



Aminonitronaphthalenes as Possible High Energy Density Materials

Rebecca J. MURAWSKI, David W. BALL*

*Department of Chemistry, Cleveland State University,
2121 Euclid Avenue, Cleveland OH 44115, USA*

** E-mail: d.ball@csuohio.edu*

Abstract: As part of a series of studies evaluating the thermodynamic properties of new potential high energy materials, a series of calculations was performed on a variety of naphthalene molecules having amino and nitro groups. Calculations on seven aminonitronaphthalene molecules were performed, determining their minimum-energy geometries, vibrational frequencies, and energies. Enthalpies of formation were determined using atomization reactions, and subsequently enthalpies of combustion or decomposition were determined. Specific enthalpies of decomposition ranged from 4.1–4.8 kJ/g, while specific enthalpies of combustion ranged more widely, from 13 to almost 21 kJ/g. Some detonation properties of some of the derivatives rival those of current HEDMs.

Keywords: high energy density materials, aminonitronaphthalenes, density functional theory calculations

1 Introduction

The search for new high energy density materials (HEDMs) to serve as new potential fuels and/or explosives is an ongoing process [1]. One of the characteristics that makes a compound a good possible candidate as an HEDM is a high nitrogen content, as one of the decomposition products of nitrogen-containing compounds is N_2 , which gives off approximately $945 \text{ kJ}\cdot\text{mol}^{-1}$ of energy upon formation from two nitrogen atoms [2].

The discovery of FOX-7 (1,1-diamino-2,2-dinitroethylene) in 1998 [3] as a new HEDM has prompted us to consider other molecular systems having amino (NH_2) and nitro (NO_2) groups as possible HEDMs. FOX-7 is relatively insensitive,

yet has explosive characteristics similar to that of cyclotrimethylenetrinitramine, or RDX. FOX-7 has a larger than expected density ($1.885 \text{ g}\cdot\text{cm}^{-3}$ [4, 5]), probably due to the intermolecular interactions between NH_2 and NO_2 groups in adjacent molecules. FOX-7 molecules have oxidizing groups (NO_2) and reducing groups (NH_2), with an overall nitrogen content of 38% by mass.

Thus inspired, we recently performed calculations on the thermodynamic properties of other aminonitro molecules: aminonitromethane [6], aminonitroethane [7], aminonitroacetylene [8], and aminonitrocyclopropane [9] among them. Although the usual trend in molar enthalpies of decomposition shows an increasing magnitude with increasing NH_2 and NO_2 substitution, the enthalpy of decomposition per gram usually decreases with the number of functional groups. Even so, the specific enthalpies of decomposition or combustion are large enough to be in the range of other, better-recognized HE materials.

Trinitrotoluene, or TNT, was discovered by J. Wilbrand in 1863 [10] and was originally used as a yellow dye. Its use as an explosive did not commence until the 1900s, partially because of the difficulty in detonation. Now, however, TNT is a common standard against which other HEDMs are compared [11].

Another benzene-based HEDM is 1,3,5-triamino-2,4,6-trinitrobenzene, known as TATB [11]. TATB has an explosive power between those of TNT and RDX, and is even more insensitive than TNT, so much so that it is thought that TATB is used in atomic weapons as the main explosive charge [12]. One of TATB's advantages is a relatively high density: $1.93 \text{ g}\cdot\text{cm}^{-3}$ for crystalline TATB, $\sim 1.80 \text{ g}\cdot\text{cm}^{-3}$ for the solidified melt [11]. The relatively high density (the density of TNT is only $1.66 \text{ g}\cdot\text{cm}^{-3}$) is thought to be due to intermolecular hydrogen bonding between NH_2 groups of one TATB molecule and NO_2 groups of another – exactly the same mechanism that is thought to contribute to the unusually high density of FOX-7. Other aromatic HEDMs of varying use include picric acid and its derivatives, tetryl (2,4,6-trinitrophenylmethylnitramine), lead styphnate (the Pb(II) salt of trinitroresorcinol), and hexanitrostilbene [11].

