

Gaussian-2 and Density Functional Studies of $\text{H}_2\text{N}-\text{NO}_2$ Dissociation, Inversion, and Isomerization

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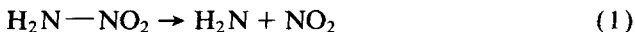
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Abstract

Several computational approaches, including Gaussian-2 (G2) and nonlocal density functional theory (DFT-GGA), have been used to calculate the energy requirements for (a) $\text{H}_2\text{N}-\text{NO}_2$ dissociation (through N—N bond scission), (b) inversion of the amine group, and (c) isomerization through the nitro-nitrite rearrangement. Taking zero-point energies into account, the G2 predictions are 53.6 kcal/mole for the dissociation energy and 1.5 kcal/mole for the inversion barrier. The corresponding DFT-GGA values are 48.4 and 0.9 kcal/mole, and an activation energy of 48.7 kcal/mole for the nitro-nitrite rearrangement. The DFT-GGA results indicate that dissociation and rearrangement should be competitive for $\text{H}_2\text{N}-\text{NO}_2$. The same conclusion was reached earlier by Saxon and Yoshimine on the basis of MRCISD/6-31G* calculations, although their computed energy requirements differ from the present ones by approximately 8 kcal/mole. © 1992 John Wiley & Sons, Inc.

Introduction

The decomposition reactions of nitramines are of considerable interest because of the importance of these compounds as energetic materials [1,2]. Among the likely unimolecular processes that they may undergo are N—N bond scission and isomerization through the nitro-nitrite rearrangement, as shown in Eqs. (1) and (2) for the smallest nitramine, $\text{H}_2\text{N}-\text{NO}_2$:



Saxon and Yoshimine have recently investigated reactions (1) and (2) computationally, at the MRCISD/6-31G*/MCSCF/4-31G level [3]. Taking zero-point energies into account, they found the N—N dissociation energy to be 40.55 kcal/mole, while the nitro-nitrite activation barrier was 40.70 kcal/mole. It was accordingly concluded that the two processes, Eqs. (1) and (2), are competitive. Melius and Binkley also studied reaction (1), using an MP4/6-31G**//HF/6-31G* procedure augmented by a bond additivity correction (BAC) [4]; they reported an N—N dissociation energy of 48.0 kcal/mole, of which more than 5 kcal/mole was the BAC contribution [3].

TABLE I. Optimized geometries (in angstroms and degrees) of the ground state of $\text{H}_2\text{N}-\text{NO}_2$.

	HF/6-31G*	MP2/6-31G*	DFT-LSDA DZVPP	DFT-GGA DZVPP	Expt. ^a	Expt. ^b
N—N	1.356	1.399	1.371	1.416	1.427	1.381
N—O	1.191	1.233	1.230	1.244	1.206 (ass.)	1.232
N—H	0.988	1.017	1.022	1.023	1.005	1.007
O—N—O	127.0	127.7	127.4	127.4	130.1	132.7
H—N—H	116.7	114.3	119.6	115.1	115.2	120.9
H—N—N—O	25.7	29.5	22.9	28.6	26.5	22.5

^a Reference [23].^b Reference [24].

As part of a continuing investigation of density functional techniques [5,6], using precise *ab initio* calculations as a frame of reference, we have now examined reactions (1) and (2) by means of (a) the Gaussian-2 (G2) procedure [7], and (b) nonlocal density-functional theory (DFT), in the generalized gradient approximation (DFT-GGA) [8,9]. G2 theory is an *ab initio* method which has been shown to yield atomization energies, ionization potentials, electron affinities, and proton affinities for molecules containing first- and second-row atoms to within an average absolute deviation of less than 1.6 kcal/mole [7], relative to experimental results having an uncertainty of less than 1 kcal/mole. However G2 imposes severe demands upon computational resources, increasing with the number of basis functions as N^7 , compared to N^3 for DFT.

Methods

Gaussian-2

The G2 procedure is based on Gaussian-1 (G1) [10,11], with corrections added to the energy. G1 uses MP2/6-31G* optimized geometries to compute

TABLE II. Optimized geometries (in angstroms and degrees) of the ground states of NO_2 and NH_2 .

