

DFT calculations on nitrodiborane compounds as new potential high energy materials

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Abstract We have used DFT methods to determine the structures and thermochemistry of several nitro-substituted diborane molecules in an attempt to rate their potential as high energy materials. The properties of nitrodiborane, three isomers of dinitrodiborane, trinitrodiborane, and tetranitrodiborane were calculated using the B3LYP density functional method. Our results indicate that the absolute enthalpy of combustion decreases with increasing nitro content, in contrast with other nitro-substituted systems that have been studied previously.

Keywords Nitrodiborane · DFT calculation · High energy material

Introduction

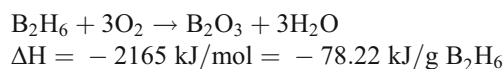
Research on new potential high energy (HE) materials is ongoing [1]. Good high energy materials need to be thermodynamically metastable with respect to decomposition/combustion products, should have a high density, and have a fast velocity of detonation [2]. They can also share certain chemical or structural properties, like high nitrogen or nitro content and strained ring systems. It is these latter properties that computational chemistry has been able to exploit in researching new potential HE materials.

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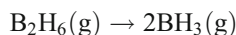
Recently we have calculated the thermochemical properties of several novel boron-containing compounds as possible HE materials, motivated by the fact that when boron oxidizes it forms B_2O_3 , and, in doing so, gives off 18.3 kJ g^{-1} [3]. Among other compounds, we considered boron-substituted spiro-pentane molecules, with [4] and without [5] nitrogen substitution as well.

Diborane, B_2H_6 , combusts spontaneously in air with one of the highest specific enthalpies of combustion known, aided by the thermodynamic stability of both of its combustion products [6]:



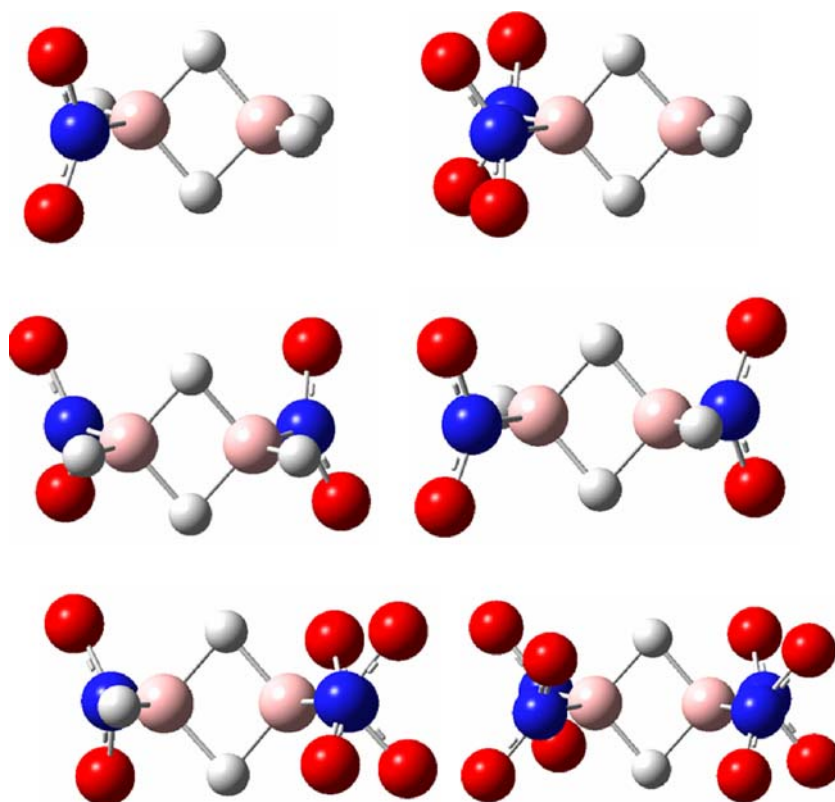
Given the tactic of including nitro groups ($-NO_2$) in HE materials, we are curious about the effect on its thermochemical properties of nitro substitution into the diborane parent molecule. Therefore, here we present calculations on the properties on a series of nitro-substituted diborane molecules. Chief among these properties are the predicted enthalpies of formation, from which we can determine enthalpies of combustion and decomposition. The molecules studied are nitrodiborane, three isomers of dinitrodiborane, trinitrodiborane, and tetranitrodiborane. The three isomers of dinitrodiborane have the nitro groups on the same boron atom, 1,1-dinitrodiborane, and the cis and trans isomers of 1,2-dinitrodiborane.

