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Structural and Thermodynamic Properties of Two Crystalline Forms of 3-Nitro-1,2,4-triazole-5-one

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Structural and thermodynamic properties of two crystalline forms of 3-nitro-1,2,4-triazole-5-one (NTO), namely α-NTO and β-NTO, have been determined by *ab initio* molecular orbital calculations at the Hartree-Fock and density functional theories at the B3LYP/6-31G level. NTO is an important high performance and a thermally stable impact insensitive explosive. Heat capacities, enthalpy, free energy and the other thermodynamic properties of α-NTO and β-NTO are also calculated. The results show that the calculated solid heats of formation and densities, as important input data for calculation of the performance of explosive by thermochemical codes or empirical methods, are comparable with the experimental reported values.

Key Words: **Structure, Thermodynamics, Properties, 3-Nitro-1,2,4-triazole, Hartree-Fock, Density functional theory.**

INTRODUCTION

A reliable quantum mechanical approach for predicting different features of new energetic materials is a modern problem of the utmost importance for a chemist concerning synthesis and formulation. The development of theoretical studies can improve capabilities to confirm various reported values or to determine unknown properties. Theoretical predictive methods are highly desirable because it is time-saving, cost-effective and environmentally desirable at an early stage of development.

The performance and sensitivity characteristics are two major factors to show the effectiveness of an energetic material for both defence and civilian applications. The performance properties of pure or mixed explosives can be measured or estimated by complicated computer codes, *e.g.*, CHEETAH[1] and empirical simple methods[2–10]. Heat of formation and density of the energetic material are

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usually needed for computer codes or some empirical procedures. Some theoretical methods also use the molecular structure to relate various molecular and bulk properties with their sensitiveness to initiation[11-15].

Since energetic materials with high performance and low vulnerability are usually selected for war head and as an oxidizer ingredient in solid propellants, to improve their performance[16]. 5-Nitro-1,2,4-triazole-3-one (NTO) can act as a suitable explosive for providing the mentioned purposes[17-21]. NTO has explosive performance characteristics similar to RDX and less sensitive than RDX, because it is able to withstand much mechanical and thermal shock without igniting. However, the attractive attributes can make it as a good candidate for a variety of defence and civilian applications[17]. Sorescu and coworkers[22] determined experimental infrared frequencies of NTO from infrared spectra of pure NTO films as well as isolated NTO molecules at low temperature (21 K). They also used *ab initio* calculations at the Hartree-Fock and second order Møller-Plesset levels to determine vibrational spectra of NTO. NTO has two crystalline forms, α and β, so that only its β crystal form has been determined experimentally [23]. The crystal structure of α-NTO was refined to only a weighted R index of 17%, whereas we expect a correct structure of a small molecule to refine to below 5%, and details of structure have not been given. Ritchie[24] has reported some of the geometric parameters based on molecular orbital calculations at AM1, 3-21G//3-21G and 6-31G*//3-21G levels for several tautomers of β-NTO and several of its conjugate bases.

Though experimental studies can provide useful information about the thermal stability and safety of energetic materials macroscopically, the main difficulty of the experimental studies is the lack of information about microscopic properties of the explosive substances, *e.g.*, molecular structure, bond angle, bond length, etc., which may be important for demonstration of thermal and performance properties as well as sensitiveness of explosives. Fortunately, development of quantum chemistry computer programs can help us as good predictive tools at molecular level. The purpose of this study was to give better characterization of geometric and thermodynamic properties of both crystal forms of NTO by a good quantum mechanical computation so that some of the predicted values were close to reported data. In this study, we will present the results of *ab initio* calculations at Hartree-Fock (HF) and density functional theories (DFT), in Kohn-Sham formulation[25], using different types of basis sets, namely, the standard basis set 6-31G and 3-21G. The local energy minimum structures and the corresponding molecular state structures are optimized to obtain the local minimum structure of NTO. DFT and Becker's three parameter exchange functional are used along with the Lee-Yang-Parr (LYP) non-local-correlation functional (B3LYP) and *ab initio* theory with HF.