	HF/6-31G*	MP2/6-31G*	DFT-LSDA DZVPP	DFT-GGA DZVPP	Experiment ^a
NO_2					
N—O	1.165	1.216	1.209	1.225	1.197
O—N—O	136.1	133.7	133.5	132.3	133.8
NH_2					
N—H	1.012	1.028	1.041	1.043	1.024
H—N—H	104.3	103.3	102.9	101.8	103.3

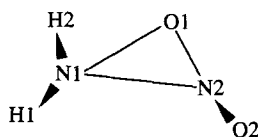
^a Reference [25].

TABLE III. Optimized geometries (in angstroms and degrees) of the planar form of $\text{H}_2\text{N}-\text{NO}_2$.

	HF/6-31G*	MP2/6-31G*	DFT-LSDA DZVPP	DFT-GGA DZVPP
N—N	1.327	1.361	1.354	1.379
N—O	1.194	1.236	1.232	1.248
N—H	0.992	1.008	1.017	1.015
O—N—O	126.8	127.6	127.3	127.4
H—N—H	126.5	126.9	126.9	126.8

energies at the MP4/6-311G** level. These are improved through subsequent MP4/6-311 + G**, MP4/6-311G (2df,p) and QCISD(T)/6-311G** calculations; the difference between each of these and the original MP4/6-311G** energy is taken to represent, respectively, the effect of diffuse *sp*-functions on the heavy atoms, additional *d* and *f* polarization functions on the latter, and correlation beyond MP4. These three corrections are assumed to be additive. Finally an empirical term is added, which depends upon the numbers of valence electrons of α and β spins. The zero-point energy is computed from scaled HF/6-31G* frequencies.

TABLE IV. Optimized geometries (in angstroms and degrees) for the transition state of the nitro-nitrite rearrangement, Eq. (2).



	DFT-GGA/DZVPP	MCSCF/4-31G ^a
N1—N2	2.831	2.845
N1—O1	3.193	3.214
N2—O1	1.229	1.212
N2—O2	1.224	1.207
N1—H	1.042	1.014
O1—N2—O1	131.7	133.1
H2—N1—H1	102.8	108.3
H2—N1—N2	95.5	96.3
H1—N1—N2	110.5	110.3
N1—N2—O1	95.5	96.4
N1—N2—O2	110.5	111.1
O2—N2—O1—N1	123.9	126.9
H1—N1—N2—O1	136.6	102.5
H2—N1—N2—O1	2.0	9.7

^a Reference [3].

TABLE V. Calculated total energies, in hartrees, for ground-state $\text{H}_2\text{N}-\text{NO}_2$, its dissociation products, and planar $\text{H}_2\text{N}-\text{NO}_2$.

	$\text{H}_2\text{N}-\text{NO}_2$ (ground state)	NH_2	NO_2	$\text{H}_2\text{N}-\text{NO}_2$ (planar)
HF/6-31G*	-259.63941	-55.55770	-204.03149	-259.63645
MP2/6-31G*	-260.35192	-55.69375	-204.56859	-260.34700
MP4/6-311G**	-260.52087	-55.75310 ^a	-204.69102	-260.51435
MP4/6-311 + G**	-260.53715	-55.75796 ^a	-204.70294	-260.53108
MP4/6-311G(2df,p)	-260.66334	-55.77971 ^a	-204.79941	-260.65872
QCISD(T)/6-311G**	-260.51069	-55.75444 ^a	-204.67501	-260.50439
G1	-260.74312	-55.80452 ^a	-204.84463	-260.73917
G2	-260.74628	-55.80738 ^b	-204.84163	-260.74239
DFT-LSDA/DZVPP	-259.20225	-55.41055	-203.65776	-259.20093
DFT-GGA/DZVPP	-261.39234	-55.95635	-205.34709	-261.38945

^a Reference [11].^b Reference [7].

G2 theory improves G1 by accounting for nonadditivity of the diffuse and polarization function corrections and by including a third *d* function on the heavy atoms and a second *p* on the hydrogens [7]. The empirical term is also modified. In the present study, the G2 calculations were carried out with the GAUSSIAN 90 program [12].

Density-Functional Theory

The Hohenberg-Kohn theorem [13] states that the energy of a system of electrons in an external potential $\nu(\mathbf{r})$ is a functional of the electronic density $\rho(\mathbf{r})$:

$$E[\rho(r)] = \int \nu(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})] \quad (3)$$

TABLE VI. Calculated dissociation energies and inversion barriers for $\text{H}_2\text{N}-\text{NO}_2$, in kcal/mole. Zero-point corrections are not included.

