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Exploring highly energetic aliphatic azido nitramines for plasticizers

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Abstract:

A set of energetic aliphatic azido nitramines was designed and studied with the B3LYP/6-31G* method of density functional theory to find new promising azido nitramines applicable to propellants as plasticizers and to investigate the effect of the methylene nitramino group ($-CH_2NNO_2-$) on performance. The reliability of the theoretical method was tested by comparing the theoretical densities with the experimental data. The thermodynamic properties (heat capacity, enthalpy, entropy, and heat of formation), density (ρ), detonation pressure (P), detonation velocity (D), specific impulse (I_s) and stability were predicted. With the increase in the number of $-CH_2NNO_2-$ groups (n), the thermodynamic properties, ρ, P, and D increase, while the stability decreases slightly. There are linear relationships between thermodynamic properties and n. A $-CH_2NNO_2-$ group improves the heat of formation by 67.59 kJ.mol^{-1} on average. I_s reaches to the maximum when $n=4$ and changes little when $n \geq 5$. It is worth noting that I_ss of all title compounds are higher than that of HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraazacyclooctane, a famous explosive).

Key words: aliphatic azido nitramine, energetic plasticizer, specific impulse, stability

1 Introduction

The common way to improve the output energy of propellants is to add certain amounts of high energetic explosives, such as, RDX (hexahydro-1, 3, 5-trinitro-1, 3, 5-trizine) and HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7- tetraazacyclooctane). However, this may also bring some problems, such as, high flame temperature and serious ablation of gun barrel. Therefore, it is necessary to mix energetic plasticizers or other additives into the propellants. Nitrate ester plasticizers have good plasticizing effects and high energy, but they also have undesired high

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volatility and impact sensitivity. Compared with nitrate ester plasticizers, azido plasticizers, especially azido nitramine plasticizers which have two kinds of energetic groups (i.e., nitramino ($-NNO_2$) and azido ($-N_3$)) in molecules have better stability and compatibility with other components of propellants (e.g. binders) [1] and have been attracting more and more attentions [2-10]. Researches found that azido nitramine plasticizers can adjust the average molecular weight of combustion products, increase the nitrogen content and hence reduce the characteristic signal, and improve the energy and specific impulse of propellants. Although this type of compounds has attracted great interests, effects of structures on their performance are still unclear. Therefore, in this paper, eight aliphatic azido nitramines (Fig. 1) were studied using the density functional theory (DFT). Thereinto, compounds 1~4 have been synthesized and reported [2-4], particularly for compound 3 (1, 7-diazido-2, 4, 6-trinitrazaheptane), extensive studies have been carried out both experimentally and theoretically [8-11].

Since the output energy (detonation pressure, detonation velocity, specific impulse) and stability are the important parameters for characterizing and evaluating the performance of energetic materials, they, together with the related thermodynamic properties and density of these compounds were investigated. In terms of the energetic property and stability, we try to (I) search for new azido nitramine plasticizers with better properties and (II) investigate the role of $-CH_2NNO_2-$ groups in the molecular design of the azido nitramines. Since specific impulse (I_s) is the most vital parameter to weigh the performance of propellants, in this work, two kinds of idealized stoichiometric decomposition reactions were designed to predict reliable I_ss. Based on the well-predicted I_ss to screen promising energetic plasticizers makes this study more meaningful.
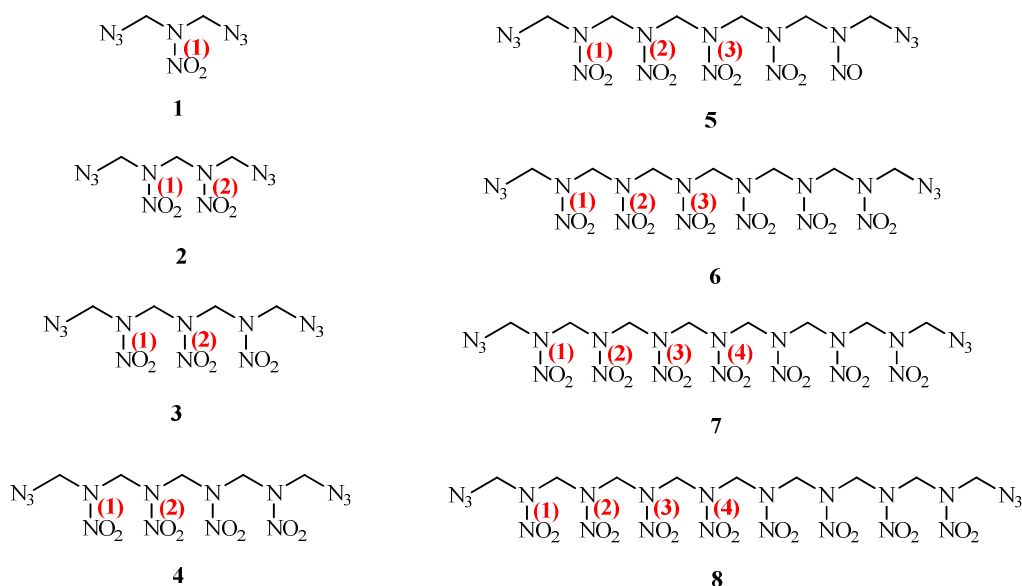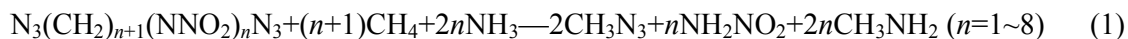
Fig. 1 Structures of title compounds with the numbering of some N-NO$_2$ bonds

