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Ab Initio Calculation of the Heats of Formation of Nitrosamides: Comparison with Nitramides

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Ab initio calculations of the structures and energies of the mono-, di-, and trinitrosamides are compared to mono-, di-, and trinitramides. Highly accurate standard heats of formation of this series of nitramides and nitrosamides are calculated using isodesmic reactions and high-level theories. The nitrosamides have heats of formation at 0 K that are 20−40 kcal/mol higher than the analogous nitramides. The N−N bond strengths are comparable whether a NO or NO_2 group is bonded to the central nitrogen atom. The data suggest that converting the nitro groups to nitroso groups will result in compounds that have lower weight, shorter N−N bond lengths, and higher energy content, at the expense of lower oxygen balance. This suggests that nitrosamides are potentially useful high-energy materials. A revised $\Delta H_f°$ for NH_2NO_2 is proposed to be 3.8 kcal/mol at 0 K, in close agreement with previous theory and very different from experiment. Recommended values for $\Delta H_f°$ are 34 and 71 kcal/mol for di- and trinitramide, respectively, and 22, 65, and 112 kcal/mol for mono-, di- and trinitrosamide, respectively. The errors in the monosubstituted molecules are estimated at 1 kcal/mol, and the errors are estimated at ±2 and ±3 kcal/mol for the di- and trisubstituted molecules, respectively. Nitrosamides have bond strengths comparable to those of the nitramides.

Introduction

The decomposition of many nitrogen-containing compounds produces N_2 molecules, thereby releasing large amounts of energy because N_2 is very stable. They can replace perchlorate oxidants that are harmful to the ozone layer. Alternative compounds may also be candidates for high-energy−density materials. In previous work, Tsai et al. pointed out that peroxynitrite ($ONOO^-$) is a high-energy form of nitrate.[1] Pure peroxynitrite ($ONOO^-$) salts have been synthesized, so such materials may be practical.[2]

The nitro group is by far the most common substituent in high-energy−density materials. Compounds with NO_2 groups have high-energy content and are useful in rocket propellants or explosives. The nitramides (also called nitramines) are nitro-substituted ammonia compounds, some of which are known. The nitramides are one of many high-energy−density materials under development.

If a nitroso group is used to replace a nitro group, higher nitrogen content will be obtained. More energy on a weight basis will result, but less oxygen will be available for oxidation. The feasibility of this approach is demonstrated by the fact that a nitroso derivative of RDX has been made, one having the same explosive power as RDX and yet less sensitivity.[3]

Shock and thermal sensitivities are related to the kinetic stability, assuming that the initiation process is a breaking of the weakest bond. This is the most likely case for the di- and trisubstituted nitramides and nitrosamides. Higher bond strengths and any additional activation energy in the bond-breaking process will give rise to safer handling characteristics. There is reason to believe that nitrosamides may be less sensitive than nitramides, on the basis of the RDX study mentioned above.

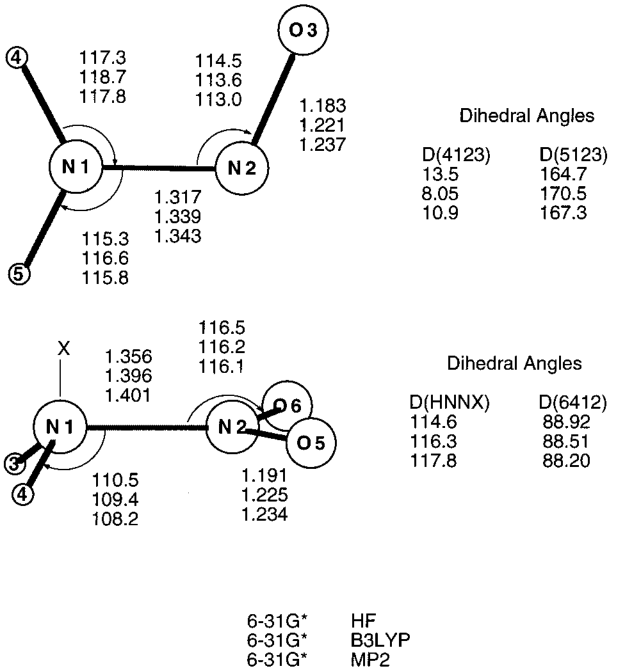

Figure 1. Energy-minimum structures of mononitrosamide and mononitramide at three levels of theory.

A survey of related compounds with NO and NO_2 groups (vide infra) reveals that most of the research has been done on nitramines. In 1963, Tyler reported the microwave spectrum of NH_2NO_2 and concluded that the NH_2NO_2 structure was nonplanar.[4] An improved experimental structure, which used a more accurate assumed N−O distance of 1.232 Å, was later published.[5] In 1989, Ritchie performed calculations on mononitramide for several structures up to the HF and MP2 levels of theory with a 6-31G* basis set.[6] Ritchie noted that lower levels of theory erroneously predicted the molecule to be planar. Ritchie predicted a rotation barrier of 10−12 kcal/mol and an inversion barrier of 2 kcal/mol. Recently, theory has been

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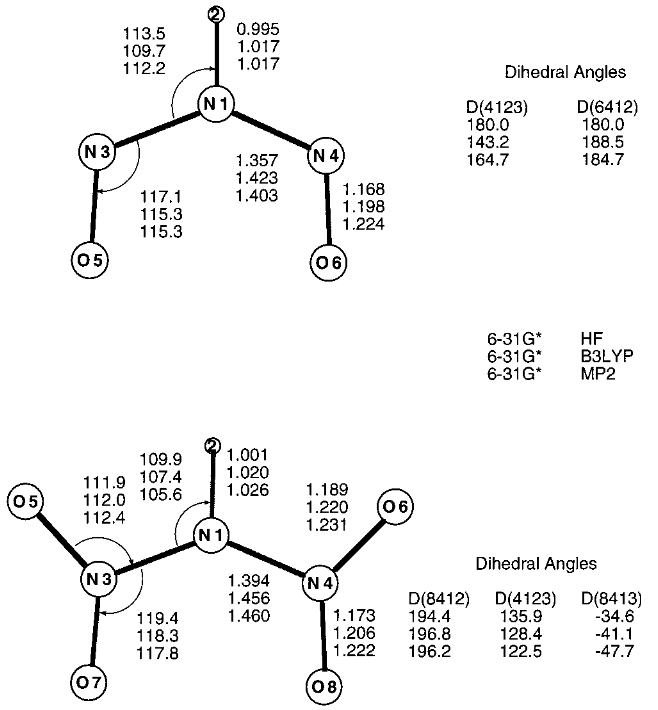

Figure 2. Energy-minimum structures of dinitrosamide and dinitramide at three levels of theory.

applied to the entire NH_2 + NO_2 reaction surface.[7-10] The highest level of theory applied was in the studies of Mebel et al.,[10] who reported a G2 N−N bond energy of 52.0 kcal/mol and a reaction barrier of 39.0 kcal/mol for the formation of H_2O + N_2O. Montgomery et al.[11] computed a $\Delta H_f°$ of 4.1 kcal/mol for NH_2NO_2, which they used in calculations of the heats of formation for di- and trinitramide.

