

Theoretical Determination of Geometrical Structures of the Nitric Oxide Dimer, (NO)₂

Jong Keun Park* and Hosung Sun*†

Department of Chemistry and Central Laboratory, Pusan National University, Pusan 609-735, Korea
†Department of Chemistry, Sungkyunkwan University, Suwon 440-746 and Center for Molecular Science, KAIST, Taejeon 305-701, Korea
Received August 26, 1999

Geometrical structures for the dimerization of (NO)₂ from (NO + NO) have been calculated using *ab initio* Hartree-Fock (SCF), second-order Møller-Plesset perturbation (MP2), and coupled cluster with the single, double, and triple substitution [CCSD(T)] methods with a triple zeta plus polarization (TZP) basis set including diffuse Rydberg basis functions. The structure of (NO)₂ can be described by two interactions (N···N, N···O). One is the ONNO structure with an (N···N) interaction. In this structure, acyclic *cis*-ONNO with C_{2v}-symmetry, acyclic *trans*-ONNO with C_{2h}, and cyclic ONNO with trapezoidal structure (C_{2v}) are optimized at the MP2 level. The other structure is the ONON structure with an (N···O) interaction. In the structure, acyclic *cis*-ONON with C_s-symmetry and cyclic ONON of the rectangular (C_{2h}), square (D_{2h}), rhombic (D_{2h}), and parallelogramic (D_{2h}) geometries are also optimized. It is found that acyclic *cis*-ONNO (¹A₁) is the most stable structure and cyclic ONNO (³A₁) is the least stable. Acyclic *trans*-ONNO (³A₁) with an (N···N) interaction, acyclic *trans*-ONON and bicyclic ONON (C_{2v}) with (N···O) interaction, and acyclic *cis*- and *trans*-NOON with an (O···O) interaction can not be optimized at the MP2 level. Particularly, acyclic *trans*-ONNO with C_{2h}-symmetry can not be optimized at the CCSD(T) level. Meanwhile, acyclic NNOO (¹A₁, C_s) and trianglic NNOO (¹A₁, C_{2v}) formed by the (O···N) interaction between O₂ and N₂ are optimized at the MP2 level. The binding energies and the relative energy gaps among the isomers are found to be relatively small.

Introduction

The relative stability and geometrical structure of N₂O₂ as a fundamental unit in photochemical processes of dinitrogen oxides (N₂O_x; x = 2-5) have been extensively studied with various experimental¹⁻³⁴ and theoretical³⁵⁻⁵⁵ methods. The dinitrogen oxides have usually a closed electronic structure. The bond strengths (N-O) of the species formed by (N···N) interaction are weaker than those of nitrogen oxides (NO_x; x = 1-3) and bond lengths are longer. As the result, the formation and dissociation of N₂O₂ can easily take place. N₂O₂ has many geometrical isomers. It combines easily with water and becomes nitric acid. And the acid dissolves in fog and rain. Although many studies for the photochemical reactions of N₂O₂ have been performed, unanimous values of the stabilities and geometrical structures have not been given. Particularly, the results calculated with the density functional theory (DFT) are different from those of the experiments and *ab initio* calculations.

By the X-ray diffraction experiment,¹⁻² the most stable structure of N₂O₂ in solid is known to be a trapezoidal geometry (C_{2v}). R_{NN}, R_{NO}, and ∠ONN of the molecule are 2.18±0.06 Å, 1.12±0.02 Å, and 101±3 degrees, respectively. By the molecular beam spectroscopy,⁴ the most stable structure of N₂O₂ in the gas phase is revealed to be an acyclic form (C_{2v}). R_{NN}, R_{NO}, and ∠ONN are 2.33 Å, 1.15 Å, and 95 degrees, respectively. Using the microwave spectroscopy,^{5,6} R_{NN}, R_{NO}, and ∠ONN of acyclic ONNO (C_{2v}) are given as 2.237 Å, 1.161 Å, and 99.6 degrees, respectively. By the result of the ¹⁵N isotopic infrared spectra,¹⁴ R_{NN}, R_{NO}, and ∠ONN of acyclic ONNO with C_{2v}-symmetry are known to

be 2.2630 Å, 1.1515 Å, and 97.17 degrees, respectively. Particularly, the structure of gaseous N₂O₂ analyzed by the infrared spectrum¹⁵ is assigned to be acyclic ONNO (C_{2v}). R_{NN} and ∠ONN are 1.75 Å and 90 degrees, respectively.

Recently, the structures and relative stabilities of N₂O₂ were investigated by Stirling *et al.*⁴⁶ and Duarte *et al.*⁵³ using the density functional theory (DFT). By the results of Duarte *et al.*, the acyclic *cis*-ONNO conformation is more stable in all case. The acyclic *cis*-ONNO with a triplet spin state is more stable than a singlet by the energy of 3.61 kcal/mol. R_{NN}, R_{NO}, and ∠ONN of acyclic *cis*-ONNO (³A₁) are 2.040 Å, 1.167 Å, and 110.37 degrees, respectively. According to the results of Stirling *et al.*, the most stable structure is also acyclic *cis*-ONNO with a triplet spin state and the most unstable one is cyclic ONON with a singlet spin. R_{NN}, R_{NO}, and ∠ONN of acyclic *cis*-ONNO (³A₁) are 2.059 Å, 1.176 Å, and 109.2 degrees, respectively. Using the various basis sets and correlated methods, the structures of acyclic *cis*-N₂O₂ were optimized by Lee *et al.*⁴² The geometrical structures are not influenced by the basis sets, but by the applied methods. At a large basis set, R_{NN}, R_{NO}, and ∠ONN are 2.186 Å, 1.170 Å, and 91.3 degrees, respectively. Configuration interaction calculation for N₂O₂ was performed by Ha.³⁹ The structure of the ground state is acyclic *cis*-ONNO (C_{2v}) with a singlet spin state. R_{NN}, R_{NO}, and ∠ONN of the ground state are 2.39 Å, 1.19 Å, and 90 degrees, respectively. The energy gap between the ground (¹A₁) and the first excited (³B₂) states is 0.43 eV.

