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## COMPUTATIONAL ANALYSES OF STRUCTURAL PROPERTIES OF THE DINITRAMIDE ION, $N(NO_2)_2^-$ , AND SOME RELATED MOLECULES: $HN(NO_2)_2$ AND $N(NO_2)_3$

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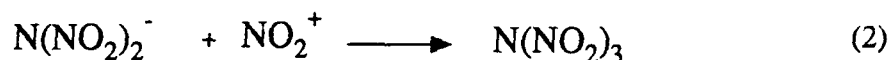
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## Introduction

In response to the interest in the dinitramide anion,  $\text{N}(\text{NO}_2)_2^-$ , that has resulted from Schmitt and Bottaro's recent synthesis of several dinitramide salts,<sup>1</sup> we have carried out a computational analysis of its structure and some of its properties. Since there is also interest in the conjugate acid,  $\text{HN}(\text{NO}_2)_2$  [the existence of which has not been established], we have included it in this study. This permits us to estimate the proton affinity of the dinitramide anion, which corresponds to  $\Delta E$  for the process,



Finally, since we had earlier investigated the possible stability of the molecule  $\text{N}(\text{NO}_2)_3$ ,<sup>2</sup> we also determined  $\Delta E$  for the reaction,



The results of these studies are summarized in this report.

## Methods

Our general approach involved *ab initio* SCF computations, using the GAUSSIAN 88 system of programs.<sup>3</sup> Geometries were optimized with the MIDI1 basis set, which is obtained by splitting the most diffuse valence s and p functions on each atom;<sup>4</sup> it is very nearly equivalent to the 3-21G basis, which is known to be generally reliable for computing structures, even for negative ions.<sup>5</sup> For  $\text{HN}(\text{NO}_2)_2$ , however, we modified this procedure because both 3-21G and MIDI1 optimizations predicted planarity for this molecule, which we considered suspect because Ritchie has shown that 3-21G calculations erroneously yield a planar structure for the related system  $\text{H}_2\text{N}-\text{NO}_2$ .<sup>6</sup> Accordingly we first determined all angles in  $\text{HN}(\text{NO}_2)_2$  at the 6-31G\* level (which had correctly predicted  $\text{H}_2\text{N}-\text{NO}_2$  to be pyramidal<sup>6</sup>) and then carried out MIDI1 optimizations of the bond lengths. The final energies for all of the systems investigated were computed by single-point runs with the MIDI1p basis set, which is obtained by enlarging the MIDI1 through the addition of a diffuse p function to each first-row atom (e.g. N, O, etc.).

While these calculations are at the *ab initio* SCF level and hence do not take account of electron correlation, it is nevertheless anticipated that the  $\Delta E$  values obtained for eqs. (1) and (2) will be meaningful, because their reactions involve only closed-shell systems and no electron pairs are disrupted. We tested this point on the nitrite ion,  $\text{NO}_2^-$ , and its conjugate acid,  $\text{HNO}_2$  (HONO),

Table 1. Proton affinity of  $\text{NO}_2^-$  calculated at various *ab initio* SCF levels.

Basis set	3-21G	MIDI1	MIDI1p	combined <sup>a</sup> MIDI1p//MIDI1	6-31+G	exp <sup>b</sup>
Proton affinity (kcal/mole)	364	364	333	333	330	338

<sup>a</sup>In this instance, MIDI1 was used for geometry optimization and MIDI1p for computing energies.

This is the approach used to obtain the results that will be presented for  $(\text{NO}_2)_2^-$ .

<sup>b</sup>S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data 17, Suppl. No. 1, (1988).

using five different basis sets. All five correctly predicted that  $\text{NO}_2^-$  is protonated on an oxygen rather than on nitrogen, and all of them predicted the energy difference between the cis and trans forms of HONO to within 2.1 kcal/mole of the experimentally-determined value. Finally, Table 1 presents the proton affinities computed for  $\text{NO}_2^-$ ; these have been corrected for the difference in zero-point energies, using a semi-empirical (AM1) estimate of 7.3 kcal/mole.

