J. Am. Chem. Soc. **1983**, *105*, 745–748

N–N Bond in Dinitrogen Tetroxide

Charles W. Bauschlicher, Jr.,[†,‡] Andrew Komornicki,[*‡] and Bjorn Roos[§]

Contribution from Polyatomics Research Institute, Mountain View, California 94043, and Department of Physical Chemistry 2, Chemical Center S220, Lund, Sweden.

Received June 21, 1982

Abstract: Dinitrogen tetroxide is a weakly bound dimer of NO_2, whose geometrical and electronic structure has been the subject of numerous experimental and theoretical investigations over the past 30 years. The molecule is characterized by two NO_2 groups whose geometrical parameters are virtually identical with those found in free NO_2 and a very long, 1.78 Å, N–N bond. Previous calculations have been unable to reproduce this geometrical structure. We report here the results of a series of CAS–SCF calculations which employ a double-ζ plus polarization quality basis set. Our most extensive CAS–SCF calculations which include 18 electrons correlated in 12 valence orbitals not only reproduce the known experimental geometry but also show that a proper description for N_2O_4 is associated with a correct description of the individual NO_2 fragments.

Introduction

The chemistry of the nitrogen oxides plays an important role in the ozone balance of the stratosphere. It is now well known that nitrous oxide is converted to nitrogen dioxide upon combination with ozone. This cycle[1] is also responsible for the formation of NO_3 and N_2O_5. In this study we have chosen to investigate the molecule N_2O_4 as a first step in our attempt to understand the nature of the bonding in these chemically interesting and environmentally important molecules.

Dinitrogen tetroxide is a weakly bound dimer of NO_2 whose geometrical structure has been the subject of numerous experimental and theoretical investigations over the past 30 years.[2–4] The molecule is characterized by two NO_2 groups whose geometrical parameters are virtually identical with those found in free NO_2. The most prominent geometrical feature found in N_2O_4 is the exceptionally long N–N bond as well as its planar structure. This geometry is based on a series of both gas-phase electron diffraction and solid-state neutron diffraction experiments. It is now generally agreed[4] that the N–N bond length lies between 1.756 and 1.782 Å. This is in stark contrast to the N–N bond length found in hydrazine,[5] N_2H_4, whose N–N bond is known to be 1.47 Å, and tetrafluorohydrazine, whose bond is also known to be short.[6] This unusual geometry has prompted a number of explanations in the literature. Smith and Hedberg had suggested[2] that the molecule was held by a "π only" bond, while Pauling pointed out the need for an N–N σ bond which would accommodate the two open-shell electrons centered on the nitrogen atoms from the two NO_2 fragments.[7]

There have also appeared several theoretical investigations of this molecule. Howell and Van Wazer performed a series of SCF calculations[8] where they compared the orbitals and the electronic structure of N_2O_4 and B_2F_4. They employed a moderate size sp basis set which predicted an N–N bond of 1.67 Å. Their analysis focused on the planarity of N_2O_4 which they ascribed primarily to a 1,4 σ interaction between the oxygen atoms. Ahlrichs et al. performed a more extensive series of calculations[9] where both an sp basis set and one with d-type polarization functions centered on the nitrogen atoms were employed. The SCF wave functions predicted an N–N bond of 1.67 and 1.59 Å with these two basis sets, respectively. There has also appeared another ab initio investigation where N_2O_4 was described with a one-pair GVB wave function[10] employing a split-valence 4-31G basis.[4] This study predicted an N–N bond length of 1.80 Å in apparent agreement with experiment. There is considerable similarity between these recently published results of Kvich et al.[4] and those found by Ahlrichs where the calculations were extended to include the correlation of the N–N σ bond electron pair. The previous investigation of Ahlrichs had shown that this one-pair treatment predicts an N–N bond length of 1.81 Å with an sp basis set, and 1.67 Å once d-type polarization functions are included on the nitrogen atoms. Thus for a larger basis set the inclusion of σ correlation lengthens the bond by about 0.1 Å relative to the SCF predicted value, or half of the 0.2 Å discrepancy between SCF and experiment. It is clear that σ correlation is only responsible for part of the SCF error. It seems unlikely that such a treatment could explain the planar structure, since it ignores correlation within the π system which we would expect to be the primary mechanism which stabilizes the planar structure. Based on these earlier investigations it becomes clear to us that a proper description of N_2O_4 must include a balanced description of both the σ and π framework for a consistent description of the geometry of N_2O_4 in terms of its electronic structure.

