) that are among the most effective and widely used explosives and monopropellants [10]. Furthermore, there have been several theoretical studies on NTO in several recent works [11–17]. It is known that intermolecular forces control diverse phenomena such as diffusion, aggregation and detonation. In recent years, we have examined the intermolecular interactions in a series of explosives and obtained some meaningful information [18–22] that is valuable for further study of energetic materials. Generally HF is product during explosives exploding. In this paper, we investigated

theoretically the intermolecular interaction between NTO and HF.

2. Computational methods

The geometries of isolated NTO and their corresponding hydrogen fluoride complexes were fully optimized at the DFT–B3LYP [23,24] level by the Berny method [25,26] with 6–311++G** basis set concluding diffusion action. Natural bond orbital analyses and frequency calculations were performed on each optimized structure. Frequency calculations are carried out on each optimized structure, and their IR spectra are discussed. Thermodynamic data and their changes upon compounding were derived from statistical thermodynamics [27] based on the frequencies.

The interaction energy of the complex is evaluated as the energy difference of the subsystem and complex. The basis sets commonly used to calculate the energies are far from being saturated. As a result, each subsystem in any complex will tend to lower its energy due to the use of the basis functions of the other subsystem. The energies obtained at the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called basis set superposition error (BSSE) that can be checked by the Boys and Bernardi's counterpoise procedure (CP) [28–30]. All calculations were performed with Gaussian03W program [31].

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Table 1
Part of fully optimized geometries of NTO and NTO–HF at B3LYP/6–311++G** level^a

Geometrical parameter	NTO	I	II	III
N1–N2	0.1358	0.1357	0.1361	0.1349
N1–C5	0.1398	0.1384	0.1381	0.1402
N1–H10	0.1009	0.1014	0.1009	0.1009
N2–C3	0.1291	0.1290	0.1291	0.1295
C3–N4	0.1366	0.1369	0.1365	0.1367
C3–N6	0.1452	0.1452	0.1456	0.1447
N4–C5	0.1403	0.1387	0.1388	0.1402
N4–H11	0.1009	0.1010	0.1016	0.1019
C5–O9	0.1205	0.1222	0.1222	0.1203
N6–O7	0.1215	0.1213	0.1214	0.1211
N6–O8	0.1230	0.1230	0.1227	0.1241
F12–H13	(0.0922)	0.0952	0.0952	0.0939

^a Bond lengths are in nm and values in parentheses are data of HF.

3. Results and discussion

3.1. Optimized geometries

Three stable structures of NTO–HF complexes were obtained (Fig. 1). After stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure found corresponds to a minimum on the potential energy surfaces (no imaginary frequencies) for all structures in Fig. 1. NTO–HF complexes I, II and III possess C_s symmetry. Obviously, the intermolecular interactions do not change the planarity of NTO molecule.

Some geometrical parameters are collected in Table 1. Compared to the monomer, the bond lengths of complexes I, II and III change large. The lengths of N1–C5 and N4–C5 of complex I decrease by 1.4 pm and 1.6 pm, respectively, while the N1–H10, C5–O9 and F12–H13 lengths increase by 0.5 pm, 1.7 pm and 3.0 pm, respectively. The lengths of complex II's N1–C5 and N4–C5 decrease by 1.7 pm and 1.5 pm, respectively, while its N4–H11, C5–O9 and F12–H13 lengths increase by 0.7 pm, 1.7 pm and 3.0 pm, respectively. The lengths of III's N4–H11, N6–O8 and F12–H13 increase by 1.0 pm, 1.1 pm, and 1.7 pm, respectively. The changes of other bond lengths of all the structures predicted are noticeably smaller. As a whole, intermolecular H-bonds elongate the X–O (X=N, C) and X–H (X=N, F) bonds. The bond angles and the dihedral angles of all three NTO–HF complexes change slightly from its monomer, which implies that the influence of interaction on bond bending or internal rotation is small.

3.2. Binding energies

Table 2 gives both the uncorrected and corrected binding energies. There are no imaginary frequencies for any of the structures in Table 2, indicating that the structures in Fig. 1 are indeed the minima on their potential energy surfaces.

