

Nitroborazines as potential high energy materials: density functional theoretical calculations

Jay D. Janning · David W. Ball

Received: 24 July 2009 / Accepted: 22 August 2009 / Published online: 23 September 2009
© Springer-Verlag 2009

Abstract As part of a search for new high energy density materials, we used density functional theoretical calculations to determine the thermochemical properties of various nitro-substituted borazine molecules. Optimized geometries, vibrational frequencies and spectra, and enthalpies of formation and combustion were determined for nitroborazine, dinitroborazine, trinitroborazine, and methyltrinitroborazine with substituents on either the boron atoms or the nitrogen atoms of the parent borazine ring. Our results indicate that the specific enthalpy of combustion ranged from 4 to 11 kJ g⁻¹, with increasing substitution of nitro groups lowering the energy of combustion per unit mass.

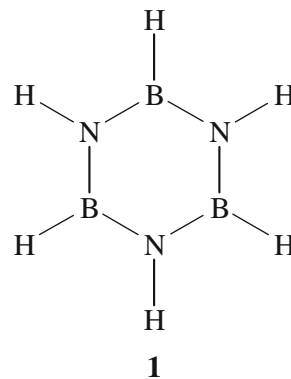
Keywords Density functional theory calculations · High energy density materials · Nitroborazines

Introduction

Research on new potential high energy (HE) materials is ongoing [1]. Good high energy materials should be thermodynamically unstable 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 content and strained ring systems. Recently we have published

several papers on small molecules having significant boron and nitrogen content [3, 4]. Results indicate that some of these hypothetical compounds have a rather high specific enthalpy of combustion or decomposition. However, because of boron's propensity to make compounds with oxygen, many of these proposed compounds would likely be air-sensitive, if not outright pyrophoric, potentially limiting their usefulness even if they are synthesized and tested as HE materials.

Borazine (1), B₃N₃H₆, is the nitroboron analog of benzene. It is apparently air-stable, as short-wavelength radiation is required to react with oxygen [5]. Although hexagonal and planar, it shows no chemical similarity to its organic analog. With an enthalpy of formation of -510 kJ mol⁻¹ [6], it is thermodynamically very stable.



Electronic supplementary material The online version of this article (doi:10.1007/s00894-009-0586-y) contains supplementary material, which is available to authorized users.

J. D. Janning · D. W. Ball (✉)
Department of Chemistry, Cleveland State University,
2121 Euclid Avenue,
Cleveland, OH 44115, USA
e-mail: d.ball@csuohio.edu

With well-known explosive compounds like trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) based on the benzene ring, we speculate on what the HE properties of similar borazine-based substances might be. Hence, we have undertaken a computational study of the thermochemical properties of a series of nitroborazines,

culminating in methyltrinitroborazine – the borazine equivalent of TNT.

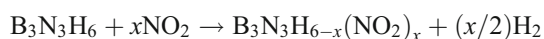
Borazine itself has a substantial enthalpy of combustion: $-2258 \text{ kJ mol}^{-1}$, or 20.1 Jg^{-1} . This is in part due to the very negative enthalpy of formation of B_2O_3 , which at $-1273 \text{ kJ mol}^{-1}$ is one of the most thermodynamically stable oxides (surpassed only by Al_2O_3) [6]. Because of boron's low atomic mass, boron compounds have a relatively large specific enthalpy of combustion, an important quantity for vehicles that have to carry their own fuel. Addition of one or more nitro groups to the borazine will make the molecule more autooxidative, improving its potential to act as an explosive.

There are no known previous studies on nitroborazine compounds.

