



A Computational Investigation of a Novel Explosive: DNTF

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Abstract: Computational investigation including molecular structure, crystal density, heat of formation, relative specific impulse, heat of detonation, detonation velocity and pressure on dinitrofurazanfuroxan (DNTF) was performed by quantum chemistry (density functional theory and Beck 3LYP hybrid density functional with 6-31G (d, p) basis set), molecular mechanics (Dreiding forcefield) and Monte Carlo methods. It can be deduced that DNTF is moderately sensitive and the N9-O10 bond is the weakest in the molecule and the trigger spot of decomposition by the molecular structure analyses. The mean values of the computational results of DNTF are: heats of formation of gas (HOF) and crystal state – 1113.8 and 992.5 kJ mol⁻¹ respectively; heat of detonation (HOD) – 7119.0 kJ kg⁻¹; relative specific impulse vs. HMX – 1.135; detonation velocity and pressure – 9.10 km s⁻¹ and 38.3 GPa respectively. As a result, DNTF is more powerful than HMX and is a promising melt-cast explosive for its possessing high power, moderate sensitivity, low melting point and thermal stability. Additionally, the simulation data is consistent with experiment. So these methods can also be applied to other HEDM (high energetic density materials) designs.

Keywords: DNTF, HOF, HOD, crystal densities, detonation velocity and pressure, relative specific impulse, computational investigation

Introduction

After having investigated on energetic furazan compounds for more than 20 years, Zelinskii Institute of Organic Chemistry, Russian Federation Academy of Science drew a conclusion that furazan group is an efficient unit in HEDM containing C, H, O and N atoms. At same time, many furazans and furoxans have been synthesized [1]. As a matter of fact, the densities and detonation velocities can increase 0.06-0.08 g cm⁻³ and about 300 m s⁻¹ respectively when a nitro group is displaced by furazan group of HEDM [2]. Additionally, that densities of most furazan compounds are usually above 1.80 g cm⁻³ is very useful to enhance detonation properties of explosives. That taking 3,4-diamino furazan (DAF) as initial material to synthesize explosives is one of the most flourishing domains in HEDM syntheses. So, DAF is regarded as a new milestone in the development history of explosives and pyrotechnics, and furazan and furoxan series are not only the important member in HEDM family, but also the important objects that we should take into account in HEDM designing. Recently, a serial of furazan and furazan compounds have been designed, and some of them have been synthesized by our team. Dinitrofurazanfuroxan (DNTF), whose application blazes a new trail for melt-cast explosives was introduced in this paper. Some properties of DNTF comparing with RDX, HMX and CL-20 are listed in Table 1 [3]. It can be found from the table that DNTF is fitly used as melt-cast explosive for its possessing high power, moderate sensitivity, low melting point and thermal stability, and being employed in warhead, owing to its high detonation sensitivity and velocity. However, there is no computational investigation of DNTF according to our knowledge. So, DNTF was studied theoretically for a complementary purpose.

Table 1. Properties of DNTF comparing with some explosives

Explosive	Density [g cm ⁻³]	Melting point [°C]	Dv/m s ⁻¹ theo./exp.	Impact sensitivity	Friction sensitivity [%]	Detonation point [(5 s) /°C]	Detonation heat [kJ kg ⁻¹]	Power (vs. TNT)
RDX	1.820	203	8800/8712 (<i>p</i> = 1.786)	80 ±8%	76 ±8	230.0	5376	140%
HMX	1.900	278	9100/8917 (<i>p</i> = 1.854)	100% <i>H</i> ₅₀ =0.32 m	100	327.0	5715	140%
DNTF	1.937	110	9250/8930 (<i>p</i> = 1.860)	94%	12	308.0	5799	168.4%
CL-20	2.035	210	9500	<i>H</i> ₅₀ =0.20 m	100	283.9	6238	-

