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Localized Molecular Orbitals for N_2O_2, N_2O_3, and N_2O_4

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Abstract: Localized molecular orbitals, LMO's, are derived from the MO's calculated by a CNDO method for N_2O_4, N_2O_2, and N_2O_3. The theoretical Lewis structures are given. The molecules have σ-type nitrogen–nitrogen bonds of high p-orbital character, but no π bonds; oxygen lone pair delocalization to both nitrogen atoms is antibonding, reducing the strength of the nitrogen–nitrogen bond. The present results from a semiempirical CNDO method are in good agreement with those from previous ab initio studies using canonical MO's.

Introduction

The nitrogen oxides, N_2O_2, N_2O_3, and N_2O_4 have many peculiar features: very long, weak N–N bonds, 2.18, 1.864, and 1.782 Å, with heats of dissociation 2.7,[1] 9.5,[2] and 12.7[3] kcal mol^{-1}; a typical N–N single bond length is 1.47 Å (hydrazine), with heat of dissociation[4] 71 kcal mol^{-1}. The molecules are planar although the O–O repulsions are a maximum for this configuration. The barrier to internal rotation about N–N is higher than would be expected for such long bonds, being 2.9 kcal mol^{-1} for N_2O_4.[3] The dinitrogen oxides are diamagnetic, whereas the building units, NO_2 and NO, are paramagnetic. The ONO bond angles in N_2O_3 and N_2O_4 are unusually large, being 129.8 and 135.4°. The nitroso NNO angles in N_2O_2, 101.3°, and N_2O_3, 105.1°, are smaller than in other NO compounds; in the nitrosyl halides, the NO halide angle ranges between 110 and 116°.

Bonding between linked groups with identical formal charges is unfavorable but occurs in N_2O_2 and in the most stable form of N_2O_4, which has three different rotational and

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structural isomers.[5,6] At liquid nitrogen temperatures, a twisted O_2NNO_2 form can be trapped in an inert matrix, while at approximately 4 °K the $ONONO_2$ isomer also exists. Similarly, N_2O_3 has two forms, the unstable ONONO isomer and the more stable $ONNO_2$ isomer.[7]

There have been many attempts to explain the geometry and electronic structures of these oxides, mainly for N_2O_4: Chalvet and Daudel[8] favored a N–N σ bond with partial π character, giving a total N–N bond order of 1.164 in N_2O_4. Smith and Hedberg[9] described the N–N bond as π only. Coulson and Duchesne[10] suggested a π-bond model with the σ and σ* levels both occupied, to give a net π bond order of 0.3. McEwan[11] superposed the separate NO_2 and charge-transfer structures. Green and Linnett,[12] by an extended Hückel calculation, concluded that the N–N bond was mainly σ, with additional π-bond stabilization. Bent[13] favored a "splayed single bond" for the central bond in N_2O_4. Brown and Harcourt[14] used the variable electronegativity SCF-MO method to suggest a σ + π model, in which the lone pair oxygen electrons delocalize into the σ* N–N orbital. Redmond and Wayland,[15] by extended Hückel theory, proposed that the barrier to internal rotation

Figure 1. N_2O_4. (a) Geometry and directions of the bond hybrid orbitals calculated from the LMO's, Table 1. (b) Electronic structure and atomic charges. Arrows indicated electron delocalization.
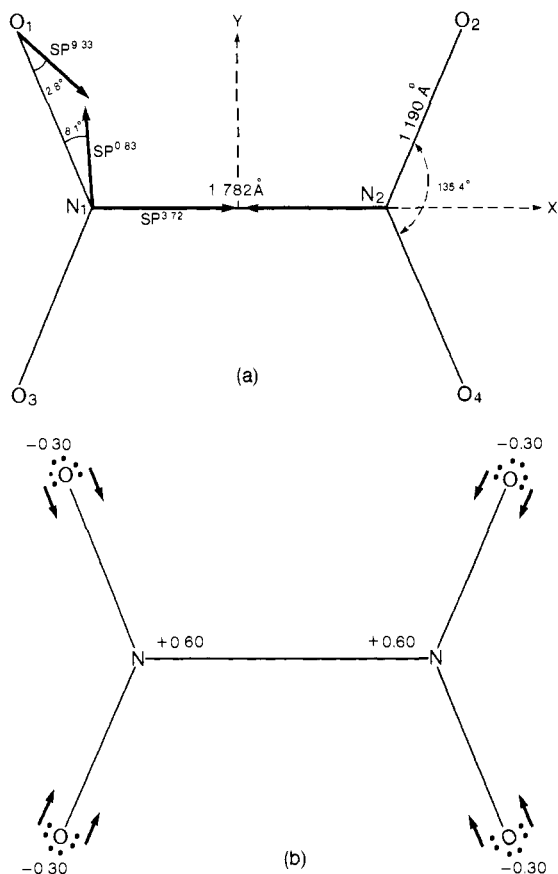