Computational Details

Our calculations are based on a standard double-ζ polarized basis formed from the Huzinaga (9s5p1d) primitive set, and contracted to a [4s2p1d] basis as suggested by Dunning.[11] The exponents for the polarization functions were chosen to be $\alpha(O) = 0.9$ and $\alpha(N) = 0.8$. We have also included some calculations with a split-valence 4-31G basis[12] and have extended these to the split-valence polarized 6-31G* basis where polarization functions were placed only on the nitrogen atoms. The latter set can be described as a (10s4p1d) primitive set on nitrogen contracted to a [3s2p1d] basis.

The MC-SCF approach used in this work is based on the CAS–SCF procedure.[14] In this approach the orbitals are classified as either inactive, active, or secondary. The inactive orbitals are doubly occupied in all configurations. Within the active space electrons are distributed in all possible ways maintaining spacial

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[†] NASA Ames Research Center, Moffett Field, CA 94035.

[‡] Polyatomics Research Institute, 1101 San Antonio Rd., Suite 420, Mountain View, CA 94043.

[§] Chemical Center, Lund.

(1) P. Connell and H. S. Johnston, *Geophys. Res. Lett.*, **6**, 553 (1979).

(2) D. W. Smith and K. Hedberg, *J. Chem. Phys.*, **25**, 1282 (1956).

(3) (a) J. S. Broadley and J. M. Robertson, *Nature (London)* **164**, 915 (1949); (b) P. Groth, *Acta Chem. Scand.*, **17**, 2419 (1963); (c) B. S. Cartwright and J. H. Robertson, *Chem. Commun.*, 82 (1966); (d) B. W. McClelland, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, **56**, 4541 (1972).

(4) A. Kvick, R. K. McMullan, and M. D. Newton, *J. Chem. Phys.*, **76**, 3754 (1982).

(5) Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Jpn.*, **33**, 46 (1959).

(6) M. M. Gilbert, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, **56**, 1691 (1972).

(7) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, NY, 1960, p 349.

(8) J. M. Howell and J. R. Van Wazer, *J. Am. Chem. Soc.*, **96**, 7902 (1974).

(9) R. Ahlrichs and F. Keil, *J. Am. Chem. Soc.*, **96**, 7615 (1974).

(10) P. J. Hay, W. J. Hunt, and W. A. Goddard, *J. Am. Chem. Soc.*, **94**, 8293 (1972).

(11) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

(12) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(13) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972); *Mol. Phys.*, **27**, 209 (1974).

(14) B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.*, **48**, 157 (1980); P. E. M. Siegbahn, J. Almlof, A. Heiberg, and B. O. Roos, *J. Chem. Phys.*, **74**, 2381 (1981); P. E. M. Siegbahn, A. Heiberg, B. O. Roos, and B. Levy, *Phys. Scr.*, **21**, 323 (1980).

0002-7863/83/1505-0745$01.50/0

Table I. Summary of N_2O_4 Results

	4-31G SCF	6-31G* SCF	DZP 18 e CAS	DZP 10 e CAS	DZP 26 e CI(SD)	exptl[b]	(NO_2, exptl)[c]
N-N, Å	1.632	1.583	1.80	1.58	1.62	1.782	-
N-O, Å	1.188	1.168	1.188	1.188[a]	1.188[a]	1.190	1.193
O-N-O, deg	133.3	132.8	133.3[a]	133.3[a]	133.3[a]	135.4	134.1

[a] Fixed at 4-31G optimum geometry. [b] Reference 3d. [c] G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand, New York, 1966.

and spin symmetry. We are further able to restrict the number of electrons in a given symmetry group of orbitals. The resulting wave function is thus a product of two full CI expansions, each within an invariant subspace.

