Structure and Bonding in Dinitrogen Tetroxide (N_2O_4)

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Abstract: *Ab initio* computations which included effects of electron correlation were performed at various N–N distances for the planar and the skew structure of N_2O_4. The results prove definitely the σ character of the bond electron pair. An investigation of the wave function by means of contour diagrams and a population analysis show that the very long N–N bond in N_2O_4 is due to the delocalization of the bond electron pair over the whole molecule and to a rather large repulsion between the doubly occupied MO's of the NO_2 fragments. The coplanarity of N_2O_4 results from a delicate balance of the repulsive forces, which favor the skew structure, and of the effects of bonding which favor the planar structure.

The structure of molecular N_2O_4, which is well known from electron-diffraction measurements,[1] poses some intriguing questions. The most peculiar feature is an unusually long, weak N–N bond with a bond distance of 1.78 Å, whereas the N–N distance in N_2H_4 is 1.47 Å. If the O–O repulsion were the main cause of the weakening of the N–N bond one would expect the molecule to adopt the skew configuration, whereas the experimental data clearly prove the planarity of N_2O_4.

We mention briefly some attempts that have been made to explain the geometry of N_2O_4 (for a recent discussion see ref 1b and references therein).

Smith and Hedberg,[1a] see also ref 2, have noted that the long N–N distance could be explained by a "π-only" bond. These authors thus presumed that no σ bond between the NO_2 fragments is formed at all. This would, of course, explain the planarity of N_2O_4. Pauling[3] has rejected this explanation by the following reasoning. The unpaired electron in NO_2 clearly occupies a σ MO and consequently a σ bond should be formed. As the odd electron in NO_2 is delocalized and is located only 42% on the nitrogen atom one would expect a bond strength of 0.42, which according to Pauling would correspond to a bond length of about 1.75 Å.[3] Pauling did not attempt to give an explanation of the planarity of N_2O_4, however.

Bent[4] tried to explain the long N–N distance and the planarity of N_2O_4 by so-called "splayed" σ bonds.

The above mentioned considerations are exclusively based on qualitative arguments or semiempirical calculations. The only rigorous computation known to the authors (on the HF level) has been published by Snyder and Basch.[5]

Since these authors used a rather limited basis set and performed a computation at the experimental geometry only, their results appeared not to be sufficient to discuss the questions mentioned above.

In order to investigate the problems of structure and bonding in N_2O_4 we have performed a series of *ab initio* computations for various N–N distances for the planar (D_{2h}) and the skew (D_{2d}) structure in using an extended basis set. The method applied goes beyond the Hartree-Fock (HF) approximation and allows one to account for the effect of electron correlation which is neglected on the HF level.

In the following section we describe briefly the method of computation and the basis set used. In sections II and III we report and discuss the results.

I. Method

To answer the questions mentioned in the introductory section requires the computation and interpretation of wave functions and energies which are sufficiently accurate to account for the changes in electronic structure that take place on formation of N_2O_4 from 2 NO_2. At present rigorous computations for large molecules are performed almost exclusively within the HF approximation.[6] The HF wave function may then be investigated by means of a population analysis[7] to gain some understanding of the actual mechanism of the chemical bonding. It should be noted, however, that none of the various methods of interpretation proposed so far appears to be really satisfactory.[8]

For the treatment of N_2O_4 it is furthermore desirable to go beyond the HF approximation and to include at least partially the effects of electron correlation. It is one of the most serious drawbacks of the HF model that it cannot describe accurately the dissociation of an electron pair bond into the open shell fragments as is well known from the treatment of processes like $H_2 \rightarrow 2H$ or $F_2 \rightarrow 2F$.[9] In order to obtain a reliable description of the long and weak bond formed in N_2O_4, the equation for the wave function should be flexible enough to yield a proper description of the dissociation $N_2O_4 \rightarrow 2NO_2$. Since only one electron pair bond is broken in this process, it is sufficient for this purpose to account for the electron correlation of the valence electron pair. This can be done in replacing $\varphi\alpha\varphi\beta$ in the HF wave function, where φ denotes the MO describing the bond under consideration, by a two-electron CI (configuration interaction) function Φ_{VP} describing the valence pair (VP = valence pair). Stated differently, we consider the following equation for the total wave function Ψ_{VP}

$$\Psi_{VP} = A[\varphi_1\alpha\varphi_1\beta \ldots \varphi_{n-1}\alpha\varphi_{n-1}\beta\Phi_{VP}] \quad (1)$$

where A is the n-electron antisymmetrizer and φ_i, $i = 1, \ldots, n-1$, are the remaining SCF-MO's.

