



## Comparative Theoretical Investigation on Energetic Substituted Furazanyl Ethers

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**Abstract:** Furazanyl ether has great potential to be an important candidate as a casting explosive and energetic plasticizer. The density functional theory (DFT) method was used to investigate the heats of formation (HOFs), molecular stability, detonation performance and melting point of a series of substituted furazanyl ethers at B3LYP/6-311G(d,p) level. The results show that the introduction of  $-N_3$  or  $-N(O)=N-$  groups significantly improves the HOFs values of the derivatives. The bond dissociation energies (BDEs) were analyzed, showing that the N–O bond in the furazan ring is the weakest for most compounds and the ring is vulnerable to cleavage in thermal decomposition. The calculation of density, detonation velocities and detonation pressures suggests that the substitution of  $-NF_2$ ,  $-CF(NO_2)_2$ , furoxan or  $-N(O)=N-$  group is an effective method for enhancing their detonation performance. The melting points were determined according to the variation of specific heat capacity, and good estimates were obtained in comparison with the available experimental data. Taking into account the detonation performance and melting point, four compounds are favoured for application in melt cast explosive or energetic plasticizers.

**Keywords:** furazanyl ethers, heats of formation, bond dissociation energy, detonation performance, melting point

**Supporting Information** (S.I.) available at: <http://www.wydawnictwa.ipw.waw.pl/CEJEM/contents/2018/vol-15-no-1.html>

## 1 Introduction

As a typical energetic heterocyclic compound, furazan-based derivatives have been studied extensively to search for promising candidates as high-energy density materials (HEDMs) due to their high densities, high positive heat of formation (HOF), and good detonation performance [1-5]. Furazanyl ethers, which possess high standard enthalpies of formation, low melting points, good oxygen balance and low impact sensitivity due to them containing an ether linkage, have a wide range of applications from liquid phase carriers of casting explosive to energetic plasticizer [6, 7]. The first symmetrical difurazanyl ether, 3,3'-dinitrodifurazanyl ether (FOF-1), was first synthesized by Sheremetev *et al.* in 1996 [8]. They reacted 3,4-dinitrofurazan in anhydrous acetonitrile. Much subsequent research has concentrated on the synthesis and properties of difurazanyl ethers, including 3,3'-dicyanodifurazanyl ether (FOF-2) [9, 10], bis-3,4-(3-nitrofurazan-4-oxy) furazan (FOF-11) [6, 11] and 3,3-bis(fluorodinitromethyl)difurazanyl ether (FOF-13) [12, 13]. However, owing to the difficulties in their synthesis and preparation on the large scale, the properties of most difurazanyl ethers are lacking. Therefore, systematic and comprehensive investigation of the relationship between molecular structure and properties of the furazanyl ethers is of important practical significance.

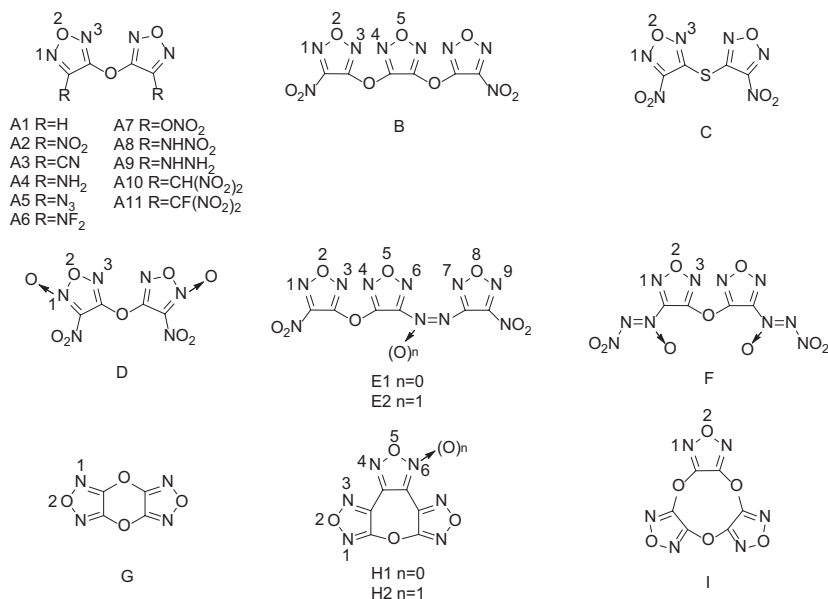
Compared to experimental approaches, theoretical studies are safe and time saving, and can also be used to calculate the essential parameters of energetic materials based on detailed insights into molecular structure. Among many computational methods, density functional theory (DFT) is a powerful approach for investigating the structure and performance of energetic materials [14-23]. Zhang *et al.* used DFT to predict HOFs, explosive properties, and molecular stability of monofurazan derivatives and bridged difurazan derivatives [24, 25]. Their results show that the  $-\text{NH}-\text{NH}-$ ,  $-\text{N}=\text{N}-$  and  $-\text{N}(\text{O})=\text{N}-$  groups are effective bridges for enhancing the thermal stability, and the  $-\text{N}=\text{N}-$  bridge plays an important role in increasing the HOF values of the difurazan derivatives. The molecular structure and performance of furazano[3,4-b]pyrazine-, difurazano[3,4-b:3',4'-e]piperazine-, and furazano [3,4-d]-pyridazine-based derivatives were also investigated by Pan *et al.* [26, 27] and Wang *et al.* [28]. They found that the substitution of  $-\text{NO}_2$ ,  $-\text{NF}_2$ , or  $\text{NO}_2$ -substituted heterocycles is the most efficient method for enhancing the detonation performance of designed compounds.

In this article, a series of furazanyl ethers (including symmetrical difurazanyl ether,  $-\text{N}=\text{N}-$  and  $-\text{N}(\text{O})=\text{N}-$  bridged furazanyl ether, cyclic furazanyl ether)

substituted with energy-rich functional groups were investigated to evaluate the effects of different substituents on the performance and stability of the derivatives. The gas phase and solid phase HOFs were estimated by designing an isodesmic reaction. The molecular stabilities were predicted using bond dissociation energy (BDE) and frontier orbit energy. By using the calculated HOFs and densities, the detonation performances of title compounds were also investigated. The impact sensitivities ( $H_{50}$ ) were investigated to better understand the safety performance of these compounds. In addition, their melting points were calculated by calculating their specific heat capacities as a function of temperature. These results may provide useful information for the application of furazanyl ether HEDMs.

