Research paper

A Theoretical Study of Polyethylene Glycol Polynitrates as Potential Highly Energetic Plasticizers for Propellants

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Abstract: Polyethylene glycol polynitrates may be used as plasticizers in propellants. In this study, ten derivatives of ethylene glycol dinitrate were investigated using the density functional theory method. The fitted densities ($\rho'_{exp.}$) were obtained and were very close to the experimental values. The detonation properties were predicted using the modified Kamlet-Jacobs equations and the specific impulse (I_s) was evaluated according to the largest exothermic principle. A new indicator, $K = I_s \cdot \rho'_{exp.}$, is proposed to evaluate the energetic characteristics of the plasticizers. Thermal stability is discussed by calculating the bond dissociation energies or energy barriers. The $O-NO_2$ bond is the trigger bond for all of the compounds studied. Considering the energetic properties and stability, diethylene glycol tetranitrate, triethylene glycol hexanitrate, tetraethylene glycol octanitrate, pentaethylene glycol decanitrate and hexaethylene glycol dodecanitrate are potential energetic plasticizers for solid propellants. The influences of the $-O-CH_2-CH_2-$ and $-O-CH(ONO_2)-CH(ONO_2)-$ groups are also discussed, which will be helpful for the design of new highly energetic plasticizers by modifying the structures as required.

Keywords: polyethylene glycol polynitrates, density functional theory, density, specific impulse, stability

1   Introduction

Solid propellants are the propulsion power behind rockets, missiles and launch vehicles. They are generally a type of highly energetic composite materials, from which hot gaseous products are ejected on combustion from the nozzle to produce forward thrust to the propulsion units. Propellant formulations usually include oxidizers, plasticizers, metallic fuels, polymeric binders, and other highly energetic additives, and the properties of propellants play an important role in the development of the aerospace industry and the survival capacity and combat efficiency of the missiles. Improving the performance, such as the energetic level of the solid propellants is the main and key point of research on propellant technology, which naturally requires the search for highly energetic dense compounds (HEDCs) [1-4].

At present, a good and widely adopted way to improve the energy is to substitute compounds with highly energetic groups, such as nitro ($-NO_2$), nitrate ($-ONO_2$), nitramine ($-NNO_2$), azido ($-N_3$) and difluoramino ($-NF_2$) groups or a combination of energetic groups into a molecule [4, 5]. Nitrate esters form an important group of organic compound with excellent plasticizing properties, and are widely used as components in industrial explosives (such as dynamites) and smokeless powders. Ethylene glycol dinitrate (EGDN), diethylene glycol dinitrate (DEGDN), and nitroglycerine (NG), for example, have received considerable attention in synthesis and analysis [6-13]. Their structures, heats of formation, pyrolysis mechanism, mechanical properties, *etc.* have been studied theoretically by the semi-empirical molecular orbital (MO) method [14, 15], *ab initio* MO method and density functional theory (DFT) [16-24], molecular dynamics (MD) [18, 25], *etc.* However, few reports have systematically studied the energetic properties, such as the density and specific impulse (I_s). In the past decade, our group has proposed and utilized quantitative criteria to design and select potential HEDCs [26], which is of great practical value in the design of composite explosives. However, the quantitative criteria for HEDCs is not directly applicable for propellants which require not only high density but also high I_s [1-4]. Previous theoretical research has rarely consider I_s. Furthermore, it is difficult to measure the I_s of propellants experimentally and even impossible for unsynthesized ones, therefore, it is of great significance to be able

to predict the I_s in seeking highly energetic plasticizers that are applicable in solid propellants.

In the present paper, polyethylene glycol polynitrates (see Figure 1), such as, ethylene glycol dinitrate (EGDN), diethylene glycol dinitrate (DEGDN), diethylene glycol tetranitrate (DEGTN), triethylene glycol hexanitrate (TriEGHN), tetraethylene glycol octanitrate (TetraEGON), pentaethylene glycol decanitrate (PEGDeN), and hexaethylene glycol dodecanitrate (HEGDoN), *etc.*, were studied using the DFT method. The theoretical density ($\rho_{cal.}$), detonation velocity (D), detonation pressure (P), specific impulse (I_s), as well as the bond dissociation energy (BDE) or bond dissociation energy barrier (BDEB) of the main bonds were predicted. The pyrolysis mechanism, thermal stability and sensitivity were also studied.
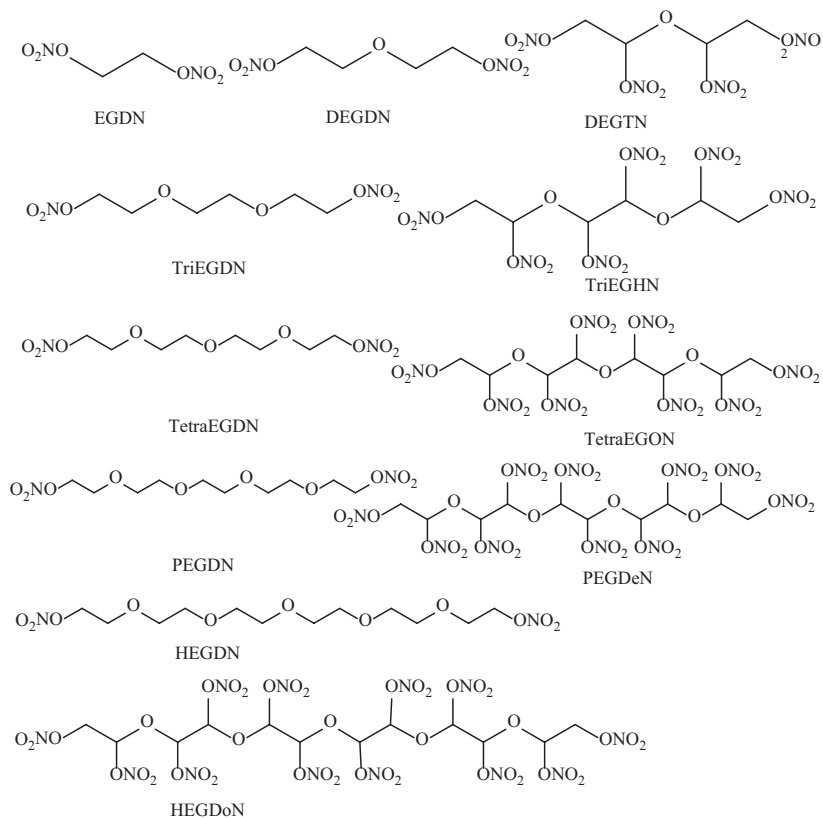