Methods and computational details

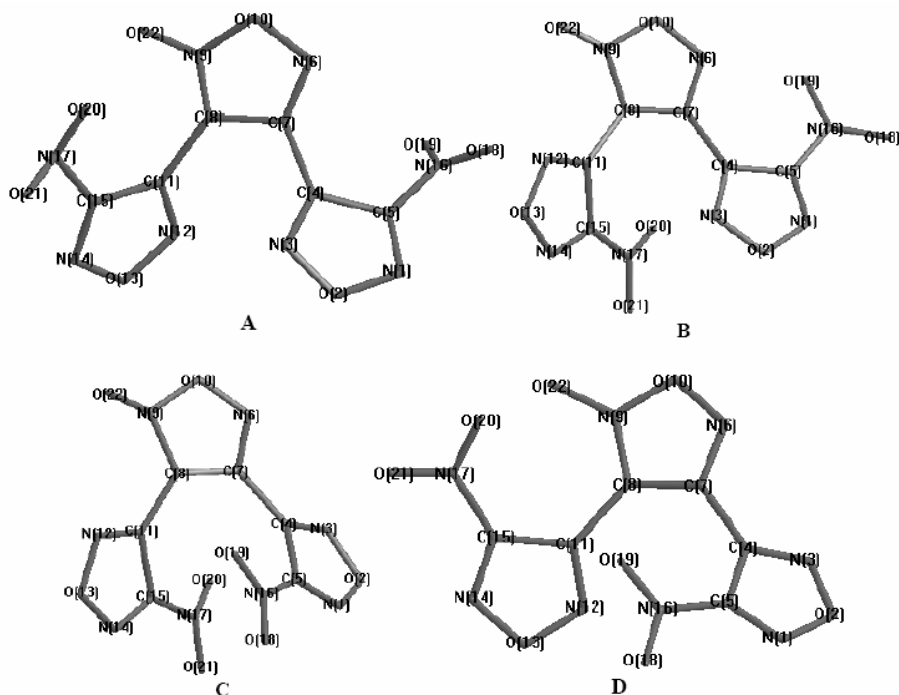
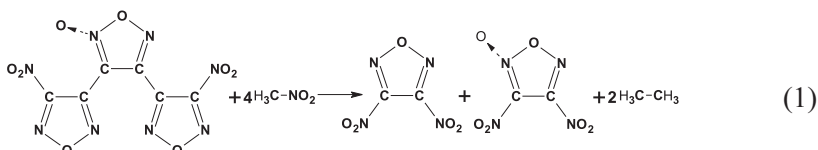


Figure 1. Four conformers of DNTF.

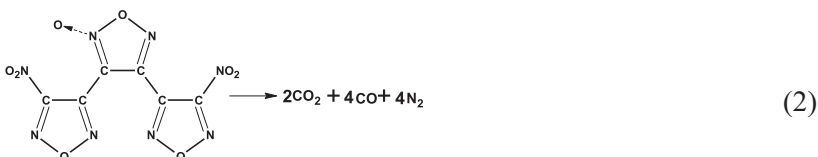
At first, by means of C8-C11 bond and C4-C7 bond spinning, DNTF possesses four conformers (Figure 1). Optimizations and frequency and natural bond orbital (NBO) analyses of these conformers were performed by the density functional theory method (DFT) and Beck 3LYP hybrid density functional with 6-31G (d, p) basis set. The normal mode analysis for each structure resulted in six zero frequencies, and no imaginary frequencies for the remaining $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. Stabilities of these four structures were discussed for finding the trigger spot of decomposition at the same time. Some properties including heats of formation (HOF), heats of detonation (HOD, $-\Delta H_D$), crystal density, detonation velocities (V_D) and pressures (P_D) and relative specific impulse (RI_s , vs. HMX) were calculated too. All the study contents and methods must be due to a design procedure of HEDM.

Because the electronic circumstances of reactants and products are similar in the reaction of equal bonds, the errors of electronic correction energies can be counteracted, and the errors of calculated *HOF* can be lessened greatly [4]. So the equal bond reaction of DNTF was designed to calculate *HOF* (equation 1). It can be found that the basic structures such as furazan and furoxan ring keep invariable.