Figure 2, N_2O_2. (a) Geometry and directions of the bond hybrid orbitals calculated from the LMO's, Table 11. (b) Electronic structure and atomic charges. Arrows indicate electron delocalization.

was not from N–N π bonding but from long-range O–O σ interactions and the dependence of N–O bonding on the dihedral angle.

Griffiths et al.,[16] from a Hartree–Fock calculation, found the lowest energy state to be N–N antibonding, but stabilized by N–N–O three-center interactions; the N–N π bonding was not large. Ahlrichs and Keil[17] from an ab initio study found the N–N bond to be σ in character, with the bond electron pair delocalized over the entire molecule. The planar structure was found stable in a delicate balance between repulsive forces favoring the twisted structure and weak O–O bonding forces favoring the planar structure, but only achieved when a double-ζ basis set with Cl and d orbitals on N were used. Howell and Van Wazer's ab initio calculations using an extended Gaussian basis set[18] suggested that the planar geometry is due to O–O σ interactions, and that there is donation of the oxygen lone pairs into the N–N σ^* orbital.

All these studies have used the conventional canonical MO's which are delocalized over the entire molecule, but better insight into the valence structure, hybridization and directional character of bonds can be obtained by transforming these MO's into localized molecular orbitals (LMO's). In Lennard-Jones theory[19] the delocalized molecular orbitals are transformed into LMO's by maximizing the interaction of two electrons in each MO. The Edmiston-Reudenberg[20] procedure to obtain LMO's within this theory has been successful,[21,22] giving a bonding picture that falls within the classical picture of chemical bonding.

The LMO's obtained from ab initio and semiempirical wave functions are very similar,[23] but the localization procedure in ab initio calculations is very time consuming and costly. In the present study the LMO's are obtained for the nitrogen oxides from canonical MO's calculated by the semiempirical
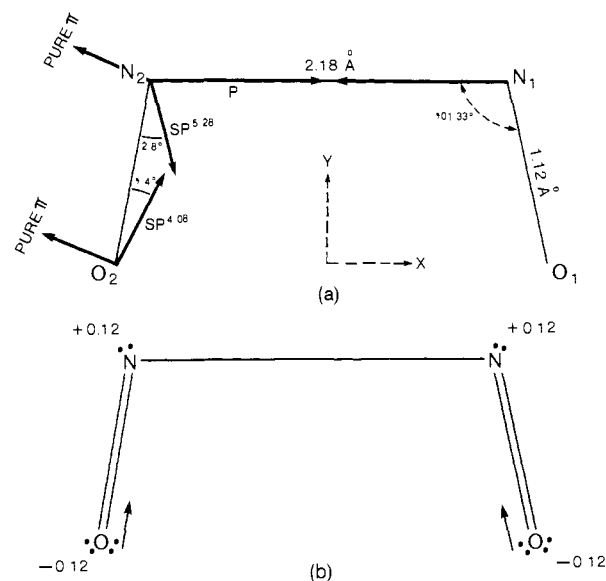
CNDO/BW method.[24] This is a version of the CNDO/2 method[25] in which bonding parameters and core repulsions are determined by extensive optimization of bond energies and bond lengths for each atom pair; the CNDO/BW method predicts quantitatively accurate dipole moments, force constants, total bond energies, energy-minimized bond lengths and angles, and ionization potentials and orbital energy levels for a wide range of molecules.[24]

Method

Parameter set 1 of Boyd and Whitehead[24] was used in the CNDO/BW theory. CNDO/2[25] calculations were performed for comparison. Gopinathan and Narasimhan's[26] method for obtaining truncated LMO's from CNDO MO's was used and the localization procedure applied until the difference in the sum of the orbital self-repulsion energies between successive iterations was less than 10^{-5} eV. Dipole moments in the CNDO/BW approximation were calculated using the method of Pople and Segal[27] and bond orders using the bond order index of Wiberg.[28,29]