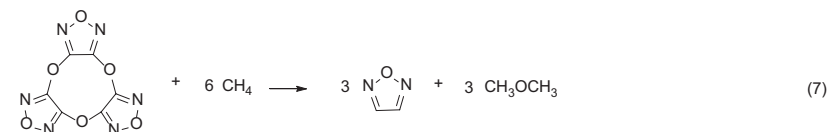
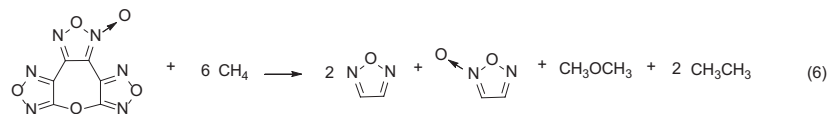
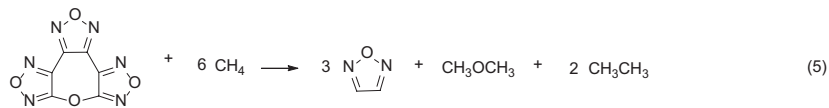
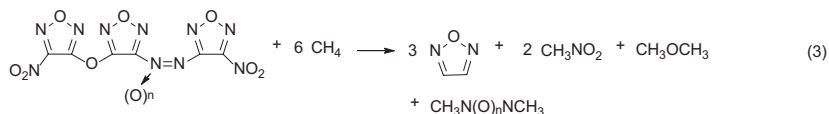
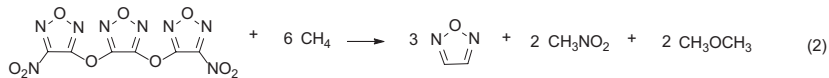
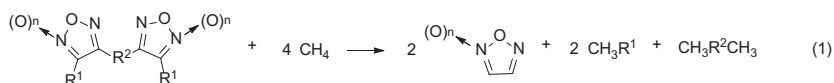
## 2 Computational Details

The target molecular frameworks of a series of furazanyl ethers are listed in Figure 1. The DFT-B3LYP method with a 6-311G(d,p) basis set, which has been demonstrated to be reliable in predicting molecular structures and energies of furazan-based energetic materials [26, 28], was used to perform the geometry optimization for all molecules using the GAUSSIAN 09 program package [29]. All optimized structures were positively identified to be truly relative energy minima of the potential surface by frequency calculation (no imaginary frequencies were found).



**Figure 1.** Molecular frameworks of a series of furazanyl ethers

Isodesmic reactions have been proved to reliably evaluate the HOFs of organic compounds due to the similar electronic nature of products and reactants [30-33]. Here, isodesmic reactions were designed to compute HOFs using total energies calculated from DFT-B3LYP/6-311G(d,p) level, in which the numbers of all kinds of bonds remain invariant, thus permitting a reduction in calculation error. The isodesmic reactions used to calculate the HOFs of furazanyl ethers at 298 K are shown in Scheme 1, where R =  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{NH}_2$ ,  $-\text{N}_3$ ,  $-\text{NF}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NHNO}_2$ ,  $-\text{NHNH}_2$ ,  $-\text{CH}(\text{NO}_2)_2$  and  $-\text{CF}(\text{NO}_2)_2$ . All heterocyclic skeletons and conjugated bonds remained constant and large molecules transformed into smaller ones.



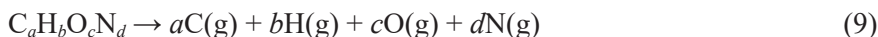
**Scheme 1.** Isodesmic reactions used to calculate the HOFs of furazanyl ethers at 298 K

For the isodesmic reaction, the heat of reaction ( $\Delta H_{298\text{K}}$ ) at 298 K can be calculated from the following equation:

$$\Delta H_{298\text{K}} = \Sigma \Delta H_{(f,P)} - \Sigma \Delta H_{(f,R)} \quad (8)$$

where  $\Sigma \Delta H_{(f,P)}$  and  $\Sigma \Delta H_{(f,R)}$  are the HOFs of products and reactants at 298 K, respectively. Meanwhile, the  $\Delta H_{298\text{K}}$  values can be calculated using our own computer code.

The HOFs of  $\text{CH}_4$ ,  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{NF}_2$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{N}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{SCH}_3$ ,  $\text{CH}_3\text{ONO}_2$ ,  $\text{CH}_3\text{NHNO}_2$ ,  $\text{CH}_3\text{LNHNH}_2$ ,  $\text{CH}_3\text{N}_2\text{CH}_3$ ,  $\text{CH}_3\text{N(O)NCH}_3$ ,  $\text{CH}_3\text{N(O)NNO}_2$ ,  $\text{CH}_2(\text{NO}_2)_2$ ,  $\text{CHF}(\text{NO}_2)_2$ , furazan and furoxan were evaluated by using an atomization approach [21, 22, 34] at the G2 level to get an accurate value. The atomization reaction can be written as:



Then, the gas state HOFs for the target molecule at 298 K can be calculated from Eq. (10):

$$\Delta H_{298\text{K}} = \Delta E_{298\text{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (10)$$

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies of the products and the reactants at 0 K;  $\Delta H_T$  is thermal correction from 0 K to 298 K. The  $\Delta(PV)$  term in Eq. (10) equals  $\Delta nRT$  for reactions of an ideal gas. For the isodesmic reactions,  $\Delta n = 0$ , so  $\Delta(PV) = 0$ .

For most energetic compounds, the accurate calculation of detonation performance demands solid state HOFs ( $\Delta H_{f,\text{solid}}$ ). These can be estimated from the gas state HOFs ( $\Delta H_{f,\text{gas}}$ ) and heats of sublimation ( $\Delta H_{\text{sub}}$ ) according to Hess's law of constant heat summation as Eq. (11) [35]:

$$\Delta H_{f,\text{solid}} = \Delta H_{f,\text{gas}} - \Delta H_{\text{sub}} \quad (11)$$

The heat of sublimation ( $\Delta H_{\text{sub}}$ ) can be evaluated by Eq. (12) developed by Politzer *et al.* [36, 37]:

$$\Delta H_{\text{sub}}(298 \text{ K}, \text{kJ}\cdot\text{mol}^{-1}) = \alpha(As)^2 + \beta(v\sigma_{\text{tot}}^2)^{0.5} + \gamma \quad (12)$$

where  $As$  is the surface area of the  $0.001 \text{ electrons}\cdot\text{Bohr}^{-3}$  isosurface of the electronic density of the molecule,  $v$  represents a measure of balance between positive and negative potential on the molecular surface, and  $\sigma_{\text{tot}}^2$  describes the variability of electrostatic potential. Parameters  $\alpha$ ,  $\beta$ , and  $\gamma$  are adopted from Ref. [38].