2 Theoretical methods

Molecular geometries of the title compounds were fully optimized using the DFT-B3LYP method [12-13] in combination with the 6-31G* basis set [14]. Many studies [15-16] have shown that accurate molecular structures and other properties can be produced at this level. The density (ρ) was evaluated with $\rho=M/V_m$, where M is the molecular weight. V_m is the average molar volume obtained with the Monte Carlo integration scheme by setting the number of points to 20000 per Bohr^3, which is basically equivalent to the average of 1000 default runs [17]. Previous studies [17-18] have indicated that the theoretical ρ calculated using this method is very close to the experimental crystal density for azido compounds.

To discuss the effect of the number (n) of -CH$_2$NNO$_2$- groups on the thermodynamic properties, heat capacity ($C^0_{p, m}$), enthalpy (S^0_m), and entropy (H^0_m) at different temperatures (200 to 800 K) were calculated using a self-compiled program and the heat of formation (HOF) was calculated from the isodesmic reaction (1). This procedure has been proved to be very successful [19] and widely used in previous studies [20-22].

$$\text{N}_3(\text{CH}_2)_{n+1}(\text{NNO}_2)_n\text{N}_3+(n+1)\text{CH}_4+2n\text{NH}_3—2\text{CH}_3\text{N}_3+n\text{NH}_2\text{NO}_2+2n\text{CH}_3\text{NH}_2 \ (n=1~8) \qquad (1)$$

The reaction enthalpy (ΔH_r) of the isodesmic reaction at 298 K was calculated using the following equation:

$$\Delta H_r = \Sigma \Delta H_{f,P} - \Sigma \Delta H_{f,R} = \Delta E_0 + \Delta E_{ZPV} + \Delta H_T + \Delta nRT \qquad (2)$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are HOFs of products and reactants at 298 K, respectively. ΔE_0 and ΔE_{ZPV} are the differences between the total energies at 0 K and between the zero-point vibrational energies of products and reactants, respectively, and ΔH_T is the thermal enthalpy correction from 0 to 298 K. The ΔH_fs of the reference compounds except CH_3N_3 and NH_2NO_2 are taken from the experimental values. For CH_3N_3 and NH_2NO_2 which lack of experimental data, additional calculations were performed at the G2 level to get accurate ΔH_f from the atomization reaction. Previous researches have verified the reliability of the procedure [23].

Detonation velocity (D) and detonation pressure (P) were predicted using the empirical Kamlet-Jacobs equations [24].

$$D = 1.01(N \overline{M}^{0.5} Q^{0.5})^{0.5}(1 + 1.30\rho) \qquad (3)$$

$$P = 1.558 \, \rho^2 N \overline{M}^{0.5} Q^{0.5} \qquad (4)$$

where ρ is the density (g.cm^{-3}), N is the moles of gas produced by per gram of reactant, $\overline{M}$ is the average molar weight of detonation products, and Q is the chemical energy of detonation (cal.g^{-1}). N, $\overline{M}$ and Q were determined according to the largest exothermicity principle [25].

Specific impulse (I_s) is the most vital parameter for characterizing and evaluating the performance of propellants. It was calculated using the following equations. First, the proportional specific impulse $I_{s,p}$ was estimated using Eq.(5) [26], which has been employed by many studies [15, 27].

$$I_{s,p} \sim T_c^{1/2} N^{1/2} \qquad (5)$$

To use Eq. (5), it is necessary to determine the combustion temperature (T_C) and the molar number of products (N) produced by per unit weight of propellant. T_C was calculated using Eq. (6).

$$\Delta H_C = C_p(T_C - T_0) \qquad (6)$$

where ΔH_C is the enthalpy of combustion and can be calculated from the HOFs of the reactant ($\Delta H_{f,R}$) and product ($\Delta H_{f,P}$).

$$\Delta H_C = \sum \Delta H_{f,R} - \sum \Delta H_{f,P} \qquad (7)$$

The HOFs of products are known and that of reactant was computed from the above mentioned isodesmic reaction.