At the SCF level, the *cis*-, *trans*-, and *gauche*-N₂O₂ were optimized by some groups.^{36,37,40,41} For small basis set, acyclic *cis*-ONNO is more stable than any others. With increas-

ing size of basis set, acyclic *trans*-ONNO is more stable than any others and the cyclic form is very unstable. According to the results of Vladimiroff³⁶ and Ritchie,⁴⁰ cyclic ONNO is the most stable structure. R_{NN} , R_{NO} , and $\angle ONN$ of the structure obtained by Vladimiroff are 1.35 Å, 1.51 Å, and 93.0 degrees, respectively. Acyclic *cis*-ONNO is more stable than the acyclic *trans*-conformer by 2.9 kcal/mol. By Skaarup *et al.*,³⁷ the most stable structure is acyclic *cis*-ONNO. R_{NN} , R_{NO} and the $\angle ONN$ of the species are 1.768 Å, 1.162 Å, and 106.6 degrees, respectively. Bock *et al.*⁴¹ predicted that acyclic *trans*-ONNO is more stable than the acyclic *cis* by 4.1 kJ/mol.

Although the structure and stability of N_2O_2 have already been studied by many groups, further investigations seem to be worth carrying out on the base of following points. (i) The structure of N_2O_2 is grouped as two possible geometrical isomers. One is a dimeric structure (ONNO) formed by an interaction between N and N. The other is a dimerization (ONON) by two interactions between O and N. Which structure is more stable form? (ii) According to the spin state in the same structure, the relative stability is different from each other. Which spin state is more stable? (iii) According to the applied methods, the geometrical parameters of N_2O_2 are quite different from the others. Why is the geometry of N_2O_2 dependent on the calculational methods? (iv) Although the binding energy of $(NO)_2$ is known to be relatively small, there are many geometrical isomers which should be all investigated. Is the binding energy between two monomers ($NO + NO$) as low as 2-5 kcal/mol?

Since the previous studies for the geometrical structure and relative stability of N_2O_2 are still limited, we have studied a schematic energy diagram for the geometrical isomers (N_2O_2) along the dimerization processes of $(NO + NO)$. Firstly, the geometrical structures of N_2O_2 are optimized at

the MP2 level and the harmonic frequencies of the structures are also analyzed. Secondly, a schematic diagram using the relative potential energies is drawn to clarify the systematic structure variation of the isomers of N_2O_2 . Last, the potential energy curves of acyclic *cis*-ONNO (1A_1) and cyclic ONNO (1A_1) near the equilibrium geometry are investigated to find the dissociation channels for the formation of N_2O_2 from $(NO + NO)$.

Computational Methods

The basis set chosen is the triple zeta basis on N (421/31) and O (421/31).^{56,57} Two extra *d* type polarization functions are added to nitrogen ($\alpha_d = 0.4, 1.6$)⁵⁶ and oxygen ($\alpha_d = 0.35, 1.5$).⁵⁸ The diffuse basis functions are additionally augmented on nitrogen ($\alpha_s = 0.028, 0.0066$; $\alpha_p = 0.025$; $\alpha_d = 0.015$)⁵⁹ and oxygen ($\alpha_s = 0.028, 0.0066$; $\alpha_p = 0.025$; $\alpha_d = 0.015$)⁶⁰ to describe the Rydberg states of N_2O_2 . The total number of contracted basis functions used is 106.

The geometrical structures of the ground states of N_2O_2 , NO, and O_2 are optimized with the Hartree-Fock (SCF) and second-order Møller-Plesset (MP2) levels using GAUSSIAN 94. To examine the appropriateness of the procedure, the geometrical structure of the species has also been optimized with the coupled cluster with the single, double, and triple substitution [CCSD(T)] method. In addition, the harmonic vibrational frequencies of the species have been analyzed to confirm the existence of the stable structure at the SCF and MP2 levels.

To find the geometrical conformers and isomers, the optimized geometrical structures from acyclic *trans*-ONNO to triangular NNOO are drawn using the MP2 results. To investigate the relative stability of the optimized geometries, a schematic energy diagram is made using the results of the

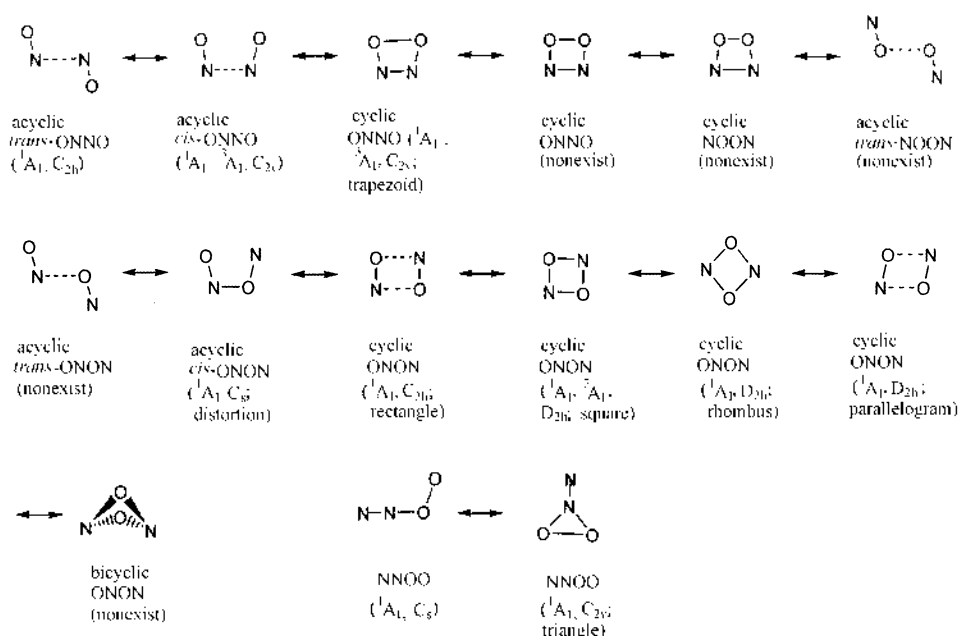


Figure 1. Optimized geometrical structures formed by the dimerization of $(NO)_2$ from $(NO + NO)$ along the orientation of the constituted atoms.

MP2 calculations. In the diagram, the potential energy of acyclic *cis*-ONNO is set to be zero. To investigate the binding energies and potential barriers from acyclic *trans*-ONNO and cyclic ONNO to the (NO + NO) asymptotes, the potential energy curves are drawn using the MP2 results. The internuclear distances ($R_{\text{N-N}}$) considered are from 1.1 to 2.4 Å. To connect the potential curves between the equilibrium geometry of N_2O_2 and the (NO + NO) asymptotes, the singly and doubly excited configuration interaction (SDCI) for NO are performed using the GAMESS package.