The geometry for N_2O_2 was taken from x-ray crystallography:[30,31] an equilateral trapezoidal structure with $R(NN)$ = 2.18 Å, $R(OO)$ = 2.62 Å, and $R(NO)$ = 1.12 Å (Figure 2a). For N_2O_3 the structure was from microwave spectra:[32] $R(N_1N_2)$ = 1.864 Å, $R(N_1O_1)$ = 1.142 Å, $R(N_2O_2)$ = 1.202 Å, $R(N_2O_3)$ = 1.271 Å, $\angle O_1N_1N_2$ = 105.1°, $\angle N_1N_2O_2$ = 112.7°, $\angle N_1N_2O_3$ = 117.5° (Figure 3a). The structure of N_2O_4 was from electron diffraction results:[33] $R(NN)$ = 1.782 Å, $R(NO)$ = 1.190 Å, $\angle ONO$ = 135.4° (Figure 1a). CNDO/BW calculations were carried out to give the *theoretical* optimum N–N bond lengths.

Results and Discussion

LMO's in N_2O_4. The LMO's for N_2O_4 are given in Table I, together with the delocalization index (d)[21] and the hybridization of the bonding orbitals on each atom in each LMO. There are five types of LMO's in N_2O_4.

(1) **Oxygen Lone Pair (I):** mainly an oxygen 2s orbital with 87.0% s character, highly localized with d = 0.27%.

(2) **Nitrogen–Oxygen σ Bond:** 61.4% (1.23 e) nitrogen orbitals and 37.6% (0.75 e) oxygen orbitals. The nitrogen orbitals are approximately sp hybrids, while the oxygen orbital is almost pure p with 9.63% s character. These orbitals are not

Table I. LMO'S in N_2O_4[a]

Type of LMO	Atom	2s	$2p_x$	$2p_y$	$2p_z$	% s character (hybridization)	Delocalization index, d,[b] %
O_1 lone pair (I)	O_1	0.931	0.043	0.357	0.0	87.03 (sp$^{0.15}$)	0.27
N_1-O_1 σ bond	N_1	−0.58	0.130	−0.511	0.0	57.49 (sp$^{0.83}$)	0.96
	O_1	−0.191	−0.247	0.528	0.0	9.63 (sp$^{9.33}$)	
O_1 lone pair (II)	O_1	0.176	−0.887	−0.354	0.0	3.30 (~p)	5.76
	N_1	−0.028	−0.201	−0.010	0.0	1.89 (~p)	
	N_2	0.050	−0.098	−0.001	0.0	21.04 (sp$^{3.75}$)	
O_1 lone pair (III)	O_1	0.0	0.0	0.0	0.891	0.0 (p)	20.67
	N_1	0.0	0.0	0.0	0.441	0.0 (p)	
	O_3	0.0	0.0	0.0	−0.109	0.0 (p)	
N_1-N_2 σ bond	N_1	0.315	0.607	0.0	0.0	21.19 (sp$^{3.72}$)	6.58
	N_2	0.315	−0.607	0.0	0.0	21.19 (sp$^{3.72}$)	
	O_1	−0.027	0.091	0.086	0.0	4.33 (~p)	
	O_2	−0.027	−0.091	0.086	0.0	4.33 (~p)	
	O_3	−0.027	0.091	−0.086	0.0	4.33 (~p)	
	O_4	−0.027	0.091	−0.086	0.0	4.33 (~p)	

[a] Refer to Figure 1 for the numbering of the atoms and for the coordinate axes. [b] $d\% = (1 - \Sigma_i C_i^2 \text{ LMO}) \times 100$ where the summation is only over orbitals on a given atom (lone pair) or atom pair (bonds); thus the delocalization for a N_1 lone pair is $(1 - \Sigma_{s,p_x,p_y,p_z} C_{N_1}^2 \text{ LMO}) \times 100$, and the amount of delocalization in a N_1O_1 bond is $(1 - \Sigma_{N_1,i} C_i^2 - \Sigma_{O_1,j} C_j^2) \times 100$. Orbitals not shown in the tables had negligible occupancy.

directed along the N–O internuclear axis. The oxygen atom orbitals are at 2.8°, and the nitrogen orbitals at 8.1° to the N–O axis. Both vectors lie in the plane of the molecule (Figure 1a). This LMO is highly localized, with $d = 0.96\%$ (0.02 e).

(3) **Oxygen Lone Pair (II):** virtually a p_x lone pair, with $d = 5.76\%$ (0.12e). The delocalization is mainly to the p_x orbitals of the nitrogen atoms and is *antibonding*, reducing the nitrogen–nitrogen bond strength.

(4) **Oxygen Lone Pair (III):** exclusively p_z orbitals, $d = 20.7\%$ (0.42 e) delocalized predominantly into the adjacent N p_z orbital, giving 20% π-bonding in the N–O bond. Because of the high delocalization of this lone pair, it could effectively be described as a highly polar N–O π bond.

