Theoretical Studies on the Properties of
4,4'-*Bis*[(2,4,6-trinitrophenyl)amino]-[3,3'4',3''-*ter*(1',2',5'-oxidiazole)]-2'-oxide

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Density functional theory (DFT) method has been used to study a novel designed molecule 4'-*bis*[(2,4,6-trinitrophenyl)amino]-[3,3'4',3''-*ter*(1',2',5'-oxidiazole)]-2'-oxide (DTNBAFF). The optimized structure and the energy gap between the HOMO and LUMO of the titled molecule have been studied based on B3LYP/6-311++G** level. The isodesmic reaction method was employed to estimate the heat of formation. The detonation velocity and detonation pressure of the titled molecule are calculated by Kamlet-Jacobs equation. The DFT method was used to study the IR spectrum of DTNBAFF and the M06L method was used to study the ^{1}H NMR spectrum. The results show that the bond of R-NO$_2$ and the N-O besides the oxygen ligand atom in the furoxan ring of the DTNBAFF are easier to break. The activity, density, heat of formation and detonation properties of DTNBAFF are particular better than 1,3,5-trinitro-2-methylbenzene and 3,4-*bis*(aminofurazano)furoxan. The relationship of thermodynamic function and temperature of DTNBAFF have been studied and it can be helpful for further study on it. The analysis of IR spectrum and ^{1}H NMR spectrum of DTNBAFF show that the structure is stable.

Keywords: Density functional method, Heat of formation, Detonation properties.

INTRODUCTION

1,3,5-Trinitro-2-methylbenzene (TNT) is a conventional explosive which was synthesized in 1863. The detonation properties is very strong because of the three nitro groups in TNT[1,2]. There are many researches studies[3-5] on 3,4-*bis*(amino-furazano)furoxan (BAFF) and found that it is a effective explosive because there are two furazan rings and a furoxan ring in the molecule. For the mother to BAFF and the group of trinitro-phenyl was even at the ends of amino group. This is the new designed compound which is called 4,4'-*bis*[(2,4,6-trinitro-phenyl)amino]-[3,3'4',3''-*ter*(1',2',5'-oxidiazole)]-2'-oxide (DTNBAFF).

Density functional method is widely used for the calculation of the properties of the designed novel explosives because the synthesis of them is dangerous and explosive[6-12]. We calculate the new designed molecule before synthesis can avoid unnecessary waste. In additional, theoretical studies on explosives can tell us the relationship of the structure and properties, this can give a hand for the research of the explosives.

In this paper, TNT, BAFF and DTNBAFF have been calculated by Gaussian 09[13] procedure. The optimized structure, energy gap, heat of formation, detonation properties were studied by density functional method on B3LYP/6-31G* level[14-16]. The

DFT method was used to study the infrared spectrum of DTNBAFF and the M06L method was used to study the ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrum. The isodesmic reaction method was employed to estimate the HOFs. The detonation velocity and detonation pressure of the titled molecule are calculated by Kamlet-Jacobs equation.

COMPUTATIONAL METHODS

Previous studies[15-18] show that density functional theoretical (DFT) method is successfully used to predict the HOF of many systems via isodesmic reactions. The isodesmic reaction processes, in which the number of each kind of formal bond is conserved, must comply with the bond separation reaction (BSR) rules. The designed isodesmic reactions of the TNT BAFF and DTNBAFF were shown in **Scheme-I**.

For the isodesmic reaction, heats of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \Delta H_{f,P} - \Delta H_{f,R} \qquad (4)$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the HOFs of products and reactants at 298 K, respectively.