Results and Discussion

Optimized geometrical structures formed by the dimerization of $(\text{NO})_2$ from (NO + NO) are drawn in Figure 1. The geometrical structures with the internuclear distance of $R \geq 2.5$ Å between constituent atoms are denoted as acyclic form. The structure of N_2O_2 is divided as two groups by (N...N) and (N...O) interactions. One is ONNO with an (N...N) interaction. Acyclic *trans*-ONNO (1A_1), acyclic *cis*-ONNO (1A_1 , 3A_1), and cyclic ONNO (1A_1 , 3A_1) are optimized at the MP2 level. The other group is ONON with the (N...O) interaction. Acyclic *cis*-ONON with C_s -symmetry and five cyclic ONON of the rectangular (1A_1), square (1A_1 , 3A_1), rhombic (1A_1), and parallelogramic (1A_1) geometries are also optimized. Although acyclic *trans*-ONNO (3A_1), acyclic *trans*-ONON (1A_1), acyclic *cis*-ONON (3A_1), and bicyclic ONON (1A_1) can not be optimized at the MP2 level, the molecules are optimized at the SCF level and the harmonic vibrational frequencies are the positive values. But cyclic and acyclic NOON with an (O...O) interaction, acyclic *trans*-ONON (3A_1), and cyclic ONON (3A_1 ; rectangle, square, rhombus, and parallelogram) with two (N...O) interactions can not be optimized at both levels. Acyclic *cis*- and *trans*-NOON and cyclic ONON (3A_1 ; rectangle) are optimized to become acyclic *cis*- and *trans*-ONNO and acyclic *cis*-ONON (3A_1) without a potential barrier, respectively. Acyclic *trans*-ONON (3A_1) are found to be the transition state having a negative imaginary vibrational frequency. Additionally, two isomers of NNOO made from the (O...N) interaction between O_2 and N_2 are also optimized at the MP2 level.

Using the density functional theory (DFT), the eight structures of N_2O_2 were optimized by Stirling *et al.*⁴⁶ Acyclic *cis*- and *trans*-ONNO (1A_1 , 3A_1) and acyclic *cis*- and *trans*-ONON (1A_1 , 3A_1) are found as stable species. The most stable one is acyclic *cis*-ONNO (3A_1) and the most unstable one is acyclic *trans*-ONON (1A_1). The geometrical structures of ONNO lie lower in potential energy than the ONON species. And the conformers with the triplet spin state are more stable than the corresponding one with the singlet state. In particular, acyclic *cis*-ONNO with the triplet state is more stable than that of the singlet state. Very recently, Duarte *et al.*⁵³ optimized four isomers of N_2O_2 using various density functional theories (DFT). For all DFT methods, the optimized geometrical structures of acyclic *cis*-ONNO (1A_1 , 3A_1) are more stable than acyclic *trans*-ONON (1A_1 , 3A_1). Acyclic *cis*-ONNO with the triplet spin state is more stable than acy-

lic *cis*-ONNO with the singlet state. Although acyclic *trans*-ONNO (3A_1), acyclic *cis*-ONON (3A_1), and *trans*-ONON (3A_1 , 1A_1) are optimized at the DFT levels, the isomers can not be optimized by our MP2 calculation.

With a relatively large basis set and the various applied methods including the DFT method, acyclic *cis*- and *trans*-ONNO were investigated by Nguyen *et al.*^{49,51} At the SCF level *trans*-ONNO is more stable than the *cis*-isomer by 2.65 kcal/mol. On the other hand at the MP2 and DFT levels, *cis*-ONNO is more stable. Two isomers [bicyclic ONON (C_{2v}) and trianglic NNOO (C_{2v}) with two (O...N) interactions] of N_2O_2 with relatively high energy with respect to 2NO were also optimized by Nguyen *et al.*^{44,47,48,52} At the SCF level, the isomers are a minimum structure having all positive frequencies. In contrast at the MP2 and MCSCF levels, bicyclic NONO and trianglic NNOO have one imaginary frequency. In our MP2 result, bicyclic ONON (1A_1) is found to be a transition state, while the trianglic NNOO is found as a local minimum species.

The eight low-lying states of N_2O_2 with four singlets and four triplets were investigated by East.⁵⁴ He suggested that the *cis*-ONNO is more stable than the *cis*-ONON and *trans*-ONNO by 0.19 and 0.21 eV, respectively. Although the ground state of *cis*-ONNO could not be definitely determined due to the narrow energy span, the ordering of the lowest four states are \tilde{X}^1A_1 , 3B_1 , 1B_1 , and 1A_1 . They concluded that the only potential minimum lying below the lowest (NO + NO) asymptotes is the *cis*-ONNO conformer with a ground \tilde{X}^1A_1 state. By the configuration interaction calculation for N_2O_2 performed by Ha,³⁹ the structure of the ground state is also acyclic *cis*-ONNO (C_{2v}) with a singlet spin state. The energy gap between the ground (1A_1) and the first excited (3B_2) states is 0.43 eV.

The geometrical structures of N_2O_2 at the SCF level were obtained by some groups.^{36,37,40,41} Ritchie⁴⁰ optimized acyclic *trans*-ONON (C_{2h}), acyclic *cis*-ONNO (C_{2v}), and cyclic ONNO (C_{2v}). Acyclic *trans*-ONON at the DZP basis set is more stable than the others. By the results of Vladimiroff,³⁶ cyclic ONNO is more stable than the others. And acyclic *cis*-ONNO is more stable than acyclic *trans*-ONNO by 2.9 kcal/mol. By Skaarup *et al.*³⁷ at a small basis set the *cis*-conformer is more stable than the *trans*. With increasing size of basis set, the *trans*-conformer is more stable than the *cis*. In the calculation of Bock *et al.*⁴¹ acyclic *trans*-ONNO is more stable than the *cis* and the *gauche* forms. The previous SCF results are similar to our SCF results.

Experimentally,^{1-10,12-23,25-34} the stable structure of N_2O_2 is acyclic *cis*-ONNO with C_{2v} -symmetry. But in the Raman and infrared spectra for four different isotopes of nitric oxide investigated by Ohlsen and Laane,¹¹ the peaks of asymmetric ONON were observed. Simultaneously the harmonic frequencies of four isomers were also analyzed with the force constant calculation. The calculated frequencies were compared with their experimental values. From the comparison, they concluded that the most stable molecule is acyclic *cis*-ONON, that is, it exists as a polymer form rather than a simple dimer. In the electron spin resonance (ESR) spectrum of

NO adsorbed in Na-A zeolite,²⁴ the spectrum of the NO monomer is observed to be well-defined form. According to the results, an unpaired electron of the nitrogen atom combines with a sodium cation. The ONON species with the triplet state in zeolite are weakly dimerized like a van der Waals complex. The internuclear distance between two monomers is 4.6 Å. But, in the absorption spectrum of (NO)₂ studied by Holland and Maier,²⁵ the infrared spectra of the red-colored ONON species were not observed.