Method of computations

Standard quantum mechanical calculations were performed with the GAUSSIAN 98 computer program[26]. Geometries were optimized by *ab initio* calculations and by using the 3-21G, 6-31G basis sets. Final energies were obtained for two crystalline forms of α-NTO and β-NTO.

The effects of electron correlation can be ignored because small differences in zero point energies of two crystalline forms that introduce an additional uncertainity. The coupled cluster method was used for the single-point energy calculations in order to ensure the reliability energy prediction.

RESULTS AND DISCUSSION

NTO is an explosive of current interest with the structure shown in Fig. 1. α-NTO is one of two crystalline forms of NTO that is soluble in water and most organic solvents. Recrystallization of NTO from water can give sizeable α-NTO crystals that are suitable for X-ray crystallography. α-NTO crystal has an interesting feature so that if one tries to cut a needle NTO crystal perpendicular to the long axis, the crystal shatters parallel to this axis[23]. However, α-NTO can have the triclinic space group. It refined only to R = 17% meanwhile a correct structure of a small organic molecule refined to below R = 5%. This phenomenon can be attributed to the poor quality of the crystals or to the existence of some kind of twining about the needle axis although the agreement between equivalent reflections was normal. In α-NTO structure, NTO molecules are joined by hydrogen bonds to form ribbons of NTO molecules in which they are duplicated by the centre of symmetry at the origin to give a parallel ribbon. The other crystal form of NTO, β-NTO, has only been found in the re-crystallization product of NTO from methanol or ethanol/methylene chloride mixture[23]. Infinite extension of H-bonding in two-dimensional sheets occurs in the monoclinic form so that β-NTO cannot have planar structure.

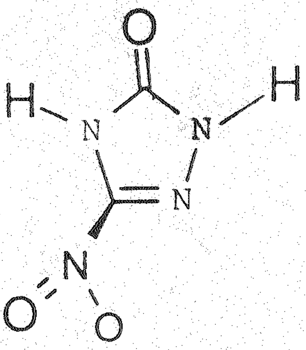

Fig. 1. Chemical structure of NTO

Theoretical studies have shown that non-local DFT techniques are superior to HF theory for calculating molecular force fields[25]. We have studied the results of *ab initio* calculations of HF and DFT using different types of basis sets for two crystalline forms of NTO.

The structures of α-NTO and β-NTO were optimized with HF/6-31G. They are shown in Figs. 2 and 3. Theoretical calculations show that α-NTO has lower minimal energy as compared to β-NTO.

B3LYP/6-31G shows 2.012 degree for C3-N2-H10 and 0.120 degree for N2-N1-C3 in α-NTO while 2.004 degree for C3-N2-H10 and 0.092 for C3-N4-C5 in β-NTO. The chemical bond angles computed by HF/6-31G and B3LYP/6-31G