Figure 1.   Molecular structures of the polyethylene glycol polynitrates studied

2 Computational Methods

The polyethylene glycol polynitrate compounds were studied with the Gaussian03 program package [27] at the B3LYP/6-31G* level of DFT [28-30] that has been widely used to study molecular structures, infrared vibrational frequencies, and other properties. Detonation velocity and pressure, the most important parameters for evaluating the detonation characteristics of explosives, were calculated using the Kamlet-Jacbos (K-J) equations [31, 32]:

$$D = (1.011 + 1.312\rho_0) (N \overline{M}^{0.5} Q^{0.5})^{0.5} \tag{1}$$
$$P = 1.558\rho_0^2 N \overline{M}^{0.5} Q^{0.5} \tag{2}$$

where P is the detonation pressure (GPa), D is the detonation velocity (km·s^{-1}), ρ_0 is the packed density (g·cm^{-3}), N is the moles of gas produced by *per* gram of explosive, $\overline{M}$ is the average molar weight of the detonation products, and Q is the chemical energy of detonation (cal·g^{-1}), which can be determined from the heats of formation (*HOFs*) of the detonation products and the explosives. N, $\overline{M}$ and Q were decided according to the largest exothermic principle.

From the K-J equations, Q has a much lower effect on D and P than ρ_0. For the unsynthesized compounds, we have recommended and used the theoretical crystalline density ($\rho_{cal.}$) and *HOF*s estimated by the semi-empirical MO PM3 [33] method, to evaluate D and P using the K-J equations [24, 26, 34-42]. Since ρ_0 is smaller than $\rho_{cal.}$, the D and P values calculated using $\rho_{cal.}$ Are generally larger than those calculated using ρ_0. Consequently the corrected density was used. Our previous studies have demonstrated a rapid and convenient way to reliably predict the crystalline densities of energetic materials [43, 44]. By using the average molar volume V estimated by the Monte-Carlo method based on the 0.001 electrons/bohr^3 density space at the B3LYP/6-31G** or B3LYP/6-31G* level, the theoretical density $\rho_{cal.}$ ($\rho_{cal.} = M/V$, M is the molecular weight) and the fitted density $\rho'_{exp.}$, which is very close to the experimental crystal density ($\rho_{exp.}$), were obtained.

The specific impulse (I_s), the impulse produced by combusting one kilogram of explosive in the engine, is widely used as a means of characterizing and evaluating explosives. Equations 3-6 can be used to predict the proportional specific impulse $I_{s,p}$. To facilitate comparisons, the $I_{s,r}$ (relative specific impulse) relative to that of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) is given (see Equation 7):

$$I_{s,p} \sim T_C^{1/2} N^{1/2} \tag{3}$$

$$N = n/M \tag{4}$$
$$T_C = T_0 - \Delta H_C / C_{P,\text{gas}} \tag{5}$$
$$\Delta H_C = \sum N_R \Delta H_{f,R} - \sum N_p \Delta H_f \tag{6}$$
$$I_{s,r} = I_{s,p} / I_{s,p(\text{HMX})} \tag{7}$$

where T_0 and T_C (K) are the initial and the combustion temperatures, respectively, n (mol) is the number of moles of gaseous products produced *per* mole of explosive, M (g·mol^{-1}) is the molecular weight of the explosive, ΔH_C (J·mol^{-1}) is the enthalpy of combustion, $C_{P,gas}$ (J·(mol·K)$^{-1}$) represents the total heat capacity of the gaseous products, N_P and N_R (mol) are the moles of combustion products and reactants, respectively, and, $\Delta H_{f,P}$ and $\Delta H_{f,R}$ (J·mol^{-1}) are the molar heats of formation of the combustion products and reactants respectively. The molar heats of formation for the gaseous products are known, and that of the explosive can be determined in a number of ways. For example, a reasonable estimate can be obtained from the standard bond enthalpies plus strain contributions. Politzer [45] has pointed out that the relative specific impulse is not highly sensitive to the method used for obtaining the heats of formation. Therefore, in our work, the gas-phase heats of formation were computed with the semiempirical MO PM3 method. Since Equation 3 is a proportional relationship, and, the $I_{s,p}$ obtained is not an absolute value, the absolute specific impulse (I_s) was predicted by multiplying the experimental I_s of HMX (265.10 s [46]) as in Equation 8.

$$I_s = 265.10 \, I_{s,r} \tag{8}$$

The BDEs of the main bonds in the molecules were predicted to measure the strength of the bonds and the relative stabilities of the molecules. Expressions for the homolysis of the A−B bond (Equation 9) and for calculating its BDE (Equation 10) are shown as follows [47]:

$$R_1A-BR_{2(g)} \rightarrow R_1A_{(g)} + R_2B_{(g)} \tag{9}$$
$$BDE_{(R1A-BR2)} = [E_{R1A} + E_{R2B}] - E_{(R1A-BR2)} \tag{10}$$

where R_1A-BR_2 stands for the neutral molecule and R_1A and R_2B are the corresponding radicals after bond dissociation; $BDE_{(R1A-BR2)}$ is the BDE of the bond R_1A-BR_2; $E_{(R1A-BR2)}$, E_{R1A}·and E_{R2B}·are the zero-point energy corrected total energies of the molecule and the corresponding radicals, respectively. The characteristic height (h_{50}) can reflect the impact sensitivity and stability of the compounds as well, *i.e.* the smaller the h_{50} a compound exhibits, the higher is the sensitivity of the compound. In this paper, h_{50} was calculated using

Equation 11 suggested by Pospíšil *et al.* [48]:

$$h_{50} = -0.0064(\sigma_+)^2 + 241.42v - 3.43 \tag{11}$$

where $(\sigma_+)^2$ is an indicator of the strengths and variabilities of the positive surface potentials, and v is an electrostatic balance parameter.

