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Density functional theory calculations on the thermodynamic properties of polynitrosoprismanes

Weijie Chi · Guangdong Sun · Tao Liu · Butong Li · Haishun Wu

Abstract A series of polynitrosoprismanes, $C_6H_{6-n}(NO)_n$ ($n=1$–6), considered as high energy density compounds (HEDCs), have been designed computationally. We calculated the electronic structures, the heats of formation, the specific enthalpies of combustion, the bond dissociation energies, and the strain energies of the title compounds using density functional theory (DFT) with the 6-311G** basis set. It was found that the $\Delta E_{\text{LUMO–HOMO}}$ values of the title compounds decrease as the number of nitroso groups increase, and the energy gaps of the prismane derivatives are much lower than that of TATB. Their high positive heats of formation indicate that polynitrosoprismanes can store a great deal of energy. Furthermore, the HOFs for the nitrosoprismane series were observed to decrease until three nitroso groups were connected to the prismane skeleton. For the polynitrosoprismanes, the trigger bond was confirmed to be the C-C bond in the skeleton. According to our calculations, all nitrosoprismanes appear to have large strain energies, and these calculations can provide basic information that may prove useful for the molecular design of novel high energy density materials.

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Introduction

The search for new high energy density compounds (HEDCs) is an ongoing process [1–6]. HEDCs have been widely used for both military and civilian applications. Researchers are constantly trying to develop HEDCs that are better than existing ones in order to meet the requirements of space-related applications [7, 8]. Polysubstituted cage compounds have been investigated as an important category of HEDCs due to their high strain energies, compact structures, and self-oxidizability [9, 10]. Examples include hexanitrohexaazaisowurtzitane (CL-20) [11], octanitrocubane [12], and polynitroprismanes [13]. Typical characteristics of these compounds are that they derive most of their energy from their heats of formation (HOFs). In addition, compounds with compact structures usually have high densities and can release additional energy upon detonation as a consequence of the cage strain present in these systems. Experimental synthesis of HEDCs is not only dangerous but also hazardous to humans and the environment. However, computer simulation—an effective way of screening promising explosives that does not suffer from these shortcomings—has been used to design various new energetic materials. Therefore, a key step towards achieving a breakthrough in HEDC research is to perform molecular design; the results from the design step are then used to synthesize new and improved HEDCs.

Highly energetic compounds that have polynitro groups are an important class of useful energetic materials. The presence of the nitro groups tends to decrease the heat of

formation but markedly enhances the overall energetic performance [14]. Also, the nitro groups enhance the oxygen balance and the density, which improves detonation performance. Studies have shown that adding other nitrogen-containing functional groups to a molecule can yield good potential candidates for high-energy materials [15]. Anther nitrogen-containing functional group, and the one we are interested in here, is the nitroso group. The main difference between a nitro group and a nitroso group is the oxygen content of the group. Although adding a nitro group helps to facilitate complete combustion, we do not believe that this is a problem in an oxygen-rich environment such as the Earth's atmosphere.

Prismane has been synthesized and fully characterized. Several substituted derivatives of this hydrocarbon have also been characterized [16, 17]. Prismane is a hydrocarbon with a large ring strain energy of 606.9 kJ mol^{-1}, which is an important requirement of HEDCs. Therefore, we used the cage compound prismane C_6H_6 (D_{3h}) to design new high-energy compounds. Lately, polyisocyanoprismanes [18], polyazidoprismanes [19], and polynitroprismanes have been studied. In addition, azaprismanes were studied by Peter Politzer et al. in 1989 [20, 21]. Their studies showed that these compounds can be used as high energy density materials. In the present work, the H atoms in prismane were replaced with nitroso groups to generate a series of molecules of formula $C_6H_{6-n}(NO)_n$ (n=1–6). The molecular electronic geometries, heats of formation, bond dissociation energies, the specific enthalpies of combustion, and strain energies of these polynitrosoprismanes were studied in detail at the B3LYP/6-311 G** level. We believe that our results could provide useful information for the laboratory synthesis of polynitrosoprismanes and the development of new novel HEDCs.