Despite the popularity of certain benzene-based HEDMs, HEDMs based on naphthalene (C_{10}H_8) are less popular, but not unknown. One of the earliest mentions of a naphthalene-containing HEDM is from 1879 in a UK patent for a gunpowder mixture containing nitronaphthalene [13]. Several other references to nitronaphthalenes, all in the name of J. H. Stebbins, relate to improvements in the performance of dyes, echoing the initial interest in TNT [14]. By 1897, Krug and Blomen [15] pointed out that even Alfred Nobel noted that adding nitronaphthalene to nitroglycerine improved its concussive stability, and they proceeded to present experimental guidelines for preparing naphthalene derivatives of undetermined nitro content. Throughout the 20th

century, nitronaphthalenes, up through at least the trinitro derivative, were minor components of HEDM mixtures in munitions.

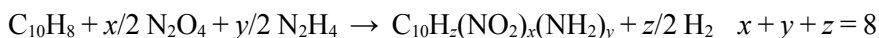
Despite the presence of nitronaphthalenes in high energy density applications, there appears to be no appearance of aminonitronaphthalenes of the sort exemplified by TATB and FOX-7. The parent hydrocarbon, naphthalene, already has a condensed-phase that is of significantly higher density than the parent hydrocarbon for TATB, which is benzene: the density of benzene is $0.876 \text{ g}\cdot\text{cm}^{-3}$ versus $1.145 \text{ g}\cdot\text{cm}^{-3}$ for naphthalene [16]. Substitution of amino and nitro groups for the hydrogen atoms in benzene more than doubles the density and, as mentioned, condensed-phase density has a significant impact on the explosive properties of a potential HEDM material. Therefore, we have performed a computational study of the thermochemical properties of some representative aminonitronaphthalene molecules to (if at least partially) assess them for their potential as HEDMs.

There are a very large number of possible aminonitronaphthalene molecules, depending on the number and relative positions of each type of substituent. As such, we have focused on aminonitronaphthalene molecules that have some regularity or symmetry of the substituents, reasoning that this would increase the chance for intermolecular interactions, increasing the solid-state density and therefore the explosive power. A total of seven diaminodinitro and tetraaminotetranitro derivatives are discussed here.

2 Computational Details

All calculations were performed using Gaussian 03 [17] 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 (abbreviated B3LYP) [18, 19] along with the standard Gaussian basis set labeled 6-31G(*d,p*) [20]. Minimum energy structures were determined for all target molecules using standard options, and minima were verified as having no imaginary vibrational frequencies, which were visualized using the GaussView program [21].

The enthalpies of formation were calculated using the following reaction:



where x , y , and z vary with the particular aminonitronaphthalene. After determining the enthalpy change of this reaction, in terms of both electronic

energies and thermal energies, the enthalpy of formation of the particular aminonitronaphthalene was determined using the known enthalpies of formation of $C_{10}H_8$, N_2O_4 , N_2H_4 , and H_2 , which were obtained from the NIST Chemistry Webbook [2]. Once the enthalpies of formation were calculated, the enthalpies of decomposition and combustion were determined. The decomposition reactions followed the modified Kistiakowsky-Wilson rules [11]: hydrogen is converted to water; then any remaining oxygen converts carbon to CO; then any remaining oxygen converts CO to CO_2 , and all nitrogen is converted to N_2 . The combustion reactions assumed that enough molecular oxygen is present to oxidize all C and H atoms, while the N atoms are converted to N_2 .

Two important explosive properties, the detonation pressure P (in kbar) and the velocity of detonation D (in km/s) were calculated using the parametrized equations of Kamlet and Jacobs [22]:

$$P = 15.58\rho^2NM^{1/2}Q^{1/2}$$

and

$$D = 1.01[NM^{1/2}Q^{1/2}]^{1/2}(1 + 1.30\rho)$$

where ρ is the density of the substance in $g\cdot mL^{-1}$, N is the number of moles of gas produced per gram of explosive, M is the grams of gas produced per gram of explosive, and Q is the energy released in calories per gram.

3 Results and Discussion

Figure 1 shows the numbering scheme for substitutions of the parent naphthalene molecule. Table 1 lists the labels and substitutions used to indicate the particular aminonitronaphthalene considered in this study.

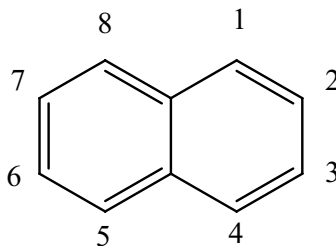


Figure 1. Numbering of positions on naphthalene.