The oxygen balance (OB_{100}), which can be used to roughly predict the impact sensitivities of explosives, was calculated using the following formula (Equation 12) [49]:

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{M} \tag{12}$$

where n_o, n_H and n_c represent the numbers of O, H and C atoms, respectively; n_{coo} is the number of COO−; here $n_{coo} = 0$ for the polyethylene glycol polynitrate compounds. All of the calculations were concluded using the default convergence criteria given in the programs.

3   Results and Discussion

3.1 Density and detonation properties

Table 1 lists V, $\rho_{cal.}$, the fitted density ($\rho'_{exp.}$), D and P of the title compounds. OB_{100}, HOF, and Q are also given in this table.

Table 1. Predicted densities and detonation properties [a]

Compound	OB_{100} [%]	Q [J·g⁻¹]	h_{50} [cm]	HOF [kJ·mol⁻¹]	V [cm³·mol⁻¹]	$\rho_{cal.}$ [g·cm⁻³]	$\rho'_{exp.}$ [b] [g·cm⁻³]	D^c [km·s⁻¹]	P^c [GPa]
EGDN	2.63	6861.39	40.2	−226.32	86.83	1.75 (1.48)[a]	1.54	8.22 (7.30)[a]	27.15
DEGDN	−1.02	5915.87	55.6	−401.83	122.41	1.60 (1.38)[a]	1.36	7.01 (6.67)[a]	18.12
DEGTN	7.11	5381.46	24.6	−594.17	168.71	1.89	1.71	8.20	28.91
TriEGDN	−3.33	5341.48	56.6	−566.56	153.88	1.56 (1.34)[a]	1.31	6.48	15.07
TriEGHN	7.79	4905.05	20.7	−962.62	256.58	1.89	1.71	7.98	27.40
TetraEGDN	−4.93	4947.26	54.8	−730.68	188.24	1.51	1.25	6.04	12.62
TetraEGON	8.46	4726.47	20.5	−1295.79	331.16	1.96	1.79	8.15	29.37
PEGDN	−6.09	4717.99	53.8	−875.48	225.65	1.45	1.17	5.63	10.42
PEGDeN	8.61	4544.61	17.6	−1690.68	417.89	1.95	1.78	8.03	28.42
HEGDN	−6.98	4347.08	53.7	−1047.84	257.68	1.44	1.16	5.49	9.86
HEGDoN	8.79	4440.62	15.1	−2069.57	500.57	1.96	1.79	8.01	28.37

[a] The bracketed experimental values are taken from Ref. [50]; [b] $\rho'_{exp.}$ is the predicted experimental density according to Ref. [24] using the fitting equation ($\rho'_{exp} = (\rho_{cal.} - 0.4768)/0.8283$); [c] D and P were predicted by using $\rho'_{exp.}$ and the K-J equations

The data in Table 1 show that the differences between $\rho'_{exp.}$ and $\rho_{exp.}$ ($0.06\,\text{g·cm}^{-3}$, $-0.02\,\text{g·cm}^{-3}$ and $-0.03\,\text{g·cm}^{-3}$) are much smaller than those between $\rho_{cal.}$ and $\rho_{exp.}$ ($0.27\,\text{g·cm}^{-3}$, $0.22\,\text{g·cm}^{-3}$ and $0.22\,\text{g·cm}^{-3}$), which indicates that the fitted density $\rho'_{exp.}$ at the B3LYP/6-31G* level can be regarded as the experimental crystal density. Comparing D and P produced from the experimental and theoretical methods, the differences between them are small, for example, the theoretical and experimental D values of EGDN and DEGDN were ($8.22/7.01$) km·s^{-1} and ($7.30/6.67$) km·s^{-1}, respectively.

Figure 2(a-c) presents the relationships between OB_{100}, Q, $\rho'_{exp.}$, HOF, V, D, P, and the number of $-\text{O}-\text{CH}_2-\text{CH}_2-$ groups (n_1). With an increasing number of $-\text{O}-\text{CH}_2-\text{CH}_2-$ groups, V increases, and OB_{100}, Q, HOF, $\rho'_{exp.}$, D and P decrease. Linear relationships were found between HOF, V and n_1. The relevant equations are:

$$HOF = -234.83 - 162.65n_1 \qquad (R = -0.9997, SD = 8.5755) \qquad (13)$$
$$V = 86.85 + 34.24n_1 \qquad (R = 0.9998, SD = 1.5113) \qquad (14)$$

The sensitivity of these compounds also increases, with the h_{50} value decreasing from 55.6 cm to 53.7 cm.