Optimized internuclear distances and angles of N₂O₂ including NO and O₂ are listed in Table 1. Our values for the species calculated with the Hartree-Fock (SCF) and second order Møller-Plesset perturbation (MP2) methods are in reasonable agreement with experimental¹⁻³⁴ or other theoretical³⁵⁻⁵⁵ values. In addition, to find more stable structure between the singlet and triplet spin states and between the *cis*- and *trans*-

conformers, the geometrical structures of acyclic *cis*- and *trans*-ONNO have also been optimized using the coupled cluster with the single, double, and triple substitution [CCSD(T)] methods. But, *trans*-ONNO can not be optimized at the CCSD(T) calculation. NO and O₂ are open shell molecules. These molecules have unpaired electrons in the antibonding orbital. Our results of NO and O₂ are in good agreement with other theoretical⁶¹⁻⁶⁴ or experimental⁶⁵⁻⁶⁷ values.

In our results, five isomers consisting of an (N...N) interaction between two NO molecules are optimized at the MP2 level. The most stable structure is acyclic *cis*-ONNO (¹A₁) with C_{2v}-symmetry. The geometrical parameters of R_{NO}, R_{NN}, and ∠NNO are in good agreement with experimental^{1,4,5,14,15} or other theoretical^{39,42,43,45,46,53,54} values. Particularly, the parameters of acyclic *cis*-ONNO (¹A₁) optimized by CCSD(T) are similar to the experimental results of

Table 1. Optimized internuclear distances (Å) and angles (degrees) of N₂O₂

	Present work				Other works				
	SCF	MP2	CCSD(T)	DFT ^a	CI ^b	CI ^c	ACPF ^d	CCSD(T) ^e	Exptl ^f
R(NO)	1.115	1.137	1.156	1.167	1.164	1.162			1.151 ^g
R(O ₂)	1.163	1.235	1.221	1.223	1.210 ^h	1.215			1.208 ⁱ 1.216 ^j
acyclic <i>cis</i> -ONNO(¹ A ₁ ; C _{2v})									
R _{NO}	1.135	1.173	1.161	1.167 ^k 1.174 ^l 1.175 ^m	1.170 ⁿ	1.19 ^o	1.149	1.169 1.180 ^p	1.161 1.12 ^q 1.15 ^r 1.1515 ^s
R _{NN}	1.613	2.218	2.203	2.089 ^t 2.119 ^l 2.121 ^m	2.186 ⁿ	2.39 ^o	2.284	2.227 2.354 ^p	2.237 2.18 ^q 2.33 ^r 2.263 ^s 1.75 ^t
ONN	109.9	91.0	96.5	99.43 ^k 97.6 ^l 100.5 ^m	91.3 ⁿ	90 ^o	96.1	96.2 95.3 ^p	99.6 101 ^q 95 ^r 97.17 ^s 90 ^t
acyclic <i>cis</i> -ONNO(³ A ₁ ; C _{2v})									
R _{NO}	1.126	1.171	1.159	1.168 ^k 1.176 ^l					1.161
R _{NN}	1.725	2.310	2.128	2.085 ^k 2.059 ^l					2.237
∠ONN	113.7	93.8	105.3	109.85 ^k 109.2 ^l					99.6
acyclic <i>trans</i> -ONNO(¹ A ₁ ; C _{2h})									
R _{NO}	1.145	1.172		1.170 ^k 1.178 ^m	1.23 ⁿ 1.170 ⁿ	1.159 ⁿ			
R _{NN}	1.516	2.017		2.013 ^k 2.066 ^m	1.53 ⁿ 1.686 ⁿ	1.501 ⁿ			
∠ONN	108.5	108.3		109.12 ^k 109.1 ^m	104.6 ⁿ 107.7 ⁿ	108.7 ⁿ			
acyclic <i>trans</i> -ONNO(³ A ₁ ; C _{2h})									
R _{NO}	1.139			1.168 ^k					
R _{NN}	1.579			2.065 ^k					
∠ONN	115.5			114.20 ^k					

Table 1. Continued

	Present work		Other works			
	SCF	MP2	SCF	SCF	MP2	MP2
cyclic ONNO(1A_1 ; C_{2v} , trapezoid)						
R_{NN}	1.211	1.275	1.224 ^a	1.35 ^b	1.2773 ^c	1.247 ^d
R_{NO}	1.349	1.391	1.349 ^a	1.51 ^b	1.3756 ^c	1.431 ^d
R_{OO}	1.391	1.489			1.4644 ^c	1.539 ^d
$\angle ONN$	93.9	94.4	93.6 ^a	93.0 ^b	93.9 ^c	95.9 ^d
$\angle NNO$	86.2	85.6				
cyclic ONNO(3A_1 ; C_{2v} , trapezoid)						
R_{NN}	1.469	1.506				
R_{NO}	1.354	1.389				
R_{OO}	1.401	1.510				
$\angle ONN$	88.6	89.0				
$\angle NNO$	91.5	91.0				
acyclic <i>trans</i> -ONON(1A_1 ; C_s)						
R_{NO}	1.135		1.159 ^a			
R_{NO}	1.673		1.501 ^a			
$\angle ONO$	110.8		108.7 ^a			
acyclic <i>cis</i> -ONON(1A_1 ; C_s)						
R_{NO}	1.245	1.296				
R_{O-N}	2.490	2.553				
$\angle NON$	120.0	118.6				
$\angle ONO$	113.1	110.7				
dihedral angle	41.9	47.1				
acyclic <i>cis</i> -ONON(3A_1 ; C_s)						
R_{NO}	1.283					
R_{O-N}	2.453					
$\angle NON$	121.5					
$\angle ONO$	112.9					
dihedral angle	0.0					
cyclic ONON(1A_1 ; C_{2v} , rectangle)						
R_{NO}	1.108	1.172	1.162 ^a			
R_{NO}	2.142	2.310	1.768 ^a			
$\angle NON$	90.0	90.0	106.6 ^a			
cyclic ONON(1A_1 ; D_{2h} , square)						
R_{NO}	1.299	1.395				
$\angle ONO$	90.0	90.0				
cyclic ONON(3A_1 ; D_{2h} , square)						
R_{NO}	1.375	1.422				
$\angle ONO$	90.0	90.0				