Since Eq. (5) is a proportion relationship, the obtained $I_{s,p}$ isn't an absolute value. So the relative specific impulse ($I_{s,r}$) to HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraazacyclooctane) was predicted with Eq. (8). Then the absolute specific impulse (I_s) of the title compounds was estimated by multiplying the experimental I_s of HMX (265.10 s [28]) with Eq. (9).

$$I_{s,r}=I_{s,p}/I_{s,p(HMX)} \tag{8}$$

$$I_s=265.10I_{s,r} \tag{9}$$

The thermal stability was investigated by evaluating the bond dissociation energy (E_{BD}). To obtain more accurate results, in this study, E_{BD}s of possible initiation bonds were calculated using Eq. (10).

$$E_{BD}(A\text{-}B)=E_{A\cdot}+E_{B\cdot}-E_{A\text{-}B}-E_{BSSE} \tag{10}$$

where A-B stands for the neutral molecule and A· and B· for the radical products of the dissociation of the A-B bond; $E_{A\text{-}B}$, $E_{A\cdot}$ and $E_{B\cdot}$ are their corresponding total energies corrected by the zero-point vibrational energies. E_{BSSE} is the basis set superposition error (BSSE) calculated with the method proposed by Boys-Bernardi counterpoise [29], which was usually neglected in pevious works [18, 21-22].

All calculations except for D, P, and I_s were performed with the Gaussian program package [30].

3. Results and discussion

3.1 Thermodynamic properties

Thermodynamic properties of the title compounds were evaluated and tabulated in Table 1. It can be seen that $C^0_{p,m}$, S^0_m, and H^0_m increase evidently with the increasing temperature (T) from 200 to 800 K. This is because at the higher temperature, the vibrations of molecules are intensified and make more contributions to the thermodynamic properties, but at the lower temperature, the main contributions are from the translation and rotation. Therefore, the increasing temperature leads to the increase of thermodynamic functions.

Table 1 Thermodynamic properties of the title compounds at different temperatures

Property	T/K	1	2	3	4	5	6	7	8
$C^0_{p,m}$/J.mol^{-1}.K^{-1}	200.00	132.32	185.11	241.09	298.40	351.11	404.18	458.81	513.45
	300.00	170.96	243.64	317.27	392.18	464.92	537.40	610.25	683.63
	400.00	205.44	295.64	385.94	477.07	567.57	657.45	747.18	837.77
	500.00	234.00	338.55	442.93	547.83	652.75	757.00	860.94	965.81

	600.00	256.98	372.88	488.59	604.62	720.88	836.55	951.89	1068.06
	700.00	275.47	400.33	525.04	649.99	775.15	899.85	1024.25	1149.36
	800.00	290.49	422.50	554.42	686.56	818.80	950.72	1082.37	1214.61
S^0_m/J.mol^{-1}.K^{-1}	200.00	425.42	475.75	575.20	637.13	729.99	811.30	880.34	968.69
	300.00	486.45	562.01	687.48	776.01	894.06	1000.60	1095.25	1209.31
	400.00	540.48	639.42	788.41	900.75	1042.24	1172.08	1290.05	1427.64
	500.00	589.50	710.17	880.88	1015.08	1178.37	1329.87	1469.45	1628.84
	600.00	634.27	775.04	965.82	1120.18	1303.64	1475.20	1634.77	1814.32
	700.00	675.32	834.66	1043.98	1216.92	1418.99	1609.08	1787.14	1985.31
	800.00	713.12	889.61	1116.07	1306.18	1525.45	1732.68	1927.84	2143.19
H^0_m/kJ.mol^{-1}	200.00	18.54	23.97	31.19	37.60	44.29	50.60	56.95	63.83
	300.00	33.72	45.44	59.14	72.17	85.14	97.73	110.47	123.75
	400.00	52.59	72.48	94.39	115.74	136.9	157.63	178.51	200.02
	500.00	74.61	104.26	135.93	167.11	198.07	228.53	259.12	290.42
	600.00	99.20	139.9	182.60	224.84	266.88	308.36	349.94	392.32
	700.00	125.86	178.61	233.35	287.65	341.78	395.30	448.88	503.34
	800.00	154.18	219.79	287.37	354.55	421.56	487.92	554.31	621.65

Taking compound 4 as an example, the relationships between the thermodynamic functions and the temperature are expressed in Fig. 2(a) and shown as follows (R^2 is the correlation coefficient and SD is the standard deviation). Obviously, the increments for $C^0_{p,m}$ and S^0_m decrease, while that for H^0_m increases with the increasing temperature. The corresponding correlation coefficients are all close to 1. These equations will be helpful for further studies on the other physical, chemical, and explosive properties of the title compounds at various temperatures.