Figure 2(d) shows the relationship between $\rho'_{exp.}$, D, P and n_2 for EGDN, DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN. With an increasing number of $-\text{O}-\text{CH}(\text{ONO}_2)-\text{CH}(\text{ONO}_2)-$ groups (n_2), OB_{100}, $\rho'_{exp.}$ and V increase, Q and HOF decrease, while D and P change little. The sensitivity of these compound also increases, with the h_{50} value decreasing from 40.2 cm to 15.1 cm. That is to say, when a compound is excessively nitrated, its Q value typically decreases while its sensitivity increases (see Figure 2(e)). This result is different from that found by Politzer et al. [51], i.e. the sensitivity tends to increase as the maximum detonation heat released increases. The reason for this may be that sensitivity is affected by many factors, such as oxygen balance, heat of formation, bond energies, bond polarities, electrostatic potentials, and more. Compared with the common plasticizers EGDN ($\rho'_{exp.} = 1.48\,\text{g·cm}^{-3}$, $D = 8.00\,\text{km·s}^{-1}$, $P = 25.07\,\text{GPa}$) and NG ($\rho'_{exp.} = 1.54\,\text{g·cm}^{-3}$, $D = 8.03\,\text{km·s}^{-1}$, $P = 25.92\,\text{GPa}$) [24], it is seen that the introduction of the $-\text{O}-\text{CH}(\text{ONO}_2)-\text{CH}(\text{ONO}_2)-$ group benefits the detonation properties.
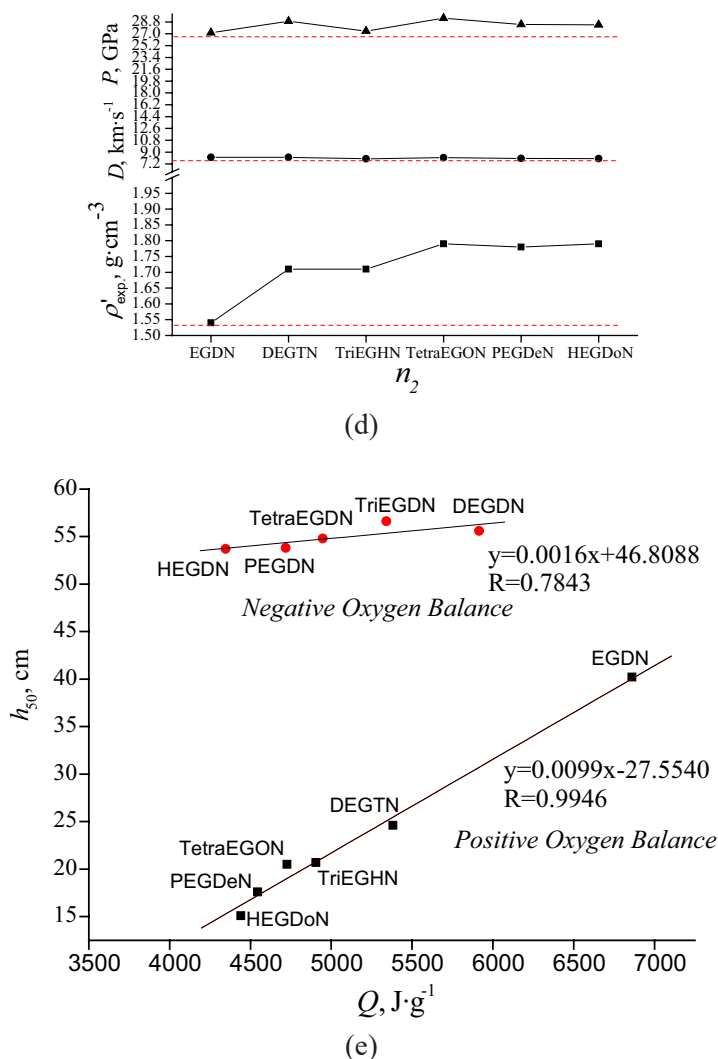
(a)

(b)

(c)

(d)

(e)
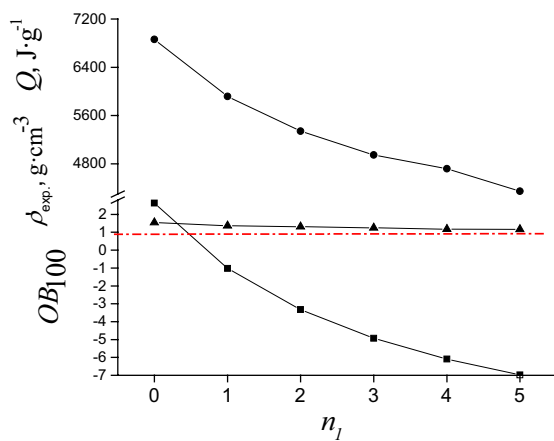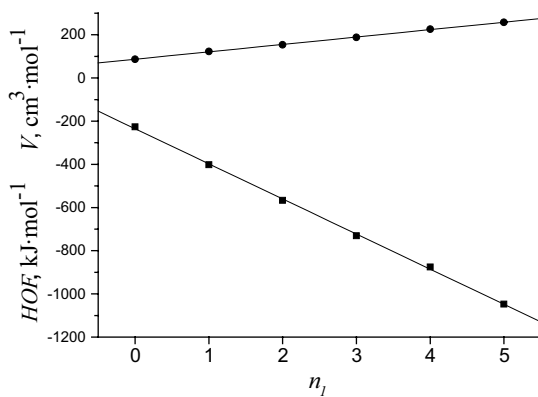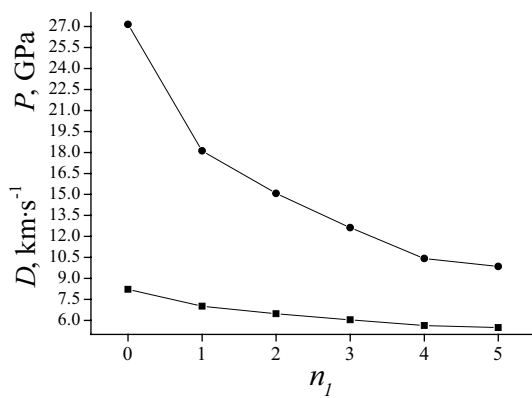
Figure 2. Correlations between OB_{100}, Q, $\rho'_{exp.}$, HOF, V, D, P and the number of $-O-CH_2-CH_2-$ groups (n_1) (a-c) and $-O-CH(ONO_2)-CH(ONO_2)-$ groups (n_2) (d), and the correlation between Q and h_{50} (e)

3.2 Specific impulse

Table 2 lists the ideal stoichiometric decomposition reactions and some properties for the title compounds, such as N, ΔH_{comb}, $C_{B,gas}$, T_c, $I_{s,p}$ and I_s. Since a solid propellant requires not only high density but also high specific impulse, to synthetically assess the energetic characteristics of a plasticizer,

a new indicator, the product of specific impulse and density, $K = I_s \cdot \rho'_{\text{exp.}}$, is introduced. The larger K is, the better the energetic properties of the solid propellant are [2].