The CI expansion for Φ_{VP} can be brought into a very compact form if it is based on the PNO's χ_i of Φ_{VP} (PNO's = pair natural orbitals)

$$\Phi_{VP} = \sum_i C_i | \chi_i\alpha \chi_i\beta |$$

The total wave function Ψ_{VP} then has the form

$$\Psi_{VP} = A\sum_i C_i | \varphi_1\alpha\varphi_1\beta \ldots \varphi_{n-1}\alpha\varphi_{n-1}\beta\chi_i\alpha \chi_i\beta | \quad (2)$$

The NO-expansion guarantees optimal convergence properties, *i.e.*, the $|C_i|$ usually form a rapidly decreasing series and one has to include only a small number (10–20) of terms in (2). In order to take advantage of this fact one has first to determine the PNO's χ_i, which are a solution of a rather complicated system of coupled integrodifferential equations. A method to solve these equations, at least ap-

Table I. Computed Energies of N_2O_4 for Various N–N Distances[a]

Geom-etry	Basis[b]	N–N distance[c]	2.707	3.007	3.307	3.607	3.907	Computed equil[e] Energy	N–N dist
D_{2h}	1	ΔE_{HF}[d]	0.0411	0.0249	0.0268	0.0380		0.0241	3.15
		ΔE_{VP}[d]	0.0347	0.0141	0.0085	0.0088		0.0082	3.42
D_{2h}	2	ΔE_{HF}	0.0142	0.0031	0.0102	0.0250		0.0031	3.00
		ΔE_{VP}	0.0072	−0.0070	−0.0071	−0.0030		−0.0080	3.15
D_{2d}	1	ΔE_{HF}			0.0398	0.0502	0.0640		
		ΔE_{VP}			0.0208	0.0193	0.0184		
D_{2d}	2	ΔE_{HF}	0.0137	0.0120	0.0220	0.0365	0.0528	0.0111	2.89
		ΔE_{VP}	0.0075	0.0017	0.0041	0.0072	0.0089	0.0016	3.06

[a] The remaining structure parameters were kept at their experimental values, see text. [b] Basis set 2 includes a d set on N, whereas basis 1 does not; see text. [c] All quantities in atomic units. [d] $\Delta E_{HF} = E_{HF}(N_2O_4) - 2E_{HF}(NO_2)$, $\Delta E_{VP} = E_{VP}(N_2O_4) - 2E_{HF}(NO_2)$. $2E_{HF}(NO_2) = -407.7495$ au (basis 1), $2E_{HF}(NO_2) = -407.8992$ (basis 2). [e] Obtained from a fit of the foregoing results to a morse like potential $E(R) = a + b\exp(-\eta R) + c\exp(-2\eta R)$ all parameters were optimized.

proximately, has been discussed in detail in ref 10. In the present computations we have, however, used a different method[11] to obtain the PNO's χ_i which is even more accurate and considerably faster than the one described in ref 10.

The computational steps to be actually performed are then as follows: (1) a conventional closed shell HF computation, (2) the computation of PNO's χ_i of the valence pair, (3) a CI calculation to determine the total energy E_{VP} and the CI coefficients C_i of the wave function Ψ_{VP} (see eq 2).

We note that the procedure just described resembles closely the OVC method developed by Das and Wahl.[9]

The program used for the computations sketched above could have also been applied to obtain the total correlation energy within the independent electron pair approximation (IEPA),[12] the coupled electron pair approximation, or the PNOCI method.[13] This would have increased the necessary computer time by a factor of 2–3. Furthermore, we did not expect these additional correlation effects to be of great significance for the understanding of the present problem.

Basis Set. The basis set consisted of groups of Gaussian lobe functions. We started from a Huzinaga 8s, 4p basis.[14] The p AO's are constructed from two lobes each. The s orbitals were contracted (5,1,1,1) with contraction coefficients as in the 1s HF AO's. For the p set we used a contraction (3,1) as in the 2p AO of the corresponding atom. Our basis is thus of so-called "double ζ" quality since we have four s- and two p-type basis functions per atom. For the nitrogen atom we also included a d set with orbital exponent $\eta = 0.75$. The construction of the d AO's from Gaussian lobes is described in ref 15. The computer facilities available to the authors did not allow for a simultaneous inclusion of a d set on oxygen. It could appear that our basis set is somewhat unbalanced, but the nitrogen d functions have a maximum at a distance of about 0.6 Å from the nitrogen atom and thus provide flexibility in the bond region where it is desired.

II. Results

The computations were performed for a fixed geometry of the NO_2 fragments for various N–N distances. The NO distance (1.18 Å) and the ONO angle (134°) were chosen as in the experimental equilibrium geometry.[1] We note that the corresponding structure parameters of NO_2 (1.19 Å, 134.1°) differ only slightly from those of N_2O_4. In the case of NO_2 we have checked by a series of HF computations that our basis set reproduces the experimental structure up to 0.01 Å and ±1°.

