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THEORETICAL INVESTIGATION OF THE HEAT OF FORMATION AND DETONATION PERFORMANCE ON 1,1,3,5,5-PENTANITRO-1,5-BIS(DIFLUORAMINO)-3-AZAPENTANE SUBSTITUTED**F. Aghabozorgi¹, M. Hamadani²**

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The density functional theory (DFT) calculation is performed on 1,1,3,5,5-pentanitro-1,5-bis(difluoramino)-3-azapentane substituted. The heat of formation (HOF) is predicted by B3LYP and B3P86 methods with the 6-311G** and 6-311++G** basis sets via isodesmic reactions. With NF₂ and ONO₂ substitution for NO₂, HOFs clearly decrease. Furthermore, we designed a detonation reaction for each compound and computed ΔH_{298} , the heat of explosion (Q), and ΔG_{298} for each reaction. The general trend is that Q increases as ONO₂ and NO₂ groups are replaced by the NF₂ groups.

Keywords: density functional calculations, heat of formation, heat of explosion.

INTRODUCTION

Interest in organic difluoramines has been predominantly due to their potential for being energetic materials in rocket propellant and explosives formulations. This potential derives from the intrinsically high energy of the difluoramino (NF₂) group relative to another substituent of oxidizing capability in energetic ingredients, such as the nitro group (NO₂) [1]. The difluoramino group strongly enhances the performance of formulations that contain boron and aluminum. 1,1,3,5,5-pentanitro-1,5-bis (difluoramino)-3-azapentane (DFAP) is a high-energy material with a potential of being an oxidizer in energetic propellants. DFAP is obtained through the reaction of bis(2,2-dinitroethyl)nitramine with NF₂OSO₂F and has an extremely high density for an acyclic compound of 2.045 g/ml [2].

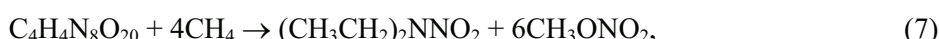
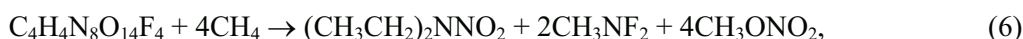
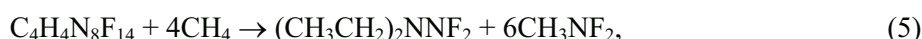
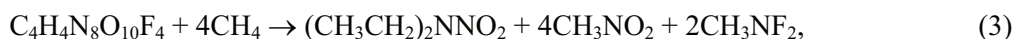
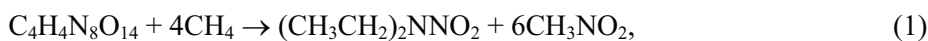
In this paper, six molecules were designed by changing the substituent of DFAP and by using the DFT calculation to calculate the explosive properties of these compounds and to investigate the effect of different groups on these properties [3, 4].

The heat of formation (HOF) is one of the most important thermochemical properties of energetic materials. Computational approaches have also been employed to obtain HOFs of these demanding materials [5–8]. To investigate the detonation performance, the detonation reaction for the corresponding compound was designed and the enthalpy (heat of detonation), Q (heat of explosion), and the Gibbs free energy have also been calculated for each reaction. These results provide useful information for the molecule design of novel high energetic density materials.

COMPUTATIONAL METHODS

The hybrid DFT-B3LYP, B3P86 methods with 6-311G** and 6-311++G** via isodesmic reaction were adopted for predicting HOFs [9–15]. The so-called isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with the application of the bond separa-

tion reaction rules (BSRR). The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds [14]. The isodesmic reactions employed to calculate HOFs of our compounds are as follows:



For isodesmic reactions (1)–(7), the heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R}, \quad (9)$$

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

Since experimental HOFs of CH_3NF_2 and NH_2NF_2 are unavailable, additional calculations were carried out for the replacement reaction $\text{CH}_3\text{NH}_2 + \text{F}_2 \rightarrow \text{CH}_3\text{NF}_2 + \text{H}_2$ using the G2 theory to get an accurate value of ΔH_f for CH_3NF_2 [16].