The theoretical density was obtained by Eq. (13), which was proposed by Politzer *et al.* [39]:

$$\rho = \alpha' \left( \frac{M}{V(0.001)} \right) + \beta' (v\sigma_{\text{tot}}^2) + \gamma' \quad (13)$$

where  $M$  is the molecular mass ( $\text{g}\cdot\text{mol}^{-1}$ ),  $V(0.001)$  is the volume of the 0.001 electrons·Bohr<sup>-3</sup> contour of electronic density estimated using Monte Carlo integration [40]. The coefficients  $\alpha'$ ,  $\beta'$ , and  $\gamma'$  are taken from Ref. [39].

The detonation velocity ( $D$ ,  $\text{km}\cdot\text{s}^{-1}$ ) and pressure ( $P$ , GPa) were calculated using empirical Kamlet-Jacobs equations [41]:

$$D = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (14)$$

$$P = 1.558\rho^2 N \bar{M}^{1/2} Q^{1/2} \quad (15)$$

where  $N$  is the amount ( $\text{mol}^{-1}$ ) of gaseous products per gram of explosive,  $\bar{M}$  is the average molecular weight of the gaseous products,  $Q$  is the heat of detonation ( $\text{cal}\cdot\text{g}^{-1}$ ) derived from HOFs of the products and reactants, and  $\rho$  is the density of explosive ( $\text{g}\cdot\text{cm}^{-3}$ ).

The oxygen balance reflects the effect on capacity of explosives, which can be calculated from Eq. (16) for a general formula  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  [42] and Eq. (17) for fluorine-containing formula  $\text{C}_a\text{H}_b\text{F}_c\text{N}_d\text{O}_e$  [43].

$$\Omega_{\text{CO}_2} = \frac{c - (2a + 0.5b)}{M} \times 1600 \quad (16)$$

$$\Omega_{\text{CO}_2} = \frac{e - 2a - [(b - c) / 2]}{M} \times 1600 \quad (17)$$

The bond dissociation energy (BDE), which represents the difference between the energy of a molecule and those of the radicals produced when a bond of this molecule is broken, is usually regarded as a compelling criterion for the molecular stability [44]. It is quite important to understand chemical change during detonation process [45]. The BDE of the trigger bond, which is

required for homolytic bond cleavage at 298 K and 1 atm, can be given in terms of the following Eq. (18):

$$\text{BDE}(\text{R-X}) = E(\text{R}) + E(\text{X}) - E(\text{R-X}) \quad (18)$$

where R-X is the designed molecule.  $E(\text{R-X})$ ,  $E(\text{R})$ , and  $E(\text{X})$  are the total energies of the parent compound and corresponding radicals, respectively.

The BDE with zero point energy correction ( $\text{BDE}_{\text{ZPE}}$ ) can be calculated from Eq. (19):

$$\text{BDE}_{\text{ZPE}}(\text{R-X}) = \text{BDE}(\text{R-X}) + \Delta E_{\text{ZPE}} \quad (19)$$

where  $\Delta E_{\text{ZPE}}$  is the zero point energy correction.

The impact sensitivity is defined as the degree of sensitivity for an explosive to the impact from a drop-hammer. It can be measured by a height of 50% initiation probability ( $H_{50}$ ). Here, we choose a computer algorithm suggested by Keshavarz *et al.* [46] to estimate  $H_{50}$ . For a general formula  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ , the  $H_{50}$  value for target compound can be calculated from Eq. (20) and Eq. (21):

$$\log H_{50} = (\log H_{50})_{\text{elem}} + \frac{111.6h_{50}^{\text{ds}} - 132.3h_{50}^{\text{is}}}{MW} \quad (20)$$

$$(\log H_{50})_{\text{elem}} = \frac{48.81a + 25.94b + 13.73c - 4.786d}{MW} \quad (21)$$

where the values of coefficients  $h_{50}^{\text{ds}}$  and  $h_{50}^{\text{is}}$  are taken from Ref. [46].

As a contrast, the HOFs, density and melting point of furazanyl ethers were also calculated by an empirical method proposed by Keshavarz *et al.* [47-49].

### 3 Results and Discussion

#### 3.1 Heats of formation

Table 1 lists the total energies, zero-point energies and thermal corrections for 19 reference compounds involved in the isodesmic reactions. The HOFs of the above-mentioned compounds were calculated by using atomization reactions at the G2 level. To validate the reliability of the computational results, the corresponding experimental HOFs were taken from Refs. [50, 51]. The

results show that the calculated HOF values of most products are quite close to experimental values with relative errors within 10% (except  $\text{CH}_3\text{NH}_2$ ). This indicates that the calculated HOFs at the G2 theory are reliable in this work.

**Table 1.** The total energies ( $E_0$ ), zero point energies (ZPE), thermal corrections ( $H_T$ ), and heats of formation (HOFs) for furazanyl ethers<sup>a</sup>

Compd.	$E_0$ [a.u.]	ZPE [a.u.]	$H_T$ [kJ·mol <sup>-1</sup> ]	$\Delta H_f(\text{g})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{sub}}$ [kJ·mol <sup>-1</sup> ]	$\Delta H_f(\text{s})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_f(\text{s})^b$ [kJ·mol <sup>-1</sup> ]
A1	-598.2415	0.0758	23.39	325.40	64.67	260.73	268.81
A2	-1007.2995	0.0801	37.53	388.94	125.41	263.53	251.97
A3	-782.7422	0.0727	32.77	667.39	131.89	535.50	566.31
A4	-708.9952	0.1094	29.19	304.79	128.13	176.66	197.65
A5	-925.4871	0.0820	37.62	1028.90	145.12	883.80	847.29
A6	-1105.7349	0.0736	38.88	318.32	121.83	196.49	183.09
A7	-1157.7330	0.0875	43.10	224.99	138.71	86.28	97.25
A8	-1118.0403	0.1148	42.60	454.29	146.70	307.59	334.11
A9	-819.6529	0.1448	37.19	519.72	167.11	352.61	310.45
A10	-1495.0532	0.1418	57.83	340.22	199.26	140.96	185.99
A11	-1693.5552	0.1240	62.76	0.24	207.24	-207.00	-152.59
B	-1343.4273	0.1106	49.21	519.72	167.11	352.61	328.10
C	-1330.2867	0.0767	38.76	550.88	130.27	420.61	251.97
D	-1157.6677	0.0876	42.65	404.78	138.18	266.60	342.53
E1	-1377.6576	0.1148	51.99	878.08	201.19	676.89	710.67
E2	-1452.8581	0.1199	54.31	853.04	215.55	637.49	648.64
F	-1376.5849	0.1069	52.21	953.60	183.62	769.98	843.03
G	-672.2466	0.0594	21.47	279.10	76.43	202.67	224.83
H1	-857.9412	0.0811	26.26	615.33	105.20	510.13	596.26
H2	-933.1246	0.0847	31.61	667.48	112.82	564.66	641.54
I	-1008.3614	0.0896	33.01	443.09	117.78	325.31	392.95

<sup>a</sup> The scaling factor is 0.98 for ZPE and 0.96 for  $H_T$  [52];

<sup>b</sup> The data calculated by the empirical method from Ref. [47].