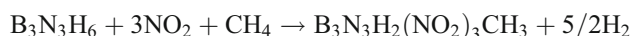
Computational details

All calculations were performed using Gaussian03 [7] on a desktop personal computer, or on an IBM Cluster 1350 supercomputer located at the Ohio Supercomputer Center in Columbus, Ohio. 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 (abbreviated B3LYP) [8, 9] along with the standard Gaussian basis set labeled 6-311+G(d,p) [10]. This basis set was chosen after testing the ability to reproduce thermochemical data on borazine itself. Minimum energy geometries were determined for all target molecules using standard options, and minima were verified as having no imaginary vibrational frequencies. No structural parameters were constrained during the geometry optimizations. Only nitro substitution on either the B atoms or the N atoms were studied, as this decreased the number of possible isomers to consider.

The following general gas-phase reaction was used to determine the enthalpy of formation of the nitroborazine molecules:



For the methyltrinitroborazine, the following reaction was used to determine the enthalpies of formation:



After the calculated electronic and thermal energy changes were determined and an overall energy change for the reaction determined, this energy change was set equal to the difference of the known enthalpies of formation of the products minus those of the reactants, and the unknown enthalpy of formation of the appropriate nitroborazine was determined. After the ΔH_f of the nitro-

borazine was determined, the enthalpy of combustion was determined, assuming that the appropriate amount of elemental oxygen were present as a reactant and that $\text{B}_2\text{O}_3(\text{s})$, $\text{H}_2\text{O}(\text{l})$, $\text{CO}_2(\text{g})$, and $\text{N}_2(\text{g})$ (as appropriate for each substance) were the products of the combustion reaction. Values for the known enthalpies of combustion were taken from the NIST Chemistry Webbook [6].

Results and discussion

Optimized geometries

Figures 1, 2, 3, and 4 show the optimized structures of B- and N-nitroborazine, B- and N-dinitroborazine, B- and N-trinitroborazine, and methyl-B- and -N-trinitroborazine, while Table 1 lists representative bonding parameters of the molecules. One issue to note immediately is that the B-bonded nitroborazine molecules have all nitro groups in the same plane as the borazine ring, while the N-bonded nitroborazine molecules have all nitro groups making an angle with the borazine ring, about $27\text{--}28^\circ$.

Figures 1, 2, 3, and 4 and Table 1 also show that the borazine ring is more closely hexagonal when nitro groups are bonded to the boron atoms than when they are bonded to the nitrogen atoms. In the B-nitroborazine molecules, the ring bond angles are closer to the 120° in a regular hexagon. However, in the N-nitroborazine molecules, the B-N-B angles are about 125° , while the N-B-N angles are about 115° . This is an obvious deviation from regularity, and it is visibly noticeable in the structures in Figs. 1, 2, 3, and 4. Other trends are a slightly smaller O-N-O bond angle in all B- nitroborazines than in N-nitroborazines, and N-N bonds between the ring and the nitro group were significantly smaller than the B-N bonds between the ring and the nitro groups. Perhaps the most significant difference in the structures are the angles of the NO_2 groups with respect to the ring. Figures 1, 2 and 3 show that the nitro groups in the

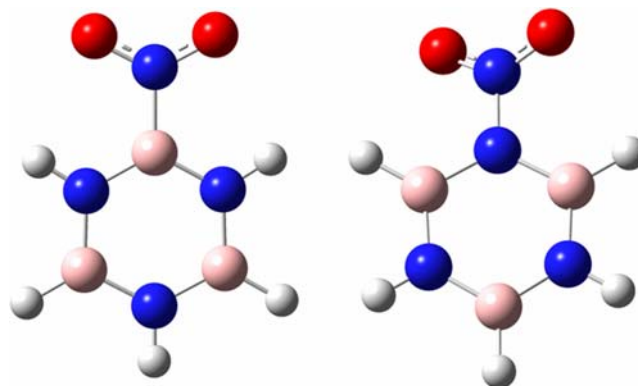
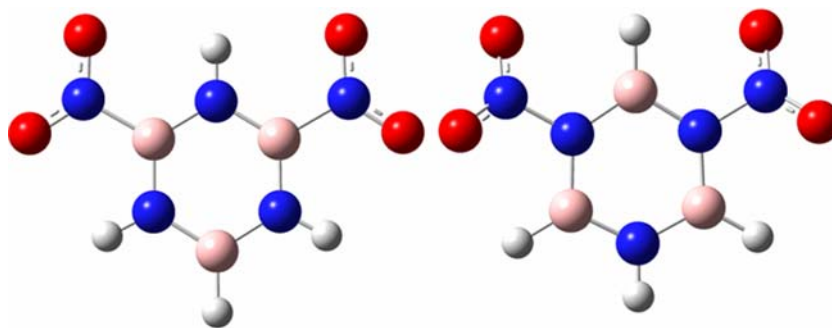