In a first series of computations, see Table I, we used s and p functions only, i.e., we excluded the d set on nitrogen. For the planar configuration we found an N–N distance of

1.67 Å on the HF level and of 1.81 Å if the valence pair correlation is included. A comparison of E_{VP} (N_2O_4) with the RHF energy of NO_2 reveals that N_2O_4 is not predicted to be stable with respect to $2NO_2$ for this basis set.

It should be noted here, that we really have to compare E_{VP} (N_2O_4), the total energy obtained with the wave function Ψ_{VP} described in eq 2, with $2E_{HF}$ (NO_2), since we included the valence pair correlation energy only in the N_2O_4 computations, which essentially guarantees a proper description of the dissociation $N_2O_4 \rightarrow 2NO_2$.

For the skew configuration, still excluding d functions, we find an attractive potential curve on the HF level, whereas inclusion of the valence pair correlation yields a purely repulsive curve. As will be seen below this repulsion is due to a basis set deficiency and disappears if d's are included. The attractive force on the HF level is an artefact of this approximation, it is solely due to the fact that this model is not capable of describing dissociation correctly, and always gives too high energies for large distances.

More reasonable results are obtained if a d set on nitrogen is included, see Table I. For the planar geometry we now get the minimum of the potential curve at an N–N distance of 1.59 Å on the HF level and 1.67 Å if the valence pair correlation is included. The HF energy of N_2O_4 is still 0.003 au = 2 kcal/mol higher than twice the RHF energy of NO_2, i.e., N_2O_4 is still predicted to be unstable with respect to $2NO_2$. Including the valence pair correlation we get a corresponding binding energy of 0.008 au = 5.0 kcal/mol. A recent experimental value[16] is 12.7 kcal/mol.

From the fit of the E_{VP} results (including the d set on N) we obtain an N–N force constant $k_1 = 1.32$ mdyn/Å, yielding an $(NO_2)–(NO_2)$ frequency $\nu_3(a_g) = 307$ cm^{-1}.

The corresponding Raman frequency has been measured only for the liquid (265 cm^{-1} at −10°) and for the solid phase (283 cm^{-1} at −190°) but not for the gas phase.[16]

Let us now comment briefly on the deviation between our best theoretical and the most recent experimental value[1] for the N–N distance, 1.67 and 1.78 Å, respectively. The theoretical value corresponds to the minimum of the potential curve (R_e^{N-N}), whereas in the electron diffraction measurement one really determines the thermodynamical average over the quantum mechanical expectation values $\langle R^{N-N} \rangle$ of the vibrational states. A quantitative account of the averaging effects requires the knowledge of the total potential hypersurface which is not available at present. Due to some uncertainties in the evaluation of electron diffraction data (deviations of up to 0.02 Å for the N–N distance of N_2H_4 have been reported[17]), due to the unharmonicity effects which always cause $\langle R \rangle - R_e > 0$ (where the difference increases with increasing vibrational quantum number), and furthermore as a result of the thermodynamical average (the measurements[1] were performed at −21° yield-

Table II. CI Coefficients, C_i Occupation Numbers, n_i, and Energy Contributions, ΔE_i, of the PNO Configurations[a]

| | NO configuration | | | | | |
	1	2	3	4	5	6
PNO-symmetry	a_g	b_{1u}	b_{3u}	b_{2u}	a_g	b_{2g}
C_i	0.98924	−0.14208	−0.02171	−0.01787	−0.01045	−0.01009
n_i	0.97860	0.020187	0.00047	0.00032	0.00011	0.00010
ΔE_i	−407.88898	−0.01444	−0.00108	−0.00024	−0.00040	−0.00039

[a] See eq 2 and text, $n_i = C_i^2$.

ing $h\nu_3/kT = 1.75$), we consider it quite conceivable that the reported electron diffraction results differ by as much as 0.04–0.08 Å from R_e.

For the skew configuration we get (including a d set on N) a minimum of E_{HF} at an N–N distance of 1.53 Å and of E_{VP} at 1.62 Å. The N–N distances for this geometry are then 0.06 and 0.05 Å shorter than for the planar structure. We note that E_{VP} for the skew configuration is still 0.0016 au = 1 kcal/mol higher than for $2NO_2$. The present authors conclude, however, that N_2O_4 in the skew configuration is predicted to be bound if a larger basis is used and the remaining structure parameters, like ∠ONO and N–O distance, were optimized.