Table 2 shows that the calculation gives the ZPE and BSSE corrections of comparable values, both sum of them account for 34.94%, 35.88% and 51.74% of corrected binding energies, respectively, which illustrates that it is necessary to correct ZPE and BSSE values. Both the uncorrected and corrected binding energies indicate that the stability of the optimized structures I and II is com-

Table 2
Total energy, zero-point energy and interaction energy (kJ/mol) at B3LYP/6–311++G** level

Energy	HF	NTO	I	II	III
E	–263816.471	–1370871.425	–1634734.365	–1634733.245	–1634719.052
ΔE			–46.467	–45.348	–31.154
ZPE			9.046	9.046	7.327
BSSE			2.889	2.829	3.193
$\Delta E_{C,ZPE}$			–34.155	–33.095	–20.329

Table 3
The calculated natural atomic charges (e) of NTO and NTO–HF complexes^a

Atom	NTO	I	II	III
N1	–0.422	–0.411	–0.407	–0.413
N2	–0.221	–0.208	–0.220	–0.211
C3	0.463	0.463	0.470	0.456
N4	–0.619	–0.601	–0.609	–0.631
C5	0.768	0.777	0.777	0.770
N6	0.463	0.463	0.464	0.473
O7	–0.322	–0.313	–0.317	–0.296
O8	–0.385	–0.382	–0.368	–0.447
O9	–0.598	–0.652	–0.654	–0.589
H10	0.423	0.451	0.427	0.424
H11	0.451	0.456	0.477	0.467
F12	(–0.548)	–0.601	–0.599	–0.571
H13	(0.548)	0.558	0.558	0.567

^a Values in parentheses are data of HF.

parable, whereas the structure III is characterized by the smallest stability.

3.3. Atomic charges and charge transfer

Table 3 lists the atomic NBO charges of NTO and its complexes. Table 3 with Fig. 1 shows that the atoms whose charges change more are primarily these atoms of the vicinity of subsystem.

Compared to free HF molecule, charges on the H13 of I's HF subsystem increase by 0.010 e, while charges on F12 decrease by 0.053 e, net charge of HF molecule decrease by 0.042 e, indicating an effect of charge transfer through molecular contacting. Charges on O9 of I's NTO subsystem decrease by 0.054 e, while charges on the other atom of I's NTO subsystem all increase. Similarly, charges on the H13 of II's HF subsystem increase by 0.010 e, while charges on F12 decrease by 0.051 e, charges on O9 of II's NTO subsystem decrease by 0.056 e, while charges on the other atom of NTO subsystem all increase, net charge of HF molecule decrease by 0.041 e. Charges on O8 and F12 of complex III decrease by 0.062 e and 0.023 e, respectively, net charge of HF molecule decrease by 0.004 e. As a whole, the atoms whose charges change more are primarily these atoms of the vicinity of subsystem and electrons in NTO–HF complexes transfer from NTO to HF.

3.4. Natural bond orbital analysis

Table 4 summarizes the second-order perturbative estimates of 'donor–acceptor' (bond–antibond) interactions in the NBO basis for all the complexes. This is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their stabilization energy by second-order perturbation theory [32–34]. The stabilization energies E are proportional to the NBO interacting intensities. When the donor and the acceptor belong to different submolecules in a complex, we call it intermolecular NBO interaction. It is the intermolecular NBO interaction that reveals the origin of intermolecular interactions.

As can be seen from the intermolecular NBO interaction in Table 4, the main NBO interacting in the complexes I and II are that the lone pairs on oxygen atom of trizole submolecule act as donor