Consensus indicates that the first step in the combustion mechanism of B_2H_6 is the scission of the diborane molecule into two borane fragments [7, and references therein]:



Thermodynamic information on these species suggests that the bridging B–H bond has a bond energy of about

Fig. 1 Optimized structures of various nitrodiborane molecules. *Top* Nitrodiborane and 1,1-dinitrodiborane; *middle* cis-1,2-dinitrodiborane and trans-1,2-dinitrodiborane; *bottom* trinitrodiborane and tetranitrodiborane



86 kJ mol⁻¹. Among other things, we are interested in determining how this bond energy changes with nitro group content, as this might yield clues on whether nitrodiboranes will be air-sensitive or not.

Computational details

All calculations were performed using Gaussian03 [8] on a desktop personal computer. The calculational method used was the density functional theoretical method using Becke's 3-parameter exchange functional plus the correlation

functional of Lee, Yang, and Parr (B3LYP) [9, 10] along with the standard Gaussian basis set labeled 6-31G(d,p) [11]. Minimum energy geometries were determined for all target molecules using standard options, and minima were

Table 1 Representative bonding parameters for the various nitrodiborane molecules. (*r* in Ångstroms, α and δ in degrees)

	mono	1,1-di	cis-1,2-di	trans-1,2-di	tri	tetra
$r(\text{B-H}_{\text{terminal}})$	1.184	1.182	1.181	1.180	1.178	—
$r(\text{B-H}_{\text{bridge}})$	1.308	1.332	1.318	1.318	1.308	1.324
$r(\text{B-N})$	1.533	1.533	1.527	1.530	1.528	1.525
$r(\text{N-O})$	1.233	1.229	1.232	1.232	1.232	1.230
$\alpha(\text{B-H-B})$	83.0	82.4	82.1	82.1	81.9	81.6
$\alpha(\text{O-N-O})$	125.3	126.0	125.9	125.8	126.5	126.8
$\alpha(\text{H-B-N})$	115.7	111.3	117.5	117.8	119.5	108.8
$\delta(\text{B-H-B-H})$	110.0	111.4	116.8	116.9	114.1	—
$\delta(\text{B-H-B-N})$	110.8	115.5	112.4	111.9	112.9	115.3

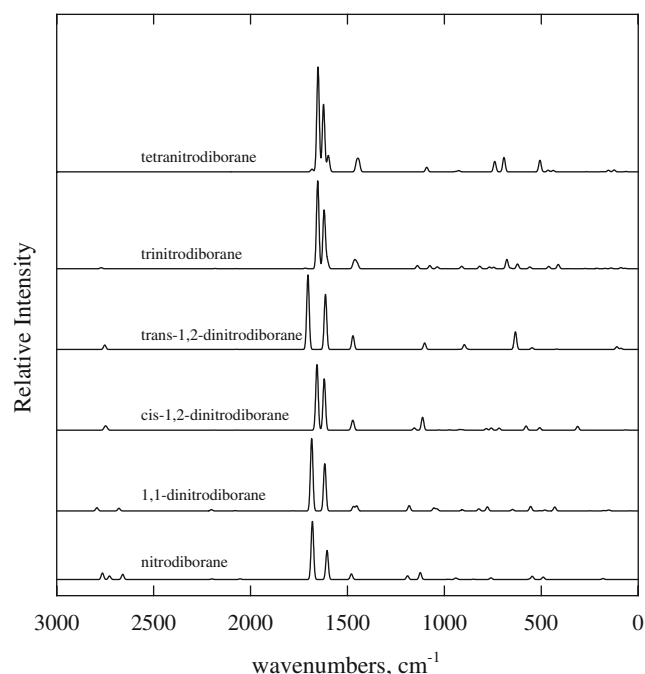


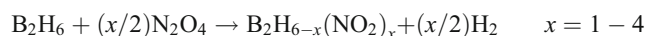
Fig. 2 Calculated unscaled vibrational spectra of the various nitrodiborane molecules