Table 1. Legend to the amino- and nitro-substituted naphthalene molecules in this study

Substitution	Label
1,5-diamino-4,8-dinitro	ANN1
1,4-diamino-5,8-dinitro	ANN2
2,3-diamino-6,7-dinitro	ANN3
1,8-diamino-4,5-dinitro	ANN4
1,4,5,8-tetraamino-2,3,6,7-tetranitro	ANN5
2,3,6,7-tetraamino-1,4,5,8-tetranitro	ANN6
1,3,5,7-tetraamino-2,4,6,8-tetranitro	ANN7

Figure 2 shows two geometry-optimized aminonitronaphthalene molecules that demonstrate some representative structural features. Although the NO₂ groups are generally planar and the NH₂ groups are generally tetrahedral about their respective nitrogen atoms, having substituents in positions alpha or beta to each other can cause significant steric hindrance, leading to twisting of the functional groups into asymmetric positions with respect to the naphthalene framework. An extreme case is seen for ANN7, which has NO₂ and NH₂ groups in alternating positions; rather than simply rotating the groups out of the C₁₀ plane (as is largely seen in ANN4 and ANN6), the C₁₀ framework is distorted significantly out of planarity, as demonstrated by the side-on view of ANN7 in Figure 2.

Vibrational frequency calculations, having no imaginary frequency values, confirmed the minimum-energy geometries. Conformational analyses were not performed, so the optimized geometries may not be absolute minima, but any conformational energy differences are expected to be minimal. Graphics of the optimized structures of all of the aminonitronaphthalene derivatives reported here, as well as lists of vibrational frequencies and their intensities, can be found in the accompanying Supplementary Material.

Table 2 lists the enthalpies of formation and, subsequently calculated, the enthalpies of decomposition and combustion for each aminonitronaphthalene, per unit mole and per unit gram. The first four entries are isomers of each other, as are the last three; hence comparisons are best made within each group. The isomer ANN1, which has the amino and nitro groups adjacent to each other, has an enthalpy of formation slightly higher than the other diaminodinitro derivatives. The isomer ANN3 is predicted to be the most stable diaminodinitro isomer; this isomer has the two nitro groups and the two amine groups in positions farthest apart from each other, minimizing steric interference that would increase the instability of the molecule.