Figure 3 presents the relationships between N, ΔH_{comb}, $C_{P,\text{gas}}$, T_c, I_s, K and the number of the $-O-CH_2-CH_2-$ groups (n_1) and the $-O-CH(ONO_2)-CH(ONO_2)-$ groups (n_2). With an increase in n_1, N and $C_{P,\text{gas}}$ increase, while ΔH_{comb}, T_c, $I_{s,p}$ and K basically decrease. Linear correlations exist between ΔH_{comb}, $C_{P,\text{gas}}$ and n_1:

$$\Delta H_{\text{comb}} = -1044.44 - 117.82 n_1 \qquad (R = -0.9975, SD = 17.6125) \qquad (15)$$
$$C_{P,\text{gas}} = 174.34 + 66.48\, n_1 \qquad (R = 0.9989, SD = 6.4763) \qquad (16)$$

With an increase in n_2, N, ΔH_{comb}, T_c, and I_s all decrease, but not for $C_{P,\text{gas}}$ and K. ΔH_{comb} and $C_{P,\text{gas}}$ both change linearly with n_2, as follows:
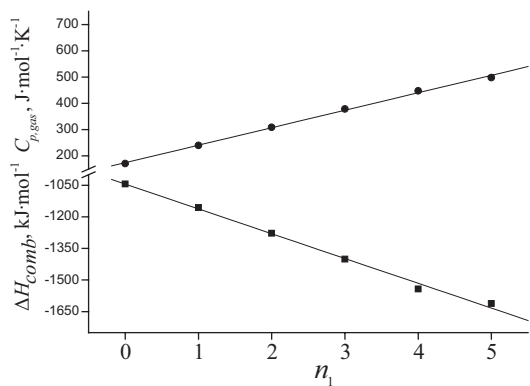
$$\Delta H_{\text{comb}} = -1047.89 - 662.02 n_2 \quad (R = -0.9999, SD = 15.7065) \qquad (17)$$
$$C_{P,\text{gas}} = 170.76 + 137.43 n_2 \quad (R = 1.0000, \; SD = 1.1369 \times 10^{-13}) \qquad (18)$$

Although the I_ss values of DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN are smaller than that of EGDN ($I_s = 266.69$ s), their K values are larger than that of EGDN ($K = 410.70$ s·g·cm^{-3}), which implies that these compounds could improve the energetic properties of solid propellants.
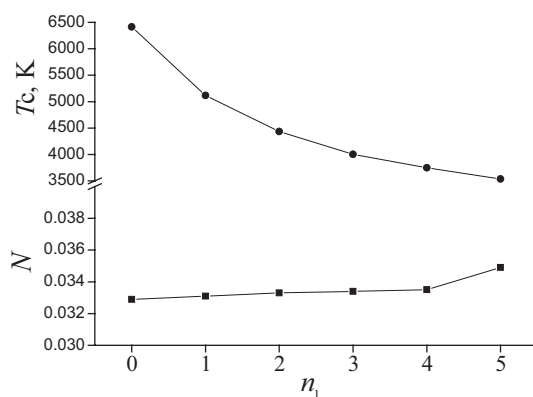
(a)

(b)
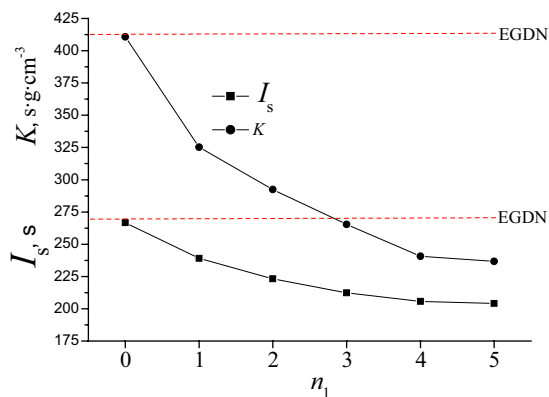
(c)

(d)

(e)

(f)

Figure 3. Correlations between N, ΔH_{comb}, $C_{B,gas}$, T_c, $I_{s,p}$, K and the number of $-CH_2-CH_2-O-$ groups (n_1) and $-O-CH(ONO_2)-CH(ONO_2)-$ groups (n_2)