The calculations of methane, ethane, ammonia, benzene, methylbenzene, nitrobenzene, aminobenzene, aminofurazan
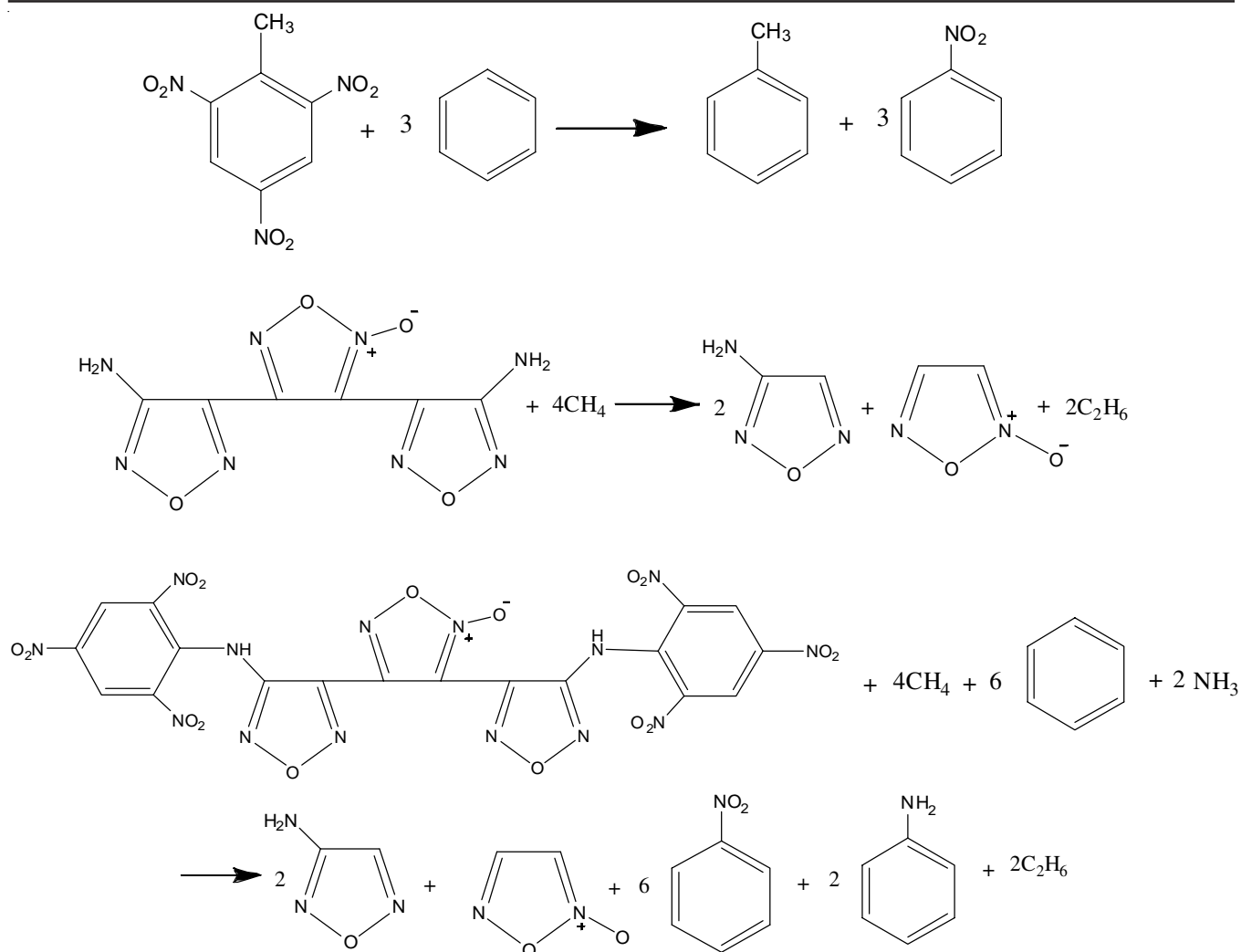
Scheme-I: Isodesmic reaction of the substances (**1-3**)

and furoxan were carried out by the atomization reaction $C_aH_bO_cN_d \rightarrow aC(g)+bH(g)+cO(g)+dN(g)$ using the G3 method to get accurate value of ΔH_f. Previous studies[17,18] show that G3 method can more accurately predict the HOFs than other methods when the number of heavy atoms is more than nine in the molecule. The ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(pV) = \Delta E_0 + \Delta E_{ZPE} + \Delta E_T + \Delta nRT \quad (5)$$

where ΔE_0 is the change in total energy between the products at reactants at 0 K, ΔE_{ZPE} is the difference between the zero-point energies (ZPE) of products and reactants at 0 K, ΔE_T is thermal correction from 0 to 298 K. $\Delta(PV)$ equals to ΔnRT in the equation. For the isodesmic reactions in this work.