NH_2NO has primarily been studied by many experimental groups because it is a transient intermediate in the reaction NH_2 + NO → N_2 + H_2O, one of the so-called deNO$_x$ processes. The reaction pathway and rate constants have been studied by many groups.[12] Under the reaction conditions in the NO$_x$ removal process, NH_2NO is very short-lived because it is formed in a vibrationally excited state.[13] There have been fewer theoretical studies of NH_2NO than of NH_2NO_2. Harrison et al. were the first to report that the NH_2NO energy-minimum structure is nonplanar,[14] rather than planar as predicted by Hartree−Fock wave functions with small basis sets.[15] More recently, the potential surface for the reaction of NH_2 + NO has been explored using theory.[16-19] The most accurate calculations (internally contracted CI from a CASSCF reference)[19] predict a N−N bond strength of 44.0 kcal/mol, and an overall activation energy of 36.6 kcal/mol for producing N_2 + H_2O. Protonated nitrosamide has also been suggested as an important intermediate in the deNO$_x$ process, and a recent theoretical study has been made on this species.[20]

The interest in di- and trinitramides has been as high-energy−density materials. Leroy et al. reported calculations on the energy-minimum structure of $HN(NO_2)_2$[21] and confirmed that the isodesmic approach[22] can reproduce heats of formation accurately even if a semiempirical procedure is used. Leroy et al. predicted a $\Delta H_f°$ of 15.8 kcal/mol for dinitramide in a later paper.[23] In 1993, Michels and Mongomery[24] reported calculations on 18 minima and transition states for the $HN(NO_2)_2$ surface and estimated the heat of formation at 0 K (28.4 kcal/mol) and the N−N bond dissociation energy (48 ± 8 kcal/mol). They also concluded that a low-energy unimolecular decomposition is the decay mechanism for dinitramide. Schmitt et al. studied the gas-phase chemistry of dinitramide and obtained the $\Delta H°_{acid}$ ($\leq$310 kcal/mol) of $HN(NO_2)_2$, concluding that it is one of the strongest gas-phase acids.[25]

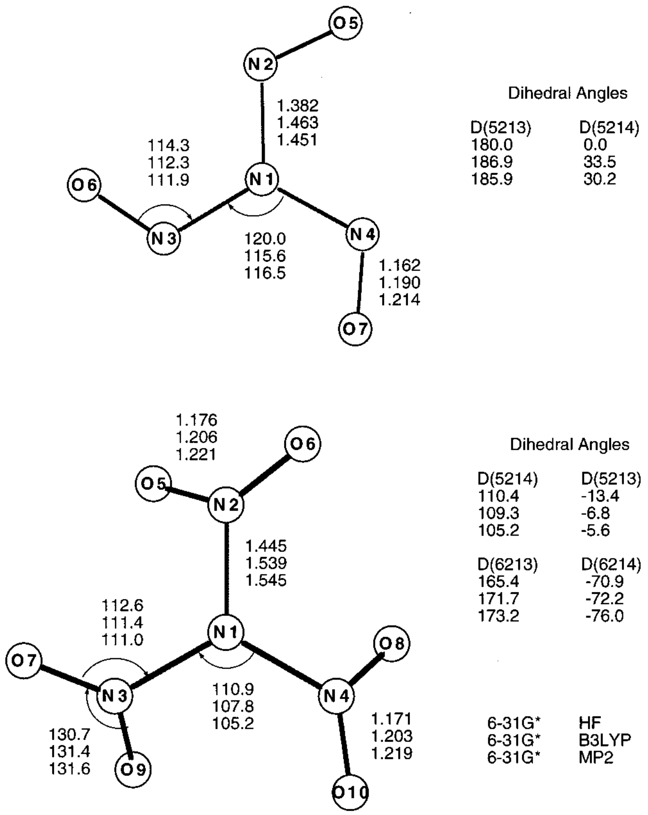

Figure 3. Energy-minimum structures of trinitrosamide and trinitramide at three levels of theory.

Politzer et al. reported the structure of $HN(NO_2)_2$ (also known as dinitraminic acid) and some possible decomposition intermediates using the MP2/6-31G* method.[26] For the reaction $HN(NO_2)_2$ → $HNNO_2$ + NO_2, they calculated ΔE as 44.0 kcal/mol using nonlocal density functional theory. Recently, Mebel et al. found that the energy for nitro elimination from $HN(NO_2)_2$ was about 38.4 kcal/mol using higher levels of theory, including the G1 method.[26] This compares to an earlier BAC-MP4 value of 46.6 kcal/mol.[27] The Politzer group has studied the energetics of the N−N bond-breaking in the dinitramide anion and concluded that the elimination of NO_2 as a neutral species is the lowest energy dissociation process (45.5 kcal/mol).[28] The anionic form may actually be stabilized by delocalization effects, and there is evidence that formation of dinitramine is the first step in the decomposition of dinitramide salts.[27]

Miroshnichenko et al. gave an estimation of 38 kcal/mol for the heat of formation of trinitramide from group additivity arguments.[29] Montgomery and Michels estimated the $\Delta H_f°$ of trinitramide as 59 kcal/mol and the N−N bond strength as 26 kcal/mol on the basis of MP2/6-31G* calculations.[11]

There is still no reported experimental observation of these compounds except NH_2NO_2, NH_2NO, $HN(NO_2)_2$, and the $N(NO_2)_2^-$ ion in salts. Christe et al. reported the infrared and Raman spectra of the NH_4^+, K^+, and Cs^+ salts of $N(NO_2)_2^-$ in the solid state.[30] In this paper, ab initio methods are used to predict the optimized geometries, atomization energies, heats of formation, and bond energies of nitramides and nitrosamides.