The orbital optimization was performed with a modified first-order process, which utilizes a simplified super-CI technique where all super-CI matrix elements are expanded in terms of an average Fock operator.[15] Convergence in all cases was found to be quite satisfactory, requiring usually six to eight iterations to yield a maximum Brillouin matrix element to be less than 1×10^{-4}.

The calculations were performed with the following programs. The initial SCF calculations on N_2O_4 which included gradient geometry optimization were performed with the GRADSCF program system.[16] The MC-SCF and CI(SD) calculations were performed with the program system MOLECULE-SWEDEN.[17] All of the calculations were carried out on either the Control Data 7600 or the CRAY-1S computers at NASA Ames Research Center.

NO_2. The molecule N_2O_4 can be viewed as a weakly bound dimer of NO_2. Current experimental estimates for the dissociation[18] energy range from 12.7 to 13.6 kcal. We therefore chose to perform a series of both SCF and CAS-SCF calculations on the fragment NO_2. The ground $^2A_1$ state of NO_2 can nominally be described as arising from the configuration: . . . $5a_1^2 1a_2^2 4b_2^2 6a_1^1$. In all these calculations we have employed the DZP basis described in the previous section. In our CAS-SCF wave function the nitrogen 1s and the oxygen 1s and 2s orbitals were treated as the inactive orbitals and the nitrogen 2s,2p and the oxygen 2p orbitals were treated as the active orbitals. Our wave function therefore contained 13 electrons distributed in 10 valence orbitals. We have also imposed the further constraint that there always be four π and nine σ symmetry electrons in all configurations. The total number of symmetry adapted configurations was 2544.

At the SCF level we found the open-shell $6a_1$ orbital has 0.57 electrons on nitrogen and 0.43 electrons distributed on the two oxygen atoms. This description is best seen by viewing NO_2 as a mixture of three neutral resonance structures and two ionic resonance structures, as seen in Figure 1. The presence of the ionic structures can be seen by the net positive charge of 0.43 electrons on the nitrogen atom as calculated on the basis of a Mulliken population analysis. At the CAS-SCF level we found the net charge on the nitrogen atom was reduced to 0.29 electrons, and the open-shell σ orbital character on nitrogen was reduced to 0.51 electrons. The primary configuration which we found responsible for this shift in electron density was seen to involve a $(\pi-\pi^*) \times$ (O lone pair (lp) $\rightarrow$ open shell) excitation which we found to be even more important than the $\pi^2 \rightarrow \pi^{*2}$ correlating excitations. Thus we found that the description at the CAS-SCF level reduced the importance of the ionic structures (4) and (5) and at the same time increased the importance of the neutral structures (1) and (2). We also noted that valence structures (1) and (2) cannot be used to form an N-N σ bond in N_2O_4. Their importance in NO_2 at the CAS-SCF level indicated that they could also play an important role in the valence description of the bonding in N_2O_4. It is therefore clear that a meaningful treatment of N_2O_4 must include all of the important configurations which balance the resonance structures of NO_2. These include the σ open-shell orbital which will form the N-N bond, the π orbitals, as well as the oxygen lone-pair orbitals.