An *ab initio* prediction method developed by Karfunkel *et al.* [5] and Dreiding forcefield [6] were used to predict crystal structures and densities. Because most organic crystals crystallize in only a few space groups [7], the five most space groups were chosen to study: P 21/c, P-1, P 21 21 21, P 21 and C 2/c.

The reaction of detonation or combustion was postulated as below for detonation property and relative specific impulse calculation purpose (equation 2).



Detonation velocity and pressure were calculated by Kamlet's formula [8]. Specific impulse introduced by Politzer *et al.* [9, 10] was adopted to evaluate detonation properties of energetic molecules. Two assumptions were taken. One is that all heats of combustion are used to heat the occurred gases. The other is that the pressure of combustion is constant when temperature changes from 298.15 K to temperature of combustion room, and the velocities of gas appearing and disappearing are equal. Additionally, HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) was regarded as the reference molecule for *RI*s calculation.

All calculations were performed by Acceryls' Serius2 package [11] and Gaussian98W package [12].

Results and discussion

Table 2. Bond lengths (\AA)/bond orders of DNTF's conformers

bond	A	B	C	D	bond	A	B	C	D
R(1,2)	1.360/1.135	1.359/1.135	1.352/1.153	1.354/1.151	R(9,10)	1.463/0.861	1.473/0.845	1.459/0.862	1.462/0.862
R(1,5)	1.303/1.619	1.303/1.623	1.305/1.598	1.304/1.604	R(9,22)	1.210/1.530	1.208/1.544	1.209/1.537	1.211/1.527
R(2,3)	1.370/1.114	1.371/1.109	1.374/1.109	1.374/1.110	R(11,12)	1.313/1.599	1.314/1.606	1.315/1.600	1.313/1.594
R(3,4)	1.311/1.610	1.311/1.602	1.312/1.613	1.312/1.618	R(11,15)	1.430/1.177	1.431/1.177	1.432/1.177	1.430/1.174
R(4,5)	1.429/1.181	1.430/1.178	1.429/1.185	1.429/1.185	R(12,13)	1.372/1.113	1.372/1.111	1.372/1.111	1.374/1.106
R(4,7)	1.463/1.030	1.459/1.039	1.470/1.020	1.468/1.018	R(13,14)	1.357/1.142	1.355/1.147	1.352/1.153	1.357/1.141
R(5,16)	1.462/0.907	1.463/0.905	1.454/0.925	1.457/0.922	R(14,15)	1.304/1.611	1.304/1.607	1.305/1.599	1.303/1.614
R(6,7)	1.310/1.603	1.310/1.600	1.313/1.608	1.311/1.612	R(15,17)	1.459/0.916	1.457/0.922	1.453/0.926	1.459/0.914
R(6,10)	1.354/1.120	1.350/1.124	1.352/1.117	1.356/1.117	R(16,18)	1.221/1.530	1.221/1.527	1.218/1.545	1.219/1.542
R(7,8)	1.425/1.182	1.427/1.176	1.431/1.184	1.425/1.181	R(16,19)	1.227/1.502	1.225/1.508	1.234/1.464	1.233/1.471
R(8,9)	1.339/1.306	1.341/1.309	1.346/1.298	1.338/1.307	R(17,20)	1.229/1.489	1.232/1.473	1.234/1.463	1.228/1.492
R(8,11)	1.453/1.043	1.456/1.038	1.458/1.042	1.449/1.050	R(17,21)	1.220/1.532	1.219/1.541	1.218/1.544	1.220/1.530

Table 3. Partial dihedral angles (deg.) of DNTF's conformers

	A	B	C	D		A	B	C	D
D(5,1,2,3)	-0.66	-0.77	0.20	-0.06	D(7,8,9,22)	178.28	179.32	179.54	177.70
D(2,3,4,5)	-0.61	-0.69	0.28	-0.19	D(22,9,10,6)	179.82	179.98	157.59	158.41
D(1,5,16,18)	-32.31	-35.58	6.40	-1.55	D(7,8,11,12)	-41.69	131.33	135.38	-36.36
D(4,5,16,19)	-29.01	-32.44	7.39	-0.15	D(9,8,11,15)	-45.51	130.86	134.68	-40.90
D(5,4,7,6)	-36.01	-25.91	130.67	129.07	D(11,12,13,14)	0.91	0.29	-0.26	0.86
D(3,4,7,8)	-35.17	-24.07	133.79	128.73	D(13,14,15,11)	0.27	0.30	0.30	0.45
D(6,7,8,9)	1.04	-0.08	-0.41	0.97	D(11,15,17,20)	-17.12	-4.37	6.55	-20.53
D(8,9,10,6)	-0.35	-1.11	2.02	-0.51	D(14,15,17,21)	-20.88	-6.18	5.40	-25.24