Computational Approaches

The GAUSSIAN 94 package of programs was used to perform the calculations on an IBM RISC 6000 workstation.[31]

TABLE 1: ΔH_f(0 K) with ZPE Correction for NH_2NO and NH_2NO_2 (kcal/mol)

	reaction	B3LYP[a]	MP2	CCSD(T)	G2	CBS-APNO
ΔH_f(0 K) of NH_2NO	$NH_2NO \rightarrow 2N + 2H + O$				20.8	
	$N_2H_4 + NO \rightarrow H_2NO + NH_2$				20.1	19.8
	$NH_3 + HNO_2$(trans) $\rightarrow NH_2NO + H_2O$	23.8 **20.9**	23.0	22.7	21.8	21.7
ΔH_f(0 K) of NH_2NO_2	$NH_2NO_2 \rightarrow 2N + 2H + 2O$				2.5	
	$N_2H_4 + NO_2 \rightarrow NH_2NO_2 + NH_2$				2.0	3.7
	$NH_3 + HNO_3 \rightarrow NH_2NO_2 + H_2O$	9.2 **5.0**	7.2	6.1	4.4	4.5
	$N_2H_4 + N_2O_4 \rightarrow 2NH_2NO_2$ (isodesmic rxn)	4.2 **3.6**	7.9			3.8

[a] The bold values are calculated from the B3LYP/6-311++G(3df,2p)//B3LYP/6-31G* level.

TABLE 2: ΔH_f(0 K) of Dinitrosamide and Dinitramide (kcal/mol)

	HF/6-31G*	B3LYP[c]/6-31G*	MP2/6-31G*	G2
	ΔH_f(0 K) of $HN(NO)_2$			
$2NH_2NO \rightarrow HN(NO)_2 + NH_3$ (isodesmic)	67.4	66.8, **68.4**	63.6	64.6
$NH_3 + 2HNO_2$(trans) $\rightarrow HN(NO)_2 + 2H_2O$	64.4	70.9, **66.8**	66.3	64.9
$2N_2H_4 + 2NO \rightarrow HN(NO)_2 + 2NH_2 + NH_3$	60.8	54.3, **64.3**	50.6	61.5
	ΔH_f(0 K) of $HN(NO_2)_2$			
$2NH_2NO_2 \rightarrow HN(NO_2)_2 + NH_3$ (isodesmic)	40.8	32.1, **34.5**	28.4	
$NH_3 + 2HNO_3 \rightarrow HN(NO_2)_2 + 2H_2O$	41.9	43.0, **37.0**	35.3	
$2N_2H_4 + 2NO_2 \rightarrow HN(NO_2)_2 + 2NH_2 + NH_3$	11.0	28.5, **35.3**	27.1	
$N_2H_4 + N_2O_4 \rightarrow HN(NO_2)_2 + NH_3$	20.6	33.0, **34.0**	36.7	

[a] A value of 28.4 kcal/mol was given at the MP2/6-311+G**//MP2/6-31G** level of theory in ref 24. Note that ref 24 uses a different $\Delta H_\mathrm{f}°$ for NH_2NO_2. [b] The experimental $\Delta_\mathrm{f}H°$(0 K)[47] values of H_2O and NO are −238.923 and 90.773 kJ/mol with 0.3 kJ/mol error. The experimental $\Delta_\mathrm{f}H°$(0 K)[47] values of NO_2, NH_3, HNO_3, N_2H_4, and HNO_2(trans) are 37.0, −38.946, −72.8, 109.337, and −124.20 kJ/mol, respectively, with 1.0 kJ/mol error. The $\Delta_\mathrm{f}H°$(0 K)[47] of N_2O_4 is 20.400 kJ/mol with 3 kJ/mol error. $\Delta_\mathrm{f}H°$(0 K) of NH_2 is 192.865 kJ/mol with 10 kJ/mol error. [c] The bold values are calculated from the B3LYP/6-311++G(3df,2p)//B3LYP/6-31G* level of theory.

TABLE 3: ΔH_f(0 K) for Trinitrosamide and Trinitramide (kcal/mol) with ZPE

	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
	ΔH_f (0 K) of $N(NO)_3$		
$3NH_2NO \rightarrow N(NO)_3 + 2NH_3$ (isodesmic rxn)	111.3	112.2 **115.2**	104.9
$NH_3 + 3HNO_2$(trans) $\rightarrow N(NO)_3 + 3H_2O$	106.9	118.4 **112.8**	108.8
$3N_2H_4 + 3NO \rightarrow N(NO)_3 + 3NH_2 + 2NH_3$	101.5	93.5 **109.1**	85.3
	ΔH_f(0 K) of $N(NO_2)_3$		
$3NH_2NO_2 \rightarrow N(NO_2)_3 + 2NH_3$ (isodesmic rxn)	89.8	67.0 **72.1**	52.5
$NH_3 + 3HNO_3 \rightarrow N(NO_2)_3 + 3H_2O$	91.5 (91.5)[a]	83.4 **75.8**	(63.1)[a]
$3N_2H_4 + 3NO_2 \rightarrow N(NO_2)_3 + 3NH_2 + 2NH_3$	45.2	61.5 **73.2**	50.5
$3N_2H_4 + 3N_2O_4 \rightarrow 2N(NO_2)_3 + 4NH_3$	59.5	68.3 **71.4**	64.7

[a] The values in parentheses are from ref 11. Note that ref 11 uses a different heat of formation at 0 K for NH_2NO_2. [b] The bold values are calculated from the B3LYP/6-311++G(3df,2p)//B3LYP/6-31G* level of theory.

The calculations of electronic energy at 0 K (E_0) and the enthalpies (H) of the molecules are based on the Hartree−Fock (HF) wave function, the Becke3−Lee−Yang−Parr (B3LYP) density functional[32] and second-order Møller−Plessett perturbation (MP2) theory, each theory using the 6-31G* basis set. Full geometry optimization and harmonic vibration calculations were performed on the structures of nitramides and nitrosamides for each level of theory.