$$\Delta n = 0, \text{ so } \Delta(PV) = 0$$

Many energetic compounds is solid-phase, so we must calculate the solid-phase HOF ($\Delta H_{f, solid}$). The solid-phase HOF ($\Delta H_{f, solid}$) can be obtained from the gas-phase HOF ($\Delta H_{f, gas}$) subtract heat of sublimation (ΔH_{sub}) due to Hess's law of constant heat summation[19]:

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub} \quad (6)$$

Recently, Politzer *et al.*[20,21] reported that the heat of sublimation correlates with the molecular surface area and the electrostatic interaction index $\nu\sigma_{tot}^2$ for energetic compounds. The empirical expression of the approach is as follows:

$$\Delta H_{sub} = aA^2 + b(\nu\sigma_{tot}^2)^{0.5} + c \quad (7)$$

where A is the surface area of the 0.001 electrons/bohr^3 isosurface of the electronic density of the molecule, ν describes the degree of balance between positive potential and negative potential on the isosurface and $\nu\sigma_{tot}^2$ is a measure of the variability of the electrostatic potential on the molecular surface. Byrd and Rice[22] have determined the coefficients a, b and c: a = 2.670×10^{-4} kcal/(mol A^4), b = 1.650 kcal/mol and c = 2.966 kcal/mol. The descriptors A, ν and $\nu\sigma_{tot}^2$ were ensured by using the computational procedures proposed by Bulat *et al.*[23]. This approach has been demonstrated to reliably predict the heats of sublimation of many energetic compounds.

The detonation velocity and pressure were estimated by the Kamlet-Jacobs equations[24] as:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+0.30\rho) \quad (8)$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2} \quad (9)$$

where D is the detonation velocity(km/s), P is the detonation pressure (GPa), N is the moles of detonation gases per gram explosive, $\overline{M}$ is the average molecule weight of these gases, Q is the heat of detonation (cal/g) and ρ is the loaded density

of explosives (g/cm^3). Therefor, we must calculate their Q and ρ before we estimate D and P of the molecules.

The theoretical density was obtained by an improved equation proposed by Politzer *et al.*[25], in which the interaction index was introduced:

$$\rho = \alpha\left(\frac{M}{V(0.001)}\right) + \beta v(\sigma_{tot}^2) + r \tag{9}$$

where, M is molecular mass (g/mol) and V (0.001) is the volume of the 0.001 electrons/bohr^3 contour of electronic density of the molecule (cm^3/molecule). The coefficients α, β and γ are 0.9183, 0.0028 and 0.0443, respectively.

The heat of detonation Q was evaluated by the HOF difference between products and explosives according to the principle of exothermic reactions. The decomposition products are supposed to be only CO_2, H_2O and N_2. So released energy in the decomposition reaction reaches its maximum. The value of D and P can be evaluated based on the ρ and Q values according to the Kamlet-Jacobs equations, the D and P can be regarded as their upper limits.

RESULTS AND DISCUSSION

Bond length: The optimized structure of the molecules can be obtained by B3LYP method on 6-31 G* basis. The bond length of the optimized structure are shown in **Scheme-II**. The longer the bond length is, the lower the bond energy is and the weaker the bond is. We can find that the bond length of R-NO_2 is longer than the bond length of C-N (1.46 Å). This indicated that the -NO_2 can elongate the bond length of C-N which the N atom is the content of -NO_2. Instead, the bond length of C19-N18, C12-N18, C8-N17 and C20-N17 are below the bond length of C-N (1.46 Å), this indicated that a big π bond was formed in the molecule. The bond length of N3-O4 which is besides the oxygen ligand atom in furoxan ring is 1.46181 Å, it is longer than another bond length of N-O in furoxan ring and N-O in furazan rings. Accordingly, the bond of R-NO_2 and the

N-O besides the oxygen ligand atom in furoxan ring of the DTNTBAFF are easier to break than other N-O bond in the ring[26].