Fig. 1 Optimized structures of B-nitroborazine (left) and N-nitroborazine (right)

Fig. 2 Optimized structures of B-dinitroborazine (left) and N-dinitroborazine (right)



B-nitroborazines lie in the plane of the ring, while the nitro groups in the N-nitroborazines are not in the same plane as the ring. In methyl-B-trinitroborazine (Fig. 4), the two nitro groups adjacent to the methyl group lie outside of the plane of the ring, obviously because of steric factors caused by the presence of the methyl group; note that the third nitro group, in a *para* position with respect to the CH₃, lies in the plane of the ring. In methyl-N-trinitroborazine, all nitro groups are out of the plane of the ring, in common with the other N-nitroborazine compounds.

Although the nitro groups in the methylnitroborazine molecules are rotated out of plane because of steric interference from the methyl group, there may be interaction between a hydrogen atom of the methyl group and an oxygen in an adjacent nitro group. The optimized geometry of the N-methyltrinitroborazine shows a closest distance of 2.57 Å, which is slightly less than the sum of the van der Waals radii of an H atom and an O atom (1.20 Å + 1.52 Å, or 2.72 Å) [11]. However, since this interatomic distance is just under the van der Waals radii, it is likely a weak intramolecular hydrogen bond and not a strong covalent interaction between the atoms. In B-methyltrinitroborazine, the shortest interatomic distance between the substituents is 3.07 Å, well outside the sum of the van der Waals radii of the two nearest atoms.

Vibrations

Figures 5, 6, 7, and 8 show the calculated vibrational spectra of the various nitroborazine molecules. The spectra

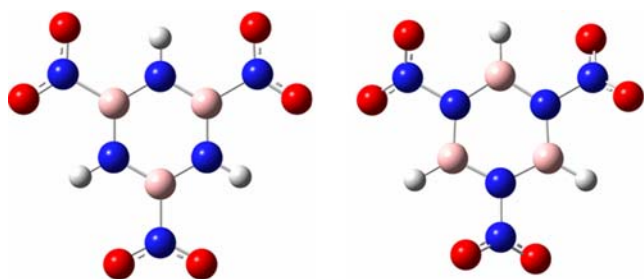


Fig. 3 Optimized structures of B-trinitroborazine (left) and N-trinitroborazine (right)

of the molecules with the same nitro content are shown together to illustrate the differences when the NO₂ groups are bonded to B atoms or N atoms in the borazine ring. The spectra for each level of substitution are qualitatively similar, although the fingerprint regions are obviously different. We note that in all cases, the boron-substituted molecules have seemingly simpler spectra than the nitrogen-substituted analogs, although this is because of near-degeneracy, as all pairs have the same number of vibrational degrees of freedom. The B-nitroborazine molecules show two relatively strong, nearly degenerate N-H stretches just under 3600 cm⁻¹, while the N-nitroborazine molecules show symmetric and asymmetric B-H stretches of decreasing intensity and energy separation around 2700 cm⁻¹.

A complete list of vibrational frequencies, infrared absorption intensities, and approximate descriptions of the normal modes is available as [Supplementary Material](#). In the case of the B- and N-trinitroborazine, because of the three-fold symmetry there are some degeneracies in the vibrational frequencies, so these tables have less than $3N-6=48$ different normal modes of vibration.