Computational method and details

The geometries of the polynitrosoprismanes were fully optimized without symmetry restriction using density functional theory (DFT) with the Becke's three-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (B3LYP) [22, 23], along with the 6-311G** basis set [24], in the Gaussian 03 program package [25]. Previous studies have shown that accurate energies, molecular structures, and vibrational frequencies that are very close to the corresponding experimental results are obtained when the basis set 6-311G** is used [26, 27]. Each optimized structure was checked to ensure that is was a local energy minimum on the potential energy surface by vibrational analysis.

The heats of formation (HOFs) of the title compounds are needed to calculate the detonation energy. In the present work [28, 29], the method of isoseismic reactions was employed very successfully to estimate the HOFs from the total energies obtained from ab initio calculations [30]. Therefore, in our work, we also designed isoseismic reactions; in them, the basic structural unit of prismane remained invariable, and the big molecules were changed into small ones to obtain the HOFs. These isoseismic reactions that were used to calculate the HOFs of the polynitrosoprismanes at 298 K are as follows:

$$C_6H_{6-n}(NO)_n + nCH_4 = C_6H_6 + nCH_3NO (n = 1 - 6). \quad (1)$$
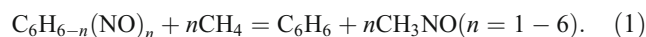
For the isoseismic reactions, the HOF (ΔH_{298}) at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \Delta H_{f,P} - \Delta H_{f,R} \quad (2)$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the heats of formation of the reactants and products at 298 K, respectively. The experimental HOFs for the reference compounds CH_4, CH_3NO, and C_6H_6 are available from the NIST Chemistry WebBook. Thus, the HOFs of the polynitrosoprismanes can be calculated when the heat of reaction ΔH_{298} is known. ΔH_{298} can be calculated using the following formula:

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT. \quad (3)$$

Using the HOFs of the polynitrosoprismanes (obtained from Eqs. 2 and 3), it is then a straightforward process to determine the enthalpy of combustion using reaction (4):

$$C_6H_{6-n}(NO)_n + (7.5 - 0.75n)O_2 \quad (4)$$
$$= 6CO_2 + (3 - 0.5n)H_2O + 0.5nN_2.$$
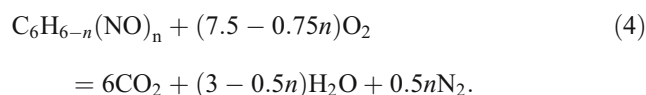
The enthalpies of formation for carbon dioxide and water were also obtained from the NIST Chemistry WebBook: −393.52 and −285.83 kJ mol^{-1}, respectively. Dividing the enthalpies of combustion obtained from reaction (4) by the mass of the molecule yields the specific enthalpies of combustion.

Thermal stability was evaluated on the basis of the bond dissociation energy (BDE), which is fundamental to understanding chemical processes [31]. The BDE values of the C–NO bonds in the title compounds can be obtained as follows:

$$BDE(A - B) = E(A\bullet) + E(B\bullet) - E(A - B). \quad (5)$$

The BDE corrected for the zero-point energy (ZPE) can be calculated via Eq. 6:

$$BDE(A - B)_{ZPE} = BDE(A - B) + \Delta ZPE, \quad (6)$$

where ΔZPE is the difference between the ZPE values of the products and the reactants.

