
Theoretical Investigation of *cis*- and *trans*-Nitric Oxide Dimers with Ab Initio and Density Functional Gaussian-Type Orbital Approach

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ABSTRACT

Structures and total energies of the *cis*-NO dimer, the *trans*-NO dimer, and the NO monomer were calculated by ab initio methods (UHF, UMP2, and MP3) and density functional theory methods (LSDA and BLYP) with different basis sets [from 3-21G* to 6-311++(3df,3pd)]. The system is especially hard to model because two NO molecules are weakly associated in a dimer that has a very long N—N bond. The results obtained by different methods are compared and the necessity of correlational methods for studying these systems is discussed. © 1995 John Wiley & Sons, Inc.

Introduction

The most valuable characteristic of computational chemistry is its accuracy and efficiency in predicting the molecular geometry, vibrational frequency, isomer stability, and reaction outcome. These predictions are becoming invaluable in planning organic synthesis, molecular biology, catalyses, and material science. For many organic compounds that include only second-row elements when bond formation-breaking and weak complexation is not involved, Hartree–Fock calculations

produce reasonable geometries, energies, and vibrations [1]. Electron correlation and multi-reference representation is not implemented in Hartree–Fock calculations needed when modeling bond formation-breaking or weakly bonded complexes. Inclusion of correlation typically increases the computational requirements dramatically and seems to be practical only for small molecules [2]. Although in many computational chemistry studies second-order Møller–Plesset perturbation theory as well as quadratic CI calculations have been used routinely [1], there are only a few density functional theory (DFT) [3] studies for loose molecular complexes. That is surprising because there is increasing evidence that DFT offers a promising alternative to the Hartree–Fock approach [4].

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A molecular system that has presented enormous difficulties for theoretical studies in regard to correctly predicting the geometry and energy is the NO (nitric oxide) dimer. The *cis*-isomer is the most stable of all NO species (monomer and *trans*-dimer). There are several different experimental studies concerning the structure of the *cis*-NO dimer. An X-ray crystallographic study [5] determined that the bond distances are 2.18 Å for N—N and 1.15 Å for N—O with a N—N—O angle of 101.3°. The second structure determination is from the IR spectrum in the gas phase. The structural parameters of 1.75 Å for the N—N bond and 90° for the bond angle were obtained by contour analyses of two IR bands [6]. This big discrepancy in the predicted values for the bond distance in solid and gas phases can be attributed to different phases with strong N—N amplitude motion because of its very weak energy. There are two more evaluations of the structural properties of the NO dimer in the gas phase. One of them predicts a N—N bond distance of 2.33 ± 0.12 Å and an angle of $95 \pm 5^\circ$ with a N—O bond assumed to be 1.15 Å [7]. The other, determined on the basis of the rotational frequencies for different isotopic contents of the NO dimer found the N—N distance to be 2.237(2) Å and the N—O bond length 1.161 Å [8]. Consequently, the NO dimer is very difficult to study experimentally as well.

SCF calculations all yield a N—N bond of ONNO which is much too short. These calculations were reviewed in several other places [9]. Correlation treatments generally do better: The most extensive studies until now were performed by Lee et al. [10]. Their calculations at various correlation levels (MP2, CISD, and CCSD) found the N—N bond significantly longer than the previously reported SCF values. Although this is the best calculation to date, it was concluded that an entirely satisfactory theoretical treatment of the ONNO structure has yet to be obtained. Here, we present our theoretical *ab initio* and DFT studies at the correlation level of the structural and energetic characteristics of the NO monomer and its dimers.

Methodology

The *ab initio* program Gaussian 92/DFT [11] was employed to fully optimize the geometries without any symmetry constraints at the unrestricted Hartree–Fock (UHF) [12] with the standard

basis sets, 3-21G*, 6-31G(*d*), 6-311+G(*d,p*), and 6-311+G(2*d,2p*) and, in one case, 6-311++G(3*df,3pd*). At the correlation level, the structures were optimized by applying second- and third-order Møller–Plesset (MP2 and MP3) theory keeping the core electrons frozen (FC) [13]. The geometries of the studied structures were also optimized by the LSDA [14] and BLYP [15] DFT methods with the same basis sets.