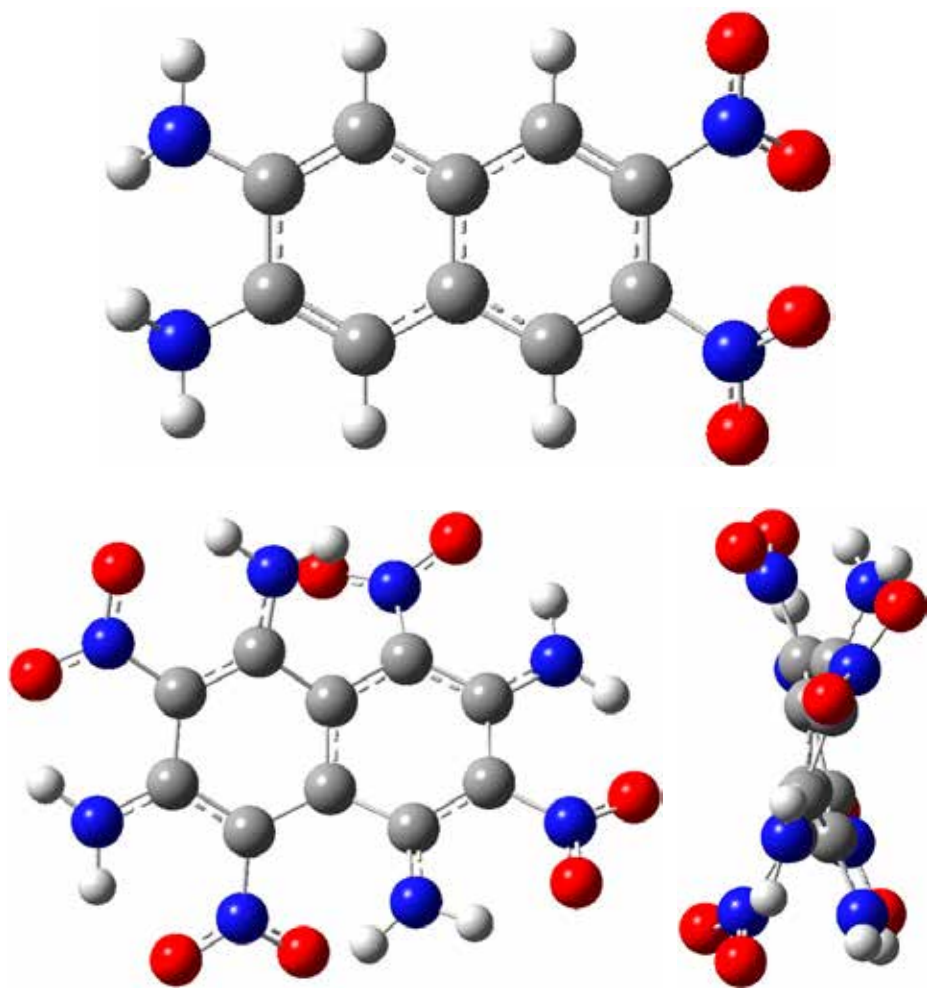


Figure 2. Representative structure of two aminonitronaphthalenes. Top: 2,3-diamino-6,7-dinitronaphthalene. Bottom left: front 1,3,5,7-tetraamino-2,4,6,8-tetranitronaphthalene. Bottom right: side view of 1,3,5,7-tetraamino-2,4,6,8-tetranitronaphthalene, showing the distortion of the naphthalene ring due to steric interference.

The three tetraaminotetranitro derivatives show thermodynamic properties closer to each other, suggesting that the maximum level of substitution, eight groups on a naphthalene framework, have minimal energetic effect versus position. Indeed, in every case there are structural modifications of the NH_2 or, more obviously, the NO_2 groups, because of neighboring groups.

Table 2. Thermodynamic properties of the various aminonitronaphthalenes (in $\text{kJ}\cdot\text{mol}^{-1}$ unless otherwise specified)

Molecule	ΔH_f	ΔH_{dec}	$\Delta H_{\text{dec}}, [\text{kJ}\cdot\text{g}^{-1}]$	ΔH_{comb}	$\Delta H_{\text{comb}}, [\text{kJ}\cdot\text{g}^{-1}]$
ANN1	221.6	-1188.9	-4.79	-5124.0	-20.66
ANN2	128.1	-1095.4	-4.42	-5030.5	-20.28
ANN3	75.2	-1042.5	-4.20	-4977.6	-20.07
ANN4	99.4	-1066.7	-4.30	-5001.8	-20.17
ANN5	120.7	-1530.1	-4.16	-5023.1	-13.65
ANN6	101.2	-1510.6	-4.11	-5003.6	-13.60
ANN7	49.56	-1459.0	-3.96	-4952.0	-13.46

Table 3 lists the other calculated properties of the aminonitronaphthalenes studied here. The data used to calculate P and D are listed in the table. In the second column, the density of the molecule, based on the results of the “volume” computational keyword, is listed; for these calculations, the average of 50 molecular volume calculations (determined as a Monte Carlo integration of the volume inside an electron density of 0.001 electrons per cubic Bohr) was determined, and the molecular volume was divided into the molar mass. The calculated densities range from $1.483 \text{ g}\cdot\text{mL}^{-1}$ for ANN3 (which has the substituents on opposite sides of the long axis of the naphthalene framework) to $1.972 \text{ g}\cdot\text{mL}^{-1}$ for ANN7, which is the alternating-group, completely substituted naphthalene shown in Figure 2. We speculate that the density of this particular aminonitronaphthalene is so high (indeed, its calculated density is over 11% higher than the next-most dense aminonitronaphthalene, ANN6) because the all-adjacent NH_2 and NO_2 groups interact electronically within a single molecule, tightening the electron density around the molecule. We note that the calculated densities in the second column of Table 3 do not account for any intermolecular interactions between NH_2 and NO_2 groups, so the experimental densities of these derivatives, should they ever be measured, are likely to be higher than predicted. The calculated densities of the aminonitronaphthalenes can be compared to those of other HEDMs like TNT ($1.654 \text{ g}\cdot\text{mL}^{-1}$), pentaerythritol tetranitrate (PETN; $1.76 \text{ g}\cdot\text{mL}^{-1}$), RDX ($1.82 \text{ g}\cdot\text{mL}^{-1}$), and cyclotetramethylenetetranitramine (HMX; $1.78\text{-}1.96 \text{ g}\cdot\text{mL}^{-1}$) [11]. Curiously, the HEDM known as TATB, or triaminotrinitrobenzene, has a density of $1.93 \text{ g}\cdot\text{mL}^{-1}$. This is the benzene counterpart of ANN7, the completely substituted naphthalene derivative with alternating NH_2 and NO_2 groups, suggesting a similar result based on alternating oxidizing and reducing groups on an aromatic framework.