Table 1 shows that both the MIDI1p basis set and the combined MIDI1p//MIDI1 yield very good  $\text{NO}_2^-$  proton affinities. The latter is the approach that was used for  $\text{N}(\text{NO}_2)_2^-$  in this work, because we found it to produce better geometries than does the MIDI1p.

## Results

Our calculated energies and structures for  $\text{N}(\text{NO}_2)_2^-$ ,  $\text{HN}(\text{NO}_2)_2$ ,  $\text{NO}_2^+$  and  $\text{N}(\text{NO}_2)_3$  are given in Table 2. The protonation of  $\text{N}(\text{NO}_2)_2^-$  to give  $\text{HN}(\text{NO}_2)_2$  could, in principle, occur on the central nitrogen or any of the four oxygens. We tested all of these possibilities and found that the site most favored energetically is the nitrogen, although the oxygen protonations are only 4 to 8 kcal/mole less stable.

Gilardi has carried out crystallographic determinations of the structures of a series of dinitramide salts synthesized by Schmitt and Bottaro. The ranges of bond lengths and bond angles obtained for two of these, ammonium dinitramide (I) and the 1,2,4,7-tetrammonio salt of cubane (II), are summarized in Table 3.

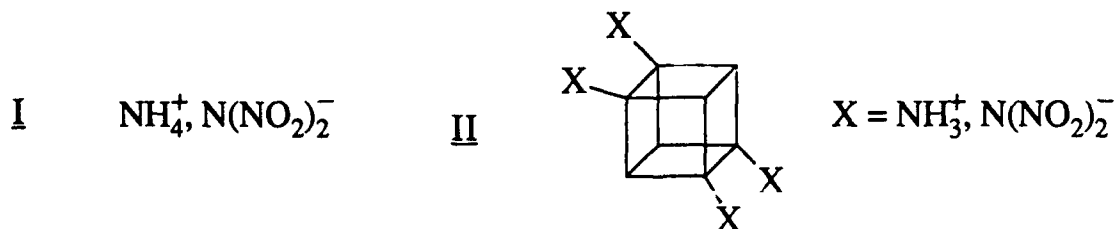


Table 2. Calculated *ab initio* SCF energies (MIDI1p) and structures (MIDI1).