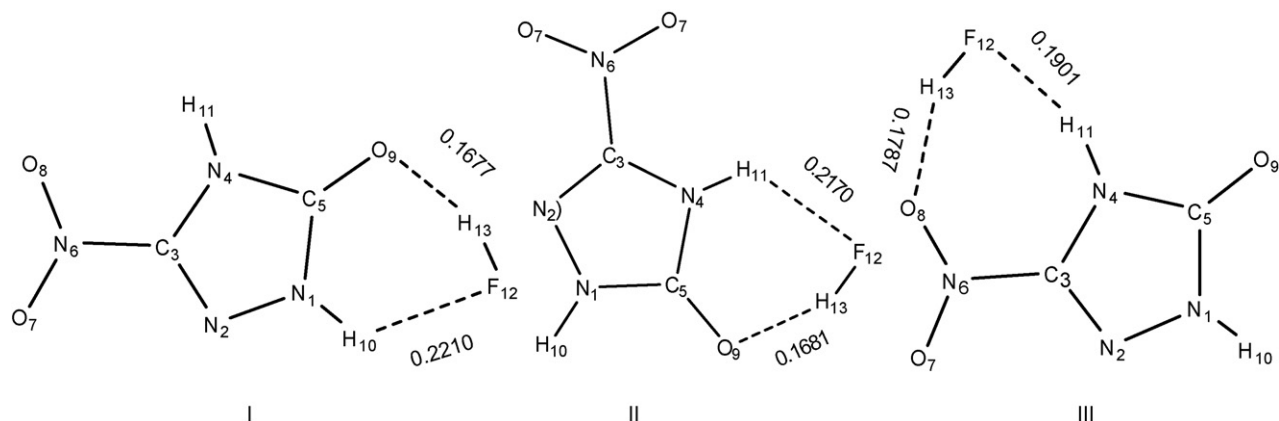


Fig. 1. Atomic number, optimized geometries and intermolecular distance (nm) of NTO–HF complexes.

and that the F–H antibond of HF submolecule as acceptor. Similarly, the main NBO interacting in the complexes III are that the lone pairs on fluorine atom of HF submolecule and oxygen atom of NTO's nitro-group act as donor and that the NTO'N–H and HF'F–H antibond as acceptor.

3.5. Vibrational frequencies

Fig. 2 shows the simulated infrared (IR) spectra for the NTO and their complexes, where the intensity is plotted against the harmonic vibrational frequencies (the scale factor is 0.96 [35]).

For the complexity of vibrational modes, it is difficult to attribute all bands, so we have only analyzed some H–X (X = N and F) vibrational frequencies in the NTO and three complexes. For the HF and NTO, it is found that the HF stretching vibrations appears at 3942.00 cm^{-1} (not listed), while NTO's N1–H10 and N4–H11 stretching vibrations appear at 3518.14 cm^{-1} and 3516.27 cm^{-1} , respectively.

Compared to HF and NTO monomer, the HF and N1–H10 stretching vibration of complex I appear at 3335.22 cm^{-1} and 3452.00 cm^{-1} , respectively, indicating large red-shifts. The HF and N4–H11 stretching vibrations of complex II appear at 3337.52 cm^{-1}

