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Calculated Thermochemistry of Aminonitroacetylene: A New High-Energy Material?

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As part of an increased interest in amino- and nitro-substituted high-energy-density materials (as exemplified by FOX-7, 1,1-diamino-2,2-dinitroethylene), here we present calculated properties of aminonitroacetylene, $NH_2{-}C{\equiv}C{-}NO_2$. Our results indicate that while the specific enthalpy of combustion is less than that of acetylene, its specific enthalpy of decomposition is greater than that of TNT, and its predicted density is large enough to predict substantial high-energy-density properties for this substance.

Since the original isolation of 1,1-diamino-2,2-dinitroethylene (also called FOX-7) in 1998,[1] there have been almost 200 experimental and theoretical studies of this new high-energy-density material. It is readily recognized that the intermolecular hydrogen bonding in the solid phase makes positive contributions to its efficacy as a high-energy-density (HED) material,[2] including increased solid-phase density, which itself contributes positively to the detonation pressure and velocity of detonation. This understanding motivated us to explore the possible high-energy-density applications of aminonitromethane and ethane molecules, considering the structural and thermodynamic properties of aminonitromethane and diaminodinitromethane[3] and mono-, di-, and triamino- and nitro-substituted ethanes.[4] Our results on the methane systems showed that the specific enthalpy of decomposition for diaminodinitromethane was almost 25% larger than that of aminonitromethane (8.1 versus 6.6 kJ g^{-1}). In the ethane series, our results showed that the greater the amount of substitution, the lesser the specific enthalpies of combustion but the greater the specific enthalpies of decomposition, suggesting that such ethane-based compounds may be good candidates for HED explosives rather than fuels.

We turn our attention now to aminonitroacetylene, the last possible two-carbon nitroamine. There have been several computational studies that have included this molecule, but in the past, most of them have focused on relative bond strengths[5] or hyperpolarizabilities.[6] Only one study reports a thermochemical property of the molecule; in a study focusing on the determination of the enthalpy of formation of the ethynyl radical, Golovin and Takhistov report[7] an enthalpy of formation for aminonitroacetylene of 43 kcal/mol, apparently determined by comparison with other molecules and not by using SCF or post-SCF methods. As such, the thermochemistry of aminonitroacetylene from first principles is still unknown.

Here, we have used the Gaussian03 package[8] with the compound G2[9] and G3[10] methods to determine optimized geometries, vibrational frequencies, and the thermochemistry of aminonitroacetylene. Both of these methods were selected because they have been parametrized to yield a ~4 kJ mol^{-1} (~1 kcal mol^{-1}) accuracy in predicting the energies of a series of test compounds. Figure 1 shows the optimized geometry of aminonitroacetylene, from orthogonal views. The figure is annotated with various structural parameters. The N−C−C−N backbone of the molecule optimizes to a linear structure, with the NO_2 group in the same plane and the NH_2 group 44.0° out of plane. Although not constrained as part of the geometry optimization, the molecule optimizes to a structure having a plane of symmetry, giving it the molecular point group C_s. The 18 normal modes of vibration of the molecule thus transform as

$$\Gamma_{\text{vib}} = 11A \oplus 7B$$

and all vibrational modes are infrared-active. Figure 2 shows the calculated vibrational absorption spectrum of aminonitroacetylene (unscaled). The spectrum is uncomplicated, and animations of the normal modes show relatively simple molecular motions. Parties interested in mode descriptions can contact the authors.

Table 1 lists the enthalpies of formation, combustion, and decomposition for aminonitroacetylene at 298.15 K. The formation reaction was determined using the reverse atomization reaction

$$2C(g) + 2H(g) + 2N(g) + 2O(g) \rightarrow NH_2{-}C{\equiv}C{-}NO_2(g)$$

and then correcting for the enthalpy of formation of the atoms to generate the proper formation reaction of aminonitroacetylene from its constituent elements in their standard states. The enthalpies of formation of the atoms were taken from the NIST Chemistry Webbook Web site.[11] The combustion reaction is assumed to be

$$NH_2{-}C{\equiv}C{-}NO_2(g) + 3/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l) + N_2(g)$$

in which everything is completely oxidized and reduced. The decomposition reaction, which is more important to consider for a high-energy explosive, is assumed to be

$$NH_2{-}C{\equiv}C{-}NO_2(g) \rightarrow H_2O(l) + CO(g) + N_2(g) + C(s)$$

Here, we are following the modified Kistiakowsky−Wilson rules,[12] which give guidelines for product formation for a substance that has an oxygen balance (OB%[13]) of less than