In the calculation of the standard heats of formation, the known experimental values, isodesmic reactions, and higher level methods were used, when possible, to get the most accurate results for the heats of formation. The G2 method,[33] one of the most accurate models employed, has been demonstrated to have an average error of 1−2 kcal/mol, and the CBS-APNO[34] method an average error of only 0.5 kcal/mol. Unfortunately, the methods are limited in scope to smaller molecules because of their computational requirements. Fortunately, B3LYP single-point energies with the 6-311++G(3df,2p) basis have only 2.7 kcal/mol average error for the G2 set of molecules,[35] and performed superbly in this work when compared to B3LYP/6-31G* energies.

The limitation to smaller molecules also applies to the CCSD(T) method,[36] which was also used with the cc-pVTZ basis set[37] to compute $\Delta H_\mathrm{f}°$ for NH_2NO and NH_2NO_2. The structures were optimized at the CCSD level of theory.[38] The coupled cluster computations were performed using the PSI[39] and ACES II programs.[40]

Accurate heats of formation for the larger molecules require judicious use of experimental data and theoretical values, i.e., using isodesmic reactions. The results from isodesmic reactions are accurate because the differences in correlation energies for similar kinds of electron pairs are partially canceled. The heats

TABLE 4: N−N Bond Energies and Strengths at 0 K (kcal/mol)[a]

molecule	N−N bond energy	N−N bond strength	molecule	N−N bond energy	N−N bond strength
$N(NO)_3$	21.8	22.5	$HN(NO_2)_2$	34.7	26.9
$N(NO_2)_3$	22.6	19.8	NH_2NO	46.1	46.1
$HN(NO)_2$	32.2	27.2	NH_2NO_2	51.2	51.2

[a] Using the most accurate heats of formation (experimental for fragments, and as reported in the text for nitramides and nitrosamides).

of formation from nonisodesmic reactions were also computed as a check, since there could be a significant error in the experimental heat of formation of a particular molecule.

Results and Discussion

Structures. Figure 1 shows the energy-minimum structures of mononitrosamide and mononitramide from three levels of theory. The energy-minimum structures of mononitrosamide and mononitramide are in agreement with the previous results of Ritchie,[6] Harrison et al.,[14] and Kulkarni et al.[20] The top structure shows the gauche shape (the point group is C_1) of NH_2NO corresponding to a minimum on the potential energy surface. The energy-minimum nonplanar structure of NH_2NO_2 has C_s symmetry. The NNOO are almost in one plane, and there is a vertical mirror plane which is perpendicular to the NH_2 and NO_2 planes. Both energy-minimum structures erroneously optimize to planar geometry (C_s for NH_2NO and C_{2v} NH_2NO_2) at the HF/3-21G level of theory. Figure 1 also reveals that the optimized N−N bond lengths of mononitrosamide are shorter than those of mononitramide at all levels of theory.

Figure 2 shows the energy-minimum structures of dinitramide and dinitrosamide from three levels of theory. The point group of the nonplanar structures is C_s. Both have a symmetry plane which contains the N−H bond and is perpendicular to the N−N−N plane. The geometry of the dinitramide is in good agreement with the previous work of Leroy et al.,[21] Michels et al.,[24] and Politzer et al.[26] The HF/6-31G* energy-minimum structures of both disubstituted molecules are of C_{2v} geometry. Again, the optimized N−N bond lengths of dinitrosamide are shorter than those of dinitramide at all levels of theory. The N−N bond lengths of dinitramide and dinitrosamide (average values 1.432 and 1.398 Å, respectively) indicate that their N−N bonds are best described as single bonds. Typical values of N−N single and double bonds are about 1.45 and 1.25 Å, respectively.[41]

The energy-minimum structures of trinitramide and trinitrosamide from three levels of theory are shown in Figure 3. Both structures have C_3 point group symmetry. At the HF/6-31G* and MP2/6-31G* levels of theory, the geometries and the energies of trinitramide are exactly the same as reported by Montgomery and Michels.[11] The N−N bond lengths of both molecules obtained at the HF/6-31G* level of theory are unreasonably short. B3LYP/6-31G* reproduces the MP2/6-31G* values quite well. The HF/6-31G* level of theory predicts that the trinitrosamide energy-minimum structure is of C_{3h} symmetry.

The optimized N−N bond lengths of trinitrosamide are shorter than those of trinitramide at all levels of theory. This raises the possibility that the trinitrosamide N−N bond might be more stable; however, actual bond energies (discussed below) must be computed to determine whether this is true. The N−N bond lengths of the trinitrosamide (average 1.432) and trinitramide (average 1.505) indicate that their N−N bonds are single bonds, despite significant conjugation in trinitrosamide.

It is noted that the central N is pyramidal in both compounds with trinitramide very similar to ammonia in this respect, whereas trinitrosamide exhibits more extensive conjugation. Each $N-NO_2$ in trinitramide is twisted such that the N−O bonds are syn and anti to one of the other N−N bonds. For the nitro group on N_3, the dihedral angles $D(9314)$ and $D(7314)$ in Figure 3 demonstrate this. At the HF/6-31G* level of theory, the energy-minimum structure of trinitrosamide is planar. Electron correlation favors a lone pair on the central nitrogen. In trinitrosamide the inversion barrier is less than 1 kcal/mol, lower than the well-known inversion barrier of 5 kcal/mol in ammonia.

The N−N bond lengths in the disubstituted ammonia are shorter than their trisubstituted counterparts. This can be explained by the progressive weakening in the bonding as more NO or NO_2 groups are added. This is reflected in the bond strength discussion below.

From Figures 1−3, three trends are observed. (1) Nitroso substitution makes the pyramidal geometry of the central N atoms flatter. Evidently, there is more interaction between the lone pairs of the central N atoms and the π orbital in NO groups. (2) All of the N−N bond lengths are well within a reasonable range for stable bonds; some known compounds have longer N−N bond lengths. The experimental N−N bond length is 1.864 Å in N_2O_3[42] and 1.794 Å in N_2O_4[43] from spectroscopy (or 1.750 Å from the *JANAF Thermochemical Tables*[44]). (3) The optimized N−N bond lengths of all nitrosamides are shorter than those of the analogous nitramides at all levels of theory. The shorter N−N bond lengths of nitrosamides hint that they might be stronger, which will be investigated later with N−N bond strengths.