	Dissociation energy	Inversion barrier
HF/6-31G*	31.5	1.9
MP2/6-31G*	56.2	3.1
MP4/6-311G**	48.2	4.1
MP4/6-311 + G**	47.8	3.8
MP4/6-311G(2df,p)	52.8	2.9
QCISD(T)/6-311G**	51.0	4.0
G1	59.0	2.5
G2	61.0	2.4
DFT-LSDA/DZVPP	84.0	0.8
DFT-GGA/DZVPP	55.8	1.8

TABLE VII. Gaussian-2 and nonlocal density functional results, in kcal/mole, for H₂N—NO₂ dissociation energy, amine group inversion barrier, and nitro-nitrite rearrangement activation energy. Zero-point corrections are included.

	Dissociation energy	Inversion barrier	Activation energy
G2	53.6	1.5	—
DFT-GGA	48.4	0.9	48.7

(In atomic and molecular calculations, the external potential is that due to the nuclei.) $F[\rho(\mathbf{r})]$ is a universal functional of the electron density. Hohenberg and Kohn also established the existence of a variational principle for $E[\rho]$. Later, Kohn and Sham [14] developed a working procedure to solve the N-electron problem, in which $F[\rho]$ was partitioned in the form,

$$F[\rho] = T_s[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] \quad (4)$$

in which $T_s[\rho]$ is the kinetic energy of a set of N noninteracting electrons having density $\rho(\mathbf{r})$ identical to the density in the real (interacting) system. $E_{xc}[\rho]$ is the exchange-correlation energy, whose functional form is unknown. Expressing $\rho(\mathbf{r})$ in terms of one-electron orbitals, and

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (5)$$

applying the variational principle to Eq. (3), subject to the condition of conserving the number of electrons, the N-particle problem is simplified eventually to solving a set of one-particle Schrödinger equations with the canonical form,

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}} \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad i = 1, 2, \dots, N \quad (6)$$

These are known as the Kohn-Sham equations. The effective potential v_{eff} is given by,

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} + \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (7)$$

Once an approximation for $E_{xc}[\rho]$ has been selected, the Kohn-Sham equations can be solved in a self-consistent manner to obtain the orbitals φ_i and eigenvalues ϵ_i , and subsequently $\rho(\mathbf{r})$, $E[\rho]$ and other properties.

In the program *deMon* that was used in this work [15], $E_{xc}[\rho]$ is separated into exchange and correlation portions; for both of these, formulations in terms of the generalized gradient approximation (GGA) were selected:

$$E_{xc}[\rho] = E_x^{\text{GGA}}[\rho, \nabla\rho] + E_c^{\text{GGA}}[\rho, \nabla\rho] \quad (8)$$

Perdew and Wang's expression was used for $E_x^{\text{GGA}}[\rho, \nabla\rho]$ [18]; when $\nabla\rho(\mathbf{r}) = 0$, this reduces to Dirac's formula for the uniform electron gas [16]. $E_c^{\text{GGA}}[\rho, \nabla\rho]$ was represented by Perdew's improved version [9] of the Langreth-Mehl functional [17]. This is made up of two terms, the first (which is the only term when $\nabla\rho = 0$) being the correlation energy of a uniform electron gas. This is expressed by the Vosco-Wilk-Nusair functional [18,19], which is based on the accurate quantum Monte Carlo calculations of Ceperley and Alder [20]. Thus our treatment of $E_{xc}[\rho]$ can be regarded as a local spin-density approximation (LSDA) plus gradient correction terms. (The LSDA assumes that $\rho(\mathbf{r})$ can be viewed as uniform locally [21].) An interesting review and comparison of nonlocal functionals implemented in *deMon* has been given by Mlynarski and Salahub [22].

A Gaussian basis set, the DZVPP, was used for the orbitals φ_i in the present computations; it is double-zeta for the valence electrons plus polarization functions (approximately equivalent to the 6-31G**). The program *deMon* also requires auxiliary basis sets for fitting the electron density and the exchange and correlation potentials; this is done to reduce the computational effort. We used the (4,3; 4,3)/(5,1; 5,1) which includes four lone *s*-type and three constrained sets of *s*-, *p*-, and *d*-type functions on the heavy atoms, and five *s*-type and one set of *s*-, *p*-, and *d*-on the hydrogens.