Kukolich,^{5,6} Salahub group^{46,53} optimized the structure of acyclic *cis*-ONNO (1A_1 , 3A_1) at the DFT level. The most stable isomer is acyclic *cis*-ONNO (3A_1) and the second stable one is acyclic *cis*-ONNO (1A_1). The geometrical parameters of acyclic *cis*-ONNO optimized with the DFT method are in good agreement with our CCSD(T) results. Using several basis sets and theoretical methods, the structures of acyclic *cis*-ONNO were calculated by Lee *et al.*⁴² The optimized parameters are greatly influenced from the applied computational methods (CCSD, CISD, CPF). At the CPF level, R_{NN} , R_{NO} , and $\angle ONN$ are 2.160 Å, 1.154 Å, and 98.1 degrees, respectively. In Table 1, the previous theoretical values of

Table 1. Continued

	Present work		Other works	
	SCF	MP2	MP2	MP2
cyclic ONON(1A_1 ; D_{2h} , rhombus)				
R_{NS}	1.871	1.172	1.9860 ^a	1.970 ^{b,1}
R_{NO}	1.299	1.394	1.3789 ^a	1.365 ^{b,1}
$\angle NON$	92.13	92.05	92.13 ^a	92.4 ^{b,1}
$\angle ONO$	87.87	87.95	87.87 ^a	87.6 ^{b,1}
cyclic ONON(1A_1 ; D_{2h} , parallelogram)				
R_{NO}	1.107	1.172		
R_{OS}	2.137	2.301		
$\angle NON$	93.84	95.82		
$\angle ONO$	86.18	84.17		
bicyclic ONON(1A_1 ; C_{2v})				
R_{NO}	1.401		1.4658 ^a	1.484 ^d
R_{NS}	1.321		1.3819 ^a	1.395 ^d
R_{OO}	2.003			
$\angle NON$	56.3		56.24 ^a	56.1 ^d
$\angle ONO$	91.2		91.53 ^a	
dihedral angle	56.9		56.71 ^a	
acyclic NNOO(1A_1 ; C_s)				
R_{NS}	1.073	1.139	1.1453 ^a	1.1008 ^b
R_{NO}	1.199	1.221	1.2166 ^a	1.2190 ^b
R_{OO}	1.708	1.521	1.5104 ^a	1.6795 ^b
R_{N-O}	2.319	2.164		
$\angle OON$	104.49	103.7	106.36 ^a	101.82 ^b
$\angle NNO$	180.0	180.0	179.74 ^a	180.63 ^b
dihedral NONO	180.0	180.0		
triangular NNOO(1A_1 ; C_{2v})				
R_{NS}	1.116	1.125	1.1296 ^a	
R_{NO}	1.352	1.490	1.4711 ^a	
R_{OO}	1.475	1.590	1.5814 ^a	
$\angle NNO$	146.9	147.8	147.49 ^a	
$\angle NCO$	56.9	57.8		
dihedral NONO	0.0	0.0		

^aRef. 61. ^bRef. 62. ^cRef. 63. ^dRef. 45. ^eRef. 54. ^fRef. 5. ^gRef. 6. ^hRef. 65. ⁱRef. 64. ^jRef. 66. ^kRef. 67. ^lRef. 53. ^mRef. 46. ⁿRef. 21. ^oRef. 42. ^pRef. 39. ^qRef. 43. ^rRef. 1. ^sRef. 4. ^tRef. 14. ^uRef. 15. ^vRef. 41. ^wRef. 37. ^xRef. 40. ^yRef. 36. ^zRef. 48. ^{aa}Ref. 52. ^{ab}Ref. 47. ^{ac}Ref. 44.

R_{NO} of acyclic *cis*-ONNO (1A_1) are longer than the experiments, while the theoretical values of R_{NN} are shorter.

At the CCSD(T) level, the geometrical structure of acyclic *trans*-ONNO (1A_1 , 3A_1) can not be optimized. On the other hand at the SCF and MP2 levels, the structure of acyclic *trans*-ONNO (1A_1) is optimized. Our parameters of the molecule are compared with the previous results^{21,37,40,41,53} calculated at the SCF and DFT levels. Our MP2 results of acyclic *trans*-ONNO (1A_1) are similar to the DFT results. Although acyclic *trans*-ONNO with the triplet spin state was optimized by Salahub group,^{46,53} we could not optimize the molecule at the MP2 and CCSD(T) levels. The structures of cyclic ONNO (1A_1 , 3A_1) with the trapezoidal geometry are optimized at the SCF and MP2 methods. Our MP2 parameters of cyclic ONNO (1A_1) are similar to the results of Nguyen *et al.*^{48,52} and Ritchie.⁴⁰

Six isomers with (N...O) interaction [acyclic *cis*-ONNO (1A_1 ; C_3), cyclic ONNO (1A_1 ; rectangle), cyclic ONNO (1A_1 ; square), cyclic ONNO (1A_1 ; rhombus), and cyclic ONNO (1A_1 ; parallelogram)] are optimized at the MP2 level, while acyclic *cis*-NONO (3A_1), acyclic *trans*-ONNO, and bicyclic ONNO (C_{2v}) are not optimized. Our optimized parameters are in good agreement with the previous results. But, R_{NN} of cyclic ONNO with the rhombic geometry is quite different from that of Nguyen *et al.*^{47,48,52} Although the structure of bicyclic NONO (1A_1 , C_{2v}) was optimized by Nguyen *et al.*, we could not optimize the structure at the MP2 level. Four isomers of *cis*- and *trans*-ONNO with the singlet and triplet states were optimized by Stirling *et al.*⁴⁶ In their results, *cis*-ONNO (3A_1) is more stable than *trans*-ONNO (1A_1). And

trans-ONNO (1A_1) is relatively unstable. But the optimized parameters were not listed in their article. At the SCF level, acyclic *trans*-ONNO was optimized by Ritchie.⁴⁰ The results are similar to our SCF results. Cyclic ONNO with the trapezoidal geometry (C_{2v}) was optimized by Skaarup *et al.*³⁷ And the geometrical parameters are quite different from our SCF results. Optimized parameters of acyclic NNOO (1A_1 ; C_3) and triangular NNOO (1A_1 , C_{2v}) are similar to the results of Nguyen *et al.*