Transition states for interconversion have been located for each of the nitrosamides and nitramides except for trinitramide. Some of their relative energies are listed in Table 1 in the Supporting Information. For the C_{3v} and D_{3h} trinitramide structures, three imaginary frequencies are obtained in the harmonic vibration calculations.

Heats of Formation. Initially, McGrath and Rowland's procedure was used to compute the heats of formation from the atomization reactions.[45] Using the G2 method[34] and Hess' law, the atomization reaction (molecule → atoms) was used to calculate the heats of formation for small molecules (NH_2NO and NH_2NO_2) from the equation

$$\Delta H_f(\text{molecule}) = \sum \Delta H_f(\text{experimental values for atoms}) - \Delta H_{rxn}(\text{theoretical value})$$

Finite temperature thermal corrections for the molecule were made using statistical mechanics contributions from translation, vibration, and rotation for ideal gases, whereas tabulated experimental data were used for atoms.[46] The $\Delta H_f°$ of mononitrosamide (20.8 kcal/mol) calculated from the G2 atomization reaction is higher than mononitramide (2.5 kcal/mol). Given the fact that errors in $\Delta H_f°$ will propagate to the di- and trinitramides and nitrosamides, we noted the disagreement among the experimental $\Delta H_f°(NH_2NO_2)$ value (−3.0 kcal/mol), our theoretical G2 $\Delta H_f°(NH_2NO_2)$ value of 2.5 kcal/mol (using the atomization reaction), and the one reported by Montgomery and Michels.[11] Theirs is 4.1 kcal/mol from using G2 and the reaction

$$NH_3 + HNO_3 \rightarrow H_2NNO_2 + H_2O$$

While a difference between 2.5 and 4.1 kcal/mol may seem small, the difference is multiplied by a factor of up to 3. The

TABLE 5: B3LYP/6-31G* Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities for H_2NNO, H_2NNO_2, $HN(NO)_2$, $HN(NO_2)_2$, $N(NO)_3$, and $N(NO_2)_3$

H_2NNO	H_2NNO_2	$HN(NO)_2$
217 (262) H_2NN umbrella	423 (29) twist	161 (1) NO twist
624 (1) NH_2 and NO rock	569 (2) NH_2 and NO_2 rock	190 (0) NNN bend
724 (7) twist	638 (87) NH_2 wag	295 (12) HNN_2 umbrella
1099 (72) NN str	730 (89) NNO_2 umbrella	504 (58) NH and NO rock
1240 (97) NH_2 rock	813 (180) H_2NN umbrella	685 (109) sym NN str
1602 (165) NH_2 sciss	1023 (18) NN str	756 (347) asym NN str
1625 (53) NO str	1256 (48) NH_2 rock	814 (16) NH wag
3466 (7) sym NH_2 str	1408 (220) sym NO_2 str	1028 (47) NNN bend
3692 (47) asym NH_2 str	1632 (65) NH_2 sciss	1395 (199) NH rock
	1718 (272) asym NO_2 str	1676 (117) out of phase NO str
	3524 (29) sym NH str	1713 (97) in phase NO str
	3658 (42) asym NH str	3570 (34) NH str

$HN(NO_2)_2$	$N(NO)_3$	$N(NO_2)_3$
43 (0) NO_2 twist	173 (1) NO twist	34 (0) NO_2 twist (e)
121 (7) HNN_2 umbrella	184 (10) NO twist (e)	96 (0) NO_2 twist
239 (2) in phase NO_2 rock	227 (10) NNN bend (e)	200 (5) NNN bend (e)
401 (18) out of phase NO_2 rock	250 (0) NN_3 umbrella	212 (3) NN_3 umbrella
423 (1) NNN bend	388 (0) sym NN str	336 (0) sym NN str
656 (33) sym NN str	418 (315) asym NN str (e)	344 (45) asym NN str (e)
716 (0) NH, NO_2 rock	746 (6) NNO bend	519 (0) NNO bend
739 (0) out of phase NNO_2 umbrella	958 (239) NNO bend (e)	631 (41) NNO bend (e)
794 (56) in phase NNO_2 umbrella	1705 (256) NO str (e)	774 (175) NO_2 scissor (e)
842 (63) in phase NO_2 scissor	1729 (0) sym NO str	794 (10) NNO_2 umbrella
854 (416) asym NN str		831 (90) NNO_2 umbrella (e)
1051 (35) NNN bend		856 (8) NO_2 scissor
1309 (397) out of phase NO_2 sym str		1316 (254) sym NO_2 str (e)
1372 (27) NH rock		1413 (20) sym NN and NO_2 str
1390 (21) in phase sym NN and NO_2 str		1765 (343) asym NO_2 str
1743 (58) out of phase asym NO_2 str		1798 (244) asym NO_2 str (e)
1772 (461) in phase asym NO_2 str		
3538 (65) NH str		

TABLE 6: Total Energies and the Electronic Energies with Zero-Point Energy Corrections for the Minimum-Energy Structures of H_2NNO, H_2NNO_2, $HN(NO)_2$, $HN(NO_2)_2$, $N(NO)_3$, and $N(NO_2)_3$

molecule	energy (au)	HF 6-31G*	B3LYP 6-31G*	MP2 6-31G*	CCSD(T) cc-pVTZ
H_2NNO (gauche)	*E* (total)	−184.826 480	−185.843 654	−185.333 616	−185.585 812
	E (0)	−184.790 396	−185.811 102	−185.300 513	
H_2NNO_2 (C_s)	*E* (total)	−259.639 406	−261.031 503	−260.339 881	−260.680 282
	E (0)	−259.595 748	−260.991 883	−260.299 516	
$HN(NO)_2$ (C_s)	*E* (total)	−313.443 142	−315.115 465	−314.293 300	
	E (0)	−313.410 028	−315.086 337	−314.264 663	
$HN(NO_2)_2$ (C_s)	*E* (total)	−463.052 814	−465.487 025	−464.303 287	
	E (0)	−463.006 010	−465.446 009		
$N(NO)_3$ (C_3)	*E* (total)	−442.061 268	−444.384 479	−443.252 554	
	E (0)	−442.032 470	−444.361 081	−443.229 870	
$N(NO_2)_3$ (C_3)	*E* (total)	−666.445 823	−669.930 384	−668.265 372	
	E (0)	−666.397 176	−669.889 727		
H_2O (C_{2v})	*E* (total)	−76.010 747	−76.408 953	−76.196 848	−76.350 296
	E (0)	−75.987 773	−76.387 793	−76.175 373	
NH_3 (C_{3v})	*E* (total)	−56.184 356	−56.547 948	−56.354 212	−56.492 337
	E (0)	−56.147 356	−56.513 414	−56.318 916	
HNO_2 (cis)	*E* (total)	−204.639 938	−205.696 797	−204.631 066	−205.433 456
	E (0)	−204.616 786	−205.676 464	−205.146 954	
HNO_2 (trans)	*E* (total)	−204.637 676	−205.695 212	−205.165 158	−205.432 686
	E (0)	−204.614 600	−205.674 909	−205.145 153	
HNO_3 (planar)	*E* (total)	−279.444 264	−280.878 552	−280.165 222	−280.519 340
	E (0)	−279.414 233	−280.852 100	−280.138 572	