(5) **Nitrogen–Nitrogen σ Bond:** between s and p_x atomic orbitals on each nitrogen atom, along the N–N axis. The nitrogen atom hybridization is sp$^{3.72}$, indicating the high p character of the bond; $d = 6.58\%$ (0.13 e) and the delocalization is over the whole molecule.

Thus the N–N bond *has no π character*, contrary to the suggestions of Chalvet and Daudel,[8] Smith and Hedberg,[9] Coulson and Duchesne,[10] Green and Linnett,[12] and Brown and Harcourt,[14] but agreeing with the ab initio study of Ahlrichs and Keil.[17]

This N–N bond is indicated experimentally by the observed diamagnetism of the molecule, compared to the paramagnetism of the constituent NO_2 molecules.

The weak N–N bond order is 0.515. From the N–N bond LMO, it would be 0.873; the bond order is reduced by the oxygen lone pair (II) *antibonding* delocalization (0.11 e from each of the four oxygens) onto the nitrogens. Howell and Van Wazer[18] and Brown and Harcourt[14] have qualitatively argued at length in favor of such delocalization, but a quantitative assessment can only be obtained easily from LMO's as in the present study.

The oxygen lone-pair I and II delocalization contributes to the N–O σ bond, bond order 1.45, and reduces the negative charge on the oxygen atoms to −0.30 from a formal charge of −1, for an oxygen atoms with three lone pairs and one σ bond. This leaves a charge of −0.60 on adjacent nitrogen, causing an electrostatic repulsion which helps to make the N–N bond long and weak.

The hybrid bond orbital directions are shown in Figure 1a, and the closest representation to a Lewis structure obtained from the present LMO's is shown (Figure 1b).

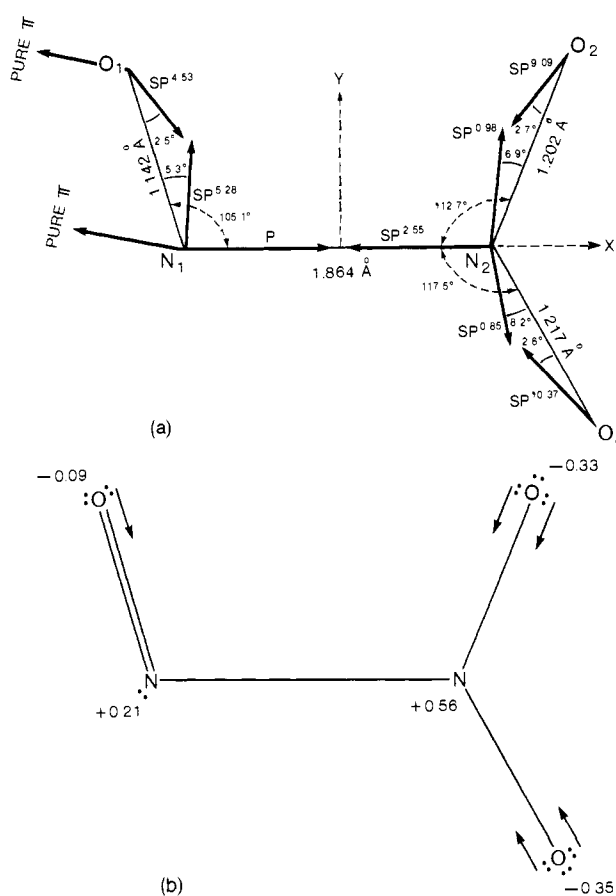The hybridization at the nitrogen atoms, sp$^{0.83}$, reflects the

Figure 3. N_2O_3 (a) Geometry and directions of the bond hybrid orbitals calculated from the LMO's, Table III. (b) Electronic structure and atomic charges. Arrows indicate electron delocalization.

large ONO angle in N_2O_4. The orbitals forming the N–O bond are not directed along the N–O axis, and the bond is bent (Figure 1a). The angle between the hybrid orbitals exceeds 120° because the p character is smaller than in sp^2 hybridization; the angle is 151.6° (Figure 1a).