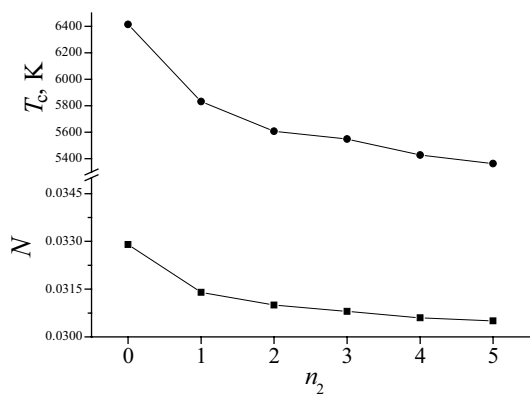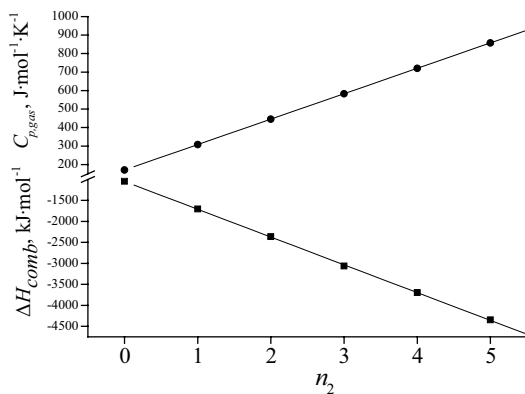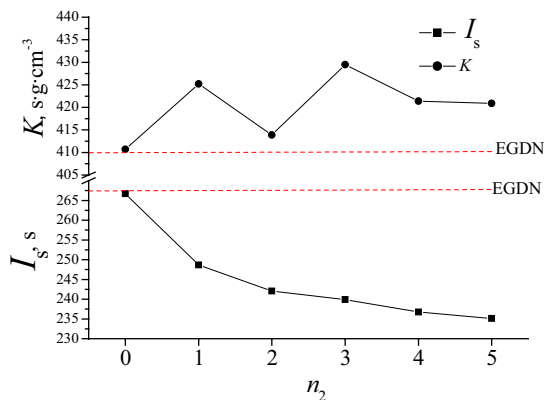**Table 2.** Idealized stoichiometric decomposition reactions and some properties of the polyethylene glycol polynitrate compounds[a]

Molecule	Idealized stoichiometric reaction	M [g·mol⁻¹]	N [mol]	N	ΔH_{comb} [kJ·mol⁻¹]	$C_{p,gas}$ [J·mol⁻¹·K⁻¹]	T_c [K]	$I_{s,p}$ [s]	$I_{s,r}$	I_s [s]	K [s·g·cm⁻³]
HMX	$C_4N_8O_8H_8 \rightarrow 4H_2O + 2CO_2 + 4N_2 + 2C$	296.16	10.00	0.0338	−2000.40	340.88	6166.49	14.43	1.000	265.10	487.78
EGDN	$C_2H_4N_2O_6 \rightarrow 2H_2O + 2CO_2 + N_2$	152.06	5.00	0.0329	−1044.36	170.76	6414.10	14.52	1.006	266.69	410.70
DEGDN	$C_4H_8N_2O_7 \rightarrow 4H_2O + 1.5CO_2 + N_2 + 2.5C$	196.12	6.50	0.0331	−1155.76	239.92	5115.40	13.02	0.902	239.12	325.20
DEGTN	$C_4H6N_4O_{13} \rightarrow 3H_2O + 4CO_2 + O_2 + 2N_2$	168.71	10.00	0.0314	−1705.36	308.19	5831.62	13.54	0.938	248.66	425.21
TriEGDN	$C_6H_{12}N_2O_8 \rightarrow 6H_2O + CO_2 + N_2 + 5C$	240.17	8.00	0.0333	−1277.93	309.08	4432.78	12.15	0.842	223.21	292.41
TriEGHN	$C_6H_8N_6O_{20} \rightarrow 4H_2O + 6CO_2 + 2O_2 + 3N_2$	256.58	15.00	0.0310	−2365.76	445.62	5607.07	13.18	0.913	242.04	413.89
TetraEGDN	$C_8H_{16}N_2O_9 \rightarrow 8H_2O + 0.5CO_2 + N_2 + 7.5C$	284.22	9.50	0.0334	−1400.72	378.24	4001.39	11.56	0.801	212.35	265.44
TetraEGON	$C_8H_{10}N_8O_{27} \rightarrow 5H_2O + 8CO_2 + 3O_2 + 4N_2$	331.16	20.00	0.0308	−3061.44	583.05	5548.88	13.06	0.905	239.92	429.46
PEGDN	$C_{10}H_{20}N_2O_{10} \rightarrow 10H_2O + N_2 + 10C$	328.28	11.00	0.0335	−1542.82	447.40	3746.56	11.20	0.776	205.72	240.69
PEGDeN	$C_{10}H_{12}N_{10}O_{34} \rightarrow 6H_2O + 10CO_2 + 4O_2 + 5N_2$	417.89	25.00	0.0306	−3695.40	720.48	5427.23	12.89	0.893	236.73	421.38
HEGDN	$C_{12}H_{24}N_2O_{11} \rightarrow 11H_2O + H_2 + N_2 + 12C$	372.33	13.00	0.0349	−1612.29	497.79	3537.05	11.11	0.770	204.13	236.79
HEGDoN	$C_{12}H_{14}N_{12}O_{41} \rightarrow 7H_2O + 12CO_2 + 5O_2 + 6N_2$	500.57	30.00	0.0305	−4345.36	857.91	5363.20	12.80	0.887	235.14	420.90

[a] C_p of the products: – H_2O: 33.33 J·(mol·K)⁻¹; – CO_2: 37.65 J·(mol·K)⁻¹; – N_2: 28.86 (mol·K)⁻¹; – C: 8.53 (mol·K)⁻¹; HOF of the products: H_2O: −241.83 kJ·mol⁻¹; CO_2: −393.51 kJ·mol⁻¹.

3.5 Pyrolysis mechanism and stability

3.5.1 Bond overlap populations

Bond overlap population mean the electron accumulation in the bonding region, and can provide us with detailed information about the chemical bond. In general, the lower the Mulliken populations (MPs) a bond has, the easier the bond breaks. Although Mulliken population analysis (MPA) [52] has some shortcomings, such as basis set dependence, the results from MPA at the same calculation conditions are still meaningful for comparing trends in the electron distribution of the homologous compounds, as is done here. The Mulliken populations of various kinds of bonds for the title compounds are listed in Table 3. For the same type of bonds, only the lowest value is given.