Strain is an important concept in structural organic chemistry. The concept of the strain energy (SE) provides a basis for correlating the structures, stabilities, and reactivities of molecules. In previous studies, the homodesmotic reaction method was employed very successfully to estimate the SE [32–34]. In the homodesmotic reaction, not only is the number of bonds of each type conserved, but the valence environment around each atom is also preserved. The homodesmotic reaction that was used to derive the SEs of the title compounds is as follows:

$$C_6H_{6-m}(NO)_m + 9CH_3CH_3 \rightarrow (6-m)(CH_3)CH + m(CH_3)CNO, \quad (7)$$
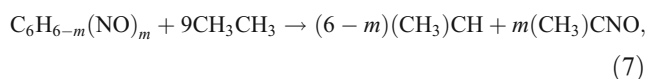
where m is the number of substituent groups in the prismane derivative $C_{6}H_{6-m}(NO)_m$. The change in energy, corrected for the zero-point vibrational energy (ZPE), during this homodesmotic reaction is

$$\Delta E_n = \sum E_{product} - \sum E_{reactant} + \Delta ZPE. \quad (8)$$

We wish to define SE as a positive quantity. Therefore, we relate the SE to $-\Delta E_n$ for Eq. 7.

Results and discussion

Electronic structure and stability

Figure 1 shows the numbering scheme for the polynitroprismanes. The numbering system used ensures that the numbers employed to label the nitro groups are the smallest numbers possible that are still consistent with the numbering pattern shown in Fig. 1. Table 1 lists the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies as well as the energy gaps ($\Delta E_{LUMO-HOMO}$) calculated at the B3LTY/6-311G** level. Form Table 1, it is clear that $\Delta E_{LUMO-HOMO}$ values decrease as the number of nitroso groups increases. It is interesting to note that all of the polynitrosoprismanes have lower $\Delta E_{LUMO-HOMO}$ values than the unsubstituted prismane. This indicates a shift toward lower frequencies in their electronic absorption spectra. In addition, the energy
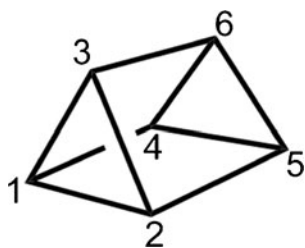

Fig. 1 Molecular framework and atomic numbering of prismane

Table 1 Calculated HOMO and LUMO energies (in a.u) as well as the energy gaps ($\Delta E_{LUMO-HOMO}$) of the title compounds, calculated at the B3LYP/6-311G** level

Compound	E_{LUMO}	E_{HOMO}	$\Delta E_{LUMO-HOMO}$
C_6H_6	0.05360	−0.23150	0.28510
1-	−0.08181	−0.21396	0.13215
1,2-	−0.12372	−0.23166	0.10794
1,4-	−0.09921	−0.22787	0.12866
1,5-	−0.10488	−0.23508	0.13020
1,2,3-	−0.14627	−0.24458	0.09831
1,2,4-	−0.13231	−0.24622	0.11391
1,2,6-	−0.13198	−0.25197	0.11999
1,2,3,4-	−0.15549	−0.26100	0.10551
1,2,4,5-	−0.14283	−0.25553	0.11270
1,2,3,4,5-	−0.16810	−0.26595	0.09785
1,2,3,4,5,6-	−0.17547	−0.27667	0.10120
TATB	−0.10280	−0.26480	0.16210

1- and 1,2- denote 1-nitrosoprismane and 1,2-nitrosoprismane, respectively; the others are similar

gaps of the prismane derivatives are much lower than that of TATB (triaminotrinitrobenzene), which suggests that the prismane derivatives are more sensitive than TATB. If we consider isomers, such as the three prismane derivatives with two nitro groups, the $\Delta E_{LUMO-HOMO}$ value of 1,2-bisnitrosoprismane is the lowest of the three, while te value for 1,5-bisnitrosoprismane is the highest of the three. This shows that 1,5-disnitrosoprismane is more stable than 1,2-bisnitrosoprismane. This is because the distance between the two nitroso groups in 1,5-bisnitrosoprismane is greater than it is in 1,2-bisnitrosoprismane. It was proposed that the molecule withthe largest energy gap should have the lowest reactivity in chemical or photochemical processes involving an electron transfer or jump [35, 36]. However, it should be pointed out that the sensitivity was estimated using $\Delta E_{LUMO-HOMO}$, which gives only a rough estimate.