For the very same reasons one cannot expect a better agreement between the experimental rotational barrier 2.9 kcal/mol[16] and the one obtained from the present computation which amounts to 0.0096 au = 6.0 kcal/mol as obtained from the respective E_{VP} values. In order to obtain more accurate energies and a better agreement with experiment it is furthermore necessary to include the total valence shell correlation energy and not just the bond pair correlation as was done in the present treatment.

At first glance it is somewhat surprising that the HF level calculations, which usually predict molecular geometries very well, yield rather poor N–N distances for N_2O_4, roughly 0.1 Å shorter than on the E_{VP} level. Since the HF energy is always too high for large internuclear distances if one or several bonds are broken, it is not unreasonable, however, that the HF approximation yields too short bond distances for the case of a long and weak bond as found in N_2O_4.

III. Discussion

In this section we first discuss the structure of Φ_{VP} in order to get a better understanding of the properties of the electron pair bond formed between the NO_2 fragments in N_2O_4. As a result of this discussion it will turn out that inclusion of electron correlation has little influence on the electron distribution in N_2O_4. In the second part of this section we will thus discuss the binding mechansim in N_2O_4 by means of a Mulliken population analysis and contour diagrams based on the HF wave function.

The discussions of the preceding section have revealed that reliable results for the N–N distance and the stability of N_2O_4 can only be obtained if (at least) a set of d functions on the nitrogen atoms is included and if the valence pair correlation is taken into account. Inclusion of the valence pair correlation results essentially in an admixture of the antibonding b_{1u} MO (which is to a good approximation the antibonding linear combination of the singly occupied MO's of the NO_2 fragments), whereas the remaining MO's contribute much less to the energy and the wave function, as can be seen from Table II. Although the admixture of the $(b_{1u})^2$ configuration is rather important as far as a quantitative computation of the binding energy is concerned, it contributes little to the wave function, the corresponding occupation number is only 0.02. This means that in the subsequent interpretation we can restrict ourselves to

the SCF wave function.

As the π^2 contribution to Φ_{VP} (configuration 4 of Table II) has an occupation number of 0.00032 only (in the planar geometry), we can definitely exclude the "π-only" bond theory of Coulson and Duchesne.[2] This conclusion has been verified in an independent way by performing an SCF computation where the bond electron pair was forced to occupy the $2b_{2u}$ MO. The SCF energy of this computation (for the experimental geometry) is 0.37 au = 232 kcal/mol above the corresponding SCF energy given in Table I (including d's on N).

We now discuss the SCF MO's and orbital energies of N_2O_4 in order to get a better understanding of the extraordinary features of the N–N bond. As the occupied MO's of N_2O_4 are to a good approximation simply the bonding and antibonding linear combinations of the NO_2 MO's, the weakness of the N–N bond can have two reasons: (i) a relatively small N–N bond order of the highest occupied MO, which essentially describes the bond between the NO_2 fragments; (ii) the repulsion of the doubly occupied MO's of NO_2. Our discussion will show that both effects are of importance.

A measure for the repulsion of the doubly occupied MO's of NO_2 is the splitting of the orbital energies of the bonding and antibonding N_2O_4 MO's arising from the corresponding NO_2 MO's. This is due to the fact that the repulsion of doubly occupied MO's of NO_2 is related to their overlap which in turn determines, at least qualitatively, the splitting of the corresponding orbital energies. In Table III we have listed the HF orbital energies of the MO's of N_2O_4 and their correspondence to the MO's of NO_2.

Inspection of Table III shows that the splitting of orbital energies is smaller than 0.02 au only for the $2b_2$, $3b_2$, and $1a_2$ MO's of NO_2, which have no s and p_z contribution (we put the molecule in the xz plane with N–N in the z direction) on nitrogen for symmetry reasons. Splitting is of intermediate size (0.04–0.06 au) for the $3a_1$, $1b_1$, and $4b_2$ MO's of NO_2, which are low lying MO's with nitrogen 2s contribution ($3a_1$) dominantly p_z on oxygen, like $4b_2$, or have a large nitrogen p_y contribution like $1b_1$. A rather large splitting (0.16–0.18 au) is found for the $4a_1$ and $5a_1$ MO's which have large s and p_z occupation on the nitrogen atoms. In agreement with this pattern we find in the Mulliken population analysis only small N–N bond charges (less than 0.04 in absolute value) for the N_2O_4 MO's except for those arising from the $4a_1$, $5a_1$, and, of course, the $6a_1$ MO's of NO_2.