Energies of reaction

Table 2 lists the calculated enthalpies of formation and the resulting enthalpies of combustion; enthalpies of decomposition (more important for considering a potential explosive rather than fuel) were not considered because of the unknown distribution of oxygen among the B, H, and C

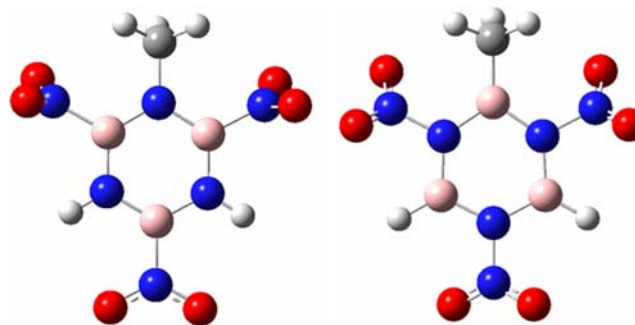


Fig. 4 Optimized structures of methyl-B-trinitroborazine (left) and methyl-N-trinitroborazine (right)

Table 1 Representative bonding parameters of the various nitroborazine molecules

Parameter	B-mono	N-mono	B-di	N-di	B-tri	N-tri	B-methyl	N-methyl
r(B-N) [ring]	1.431	1.431	1.413	1.442	1.413	1.441	1.419	1.440
r(B-H)	1.188	1.180	1.185	1.178	—	1.171	—	1.173
r(N-H)	1.011	1.010	1.012	1.010	1.015	—	1.014	—
r(B-N) [nitro]	1.563	—	1.557	—	1.551	—	1.540	—
r(N-N) [nitro]	—	1.437	—	1.452	—	1.467	—	1.460
r(N-O)	1.230	1.215	1.230	1.211	1.229	1.208	1.228	1.209
r(B-C)	—	—	—	—	—	—	1.559	—
r(N-C)	—	—	—	—	—	—	—	1.485
r(C-H)	—	—	—	—	—	—	1.089	1.092
α (B-N-B) [ring] 120.4	—	124.2	121.6	124.6	119.3	125.6	119.3	127.2
α (N-B-N) [ring] 116.6	—	115.7	116.51	114.8	120.7	114.4	121.9	115.0
α (N-B-N) [nitro] 119.0	—	—	119.5	—	119.6	—	118.1	—
α (B-N-N) [nitro] —	118.3	—	118.0	—	117.2	—	117.9	—
α (O-N-O)	124.1	126.4	124.5	127.2	124.9	128.0	125.2	127.7
α (H-C-H)	—	—	—	—	—	—	109.1	106.7
δ (N-B-N-O)	180.0	—	180.0	—	180.0	—	108.2	—
δ (B-N-N-O)	—	153.1	—	153.1	—	151.8	—	133.6
δ (N-B-C-H)	—	—	—	—	—	—	—	26.7
δ (B-N-C-H)	—	—	—	—	—	—	31.7	—

(The names have been abbreviated for clarity. Distances in angstroms, angles in degrees.)

for those molecules with a negative oxygen balance (OB%; [12]), which implies that the molecular formula does not have enough oxygen to completely oxidize. Of the four molecular formulas studied here, the nitroborazines, dinitroborazines, and methyltrinitroborazines have a negative

OB% (−63.7%, −23.5%, and −20.9%, respectively); if they decompose, they would not have sufficient oxygen to oxidize the substance completely, and may need external sources of oxidant. However, the trinitroborazines have an OB% of 0%, implying that these molecular formulas have