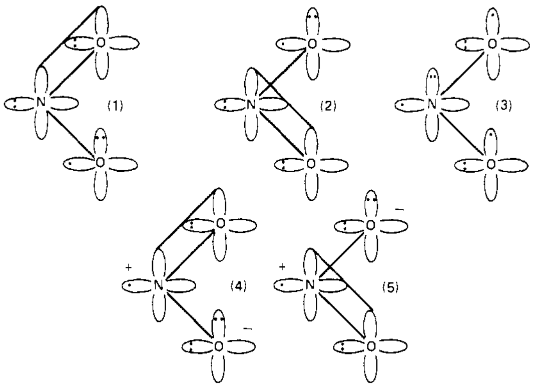

Figure 1. Depicted are the five resonance structures of NO_2. Structures 1, 2, and 3 are the neutral valence structures while structures 4 and 5 are ionic. The total number of electrons represented is 13. (The nitrogen 1s and the oxygen 1s and 2s orbitals are not explicitly shown.) Each of the bonds depicted represents two electrons plus the seven dots for the remaining electrons.

We would like to note that there does not exist a one to one mapping between configurations and resonance structures. The SCF reference configuration itself represents a combination of several resonance structures. An example of this is achieved by delocalizing the orbitals such that the open shell is part of both the nitrogen and oxygen atoms. We can however infer from the resonance structures which electrons should be more highly correlated. We can also infer from such overall properties as charge density and open-shell character on the nitrogen atom the relative importance of the various resonance structures. Therefore it is from the analysis of the CAS-SCF results, as well as the resonance structures, that we conclude that the oxygen atom lone-pair electrons must be included in the active space of the CAS-SCF wave function. Thus the resonance structures serve as a useful guide which helps us to understand this system, and as a vehicle which helps to determine the active space in other systems.

N_2O_4. The molecule N_2O_4 contains 46 electrons. When two NO_2 groups are brought together, the resulting closed-shell singlet ground state can be described within the SCF model as 23 doubly occupied orbitals which, within D_{2h} symmetry, were designated as follows: $6a_g$, $1b_{1g}$, $4b_{2g}$, $1b_{3g}$, $1a_u$, $5b_{1u}$, $1b_{2u}$, and $4b_{3u}$. If we remove the six doubly occupied orbitals which form the 1s core space we are left with 34 electrons in the valence space.

We first chose to perform a series of preliminary calculations at the SCF level. The geometry was optimized with the gradient methods available in the GRADSCF program system.[19] These initial

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(15) B. O. Roos, *Int. J. Quantum Chem.*, **S14**, 175 (1980).

(16) GRADSCF is a gradient program system developed by A. Komornicki at Polyatomics Research and funded by NASA Ames Research Center.

(17) Sweden is a vectorized SCF, MCSCF, direct CI program system written by P. E. M. Siegbahn, B. O. Roos, and C. W. Bauschlicher. MOLECULE is a Gaussian integral program written by J. Almlof of the University of Uppsala, Sweden. For a description of MOLECULE see J. Almlof, "Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry", Max-Planck Institute, Munich, 1973, p 14.

(18) R. G. Snyder and I. C. Hisatsune, *J. Mol. Spectrosc.*, **1**, 139 (1957); I. C. Hisatsune, *J. Phys. Chem.*, **65**, 2249 (1961).

(19) A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield, and M. Conrad, *Chem. Phys. Lett.* **45**, 595 (1977); A. Komornicki, C. E. Dykstra, M. A. Vincent, and L. Radom, *J. Am. Chem. Soc.*, **103**, 1652 (1981); A. Komornicki, J. D. Goddard, and H. F. Schaefer, *ibid.*, **102**, 1763 (1980).

calculations were carried out with the split-valence and the split-valence polarized basis sets described above. A summary of these results is presented in Table I. Our results are in agreement with previous calculations at this level, where we found the N–O bond length and the O–N–O angle to be in quite good agreement with experiment, while the N–N bond is far too short. We also noticed the well-known trend that calculations which include polarization functions at the SCF level tend to predict bonds which are shorter than those found in experiment, or with basis sets which only contain sp basis functions. In this case the effect is quite pronounced, in that the N–N bond shortens by about 0.05 Å. The results at this level point out the difficulty of an SCF description which predicts a bond which is 0.2 Å too short. Since the major discrepancy between theory and experiment lies with the N–N bond we chose to freeze both the N–O bond length, as well as the O–N–O angle at the 4-31G SCF values for all subsequent calculations and focus on only the N–N bond.

