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Structure and Force Fields of the Isomers of Dinitrogen Dioxide

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Abstract: The fully optimized geometries of the cis and trans isomers of dinitrogen dioxide, $(NO)_2$, have been calculated ab initio. No other minima in the potential surface corresponding to other possible stable isomers could be found. Vibrational force fields, compliance constants, and vibrational frequencies were computed. The localized orbital wave functions, structures, and force fields all show the importance of lone pair delocalization in weakening the N-N bond and of a weak O···O bond in stabilizing the cis form.

Although the nitric oxide dimer has been observed by many types of experiments,[2-10] its structure is not well known, the only two determinations being an x-ray study of the solid[10] and a gas phase infrared band shape analysis.[6] These two structure determinations differ greatly from each other and have large experimental uncertainties.[11,12] Two previous ab initio calculations using minimum basis sets[13,14] yielded results disagreeing both with each other and with experiment, the most important error being the failure to reproduce the uncommonly long N-N bond. We therefore decided to extend our preliminary studies which used a double ζ basis set[15] to a systematic calculation of the structures, force fields, and relative stability of the isomers of $(NO)_2$.

Method of Calculation

The SCF calculations employed the FORCE method of Pulay,[16] by which the forces acting on the atoms are calculated analytically as derivatives of the energy with respect to the coordinates. All calculations, unless otherwise stated in the discussion of the results, were done with a (7,3) basis set of Gaussian lobe functions contracted to ⟨4,2⟩.[17] The resulting canonical molecular orbitals were transformed into localized orbitals using the criterion of Boys.[18] The relative energies of the isomers found to be stable with this basis set were also calculated using (9,5), (9,5,1) and (10,6,1) basis sets[19] contracted to ⟨4,2⟩, ⟨4,2,1⟩, and ⟨5,3,1⟩.

Structures of the Stable Isomers

Only two isomers of $(NO)_2$ having minima in the energy surfaces were found, the planar cis and the planar trans species with energies of −257.988 379 6 and −257.986 168 8 au, respectively. Various other structures were calculated. A peroxide structure, Figure 1a, with O–O = 1.48 Å, N–O = 1.16 Å, and ∠OON = 107° was 87 kcal above the cis form. The cyclic structure of ref 14, shown in Figure 1b, was 48 kcal less stable than the cis form. A rectangular structure, Figure 1c, with N–O = 1.77 Å and N=O = 1.16 Å was 65 kcal less stable than the cis structure. All of these forms have very large forces

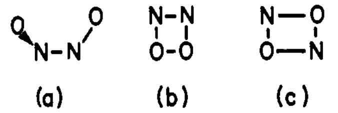

Figure 1. Calculated unstable geometries of $(NO)_2$.

Table I. Structures of $(NO)_2$ Isomers[d]

	Ab initio values			Exptl values	
	Trans	90°	Cis	Infrared[a] gas phase	X-ray[b] solid
N-N	1.686	1.694	1.768	~1.75	~2.18
N=O	1.170	1.173	1.162	1.15[c]	1.12
∠NNO	107.7	108.9	106.5	~90	~101

[a] C. E. Dinerman and G. E. Ewing, *J. Chem. Phys.*, **53**, 626 (1970). [b] W. N. Lipscomb, F. E. Wang, W. R. May, and E. L. Lippert, *Acta Crystallogr.*, **14**, 1100 (1961). [c] Assumed. [d] Bond lengths in Å and angles in degrees. Internal accuracy of ab initio values better than 0.001 Å and 0.1°.

acting on the atoms, showing that they are not near a minimum in the energy surface. The forces on the x-ray structure of ref 10 pull it toward the cis form. The energies of both the cis and trans forms increase when they are tilted 5 or 10° out of plane, showing that both planar forms represent energy minima. It is thus highly unlikely that there are any other stable isomers. The possible third isomer observed in matrix isolation by Guillory and Hunter[20] is probably a site-affected cis form.

The calculated structures of the cis and trans isomers, as well as that of the rotamer with a dihedral angle of 90°, are shown in Table I. The cis N-N bond length is close to the infrared value but is far shorter than the x-ray result. It is near the electron diffraction value for N_2O_4 (1.782 Å)[21] and somewhat shorter than the microwave value for N_2O_3 (1.864 Å).[22] Judging by the results of Ahlrichs and Keil[23] on N_2O_4, the calculated N-N bond lengths may be underestimated by as much as 0.1 Å. The cis NNO angle is close to the corresponding angle in N_2O_3 (105.1°).