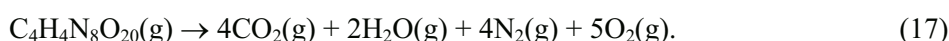
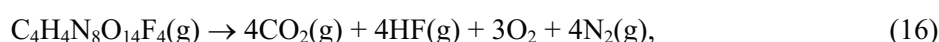
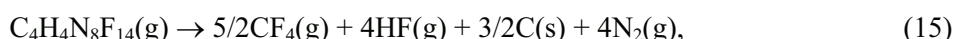
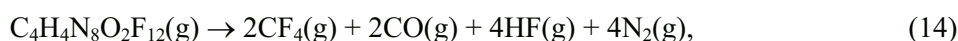
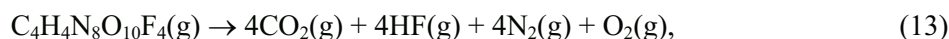
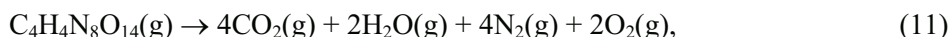
The HOF value for NH_2NF_2 was found at the G2 level from the atomization reaction: $\text{NH}_2\text{NF}_2(\text{g}) \rightarrow 2\text{N}(\text{g}) + 2\text{H}(\text{g}) + 2\text{F}(\text{g})$ [17]. Experimental HOFs of the reference compounds such as $(\text{CH}_3\text{CH}_2)_2\text{NH}$, CH_4 , CH_3NO_2 , CH_3ONO_2 , $(\text{CH}_3\text{CH}_2)_2\text{NH}$, and NH_3 are available.

The HOFs of corresponding compounds can be found when the heat of reaction ΔH_{298} is known. Therefore, the most important matter here is to compute the ΔH_{298} that can be calculated using the following formula:

$$\Delta H_{298} = \Delta E + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT, \quad (10)$$

where ΔE_0 is a change in the total energy between the products and reactants at 0 K; ΔZPE is the difference between zero-point energies (ZPE) of the products and reactants; ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in equation (10) is the PV work term. It equals ΔnRT .

To determine the performance of detonation of each compound the detonation reactions should be designed. Depending on the composition of the propellant, the major components of the gaseous products may include CO , CO_2 , H_2O , N_2 , or HF with less quantities of other molecules and radicals such as H_2 , NO , H , O , CHO , and N_2O . Unused carbon is present as the solid [18–21]. Thus, we designed the detonation reactions for our compounds as follows:



Our goal was to compute ΔH_{298} (the heat of detonation), Q (the heat of explosion) and then ΔG_{298} for each detonation reaction. ΔH_{298} can be computed by equation (10) and ΔG_{298} can be calculated by equation (18).