Heats of formation

It is well known that evaluating the explosive performance of an energetic material requires a knowledge of its HOF. Moreover, HOFs are of great importance in thermochemical research. The total molecular energies, the zero-point energies, and the values for the thermal correction calculated at the B3LYP/6-311G** level for three reference compounds are listed in Table 2. To the best of our knowledge, no experimental HOF values for these newly designed molecules are available in the literature. However, the HOFs can be obtained via isodesmic reactions. Previous studies [37, 38] have shown that theoretically predicted HOFs agree well with the corresponding experimental values when the

Table 2 Calculated total energies (E_0, a.u), thermal corrections (H_T, a.u), zero-point energies (ZPE, a.u), and HOFs (kJ mol^{-1}) for the reference compounds, calculated at the B3LYP/6-311G** level

Compound	E_0	ZPE	H_T	HOF
C_6H_6	−232.11118	0.09670	0.00504	567.7
CH_4	−40.53374	0.04460	0.00382	−74.6
CH_3NO	−169.84396	0.04301	0.00472	−66.9

appropriate reference compounds are chosen for the isodesmic reaction. Table 3 lists the total energies, the zero-point energies, the values for the thermal correction, the HOFs, and the specific enthalpies of combustion of the polynitrosoprismanes calculated at the B3LYP/6-311G** level.

In Table 3, the HOFs are all highly positive values, which is one of the requirements for energetic materials. The HOFs for the nitrosoprismane series decrease until about three nitroso groups are present on the prismane skeleton. The series reaches its minimum HOF value of 476.19 kJ mol^{-1} at 1,2,6-trinitrosoprismane. The HOFs then increase as additional nitroso groups are added to the prismane skeleton. In our previous study, we mentioned the trend in the HOFs of nitroprismanes (the HOFs of polynitroprismanes increase as the number of nitro groups increases). However, the same trend is not seen for the nitrosoprismane series. Since isomers with the same number of nitroso groups have different HOF values, it is clear that the HOF is also affected by the position of the nitroso group. For instance, for the three isomers with two nitroso groups, the HOF of 1,2-dinitrosoprismane is slightly higher than those of 1,4-dinitrosoprismane and 1,5-dinitrosoprismane. This indicates that 1,2-dinitrosoprismane stores the most energy among all of the dinitrosoprismanes; in other words, 1,2-dinitrosoprismane is not stable. Strong repulsion energy is present, which leads to an increase in the total energy and the HOF for 1,2-dinitrosoprismane.

The sixth column in Table 3 relates to the specific enthalpy of combustion, which is the molar enthalpy of combustion divided by the molar mass of the substance. As the number of nitroso groups in the molecule increases, the specific enthalpy of combustion decreases. This is due to the fact that we are replacing hydrogen atoms, each of which contributes roughly about 8 kJ/g of energy during combustion through the formation of water. Steric hindrance compensates for some of this lost 8 kJ/g, but not enough to compensate for the energy lost when a hydrogen atom is replaced by a nitroso group. This means that highly nitroso-substituted molecules release less combustion energy than less substituted molecules.

Bond dissociation energies

Another important issue for the explosives is whether they are kinetically stable enough to be of practical interest. Studying the bond dissociation energy (BDE) is therefore a crucial step in elucidating the decomposition process of a high-energy material. Generally, the smaller the BDE, the easier it is to break the bond.

The bond order is a measure of the overall bond strength between two atoms. A high value for the bond order indicates a covalent bond, while a low value shows an ionic nature. We obtained the bond orders of the polynitrosoprismanes by natural bond orbital (NBO) analyses. A smaller Wiberg bond index (WBI) generally indicates a weaker bond. Actually, for these molecules we should consider the energies of all of the bonds in order to determine the weakest bonds. However, to save time, two possible bond dissociations were considered: (1) the C–NO bond on the side chain; (2) the C–C bond in the ring. It should be pointed out that, among bonds of the same type, the weakest bond was selected as the breaking bond, according to the principle of the smallest bond order (PSBO) [39].