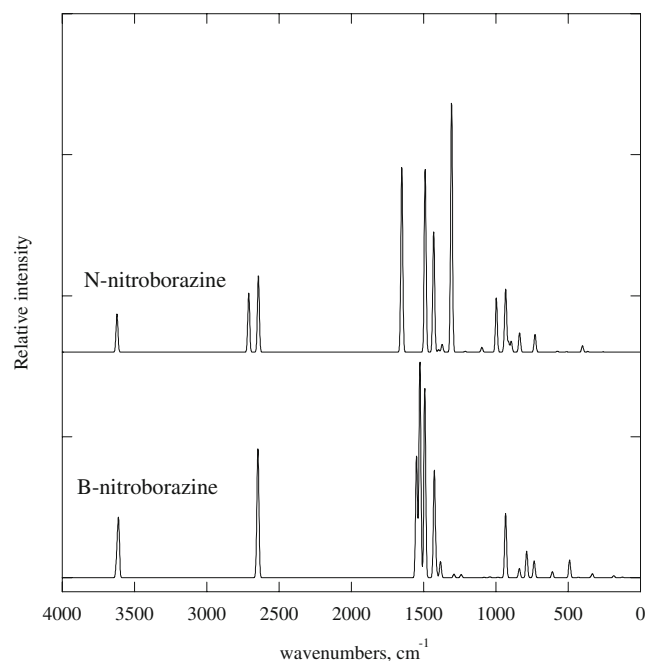


Fig. 5 Calculated vibrational spectra of B-nitroborazine and N-nitroborazine

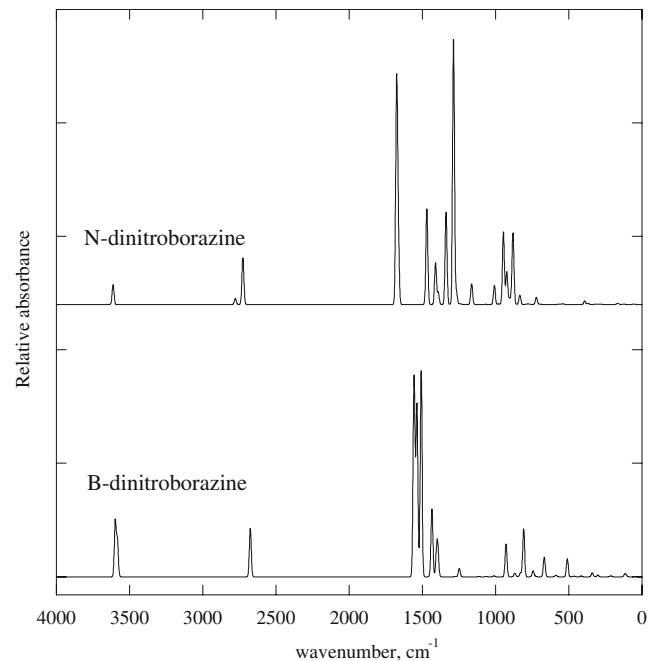


Fig. 6 Calculated vibrational spectra of B-dinitroborazine and N-dinitroborazine

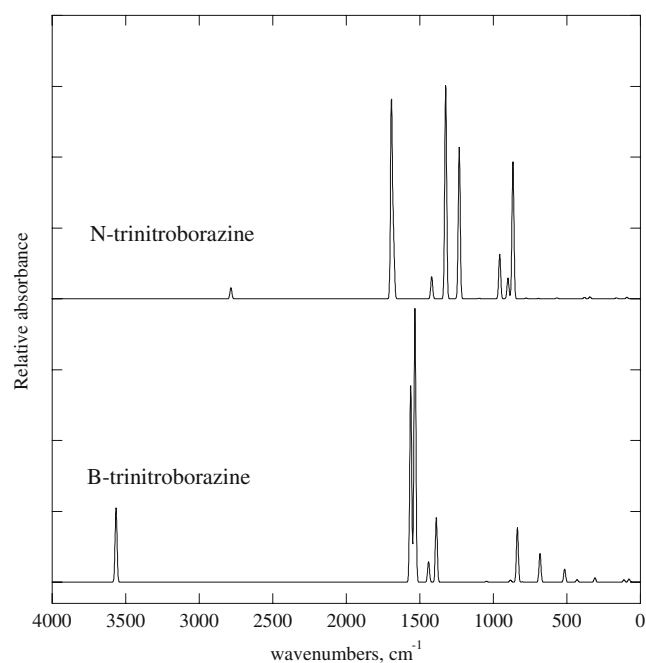


Fig. 7 Calculated vibrational spectra of B-trinitroborazine and N-trinitroborazine