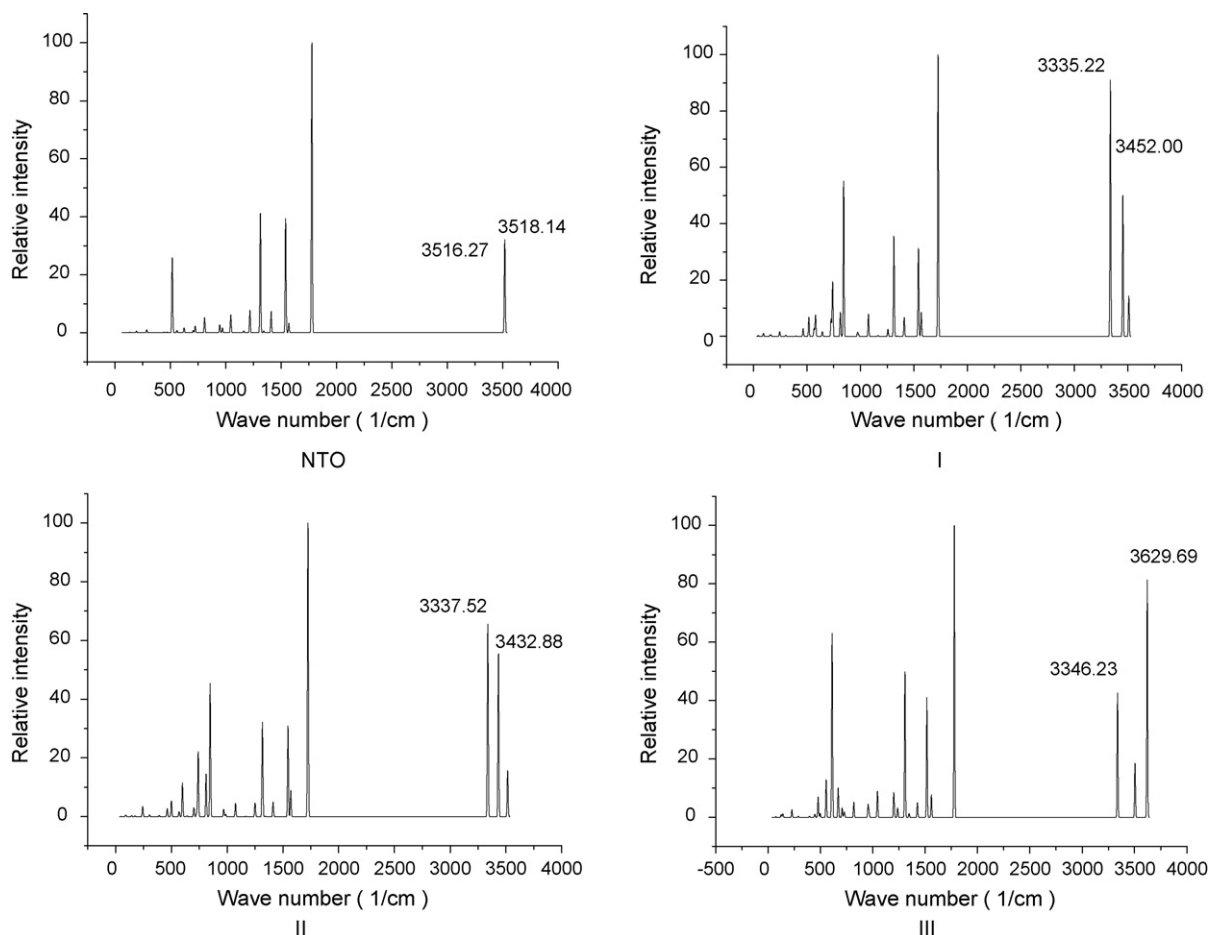


Fig. 2. IR spectra of NTO and NTO–HF complexes.

Table 4
Part of calculated results of NTO–HF at the B3LYP/6–311++G** level by NBO analysis^a

Structure	Donor NBO (i)	Acceptor NBO (j)	E (kJ mol ⁻¹)
I	LP(1)O9	BD*(1)F12–H13	18.660
	LP(2)O9	BD*(1)F12–H13	73.136
	LP(3)F12	BD*(1)N1–N2	1.129
II	LP(3)F12	BD*(1)N1–H10	7.447
	LP(1)O9	BD*(1)F12–H13	18.493
	LP(2)O9	BD*(1)F12–H13	70.082
III	LP(3)F12	BD*(1)N4–H11	9.372
	LP(1)O8	BD*(1)F12–H13	17.321
	LP(2)O8	BD*(1)F12–H13	32.928
	BD(1)F12–H13	BD*(1)N4–H11	2.677
	LP(1)F12	BD*(1)N4–H11	1.757
	LP(3)F12	BD*(1)N4–H11	37.446

^a E denotes the stabilization energy, BD denotes bonding orbital, BD* denotes antibonding orbital, LP denotes lone pair. For BD and BD*: (1) denotes σ orbital. For LP: (1), (2) and (3) denote the first, the second and the third lone pair electron, respectively. Only the stable energies over 1.00 kJ mol⁻¹ are listed.

and 3432.88 cm⁻¹, respectively. Those of complex III appear at 3629.69 cm⁻¹ and 3346.23 cm⁻¹, respectively. All calculation show that there are strong interactions in the O...H–X (X=N and F) hydrogen bond and there are large red-shifts for H–X stretching vibrational frequencies in the NTO and HF complexes.

Table 5
The thermodynamic properties of HF, NTO and NTO–HF complexes at different temperatures^a