Results and Discussion

The equilibrium structural parameters for the *cis*- and the *trans*-NO dimer as well as the NO monomer are presented in Table I.

Although some RHF [9] and MP2 [10] calculations are known, our own will be used for comparison, because the calculation between different methods is performed with the same basis sets. Unrestricted Hartree–Fock calculations at all three applied theory levels predict for the *cis*-NO dimer consistently too small N—N distances (1.606–1.709 Å) in comparison with experimental data in both the solid and the gas phases. The angle (107.2–110.1°) is considerably wider than what was predicted experimentally (Table I). Furthermore, to our surprise, the UHF prediction is actually that the *trans*-isomer is the more stable species, rather than the *cis*-NO dimer [by 2.65 kcal/mol at UHF/6-311+G(2*d,2p*)] (Table II). The greatest disappointment is the prediction that the *cis*-NO dimer is by around 50 kcal/mol less stable than are the two separated NO molecules. Therefore, UHF calculations incorrectly predict both the geometry and the relative stability of the *cis*-NO dimer in comparison with the *trans*-NO dimer and the NO monomer. The geometry of the *trans*-dimer is not available, but on the basis of the previous results, we can assume that the UHF calculations generate geometries and energies for the *trans*-dimer that are far from the “real” structure. These calculations demonstrate an absolute failure of the HF method for the prediction of both the geometry and energy of polarized loose complexes like the NO dimer.

The results of the correlational methods applied in this work are presented in Table I. The N—N distance calculated by UMP2/6-31(*d*), UMP2/6-311+G(*d,p*), and UMP2/6-311+G(2*d,2p*) is 2.238, 2.235, and 2.219 Å, respectively. These values are in excellent agreement with the N—N distance of

2.237 Å determined by microwave spectroscopy for the *cis*-NO dimer in the gas phase [8]. The difference of the distance is below 1%, which is extraordinary considering the fact that the modeling of a very weak molecular associate is carried out. Contrary to our expectations, the error in the prediction of the N—O bond distance and especially the N—N—O angle are much higher. The differences are 2.2% for the N—O bond and

8.2% for the N—N—O angle at the UMP2/6-311+G(2*d*,2*p*) level (Table I). It is quite interesting to point out that the geometry parameters at the MP2 theory level are not very sensitive to the basis set. MP3 seems to give a little better agreement with the experimental data. For example, even though the predicted N—N bond distance for the *cis*-NO dimer at MP3/6-311+G(*d*,*p*) is worse (7.3%) than the one predicted at the MP2 level with the same

TABLE I
Geometries and total energies (au) of the *cis*- and the *trans*-NO dimer and the NO monomer calculated by *ab initio* and DFT method at various basis sets.

Theoretical model	NO monomer		
	<i>E</i>	<i>r</i> (N—O)	
UMP2-FC/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−129.651175	1.137	
UMP2-FC/6-311+G(<i>d</i> , <i>p</i>)	−129.625128	1.135	
UMP2-FC/6-31G(<i>d</i>)	−129.558900	1.143	
UHF/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−129.290288	1.117	
UHF/6-31G(<i>d</i>)	−129.247883	1.127	
UHF/3-21G*	−128.494968	1.150	
BLYP/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−129.927797	1.165	
BLYP/6-311+G(<i>d</i> , <i>p</i>)	−129.925553	1.165	
BLYP/6-31G(<i>d</i>)	−129.878981	1.176	
BLYP/3-21G*	−129.140727	1.219	
LSDA/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−129.256430	1.147	
LSDA/6-31G(<i>d</i>)	−129.209464	1.160	
LSDA/3-21G*	−128.475757	1.198	
Experimental [8]		1.151	