Table 2 Enthalpies of formation and combustion or decomposition for the various nitrodiborane molecules

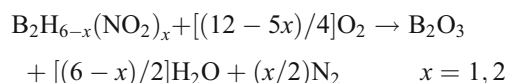
	ΔH_f , kJ mol ⁻¹	ΔH_{comb} , kJ mol ⁻¹	ΔH_{comb} , kJ g ⁻¹
Nitrodiborane	-15.4	-1,972.7	-27.17
1,1-Dinitrodiborane	-44.7	-1,800.2	-15.31
Cis-1,2-dinitrodiborane	-54.1	-1,790.8	-15.23
Trans-1,2-dinitrodiborane	-56.2	-1,788.4	-15.21
	ΔH_f , kJ mol ⁻¹	ΔH_{decomp} , kJ mol ⁻¹	ΔH_{decomp} , kJ g ⁻¹
Trinitrodiborane	-72.9	-1,629.3	-10.02
Tetranitrodiborane	-71.8	-1,487.5	-7.165

verified as having no imaginary vibrational frequencies, which were visualized using the GaussView program [12].

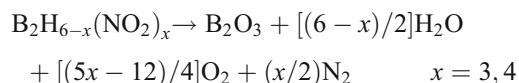
Because there are no good data on species that would provide for a reliable isodesmic or homodesmic reaction, the enthalpies of formation were determined by calculating the electronic and thermal energy changes for the following reactions:



Once the total energy change for this reaction was calculated, this energy change was equated to the change in enthalpy from the known enthalpies of formation of all but the title species, and the enthalpy of formation of the nitrodiborane was determined. Known enthalpies of formation were taken from the NIST Chemistry Webbook [3]. Once enthalpies of formation were determined for the various nitrodiborane species, the enthalpies of combustion or decomposition were determined. The general combustion reaction for nitrodiborane and dinitrodiborane is



The general decomposition reaction for trinitrodiborane and tetranitrodiborane is



in which excess oxygen is also a product.

For trinitrodiborane and tetranitrodiborane, there is too much oxygen present as a reactant, so molecular oxygen will be a product of the decomposition. Specific enthalpies of combustion or decomposition were determined by dividing the molar enthalpy change by the molar mass of the nitrodiborane.

Results and discussion

Figure 1 shows the optimized geometries of the various nitrodiborane molecules, while Table 1 lists representative

structural parameters. A review of the structural parameters shows some trends. For example, the bridging B–H–B bond becomes slightly elongated when two nitro groups are on the same boron atom, while the B–H–B bond angle becomes slightly smaller with increasing nitro content. Most other bonding parameters presented here show little deviation from one derivative to another, and vary without obvious trends. The calculations are all fairly accurate, coming very close to the experimental B–H_t and B–H_b bond distances of 1.184 and 1.314 Å, respectively, in diborane itself [13, 14].

The three isomers of dinitrodiborane have surprisingly similar bonding parameters. The largest variation is seen in the H–B–N bond angle, which is smaller in the 1,1-dinitrodiborane, at 111.3°, than it is in either the cis- or trans-1,2-dinitrodiborane isomers, both of which are approximately 117°. This suggests that the nitro groups on the same boron atom are sterically repelling each other slightly, as would be expected. The bonding parameters of the cis- and trans-1,2-dinitrodiborane show little difference, indicating that the nitro groups are far enough apart that the differing bonding arrangements do not cause dramatically different bond distances and angles.