$$C^0_{p,m}=71.68+1.23T-6.09\times10^{-4}T^2 \qquad R^2=0.99994, SD=1.31035$$

$$S^0_m=339.32+1.59T-4.84\times10^{-4}T^2 \qquad R^2=0.99996, SD=1.82154$$

$$H^0_m=-18.64+0.21T+3.22\times10^{-4}T^2 \qquad R^2=0.99988, SD=1.55821$$

In addition, the thermodynamic properties increase with the increasing number of -CH_2NNO_2- group under the same temperature, and there are good linear relationships between $C^0_{p,m}$ S^0_m, H^0_m and n. As an example, relationships between n and thermodynamic properties at 298 K are depicted in Fig. 2(b) and shown as follows:

$$C^0_{p,m}=97.45+71.94n \qquad R=0.99999, SD=0.73798$$

$$S^0_m=367.34+104.11n \qquad R=0.99930, SD=10.34251$$

$$H^0_m=20.19+12.77n \qquad R=0.99993, SD=0.39382$$

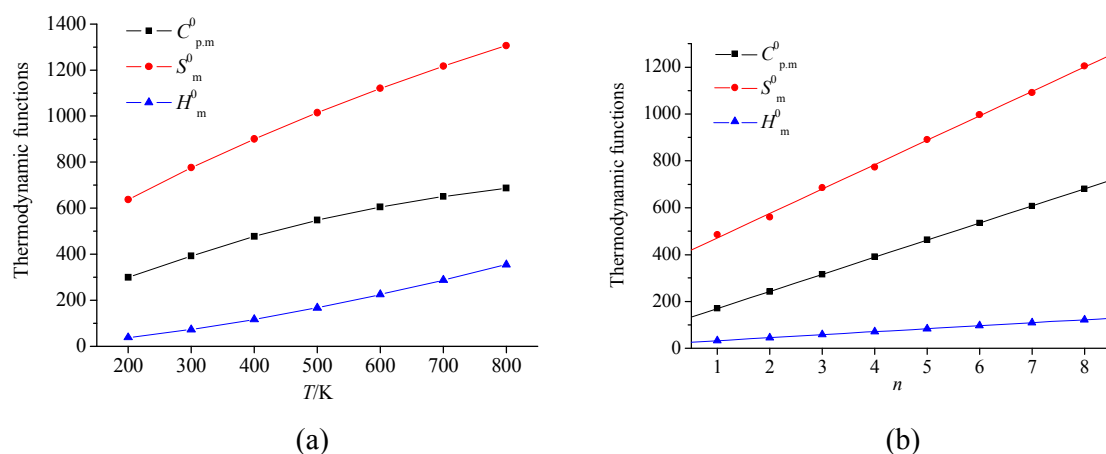Obviously, incorporation of the -CH$_2$NNO$_2$- group exhibits a positive effect on thermodynamic properties.

Fig. 2 Relationships between $C^0_{p,m}$(J.mol^{-1}.K^{-1}), S^0_m(J.mol^{-1}.K^{-1}), H^0_m(kJ.mol^{-1}) and T(K) for compound 4 (a), and n at 298 K (b)

3.2 Energetic properties

Table 2 lists the molecular weight, oxygen balance (OB=[16×(c-2a-b/2)]×100/M, where a, b and c are respectively the number of C, H, and O atoms of the compound C$_a$H$_b$O$_c$N$_d$), calculated density, HOF, detonation pressure, and detonation velocity. For comparison, the calculated and experimental detonation properties of HMX are also summarized in Table 2. Evidently, the calculated detonation properties basically agree with the available experimental values. For example, the predicted ρ, D, and P of HMX are 1.90 g.cm^{-3}, 9.08 km.s^{-1}, 37.66 GPa, respectively and the corresponding experimental results are 1.91 g.cm^{-3}, 9.10 km.s^{-1} and 39.00 GPa [31]; The predicted ρ of 1, 2, and 3 are 1.45, 1.70, and 1.71 g.cm^{-3}, respectively and the corresponding experimental results are 1.43, 1.70, and 1.71 g.cm^{-3} [32]. The calculated and experimental densities of 4 have a relative big deviation, for which we can not provide a definite reason. One possible reason is that the experiment has provided the density of one of the polymorphs for 4. Comparing the D and P of 3 and 4 obtained in this work with those of Zhou, et al [33], a slight deviation exists, which can be attributed to the different fomulas for calculating D and P. Our results are much closer to those reported in references [3] or [9].

Table 2 Detonation properties of the title compounds

Compound	M/g.mol^{-1}	OB/%	ρ/g.cm^{-3}	ΔH_f/kJ.mol^{-1}	D/km.s^{-1}	P/GPa
1	172.11	-37.19	1.45 (1.43 [32])	651.04	7.65	22.59

2	246.15	-32.50	1.70 (1.70 [32])	713.95	8.55	31.36
3	320.18	-29.98	1.71 (1.71 [32], 1.65 [33])	778.56	8.59 (8.30 [9], 8.105 [33])	31.76
4	394.22	-28.41	1.74 (1.67 [3], 1.56 [33])	864.83	8.73 (8.30 [3], 7.839 [33])	33.11 (29.5 [3])
5	468.26	-27.34	1.77	933.76	8.83	34.22
6	542.30	-26.55	1.78	996.61	8.90	35.00
7	616.34	-25.96	1.79	1047.81	8.92	35.24
8	690.38	-23.18	1.80	1120.38	8.97	35.74
HMX	296.16	-21.61	1.90 (1.91 [31])	73.31	9.08 (9.10 [31])	37.66 (39 [31])