Structure	Temperature (K)	C_p^0 (J mol ⁻¹ K ⁻¹)	S_m^0 (J mol ⁻¹ K ⁻¹)	H_m^0 (kJ/mol)	ΔS_T (J mol ⁻¹ K ⁻¹)	ΔH_T (kJ/mol)	ΔG_T (kJ/mol)	
HF	200.00	29.10	161.90	5.82				
	298.15	29.10	173.51	8.68				
	500.00	29.11	188.55	14.55				
	700.00	29.27	198.36	20.39				
	900.00	29.72	205.76	26.28				
	1100.00	30.40	211.79	32.29				
	1300.00	31.18	216.93	38.45				
	1500.00	31.95	221.44	44.76				
	NTO	200.00	87.36	315.95	11.45			
		298.15	117.38	356.54	21.53			
500.00		164.28	429.23	50.32				
700.00		192.41	489.38	86.23				
900.00		209.65	539.97	126.57				
1100.00		220.97	583.21	169.70				
1300.00		228.82	620.80	214.72				
1500.00		234.50	653.96	261.09				
I		200.00	110.03	355.99	14.55	-121.86	-40.14	-15.77
		298.15	144.93	406.55	27.09	-123.50	-40.54	-3.71
	500.00	198.66	495.30	62.21	-122.48	-40.08	21.15	
	700.00	230.29	567.62	105.38	-120.12	-38.66	45.42	
	900.00	249.85	628.03	153.53	-117.70	-36.74	69.18	
	1100.00	262.94	679.51	204.89	-115.49	-34.52	92.51	
	1300.00	272.21	724.23	258.46	-113.50	-32.13	115.41	
	1500.00	279.00	763.68	313.61	-111.72	-29.66	137.91	
	II	200.00	110.17	356.06	14.54	-121.79	-39.03	-14.67
		298.15	144.98	406.65	27.09	-123.40	-39.42	-2.62
500.00		198.63	495.41	62.21	-122.37	-38.96	22.22	
700.00		230.25	567.72	105.37	-120.02	-37.55	46.46	
900.00		249.82	628.11	153.52	-117.62	-35.63	70.22	
1100.00		262.92	679.59	204.88	-115.41	-33.41	93.53	
1300.00		272.20	724.31	258.44	-113.42	-31.03	116.41	
1500.00		279.00	763.76	313.59	-111.64	-28.56	138.89	
III		200.00	114.14	358.99	14.88	-118.86	-26.21	-2.44
		298.15	149.21	411.29	27.85	-118.76	-26.18	9.22
	500.00	201.20	501.85	63.66	-115.93	-25.03	32.92	
	700.00	231.66	574.82	107.21	-112.92	-23.23	55.80	
	900.00	250.56	635.48	155.57	-110.25	-21.10	78.11	
	1100.00	263.28	687.07	207.03	-107.93	-18.78	99.93	
	1300.00	272.34	731.83	260.64	-105.90	-16.35	121.31	
	1500.00	279.02	771.29	315.80	-104.11	-13.87	142.28	

^a $\Delta S_T = (S_T^0)_i - (S_T^0)_{\text{NTO}} - (S_T^0)_{\text{HF}}$, $\Delta H_T = (H_T^0 + E + \text{ZPE})_i - (H_T^0 + E + \text{ZPE})_{\text{NTO}} - (H_T^0 + E + \text{ZPE})_{\text{HF}}$, $\Delta G_T = \Delta H_T - T\Delta S_T$, ($i=I, II$ and III).

3.6. Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamic, the standard thermodynamic functions, heat capacities (C_p^0), entropies (S_m^0) and enthalpies (H_m^0), were obtained and listed in Table 5. It can be seen that the values of the calculated functions of all structures increase with the increasing temperature. The magnitudes of the heat capacities (C_p^0) of complexes I, II and III are approximately the same at each temperature. In the course of monomer to complexes, the entropy changes (ΔS_T) and the enthalpy changes (ΔH_T) decrease at any temperature from 200 K to 1500 K. At the same temperature, the enthalpy change (ΔH_T) value of I is lower than that of II and III, which is consistent with the results of binding energy. The intermolecular interaction is therefore an exothermic process accompanied by a decrease, and the interactions weaken as temperature increases.

Using the $\Delta G = \Delta H - T\Delta S$ equation, the changes of Gibbs free energies (ΔG) were obtained at various temperatures. It can be seen that ΔG_T in the processes from the monomer to the complexes I, II and III under 200 K are -15.77 kJ/mol, -14.67 kJ/mol and -2.44 kJ/mol, respectively. They are all negative, indicating complexes can be spontaneously produced from the isolated monomer under 200 K. Moreover, the complexes I and II can be spontaneously produced from the isolated monomer under 298.15 K. The ΔG_T value increases as temperature increases for each complex, thus the interactions weaken as temperature increases.

4. Conclusions

From the DFT-B3LYP calculations reported in the paper, the following conclusions can be drawn:

- (1) The greatest corrected intermolecular interaction of the NTO–HF complexes is -34.155 kJ/mol.
- (2) Vibrational analysis show that there are strong interactions in the $O \cdots H-X$ ($X=N$ and F) hydrogen bonds and there are large red-shifts for $H-X$ stretching vibrational frequencies in the NTO–HF complexes.
- (3) The interaction is an exothermic process along with the decreases of entropies. The values of free energy of the complex formation became more positive as temperature increases. The process of forming NTO–HF complexes I and II from NTO and HF is spontaneous at room temperature.

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