The CNDO/2 LMO's quantitatively agree with the CNDO/BW results for N_2O_4, except that the N–N bond delocalization index is 2.58% compared with 6.58% in CNDO/
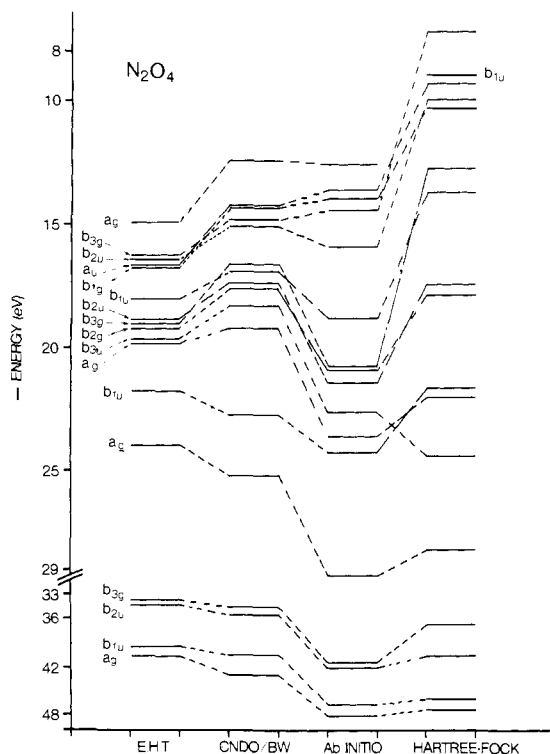
Figure 4. The MO orbital energy diagram for N_2O_4: EHT, ref 15; Hartree-Fock, ref 16; ab initio, ref 18. The choice of the ab initio results from ref 18 instead of those from ref 17 is arbitrary. It is not possible to decide between the significance of the two calculations: neither uses the correct experimental N-N bond distance of 1.782 Å, but a variationally minimized bond length of 1.67 Å. The orbital energy levels from ref 17 differs from those shown: the 7th level (b_{3g}) is b_{2g}, the 8th level (b_{2g}) is b_{3u} and the 14th level (b_{3g}) is b_{3u}. Levels 1 through 9 are more stable by about 0.5 eV; levels 10 through 17 are less stable by about 1 eV. The axes used were standardized with ref 18. CNDO/BW energies: a_g −12.50, a_u −14.33; b_{1g} −14.36; b_{3g} −14.90; b_{2u} −15.16; b_{3g} −16.69; b_{1u} −16.99; b_{2u} −17.45; b_{2g} −17.71; b_{3u} −18.40; a_g −19.29; b_{2u} −22.77; a_g −25.27; b_{3g} −34.79; b_{2u} −35.74; b_{1u} −40.59; and a_g −43.00 eV. CNDO/2 energies: a_g −12.54; a_u −15.46; b_{1g} −15.51; b_{3g} −17.39; b_{2u} −17.83; b_{1u} −21.83; b_{3g} −22.73; b_{2u} −23.92; b_{2g} −24.45; b_{3u} −26.53; a_g −26.76; b_{1u} −27.14; a_g −32.73; b_{3g} −41.85; b_{2u} −44.25; b_{1u} −48.62; and a_g −51.62 eV. The sixth and seventh are the reverse of CNDO/BW.

BW, and the oxygen p_z lone pair d is 25.5% compared to 20.7% in CNDO/BW.

Minimization of the total energy with bond length gives a theoretical N-N bond length of 1.46 Å, compared to 1.78 Å experimentally. Shorter theoretical equilibrium bond lengths are common to all SCF-MO studies, ab initio[17,18] and semiempirical.[34]

The LMO's above are for 1.78 Å; however, the LMO's for an N-N bond length of 1.46 Å are almost identical: the bonding is essentially unchanged.

The binding energy from CNDO/BW is 408 kcal mol^{-1} for N-N at 1.78 Å and 425 for N-N at 1.46 Å in good agreement with the 455 kcal mol^{-1} from thermochemical measurements[35] (Table IV).

The experimental dissociation energy $\Delta E = 2E_{NO_2} - E_{N_2O_4}$ is 12.0 kcal mol^{-1}.[3] CNDO/BW predicts −1.6 kcal mol^{-1} for the theoretical N-N bond distance, showing N_2O_4 to be unstable relative to $2NO_2$. Similar results are obtained from HF ab initio studies[17] where $\Delta E = -2$ kcal mol^{-1}: it is true that inclusion of valence electron configuration interaction, CI, gives $\Delta E = +5$ kcal mol^{-1}, but ab initio studies with or without CI predict the staggered conformation of N_2O_4 to be less stable than $2NO_2$.[17,18] Therefore energy differences of a few kcal mol^{-1} are not predictable by either ab initio or semiempirical methods.