Table 3 Calculated total energies (E_0, a.u), thermal corrections (H_T, a.u), zero-point energies (ZPE, a.u), HOFs (kJ mol^{-1}), and specific enthalpies of combustion (H_c) for polynitrosoprismances, calculated at the B3LYP/6-311G** level

1- and 1,2- denote 1-nitrosoprismane and 1,2-nitrosoprismane, respectively; the others are similar

Compound	E_0	ZPE	H_T	HOF	H_c
1-	−361.43788	0.09299	0.00707	529.06	−33.69
1,2-	−490.75705	0.08946	0.00914	511.72	−25.46
1,4-	−490.76144	0.09012	0.00892	501.34	−25.25
1,5-	−490.76252	0.08960	0.00906	497.51	−25.22
1,2,3-	−620.06387	0.08536	0.01134	525.16	−20.09
1,2,4-	−620.07544	0.08576	0.01124	495.57	−19.91
1,2,6-	−620.08246	0.08643	0.01097	476.19	−19.79
1,2,3,4-	−749.38534	0.08179	0.01342	501.22	−16.23
1,2,4,5-	−749.38547	0.08225	0.01321	501.54	−16.23
1,2,3,4,5-	−878.68792	0.07732	0.01580	525.31	−13.58
1,2,3,4,5,6-	−1007.99160	0.07342	0.01795	547.40	−11.54

Table 4 Calculated bond dissociation energies (kJ mol^{-1}) for the possible rupture of the weakest C–NO and C–C bonds, calculated at the UB3LYP/6-311G** level

Compound	C–NO	BDE_{C-NO}	BDE^0_{C-NO}	C–C	BDE_{C-C}	BDE^0_{C-C}
1-	1.1630	252.52	234.42	0.8523	130.12	126.37
1,2-	1.1085	218.70	201.27	0.7741	135.79	134.53
1,4-	1.1468	239.87	221.60	0.7737	222.64	219.65
1,5-	1.1303	235.69	216.99	0.8583	130.07	128.23
1,2,3-	1.0814	200.25	182.72	0.7948	127.02	124.87
1,2,4-	1.1047	219.15	201.63	0.8067	154.38	152.41
1,2,6-	1.1156	220.91	202.67	0.8067	151.78	150.65
1,2,3,4-	1.0883	207.20	189.95	0.8567	149.60	146.45
1,2,4,5-	1.0985	213.21	195.21	0.8136	151.73	149.89
1,2,3,4,5-	1.0522	190.43	172.53	0.8488	149.81	148.24
1,2,3,4,5,6-	1.0383	186.57	168.68	0.8511	68.66	67.74

1- and *1,2-* denote 1-nitrosoprismane and 1,2-nitrosoprismane, respectively; the others are similar. BDE^0_{C-NO} and BDE_{C-NO} denote the bond dissociation energy of the C–NO bond without and with zero-point energy correction, respectively; BDE^0_{C-C} and BDE_{C-C} denote the bond dissociation energy of the C–C bond without and with zero-point energy correction, respectively

In Table 4, it is apparent that the BDE_{C-NO} values shift downwards by ca. 18 kJ mol^{-1} when the ZPE is included, while the BDE_{C-C} values shift downwards by ca. 1–3 kJ mol^{-1} when the ZPE is included. However, the trend in the dissociation energies is not affected by the correction for the zero-point energy. Comparing BDE_{C-NO} and BDE_{C-C}, it is clear that the BDE_{C-C} value is much smaller than the BDE_{C-NO} value for the same molecule, which shows that the trigger bond for polynitrosoprismanes is the C–C bond in the skeleton. This is because the prismane skeleton has a high strain energy (609.9 kJ mol^{-1}). Therefore, it is noticeable that the mechanism for the pyrolysis of cage compounds is linked to their molecular structure, including the strain energy of the cage skeleton as well as the number and positions of substituent groups. We then studied the strain energies of the polynitrosoprismanes in detail.