Structures of conformers

The bond lengths and bond orders, and partial dihedral angles of optimized DNTF molecular structures were showed in Table 2 and Table 3. Firstly, it can be found there are not large bond length and bond order differences of the same bonds of different isomers (Table 2). It indicated there are no more changes of molecular frame when C8-C11 bond and C4-C7 bond spinning. Additionally, that C-C bond lengths are within 1.425-1.470 Å, C-N bond lengths are within 1.303-1.463 Å, N-O bond lengths are within 1.208-1.473 Å, and their isolated single and double bond lengths are 1.39 Å and 1.54 Å, 1.27 Å and 1.47 Å, 1.19 Å and 1.36 Å respectively shows that conjugated effect of N-O bonds is weaker than that of C-C and C-O bond. Especially, that N9-O10 bond length is more than that of isolated single N-O bond and its bonds order is less than 1 indicates it is the feeblest point of DNTF.

Secondly, two furazan rings in DNTF were discussed. From Table 2, it can be concluded that all bonds on the furazan ring are conjugated for their bond orders are in 1.109-1.623. From Table 3, it can be deduced that all atoms on the ring are almost on the same plane for dihedral angles such as D(5,1,2,3), D(2,3,4,5), D(11,12,13,14) and D(13,14,15,11) on the ring are close to zero. These planar and conjugated structures of furazan rings are helpful of ring stability.

Thirdly, the furoxan ring on DNTF was discussed. We can find five atoms on the ring are closely on the same plane for and the dihedral angles such as D(6,7,8,9) and D(8,9,10,6) on the ring are close to zero. But as mentioned above, N9-O10 bond is the weakest on the ring. This should be due to O22 atom, which is a strong attract-electron one. Electron clouds will transfer from N9-O10 bond to N9-O22 bond when the latter forms. Moreover, it can be found O22 atom is not on the plane of the ring such as conformer C and D. As a result, furoxan ring is less planar, conjugated and stable than furazan ring and N9-O10 bond must be the “trigger point” of the molecular decomposition.

At last, two nitro groups were discussed. For most nitro compounds, C-NO₂ bonds must be the weakest in the molecules. But it is not always the case. From Table 2, it can be found that two C-NO₂ bonds are stronger than N9-O10 bond for they have more bond orders, 0.905-0.926 and 0.845-0.862 respectively. So, it can be concluded that the weakest bond is not C-NO₂ bond but N9-O10 bond in DNTF molecule. Additionally, Table 3 shows there is no apparent conjugated effect between nitro group and furazan ring, furazan ring and furoxan ring. That is to say, there is only local conjugated effect on the ring but not on the entire molecule. This must be one of the reasons for why DNTF possess not low sensitivity. Moreover, total energies of four conformers listed in Table 4 showed that D is the most stable

conformer for its lowest total energy. It was used to predict DNTF crystal structure.

Table 4. Total energies (including zero point correction, *hartree*) of four conformers of DNTF

A	B	C	D
-1267.753334	-1267.753031	-1267.750633	-1267.754474

Crystal structures

Molecular electrostatic potentials (ESP) developed by Singh and Kollman [19] is very important to predict crystal structure. The calculated ESPs of DNTF were listed in the Table 5 and predicted crystal structures according to them were listed in the Table 6. It should be explained that about 90 per cent of the organic molecular crystal structures published between 1929 and 1975 belonged to one of the following space groups (the occurrence per cent in bracket): P 21/c (35.9), P-1 (13.7), P 21 21 21 (11.6), P 21 (6.7), C 2/c (6.6), P b c a (4.3), P n m a (1.9), P n a 21 (1.8), P b c n (1.2), P 1 (1.0), C c (0.9), C 2 (0.9), P c a 21 (0.8), P 21/m (0.8), C 2/m (0.6), P 21 21 2 (0.6), P 2/c (0.5) according to Karfunkel's Statistical data [7]. So, five in the front of them were chosen to calculate.