In order to get a quantitative, or at least semiquantitative, measure of the repulsion of the doubly occupied MO's of NO_2 we have performed HF computations for CO_2 and C_2O_4 at the corresponding NO_2 and N_2O_4 equilibrium geometries. The occupied MO's of C_2O_4 have in fact a very close resemblance to the corresponding MO's of N_2O_4, as is shown by the results of the Mulliken population analysis and by comparison of the corresponding orbital energies; see Table III. The repulsion of doubly occupied MO's of O_2C-CO_2 (or $O_2N^+-NO_2^+$) depends essentially on the asymptotic behavior of the CO_2 (or NO_2^+) wave functions,

Table III. HF Orbital Energies of Valence Shell MO's in N_2O_4 and $C_2O_4{}^a$ in au

No.	Symmetry of the N_2O_4 orbitals	Correspondence to the NO_2 MO's[b]	N_2O_4	C_2O_4
1	$1a_g$	$1a_1(g)$	−20.70600	−20.70615
2	$1b_{1u}$	$1a_1(u)^*$	−20.70599	−20.70613
3	$1b_{3u}$	$1b_2(g)$	−20.70593	−20.70608
4	$1b_{2g}$	$1b_2(u)^*$	−20.70592	−20.70605
5	$2a_g$	$2a_1(g)$	−15.93930	−11.53550
6	$2b_{1u}$	$2a_1(u)^*$	−15.93916	−11.53540
7	$3a_g$	$3a_1(g)$	−1.73794	−1.62105
8	$3b_{1u}$	$3a_1(u)^*$	−1.70012	−1.58940
9	$2b_{3u}$	$2b_2(g)$	−1.53686	−1.50809
10	$2b_{2u}$	$2b_2(u)^*$	−1.51745	−1.48822
11	$4a_g$	$4a_1(g)$	−1.04878	−0.93085
12	$4b_{1u}$	$4a_1(u)^*$	−0.89213	−0.81807
13	$5a_g$	$5a_1(g)$	−0.86743	−0.81351
14	$1b_{2u}$	$1b_1(g)$	−0.82650	−0.78013
15	$3b_{3u}$	$3b_2(g)$	−0.79658	−0.75554
16	$3b_{2u}$	$3b_2(u)^*$	−0.78136	−0.73934
17	$1b_{3g}$	$1b_1(u)^*$	−0.77664	−0.73224
18	$5b_{1u}$	$5a_1(u)^*$	−0.71754	−0.62804
19	$4b_{3u}$	$4b_2(g)$	−0.60106	−0.56972
20	$4b_{2g}$	$4b_2(u)^*$	−0.54770	−0.51642
21	$1b_{1g}$	$1a_2(g)$	−0.53749	−0.55708
22	$1a_u$	$1a_2(u)^*$	−0.52625	−0.54715
23	$6a_g$	$6a_1(g)$	−0.48001	

^{a} At the N_2O_4 equilibrium geometry[1] (planar). ^{b} An asterisk refers to the corresponding antibonding MO and no asterisk refers to a bonding MO.

which is determined by the corresponding ionization potentials of CO_2 or $NO_2{}^+$.[18] As the ionization potentials are, *via* Koopman's theorem, given by the HF orbital energies, we are confident that a C_2O_4 computation gives a reliable estimate of the repulsion of the doubly occupied MO's of NO_2 in N_2O_4.

One could have also performed a computation on $N_2O_4{}^{2+}$ to determine this repulsion, but the presence of the positive charges leads to Coulomb interactions, polarization effects, etc., which would obscure the interpretation. The computations on CO_2 (with NO_2 geometry) and C_2O_4 with the corresponding N_2O_4 geometry yields the following repulsive energies ΔE_r: planar $d(C-C) = 1.75$ Å, $\Delta E_r = 0.97$ au $= 61$ kcal/mol; the same with a C–C distance of 1.6 Å, $\Delta E_r = 0.143$ au $= 90$ kcal/mol; skew $d(C-C) = 1.75$ Å, $\Delta E_r = 0.074$ au $= 46$ kcal/mol.

These numbers clearly demonstrate the great importance of the repulsion of doubly occupied NO_2 MO's on the structure of N_2O_4, especially the long N–N distance. As expected, this repulsion is considerably smaller for the skew configuration, 46 kcal/mol *vs.* 61 kcal/mol for the planar geometry.