Results

Tables I to IV present optimized geometries, at different computational levels, for (a) ground-state $\text{H}_2\text{N}-\text{NO}_2$, (b) its dissociation products in Eq. (1), (c) its planar form that is the transition state for the inversion of the amine group, and (d) the transition state for the nitro-nitrite rearrangement, Eq. (2). Experimental data are included where available; Table I shows that there are some discrepancies in the latter. There is consistently good agreement between the MP2/6-31G* and the DFT-GGA results. In optimizing the transition state for Eq. (2), we took Saxon and Yoshimine's geometry [3] as our starting point. The major changes are in some of the angles involving the hydrogens (Table IV). Saxon and Yoshimine had already noted that the 4-31G basis set does not position the hydrogens properly [3]. For ground-state and planar $\text{H}_2\text{N}-\text{NO}_2$, and for NH_2 and NO_2 , the HF/6-31G* and MP2/6-31G* optimized geometries were confirmed to correspond to local energy minima by verifying that they have no imaginary frequencies.

Table V contains total energies, calculated at several computational levels, for ground-state $\text{H}_2\text{N}-\text{NO}_2$, its dissociation products in Eq. (1), and its planar form. Zero-point energies are not included. These data were used to obtain the $\text{H}_2\text{N}-\text{NO}_2$ dissociation energies and inversion barriers that are in Table VI. In the G1 and G2 procedures, zero-point energies are computed from scaled HF/6-31G* frequencies. These give correction terms of -7.4 kcal/mole for the dissociation energy and -0.9 kcal/mole for the inversion barrier. If we take the G2 results as our standard, then our predictions for the $\text{H}_2\text{N}-\text{NO}_2$ dissociation energy and inversion barrier are

53.6 and 1.5 kcal/mole, respectively (Table VII). Using the same zero-point corrections, our DFT-GGA/DZVPP values are 48.4 and 0.9 kcal/mole.

Finally, the DFT-GGA/DZVPP energy for the transition state in the nitro-nitrite rearrangement, Eq. (2), is -261.30519 hartrees. Using the zero-point correction term calculated by Saxon and Yoshimine [3], we find an activation energy of 48.7 kcal/mole (Table VII).

Discussion

The DFT-GGA/DZVPP dissociation energy for $\text{H}_2\text{N}-\text{NO}_2$ underestimates the G2 value by 5.2 kcal/mole. This may indicate a need for a larger basis set for the DFT calculations. Nevertheless, both the dissociation energy and the inversion barrier computed by the DFT-GGA/DZVPP procedure are closer to the G2 results than are most of the correlated *ab initio* values.

As anticipated, the DFT-LSDA/DZVPP dissociation energy is much too large. It is well known that density functional theory in the local approximation overestimates dissociation energies [5,6,26-29]. This is apparently a reflection of size inconsistency in the LSDA approach; an undissociated molecule and its fragments are not treated at the same level of accuracy [29]. As can be seen in Table VI and has been shown elsewhere [26,29,30], this problem can be handled quite well by treating exchange and correlation in a nonlocal manner, as was done in this work through the gradient terms in Eq. (8). We have shown that the total energy errors in the local approximation vary in a systematic fashion with the numbers of electrons and nuclei [5,6], so that the resulting dissociation energies can also be corrected empirically. Size inconsistency is not a problem when a molecule is undergoing rearrangement rather than fragmentation; thus the DFT-LSDA inversion barrier in Table VI is reasonably close to the G2.

Our DFT-GGA calculations indicate that the energy requirements for Eqs. (1) and (2) are very similar, 48.4 and 48.7 kcal/mole, respectively (Table VII). (Both values include zero-point corrections.) Thus we reach the same conclusion as did Saxon and Yoshimine [3], that the two processes, $\text{H}_2\text{N}-\text{NO}_2$ dissociation and its rearrangement to $\text{H}_2\text{N}-\text{ONO}$, are competitive. However we find the energies needed to be significantly larger, by about 8 kcal/mole, than did they. Our predicted dissociation energy is in fact very close to that obtained by Melius and Binkley [4], 48.0 kcal/mole, which supports their inclusion of the BAC term.

Summary

We have used the highly accurate G2 procedure to compute the N-N dissociation energy and the inversion barrier of $\text{H}_2\text{N}-\text{NO}_2$; our results are 53.6 and 1.5 kcal/mole, respectively. Nonlocal density functional calculations (DFT-GGA/DZVPP) yield 48.4 and 0.9 kcal/mole, both of which are closer to the G2 than are most of the results obtained by other correlated *ab initio* methods. Our DFT-GGA value for the activation barrier of the nitro-nitrite rearrangement of $\text{H}_2\text{N}-\text{NO}_2$ is 48.7 kcal/mole, indicating that it should be competitive with scission of the N-N bond.

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