Fig. 3 presents the relationships between ρ, ΔH_f, P, D, OB and n. Obviously, all the parameters increase with n, suggesting that incorporating the -CH_2NNO_2- group has a positive effect on the energy performance of aliphatic azido nitramines. There exists a good linear relationship between HOF and n, one -CH_2NNO_2 group increases the HOF by 67.59 kJ.mol^{-1} on average. Compared with the energetic plasticizers widely used in solid propellants, such as ethylene glycol dinitrate (EGDN, ρ=1.48 g.cm^{-3}, D=8.00 km.s^{-1}, P=25.07 GPa) and nitroglycerine (NG, ρ=1.54 g.cm^{-3}, D=8.03 km.s^{-1}, P= 5.92 GPa) [27], all title compounds have better detonation performance and may be potential energetic plasticizers. When n=8, OB, D, and P (-23.18%, 8.97 km.s^{-1}, and 35.74 GPa, respectively) are very close to the values of HMX. Since using compound 3 as a high-energy oxidant to replace RDX in the modified double-base propellants partly can markedly enhance the burning rate, reduce the pressure exponent, and improve the performance level [10], the higher OBs of 4~8 make them more attractive.
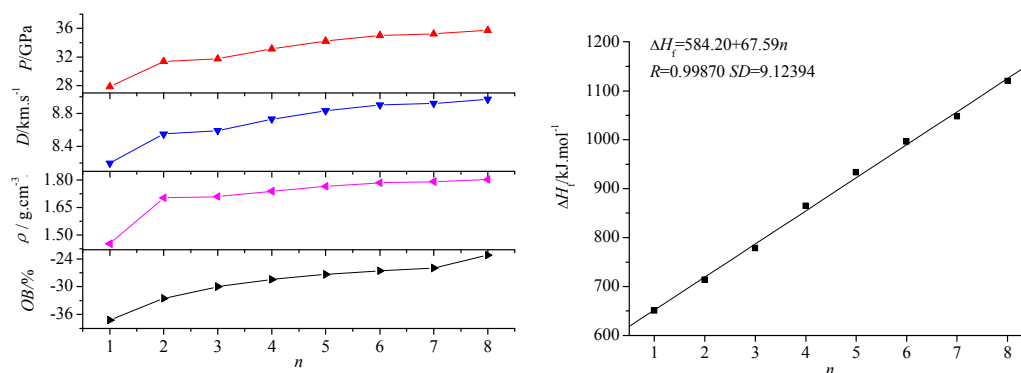

**Fig. 3** Relationships between OB, ρ, D, P, ΔH_f and n

For evaluating the I_s using Eq. (5), it is necessary to establish the identities and amounts of gaseous products. In this paper, two kinds of idealized stoichiometric decomposition

reactions (I and II in Table 3) were designed. Reaction (I) is obtained according to the largest exothermicity principle [25], i.e., all the N atoms turn into N_2, the O atoms react with the H atoms to give H_2O at first, and then form CO_2 with the C atoms. If the number of O atoms is more than that needed to oxidize H and C atoms, the redundant O atoms will convert into O_2. If the content of O is not enough to fully oxidize H and C atoms, the remaining H atoms will convert into H_2, and C atoms will exist as solid-state C. Reaction (II) is obtained according to the principle proposed by Politzer, et al [26], i.e., O atoms form H_2O with the H atoms first and then CO with the C atoms, rather than CO_2 to achieve the maximum of gas products. For the limitation of the quantity of O, the C atoms do not completely convert into CO_2, nor CO, that means the true I_s may be between the values obtained from the reactions (I) and (II). Table 3 gives ΔH_C, C_p, T_C, N, $I_{s,p}$, I_s and corresponding reactions. Fig. 4 shows the variation of I_s with n. Obviously, the designed reactions have a significant effect on I_ss. I_ss obtained from (II) are higher than those obtained from (I). However, the variation trends are consistent, that is, I_s varies up and down with the changes of n from 1 to 8 and it reaches the maximum value at $n=4$, and when n exceeds 5, I_s essentially keeps the constant. It is worth noting that all title compounds possess higher I_s than HMX, which makes these compounds more attractive.