	<i>cis</i> -(NO) ₂			
	<i>E</i>	<i>r</i> (N—N)	<i>r</i> (N—O)	<i>a</i> (N—N—O)
MP3-FC/6-311+G(<i>d</i> , <i>p</i>)	−259.226667	2.074	1.140	99.22
MP3-FC/6-31G(<i>d</i>)	−259.103879	2.119	1.154	96.58
UMP2-FC/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−259.316117	2.219	1.172	91.48
UMP2-FC/6-311+G(<i>d</i> , <i>p</i>)	−259.259781	2.235	1.171	92.10
UMP2-FC/6-31G(<i>d</i>)	−259.132463	2.238	1.187	90.35
UHF/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−258.502204	1.612	1.134	110.10
UHF/6-31G(<i>d</i>)	−258.416569	1.606	1.145	109.72
UHF/3-21G*	−256.924159	1.709	1.174	107.23
BLYP/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−259.867757	2.089	1.165	99.58
BLYP/6-311+G(<i>d</i> , <i>p</i>)	−259.862726	2.100	1.165	99.72
BLYP/6-31G(<i>d</i>)	−259.773293	2.089	1.176	98.36
BLYP/3-21G*	−258.304321	2.049	1.222	98.05
LSDA/6-311++G(3 <i>df</i> ,3 <i>pd</i>)	−258.565305	1.976	1.146	99.01
LSDA/6-311+G(2 <i>d</i> ,2 <i>p</i>)	−258.553965	1.976	1.149	99.16
LSDA/6-31G(<i>d</i>)	−258.462040	1.982	1.161	98.18
LSDA/3-21G*	−257.001705	1.986	1.200	96.49

(continued)

TABLE I (Continued)

	<i>trans</i> -(NO) ₂			
	<i>E</i>	<i>r</i> (N—N)	<i>r</i> (N—O)	<i>a</i> (N—N—O)
UMP2-FC/6-311+G(2 <i>d</i> ,2 <i>p</i>)	-259.298921	2.064	1.170	109.03
UMP2-FC/6-311+G(<i>d</i> , <i>p</i>)	-259.244899	2.101	1.169	109.41
UMP2-FC/6-31G(<i>d</i>)	-259.112417	2.147	1.185	108.91
UHF/6-311+G(2 <i>d</i> ,2 <i>p</i>)	-258.506435	1.514	1.144	108.78
UHF/6-31G(<i>d</i>)	-258.419698	1.508	1.155	108.25
UHF/3-21G*	-256.923391	1.639	1.182	107.20
LSDA/6-31G(<i>d</i>)	-258.451581	1.857	1.168	107.67
LSDA/3-21G*	-256.991201	1.892	1.207	106.89
Experimental [8]		2.237	1.161	99.6

basis set (0.04%), the other parameters, the N—O distance and the N—N—O bond angle, are much closer to the experimental value. The differences are only 1% for the N—O bond and 0.6% for the N—N—O bond angle.

The relative energies of the dimers and the monomer of NO calculated at the MP2 level follow the expected trend (Table III). The binding energy of the dimer is determined experimentally to be around 4 kcal/mol [8]. The UMP2/6-311+(*d*,*p*) is the closest one, but still ~ 2 kcal/mol higher. Although the geometries from the MP2 theory models are not fully in agreement with experimental values, the results demonstrate a necessity of correlation for modeling this kind of system.

Density function theory (DFT) includes correlation interactions and for many cases predicts very accurate geometry [16]. The results of the *cis*- and *trans*-NO dimer calculations are presented in Table I. The structures and energies were calculated by using the localized spin density approximation (LSDA) and nonlocalized functional BLYP as implemented in Gaussian 92/DFT.

TABLE II
Stabilization energy (kcal/mol) of the *cis*-NO dimer in regard to the NO monomer and the *trans*-NO dimer calculated at UHF theory level.

Theoretical model	ΔE_I	ΔE_{II}
UHF/6-311+G(2 <i>d</i> ,2 <i>p</i>)	49.17	2.65
UHF/6-31G(<i>d</i>)	49.70	1.96
UHF/3-21G*	41.27	-0.48

ΔE_I , relative to the NO monomer; ΔE_{II} , relative to the *trans*-NO dimer.