$$\Delta G_{298} = \Delta H_{298} - T\Delta S_{298}. \quad (18)$$

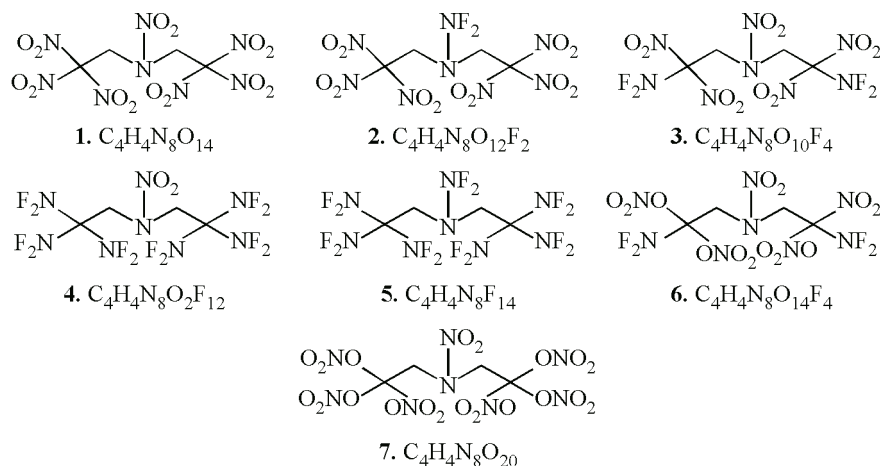


Fig. 1. Molecular frameworks of the corresponding compounds

In equation (18), ΔS_{298} is the entropy difference between the products and reactants at 298 K, and ΔG_{298} is the Gibbs free energy difference between the products and reactants at 298 K.

Computations were also performed using the Gaussian03 [22] package at the B3LYP and B3P86 levels.

RESULTS AND DISCUSSION

Heat of formation. Fig. 1 shows the molecular frameworks of our compounds. The total energies, zero-point energies, and the thermal correction values calculated at the B3LYP/6-311G** and B3P86/6-311G** levels for the reference compounds are listed in Table 1. Experimental HOFs of the reference compounds CH_4 , CH_3NO_2 , CH_3ONO_2 , $(CH_3CH_2)_2NNO_2$, $(CH_3CH_2)_2NH$, and NH_3 are taken from [23, 24]. The HOF value for $(CH_3CH_2)_2NNF_2$ at 298.15 K was calculated through the isodesmic reaction (8): $(CH_3CH_2)_2NNF_2 + NH_3 \rightarrow (CH_3CH_2)_2NH + NH_2NF_2$. The accurate value of ΔH_f for CH_3NF_2 and NH_2NF_2 were calculated through the G2 method from [16, 17]. Table 2 represents the total energies, zero-point energies, the thermal correction values for the title compounds, and the HOFs values calculated through equation (9).

As for HOFs obtained at the B3LYP/6-311G** level, it can be seen from Table 2 that in 1—5 compounds, the HOFs values decrease when NF_2 groups substitute for the NO_2 groups. For instance,

Table 1

Calculated total energy (E_0), zero-point energy (ZPE), thermal correction values (H_T), and heats of formation (HOF) of the reference compounds

Compound	E_0	ZPE	H_T	E_0	ZPE	H_T	HOF(exp)
	B3LYP/6-311G**			B3P86/6-311G**			
CH_4	-40.5337	114.70	10.02	-40.7139	115.00	10.02	-74.87 [23]
CH_3NO_2	-245.0817	127.96	13.86	-245.6491	128.88	13.80	-81.00 [23]
CH_3NF_2	-294.2983	120.29	13.61	-294.8950	121.15	13.61	-115.23 [16]
NH_3	-56.5760	88.22	10.01	-56.75632	88.73	10.01	-46.00 [23]
NH_2NF_2	-310.3268	91.72	13.28	-310.9235	92.21	13.15	-29.90 [17]
CH_3ONO_2	-320.2827	139.38	15.56	-320.9911	140.83	15.41	-122.10 [23]
$(CH_3CH_2)_2NNO_2$	-418.4070	390.43	26.45	-419.5586	392.24	26.35	-53.13 [24]
$(CH_3CH_2)_2NH$	-213.8605	382.78	20.69	-214.6231	383.91	20.70	-99.8 [23]

Note: E_0 is in a.u., ZPE, HOF and H_T are in kJ/mol. The scaling factor for ZPE is 0.98 [25].

Table 2

Total energy (E_0), zero-point energy (ZPE), thermal correction values (H_T), and heats of formation (HOFs) of the compounds at the B3LYP and B3P86 levels with 6-311G**