At the correlated wave function level we employed the same DZP basis as that used on NO_2. At this level we would ideally like to have performed the same level of calculation on N_2O_4 as we had carried out on NO_2. However, a full active space CI with this large number of electrons and orbitals becomes prohibitively large. We therefore had to reduce the CI expansion to more tractable size. We first observed that within the σ framework the N–O bonds were well described by SCF orbitals and could therefore be included in the inactive space. This partition then defined the active space as consisting of 18 electron in 12 orbitals. We further partitioned the full CI space into σ and π components. The N–N bonding and antibonding orbitals are classified as a_g and b_{1u}. There are six π-type orbitals in the active space designated as b_{1g}, $2b_{3g}$, $2b_{2u}$ and a_u. The four remaining orbitals which describe the oxygen lone pair orbitals and are designated as a_g, b_{2g}, b_{3u}, and b_{1u}. Our final wave function thus consisted of a product of a full CI of the eight π electrons in six orbitals, times a full CI of the ten σ electrons in six orbitals which resulted in a CI expansion of 976 symmetry adapted configurations.

The decision to include the N–O bonding orbitals into the inactive space was dictated by the fact that the orbitals are easily identified as to their character. When orbitals are equivalent some mixing occurs, but once they are made inequivalent they become extremely localized in character. For example, the N–N σ bond has only 0.002 electrons on the oxygen atom (18-electron CAS–SCF) and the oxygen lone pair orbitals have the sum of only 0.02 oxygen 2s character (18-electron CAS–SCF), while the bonding orbitals show more than 1.5 oxygen 2s electrons.

At this level the N–N bond length was optimized and found to be 1.80 Å. We also found that the dissociation energy to form two NO_2 fragments to be 7 kcal. Although our predicted bond length is slightly too long and the D_e is too low when compared with experiment, we consider our results to be consistent with the expected behavior of the CAS–SCF model, and also to be consistent with prior experience.[14]

For such weak bonds the difference between r_e and r_0 can be fairly large. Thus the error inherent in the CAS–SCF result is actually larger than the 1.8 Å vs. 1.782 Å difference might suggest. The experimental r_e is probably closer to 1.75 Å as originally suggested by Hedberg. Previous experience leads us to expect that a CAS–SCF wave function will predict larger bond length errors for weak bonds than for strong bonds. However, our goal here is to obtain a qualitative understanding of the bonding and not a quantitative bond length. Better quantitative agreement with experiment can only be expected with a substantially larger AO basis set, and a more extensive level of correlation, e.g., by performing a multireference singles and doubles CI calculation based on the present CAS–SCF results.

We can now turn to an examination of this CAS–SCF wave function and compare it to the previously found results on NO_2. We summarize the most important configurations found in Table II, and present the orbital occupations in Table III. An examination of these results shows that the σ^2–σ^{*2} configuration comprises 3.8% of the wave function, while the π^2–π^{*2} configurations, all with coefficients greater than 0.05, account for 5.5% of the wave function. We also find that there appears a series of configurations which are the product of singles of the type (lp–σ^*) × (π–π^*). These configurations we find to be equivalent to those found in NO_2 where we found configurations of the type (lp–open shell) × (π–π^*) to be very important. Finally, we consider it important to note that the SCF configuration accounts for only 81.6% of the wave function and that 6.7% of the wave function is contained in the sum of configurations which have coefficients less that 0.05.