It can be found that the values of HOFs calculated by isodesmic reactions and an empirical method vary in the same pattern. For the A series, it is noted that the compounds with  $-\text{N}_3$  or  $-\text{CN}$  have higher HOF values than the others, whereas for those with substituents  $-\text{NH}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ , or  $-\text{CF}(\text{NO}_2)_2$ , the HOF values of those with substituted difurazanyl ether decrease compared with the unsubstituted difurazanyl ether (A1). In addition, the substitution of a fluorine-containing  $-\text{CF}(\text{NO}_2)_2$  group greatly decreases its HOF value to  $-207.00 \text{ kJ}\cdot\text{mol}^{-1}$ . This phenomenon has been observed previously for other groups and was ascribed to the low HOF value of fluorine atoms [22]. Among the same series, the  $\text{N}_3$ -substituted difurazanyl ethers exhibit the largest HOF



value, which is in agreement with a previous study [53] which showed that the substitution of  $-N_3$  results in an obvious increase in energy content of a molecule by 293-320  $\text{kJ}\cdot\text{mol}^{-1}$ .

By comparing compound A2 and B, G and I, it is found that the HOF value increases with increase in the number of furazan rings. The replacement of an ether ( $-O-$ ) by a thioether bond ( $-S-$ ) makes the HOF of C increase to 420.61  $\text{kJ}\cdot\text{mol}^{-1}$  compared with A2. Moreover, the results of A2, D, H1, and H2 show that the substitution of a furazan ring by a furoxan ring has no effect on HOF values. It is worth noting that the furazanyl ethers linked with an azo bond ( $-N=N-$ ) and an azoxy bond ( $-N(O)=N-$ ) have relatively high HOF values (637.49-769.98  $\text{kJ}\cdot\text{mol}^{-1}$ ). Therefore, incorporation of the  $-N=N-$  and  $-N(O)=N-$  groups is effective in enhancing the HOFs for furazanyl ethers.

### 3.2 Molecular stability

Generally, the molecular stability of energetic materials can be evaluated by bond dissociation energy (BDE). When a certain bond is weak, the energy for breaking it is small and the bond becomes a trigger bond. For the furazanyl ethers, there are two possible bond dissociations that should be considered: (1) the two N–O bonds in a furazan (furoxan) ring; (2) the C(N, O)–NO<sub>2</sub> bonds. Meanwhile, it is also accepted that the Wiberg bond order value can be used as a quantitative index for the strength of trigger bond. A large Wiberg bond order suggests that the bond is hard to rupture, which corresponds to good molecular stability. Table 2 lists the bond dissociation energies (BDEs) and the Wiberg bond orders (BOs) of the relatively weaker bonds of the furazanyl ethers.

**Table 2.** Bond dissociation energy (BDE) and Wiberg bond order (BO) of the relatively weak bonds of furazanyl ethers

Compound	Bond	Length [Å]	Wiberg BO	BDE [ $\text{kJ}\cdot\text{mol}^{-1}$ ]
A1	N1–O2	1.3709	1.1104	186.907
	N3–O2	1.3751	1.0838	164.380
A2	N1–O2	1.3537	1.1466	168.859
	N3–O2	1.3781	1.0785	146.078
	C–NO <sub>2</sub>	1.4650	0.9096	257.892
A3	N1–O2	1.3558	1.1458	199.509
	N3–O2	1.3772	1.0775	165.918
A4	N1–O2	1.3928	1.0534	141.352
	N3–O2	1.3639	1.1036	179.395

Compound	Bond	Length [Å]	Wiberg BO	BDE [kJ·mol <sup>-1</sup> ]
A5	N1–O2	1.3773	1.0817	184.300
	N3–O2	1.3751	1.0827	180.724
A6	N1–O2	1.3668	1.1122	177.694
	N3–O2	1.3757	1.0814	163.571
A7	N1–O2	1.3601	1.1245	196.204
	N3–O2	1.3765	1.0863	164.792
	O–NO <sub>2</sub>	1.6144	0.6047	56.708
A8	N1–O2	1.3708	1.1011	183.845
	N3–O2	1.3653	1.1063	172.409
	N–NO <sub>2</sub>	1.4268	0.9592	129.975
A9	N1–O2	1.3903	1.0571	159.097
	N3–O2	1.3548	1.1231	161.316
A10	N1–O2	1.3556	1.1434	188.689
	N3–O2	1.3773	1.0783	162.679
	C–NO <sub>2</sub>	1.5351	0.8357	137.860
A11	N1–O2	1.3520	1.1492	195.752
	N3–O2	1.3748	1.0796	166.556
	C–NO <sub>2</sub>	1.5661	0.7791	104.474
B	N1–O2	1.3545	1.1469	172.396
	N3–O2	1.3781	1.0793	148.826
	N4–O5	1.3722	1.1027	164.937
	C–NO <sub>2</sub>	1.4609	0.9105	261.715
C	N1–O2	1.3454	1.1604	164.976
	N3–O2	1.3867	1.0695	151.084
	C–NO <sub>2</sub>	1.4572	0.9232	257.785
D	N1–O2	1.4811	0.8386	118.849
	N3–O2	1.3619	1.0884	169.725
	C–NO <sub>2</sub>	1.4411	0.9605	93.397
E1	N1–O2	1.3528	1.1478	171.025
	N3–O2	1.3802	1.0741	148.270
	N7–O8	1.3877	1.0701	152.570
	C–NO <sub>2</sub>	1.4650	0.9104	258.575
E2	N1–O2	1.3519	1.1503	171.569
	N3–O2	1.3802	1.0743	149.640
	N7–O8	1.3748	1.0882	165.207
	C–NO <sub>2</sub>	1.4653	0.9117	259.129