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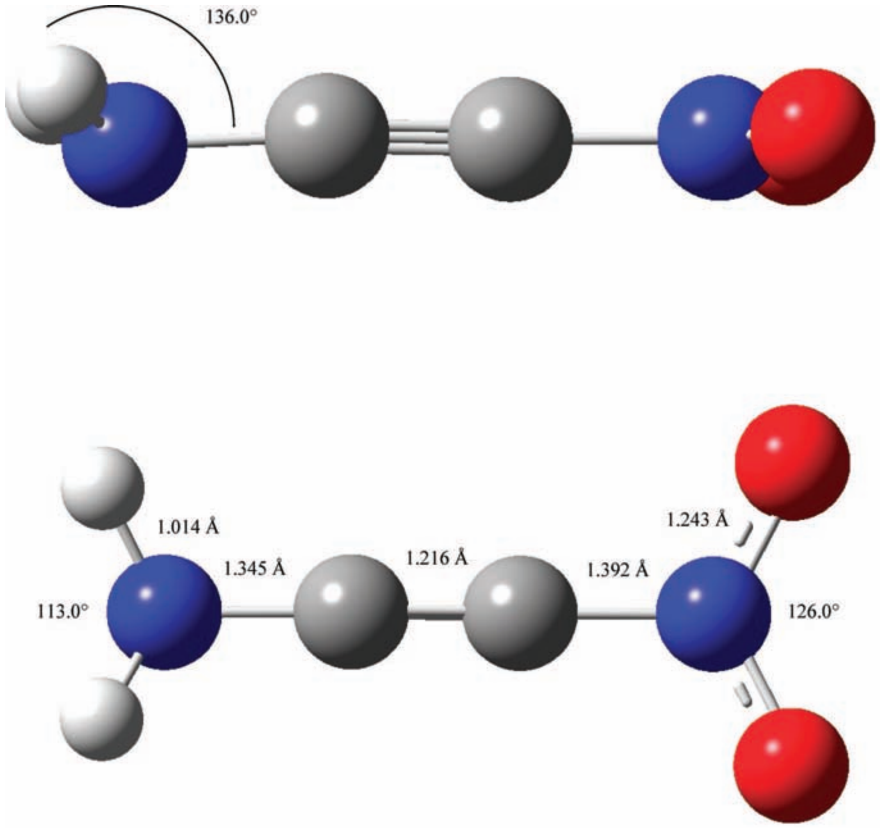

Figure 1. Optimized geometry of aminonitroacetylene, with structural parameters marked.

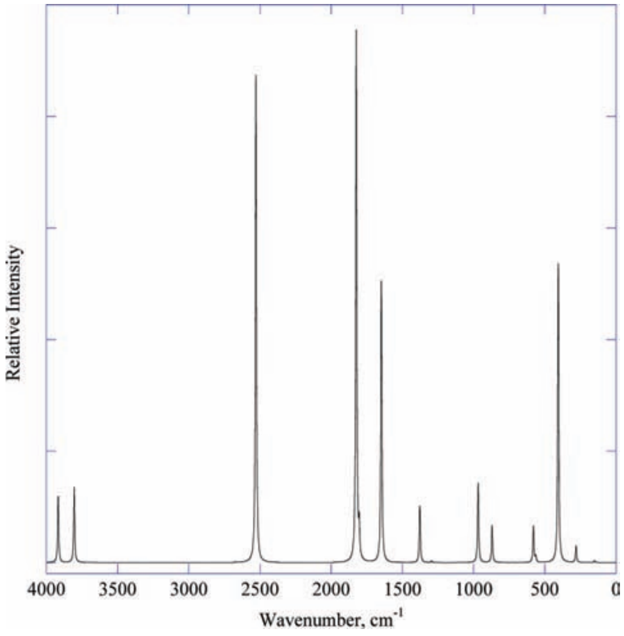

Figure 2. Calculated vibrational spectrum (unscaled) of aminonitroacetylene.