Electronic properties: The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the frontier molecular orbitals which are called the most important orbitals in a molecules. The energy gap (ΔE) is defined as E_{LUMO}–E_{HOMO} and it is related to the stability of the molecule, the smaller the energy gap is, the more active of the molecule, also the larger the energy gap is, the more stability of the molecule. The ionization potentials (IP) means the difference between the energies of mono positive valent ion and neutral molecule. The value of ionization potential reflected the the ability of electron donating, the bigger the value of ionization potential is, the more hardly the molecule offer electrons. The electron affinities (EA) means the difference between the energies of neutral molecule and mono negative valence ion. The value of electron affinities reflected the ability of electron accepting, the bigger the electron affinities value is, the more easily the molecule accept electrons[7,27]. The calculated energies of HOMO (E_{HOMO}) and LUMO (E_{LUMO}), the energy gap, ionization potentials and electron affinities of the titled molecules are listed in Table-1. We can find that the energy gap of DTNBAFF is the smallest in three molecules and it is more active than TNT and BAFF. We also find that the ionization potential of the DTNBAFF is smaller than TNT and there is no obvious different between DTNBAFF and BAFF, the electron affinities value of DTNBAFF is biggest in the three compounds. This indicated that the ability of detonating electrons and accepting electrons are very great.

Heat of formation: Heat of formation (HOF) is an important index because it was seen as the "energy content" of the energetic materials. We get the value of HOFs of TNT, BAFF and DTNTBAFF by isodesmic reaction. Table-2 lists the total energies (E_0), zero-point energies (ZPEs) and thermal corrections (H_T) at the B3LYP/6-31 G* level for the reference compounds in the isodesmic reaction (1-3). The calculations
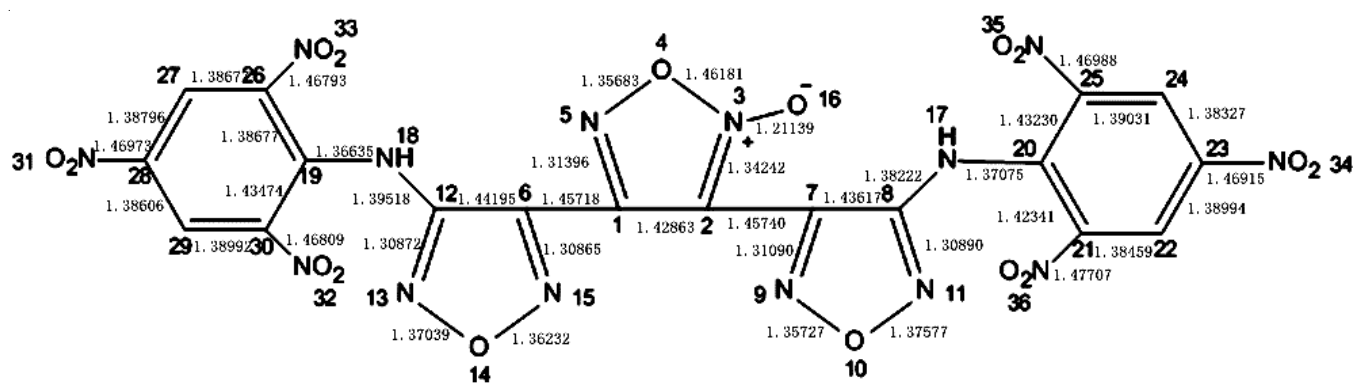
Scheme-II the bond length of DTNTBAFF

TABLE-1
CALCULATED ENERGIES OF HOMO (E_{HOMO}, eV), ENERGIES OF LUMO (E_{LUMO}, eV), THE ENERGIES GAP (ΔE, eV), IONIZATION POTENTIAL (IP, eV) AND ELECTRON AFFINITIES (EA, eV) OF THE TNT, BAFF, DTNTBAFF AT B3LYP/6-31G* LEVEL

Compound	E_{HOMO}	E_{LUMO}	ΔE	IP	EA
TNT	-8.49	-3.55	4.95	10.03	2.07
BAFF	-7.08	-2.74	4.34	8.44	2.12
DTNBAFF	-7.74	-3.89	3.85	8.67	6.12

TABLE-2
CALCULATED TOTAL ENERGIES (E_0, au), ZERO-POINT ENERGIES (ZPE, au), THERMAL CORRECTIONS (H_T, kJ/mol),
ENTHALPY BY G3 METHOD (H_{G3}, au) AND HOFs (kJ/mol) OF THE REFERENCE COMPOUNDS