Various effects have been suggested as the cause of the very long N-N bond in N_2O_4, which is the most studied of these unusual oxides. Brown and Harcourt[24] proposed delocalization of oxygen lone pairs into an antibonding N-N σ orbital. Figure 2 shows that the ab initio results provide support for such an explanation in $(NO)_2$ also. The other oxygen and the nitrogen lone pairs are delocalized in the same manner, making the N-N bond weak in both the cis and the trans isomers.

Several investigators[23,25] have suggested a delocalization of the N-N σ bond to form a weak bond between the oxygen atoms. This suggestion can also be investigated making use of the ab initio results. The plot of the localized orbital corresponding to the N-N bond in Figure 3 shows that this weak O···O bond is indeed present in cis $(NO)_2$. The resulting stabilization is the reason for the planar cis being the most stable form. The bonding interaction is also shown by an O-O overlap population of +0.06. By far the largest part of the electron density is, however, concentrated between the nitrogen atoms, the maximum value being about 0.30 as compared with only 0.015 between the oxygen atoms, showing that the delocalization is not responsible for the very long N-N bond. This is also demonstrated by the fact that the N-N bond in the trans form is unusually long too, although no O···O bond is present.

The localized N-N orbital of Figure 3 is qualitatively similar to the plot of the highest occupied canonical orbital of N_2O_4 in ref 23. It is, however, difficult to estimate delocalization on the basis of canonical orbitals, which are usually strongly delocalized. Use of the highest occupied canonical orbital of cis $(NO)_2$ would have indicated a much stronger delocalization than that shown by the localized orbital. The O···O bond is probably the main reason for the planarity of the cis form. The reason for the planarity of the trans form may be a weak N-N π bond (overlap population +0.01).

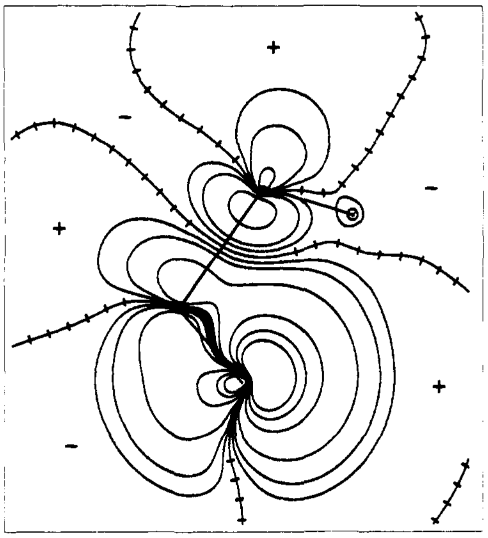

Figure 2. Localized molecular orbital corresponding to one of the oxygen lone pairs in the cis form. The zero contour is hashed.

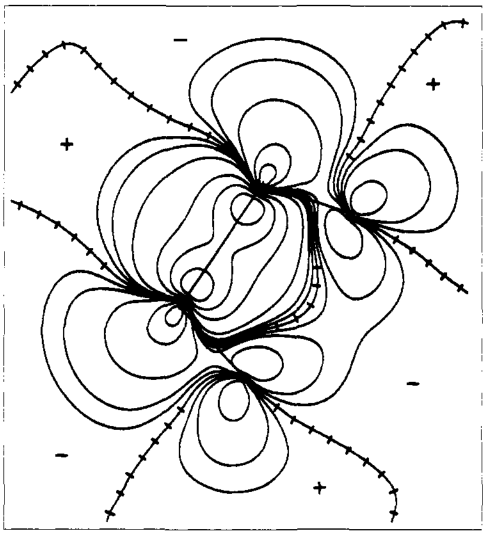

Figure 3. Localized molecular orbital corresponding to the N-N bond in the cis form. The zero contour is hashed.

It seems surprising that the cis isomer would have an N-N bond 0.08 Å longer than the trans. One explanation could be that the cis O···O distance of 2.43 Å represents an energy minimum, and a smaller N-N distance would, for unchanged valence angles, push the oxygen atoms too close together. Consideration of the molecular force fields tends to support this idea, as is shown below.