Table II. Important Configurations for N_2O_4 CAS–SCF Wave Function CI Coefficients

config type	18-electron 6 π, 2 σ, 4 lp	10-electron 6 π, 2 σ
SCF	0.903	0.926
(π–π^*) × (π–π^*)	0.182	0.218
(σ^2–σ^{*2})	0.194	0.141
(π^2–π^{*2})	0.105	0.131
(π^2–π^{*2})	0.103	0.128
(lp–σ^*) × (π–π^*)	0.083	
(lp–σ^*) × (π–π^*)	0.089	
(lp–σ^*) × (π–π^*)	0.075	
(lp–σ^*) × (π–π^*)	0.068	

Table III. N_2O_4 CAS–SCF Orbital Occupations

orbital	type	18 electron		10 electron
a_g	lp	1.993		
	σ	1.927	σ	1.928
b_{3u}	lp	1.987		
b_{2u}	π	1.975		1.983
	π^*	0.137	π^*	0.128
b_{1g}	π	1.903		1.902
b_{1u}	lp	1.981		
	σ^*	0.132	σ^*	0.071
b_{2g}	lp	1.980		
b_{3g}	π	1.973		1.984
	π^*	0.111	π^*	0.104
a_u	π	1.899		1.897

The inclusion of the lone-pair orbitals in the active space is seen to lead to a significant increase in the electron density in the N–N antibonding orbital, which in turn produces the required bond lengthening. The effect of these configurations is seem most dramatically in the occupation of the σ^* orbital. We find the occupation of this orbital to be 0.13 electrons, while the sum of the occupations in the σ and σ^* orbitals is found to be greater than 2. This shift is electron density is also seen once we examine the charge distribution in N_2O_4. At the SCF level we find a charge of 0.92 electrons on the nitrogen atoms, while at the CAS–SCF level this charge is reduced to 0.73 electrons. This charge distribution produces a much more polar structure than would be expected on the basis of two noninteracting NO_2 fragments. Of the three open-shell resonance structures of NO_2 which can lead to formation of N_2O_4, two are ionic. We find that the CAS–SCF description includes an admixture of resonance structures (1) and (2), but not to the extent found in NO_2. It is natural to expect these configurations to lead to a lengthening of the N–N bond relative to that found in the SCF description.

A further analysis requires us to attempt to separate the various components responsible for the observed bond lengthening. Our calculations, which now include the three components of σ bonding, π correlation, and lone pair antibonding interaction, cause the N–N bond to lengthen by 0.2 Å. The correlation of the N–N σ bond is known from the previous work of Ahlrichs et al.[9] to produce a repulsive interaction between the two NO_2 groups yielding a net increase of only 0.1 Å. The lowest π^* orbital is N–O antibonding but N–N bonding. The second π^* orbital is both N–O and N–N antibonding. Thus excitations from the π to the lowest π^* orbital can result in a weakening of the N–O bond and the formation of an N–N bond. Therefore we would expect π electron correlation to be attractive through the buildup of N–N π bonding which would also be used to reinforce the planar

Table IV. Summary of Results for N_2O_4

R(N-N), bohrs	*E*(SCF)	*E*(CI)	*E*(CI + Davidson)	*E*(CAS-SCF 10 e)	*E*(CAS-SCF 18 e)
2.883934				−408.267478	
2.983934	−408.135025	−408.807710	−408.914092	−408.268339	
3.083934	−408.133722	−408.808560	−408.915974	−408.267349	−408.304824
3.183934	−408.130955	−408.807883	−408.916339		
3.283934	−408.127099	−408.806093	−408.915641	−408.261923	−408.307801
3.383934					−408.308222
3.483934					−408.308066
99					−408.297153

structure. We tested this possibility by removing the eight lone-pair electrons and the four orbitals from the active space. The resulting wave function consisted of 10 electrons distributed in six π and two σ orbitals. Since we placed no further constraints on this wave function the CI expansion consisted of 176 symmetry adapted configurations. The N–N bond was reoptimized at this level and found to be 1.58 Å, in essential agreement with the original SCF results. Our assumption was thus reinforced in that correlation within the π framework serves to balance the repulsive σ correlation and brings the bond back to the SCF value. A more quantitative analysis of these changes is seen in the comparison of this 10 electron CAS–SCF wave function with our original 18-electron description. Here we see that the CAS procedure places greater weight on the π correlation and less on the σ^2–σ^{*2} configurations. Most importantly, exclusion of the lone-pair interactions reduces the occupation of the σ^*, antibonding orbital to about half that found in the original description.