No	E_0	ZPE	H_T	HOF	E_0	ZPE	H_T	HOF
	B3LYP/6-311G**				B3P86/6-311G**			
1	-1645.6085	432.17	65.11	104.62 (159.70)	-1649.0864	430.01	64.35	98.06 (136.50)
2	-1694.8245	413.22	66.73	39.88 (94.94)	-1698.3304	419.40	66.06	23.19 (70.33)
3	-1744.0426	407.56	66.07	34.68 (74.32)	-1747.5784	413.77	65.35	32.99 (50.43)
4	-1940.9025	375.46	68.35	-82.61 (-18.52)	-1944.5551	381.39	67.47	-89.63 (-41.33)
5	-1990.1196	365.97	69.57	-149.85 (-104.78)	-1993.8008	371.60	68.74	-160.03 (-134.81)
6	-2044.8692	441.09	80.32	-204.11 (-169.33)	-2048.9633	449.76	78.23	-197.313 (-176.31)
7	-2096.8861	481.72	82.26	-348.31 (-316.98)	-2101.2039	490.50	80.87	-342.25 (-324.78)

Note: E_0 is in a.u., ZPE, HOF, and H_T are in kJ/mol. The scaling factor for ZPE is 0.98 [25]. The values in parenthesis are HOFs calculated with 6-311++G**.

HOF for compound 4 is larger than that for compound 5 and HOF for compound 3 with two NF_2 groups is about 83 KJ/mol less than that for compound 1. The results show that bonding NF_2 groups on C or N atoms have no considerable effect on HOFs in these compounds.

The replacement of NO_2 groups by ONO_2 groups in compounds 1 and 3 respectively, and the construction of 7 and 6, leads to a high reduction in the HOFs values. Thus, HOF of 7 is the smallest and HOF of 1 is the largest. We also calculated HOFs at the B3LYP/6-311++G**, B3P86/6-311G**, and B3P86/6-311++G** levels to evaluate the method and dependence on the basis set. A comparison of the values of two DFT levels (B3LYP and B3P86) shows that HOFs calculated using B3LYP are larger than those yielded by B3P86 with the same basis set. There is a significant linear relationship between HOFs from the B3LYP and B3P86 methods with the 6-311G** basis set. The insertion of diffuse functions to the basis sets (6-311++G**) increased HOFs in all compounds. This shows that HOFs are clearly affected by the basis sets.

Investigation of detonation performance. The total energies, zero-point energies, and the thermal correction values calculated at the B3LYP/6-311G** and B3P86/6-311G** levels for gaseous products are listed in Table 3. Tables 4 and 5 show the computed values of ΔE_{298} , ΔS_{298} , ΔH_{298} , the heat of explosion (Q), and ΔG_{298} for the detonation reaction of the corresponding compounds in the methods used. The negative sign for the heat of explosion is generally omitted since it only denotes an exothermic reaction [19].

Table 3

Calculated total energy (E_0), zero-point energy (ZPE), and thermal correction values (H_T) for gaseous products calculated at the B3LYP and B3P86 levels with 6-311G**

Compound	E_0	ZPE	H_T	E_0	ZPE	H_T
	B3LYP/6-311G**			B3P86/6-311G**		
CO_2	-186.6417	30.10	9.36	-189.0220	30.48	9.36
CO	-113.3462	13.07	8.98	-113.5831	13.07	8.68
O_2	-150.3026	9.54	8.68	-150.5766	9.78	8.68
HF	-100.4697	24.13	8.68	-100.6447	24.39	8.68
N_2	-109.5559	14.35	8.67	-109.7952	14.45	8.67
CF_4	-437.6136	43.49	12.81	-438.3449	44.18	12.74
H_2O	-76.4474	54.85	9.93	-76.6252	55.32	9.82

Note: E_0 is in a.u., ZPE and H_T are in kJ/mol. The scaling factor for ZPE is 0.98 [25].