Table 3 Two kinds of idealized decomposition reactions and some I_s related parameters for the title compounds [a]

Compound	Idealized reaction	ΔH_C /kJ.mol^{-1}	C_p /J.mol^{-1}K^{-1}	T_C /K	N	$I_{s,p}$	I_s /s
1	$C_2H_4N_8O_2=4N_2+2H_2O+2C$	-1134.64	232.20	5184.63	0.0349	13.44	268.83
2	(I) $C_3H_6N_{10}O_4=5N_2+3H_2O+1/2CO_2+5/2C$	-1636.10	286.10	6016.78	0.0345	14.41	276.79
	(II) $C_3H_6N_{10}O_4=5N_2+3H_2O+CO+2C$	-1549.85	292.40	5598.59	0.0366	14.31	286.10
3	(I) $C_4H_8N_{12}O_6=6N_2+4H_2O+CO_2+3C$	-2139.26	371.60	6055.04	0.0344	14.42	276.95
	(II) $C_4H_8N_{12}O_6=6N_2+4H_2O+2CO+2C$	-1966.76	384.20	5417.25	0.0375	14.25	284.92
4	(I) $C_5H_{10}N_{14}O_8=7N_2+5H_2O+3/2CO_2+7/2C$	-2694.08	457.10	6192.00	0.0342	14.56	279.61
	(II) $C_5H_{10}N_{14}O_8=7N_2+5H_2O+3CO+2C$	-2435.33	476.00	5414.39	0.0380	14.35	287.01
5	(I) $C_6H_{12}N_{16}O_{10}=8N_2+6H_2O+2CO_2+4C$	-3171.56	542.60	6143.27	0.0342	14.49	278.20
	(II) $C_6H_{12}N_{16}O_{10}=8N_2+6H_2O+4CO+2C$	-2826.56	567.80	5276.24	0.0384	14.24	284.77
6	(I) $C_7H_{14}N_{18}O_{12}=9N_2+7H_2O+5/2CO_2+9/2C$	-3672.96	628.10	6145.88	0.0341	14.48	278.04
	(II) $C_7H_{14}N_{18}O_{12}=9N_2+7H_2O+5CO+2C$	-3241.71	659.60	5212.81	0.0387	14.21	284.10
7	(I) $C_8H_{16}N_{20}O_{14}=10N_2+8H_2O+3CO_2+5C$	-4162.71	713.60	6131.54	0.0341	14.45	277.54
	(II) $C_8H_{16}N_{20}O_{14}=10N_2+8H_2O+6CO+2C$	-3645.21	751.40	5149.37	0.0389	14.16	283.15
8	(I) $C_9H_{18}N_{22}O_{16}=11N_2+9H_2O+7/2CO_2+11/2C$	-4673.83	799.10	6147.02	0.0340	14.47	277.76
	(II) $C_9H_{18}N_{22}O_{16}=11N_2+9H_2O+7CO+2C$	-4070.08	843.20	5125.09	0.0391	14.16	283.10
HMX	(I) $C_4H_8N_8O_8=4N_2+4H_2O+2CO_2+2C$	-1827.51	342.00	5641.75	0.0338	13.81	265.10 [28]

| (II) $C_4H_8N_8O_8$=4N_2+4H_2O+4CO | -1482.51 | 367.20 | 4335.49 | 0.0405 | 13.26 |
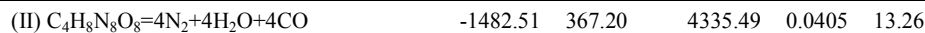
[a] C_p of H_2O, CO_2, CO, N_2, and C are 33.33, 37.65, 29.1, 28.86, 8.53 J.mol^{-1}.K^{-1} and HOF are -241.83, -393.51, -110.50, 0, 0 kJ.mol^{-1}, respectively.
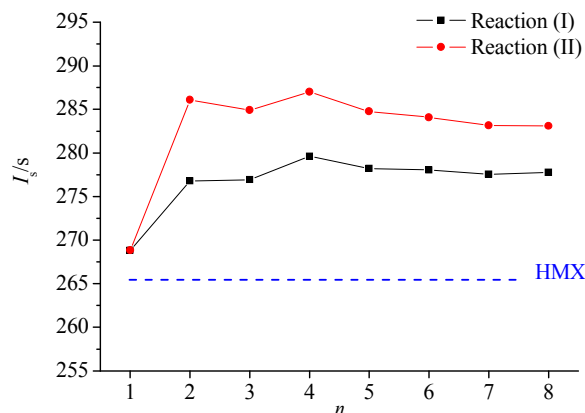