Table 5. ESPs (*e*) of DNTF

N1	O2	N3	C4	C5	N6	C7	C8	N9	O10	C11
-0.298	0.156	-0.286	0.272	0.265	-0.252	0.237	-0.267	0.527	-0.032	0.418
N12	O13	N14	C15	N16	N17	O18	O19	O20	O21	O22
-0.348	0.141	-0.289	0.285	0.649	0.575	-0.325	-0.426	-0.334	-0.328	-0.346

Table 6. The predicted crystal structures of DNTF

No.	Space group	a [Å]	b [Å]	c [Å]	α [deg.].	β [deg.].	γ [deg.].	Density, [g cm ⁻³]
1	P 21/c	8.09	13.05	10.93	90.00	111.07	90.00	1.925
2	P-1	6.96	9.39	10.70	94.80	115.96	116.67	1.969
3	P 21 21 21	12.92	10.18	8.28	90.00	90.00	90.00	1.904
4	P 21	7.30	7.23	10.52	90.00	103.10	90.00	1.916
5	C 2/c	8.43	12.98	19.62	90.00	91.07	90.00	1.931

It can be found from Table 6 that computational crystal densities of DNTF are within 1.916-1.969 g cm⁻³. Compared with the value of experiment, there is a relative error within 1.70-1.65%. It shows the value of simulation is very consistent with that of experiment for crystal density. But the predicted crystal structures cannot be evaluated for the deficiency of experimental data.

Detonation properties

Table 7. The predicted detonation properties of DNTF

No.	HOFs [kJ mol ⁻¹]	HOD [kJ kg ⁻¹]	RI _s vs. HMX	V _D [km s ⁻¹]	P _D [GPa]
1	980.97	7081.47	1.133	9.08	38.02
2	992.87	7119.62	1.135	9.24	39.89
3	986.14	7100.19	1.134	9.01	37.27
4	1019.05	7203.53	1.141	9.08	37.99
5	983.68	7090.16	1.133	9.10	38.28
AV	992.54	7118.99	1.135	9.10	38.29

The computational *HOF* of gas phase is 1113.81 kJ mol⁻¹, and those of crystal calculated by molecular mechanics method are listed in Table 7. These simulation values may be instructive and helpful to understand the thermodynamics characteristics of DNTF in different state, for lacks of relevant experimental data. The calculated *HOD* are higher 22.16-22.27% than experiment data. These much differences must be mainly owing to following factors: (1) calculation errors of *HOF*; (2) calculation errors of sublimation energies including crystal structure simulation and algorithmic accuracy of energy; (3) experimental errors. Apparently, DNTF is more powerful than HMX, for it can be deduced from Table 1 that DNTF is more powerful 20.3% than HMX and the *RI_s* vs. HMX are within 1.133-1.141. At the same time, it also shows that DNTF has good detonation properties for its detonation velocity above 9.01 km s⁻¹ and detonation pressure above 37.27 GPa according to the simulation results.

Conclusion

DNTF is fitly used as melt-cast explosive for its possessing high power, moderate sensitivity, low melting point and thermal stability, and being employed in warhead owing to its high detonation sensitivity and velocity. And the mean values of the computational results of DNTF are: heats of formation of gas and crystal state 1113.8 and 992.5 kJ mol⁻¹ respectively; heat of detonation 7119.0 kJ kg⁻¹; relative specific impulse vs. HMX 1.135; detonation velocity and pressure 9.10 km s⁻¹ and 38.3 GPa respectively. As a result, DNTF is more powerful than HMX and is a promising melt-cast explosive. Additionally, the simulation data is consistent with experiment. So these methods can also be applied on other HEDM design.

Acknowledgements

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