Let us now consider the highest occupied MO of N_2O_4 which is the only bonding MO without an antibonding counterpart (with respect to the NO_2 fragments). The contour diagram of the corresponding $6a_1$ MO of NO_2, see Figure 1, and the results of the Mulliken population analysis (which gives the following gross populations (only gross populations larger than 0.03 are given) $s(N) = 0.14$, $p_z(N) = 0.37$, $p_z(O) = 0.23$, in good agreement with the results of Schaefer and Rothenberg[19]) clearly demonstrate the delocalization of the unpaired electron of NO_2 over the whole molecule. These features of the $6a_1$ MO support in a quantitative way the suggestion of Pauling[3] that the unpaired electron is localized 50% on the nitrogen atom (Paulings estimate was 42%) which consequently leads to an N–N bond order of about 0.5 in N_2O_4. This conclusion is also support-
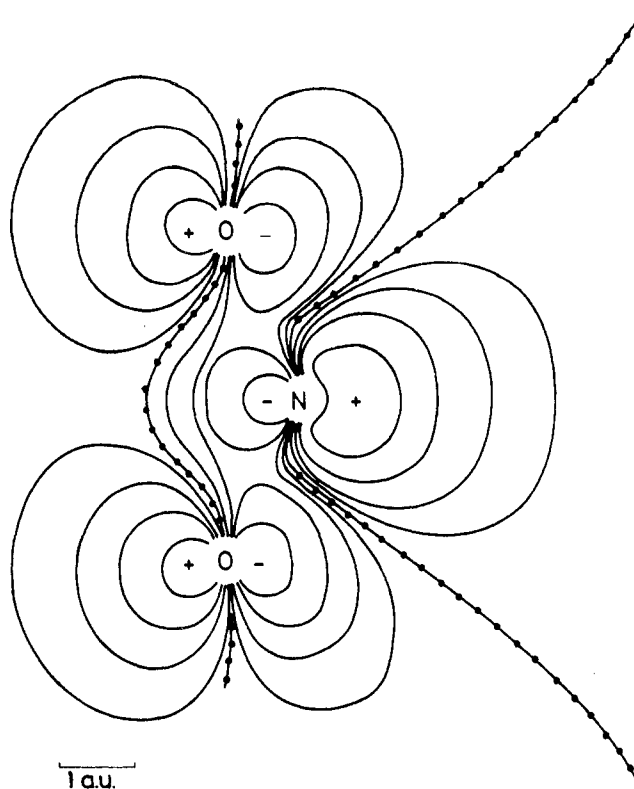

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Figure 1. Contour lines of the $6a_1$ MO of NO_2. The corresponding numerical values of the contour lines are (in atomic units): 0.0 (dotted), ±0.028, ±0.07, ±0.14, ±0.28, ±0.7. The data of all plots were taken from RHF computations. The basis included a d set on N.

ed by the contour diagram of the highest occupied MO of N_2O_4 (see Figure 2), which demonstrates that no significant change takes place on the formation of N_2O_4 from $2NO_2$ in this respect. This contour diagram also shows the presence of a weak O_1–O_2 and O_3–O_4 binding, which stabilizes the planar geometry.

Although the $6a_g$ MO of N_2O_4 is a σ-type MO, this does not mean, of course, that it is spherically symmetric with respect to the N–N axis. Hence, one cannot expect this kind of bond to allow for a free rotation of the NO_2 fragments. The contour diagram of the $6a_g$ MO in the plane perpendicular to the N–N axis (see Figure 3) also shows the ellipsoidal character of the contour lines. This implies that overlap between the $6a_1$ MO's of NO_2 and hence bonding is strongest in the planar geometry of N_2O_4.

This can also be seen from a comparison of the contour diagrams of the highest occupied MO for the D_{2d} geometry, Figures 4 and 5, with the corresponding Figures 2 and 3 for the D_{2h} geometry.

In order to support this conclusion we note that the orbital energy of the highest occupied molecular orbital (ϵ_{23}) increases from -0.4800 (D_{2h}) to -0.4696 au for the D_{2d} geometry.

We thus see that the planarity of N_2O_4 and the rather small rotational barrier is due to a rather delicate balance of two effects: the nonspherical character of the $6a_g$ MO and the weak O–O bond favor the planar structure, whereas the repulsion of the doubly occupied MO's of the NO_2 fragments favors the skew configuration by about 15 kcal/mol.