Compound	Bond	Length [Å]	Wiberg BO	BDE [kJ·mol <sup>-1</sup> ]
F	N1–O2	1.3640	1.1184	168.712
	N3–O2	1.3768	1.0830	160.707
	N–NO <sub>2</sub>	1.4771	0.8961	100.231
G	N1–O2	1.3809	1.0840	175.360
H1	N1–O2	1.3665	1.0978	182.950
	N3–O2	1.3578	1.1385	202.507
	N4–O5	1.3639	1.1245	196.821
H2	N1–O2	1.3670	1.0981	185.633
	N3–O2	1.3585	1.1369	203.941
	N4–O5	1.3463	1.1330	167.788
	N6–O5	1.4937	0.8181	78.754
I	N1–O2	1.3701	1.1054	168.449

For furazanyl ethers, we found using computational methods that the N–O bonds in the furazan ring have smaller BDE values than other bonds. From Table 2, it can be seen that the substituted groups have great influence on the BDE of the N–O bond. For instance, the BDE value of the N1–O2 bond (168.859 kJ·mol<sup>-1</sup>) is much higher than that of the N3–O2 bond (146.078 kJ·mol<sup>-1</sup>) for A2. Meanwhile the former has a shorter bond length and higher bond order than the latter. On the other hand, the N1–O2 bond in A4 has a lower BDE, a longer bond length and a lower bond order than the N3–O2 bond. That is to say, the N1–O2 bond is stronger than the N3–O2 bond for the furazanyl ethers substituted by an electron-withdrawing group, while for an electron-donating group, the case is quite the opposite. For the furoxanyl ethers, the BDE and BO values of the N(O)–O bond is much smaller than that of the N–O bond in the furoxan ring, indicating that the N(O)–O bond should be the trigger bond during the thermolysis initiation process. By observing the BDEs of N–O bonds in compounds E, F, G, H and I, it can be learned that the bridged furazanyl ethers and cyclic furazanyl ethers exhibit similar BDEs compared with A1 and A2. Among all the derivatives containing C–NO<sub>2</sub> bonds, it is interesting to find that the BDE values of the C–NO<sub>2</sub> bonds are much lower than the N–O bonds for A10, A11 and D, while the opposite is true for other compounds. In general, most of the furazanyl ethers possess high BDEs and conform to the stability requirement of HEDMs (BDE > 120 kJ·mol<sup>-1</sup>) suggested by Chung *et al.* [54]. Moreover, the introduction of the –ONO<sub>2</sub>, –NHNO<sub>2</sub>, –CH(NO<sub>2</sub>)<sub>2</sub>, –CF(NO<sub>2</sub>)<sub>2</sub> and furoxan groups will decrease the thermal stability of furazanyl ethers.

**Table 3.** The frontier orbital energy of furazanyl ethers

Compound	HOMO [kJ·mol <sup>-1</sup> ]	LUMO [kJ·mol <sup>-1</sup> ]	$\Delta E$ [kJ·mol <sup>-1</sup> ]
A1	-787.177	-198.199	588.978
A2	-890.911	-374.344	516.567
A3	-875.972	-317.082	558.890
A4	-686.752	-147.894	538.858
A5	-740.732	-230.939	509.793
A6	-845.306	-277.253	568.053
A7	-840.134	-309.809	530.325
A8	-817.817	-271.844	545.973
A9	-689.483	-181.370	508.113
A10	-895.217	-379.516	515.701
A11	-887.524	-373.766	513.758
B	-910.891	-385.817	525.073
C	-805.792	-281.748	524.045
D	-819.707	-394.140	425.567
E1	-816.741	-422.574	394.166
E2	-853.051	-399.864	453.188
F	-878.650	-416.588	462.062
G	-800.042	-239.393	560.649
H1	-818.893	-336.799	482.094
H2	-768.011	-338.164	429.847
I	-921.866	-284.762	637.104

The molecular frontier orbital energy and gap energy of furazanyl ethers were also investigated. The stability of compounds with similar frameworks can be evaluated by the band gap ( $\Delta E = |\epsilon(\text{HOMO}) - \epsilon(\text{LUMO})|$ ). Usually, the smaller the gap, the higher the molecular reactivity, and the easier the molecules decompose during chemical and photochemical processes due to the easy electron transition from HOMO to LUMO [55]. It is seen from Table 3 that the  $\Delta E$  of all substituted furazanyl ethers decrease compared with the parent compound A1, and the  $-\text{NO}_2$ ,  $-\text{N}_3$ ,  $-\text{NHNH}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ , and  $-\text{CF}(\text{NO}_2)_2$  groups produce great influence on  $\Delta E$  values. The compounds D, E1, E2, F, and H2 possess relatively low  $\Delta E$  values, which suggests that the compounds will be made less stable by introducing  $-\text{N}=\text{N}-$ ,  $-\text{N}(\text{O})=\text{N}-$ , or furoxan groups. Compound I can be considered as the most stable among these furazanyl ethers because it has the highest  $\Delta E$  value (637.104 kJ·mol<sup>-1</sup>).