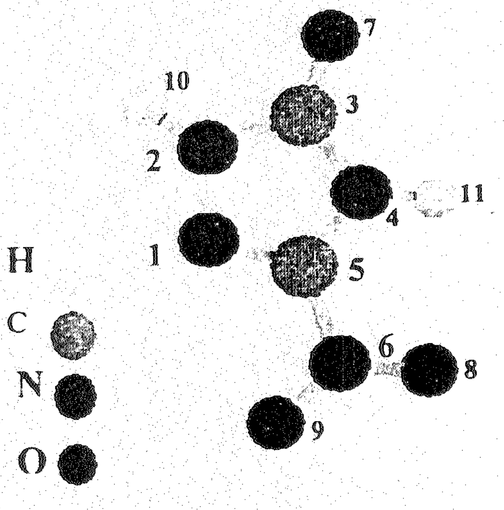

Fig. 2. Optimized geometry structure of α-NTO with HF/6-31G

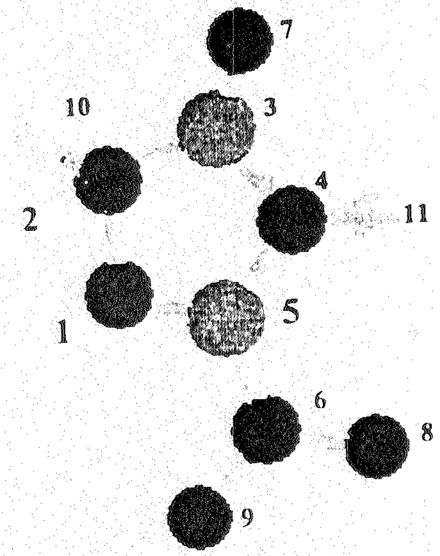

Fig. 3. Optimized geometry structure for β-NTO with HF/6-31G

for two crystal forms are given in Table-1. Table-1 also shows some calculated dihedral angles of the crystal structure based on the atomic positions and group theory reported. These results indicate that the crystal structures of α-NTO and β-NTO are planar and non-planar respectively.

The chemical bond lengths for two crystalline structures are also given in Table-2. As seen, the bond length of N—O, N—N, N—C, N—H and C—O calculated by two computation methods with two basis sets (6-31G and 3-21G) are the same. However, there is no meaningful difference between computed values at HF and DFT theory for two crystalline forms as compared to reported experimental values of β-NTO.

Energy consideration

The total energy, zero point vibrational energy (ZPVE), enthaply, SCF done energy, Gibbs free energy, entropy, thermal energy and heat capacities for two crystalline forms are calculated and listed in Table-3. The results of HF and DFT show total energy of α-NTO as slightly lower than β-NTO, which indicate α-NTO is more stable.

TABLE-1
INTERATOMIC ANGLES COMPUTED BY HF/6-31G AND B3LYP/6-31G

	Values of interatomic angles of NTO isomers				
	α-NTO		β-NTO		Exp[23]
	HF/6-31G	B3LYP/6-31G	HF/6-31G	B3LYP/6-31G	
N2-C3-N4	101.4830	100.486	101.4960	100.4860	101.60
C3-N2-N1	113.8440	114.796	—	—	112.60
N2-N1-C3	103.6460	103.070	—	—	103.20
N4-C3-O7	129.2330	130.048	129.2210	130.0420	129.30
N1-C5-N6	124.5130	124.473	124.5080	124.4720	124.90
C5-N6-O8	114.7560	114.704	114.7560	114.7060	114.50
C5-N6-O9	118.0370	118.332	118.0290	118.3300	118.10
C3-N4-H11	125.9400	126.098	125.9380	126.0660	126.60
C3-N2-H10	125.9140	125.288	125.9390	125.2960	127.30
N2-C3-O7	129.2850	129.456	129.2830	129.4720	129.10
C3-N4-C5	—	—	107.0540	107.9080	108.00
C5-N4-H11	—	—	127.0080	126.0260	125.40
N4-N3-H11	120.2420	119.916	—	—	119.80
N4-C5-N1	—	—	113.9720	113.7410	114.30
N4-C5-N6	—	—	121.5200	121.7880	120.80
O8-N6-O9	127.2070	126.964	127.2140	126.9640	127.40
O7-C3-N4	0	0	−3.3550	−3.3550	—
N1-N2-C3	0	0	1.8450	1.8450	0.06
C5-N1-N2	−0.0001	0	−1.4910	−1.4910	0.44
N6-C5-N1	+180.0000	180.000	178.8690	178.8690	178.92
O9-N6-C5	−0.0014	0	0.3853	0.3853	3.33
O8-N6-C5	+179.9980	180.000	−179.9263	−179.9263	−2.53
N4-C3-N2	180.0000	180.000	159.7423	159.7423	—
N2-C3-N4	−180.0000	−180.000	−153.2771	−153.2771	—
H11-N4-C5	180.0000	180.000	152.5000	152.5000	—