Strain energies

Strain is an important concept in structural organic chemistry [40]. The concept of strain and strain energy (SE) provides a basis for correlating the structures, stabilities, and reactivities of molecules. The advantage of using a homodesmotic reaction is that it is possible to cancel out errors associated with the truncation of the basis set and incomplete electron correlation recovery to a large extent. This method, which was used to obtain the strain energies of cubane and cubane derivatives, has been used very successfully [41]. The SE values of the polynitrosoprimanes studied in this work were therefore obtained using a homodesmotic reaction. The values of the reference compounds included in the reaction are listed in Table 5. Table 6 lists the SE values of the title compounds. In order to verify that the results calculated at the B3LYP/6-311G** level using a homodesmotic reaction are reliable for calculated the SE values of prismane derivatives, we obtained the SE value of prismane, which is 619.52 kJ mol^{-1}. This value is in agreement with

Table 5 Total energies (E_0, a.u) and zero-point energies (ZPE) of the reference compounds, calculated at the B3LYP/6-311G** level

Compound	E_0	ZPE
CH$_3$CH$_3$	−79.85626	0.07437
(CH$_3$)$_3$CH	−158.50589	0.13095
(CH$_3$)$_3$CNO	−287.82606	0.12725

Table 6 Calculated strain energies (SE, kJ mol^{-1}) of the title compounds calculated at the B3LYP/6-311G** level via homodesmotic reactions

Compound	SE
C$_6$H$_6$	619.52
1-	606.41
1,2-	608.59
1,4-	595.33
1,5-	593.87
1,2,3-	644.68
1,2,4-	614.31
1,2,6-	593.07
1,2,3,4-	640.93
1,2,4,5-	639.39
1,2,3,4,5-	689.14
1,2,3,4,5,6-	732.96

1- and *1,2-* denote 1-nitrosoprismane and 1,2-nitrosoprismane, respectively; the others are similar

the reference value of 606.9 kJ mol^{-1} [42]. Inspecting the SE values of the monosubstituted and disubstituted polynitroso-primanes, it is clear that the SE values for these compounds are smaller than the calculated SE value for prismane. However, the SE increases as additional nitroso groups are added to the prismane skeleton when m is larger than 2. Generally speaking, for isomers with same value of m, the shorter the distance between the nitroso groups, the stronger the repulsive energy, and the larger the SE. For instance, if we consider the trinitrosoprismanes, the SE value of 1,2,3-trinitrosoprismane is slightly larger while the SE values of 1,2,4- trinitrosoprismane and 1,2,6- trinitrosoprismane are smaller than that of 1,2,3-trinitrosoprismane. This indicates that the SE values are affected by the positive charge on the substituent group. In other words, the SE value is small when the substituent groups are kept well away from each other.

Conclusions

We have computationally investigated a series of nitroso-prismanes that have the potential to be new high-energy compounds. Their electronic structures, heats of formation, specific enthalpies of combustion, and strain energies were calculated at the B3LYP/6-311G** level. Based on this theoretical study, the following conclusions can be drawn.

The $\Delta E_{\mathrm{LUMO-HOMO}}$ values of the title compounds decrease as the number of nitroso groups increases, and the energy gaps for the prismane derivatives are much lower than that for TATB. All of the polynitrosoprismanes have highly positive HOFs, and these HOFs are affected by the positions of the nitroso groups (as demonstrated by a comparison of isomers). The closer the nitroso groups are to each other, the larger the HOF. Furthermore, as the number of nitroso groups in the molecule increases, the specific enthalpy of combustion decreases. The bond dissociation energy for C–NO is larger than that for C–C bonds in all of the polynitrosoprismanes, which implies that the trigger bond is a C–C bond in the skeleton. All of the polynitroso-prismanes exhibit large strain energies, ranging from 593.07 to 732.96 kJ mol^{-1}.

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