Table 3. Detonation data and properties of the various aminonitronaphthalene derivatives. (ρ in $\text{g}\cdot\text{mL}^{-1}$, N in mol, M in g, Q in cal/g)^a

Molecule	ρ	N	M	Q	P , [kbar]	D , [$\text{km}\cdot\text{s}^{-1}$]
ANN1	1.652	0.02416	21.35	1144.95	160.6	6.179
ANN2	1.767	0.02416	21.35	1054.91	176.4	6.341
ANN3	1.483	0.02416	21.35	1003.96	121.2	5.562
ANN4	1.591	0.02416	21.35	1027.27	141.1	5.862
ANN5	1.775	0.03259	24.67	993.27	250.4	7.545
ANN6	1.614	0.03259	24.67	980.61	205.7	7.045
ANN7	1.972	0.03259	24.67	947.12	301.8	8.033
TATB	1.840	0.03486	24.68	835.9	264.1	7.879
TATB (exp [24])	1.80					7.95

^a ρ = density of the substance, N = moles of gas produced per gram of explosive, M = average molar mass of all molecules of gas produced upon decomposition, Q = energy released, expressed as a positive value. Molar masses used to determine Q were $248.18 \text{ g}\cdot\text{mol}^{-1}$ and $368.18 \text{ g}\cdot\text{mol}^{-1}$, depending on the level of substitution.

The last two columns in Table 3 list the detonation pressure, P , and the detonation velocity, D , for the decomposition of the seven derivatives studied here. (Because combustion typically occurs under different circumstances than explosion, the Q values used to calculate P and D used ΔH_{dec} values from Table 2, not ΔH_{comb} values.) For comparison, we have calculated Q , P , and D for TATB using the same methods used for the naphthalene derivatives and have included them here for comparison. Again, the detonation properties are similar among the diaminodinitro derivatives and among the tetraaminotetranitro derivatives. For ANN1-ANN4, the detonation pressures are on the low side when compared to current HEDMs: for example, 340 kbar for FOX-7 and 347 kbar for RDX [22]. Their detonation velocities are reasonable, however, when compared to other HEDMs; many primary explosives have values of D around $5000 \text{ m}\cdot\text{s}^{-1}$, while secondary explosives have D values ranging from 6800 – $9100 \text{ m}\cdot\text{s}^{-1}$ [9]. All four of these isomers have detonation characteristics lower than those calculated for TATB, which are reasonable when compared to available experimental values. The all-substituted naphthalene derivatives ANN5-ANN7 have detonation pressures that are predicted to be also on the low side, but larger than the less-substituted naphthalenes ANN1-ANN4. The velocities of detonation are good, well in the range of known secondary explosives. The dependence of these parameters on density is illustrated by the values of P and D for ANN7, which are markedly larger than those for the other two isomers and even higher than TATB. In addition, in the solid state even a slightly increased density caused by intermolecular NH_2 – NO_2 interactions can lead to significantly improved performance.

4 Conclusions

We reported on the calculated thermochemical properties of seven possible amino- and nitro-substituted naphthalene molecules. The calculated enthalpies of formation, which are fundamental thermodynamic properties, are all positive but not hugely so. The enthalpies of decomposition, assuming the modified Kistiakowsky-Wilson rules apply, are close to that of TNT ($4.25 \text{ kJ}\cdot\text{g}^{-1}$ [11]). Using the Kamlet-Jacobs relations, we calculated the detonation pressures and velocities. The calculated detonation pressures are on the low side with respect to current HE materials, but the velocities of detonation are well in the range of known secondary explosives. One of the studied derivatives, which has alternating amino and nitro groups, actually has very good predicted properties, largely because its predicted density is significantly larger than the other derivatives. As such, our results suggest that highly substituted naphthalene derivatives may be valid experimental targets for new high energy density materials. Synthesis of these compounds may be challenging: TATB itself is synthesized from 1,3,5-trichlorobenzene, which is nitrated to replace the remaining hydrogen atoms, then aminated to replace the chlorine atoms [11]. As such, synthesizing a specific aminonitronaphthalene would require the proper precursor. Perhaps a more effective (albeit messier) method would be random nitration, followed by amination, followed by separation using an appropriately careful technique.

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