Force Fields

Table II contains the force and compliance constants calculated for the cis and trans isomers. The compliance constants are included since they provide an adiabatic measure of bond strengths corresponding to a minimum energy path on the potential surface, whereas force constants correspond to the physically unrealistic deformation of one coordinate while keeping all others constant.[26] Furthermore, the compliance constants are invariant to the coordinate set chosen, in contrast

Table II. Force and Compliance (in parentheses) Constants of Cis and Trans $(NO)_2$[a]

			Cis			
N-N	2.292 (0.621)					
N=O	0.988 (−0.0419)	14.497 (0.0739)				
N=O	0.988 (−0.0419)	1.068 (−0.0040)	14.497 (0.0739)			
∠NNO	0.817 (−0.208)	0.432 (−0.0054)	−0.617 (0.0383)	2.173 (0.551)		
∠NNO′	0.817 (−0.208)	−0.617 (0.0383)	0.432 (−0.0054)	0.303 (−0.0079)	2.173 (0.551)	
τ						0.067 (14.93)
			Trans			
N-N	1.544 (0.711)					
N=O	0.996 (−0.0486)	13.474 (0.0790)				
N=O′	0.996 (−0.0486)	1.001 (−0.0021)	13.474 (0.0790)			
∠NNO	0.073 (−0.0068)	0.538 (−0.0276)	0.203 (0.0064)	1.576 (0.849)		
∠NNO′	0.073 (−0.0068)	0.203 (0.0064)	0.538 (−0.0276)	0.777 (−0.417)	1.576 (0.849)	
τ						0.041 (24.39)

[a] Stretching constants in mdyn/Å. Bending constants in (mdyn Å) / rad^2. Compliance constants in reciprocal units.

Table III. Vibrational Frequencies of Cis and Trans $(NO)_2$ (cm^{-1})

	Calcd				Obsd[a]	
	Trans		Cis		Trans	Cis
1	122	A_u	190	A_2		b
2	362	B_u	439	A_1		
3	426	A_g	635	A_1		
4	933	A_g	768	B_1		
5	1685	B_u	1709	B_1	1764	1776
6	1796	A_g	1858	A_1		1870

[a] W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **50**, 3516 (1969). [b] Various low-lying frequencies reported in A. L. Smith, W. E. Keller, and H. L. Johnston, *ibid.*, **19**, 189 (1951), are not included since later work has failed to reproduce the results.

to force constants, and the interaction compliance constants are directly related to the interaction displacement coordinates $(i)_j$ (the change in coordinate i as coordinate j is displaced one unit), whereas the interaction force constants are not. The only known experimental force constant values are 14.65 for the cis N=O stretch and 0.75 for the N=O, N=O interaction constants,[20] in very good agreement with the ab initio results.

All the cis force constants are larger than the corresponding trans values. This observation can be explained by the weak O···O bond that makes the cis a more tightly bound molecule and makes torsion more difficult.

The N=O bond lengths and force constants are close to those calculated for cis and trans HNO_2 by the same method (1.179 and 1.169 Å, 13.6 and 14.6 mdyn/Å),[27] and they also correspond closely to the empirical relationship between bond lengths and force constants.[28] Of the N-N bonds, however, only the trans form falls close to the empirical curve,[29] the cis force constant being much too high, nearly 50% larger than the trans although the bond is considerably longer. This apparent paradox is resolved by looking at the compliance constants. The reciprocals of the N-N compliants (the relaxed force constants) are 1.61 for the cis and 1.41 for the trans. The large difference between the normal and relaxed cis force constants shows that the N-N stretch is accompanied by large changes in other coordinates. The signs and magnitudes of these changes can be estimated by calculating the minimum energy coordinate from the compliance constants:[30]

$$\text{cis } \mathcal{R}_{N\text{-}N} = \Delta R_{N\text{-}N} - 0.068(\Delta R_{N=O} + \Delta R_{N=O'}) - 0.335(\Delta\alpha_{NNO} + \Delta\alpha_{NNO'})$$

$$\text{trans } \mathcal{R}_{N\text{-}N} = \Delta R_{N\text{-}N} - 0.068(\Delta R_{N=O} + \Delta R_{N=O'}) - 0.010(\Delta\alpha_{NNO} + \Delta\alpha_{NNO'})$$

In the cis form, the N-N stretch is accompanied by large changes in the NNO angles. The net result is that a change of 0.10 Å in the N-N bond length only leads to a change of 0.02 Å in the O···O distance. The large value of the cis force constant is thus caused by the weak O···O bond. This result also lends support to the idea that the cis O···O distance corresponds to a minimum in the interaction energy.