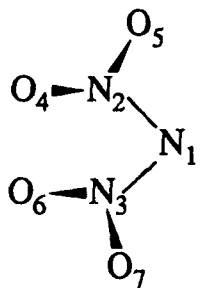
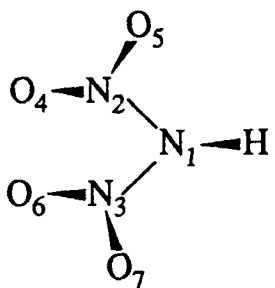
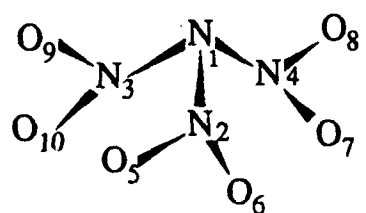
Molecule and Energy, hartrees	Distance, Å	Angle, deg.
$\text{N}(\text{NO}_2)_2^-$ : $C_2$ symmetry $E = -459.7946$	N-N: 1.410 N <sub>2</sub> -O <sub>4</sub> , N <sub>3</sub> -O <sub>6</sub> : 1.254 N <sub>2</sub> -O <sub>5</sub> , N <sub>3</sub> -O <sub>7</sub> : 1.258	N-N-N: 110 N <sub>1</sub> -N <sub>2</sub> -O <sub>4</sub> } 124 N <sub>1</sub> -N <sub>3</sub> -O <sub>6</sub> } N <sub>1</sub> -N <sub>2</sub> -O <sub>5</sub> } 113 N <sub>1</sub> -N <sub>3</sub> -O <sub>7</sub> } O-N-O: 123 O <sub>4</sub> -N <sub>2</sub> -N <sub>1</sub> -N <sub>3</sub> } -28 O <sub>6</sub> -N <sub>3</sub> -N <sub>1</sub> -N <sub>2</sub> }
	HN(NO <sub>2</sub> ) <sub>2</sub> : $C_s$ symmetry $E = -460.2664$	N-N: 1.433 N-H: 1.007 N <sub>2</sub> -O <sub>4</sub> , N <sub>3</sub> -O <sub>6</sub> : 1.221 N <sub>2</sub> -O <sub>5</sub> , N <sub>3</sub> -O <sub>7</sub> : 1.243
	NO <sub>2</sub> <sup>+</sup> : linear, O-N-O $E = -202.4039$	N-N-N: 121 N <sub>2</sub> -N <sub>1</sub> -H } 110 N <sub>3</sub> -N <sub>1</sub> -H } N <sub>1</sub> -N <sub>2</sub> -O <sub>4</sub> } 119 N <sub>1</sub> -N <sub>3</sub> -O <sub>6</sub> } N <sub>1</sub> -N <sub>2</sub> -O <sub>5</sub> } 112 N <sub>1</sub> -N <sub>3</sub> -O <sub>7</sub> } O-N-O: 129 H <sub>4</sub> -N <sub>1</sub> -N <sub>2</sub> -N <sub>3</sub> : 110 O <sub>4</sub> -N <sub>2</sub> -N <sub>1</sub> -N <sub>3</sub> : -36 O <sub>6</sub> -N <sub>3</sub> -N <sub>1</sub> -N <sub>2</sub> : 36
$\text{N}(\text{NO}_2)_3$ : $C_3$ symmetry; pyramidal $E = -662.4265$	N-N: 1.524 N <sub>2</sub> -O <sub>5</sub> , N <sub>3</sub> -O <sub>7</sub> , N <sub>4</sub> -O <sub>9</sub> : 1.213 N <sub>2</sub> -O <sub>6</sub> , N <sub>3</sub> -O <sub>8</sub> , N <sub>4</sub> -O <sub>10</sub> : 1.223	N-N-N: 107 O-N-O: 133 N <sub>1</sub> -N <sub>2</sub> -O <sub>5</sub> } 111 N <sub>1</sub> -N <sub>3</sub> -O <sub>7</sub> } N <sub>1</sub> -N <sub>4</sub> -O <sub>9</sub> } N <sub>1</sub> -N <sub>2</sub> -O <sub>6</sub> } 116 N <sub>1</sub> -N <sub>3</sub> -O <sub>8</sub> } N <sub>1</sub> -N <sub>4</sub> -O <sub>10</sub> }
		

Table 3. Crystallographically-determined ranges of bond lengths and bond angles in  $\text{N}(\text{NO}_2)_2^-$  ions of I and II.

Bond length, Å	Bond angle, deg.
N-N: 1.356 - 1.390	N-N-N: 113.2 - 115.9
N-O <sub>a</sub> : 1.227 - 1.251	N-N-O <sub>a</sub> : 110.9 - 113.0
N-O <sub>b</sub> : 1.210 - 1.228	N-N-O <sub>b</sub> : 123.4 - 127.0
	O-N-O: 121.3 - 123.3

<sup>a</sup>The crystallographic data were kindly provided by Dr. Richard Gilardi.

A comparison of Tables 2 and 3 shows that there is generally good agreement between the calculated and experimental structures of  $\text{N}(\text{NO}_2)_2^-$ , particularly in view of the fact that the latter are for the ion in crystalline environments, subject to packing effects, while the former corresponds to the gaseous phase. In particular, the computed structure reproduces the observed difference of approximately  $10^\circ$  between the two N-N-O angles of each nitro group. This can probably be attributed to steric interference between O<sub>4</sub> and O<sub>6</sub> (Table 2), and the consequent tendencies of these two oxygens to move away from each other; their separation is 2.61 Å, significantly less than the sum of their van der Waals radii, 3.0 Å.<sup>7</sup> Thus the steric factor remains important.