[a] The CCSD(T)/pVTZ calculations of H_2O and NH_3 were carried using the ACES II ab initio program, and other CCSD(T) calculations were carried using the PSI program package.

difference in the theoretical numbers arises from the fact that while the ΔH_f experimental values of atoms is known to extremely high accuracy, ΔH_{rxn} is difficult to obtain accurately, even with the G2 method. The reaction immediately above should provide a better estimate of ΔH_f° for H_2NNO_2, as ΔH_{rxn} is more accurate and the heat of formation for NH_3, HNO_3, and H_2O are known with small error (see Table 2). To obtain the most accurate ΔH_f° possible for H_2NNO_2 and H_2NNO, computations were carried out at the CBS-APNO level of theory. As an illustration of the sensitivity of ΔH_f° for the larger compounds on the ΔH_f° of nitramide and nitrosamide, the difference between using experimental and CBS-APNO values results in a change of 20 kcal/mol in the predicted ΔH_f° for trinitramide. Our most accurate values of ΔH_f° are $+3.8 \pm 1$

kcal/mol for H_2NNO_2 and +21.7 ± 1 kcal/mol for H_2NNO. The high accuracy of ±1 comes from using a high level of theory and a reaction with the same number of bonds and lone pairs of each type on each side.

From Table 1, all levels of theory and reactions are very consistent for H_2NNO. The scatter is greater for H_2NNO_2, with a difficult choice to be made between 4.5 and either 3.7 or 3.8 for $\Delta H_f°$ (all CBS-APNO derived). We selected 3.8 because this reaction has the most similar types of bonds ($-NH_2$ and $-NO_2$ groups only), and the experimental errors for N_2H_4 and N_2O_4 were small. B3LYP/6-311++G(3df,2p)//BLYP/6-31G* energies give outstanding agreement with the highest level of theory, so it is used for computing energies for the larger molecules. The large basis set single-point energy is necessary, because the B3LYP/6-31G* energy exhibited unacceptable scatter. Finally, an analogous isodesmic reaction for H_2NNO cannot be done because N_2O_2 has significant O−O bonding.

The heats of formation of the larger molecules (di- and trinitramides and nitrosamides) were calculated from each of the following isodesmic reactions, using the best experimental heat of formation[47] of ammonia in addition to the calculated $\Delta H_f°(NH_2NO$ and $NH_2NO_2)$ values from CBS-APNO:

$$3NH_2NO_2 \rightarrow N(NO_2)_3 + 2NH_3$$

$$3NH_2NO \rightarrow N(NO)_3 + 2NH_3$$

$$2NH_2NO \rightarrow HN(NO)_2 + NH_3$$

$$2NH_2NO_2 \rightarrow HN(NO_2)_2 + NH_3$$

In isodesmic reactions, the reactants and products contain the same numbers and same kinds of chemical bonds. Errors from energy calculations are largely canceled between the reactants and products. Thus, a theoretical ΔH_{rxn} for an isodesmic reaction is very close to the experimental result. Leroy et al. have confirmed that the isodesmic method allows the calculation of $\Delta H_f°$ with an average error of 3−4 kcal/mol compared with experimental $\Delta H_f°$, even with lower levels of theory (HF/6-31G and semiempirical procedures.)[23] If isodesmic reactions are used with higher levels of theory, even higher accuracy for $\Delta H_f°$ can be obtained. The larger molecules cannot be studied with CBS-APNO, because of the limitations of computer resources. The error estimates of ±2 kcal/mol for the disubstituted compounds and ±3 kcal/mol for the trisubstituted compounds come from the average of the disagreement between the isodesmic reactions and nonisodesmic ones.

For comparison, the heats of formation were computed from four nonisodesmic reactions:

$$NH_3 + 3HNO_3 \rightarrow N(NO_2)_3 + 3H_2O$$

$$NH_3 + 3HNO_2 \rightarrow N(NO)_3 + 3H_2O$$

$$NH_3 + 2HNO_3 \rightarrow HN(NO_2)_2 + 2H_2O$$

$$NH_3 + 2HNO_2 \rightarrow HN(NO)_2 + 2H_2O$$

These reactions were chosen because the experimental heats of formation of NH_3, H_2O, HNO_2, and HNO_3 are known to high accuracy.

Table 2 lists the calculated $\Delta H_f°$ values of the energy-minimum structures of dinitramide and dinitrosamide. The $\Delta H_f°$ values of dinitrosamide from different levels of theory are always higher than those of dinitramide. The average $\Delta H_f°$ of dinitrosamide is higher than that of dinitramide by 31 kcal/mol. Our $\Delta H_f°$ value for dinitramide (28.5 kcal/mol) from the B3LYP/6-31G* level of theory is very close to Michels and Montgomery's previous results at the MP2/6-311+G**//MP2/6-31G** level of theory (28.4 kcal/mol at 0 K).[24] With the accurate $\Delta H_f°$ for nitramide and the large basis set for B3LYP, the best value is 34.5 kcal/mol, which agrees with the nonisodesmic results of 35.3 and 37.0. The predicted heats of formation are less scattered in the dinitrosamide case, with the best value around 64.6 kcal/mol (using G2 energies).