Fig. 4 Correlations between n and I_s obtained from two kinds of reactions

Fig. 5 depicts the variation of C_p, ΔH_C, T_C, N with n for Reaction (I). Clearly, there are good linear correlations between C_p, ΔH_C and n (Fig. 5(a)). The correlation equations are ΔH_C=-634.61-505.79n (R=-0.99991, SD=17.78174) and C_p=130.90+82.87n (R=0.99899, SD=9.85303). T_C increases rapidly with n from 1 to 2 and changes little when n exceeds 4, while N decreases continuously with n from 1 to 8 (Fig. 5(b)).
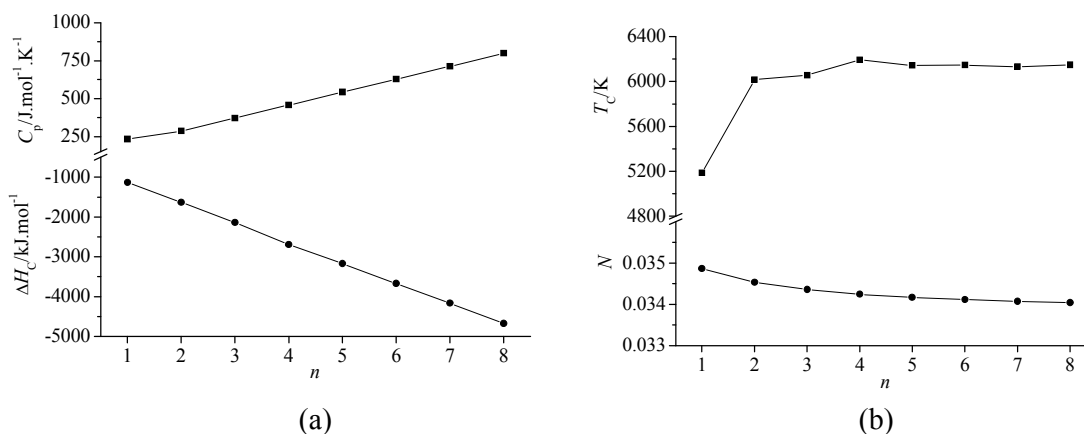

(a)   (b)

Fig. 5 Correlations between C_p, ΔH_C, N, T_C and n for the reaction (I)

3.3 Stability

3.3.1 Energy gap between frontier orbitals

Based on the frontier orbital theory [34], the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) determines

the molecular reactivity, such as the ability to absorb light and to react with other species. The molecule with a smaller energy gap is expected to have a higher reactivity and a lower stability in the chemical or photochemical processes with electron transfer or leap [35]. Table 4 summarizes the energies of HOMO and LUMO (E_{HOMO} and E_{LUMO}), and their energy gaps (E_g). According to the calculated results, the E_gs of the title compounds slightly decrease sequentially from 5.55 eV to 5.02 eV with n from 1 to 8, which shows that incorporation of the -CH_2NNO_2- group will slightly decrease the chemical or photochemical stability.

Table 4 Energies of the frontier orbits and their gaps

	1	2	3	4	5	6	7	8
E_{HOMO}/a.u.	-0.27675	-0.27860	-0.28111	-0.27502	-0.28227	-0.27649	-0.27547	-0.27452
E_{LUMO}/a.u.	-0.07293	-0.08014	-0.08332	-0.08728	-0.09506	-0.09000	-0.08996	-0.08993
E_g/eV	5.55	5.40	5.38	5.11	5.09	5.07	5.05	5.02

3.3.2 Stabilization interaction energy

The stabilization interaction energy (E_2) between the donor (i) and acceptor (j) was estimated based on the NBO analysis using the following equation [36].

$$E_2 = q_i F(i,j)^2/(E_j - E_i) \qquad (11)$$

where q_i is the donor orbital occupancy; E_i and E_j are diagonal elements (orbital energies) and $F(i,j)$ is the off-diagonal NBO Fock matrix element. To elucidate the effect of the number of -CH_2NNO_2- groups on the stability of the N-N bond in -NNO_2 groups, the delocalization from the lone pair of oxygen (n_O) into σ^* antibonding orbital of N-NO_2 (σ^*_{N-N}) was studied. The corresponding E_2 of $n_O \rightarrow \sigma^*_{N-N}$ are summarized in Table 5. The lowest E_2s of $n_O \rightarrow \sigma^*_{N-N}$ in each compound are 48.75, 48.60, 47.74, 47.58, 45.76, 45.02, 44.68, and 43.88 kcal.mol^{-1}, respectively. Since E_2 reflects the delocalization trend of electrons from i to j, and the lower the E_2, the weaker the interaction [37], we can find that the delocalization trend of electrons from n_O to σ^*_{N-N} decreases with n from 1 to 8. In addition, the lower E_2 corresponds to the longer r_{N-N}. For example, compound 8 has the lowest E_2 of $n_O \rightarrow \sigma^*_{N-N(4)}$ (see Fig. 1 for the numbering of N-N bonds) and the longest $r_{N-N(4)}$ (1.401 Å), while compound 1 possesses the highest E_2 of $n_O \rightarrow \sigma^*_{N-N(1)}$ and the shortest $r_{N-N(1)}$ (1.376 Å). Generally, the larger the bond length is, the lower stability the bond has. This suggests that the stability of the title compounds may slightly decrease with the increasing number of -CH_2NNO_2- groups.