As a point of interest, we also computed the energy of the non-equilibrium form of the dinitramide ion in which the N-N-N angle is forced to be  $180^\circ$ . In this situation, the NO<sub>2</sub> groups are observed to rotate so as to be in perpendicular planes. This  $\text{N}(\text{NO}_2)_2^-$  structure was found to be 51 kcal/mole less stable than the equilibrium form shown in Table 2.

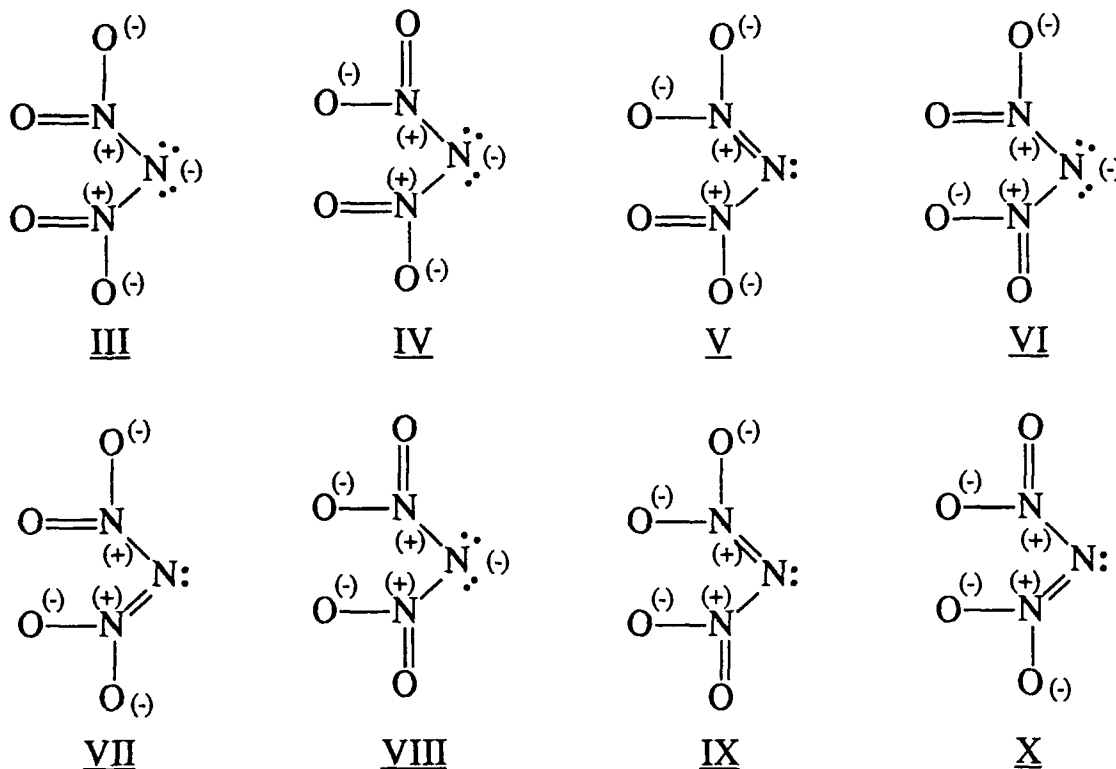
Both  $\text{HN}(\text{NO}_2)_2$  and  $\text{N}(\text{NO}_2)_3$  show differences between the two N-N-O angles within each nitro group, but they are smaller than in  $\text{N}(\text{NO}_2)_2^-$ ,  $7^\circ$  and  $5^\circ$  respectively. Presumably steric factors are again responsible; the relevant O...O separations in the two molecules are 2.69 Å and 2.78 Å.

The proton affinity of  $\text{N}(\text{NO}_2)_2^-$  is predicted to be 289 kcal/mole, based again upon an AM1 estimate of the difference in zero-point energies (7.2 kcal/mole). This indicates that the gaseous phase acidity of  $\text{HN}(\text{NO}_2)_2$  is greater than that of  $\text{HNO}_2$ . Finally,  $\Delta E$  for reaction (2) is found to be -143 kcal/mole (uncorrected for zero-point energy differences).