To find the minimum in the potential energy surfaces of the various geometrical structures of N_2O_2 , the harmonic vibrational frequencies are analyzed at the SCF and MP2 levels and listed in Table 2. In the frequencies of acyclic *cis*-ONNO (1A_1), our frequencies are similar to other theoretic

Table 2. Calculated harmonic vibrational frequencies (cm^{-1}) of N_2O_2 at the SCF and MP2 levels

acyclic <i>cis</i> -ONNO(1A_1)	$1A_2$	$1A_1$	$2A_1$	$1B_2$	$2B_2$	$3A_1$
SCF	158	432	578	978	1963	2051
MP2	285	326	353	627	1721	1846
CCSD(T) ^a	191	201	279	536		
LSD ^b	243	310	375	644	1684	1845
BPW91 ^c	226	257	386	659	1693	1837
GGA-PP ^d	230	264	381	652	1680	1839
SCF ^e	137	437	619	976	2008	2056
SCF ^f	190	439	635	768	1707	1858
Exptl ^g	161	262	202			1858
Exptl ^h		264	176	489		1866
Exptl ⁱ	117	239,361	134,503	429,140	1788 ^j	1860 ^j
Exptl ^k	97	268	189	215	1762	1866
Exptl ^l	119.2	258.9	127.2	430.0	1789.1	1868.3
acyclic <i>cis</i> -ONNO(3A_1)	$1A_2$	$1A_1$	$2A_1$	$1B_2$	$2B_2$	$3A_1$
SCF	298	393	553	650	1930	2064
MP2	225	277	435	524	1808	1855
LSD ^b	182	248	252	467	1650	1820
GGA-PP ^d	253	157	333	461	1651	1825
Exptl ^h	161	202	262			1858
Exptl ^h		176	264	489		1866
Exptl ⁱ	117	134,503	239,361	429,140	1788 ^j	1860 ^j
Exptl ^k	97	189	215	268	1762	1866
Exptl ^l	119.2	127.2	258.9	430.0	1789.1	1868.3
acyclic <i>trans</i> -ONNO(1A_1)	$1A_u$	$1B_u$	$1A_g$	$2A_g$	$2B_u$	$3A_g$
SCF	65	499	575	1064	1976	2018
MP2	78	134	157	670	1698	1739
BPW91 ^c	67	208	248	717	1692	1807
SCF ^e	132	428	448	919	1850	1920
SCF ^f	122	362	426	933	1685	1796
acyclic <i>trans</i> -ONNO(3A_1)	$1A_u$	$1B_u$	$1A_g$	$2A_g$	$2B_u$	$3A_g$
SCF	298	346	423	726	1928	1940
cyclic ONNO(1A_1 ; trapezoid)	$1A_2$	$1B_2$	$1A_1$	$2B_2$	$2A_1$	$3A_1$
SCF	464	1372	1419	1500	1674	2242
MP2	639	734	788	1078	1089	1325
SCF ^e	740	1026	1128	1328	1338	1856
cyclic ONNO(3A_1 ; trapezoid)	$1A_2$	$1B_2$	$1A_1$	$2B_2$	$2A_1$	$3A_1$
SCF	173	991	1077	1116	1193	1296
MP2	96	761	777	959	962	1143

Table 2. Calculated harmonic vibrational frequencies (cm^{-1}) of N_2O_2 at the SCF and MP2 levels

acyclic <i>cis</i> -ONON(1A_1 ; distortion)	1A'	1A''	2A'	2A''	3A'	4A'
SCF	224	503	954	1308	1398	1464
MP2	264	438	798	946	1045	1163
acyclic <i>trans</i> -ONON(1A_1)	1A'	1A''	2A'	2A''	3A'	4A'
SCF	91	209	387	925	1732	1972
cyclic ONON(1A_1 ; rectangle)	1A ₂	1B ₂	1A ₁	2B ₂	2A ₁	3A ₁
SCF	227	353	453	814	1736	2265
MP2	259	280	425	593	1758	2084
cyclic ONON(1A_1 ; square)	1B _{1u}	1B _{1g}	1A _g	2B _{2u}	3B _{3u}	2A _g
SCF	691	871	1122	1362	1443	1520
MP2	706	904	915	1070	1100	1873
cyclic ONON(3A_1 ; square)	1B _{1u}	1B _{1g}	1A _g	2B _{2u}	3B _{3u}	2A _g
SCF	93	1079	1095	1125	1138	1258
MP2	73	895	933	963	973	1127
cyclic ONON(1A_1 ; rhombus)	1B _{1u}	1B _{1g}	1A _g	2B _{2u}	3B _{3u}	2A _g
SCF	700	865	1117	1422	1452	1489
MP2	701	913	968	1081	1084	1850
cyclic ONON(1A_1 ; parallelogram)	1B _{1u}	1B _{1g}	1A _g	2B _{2u}	3B _{3u}	2A _g
SCF	239	353	468	802	1747	2270
MP2	283	287	435	580	1747	2096
bicyclic ONON(1A_1)	1A ₂	1B ₂	1A ₁	2B ₂	2A ₁	3A ₁
SCF	675	844	873	994	1143	1591
acyclic NNOO(1A_1)	1A'	1A''	2A'	2A''	3A'	4A'
SCF	204	328	663	712	1222	2644
MP2	216	495	560	689	1175	2105
trianglic NNOO(1A_1)	1A ₂	1B ₂	1A ₁	2B ₂	2A ₁	3A ₁
SCF	373	527	674	894	1166	2171
MP2	203	533	633	1102	1161	2326

^aRef. 20. ^bRef. 46. ^cRef. 21. ^dRef. 53. ^eRef. 40. ^fRef. 37. ^gRef. 11. ^hRef. 10. ⁱRef. 15. ^jRef. 17. ^kRef. 14. 16.

cal^{21,46,53} and experimental^{10,12,15} results. But, three low frequencies of this molecule are larger than those of the experiment by about 100 cm^{-1} . Particularly, our bending frequency (627 cm^{-1}) of $\angle \text{NNO}$ is larger than that (268 cm^{-1}) of Nour *et al.*¹⁷ The frequencies in relation to the geometrical structure of acyclic *cis*-ONNO were extensively analyzed by Salahub group,^{46,53} East *et al.*,^{20,54} and McKellar group.^{14,16,31} By the previous results, the calculated N-N stretching frequencies are larger than that of the symmetric $\angle \text{NNO}$ bending mode, while the experimental N-N stretching frequencies are smaller. In the N-N stretching motion, the elongation of the N-N bond length leads to the decrease of the angle of $\angle \text{NNO}$, while the decrease of the N-N bond length leads to the increase of the angle. But, the length between two oxygen atoms is not changed along the N-N stretching motion. In acyclic *cis*-ONNO (3A_1), our symmetric and asymmetric NO stretchings and symmetric bending of NNO are different from the values of Duarte *et al.*⁵³ In acyclic *trans*-ONNO (1A_1), our frequencies are also similar to the results of Canty *et al.*²¹ By the extensive analysis of the anharmonic vibrational frequency, the geometrical structures of N_2O_2 have been clarified.