In Table 3 the calculated $\Delta H_f°$ values of the energy-minimum structures of trinitramide and trinitrosamide are listed. It was found that the predicted heats of formation of trinitrosamide are always higher (38 kcal/mol on average) than those of trinitramide with each method. The $\Delta H_f°$ data in trinitramide have some scatter because they magnify the uncertainty in the $\Delta H_f°$ of mononitramide by a factor of 3. However, B3LYP with a large basis again shows excellent consistency. The best values for the heats of formation at 0 K are 71 kcal/mol for trinitramide and 112 kcal/mol for trinitrosamide. This predicts more energy content than the lower estimate of Miroschnichenko et al.[29] or Montgomery and Michels.[11]

At all levels of theory, an individual $\Delta H_f°$ value of any nitrosamide is always higher than that of the corresponding nitramide. The best $\Delta H_f°$ values of mono-, di-, and trinitrosamide are higher than those of nitramides by 18, 31, and 44 kcal/mol, respectively. This trend indicates that all of the nitrosamides have more energy content compared to the corresponding nitramides.

It is also found that the heats of formation increase in the order mono-, di-, and trisubstitution. This trend is due to the increasingly weaker N−N bonds as the central nitrogen has more electronegative groups attached to it.

N−N Bonds Energies and Strengths. The distinction between a bond energy and a bond strength is that a bond strength is the energy required to break one bond, and a bond energy is the average energy needed to break all of the bonds that are equivalent in the original molecule. The energies and strengths of the N−N bonds will reflect the stability of the nitrosamides and nitramides, as decomposition via N−N bond cleavage is the likely decomposition mechanism. To calculate the N−N bond energies, the following reactions were used:

$$N(NO)_3 \rightarrow N + 3NO$$

$$N(NO_2)_3 \rightarrow N + 3NO_2$$

$$HN(NO)_2 \rightarrow NH + 2NO$$

$$HN(NO_2)_2 \rightarrow NH + 2NO_2$$

$$H_2NNO \rightarrow NH_2 + NO$$

$$H_2NNO_2 \rightarrow NH_2 + NO_2$$

Computing the enthalpies directly using ab initio methods will give large errors, so the N−N bond energies are computed from the above reactions using $\Delta H_f°$. The experimental $\Delta H_f°$ values were used for the products, and theoretical $\Delta H_f°$ values were used for the reactants. The calculated N−N bond energies and strengths at 0 K are listed in Table 4. The $\Delta H_f°$ values of 112.2, 71.4, 64.6, and 34.5 kcal/mol recommended above for $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$, respectively, were used to find that the N−N bond energies of $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$ are 21.8, 22.6, 32.2, and 34.7 kcal/mol, respectively. The bond energy of $HN(NO_2)_2$ compares to the energy value of 39 kcal/mol Mebel et al. predicted from the G1 method.[27] In their paper, though CCSD(T) gave 30 and

B3LYP 35 kcal/mol, only B3LYP predicted that the second NO_2 group is substantially more difficult to dissociate, as we find in this study.

For H_2NNO_2 and H_2NNO, the N−N bond energies and the strengths are identical by definition. Using the ΔH_f° of H_2NNO_2 and H_2NNO (3.8 and 21.7 kcal/mol, respectively) and the experimental ΔH_f° of NH_2, NO, and NO_2,[47] the N−N bond energies and strengths are 46.1 and 51.2 kcal/mol, respectively. The N−N bond strength of H_2NNO_2 is very close to Michels and Montgomery's result (50.3 ± 4 kcal/mol).[24]

For $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$ the N−N bond strengths will differ from the N−N bond energies. The N−N bond strengths are calculated using the following reactions:

$$N(NO)_3 \rightarrow N(NO)_2 + NO$$

$$N(NO_2)_3 \rightarrow N(NO_2)_2 + NO_2$$

$$HN(NO)_2 \rightarrow HN{-}NO + NO$$

$$HN(NO_2)_2 \rightarrow HN{-}NO_2 + NO_2$$

First of all, the ΔH_f° values of $N(NO)_2$, $N(NO_2)_2$, HNNO, and $HNNO_2$ radicals need to be obtained to compute the N−N bond strengths of the products. Using the following reactions, the estimated N−H bond strength of 100 kcal/mol, the experimental ΔH_f° values of the H atom, and the recommended ΔH_f° of the reactants, it was found that the ΔH_f° values of $N(NO)_2$, $N(NO_2)_2$, HNNO, and $HNNO_2$ radicals are 116.9, 85.2, 71.1, and 54.5 kcal/mol, respectively.

$$HN(NO)_2 \rightarrow N(NO)_2 + H$$

$$HN(NO_2)_2 \rightarrow N(NO_2)_2 + H$$

$$H_2NNO \rightarrow HN{-}NO + H$$

$$H_2NNO_2 \rightarrow HN{-}NO_2 + H$$

Then, using the ΔH_f° of these radicals and the recommended ΔH_f° for $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$, the N−N bond strengths of $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$ are calculated from the N−N bond dissociation reactions above. The N−N bond strengths are 22.5, 19.8, 27.2, and 26.9 kcal/mol, respectively.

The N−N bond strengths and energies of trinitrosamide are higher than those of trinitramide. This is reasonable, because there might be delocalization over the whole trinitrosamide. In the disubstitution case, the stability trend is the reverse, even though the N−N bond lengths of the dinitrosamide are shorter than those of the dinitramide. The differences in the N−N bond strengths and energies between NO and NO_2 substitution are not large, especially in light of the approximation of using 100 kcal/mol N−H bond energy.

Compared to the typical N−N bond energy (∼40 kcal/mol),[41] the N−N bond energies and strengths of $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$ are low. More exploration is needed to determine their thermodynamic and kinetic stability more precisely. It appears that trinitrosamide may be less sensitive than trinitramide, on the basis of the N−N bond strengths. The N−N bond energies and strengths are all much smaller than those of H_2NNO and H_2NNO_2 (46.1 and 51.2 kcal/mol, respectively). This suggests that the decomposition of $N(NO)_3$, $N(NO_2)_3$, $HN(NO)_2$, and $HN(NO_2)_2$ occurs more readily via N−N bond cleavage. The exact decomposition mechanism of $N(NO)_3$ and $HN(NO)_2$ is an area for future research.

The heats of formation at 298.15 K are 2−4 kcal/mol lower than those at 0 K, and are reported in the Supporting Information. Vibrational frequencies and absolute energies are presented in Tables 5 and 6.