While the CNDO/2 LMO picture is similar to that from CNDO/BW, the binding energies differ: CNDO/2 gives 1527 kcal mol^{-1}, three and one-half times the thermochemical results. Similar errors occur in the binding energies of N_2O_3 and N_2O_2 (below) and other small molecules.[24,25,36]

The present MO energy levels and symmetries for N_2O_4 are compared to those from the extended Hückel theory, EHT,[15] ab initio results,[18] and Hartree-Fock results[16] (Figure 4). The CNDO/BW results agree well with those from ab initio and EHT calculations; CNDO/BW gives two small energy level crossovers with respect to the ab initio results.

The Hartree-Fock results[16] disagree in ordering the 12 highest occupied orbitals compared to ab initio and have one level of unique symmetry: there was no convergent solution for the proper symmetry of the molecule; a symmetry basis with arbitrarily selected occupied orbitals was used. This gave negative N-N overlap population and an antibonding N-N MO; there was some stabilization from ONN three-center interactions. Our results show that these ONN interactions are *antibonding*, and the N-N interaction is definitely bonding. This Hartree-Fock calculation, including its Foster-Boys localization results, contradicts most previous studies and is of questionable validity.

CNDO/BW gives staggered N_2O_4 more stable than planar N_2O_4 by 3.2 kcal mol^{-1} contrary to experiment. While there is the *expected loss* of electronic energy going from the planar to the staggered conformation, from −4710.45 to −4697.76 eV, the core repulsion energy also decreases from 2944.84 to 2932.01 eV. In CNDO/BW the core repulsion energy is[24]

$$N_{AB} = e^{-\alpha_{AB}R_{AB}}\frac{Z_A Z_B}{R_{AB}} + (1 - e^{-\alpha_{AB}R_{AB}})Z_A Z_B \gamma_{AB}$$

where Z_A and Z_B are the atomic core charges, R_{AB} is the internuclear distance, γ_{AB} the electron repulsion integral, and α_{AB} an empirical core repulsion parameter specific for each pair of interacting atoms, chosen to give the correct bond length of an AB bond and bonding energy of a molecule containing one or more AB bonds. The same α_{AB} is used regardless of the bond order or length;[19,34] thus in N_2O_4 the N_1-O_1 interaction has the same α_{NO} as the N_1-O_4 interaction (Figure 1a). Since it might be more realistic to use an α dependent on interatomic distance, a variable $\alpha(R_{AB})$ was tested.

On rotating about the N-N bond, only the long-range O-O interatomic distances change. Therefore α_{OO} was expressed as a linear function of R_{OO} by fitting the calculated binding energies in oxygen and ozone molecules to experiment, giving the following empirical relationship:

$$\alpha_{OO}(R_{OO}) = -0.1123R_{OO} + 1.7373$$

Using this $\alpha_{OO}(R_{OO})$ the planar conformer became more stable by 1.4 kcal mol^{-1}. This variable $\alpha_{OO}(R_{OO})$ may be unreliable because (i) the computational numerical error may exceed this difference, and (ii) N_2O_2 and N_2O_3 are still predicted to have the nonplanar conformation. It must be remembered that most calculations, including ab initio calculations, cannot give chemical accuracy of a few kcal mol^{-1}, and these methods should not be pushed beyond their valid limits.

The LMO bonding picture of N_2O_4 in D_{2d} symmetry is almost the same as in D_{2h} symmetry; this is also true for planar and staggered N_2O_2 and N_2O_3. Consequently, the LMO's do not reflect the cause of the barrier of rotation about the N-N bonds. Nevertheless, the planarity of the molecule and the high barrier to rotation are *not* due to π bonding, nor direct breaking of long-range oxygen-oxygen bonding, as these do not occur in the LMO picture.

LMO's in N_2O_2. Previous studies[37-39] of the NO dimer gave the energy minimized structure, but each favored a different

Table II. LMO'S in N_2O_2[a]

Type of LMO	Atom	2s	$2p_x$	$2p_y$	$2p_z$	% s character (hybridization)	Delocalization index, d, %
O_1 lone pair (I)	O_1	0.896	0.072	−0.439	0.0	80.25 ($sp^{0.25}$)	0.00
N_1 lone pair	N_1	0.914	0.014	0.404	0.0	83.62 ($sp^{0.20}$)	0.00
O_1 lone pair (II)	O_1	0.023	−0.915	0.195	0.0	0.06 (~p)	12.48
	N_1	−0.020	−0.303	0.035	0.0	0.43 (~p)	
	N_2	0.013	−0.166	−0.024	0.0	0.62 (~p)	
N_1–O_1 σ bond	O_1	0.0	0.0	0.0	−0.782	0.00 (p)	0.01
	N_1	0.0	0.0	0.0	−0.623	0.00 (p)	
N_1–O_1 σ bond	O_1	0.332	−0.147	0.654	0.0	19.69 ($sp^{4.08}$)	0.01
	N_1	0.265	0.090	−0.601	0.0	15.93 ($sp^{5.28}$)	
N_1–N_2 σ bond	N_1	−0.057	0.690	0.104	0.0	0.65 (~p)	1.91
	N_2	−0.057	−0.690	0.104	0.0	0.65 (~p)	