A schematic energy diagram of the structural change from

acyclic *trans*-ONNO to trianglic NNOO at the MP2 level is drawn in Figure 2. In the diagram, the potential energy of acyclic *cis*-ONNO (1A_1) is set to zero. All energies are adiabatic values and are in units of eV. Acyclic *cis*-ONNO (1A_1) is the most stable, while cyclic ONNO (3A_1) with the trapezoidal geometry is the least stable. The second most stable one is the parallelogramic form of cyclic ONON (1A_1) and the third one is acyclic *cis*-ONNO (3A_1) with the rectangular structure. Our results for the relative stabilities of $(\text{NO})_2$ are different from those of Stirling *et al.*⁴⁶ In the results of Stirling *et al.*, the most stable isomer is acyclic *cis*-ONNO with a triplet spin state and the least stable one is cyclic ONON with a singlet state. The structures with the triplet spin state are more stable than those with the singlet state. Particularly, acyclic *trans*-ONNO and acyclic *cis*- and *trans*-ONON with a triplet spin state have not been optimized by us. In the triplet and singlet, their dissociation energies are 14.9 and 10.7 kcal/mol, respectively. Some conformers (*cis*-, *gauche*-, and *trans*- N_2O_2) are optimized at the SCF level. The results are different from each other. Although the energy difference is small, the *cis*-conformer calculated with small basis set is more stable than the *trans*-conformer. With increasing size of basis sets, the *trans*-conformer is more sta-

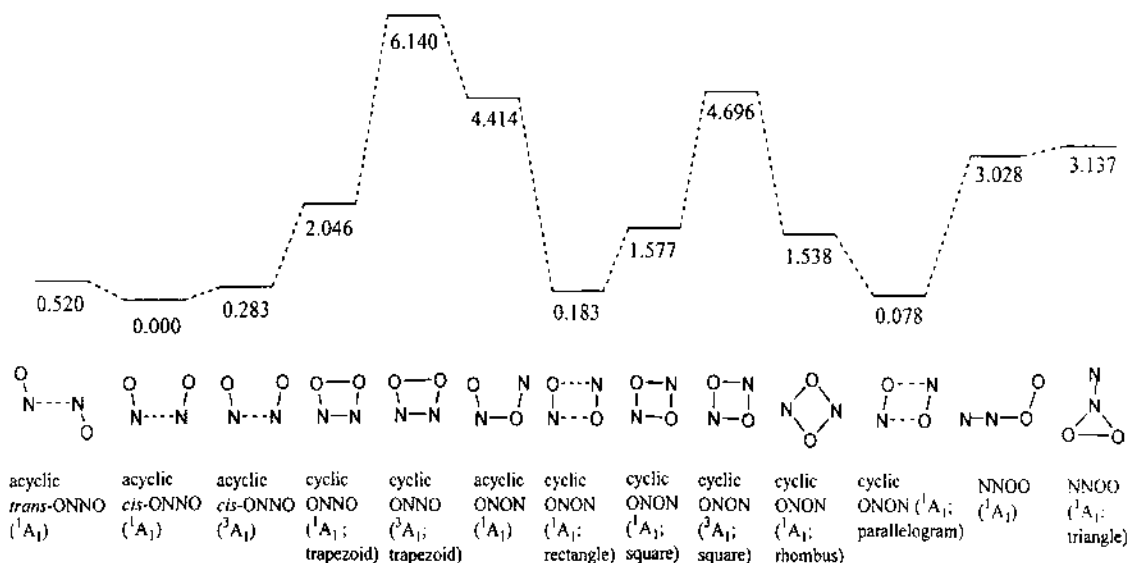


Figure 2. Schematic energy diagram of the structural change from the acyclic conformer to the cyclic. All energies are adiabatic values and are in units of eV.

ble than the *cis*-conformer. In Vladimiroff and Ritchie's calculations,^{36,40} cyclic ONNO is more stable than the others.

The geometrical orientations of the constituent atoms of acyclic *cis*-ONNO, cyclic ONNO, and cyclic NOON are the same, while the distances (R_{NN} , R_{NO} , R_{OO}) and the angle ($\angle ONN$) of the molecules are different from each other. As a result, if the internuclear distance of R_{NN} increases, the geometrical form will be changed from cyclic ONNO to acyclic *cis*-ONNO and acyclic *cis*-NOON. But, acyclic *cis*-NOON is not optimized.

As the internuclear distance of R_{NN} increases, the geometrical form does not convert from cyclic ONNO to acyclic *cis*-ONNO because acyclic *cis*-ONNO (¹A₁) and cyclic ONNO (¹A₁) dissociate into the two different dissociation limits of $[\text{NO}(\tilde{X}^2 I)] + \text{NO}(\tilde{X}^2 I)]$ and $[\text{NO}(\tilde{X}^2 I)] + \text{NO}(\tilde{A}^2 \Sigma^+)]$, respectively. Cyclic ONNO (¹A₁) dissociates into the excited state of NO. The equilibrium bond lengths (R_{NN}) of acyclic *cis*-ONNO (¹A₁) and cyclic ONNO (¹A₁) are 2.218 and 1.275 Å, respectively. The parameters, i.e., R_{NN} , R_{NO} , and the $\angle NNO$ at the equilibrium geometry are listed in Table 1. At the MP2 level, the energy gap between the two isomers is 2.05 eV and the dissociation energy of acyclic *cis*-ONNO (¹A₁) is 0.20 eV. Particularly, at the CCSD(T) level our dissociation energy is 0.08 eV (1.84 kcal/mol). This value is very close to the experimental values.