## Discussion

The dinitramide ion,  $\text{N}(\text{NO}_2)_2^-$ , can be described in terms of the resonance structures III-X. Their contributions are far from equal however. The formal charges suggest that VIII - X are rather unlikely, due to proximities of strongly negative oxygens, whereas III should be favored. These expectations are confirmed by the calculated structures (the N<sub>2</sub>-O<sub>4</sub> and N<sub>3</sub>-O<sub>6</sub> bonds are

shorter than the  $N_2-O_5$  and  $N_3-O_7$ ) and especially by the crystallographic results (the  $N-O_b$  bonds are shorter than the  $N-O_a$ ).



Our calculations show the two nitro groups in  $N(NO_2)_2$  to be rotated out of the N-N-N plane by  $28^\circ$ . This may in part represent a further effort by  $O_4$  and  $O_6$  to increase their separation; however we believe that it also reflects some delocalization of the two lone pairs on the central nitrogen, leading to contributions from V and VII. Assuming that the electron pairs around the central nitrogen are distributed tetrahedrally (which is supported by the N-N-N angle of  $110^\circ$ ), then a  $28^\circ$  rotation of the  $NO_2$  planes makes them essentially perpendicular (dihedral angles =  $92^\circ$ ) to the lone pair orbitals, thereby optimizing conjugation. This reasoning provides an explanation for the fact that in  $HN(NO_2)_2$  the nitro groups are rotated by  $36^\circ$  in *opposite* directions, rather than in the same direction as in  $N(NO_2)_2$ ; in  $HN(NO_2)_2$  there is only one lone pair available for conjugation, and opposite rotations allow both nitro groups to interact with it.

Somewhat surprisingly, we found that when the  $NO_2$  groups in  $N(NO_2)_2$  are forced to be in the N-N-N plane, the molecular energy increases by only 1.1 kcal/mole, suggesting that the conjugation has been only slightly impaired. Even when one of the groups is subsequently made to rotate by  $90^\circ$ , so that it is perpendicular to the N-N-N plane, the energy goes up by only an additional 0.2 kcal/mole; evidently the other  $NO_2$  is now able to conjugate with *both* lone pairs. Only when both  $NO_2$  groups are forced to be perpendicular to the N-N-N plane is there significant

destabilization, by 21 kcal/mole relative to the ground state. Our finding that there is very little energy barrier to small rotations of the nitro groups in  $N(NO_2)_2$  is consistent with Gilardi's observation that the degrees of  $NO_2$  rotation vary from one dinitramide salt to another; for example they are roughly  $20^\circ - 25^\circ$  in I but less than  $10^\circ$  in II.

Another aspect of the conjugation between the  $NO_2$  groups and the lone pairs in  $N(NO_2)_2$  is brought out by our observation that when the N-N-N angle is forced to be  $180^\circ$ , the nitro groups rotate so as to be in perpendicular planes. In this linear arrangement, the two lone pairs are expected to be in perpendicular p-type orbitals; thus, conjugation with the nitro groups can occur most effectively when these are also perpendicular. We have used analogous reasoning in the past to explain why the  $NO_2$  substituents in dinitroacetylene are in perpendicular planes.<sup>8</sup>

It is interesting to observe the marked increase in the N-N bond length, about  $0.1 \text{ \AA}$ , in going from  $N(NO_2)_2$  and  $HN(NO_2)_2$  to  $N(NO_2)_3$ . This is probably at least partially due to the fact that three  $NO_2$  groups are now competing to conjugate with the single lone pair on the central nitrogen; thus the degree of conjugatively-produced double bond character in each N-N bond is considerably reduced. The nitro groups in  $N(NO_2)_3$  are rotated more ( $41^\circ$ ) than in either  $N(NO_2)_2$  or  $HN(NO_2)_2$ . While our calculations do indicate that there is at least a local energy minimum corresponding to  $N(NO_2)_3$ , the lengths of the N-N bonds suggest that the molecule may be rather unstable. (For comparison, our calculated N-N distance in hydrazine,  $N_2H_4$ , at essentially the same computational level, is  $1.449 \text{ \AA}$ , in exact agreement with the experimentally-determined value.<sup>9</sup>)



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