[a] Refer to Figure 2 for the numbering of the atoms and for the coordinate axes.

geometry, differing in energy by a few kcal mol^{-1}; the complete electronic structure of N_2O_2 was not described.

The structure most consistent with the x-ray crystallographic results was the cis form of the ab initio study by Skancke and Boggs,[38] which gave atomic charges on nitrogen and oxygen of +0.128 and −0.128, and a dipole moment of 0.63 D. The CNDO/BW calculation gives atomic charges of +0.12 and −0.12 for nitrogen and oxygen, but a dipole moment of 0.397 D (Table IV).

There are six types of LMO's in N_2O_2 (Table II).

(1) Oxygen Lone Pair (I): having 80.3% s character, 100% localized.

(2) Nitrogen Lone Pair: Very similar to the oxygen lone pair (1), with 83.6% s character and d = 0%.

(3) Oxygen Lone Pair (II): pure p lone pair localized mainly in the p_x orbital, d = 12.5% (0.25 e) delocalized mainly into the N_{p_x} orbitals. This delocalization is antibonding between the three atoms.

(4) Nitrogen–Oxygen π Bond: pure π bond, 61.1% (1.22 e) oxygen atomic orbitals, and 38.8% (0.78 e) nitrogen orbitals, d = 0.01% (0.00 e).

(5) Nitrogen–Oxygen σ Bond: 56.02% (1.12 e) oxygen atomic orbitals, and 43.97% (0.88 e) nitrogen atomic orbitals, d = 0.01% (0.00 e). The hybridization is $sp^{4.08}$ on oxygen and $sp^{5.28}$ on nitrogen. The oxygen atomic orbitals are at 1.4° to the N–O bond axis, those of nitrogen at 2.8°; both vectors lie in the molecular plane (Figure 2a).

(6) Nitrogen–Nitrogen σ Bond: between almost pure N_{p_x} orbitals; highly localized, with d = 1.19% (0.02 e).

As in N_2O_4 there is no π character in the nitrogen-nitrogen bond, but oxygen lone-pair delocalizations reduce the bond order from 0.962 to 0.600.

The smaller than normal NNO angle is reflected in the central N atom hybridization. There are three bonds and one lone pair at each nitrogen atom. The nitrogen hybrid orbitals forming the N–O and N–N bonds are nearly pure p in character and the angle is consequently close to 90° (Table II, Figure 2a). The hybridizations are lone-pair $sp^{0.20}$ and N–O σ-bond $sp^{5.28}$.

The Lewis structure for N_2O_2 is shown in Figure 2b, and the MO energy levels and symmetries are given in Figure 5.

The CNDO/2 LMO results are similar: the binding energy is unacceptable at 864 kcal mol^{-1}. The CNDO/BW binding energy is 263 kcal mol^{-1} (Table IV).

The energy optimized CNDO/BW N–N bond length, 1.40 ± 0.03 Å, gave a binding energy of 301 kcal mol^{-1} compared to the binding energy of O ($N_2O_2 \rightarrow$ 2NO) of 2(152.8) = 305.6 kcal mol^{-1}.

LMO's in N_2O_3. The results for N_2O_3 are given in Tables III and IV and Figure 3a, 3b, and 5. The binding in the nitro and nitroso units is very similar to that in N_2O_4 and N_2O_2, as
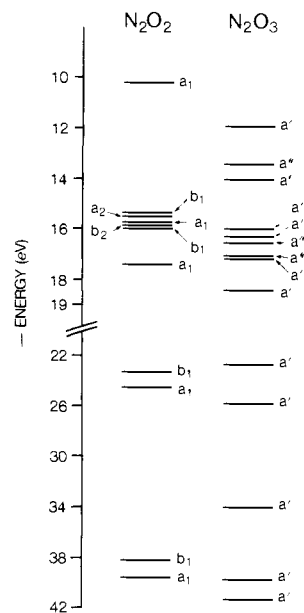