By the molecular beam techniques, the binding energy of the gaseous acyclic *cis*-ONNO (¹A₁) observed by Kukolich⁵ is about 4 kcal/mol (about 700 cm⁻¹). And the energy (D_0) of the dimer reported by Hetzler *et al.*¹⁹ is 710±40 cm⁻¹ (2.03 ±0.12 kcal/mol). The dissociation energies (D_0) of ONNO in the gas phase using the Fourier transform infrared spectrometer are 639±35 cm⁻¹ (1.83±0.1 kcal/mol) and 764±18 cm⁻¹ (2.18±0.05 kcal/mol).^{26,31} Using the electron impact method, the binding energy estimated by Casassa *et al.*²⁹ is 800±150 cm⁻¹ (2.29±0.43 kcal/mol). Fischer *et al.*²⁸ measured the binding energy of 787 cm⁻¹ (0.098 eV) using the high reso-

lution photoelectron spectra. The heats of formation of ONNO from 2NO analyzed by the infrared spectrum¹⁵ and the far ultra-violet spectrum²³ are 2.45 and 2.24 kcal/mol, respectively. By the above experimental results, the binding energies of acyclic *cis*-ONNO with a very weak N-N bond are in the range of 2-4 kcal/mol.

Recently, at the various DFT levels, the dimerization energies (D_c) of acyclic *cis*-ONNO with the triplet and singlet spin states were calculated by some groups.^{21,46,51,53} In the result of Duarte *et al.*,⁵³ the energies are in the range from 6.12 to 14.62 kcal/mol. Canty *et al.*²¹ calculated the dimerization energies of 9.75 and 10.2 kcal/mol with the BLYP and B3LYP methods, respectively. Jursic *et al.*^{49,51} calculated the energies of 7.63 kcal/mol with the BLYP method, while 2.3 kcal/mol with the *ab initio* MP2 method. The dissociation energies of N₂O₂ with the triplet and singlet states determined by Stirling *et al.*⁴⁶ are 14.9 and 10.7 kcal/mol, respectively. Meanwhile, using *ab initio* MRCI method, the binding energy of acyclic *cis*-ONNO obtained by Roos group⁴⁵ is 3.3 kcal/mol. The previous calculated values are higher than those (the range from 2.0 to 4 kcal/mol) of the experimental results. Our binding energies calculated by the *ab initio* method are relatively close to the experimental values.

The conversion of cyclic ONNO to acyclic *cis*-ONNO or (N₂ · O₂) was examined by the two-by-two configuration interaction calculations.⁵⁴ The barrier height from cyclic ONNO at $R_{NN} = 1.59$ Å, $R_{NO} = 1.24$ Å, and the $\angle NNO = 104$ degrees to acyclic *cis*-ONNO is 59 kcal/mol. And the barrier from cyclic ONNO to the dissociation limits of (N₂ + O₂) is 40 kcal/mol. The reactions from cyclic ONNO to acyclic *cis*-ONNO and (N₂ + O₂) are both exothermic. From the two potential barriers (59 and 40 kcal/mol), we know that the conversion of cyclic ONNO to (N₂ · O₂) takes place faster than that to acyclic *cis*-ONNO. Using *ab initio* SCF method,⁴⁰ the conversion of cyclic ONNO to acyclic *cis*-

ONNO was examined as a function of the bond length of R_{OO} . At the bond length of 1.7903 Å, the geometry was verified as a transition state. The activation energy of the reaction is 29.2 kcal/mol. Estimated potential barrier of the reverse reaction (from acyclic *cis*-ONNO to cyclic ONNO) is 55.9 kcal/mol. The barrier from cyclic ONNO to the dissociation limits of ($N_2 + O_2$) is 22.1 kcal/mol. According to the results, the reactions from cyclic ONNO to acyclic *cis*-ONNO or ($N_2 + O_2$) are also both exothermic. The experimental values²⁰⁻²³ for the reaction are in the range of 57 to 64 kcal/mol.

Conclusions

Geometrical structures for the dimeric form of (NO)₂ from ($NO + NO$) have been calculated using *ab initio* Hartree-Fock (SCF), second-order Møller-Plesset perturbation (MP2), and coupled cluster with single, double, and triple excitations [CCSD(T)] methods with a triple zeta plus polarization (TZP) basis set including diffuse Rydberg basis functions. In addition, the harmonic vibrational frequencies of the species have been analyzed to confirm the potential energy minima of the structures. The geometrical structure of N_2O_2 is divided by the two categories. One is N_2O_2 with an ($N \cdots N$) interaction. In this category, acyclic *cis*-ONNO (C_{2v}), acyclic *trans*-ONNO (C_{2h}), and cyclic ONNO with trapezoidal form are optimized at the MP2 level. But, at the CCSD(T) level, acyclic *trans*-ONNO (C_{2h}) can not be optimized. The other is N_2O_2 with two ($N \cdots O$) interactions. Acyclic *cis*-ONON (C_s) and cyclic ONON of the rectangular (C_{2h}), square (D_{2h}), rhombic (D_{2h}), and parallelogramic (D_{2h}) geometries are also optimized. Acyclic *trans*-ONNO (3A_1), acyclic *trans*-ONON, bicyclic ONON (C_{2v}), and acyclic *cis*- and *trans*-NOON with an ($O \cdots O$) interaction can not be optimized at the MP2 level, while two structures of NNOO formed by the ($O \cdots N$) interaction between O_2 and N_2 are also optimized.

Acyclic *cis*-ONNO (1A_1) is the most stable and cyclic ONNO with trapezoidal form is the least stable. The second stable one is the parallelogramic form of cyclic ONON (1A_1) and the third one is acyclic *cis*-ONNO (3A_1) with the rectangular structure. At the MP2 level, the structures of ONNO and ONON with the singlet state are more stable than those of ONNO and ONON with the triplet. Our results for the relative stabilities of (NO)₂ are different from those of Stirling *et al.* and Duarte *et al.* That is, the energetically most stable isomer is acyclic *cis*-ONNO with a triplet spin state.

The binding energies and the relative energy gaps between the isomers are found to be relatively small. NO has an unpaired electron in the nitrogen atom. A monomer combines with the other and makes an electron pair in the dimeric form of (NO)₂. But, this interaction is very weak like a van der Waals complex. Due to the small binding energy, the formation and dissociation of N_2O_2 from ($NO + NO$) occur easily. As the result, N_2O_2 has many geometrical isomers. Our binding energy of acyclic *cis*-ONNO (1A_1) is 0.2 eV at the MP2 level, while it is 0.08 eV (645 cm^{-1}) at the CCSD(T) level. This value is similar to the experimental

value. In the formation of (NO)₂ from the ($NO + NO$) asymptotes, the energy barrier is found to be very low.

Acknowledgment. The Ministry of Science and Technology (KOSEF, FOTD) and the Ministry of Education (BSRI-98-3409), Korea are acknowledged for financial support.

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