Table 5 Stabilization interaction energy (E_2/kcal.mol^{-1}) of $n_O \rightarrow \sigma^*_{N-N}$

	1	2	3	4	5	6	7	8
$n_O \rightarrow \pi^*_{N-N(1)}$	48.75	48.60	47.74	50.84	50.62	46.64	44.88	46.72
$n_O \rightarrow \pi^*_{N-N(2)}$		48.64	48.62	47.58	54.3	49.38	46.94	48.54
$n_O \rightarrow \pi^*_{N-N(3)}$					45.76	45.02	52.06	47.62
$n_O \rightarrow \pi^*_{N-N(4)}$							44.68	43.88

3.3.3 Bond dissociation energy

The bond dissociation energy (E_{BD}) is often used to investigate the thermal stability and pyrolysis mechanism for energetic compounds. Generally, the bond that requires the minimum energy to break is the weakest bond and is most likely to be the trigger bond. Our previous research [11] on the pyrolysis mechanism of compound 3 showed that the rupture of N-NO$_2$ and N-N$_2$ (via the hydrogen transfer) may happen simultaneously as the initial step of pyrolysis. Since the basis set superposition error has not been considered for the calculation of E_{BD}, E_{BD}(N-NO$_2$) is overestimated. E_{BD}(N-NO$_2$) with and without correction of BSSE are 135.62 and 154.83 kJ.mol^{-1} [11], respectively. According to the BSSE-corrected E_{BD}, the pyrolysis may proceed much easier. The BSSE-corrected E_{BD}s of N-NO$_2$ for all title compounds were listed in Table 6. Clearly, when $n \leq 3$, the pyrolysis is initiated from the rupture of the outside N-N bond, i.e., N-N(1), while when $n > 3$, it starts from the breaking of the inner N-N bond. The lowest E_{BD}(N-NO$_2$) decreases from compound 1 to compound 8, suggesting that incorporating more -CH$_2$NNO$_2$- groups into the molecule decrease the stability of the compound. It is noteworthy that all E_{BD}(N-NO$_2$) of the title compounds satisfy the stability requirement of energetic compounds ($E_{BD} \approx 80 \sim 120$ kJ·mol^{-1} [38]). To show the variation of the chemical and thermal stability more intuitively, Fig. 6 was plotted. Obviously, the variation trends of E_g, E_{BD}, and E_2 are the same, i.e., they all decrease with the increase of n.

Compared with the synthesized 1~4, compounds 5, 6, 7, and 8 all have good energetic properties, which suggests that they are attractive candidates as the components of propellants. In fact, to be a good energetic additive, it needs to have not only good energetic properties but also good compatibility with other components in the propellants. Since the main purpose of this work is to screen new azido nitramines from the viewpoint of energetic properties and

stabilities and to investigate the role of $-CH_2NNO_2-$ groups in the design of the azido nitramines, the compatibility of the screened compounds with binders (such as GAP) will be investigated in the coming works. We will also investigate whether they are helpful for improving the mechanical properties of propellants.

Table 6 Bond dissociation energy (E_{BD}/kJ.mol^{-1}) of N-NO$_2$

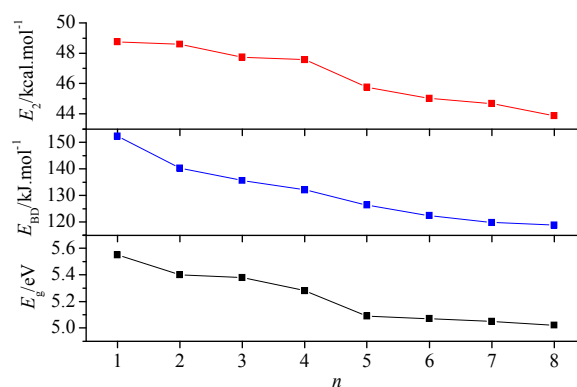|	1	2	3	4	5	6	7	8
N-N(1)	152.36	140.35	135.62	138.73	135.63	134.84	135.25	144.55
N-N(2)		148.27	145.05	132.08	130.56	128.32	139.26	134.95
N-N(3)					126.34	122.43	126.68	125.70
N-N(4)							119.87	118.83

Fig. 6 Variation of E_g, E_2, and E_{BD} with n

4. Conclusions

Eight aliphatic azido nitramines were studied using the B3LYP/6-31G* method of density functional theory. Their thermodynamic properties, density, detonation pressure, and detonation velocity increase while stability decreases with the increasing number of $-CH_2NNO_2-$ groups. Specific impulse (I_s) varies up and down, and it reaches the maximum value when $n=4$ and maintains essentially a constant value when $n>5$. All title compounds satisfy the stability requirement of energetic compounds. Compared with the synthesized compounds 1~4, compounds 5~8 are all potential promising plasticizers for propellants. This paper demonstrates how the $-CH_2NNO_2-$ group affects the performance of azido nitramines and provides guidance for the molecular design for this kind of compounds.

Acknowledgments

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