TABLE 1: Enthalpies of Reaction for Aminonitroacetylene

	G2	G3
enthalpy of formation, kJ mol^{-1}	284.0	285.6
enthalpy of combustion, kJ mol^{-1}	−1356.8	−1358.4
specific enthalpy of combustion, kJ g^{-1}	−15.8	−15.8
enthalpy of decomposition, kJ mol^{-1}	−680.3	−681.9
specific enthalpy of decomposition, kJ g^{-1}	−7.91	−7.93

−40%; aminonitroacetylene has an OB% of −55.8%, indicating that it is oxygen-deficient with regard to complete combustion.

Table 1 shows that the G2 and G3 values for the enthalpy of formation of aminonitroacetylene are very close, around 285 kJ mol^{-1}, and substantially larger than that predicted by Golovin and Takhistov.[7] This compares to an enthalpy of formation of 226 kJ mol^{-1} for acetylene itself. This trend is consistent with the differences in the enthalpies of formation of methane, nitromethane, and aminomethane,[11] whose values of ΔH_f are −74.8, −81, and −23.5 kJ mol^{-1}, respectively. The addition of a nitro group slightly lowers the enthalpy of formation, while the addition of an amino group increases the enthalpy of formation noticeably. A net increase of ~60 kJ mol^{-1} for adding both an amino group and a nitro group is consistent and fits well with the group additivity concept for thermodynamic properties.

At −1358 kJ mol^{-1}, the enthalpy of combustion of aminonitroacetylene is not significantly different from that of acetylene, which is −1301.1 kJ mol^{-1}.[14] Because of this and the fact that aminonitroacetylene has a significantly higher molar mass than acetylene, the specific enthalpy of combustion for aminoacetylene is much lower than acetylene, −15.8 kJ g^{-1} for aminonitroacetylene versus −50.0 kJ g^{-1} for acetylene. However, because aminonitroacetylene has an oxidizing group, it has a separate enthalpy of decomposition; acetylene relies on external oxidizers for reaction. At a calculated −7.9 kJ g^{-1}, the specific enthalpy of decomposition of aminonitroacetylene is significantly larger than that for trinitrotoluene (TNT), which is −4.7 kJ g^{-1}, and HMX (tetrahexamine tetranitramine), which is −5.6 kJ g^{-1}.[12] The specific enthalpy of decomposition of aminonitroacetylene would rank up with octanitrocubane, whose decomposition energy is expected to be 15−30% greater than that of HMX (which would make it −6.4 to −7.3 kJ g^{-1})[15] and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), which at −6.2 kJ g^{-1} has one of the largest specific detonation energies of any non-nuclear explosive.[16] This suggests that aminonitroacetylene has at least one desirable property for a HED material, a reasonable specific decomposition energy.

Solid-state density is also an important property when considering a HED material. For example, Kamlet and Jacobs[17] use a simple model to demonstrate that the detonation pressure is proportional to the square of the density while the detonation velocity is directly proportional to density itself. There are several methods for estimating the density of a new compound. For example, Ammon[18] determined an atom/functional group volume additivity scheme based on an analysis of 26000 structures of organic compounds. Using his parameters, we estimate a density of 1.620 g mL^{-1} for aminonitroacetylene. Using the parameters from the fast estimation method of Hofmann,[19] we estimate a density of 1.696 g mL^{-1}, a similar value. We suggest that these values may be lower limits as intermolecular hydrogen bonding may increase the packing of the molecules in the solid state.

Using the parametrized equations of Kamlet and Jacobs,[17] we use these densities to calculate detonation pressures P (in bar) and velocity of detonation D (in mm/μs) for aminonitromethane. These equations are[15]

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

and

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

where ρ is the density of the substance in g mL^{-1}, N is the 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. Assuming that H_2O comes off in the gas phase upon detonation, we calculate $P = 308-338$ bar and $D = 8613-8887$ m/s for aminonitroacetylene. For the set of high-energy materials studied by Kamlet and Jacobs, this detonation pressure is exceeded only by HMX (cyclotetramethylene tetranitramine), and this velocity of detonation is exceeded only by HMX and RDX (cyclotrimethylene trinitramine). A D value in excess of 8000 m/s definitely qualifies a substance as a high explosive.[12]

We conclude that aminonitroacetylene has some thermochemical properties that may qualify it as a legitimate high-energy-density material. We urge that any experimentalist willing to investigate this compound exercise due caution.

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