Compound	E_0	ZPE	H_T	H_{G3}	HOFs
Methane	-40.52	0.045	10.02	-40.45	-75.57
Ethane	-79.83	0.075	11.73	-79.72	-84.55
Ammonia	-56.54	0.033	9.94	-56.50	-47.00
Benzene	-232.25	0.10	14.42	-232.05	87.45
Aminobenzene	-287.60	0.12	17.63	-287.37	88.72
Nitrobenzene	-436.75	0.10	20.86	-436.46	63.61
Methylbenzene	-271.57	0.13	17.03	-271.32	51.85
Aminofurazan	-317.40	0.062	14.84	-317.21	204.23
Furoxan	-337.21	0.050	14.26	-337.01	210.10

TABLE-3
CALCULATED TOTAL ENERGIES (E_0, au), ZERO-POINT ENERGIES (ZPE, au), THERMAL CORRECTIONS (H_T kJ/mol),
MOLECULAR PROPERTIES, HEATS OF SUBLIMATION (ΔH_{sub}, kJ/mol) AND GAS-PHASE AND
SOLID–PHASE HOFs OF THE TITLE MOLECULES ($\Delta H_{f,gas}$, $\Delta H_{f,solid}$, kJ/mol)

Compound	E_0	ZPE	H_T	$\Delta H_{f,gas}$	A	ν	σ^2_{tot}	ΔH_{sub}	$\Delta H_{f,solid}$
TNT	-885.03	0.14	34.54	61.59	214.42	0.23	90.34	95.43	-33.84
BAFF	-969.64	0.14	40.49	640.57	230.91	0.20	191.62	115.18	525.39
DTNBAFF	-2658.56	0.31	107.64	1314.02	319.73	0.18	272.12	174.47	1139.55

were carried out by G3 method which can give accurate value of heat of formations. Table-3 presents the total energies (E_0), zero-point energies (ZPEs), thermal corrections (H_T), molecular properties, heats of sublimation and gas-phase and solid-phase heat of formations of the titled compounds. We can find that the gas-phase heat of formation and solid-phase heat of formation of DTNBAFF are better than that of TNT and BAFF. According to that there are many nitro-groups, furazan and furoxan rings in DTNBAFF, they have good contribution to enhance the heat of formation of a molecule.

The thermodynamics functions such as $C^{\theta}_{p,m}, S^{\theta}_m, H^{\theta}_m, G^{\theta}_m$, which are called standard molar heat capacity, standard molar entropy, standard molar thermal enthalpy and standard molar Gibbs free energy (from 200 K to 800 K) of DTNBAFF are obtained by fitting harmonic vibrational analysis result at B3LYP level. The results are given in Table-4. It is seen that the $C^{\theta}_{p,m}, S^{\theta}_m, H^{\theta}_m$ are increase with the increasing temperature. However, the G^{θ}_m is on the contrary. This is because the main contribution to them are from the translations and rotations of the molecules at lower temperature, the vibrational motion is increasing with the increasing temperature and than it is the main contribution[17,27]. The temperature-dependent relations for $C^{\theta}_{p,m}, S^{\theta}_m, H^{\theta}_m, G^{\theta}_m$ in the range of 200-800 K are as follows and they are displayed in Fig. 1. The fitting equations of thermo-dynamics functions and temperature are as follows:

$$C^{\theta}_{p,m} = 66.57364 + 2.2160T - 0.0012 \times 10^{-4} T^2$$
$$R^2 = 0.99966; SD = 9.96546$$

$$S^{\theta}_m = 389.1721 + 2.54053T - 7.76551 \times 10^{-4} T^2$$
$$R^2 = 0.99998; SD = 3.79276$$

$$H^{\theta}_m = 741.29418 + 0.34568T + 5.01914 \times 10^{-4} T^2$$
$$R^2 = 0.99975; SD = 7.10119$$

$$G^{\theta}_m = 811.69787 - 0.56808T - 8.79797 \times 10^{-4} T^2$$
$$R^2 = 0.99997; SD = 4.44707$$

TABLE-4
THERMODYNAMIC PROPERTIES OF
DTNBAFF AT DIFFERENT TEMPERATURES

Temp. (K)	$C^{\theta}_{p,m}$ (J/(K mol))	S^{θ}_m (J/(K mol))	H^{θ}_m (kJ/mol)	G^{θ}_m (kJ/mol)
200	458.43	864.48	833.77	660.88
298	621.85	1078.64	886.95	565.36
300	624.72	1082.49	888.11	563.36
400	764.77	1282.10	957.83	444.99
500	875.35	1465.16	1040.07	307.49
600	960.19	1632.60	1132.04	152.48
700	1025.05	1785.70	1231.44	-18.55
800	1075.12	1925.99	1336.56	-204.23