The calculated vibrational frequencies are shown in Table III. The cis force field reproduces the experimental observation that the symmetric N=O stretch has a higher frequency than the asymmetric. The force field also reproduces all the experimental isotope shifts[20] within a few reciprocal centimeters.

Relative Stability and Rotational Barrier

The cis form is correctly calculated with the (7,3) basis set to be more stable than the trans (by about 1.4 kcal). The energy difference turns out to be very sensitive to the choice of basis set, however, with larger basis sets predicting the trans form to be more stable, in disagreement with experiment. The results obtained are summarized in Table IV. It is apparent that the difference in energy of the two forms is not well determined by this approach. While molecular geometries and force fields appear to be well determined within the Hartree-Fock approximation, it is highly likely that configuration interaction must be considered to obtain an accurate numerical value for the energy difference between the two forms of N_2O_2.

Table IV. Calculation of $(NO)_2$ Cis-Trans Energy Difference with Expanded Basis Sets

Basis	$-E$(cis), au	$-E$(trans), au	ΔE, kcal/mol
$(9,5) \rightarrow \langle 4,2 \rangle$	258.250 09	258.254 73	−2.91
$(9,5,1) \rightarrow \langle 4,2,1 \rangle$	258.432 29	258.432 41	0
$(10,6,1) \rightarrow \langle 5,3,1 \rangle$	258.475 71	258.478 39	−1.68

With the (7,3) basis set, the cis rotational barrier is calculated to be 5.0 kcal and the trans barrier 3.6 kcal. The experimental estimates of the barriers in N_2O_3 and N_2O_4 are 1[31] and 2-3[32] kcal, so the ab initio barriers are quite probably too high, as was also the ab initio N_2O_4 barrier.[23]

Conclusion

The nitric oxide dimer has been shown to have two preferred conformations: planar cis and planar trans. The wave functions, structures, and force fields show the importance of lone pair delocalization in weakening the N-N bond and a weak O···O bond in stabilizing the cis form. The calculations form a basis for possible experimental observation of the low-lying vibrations involving the interesting N-N bond and of a direct determination of the structures by microwave spectroscopy (cis dipole moment of 0.6 D) or electron diffraction.

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Vapor Phase Hydrogen Bonding of 2,2,2-Trifluoroethanol with Acetone

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Abstract: Thermodynamic data for the 1:1 hydrogen bonded complex of trifluoroethanol with acetone have been obtained from vapor density measurements at 25, 35, and 45 °C. The equilibrium constant for formation of the 1:1 vapor complex at 25 °C is 47.3 M^{-1}. $\Delta E°$ for complex formation is −6.79 kcal/mol. A comparison of these thermodynamic data with previously reported data for the 1:1 complex in CCl_4 solution shows that the complex is significantly more stable in the vapor phase than in CCl_4 solution. With the aid of literature data the complete thermodynamic cycle for transfer of monomers and the 1:1 complex between vapor and CCl_4 has been constructed to illustrate solvation effects on the trifluoroethanol-acetone complex.

There have been literally hundreds of published reports of molecular orbital calculations of the energy of formation of hydrogen bonded complexes. Yet, there are almost no experimental vapor data with which to compare the theoretical results. In the entire chemical literature there are no more than ten publications which claim to give reliable thermodynamic data for 1:1 hydrogen bonded complexes in the vapor phase. Good thermodynamic data for vapor phase complexes are important not only because they offer experimental energies which can be directly compared with the theoretical calculations but also because they give a firm foundation on which to base considerations of solvent effects on hydrogen bond formation.[1]

Previous reports from this and other laboratories have shown that thermodynamic constants for hydrogen bonding and charge-transfer reactions are generally dependent upon the medium in which reaction occurs.[2] In particular, no solvent has been found which is truly inert in comparison with the gas phase as a reference medium. For example, thermodynamic data for hydrogen-bonded complexes which have been studied in both vapor and condensed phases indicate that carboxylic acid dimers[3,4] and methanol-amine complexes[1,5] are less stable in relatively inert solvents than in the vapor phase.[6] Moreover, in the case of most hydrogen-bonded complexes, stabilities decrease as the solvent is varied from aliphatic hydrocarbon, to chlorinated or aromatic hydrocarbon, to polar liquid.

Many workers continue to hope, however, that solvent effects on complex formation equilibria will nearly cancel as the