The LSDA gives better geometries and energies of the studied molecules than does the HF methods. For example, the difference for the N—N distance is 27.94%, for the N—O bond, it is 2.3%, and for the N—N—O angle, it is 10.54% at the UHF/6-311+G(2*d*,2*p*). As already stated, the HF calculations with a relatively large basis set give extremely unreliable results. LSDA with the same basis set gives the following results: The difference for the N—N distance is 11.67%, for the N—O bond distance, 1.0%, and for the N—N—O angle, 0.4% from experimental value. That is considerable improvement over the HF methods. Although the N—O bond distance and the N—N—O angle are in excellent agreement with experimental data, the most sensitive structural parameter computationally, the N—N distance, is underestimated. Concerning the energy evaluation, LSDA proves also to be more reliable than is HF; at all applied levels, the *cis*-NO dimer has lower energy than both the *trans*-NO dimer and the NO monomer (Table IV). However, the absolute energies are more than 20 kcal/mol above the experimental value [8]. Although the geometry parameters do not show dramatic changes with the basis set, the larger basis sets seem to give better energies (Table IV).

To improve these results, further calculations were performed with BLYP as a method of nonlocalized DFT. The obtained geometry parameters for the *cis*-NO dimer are presented in Table I. The geometry parameters are much closer to experimental values than are the ones predicted with LSDA. In many aspects, the parameters obtained with BLYP are better or comparable to the ones obtained by MP2 calculations. For example, although the N—N bond distance is underestimated with BLYP, the

TABLE III
Energies (kcal/mol) of the *cis*-NO dimer relative to the NO monomer and the *trans*-NO dimer calculated at UMP2 level.

Theoretical model	ΔE_I	ΔE_{II}
UMP2/6-311+G(2d,2p)	-8.84	-10.79
UMP2/6-311+G(d,p)	-5.98	-9.34
UMP2/3-21G(d)	-9.20	-12.57

ΔE_I , relative to the NO monomer; ΔE_{II} , relative to the *trans*-NO dimer.

angle is much closer to the experimental value [8]. Comparison of the geometry parameters at the MP2, MP3, and BLYP with the same basis set [6-311+G(d,p)] shows that the ones obtained by BLYP are closest to MP3. Thus, the N—N bond distance calculated with BLYP/6-311+G(d,p) varies 6.1%, the N—O bond, 0.3%, and the N—N—O angle, 0.1% from the experimental data. Although MP2/6-311+G(d,p) predicts a much better N—N distance for the *cis*-dimer, all other parameters obtained by BLYP/6-311+G(d,p) are in excellent agreement with experimental results.

The stability of the *cis*-NO dimer in regard to the NO monomer calculated by BLYP is presented in Table V. Although the BLYP energies are much better than the ones obtained with localized DFT (Table IV), they are still around 3–4 kcal/mol higher than the experimental values. The zero-point vibrational energy correction brings the binding energy almost within 1 kcal/mol from the experimental value.

It is interesting to point out that considerable differences in geometry and energies of the studied molecules were obtained going from one method to the other, while these values are relatively constant in the same method with different basis sets.

TABLE IV
Energies (kcal/mol) of the *cis*-NO dimer relative to the *trans*-NO dimer and NO monomer calculated at the LSDA theory level.

Theory model	ΔE_I	ΔE_{II}
LSDA/6-311+G(d,p)	-25.79	
LSDA/6-31+G(d)	-27.05	-6.56
LSDA/3-21G*	-31.49	-6.59

ΔE_I , relative to the NO monomer; ΔE_{II} , relative to the *trans*-NO dimer.

TABLE V
Stabilization energy (kcal/mol) of the *cis*-NO dimer relative to the NO monomer calculated with BLYP.

Theoretical model	ΔE_I	$\Delta E + \text{ZVPE}$
BLYP/6-311+G(2d,2p)	-7.63	-5.75
BLYP/6-311+G(d,p)	-7.29	-5.44
BLYP/6-31G(d)	-9.62	-7.26

Conclusion

In conclusion, the predicted structural parameters and the binding energy for the *cis*-NO dimer differ considerably with the level of theory applied. Using a large basis set without correlation interactions results in total failure in predicting both the geometry and the energy. Localized density function theory slightly improves the obtained values, especially in regard to the geometry but drastically overestimates the NO binding energy. Methods that include correlation interactions like MP2 and MP3 give much better agreement with experimental results. MP2 correctly predicts the bond distances but not the angle. The difference with the experiment is about 6% and the energy is 2 kcal/mol higher. Nonlocalized DFT methods like BLYP improve the prediction of both the geometry and binding energy. The results are comparable to those obtained at MP3 with the same basis sets.

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