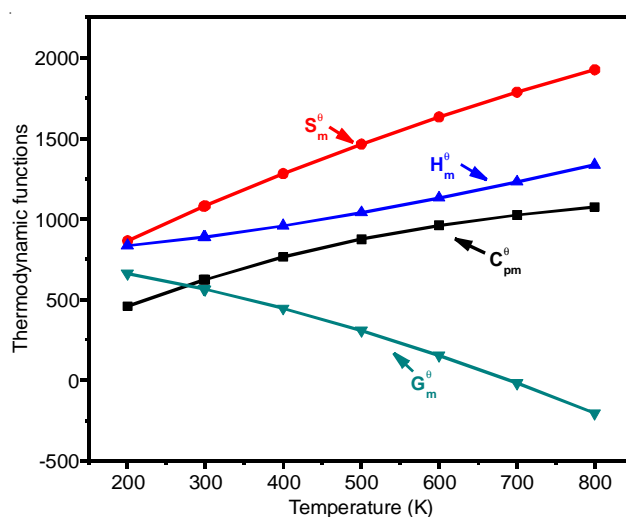Fig. 1.   Temperature-dependent relations for $C^{\theta}_{p,m}, S^{\theta}_m, H^{\theta}_m, G^{\theta}_m$ of DTNBAFF in the range of 200-800 K

The symbol R means variance and the equation is more reliable when the value of R is more near 1. The symbol SD means standard deviation and the value are not big for the equations. We can find the equations are reliable and can be used for further study on DTNBAFF.

Energetic properties: Table-5 lists the calculated density (ρ), heats of explosive (Q), detonation velocities (D), detonation pressure (P) and oxygen balance (OB) values of the titled molecules. Oxygen balance is an important parameter for energetic materials. As we know, the higher the oxygen balance is, the larger the detonation velocity and pressure are and the better the performances of energetic compounds are. However, too much oxygen balance is not good for energetic materials. The reason is that over much oxygen will produce O_2 that takes away a great deal of energy. Therefore, the value of oxygen balance near zero is the best. We can find that the detonation properties of DTNBAFF are very good, the oxygen balance, density, detonation velocity and detonation pressure of DTNBAFF is the best in three compounds.

TABLE-5
OXYGEN BALANCE (OB, %), PREDICTED DENSITIES (ρ, g/cm³), HEATS OF EXPLOSIVE (Q, cal/g), DETONATION VELOCITIES (D, km/s) AND DETONATION PRESSURE (P, GPa) FOR THE TITLED COMPOUNDS

Compound	OB	ρ	Q	D	P
TNT	-73.97	1.65	1425.64	7.19	21.73
BAFF	-63.45	1.66	1438.63	7.52	23.94
DTNBAFF	-54.57	1.79	1428.15	7.66	25.97

IR: The peak of 3300-3400 cm^{-1} is the characteristic peak of benzene. The peak of 3272 cm^{-1} represents the bond –NH. The peak of 1350-1400 cm^{-1} is the bending vibration peak of C-N bond and the peak of 1600 cm^{-1} is the bending vibration peak of N-H bond[18]. The peak of 1615 cm^{-1} and 1299 cm^{-1} represent the group of -NO_2. The peak of 1488 cm^{-1} and 1376 cm^{-1} means the group of –C=N-O and the peak of 947 cm^{-1} means the bond N-O.

^{1}H NMR: There are six atom in the molecule. We can find five H-type in ^{1}H NMR spectrum of DTNBAAF, The N17-H and N18-H are identical, the other four H-type are C22-H, C24-H, C27-H and C29-H, which is suitable of the structure. These means the structure is stable.

Conclusion

In this work, we have studied the bond length, energy properties, heat of formations and detonation properties of TNT, BAFF and DTNBAFF. The bond of R-NO_2 and the N-O besides the oxygen ligand atom in furoxan ring of the DTNBAFF are easier to break. The IR spectrum and ^{1}H NMR spectrum show that the molecule is stable. The ability of detonating and accepting electrons of DTNBAFF are better than TNT and BAFF. The activity, heat of formation and detonation properties of DTNBAFF are particular better than TNT and BAFF.

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