The Mulliken gross populations of the $6a_g$ MO of N_2O_4 give the following results: $s(N) = 0.05$, $p(N) = 0.14$, $d(N) = 0.05$, $p_z(O) = 0.38$ (remaining gross populations are smaller than 0.01). A comparison with the corresponding numbers for the $6a_1$ MO of NO_2 indicates a shift of elec-
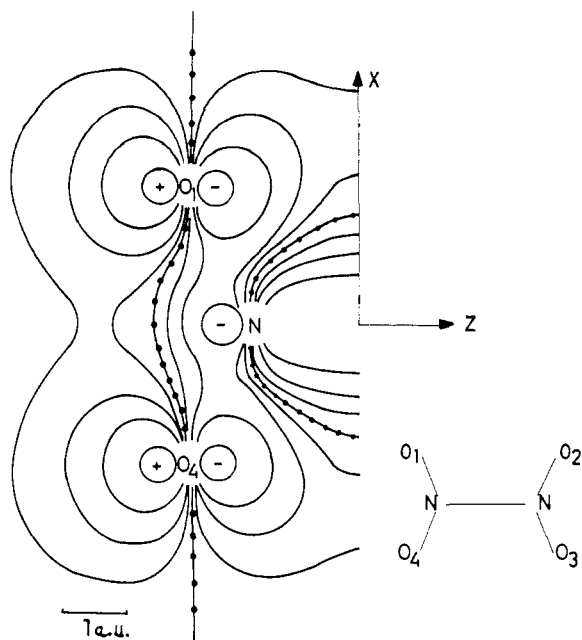
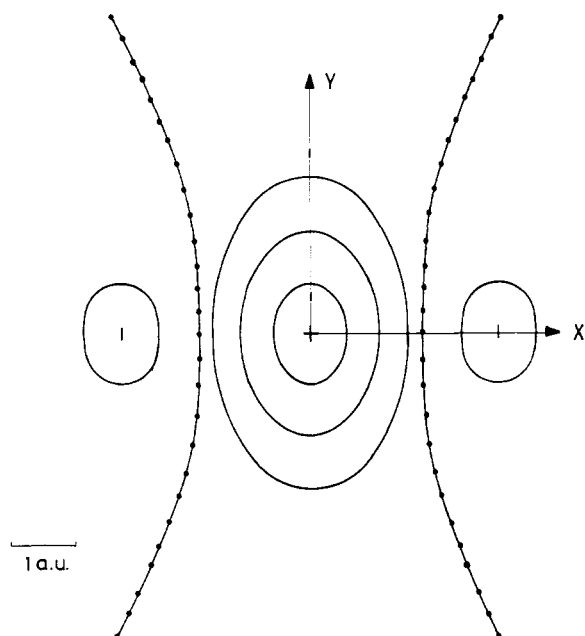**Figure 2.** Contour lines of the $6a_g$ MO of N_2O_4, (D_{2h}) d (N–N) = 1.75 Å. See also Figure 1.

Figure 3. Contour lines of $6a_g$ MO of N_2O_4 in the plane perpendicular to the N–N axis. See also Figures 1 and 2.

Figure 4. Contour lines of the highest occupied MO of N_2O_4 in D_{2d} geometry, compare also Figure 2.

Figure 5. Contour lines of the highest occupied MO of N_2O_4 in D_{2d} geometry, compare Figure 3.

tronic charge in this MO from N to O on formation of N_2O_4. Figures 6 and 7 show a plot of the density difference N_2O_4 vs. two unperturbed NO_2 (computed at the corresponding N_2O_4 geometry) for the total wave functions and for twice the $6a_g$ MO of N_2O_4 vs. the two $6a_1$ MO's of NO_2. The dominant feature of these contour diagrams is clearly the shift of electronic charge from nitrogen to oxygen. The slight accumulation of charge in the middle of the N–N bond which occurs for the total density (Figure 6), but not in Figure 7, is probably due to a slight mixture of the "unperturbed" $6a_g$ with the $4a_g$ and $5a_g$ MO's of N_2O_4, which makes the lower lying MO's more bonding and the highest MO $6a_g$ slightly less bonding. This effect leads to the conclusion that the N–N bond in N_2O_4 is even weaker than was anticipated from the discussion of the $6a_1$MO of NO_2.
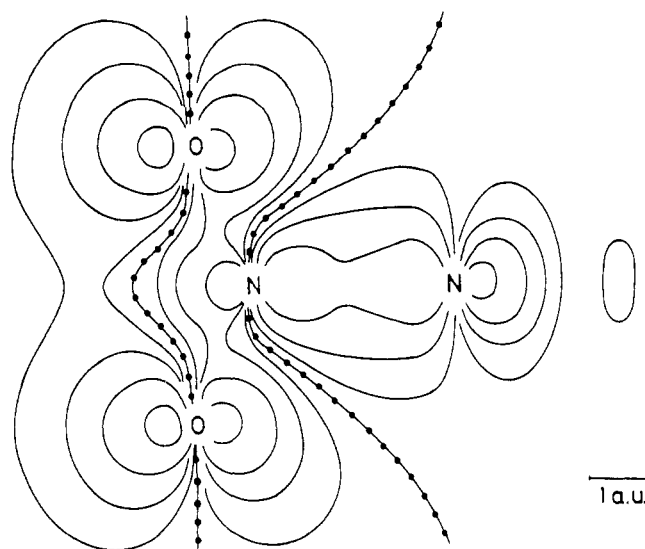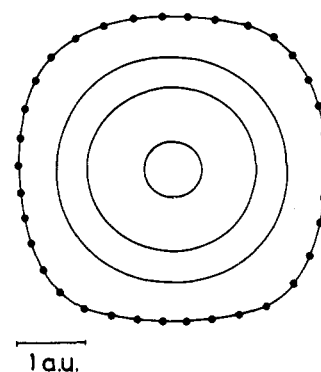
The shift of electronic charge from nitrogen to oxygen within the $6a_g$ MO, as compared to the $6a_1$ MO of NO_2, is probably due to the interaction of the $6a_1$ MO on one NO_2 with the doubly occupied $4a_1$ and $5a_1$ MO's on the other NO_2 which forces the $6a_g$ electrons out of the N–N area. Similar effects have been observed in other molecules, like N_2, where the $2p\sigma_g$ MO is actually formed from sp hybrids (with small s contribution) which point away from the other nitrogen.[7]