TABLE-2
COMPUTED CHEMICAL BOND LENGTHS

Method	HF (α-NTO)		DFT (α-NTO)		HF (β-NTO)		DFT (β-NTO)		Exp[23]
Basis sets	6-31G	3-21G	6-31G	3-21G	6-31G	3-21G	6-31G	3-21G	
C1-N2	1.366	1.400	1.366	1.366	1.366	1.400	1.366	1.366	1.400
C1-N5	1.272	1.266	1.295	1.295	1.272	1.266	1.293	1.293	1.266
N4-C5	1.369	1.364	1.413	1.413	1.369	1.364	1.413	1.413	1.364
N4-C3	1.383	1.391	1.400	1.400	1.383	1.391	1.408	1.408	1.392
C3-N2	1.378	1.385	1.405	1.405	1.378	1.385	1.411	1.411	1.385
C5-N6	1.422	1.419	1.408	1.408	1.421	1.419	1.408	1.408	1.419
N6-O8	1.232	1.251	1.276	1.276	1.232	1.251	1.276	1.276	1.251
N6-O9	1.214	1.229	1.276	1.276	1.214	1.230	1.276	1.276	1.230
N2-H10	0.992	0.996	0.990	0.990	0.989	0.993	0.993	0.993	0.994
N4-H11	0.990	0.993	0.991	0.991	0.992	0.996	0.993	0.993	0.996
C3-O7	1.204	1.204	1.228	1.228	1.204	1.204	1.230	1.230	1.204

TABLE-3
THERMAL FUNCTION VALUE

Method	HF (α-NTO)		DFT (α-NTO)		HF (β-NTO)		DFT (β-NTO)	
Basis set	6-31G	3-21G	6-31G	3-21G	6-31G	3-21G	6-31G	3-21G
Total energy (Hartree)	–518.760	–516.084	–512.693	–518.963	–518.732	–516.059	–521.672	–518.942
ZPVE (kcal mol^{-1})	44.005	43.075	41.009	40.049	43.826	42.703	40.928	39.645
E (Thermal) (kcal mol^{-1})	47.886	47.105	45.138	44.378	47.755	46.831	45.080	43.587
H (Hartree)	–518.755	–516.083	–512.692	–518.961	–518.732	–516.058	–521.671	–518.058
G (Hartree)	–518.793	–516.122	–512.731	–518.002	–518.770	–516.097	–521.710	–516.941
C_V (cal mol^{-1} K^{-1})	23.222	23.95	24.184	24.808	23.457	24.322	24.107	23.051
S (cal mol^{-1} K^{-1})	80.065	81.185	81.932	83.692	80.387	81.827	82.380	80.271
SCF done [E(RB + HF – LYP)]	–518.832	–516.159	–521.776	–519.034	–518.808	–516.134	–521.744	–519.0112
Nuclear repulsion energy	440.437				441.508			

Solid heats of formation (calculation with PM3 and *ad hoc* correction) and densities for α-NTO and β-NTO were obtained –26.282 kcal/mol, –25.494 kcal/mol, 1.872 g/cm^3 and 1.764 g/cm^3 respectively. However, the computed results for β-NTO are close to the experimental values[27], *i.e.*, –28 kcal/mol and 1.878 g/cm^3.

Conclusions

5-Nitro-1,2,4-triazole-3-one, NTO, is one of the most important explosives because it has high detonation performance as well as is a thermally stable impact insensitive explosive. It is similar to high performance explosives such as RDX and its stability is close to TATB, which is a very stable insensitive explosive. *Ab initio* molecular orbital calculations at HF and DFT at the B3LYP/6-31G level are used to optimize the geometry structure of α-NTO and β-NTO. Results of Tables 1 and 2 show that the optimized bond angles and bond lengths for β-NTO, where experimental data exist, are consistent with measured values especially in using DFT. Calculations show that β-NTO is not planar whereas α-NTO is planar. The total energy, zero point vibrational energy (ZPVE), specific heat, enthalpy, free energy and entropy, thermal energy, specified heat and entropy of NTO at 298 K are computed and given in Table-3. Since energy differences between α and β-NTO are low, tranformation of one form to the other is possible.

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