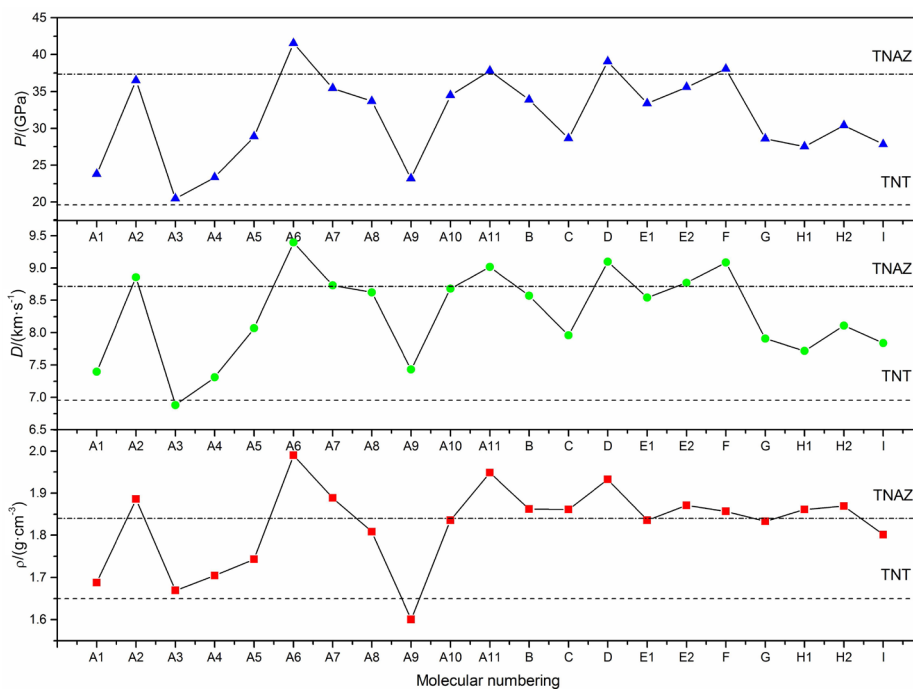
### 3.3 Detonation performance

Table 4 presents the calculated detonation performance of furazanyl ethers with some available experimental values, including densities ( $\rho$ ), heats of detonation ( $Q$ ), detonation velocities ( $D$ ), detonation pressures ( $P$ ), and oxygen balance (OB). Both quantum chemistry and empirical method were used to predict the density of the designed molecules. The widely used empirical Kamlet-Jacobs equations have been used to calculate the performance of energetic compounds [19, 20, 41]. The detonation velocity and detonation pressure of CHNOF explosives (A6, A11) have also been investigated by empirical methods [56, 57]. The experimental detonation performance of two known melt cast explosives 1,3,3-trinitroazetidide (TNAZ) and 2,4,6-trinitrotoluene (TNT) are also listed in this table for comparison.

The results show that the predicted densities of A2, A3, A11, C, F, H2 provide a reasonable match to that of the experimental values for both methods. Therefore, the calculation results for the densities of furazanyl ethers are credible. For the A series, all the densities of the substituted furazanyl ethers increase compared with the parent molecule A1 except for A3 and A9. The compounds with a combination of  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{ONO}_2$ , and  $-\text{CF}(\text{NO}_2)_2$  have higher  $\rho$  values compared with combinations of other substituents. In particular, the densities of derivatives with  $-\text{NF}_2$ , and  $-\text{CF}(\text{NO}_2)_2$  groups are higher than the derivatives with  $-\text{NH}_2$  and  $-\text{CH}(\text{NO}_2)_2$  groups. That is because the substitution of the H atoms of  $-\text{NH}_2$  and  $-\text{CH}(\text{NO}_2)_2$  with fluorine atoms not only enhances the molecular mass but also affects the volume relatively little. It is also clear that the substitution of a furazan ring by a furoxan ring is helpful for increasing its  $\rho$  value by comparison with A2 and D. In addition, for the azo (azoxy)-bridged and macrocycle furazanyl ethers, there are no appreciable changes in the values of the density.

Usually, there is a positive correlation for explosives between heat of detonation and capacity. The calculated heats of detonation reveal that the introduction of  $-\text{NO}_2$  and  $-\text{NF}_2$  significantly increases its  $Q$  value compared with the parent molecule, while the substitution of  $-\text{CN}$ ,  $-\text{NH}_2$ , and  $-\text{NHNH}_2$  are proved to be counter-productive. Furazanyl ethers linked by the  $-\text{N}=\text{N}-$  or  $-\text{N}(\text{O})=\text{N}-$  group also have high  $Q$  values, indicating that azo and azoxy group are effective bridges for improving the heat of detonation. Oxygen balance (OB) is another important factor for the application of energetic materials. In general, explosives with a value for oxygen balance around zero exhibit the best energetic performance. It is found from Table 4 that the nitro-containing groups ( $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NHNO}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ , and  $-\text{CF}(\text{NO}_2)_2$ ) play an important role in elevating the OB value for substituted difurazanyl ethers. The same is true with the introduction of the bridge group  $-\text{N}(\text{O})=\text{N}-$  and furoxan ring. On the whole, benefiting from the introduction of ether linkage, most furazanyl ethers display good oxygen balance.

Table 4 lists the predicted detonation velocities and detonation pressures for all furazanyl ethers. It can be seen that the calculated detonation velocities of A11 ( $9.02 \text{ km}\cdot\text{s}^{-1}$  or  $8.95 \text{ km}\cdot\text{s}^{-1}$ ) and H2 ( $8.11 \text{ km}\cdot\text{s}^{-1}$ ) are close to their experimental values ( $8.50 \text{ km}\cdot\text{s}^{-1}$ , at  $1.69 \text{ g}\cdot\text{cm}^{-3}$  and  $8.25 \text{ km}\cdot\text{s}^{-1}$ , at  $1.85 \text{ g}\cdot\text{cm}^{-3}$ ), so the predictions for these compounds are considered to be reliable. For the series A, all the substituted derivatives have higher  $D$  and  $P$  values than the parent compound A1 except for A3 and A4. In particular, the fluorine-containing explosives (A6 and A11) have excellent detonation properties among the derivatives investigated. It is also found that the oxygen-enriched groups  $-\text{N}(\text{O})=\text{N}-$  and furoxan have a positive effect on increasing the detonation properties. Although the density of F is lower than D, the  $D$  and  $P$  values of the two compounds are almost equivalent, indicating that the detonation properties are greatly influenced by the heat of detonation. Moreover, compound A2, A7, A11, D, and F with oxygen balance around zero have relative high  $D$  and  $P$  values, showing that oxygen balance also plays an important role in improving the detonation performance.



**Figure 2.** Density, detonation velocity, and detonation pressure of the furazanyl ethers

**Table 4.** The predicted densities ( $\rho$ ), heats of detonation ( $Q$ ), detonation velocities ( $D$ ), detonation pressures ( $P$ ) and oxygen balance (OB) for furazanyl ethers<sup>a</sup>

Compd.	$\rho$ [g·cm <sup>-3</sup> ]	$\rho^k$ [g·cm <sup>-3</sup> ]	$Q$ [J·g <sup>-1</sup> ]	$D$ [km·s <sup>-1</sup> ]	$P$ [GPa]	OB [%]
A1	1.688	1.699	5895.85	7.40	23.79	-62.30
A2	1.886 (1.898) <sup>b</sup>	1.891	6793.46	8.86	36.49	-6.55
A3	1.669 (1.64) <sup>c</sup>	1.670	5588.42	6.88	20.45	-70.55
A4	1.704	1.708	4735.96	7.31	23.35	-60.84
A5	1.743	1.796	6326.96	8.07	28.89	-33.88
A6	1.990	–	6960.29	9.40 (9.49) <sup>l</sup>	41.52 (41.23) <sup>m</sup>	-18.74
A7	1.889	1.924	6081.18	8.73	35.42	5.80
A8	1.808	1.826	6392.48	8.62	33.68	-11.67
A9	1.600	1.667	5456.00	7.43	23.20	-59.79
A10	1.836	1.876	6565.59	8.68	34.45	-8.84
A11	1.949 (1.91) <sup>d</sup>	–	6167.25	9.02 (8.95) <sup>l</sup> (8.50) <sup>d</sup>	37.78 (36.08) <sup>m</sup>	0
B	1.862 (1.859) <sup>e</sup>	1.859	6547.03	8.57	33.88	-14.63
C	1.861 (1.867) <sup>f</sup>	–	6179.29	7.96	28.65	-12.30
D	1.933	1.924	6734.34	9.10	39.05	5.80
E1	1.836	1.867	6697.95	8.54	33.39	-18.82
E2	1.871	1.881	6838.90	8.77	35.57	-13.48
F	1.857 (1.845) <sup>g</sup>	1.885	7128.85	9.09	38.05	4.82
G	1.833	1.804	5977.05	7.91	28.59	-38.07
H1	1.861	1.850	5972.14	7.72	27.51	-58.16
H2	1.869 (1.866) <sup>h</sup>	1.882	6642.25	8.11 (8.25) <sup>h</sup>	30.39	-47.44
I	1.801	1.804	6061.52	7.84	27.80	-38.08
TNAZ <sup>i</sup>	1.84	–	6134	8.73	37.2	-16.7
TNT <sup>j</sup>	1.65	–	4384	6.95	19.5	-74.0