In summary, our investigations give two reasons for the weakness of the N–N bond in N_2O_4: (i) the repulsion of the doubly occupied MO's of NO_2, and (ii) the delocalization of the bond electron pair over the whole molecule and a shift of charge from N to O which further weakens the N–N bond.

V. Conclusion

The present investigations show that the extraordinary long N–N bond in N_2O_4 is due to two reasons: (i) the delocalization of the bond electron pair over the whole molecule, which leads to a weak N–N bond only; and (ii) the rather strong repulsion between the doubly occupied MO's of the NO_2 fragments.

The coplanarity of N_2O_4 results from a delicate balance of two effects. The repulsive forces favor, of course, the skew structure, whereas bonding forces stabilize the planar structure.
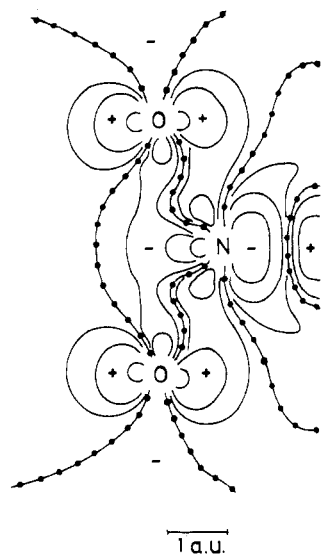
Figure 6. Contour plot of electron density differences of planar N_2O_4 (d(N-N) = 1.75 Å) vs. 2 unperturbed NO_2. The corresponding numerical values are: 0.0 (dotted), ±0.005, ±0.015, ±0.045 (see also Figure 1).

Figure 7. Contour plot of electron density differences of the $6a_g$ MO of N_2O_4 (doubly occupied) vs. the singly occupied $6a_1$ MO's of NO_2; see also Figure 6.

Let us finally compare briefly bonding in N_2O_4 with bonding in nitrocompounds RNO_2, where R is, e.g., CH_3, F, or Cl. In these compounds we have no delocalization of the orbital describing the unpaired electron on R involved in bond formation. Due to the electronic structure of NO_2, as was discussed in detail above, one could still expect a rather weak R–N bond in these molecules, which would be intermediate in bond strength between a single bond and the N–N bond in N_2O_4.

The R–N bond strength in nitro compounds can, however, be increased by a rearrangement of the NO_2 MO's leading to a better localization of the unpaired electron in this molecule. Such a rearrangement process would be too "expensive" in N_2O_4 since it requires the corresponding changes in both NO_2 fragments.

Details of Computation. The computations were performed on a UNIVAC 1108. The method of evaluation and further processing of two-electron integrals has been described elsewhere.[20] One N_2O_4 (D_{2h} symmetry) computation with a basis set of 70 groups, which included a d set on nitrogen, required the following CPU times: integrals, 127 min; HF part, 20 min (16 iterations if no starting vectors were provided, E_{HF} converged to 10^{-7} au); determination of PNO's, 0, 8 min; CI-matrix elements, 12 min; total, 160 min. Double precision arithmetic was used throughout. The computation times are reduced by about 40% if the d set on nitrogen is left out. Computations for the skew structure require about 40% more CPU time than those for the planar structure.
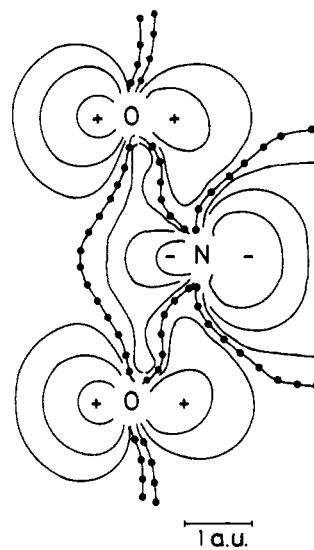
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