Figure 2 shows the unscaled vibrational spectra calculated for the various nitrodiborane molecules. In all cases, the N–O asymmetric stretching and bridging H stretching modes dominate the spectrum in the 1,600–1,700 cm⁻¹ range. The B–H stretching region, about 2,650–2,800 cm⁻¹, consistently shows some weak absorptions for all except the tetra-substituted molecule. Two absorptions in the 1,450–1,470 cm⁻¹ range represent the symmetric and

Table 3 Energy of fragmentation of the diborane molecules into two borane fragments

	ΔH_{frag} , kJmol ⁻¹
Nitrodiborane	77.1
1,1-Dinitrodiborane	81.7
Cis-1,2-dinitrodiborane	70.3
Trans-1,2-dinitrodiborane	70.2
Trinitrodiborane	67.6
Tetranitrodiborane	60.7

asymmetric NO₂ stretches, which get closer together and more intense as the number of nitro groups on the diborane grows. The fingerprint regions are dominated by a series of low-intensity absorptions, especially the trinitrodiborane, which lacks the higher symmetry of the other molecules, which thus have several absorptions with exactly zero infrared absorption intensity.

A numerical list of the vibrational frequencies, their infrared absorption intensities, and approximate descriptions of the normal modes is given in the [electronic supplementary material](#).

Table 2 lists the enthalpies of formation and combustion for the various nitrodiborane molecules. Nitrodiborane and the dinitrodiboranes have a negative oxygen balance (OB%; [15]) of -77.1 and -13.6, respectively, so they require additional oxygen to completely oxidize. Tri- and tetranitrodiborane both have positive OB% values (14.8 and 30.8, respectively), so their combustion reactions are actually decomposition reactions with extra molecular oxygen as a decomposition product.

Table 2 shows that the enthalpies of formation decrease with increasing nitro content. This trend is consistent with that seen between alkanes and nitroalkanes, which show decreasing ΔH_f upon nitration [3]. The three isomers of dinitrodiborane have similar ΔH_f values, with the trans-1,2-dinitrodiborane being the most stable, as expected from steric issues. At -72.9 and -71.8 kJ mol⁻¹ for trinitrodiborane and tetranitrodiborane, respectively, the enthalpies of formation of these two compounds are remarkably close together; apparently the steric repulsion upon adding a fourth nitro group overcomes any additional stability when forming the B–N bond.

Table 2 shows that the enthalpies of combustion (decomposition for tri- and tetranitrodiborane) show a trend to lower ΔH_{comb} values as the nitro content of the diborane increases. This is consistent with results of other polynitro compounds, like the nitroborazines [16] and nitrocyclopropanes (A. Lawong and D.W.B., manuscript submitted), and is due in part to the fact that for each nitro group that is added to the parent molecule, one half less of a water molecule is made as a product. The final column in Table 2 lists the specific enthalpy of combustion, i.e., the amount of energy given off per unit gram. Again, as the nitro content of the molecules increase, the specific enthalpy of combustion (or decomposition) decreases. Here, two factors are working in the same direction: not only are the enthalpies of formation going down with increasing nitro content, but the mass of the molecule increases by a net 45 g mol⁻¹ per nitro group added. Despite the fact that the specific enthalpy of combustion/decomposition is decreasing, the absolute numbers suggest that some nitrodiboranes may be acceptable energy sources if other factors (velocity of detonation, density, figure of insensitivity, etc.) are worthwhile.

In order to assess the nitrodiboranes' ability to be air-stable, we calculated the enthalpy change of the reaction in which the diborane became two borane fragments of the same or slightly different formulas. Enthalpies of fragmentation are listed in Table 3. The trend is clear: as the nitro content increases, the two borane fragments are held together less strongly. The values in Table 3 should also be considered in context with the fragmentation enthalpy of diborane, which is 86 kJ mol⁻¹, as determined from enthalpy data found in [3]. Thus it seems unequivocal that the addition of the electron-withdrawing nitro groups are weakening the hydrogen bridges between the boron atoms. This suggests that nitrodiboranes, should they ever be synthesized, will also be pyrophoric.

Conclusions

We have determined optimized geometries, vibrational spectra, and enthalpies of formation, combustion/decomposition, and fragmentation for a series of nitrodiborane molecules. We find that the greater the nitro content, the more stable the molecule, and the less the combustion enthalpy and specific enthalpy of combustion or decomposition. Despite this, the numerical values of the specific enthalpy of combustion put nitrodiboranes in the region of possible new HE materials, although we caution future experimentalists that we also predict that nitrodiboranes will, like their parent compound diborane, be extremely air-sensitive.

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