Table 3. Mulliken populations (e) of various bonds

Compound	$M_{O–NO2}$	$M_{C–ONO2}$	$M_{C–OCH2}$	$M_{C–C}$	$M_{C–H}$	$M_{N=O}$
EGDN	0.1459	0.1441	–	0.3281	0.3593	0.3045
DEGDN	0.1518	0.1611	0.2317	0.3516	0.3425	0.3071
DEGTN	0.1405	0.1118	0.2100	0.3219	0.3412	0.2955
TriEGDN	0.1533	0.1598	0.2200	0.3505	0.3414	0.3065
TriEGHN	0.1338	0.1152	0.2107	0.3287	0.3433	0.2972
TetraEGDN	0.1556	0.1559	0.2168	0.3503	0.3309	0.3030
TetraEGON	0.1281	0.1281	0.1854	0.2679	0.3384	0.2900
PEGDN	0.1517	0.1460	0.2177	0.3542	0.3418	0.3035
PEGDeN	0.1319	0.1267	0.1923	0.3263	0.3438	0.2960
HEGDN	0.1533	0.1582	0.2165	0.3534	0.3402	0.3074
HEGDoN	0.1322	0.1301	0.1948	0.3020	0.3407	0.2947

The data in Table 3 show that the electron populations of the O−NO$_2$ and C−ONO$_2$ bonds are relatively small, which indicates that they are weak and might be the trigger bonds in thermolysis processes. Meanwhile, as the number of −O−CH$_2$−CH$_2$− groups increases, $M_{O–NO2}$ and $M_{C–ONO2}$ generally increase, and with an increase in the number of −O−CH(ONO$_2$)−CH(ONO$_2$)− groups, they initially decrease and then increase.

3.5.2 Bond dissociation energies

In Ref. [24], the MPs and BDEs of some nitrates have been discussed. For NG, the result of MP was consistent with that of BDE, which indicates that the O−NO$_2$ bond is the trigger bond. So only the BDEs of the O−NO$_2$

bond have been calculated for the other compounds. According to the results of MPA in the present study, both $O-NO_2$ and $C-ONO_2$ bonds are weak and should be considered. Furthermore, there exist $C-O$ bonds in the linear chain of the title compounds which are not presented in Ref. [24]. Therefore, the BDE of the $C-O(C)$ bond in the linear chain is also discussed in this study. It should be noted that the weakest $O-NO_2$, $C-ONO_2$, and $C-O(C)$ bonds are selected according to the MPs. During the calculation process, it was found that when the $(H_2)C-O(C)$ bond breaks, two radicals are produced. However, for DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN, since each carbon atom has a nitrate group attached, when the $(ONO_2H)C-O(C)$ bond breaks, a transition state (TS) exists and the products are aldehydes and N_2O_5. Taking TriEGHN as an example, Figure 4 shows the structures of the reactant (TriEGHN), the TS and the products, including part of the geometric parameters. The reliability of the TS has been verified by the IRC analysis. From Figure 4, when the C_7-O_6 bond breaks, the $O_{25}-N_{29}$ and C_5-O_{26} bonds break at the same time. In this process, the C_5-O_6, C_7-O_{25} and $O_{26}-N_{32}$ bonds become shortened. The bond lengths of C_7-O_6, $O_{25}-N_{29}$, C_5-O_{26}, C_5-O_6, C_7-O_{25} and $O_{26}-N_{32}$ bonds change from 1.403 Å, 1.465 Å, 1.426 Å, 1.398 Å, 1.435 Å and 1.471 Å in the reactant to 1.951 Å, 1.937 Å, 1477 Å, 1.345 Å, 1.258 Å and 1.413 Å in the TS, respectively. The distance between N_{29} and O_{33} atoms decreases from 3.408 Å to 2.983Å. In the products, the C_7-O_6, $O_{25}-N_{29}$ and C_5-O_{26} bonds break and the distances are 3.324 Å, 3.300 Å and 3.224 Å, respectively, N_{29} and O_{33} atoms form a single bond (1.560 Å), and the $N_{32}-O_{33}$ bond goes from a delocalized bond (1.206 Å) to a single bond (1.445 Å), while the length of $O_{26}-N_{32}$ decreases from 1.471 Å to 1.203 Å. Of course, other bonds also change a little. The final products are two aldehydes and N_2O_5. The full geometric parameters of reactant, TS and products are listed in Tables 1S-S4 of the Supporting Information.
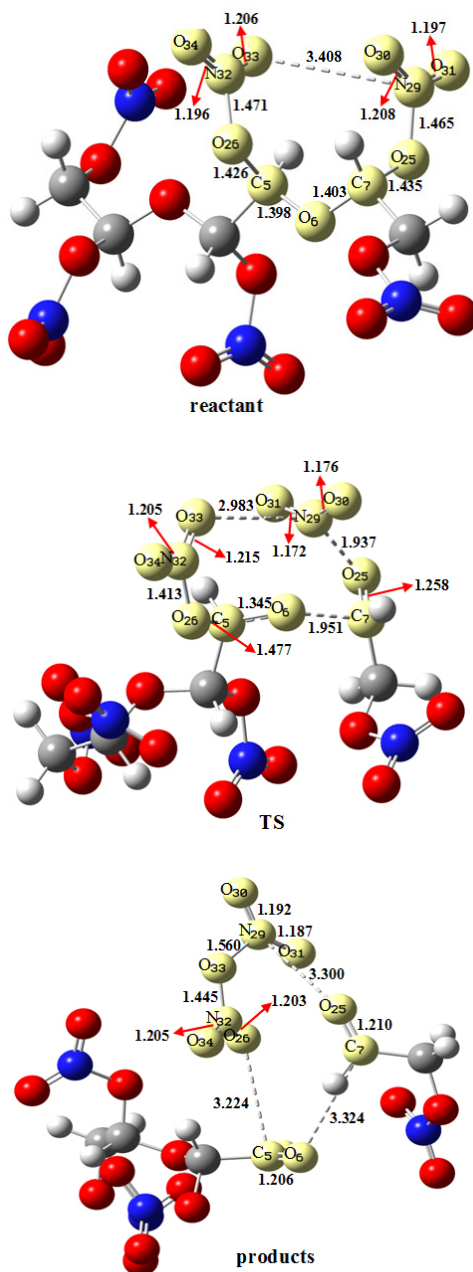
Figure 4. The structures of the reactant, TS and products for the C_7-O_6 bond breaking process of TriEGHN and some related bond lengths (Å)