Table 4

Values of ΔE_{298} , ΔS_{298} , ΔH_{298} , Q , and ΔG_{298} calculated using B3LYP and B3P86 methods with 6-311G**

No	ΔE_{298}	ΔS_{298}	ΔH_{298}	Q	ΔG_{298}	ΔE_{298}	ΔS_{298}	ΔH_{298}	Q	ΔG_{298}
	B3LYP/6-311G**					B3P86/6-311G**				
1	-1857	1.71	-1830	1.13	-2340	-1600	1.71	-1573	0.95	-2082
2	-2184	1.75	-2156	1.31	-2677	-1952	1.75	-1924	1.17	-2445
3	-2508	1.82	-2478	1.48	-3021	-2297	1.82	-2267	1.36	-2810
4	-3003	1.70	-2976	1.68	-3483	-2851	1.71	-2823	1.59	-3333
5	-2976	1.44	-2952	1.64	-3334	-2826	1.44	-2802	1.56	-3187
6	-1938	2.09	-1904	0.96	-2526	-1700	2.09	-1666	0.86	-2289
7	-907	2.14	-872	0.43	-1510	-603	2.16	-569	0.28	-1212

Note: ΔE_{298} , ΔS_{298} , ΔH_{298} , and ΔG_{298} are in kJ/mol and Q is in kcal/gr.

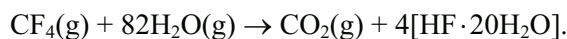
Table 5

Values of ΔE_{298} , ΔS_{298} , ΔH_{298} , Q , and ΔG_{298} calculated using the B3LYP and B3P86 methods with 6-311++G**

No	ΔE_{298}	ΔS_{298}	ΔH_{298}	Q	ΔG_{298}	ΔE_{298}	ΔS_{298}	ΔH_{298}	Q	ΔG_{298}
	B3LYP/6-311++G**					B3P86/6-311++G**				
1	-1927	1.71	-1899	1.18	-2409	-1659	1.71	-1632	1.01	-2141
2	-2273	1.74	-2244	1.36	-2766	-2020	1.71	-1991	1.21	-2501
3	-2609	1.82	-2579	1.54	-3121	-2380	1.82	-2350	1.41	-2892
4	-3112	1.69	-3085	1.75	-3588	-2923	1.69	-2896	1.64	-3399
5	-3068	1.43	-3045	1.69	-3424	-2878	1.44	-2854	1.59	-3236
6	-2064	2.08	-2030	1.05	-2649	-1787	2.09	-1752	0.91	-2375
7	-998	2.14	-963	0.48	-1601	-675	2.15	-641	0.32	-1281

Note: ΔE_{298} , ΔS_{298} , ΔH_{298} , and ΔG_{298} are in kJ/mol and Q is in kcal/gr.

When NO_2 is replaced by NF_2 , ΔH_{298} and Q increase gradually. The highest heat of explosion (Q) value belongs to compound **4**. It is expected that compound **5** with seven difluoroamino groups has a higher heat of explosion than compound **4**, but the calculated results show that the heat of explosion for compound **5** is less than that for compound **4** because compound **5** produces solid carbon in its explosive reaction. If there is enough water in the explosion environment, CF_4 can be hydrolyzed and CO_2 and HF are produced due to the following reaction:



The amount of the calculated enthalpy for this reaction is -173.97 kJ/mol [21].

Since the ONO_2 substitution for NO_2 and NF_2 in compounds **6** and **7** reduces ΔH_{298} and Q , compound **7** has the lowest Q value amongst all compounds. The computed ΔG_{298} values are negative for all compounds. This shows that all explosive reactions are spontaneous. The B3P86 method shows more negativity for ΔH_{298} and ΔG_{298} in comparison to B3LYP. Moreover, a larger basis set (6-311++G**) slightly increases (making more negative) ΔH_{298} and ΔG_{298} .

CONCLUSIONS

This study presents the DFT calculation for 1,1,3,5,5-pentanitro-1,5-bis(difluoroamino)-3-azapentane substituted in order to investigate the explosive performance of these compounds. According to the obtained results, when NO_2 groups are replaced by NF_2 and ONO_2 groups, HOFs decrease gradually. All considered compounds showed the appropriate values for HOFs as explosive molecules. Furthermore, it was found that the NF_2 group increased dramatically the heat of explosion (Q). It seems

that a balance between the number of fluorine and carbon atoms in acyclic explosive compounds can provide explosive molecules with high explosive performance.

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