Conclusions

Converting the nitro groups in nitramines to nitroso groups can result in compounds which have lower weights, shorter N−N bond lengths, and higher heats of formation. The bond energies indicate that nitrosamides will have stabilities comparable to those of the analogous nitramides, which are known high-energy−density materials. Further mechanistic exploration needs to be done to examine the kinetic stability of these NO-containing compounds.

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Supporting Information Available: Table giving the relative energies of mono-, di-, and trinitrosamides and mono- and dinitramides. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tsai, H.-H.; Hamilton, T. P.; Tsai, J.-H. M.; van der Woerd, M.; Harrison, J. G.; Jablonsky, M. J.; Koppenol, W. H.; Beckman, J. S. *J. Phys. Chem.* **1996**, *100*, 15087.

(2) Bohle, D. S.; Hansert, B.; Paulson, S. C.; Smith, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 7423.

(3) Iyer, S. *Propellants Explos. Pyrotechnics* **1982**, *7*, 37.

(4) Tyler, J. K. *J. Mol. Spectrosc.* **1963**, *11*, 39.

(5) Sadova, N. I.; Slepnev, G. E.; Tarasenko, N. A.; Zenkin, A. A.; Vilkov, L. V.; Shishkov, I. F.; Pankrushev, Y. A. *Zh. Strukt. Khim.* **1977**, *18*, 865.

(6) Ritchie, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 2517.

(7) Saxon, R. P.; Yoshimine, M. *J. Phys. Chem.* **1989**, *93*, 3130.

(8) Seminario, J. M.; Politzer, P. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 497.

(9) Melius, C. F. In *Chemistry and Physics of Energetic Materials*; Bulusu, S., Ed.; NATO ASI Series 309; 1990; p 21.

(10) Mebel, A. M.; Hsu, C.-C.; Lin, M. C.; Morokuma, K. *J. Chem. Phys.* **1995**, *103*, 5640.

(11) Montgomery, J. A.; Michels, H. H. *J. Phys. Chem.* **1993**, *97*, 6744.

(12) Diau, E. W.; Yu, T.; Wagner, M. A. G.; Lin, M. C. *J. Phys. Chem.* **1994**, *98*, 4034 and references therein.

(13) Phillips, L. F. *Chem. Phys. Lett.* **1987**, *135*, 269.

(14) Harrison, J. A.; MacLagan, R. G.; Whyte, A. R. *Chem. Phys. Lett.* **1986**, *130*, 98.

(15) Casewit, C. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3280.

(16) Abou-Rachid, H.; Pouchan, C.; Chaillet, M. *Chem. Phys.* **1984**, *90*, 243.

(17) Melius, C. F.; Binkley, J. S. *20th Symposium (International) on Combustion*; Combustion Institute: Pittsburgh, 1985; p 575.

(18) Harrison, J. A.; MacLagan, R. G. A. R.; Whyte, A. R. *J. Phys. Chem.* **1987**, *91*, 6683.

(19) Walch, S. P. *J. Chem. Phys.* **1993**, *99*, 5295.

(20) Kulkarni, S. A.; Pundlik, S. S. *Chem. Phys. Lett.* **1995**, *245*, 143.

(21) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D.; Dogimont, C. *J. Mol. Struct.: THEOCHEM* **1987**, *153*, 249.

(22) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(23) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D.; Bourasseau, S. *J. Mol. Struct.: THEOCHEM* **1989**, *187*, 251.

(24) Michels, H. H.; Montgomery, J. A., Jr. *J. Phys. Chem.* **1993**, *97*, 6602.

(25) Schmitt, R. J.; Krempp, M.; Bierbaum, V. M. *Int. J. Mass Spectrom.* **1992**, *117*, 621.

(26) Politzer, P.; Seminario, J. M. *Chem. Phys. Lett.* **1993**, *216*, 348.

(27) Mebel, A. M.; Lin, M. C.; Morokuma, K. *J. Phys. Chem.* **1995**, *99*, 6842.

(28) Politzer, P.; Seminario, J. M.; Concha, M. C.; Redfern, P. C. *J. Mol. Struct.*: *THEOCHEM* **1993**, *287*, 235.

(29) Miroshnichenko, E. A.; Korchatova, L. I.; Korsunskii, B. L.; Fedorov, B. S.; Orlov, Yu D.; Eremenko, L. T.; Lebedev, Yu A.; Dubovitskii, F. I. *Dokl. Akad. Nauk SSSR* **1987**, *295*, 419.

(30) Christe, K. O.; William, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. *Inorg. Chem.* **1996**, *35*, 5068.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(32) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1993**, *98*, 5648.

(33) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(34) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(35) Foresman, J. B.; Frisch, A. In *Exploring Chemistry With Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996; Chapter 7.

(36) (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Scuseria G. E.; Lee T. J. *J. Chem. Phys*. **1990**, *93*, 5851.

(37) Dunning, T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007.

(38) Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5361.

(39) PSI 2.0.8: C. L. Janssen, E. T. Seidl, G. E. Scuseria, T. P. Hamilton, Y. Yamaguchi, R. B. Remington, Y. Xie, G. Vacek, C. D. Sherrill, T. D. Crawford, J. T. Fermann, W. D. Allen, B. R. Brooks, G. B. Fitzgerald, D. J. Fox, J. F. Gaw, N. C. Handy, W. D. Laidig, T. J. Lee, R. M. Pitzer, J. E. Rice, P. Saxe, A. C. Scheiner, and H. F. Schaefer, PSITECH, Inc., Watkinsville, GA 30677, 1995.

(40) ACES II, an ab initio program system authored by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integrals derivative program of T. U. Helgaker, H. J. A. Jensen, P. Jørgensen, and P. R. Taylor, and the PROPS property integral package of P. R. Taylor.

(41) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins College Publishers: New York, 1993; Appendix E.

(42) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(43) McClelland, B. W.; Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1972**, *56*, 4541.

(44) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, 2nd ed.; US National Bureau of Standards: Washington, D.C., 1971.

(45) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, *98*, 1061.

(46) McQuarrie, D. A. *Statistical Thermodynamics*; Harper & Row: New York, 1973; Chapter 8.

(47) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; 4th Hemisphere Publishing Corp.: New York, 1989; Part 2, Chapter 1.