The BDEs or BDEBs of some bonds are listed in Table 4. Obviously, the BDEs or BDEBs of the C−ONO$_2$ and C−O(C) bonds are larger than those of the O−NO$_2$ bonds (113.02-145.72 kJ·mol^{-1}), which proves that the O−NO$_2$ bond is the trigger bond, excluding the possibility of the C−ONO$_2$ and C−O(C) bonds. With an increase in n_1, BDE$_{O−NO2}$s (138.89 → 145.72 kJ·mol^{-1}) and h_{50}s (40.2 → 53.7 cm) all increase, which indicates that the stability increases and the sensitivity decreases with an increase in the number of −O−CH$_2$− CH$_2$− groups. With an increase in n_2, for DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN, BDE$_{O−NO2}$s and h_{50}s all decrease, which shows that more −O−CH(ONO$_2$)−CH(ONO$_2$)− groups lead to higher sensitivity and worse safety (see Figure 5). Compared with the h_{50} value of the famous explosive 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtitane (CL-20), 12 cm [53], it is found that the title compounds are less sensitive than CL-20. According to the previously proposed quantitative criteria for stability, *i.e.* BDE ≈ 80-120 kJ·mol^{-1}, all of the title compounds have good stabilities. However, considering the energetic property (K), only DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN are expected to be new energetic plasticizers applicable for the solid propellant.

Table 4.   BDEs^a or BDEBs^a, h_{50} and related parameters

Compound	BDE$_{(C−ONO2)}$ [kJ·mol^{-1}]	BDE$_{(C−O(C))}$ [kJ·mol^{-1}]	BDEB$_{(C−O(C))}$ [kJ·mol^{-1}]	BDE$_{(O−NO2)}$ [kJ·mol^{-1}]	h_{50} [cm]	v	$(\sigma_+)^2$ [(kcal·mol^{-1})^2]
NG	220.70^b	–	–	136.77^b	25.1	0.12	111.72
EGDN	303.77	–	–	138.89	40.2	0.18	70.24
DEGDN	313.48	325.04	–	143.88	55.6	0.25	52.44
DEGTN	292.56	–	170.49	113.02	24.6	0.12	111.63
TriEGDN	315.32	328.19	–	145.72	56.6	0.25	39.73
TriEGHN	293.55	–	160.75	119.94	20.7	0.10	110.76
TetraEGDN	316.11	321.62	–	145.19	54.8	0.24	28.72
TetraEGON	291.43	–	215.31	122.70	20.5	0.10	133.05
PEGDN	313.75	324.77	–	142.56	53.8	0.24	26.91
PEGDeN	293.09	–	169.08	119.28	17.6	0.09	111.72
HEGDN	314.01	323.99	–	145.72	53.7	0.24	28.93
HEGDoN	284.94	–	166.57	123.78	15.1	0.08	122.98

^{a} BDEs and BDEBs include zero-point energy corrections; ^{b} The values are taken from Ref. [24].
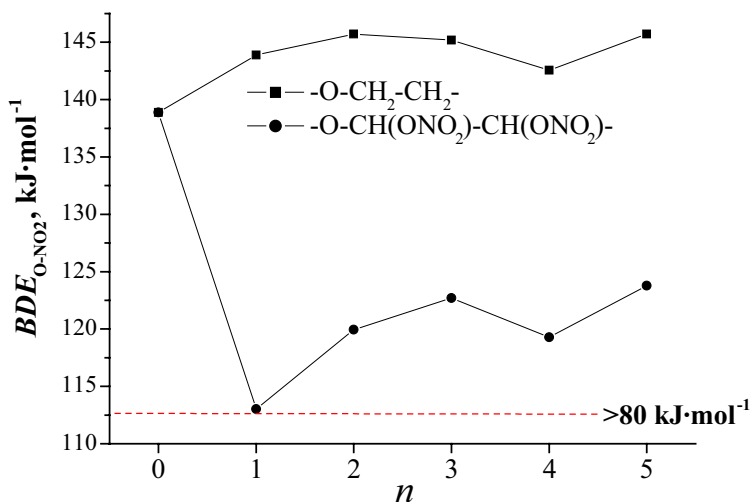
Figure 5.   Correlations between BDE_{O-NO2} and the number of $-O-CH_2-CH_2-$ and $-O-CH(ONO_2)-CH(ONO_2)-$ groups

4   Conclusions

Eleven polyethylene glycol polynitrates have been studied theoretically at the B3LYP/6-31G* level and the conclusions of this work are as follows:

(1) With an increasing number of $-O-CH_2-CH_2-$ and $-O-CH(ONO_2)-$ $CH(ONO_2)-$ groups, OB_{100}, Q, and HOF decrease, while the sensitivity of the compounds increase. The well-known inverse proportional rule between performance and sensitivity of energetic materials does not exist in this kind of compound.

(2) DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN have much higher densities ($\rho'_{exp.}$) than EGDN and their D and P values are comparable to those of EGDN. Although their is values are smaller than that of EGDN, their K values, *i.e.* the product of I_s and ρ, are larger than that of EGDN.

(3) The $O-NO_2$ bond is the trigger bond and its strength determines the thermal stability of the title compounds. According to the values of K and BDE/ BDEB, DEGTN, TriEGHN, TetraEGON, PEGDeN and HEGDoN are potential energetic plasticizers applicable for solid propellants.

(4) With an increase in the number of $-O-CH_2-CH_2-$ groups, $\rho'_{exp.}$ and I_s decrease. With an increase in the number of $-O-CH(ONO_2)-$ $CH(ONO_2)-$ groups, $\rho'_{exp.}$ increases while I_s decreases.

Acknowledgment

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