enough oxygen in them to completely oxidize the other elements present. Hence, the reactions for the trinitroborazines are more properly decomposition reactions, not combustion reactions.

The data in Table 2 show some obvious trends. First, the enthalpies of formation for the B-bonded nitroborazines get more negative with increasing nitro content, while for the

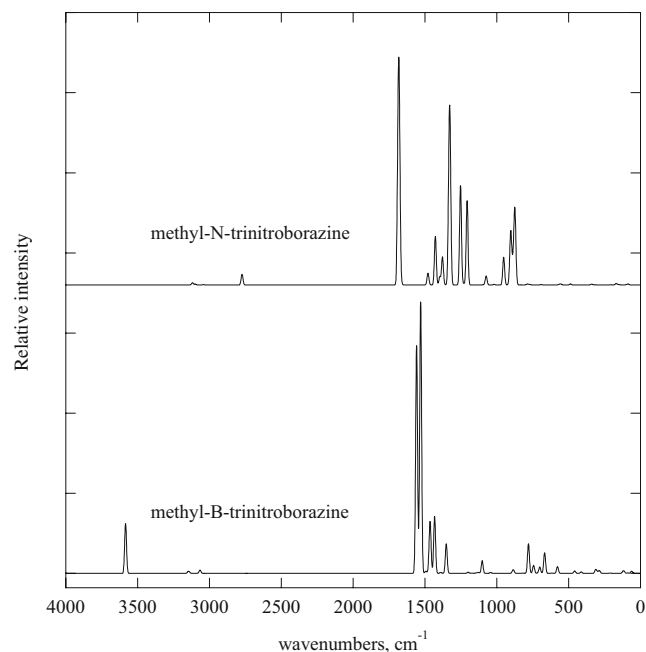


Fig. 8 Calculated vibrational spectra of methyl-B-trinitroborazine and methyl-N-trinitroborazine

Table 2 Calculated enthalpies of reaction for the various nitroborazine molecules (in kJ mol^{-1} unless otherwise stated)

Molecule	ΔH_f	ΔH_{comb}	$\Delta H_{\text{comb, kJ g}^{-1}}$
B-nitroborazine	-593.5	-1265.0	-10.1
N-nitroborazine	-418.6	-1439.9	-11.5
B-dinitroborazine	-677.1	-1060.5	-6.22
N-dinitroborazine	-326.4	-1411.2	-8.28
B-trinitroborazine ^a	-720.5	-896.2	-4.16
N-trinitroborazine ^a	-195.5	-1421.2	-6.59
methyl-B-trinitroborazine	-680.3	-1571.8	-6.85
methyl-N-trinitroborazine	-245.7	-2006.3	-8.74

^a The ΔH values for the trinitroborazine molecules are more properly labeled ΔH_{decomp} , not ΔH_{comb} . See discussion in text