<sup>a</sup> The average volumes are from 100 single-point calculations at the B3LYP/6-311G(d,p) level;

<sup>b</sup> Ref. [8]; <sup>c</sup> Ref. [10]; <sup>d</sup> Ref. [13]; <sup>e</sup> Ref. [11]; <sup>f</sup> Ref. [58]; <sup>g</sup> Ref. [59]; <sup>h</sup> Ref. [60]; <sup>i</sup> Ref. [61];

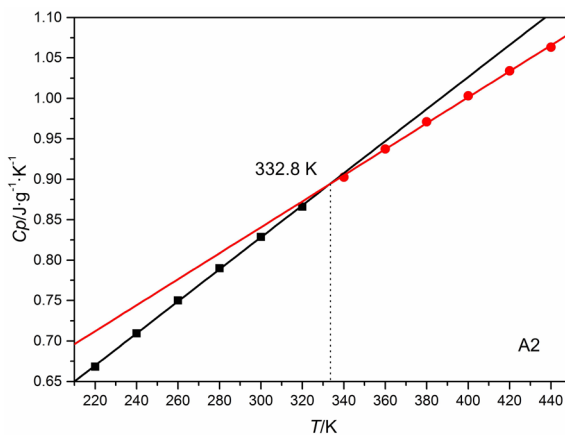
<sup>j</sup> Ref. [62]; <sup>k</sup> The data calculated by empirical method from Ref. [48]; <sup>l</sup> The data calculated by empirical method from Ref. [56]; <sup>m</sup> The data calculated by empirical method from Ref. [57].

Figure 2 displays a comparison of the  $\rho$ ,  $D$ , and  $P$  values for furazanyl ethers calculated using the DFT method as do the commonly used melt-cast explosives TNAZ and TNT. It can be seen that the  $\rho$ ,  $D$ , and  $P$  values have the same tendency to vary with the molecular number, demonstrating that detonation performance is predominantly controlled by density. It is worth noting that almost all furazanyl ethers possess higher  $D$  and  $P$  than TNT except for A3. Yet only A2, A6, A7, A11, D, and F have good detonation properties ( $D$  and  $P$ ) near or over TNAZ. Overall, it can be concluded that the introduction of fluorine-containing groups ( $-\text{NF}_2$ ,  $-\text{CF}(\text{NO}_2)_2$ ), nitro group, furoxan group, or azoxy group can lead to a significant improvement in density and hence enhance the detonation performance.

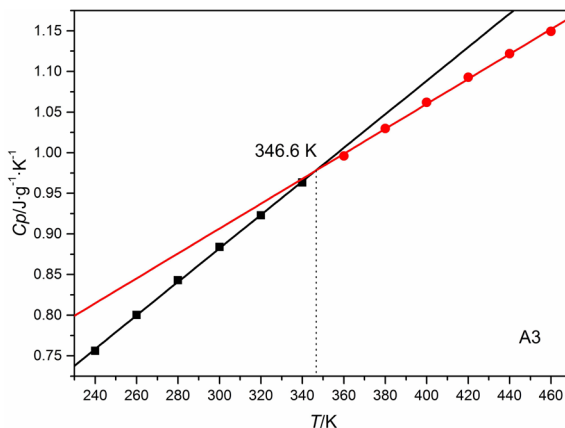
### 3.4 Melting point

The melting point ( $T_m$ ) is a crucial factor for melt cast explosives and energetic plasticizers. Usually, the melting point requirement for melt cast explosive is in the temperature range 70 °C to 120 °C [63]. The specific heat capacity  $C_p$  of a compound is the quantity of heat required to raise the temperature of unit mass by 1 K at constant pressure. Because of the different molecular packing, the value of  $C_p$  will display a different rate of change in the course of the melting phase transition. We have successfully predicted the melting points of DNTF/TNAZ eutectic compositions through calculation of  $C_p$  by using MD simulations [64]. Here, the  $C_p$  values of all furazanyl ethers at different temperatures have been calculated based on vibration frequencies and statistical thermodynamic principles (detailed results are listed in Supplementary Material). By observing the inflection point on different curves of specific heat capacity vs. temperature, the melting points of furazanyl ethers are predicted and compared with the experimental values as shown in Table 5. The corresponding graphs of  $C_p$  vs. temperature data are depicted in Figures 3 and 4 by taking A2 and A3 as examples. The empirical method based on the elemental composition and specific groups of energetic compounds was also applied for the prediction of melting points.





**Figure 3.** The specific heat capacity versus temperature relationship for A2



**Figure 4.** The specific heat capacity versus temperature relationship for A3

As shown in Table 5, the calculated  $T_m$  values are in reasonable agreement with experimental values, which proved that both methods are reliable. Compared to the parent compound A1, the substitution of  $-\text{NH}_2$ ,  $-\text{NF}_2$ , or  $-\text{NHNH}_2$  groups is helpful for improving melting points for furazanyl ethers, whereas the substitution of  $-\text{N}_3$ ,  $-\text{ONO}_2$ , and  $-\text{CF}(\text{NO}_2)_2$  produce the opposite effect. With the increase in the number of ether bonds, the  $T_m$  values of furazanyl ethers decrease remarkably. Results also show that the introduction of  $-\text{N}=\text{N}-$  or  $-\text{N}(\text{O})=\text{N}-$  groups is effective in elevating  $T_m$  values, and for  $-\text{N}=\text{N}-$  group the impact is more pronounced. Considering the detonation performance and melting point, it may be concluded that H2 possesses good  $D$  and  $P$  values and a moderate

$T_m$  value and has the potential to be used in melt cast explosives. On the other hand, the low melting point and good detonation properties make A11, E1, and E2 important candidates for energetic plasticizers.