We also chose to extend our analysis of this system in order to find out the extent of which a CI including all single and double excitations, CI(SD), from the SCF reference is able to describe the N–N bond. This resulted in 26 electrons being explicitly treated in the valence space and yielded a CI expansion of 58 618 symmetry-adapted configurations. Our results at the CI(SD) level predicted an N–N bond length of 1.62 Å. If we included the additional energy gained by the approximate treatment of higher order excitations by using Davidson's[20] correction we predicted a bond length of 1.68 Å. Both lengths are substantially shorter than the experimental values. This failure of the CI(SD) from an SCF reference is consistent with the CAS–SCF results which show that the SCF reference configuration accounts for 80% of the wave function. It is well known that for a CI(SD) calculation to work well the reference space, ψ_0, must include all important configurations. In this case the reference space should include the important configurations found in the 18-electron CAS–SCF. The results are summarized in Table IV.

Our calculations have shown that there appear to be three competitive effects which determine the N–N bond length. The first we ascribe to σ^2–σ^{*2}, bonding to antibonding correlation which lengthens the bond. The second effect involves correlation in the π space which we found causes some N–N π-bond formation and produces an attractive interaction. The third effect is seen once configurations of the type (lp–σ^*) × (π–π^*) are included. These configurations serve to balance the important NO_2 resonance structures and lengthen the bond.

Conclusion

We have examined the electronic structure of N_2O_4 in light of the difficulty that theory has had in correctly predicting the N–N bond length. Our calculations show that it is most appropriate to describe the formation of N_2O_4 as the result of the relatively weak interaction of two NO_2 groups. Each of the NO_2 groups is described in terms of five resonance structures, three covalent and two ionic. In N_2O_4 we find that one of the covalent and both ionic structures can lead to the formation of an N–N σ bond. The formation of N_2O_4 leads to a much larger charge buildup on nitrogen than found in NO_2. Using a variety of basis sets we find that even at the DZP level an SCF wave function is a poor description and predicts a bond length which is much too short (~0.2 Å). Correlation at the CI(SD) level also yields a short bond and demonstrates that the SCF accounts for only 84% of the wave function. One of the most pronounced effects which we find at the CAS–SCF level relative to that observed at the SCF level is the shift in relative importance of the five resonance structures of NO_2. Inclusion of correlation, equivalent to that used in NO_2, for N_2O_4 results in the mixing of the two nonbonding resonance structures and an N–N bond which is 0.2 Å greater than that found at the SCF level and in essential agreement with experiment.

The primary constituents which are responsible for N–N bond formation can be divided into three components. The first involves a σ bonding to antibonding correlation which lengthens the bond. The second involves correlation of the π space allowing the formation of some N–N π bonding which shortens the N–N bond and presumably is responsible for the observed planar structure. The third effect involves the interaction of the oxygen lone pair orbitals with the σ space and results in a mixing of the nonbonding resonance structures of NO_2. This in turn is responsible for bond lengthening. This 0.2 Å bond lengthening is surprisingly large, especially when one considers that the lone-pair orbitals might have been treated as inactive, if all of the important resonance structures were not treated explicitly.

Acknowledgment. We thank Drs. M. Dupuis, B. Liu, and B. Lengsfield for a critical reading of the manuscript. C. W. Bauschlicher and Andrew Komornicki were supported on NASA Grants NCC2-158 and NCC2-154, respectively.

Registry No. N_2O_4, 10544-72-6; N_2, 7727-37-9.

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(20) S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974).