N-bonded nitroborazines the enthalpies of formation get more positive (*i.e.* less negative) with increasing nitro content. This may be due to the participation of the empty p orbital on the B atom to interact not only with the lone pair of electrons on the ring N atoms, but on the nitro group's N atoms as well. The regularity of the trend is surprising: for each nitro group added to the borazine ring, the difference between the B-bonded and N-bonded nitroborazines increases by about 175 kJ mol^{-1} . The trend is just the opposite with the addition of a methyl group, however. In going from B-trinitroborazine to methyl-B-trinitroborazine, the molecule gets less stable by about 40 kJ mol^{-1} , while in going from N-trinitroborazine to methyl-N-trinitroborazine, the molecule get more stable by 50 kJ mol^{-1} . We find this result difficult to rationalize. Both the B-C and N-C bonds are stronger than the B-H and N-H bonds, at least in the diatomic molecules [13]. Intramolecular interactions may be a contributing factor, as Fig. 4 shows the NO_2 groups rotated closer to the methyl group in the N-methyl isomer than in the B-methyl isomer, suggesting that there may be some O—H interactions. However, there is nothing precluding such an interaction in the B-methyl isomer; this molecule optimized with nitro groups almost perpendicular to the B_3N_3 ring; and if this is because of a very shallow potential energy curve with respect to NO_2 internal rotation, changing the NO_2 angles with respect to the methyl group would not contribute significantly to an increased stability of the molecule. We would welcome any suggestions for the reason behind this particular result.

The final column in Table 2 lists the specific enthalpy of combustion of the nitroborazines in units of kJ g^{-1} . The numbers show that the N-bonded nitroborazine molecules are invariably more energetic per unit mass than the B-bonded nitroborazines, again likely due to a more stable B-N bond. The specific enthalpies of formation decrease with increasing nitro content, indicating that the change in stability of the parent compound does not keep up with the mass increase accompanying the greater number of nitro

groups. We have noted this trend before in other nitro-derived compounds [14, 15].

The reported specific enthalpy of decomposition of trinitrotoluene, TNT, varies from 4.25 [2] to 5.3 kJ g⁻¹ [16]. Hence, all but one nitroborazine has a greater specific enthalpy than TNT. However, TNT has an OB% of -74%, implying a significant lack of oxygen for complete combustion. The enthalpy of combustion of TNT is about 15 kJ g⁻¹, based on information from the NIST Chemistry Webbook [6]. Hence, from a complete combustion standpoint, TNT is a more energetic fuel than all of the nitroborazine molecules presented here. As an explosive, however (assuming that an additional oxidant is not present), the two trinitroborazine derivatives have energy contents that rival or exceed that of TNT, suggesting that if other factors like density and velocity of explosion are comparable, such compounds may have promise as new high energy density materials.

Acknowledgments JDJ thanks the Provost's Office, Cleveland State University, for providing funds to perform this research. We also thank the Ohio Supercomputer for a grant of resources with which some of this work was performed.

References

1. Badgujar DM, Talawar MB, Asthana SN, Mahulikar PP (2008) *J Hazard Mater* 151:289–305
2. Kahavan J (2004) *The chemistry of explosives*. Royal Society of Chemistry, Cambridge
3. Richard RM, Ball DW (2008) *Theochem* 851:284–923
4. Richard RM, Ball DW (2008) *J Mol Model* 14:871–878
5. Lee GH, Porter RF (1967) *Inorg Chem* 6:648–652
6. NIST Chemistry Webbook. <http://webbook.nist.gov/chemistry/>. Accessed 19 June 2009
7. Frisch MJ et al. (2004) *Gaussian 03*, Revision D.01. Gaussian Inc, Wallingford, CT
8. Becke AD (1993) *J Chem Phys* 98:5648–5652
9. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
10. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) *J Chem Phys* 72:650–654
11. Bondi A (1954) *J Phys Chem* 68:441–451
12. Persson PA, Holmberg R (1993) *Rock blasting and explosives engineering*. CRC Press, Boca Raton, FL
13. Lide DR (2008) *CRC handbook of chemistry and physics*. CRC Press, Boca Raton, FL
14. Mathews K, Ball DW (2008) *Theochem* 868:78–81
15. Mathews K, Ball DW (2009) *Theochem* 902:15–20
16. Yates JT, Johnson JK (2007) *Molecular physical chemistry for engineers*. University Science Books, Sausalito, CA