**Table 5.** The predicted and experimental melting points ( $T_m$ ) of furazanyl ethers

Compound	$T_m$ [K] (Cal.)	$T_m$ [°C] (Cal.)	$T_m^k$ [°C] (Cal.)	$T_m$ [°C] (Exp.)
A1	342.2	69.1	73.2	–
A2	332.8	59.7	59.7	63-64 <sup>a</sup>
A3	346.6	73.5	70.8	68.5-69.0 <sup>b</sup>
A4	369.7	96.5	149.3	–
A5	292.8	19.7	20.9	–
A6	408.5	135.4	134.7	–
A7	312.5	39.4	33.5	–
A8	333.2	60.1	65.5	–
A9	371.9	98.8	104.5	–
A10	334.6	61.5	65.2	68-69 <sup>c</sup>
A11	311.1	38.0	38.2	43-44 <sup>c</sup>
B	314.8	41.7	44.8	38-40 <sup>d</sup>
C	350.9	77.8	85.8	72-73 <sup>e</sup>
D	329.1	56.0	59.7	–
E1	295.3	22.2	18.9	–
E2	312.3	39.2	45.1	41-42 <sup>d</sup>
F	332.2	59.1	60.2	66 <sup>f</sup>
G	292.2	19.1	20.1	16 <sup>d</sup>
H1	352.5	79.4	83.8	76.5-77 <sup>g</sup>
H2	370.1	97.0	96.9	92-94 <sup>h</sup>
I	298.6	25.5	31.4	–
TNAZ	–	–	–	100 <sup>i</sup>
TNT	–	–	–	81 <sup>j</sup>

<sup>a</sup> Ref. [8]; <sup>b</sup> Ref. [10]; <sup>c</sup> Ref. [13]; <sup>d</sup> Ref. [6]; <sup>e</sup> Ref. [58]; <sup>f</sup> Ref. [59]; <sup>g</sup> Ref. [65]; <sup>h</sup> Ref. [60];

<sup>i</sup> Ref. [61]; <sup>j</sup> Ref. [62]; <sup>k</sup> The data calculated by empirical method from Ref. [49].

### 3.5 Impact sensitivity

**Table 6.** The predicted impact sensitivity ( $H_{50}$ ) for furazanyl ethers

Compound	$\log H_{50}$	$H_{50}$ [cm]
A1	1.868	73.8
A2	1.412	25.8
A3	2.043	110.3 (125.9) <sup>a</sup>
A4	2.298	198.6
A5	1.494	31.2
A6	1.421	26.3
A7	1.214	16.4
A8	1.547	35.2
A9	2.347	222.1
A10	1.881	76.0
A11	1.581	38.1 (57.1) <sup>b</sup>
B	1.403	25.3
C	1.511	32.5
D	1.214	16.4
E1	1.448	28.1
E2	1.369	23.4
F	1.174	14.9
G	1.973	94.0
H1	1.872	74.5 (72.4) <sup>c</sup>
H2	1.725	53.1 (57.5) <sup>d</sup>
I	1.774	59.4
TNAZ	–	26 <sup>e</sup>
TNT	–	103 <sup>f</sup>

<sup>a</sup> Ref. [7]; <sup>b</sup> Ref. [13]; <sup>c</sup> Ref. [65]; <sup>d</sup> Ref. [60]; <sup>e</sup> Ref.[69]; <sup>f</sup> Ref. [70].

The sensitivity of an explosive greatly affects the safety of its preparation, transportation, storage and practical application. For a given compound, the degree of sensitivity is closely related to its molecular structure [66-68]. Generally, the larger  $H_{50}$  value an explosive has, the lower its impact sensitivity. Table 6 lists the predicted characteristic height  $H_{50}$  for all furazanyl ethers. Good agreements can be observed from the comparison between calculated  $H_{50}$  values and experimental data for A3, A11, H1 and H2. Overall, for furazanyl ethers, the high level of detonation performance means the low degree of  $H_{50}$  value. The introduction of  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{ONO}_2$ ,  $-\text{N}=\text{N}-$  and  $-\text{N}(\text{O})$  groups may lead to a substantial increase in sensitivity, whereas  $-\text{CN}$  and  $-\text{NH}_2$  derivatives present

quite low impact sensitivity. Moreover, it is suggested that the replacement of one nitro group by fluorine for fluorodinitromethyl may decrease the sensitivity, which coincides with the report from Ma *et al.* [22]. Most furazanyl ethers maintained lower sensitivity compared to that of TNAZ, some of them even lower than that of TNT. In particular, the high energy level and low impact sensitivity make A11 a very attractive candidate in high energy density materials (HEDMs).

## 4 Conclusions

In summary, a detailed theoretical study of HOFs, molecular stability, energetic properties and melting point of energetic substituted furazanyl ethers was performed by the DFT-B3LYP method at 6-311G(d,p) level. By designing isodesmic reactions, the gas state and solid state HOFs were predicted. The results show that incorporating the  $-N_3$  or  $-N(O)=N-$  groups into the furazan ring is favorable for increasing the HOFs. An analysis of the bond dissociation energies suggests that the N–O bond in the furazan ring is the weakest and most compounds meet the stability requirement of HEDMs. In addition, the calculated frontier orbital energy shows that the introduction of  $-N=N-$ ,  $-N(O)=N-$ , or furoxan groups lowers molecular stability. From calculation of detonation velocities and detonation pressures, it was found that  $-NF_2$ ,  $-CF(NO_2)_2$ , furoxan, and  $-N(O)=N-$  groups are effective substituents for enhancing the detonation performance in comparison with the parent compounds. The study of melting point shows that the incorporation of  $-NH_2$ ,  $-NF_2$ ,  $-NHNH_2$ ,  $-N=N-$ , or  $-N(O)=N-$  groups is helpful for increasing the melting point, but the  $-N_3$ ,  $-ONO_2$ , and  $-CF(NO_2)_2$  groups have the opposite effect. The calculated  $H_{50}$  values suggest that the introduction of the  $-CN$  or  $-NH_2$  groups greatly decreases the impact sensitivity of furazanyl ethers. Considering the detonation performance and melting point, H2 is suitable to be used as a melt cast explosive, while A11, E1 and E2 are expected to be applied as energetic plasticizers. These results may provide useful thoughts and a theoretical basis for the molecular design of energetic materials.

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