Figure 5. The MO energy diagram for N_2O_2 and N_2O_3 from CNDO/BW. In N_2O_2 the axis system of Figure 2a is transformed to the symmetry axis system for this figure; the y axis of Figure 2a becomes z. N_2O_2 CNDO/BW energies (CNDO/2 energies): a_1 −10.24 (−8.36); b_1 −15.39 (−19.63); a_2 −15.58 (−20.40); a_1 −15.78 (−21.07); b_2 −15.87 (−21.13); b_1 −15.98 (−21.49); a_1 −17.44 (−24.87); b_1 −23.34 (−27.52); a_1 −24.51 (−29.04); b_1 −38.27 (−45.87); and a_1 −39.64 (−47.73) eV. N_2O_3 CNDO/BW energies (CNDO/2 energies): a' −11.89 (−11.70); a" −13.40 (−13.74); a' −14.00 (−15.74); a' −16.00 (−20.79); a' −16.30 (−21.38); a" −16.52 (−22.06); a" −17.10 (−23.74); a' −17.11 (−23.74); a' −18.41 (−25.06); a' −22.70 (−28.14); a' −25.83 (−31.89); a' −33.96 (−40.40); a' −39.28 (−47.05); and a' −41.20 (−49.71) eV.

is the antibonding oxygen lone-pair delocalization. The only difference is the N–N bond, which is a pure σ bond with 40.1% (0.80 e) nitroso nitrogen (N_1) atomic orbitals and 55.9% (1.12 e) nitro nitrogen (N_2) orbitals with d = 3.96% (0.08 e). The N_2 orbitals are $sp^{2.55}$ hybridized; the N_1 orbital is pure p_x. In the CNDO/2 LMO picture the O_3 "lone pair" III has d = 23.3% (0.46 e) compared to CNDO/BW with d = 18.6% (0.37 e), while the O_2 lone pair II has d = 26.0% (0.52 e) instead of 21.1% (0.42 e). The N–N bond d = 1.54% (0.03 e) instead of 3.96% (0.08 e). Again the CNDO/2 binding energy is too large, 1235 kcal mol^{-1} at R(NN) = 1.86 Å. The CNDO/BW binding energy is 351 compared to the experimental 380 kcal mol^{-1} [33] (Table IV). The energy-optimized CNDO/BW N–N bond length is 1.53 ± 0.001 Å, with a binding energy of 386 kcal mol^{-1} combined to the binding energy of NO + NO$_2$ → N_2O_3 of 152.8 + 213.1 = 365.9 kcal mol^{-1}.

Table III. LMO'S in N_2O_3[a]

Type of LMO	Atom	2s	$2p_x$	$2p_y$	$2p_z$	% s character (hybridization)	Delocalization index, d, %
O_2 lone pair (I)	O_2	0.928	−0.052	0.366	0.0	86.30 ($sp^{0.16}$)	0.22
O_1 lone pair (I)	O_1	−0.904	0.072	−0.423	0.0	81.63 ($sp^{0.22}$)	0.00
O_3 lone pair (I)	O_3	0.927	−0.059	−0.367	0.0	86.17 ($sp^{0.16}$)	0.26
N_1 lone pair	N_1	0.909	−0.058	−0.412	0.0	82.71 ($sp^{0.21}$)	0.03
N_2−O_3 σ bond	N_2	−0.579	−0.176	0.503	0.0	54.10 ($sp^{0.85}$)	1.16
	O_3	−0.180	0.291	−0.502	0.0	8.80 ($sp^{10.37}$)	
O_1 lone pair (II)	O_1	−0.052	0.913	0.265	0.0	0.30 ($\sim$p)	9.32
	N_1	0.031	0.271	0.031	0.0	1.30 ($\sim$p)	
	N_2	−0.057	0.101	0.004	0.0	24.37 ($sp^{3.10}$)	
N_1−O_1 σ bond	N_1	0.268	−0.105	0.606	0.0	15.91 ($sp^{5.28}$)	0.02
	O_1	0.315	0.203	−0.639	0.0	18.07 ($sp^{4.53}$)	
O_2 lone pair (II)	O_2	0.0	0.0	0.0	0.888	0.0 (p)	21.08
	N_2	0.0	0.0	0.0	0.448	0.0 (p)	
	O_3	0.0	0.0	0.0	−0.101	0.0 (p)	
N_1O_1 π bond	O_1	0.0	0.0	0.0	0.760	0.0 (p)	
	N_1	0.0	0.0	0.0	0.650	0.0 (p)	
O_3 lone pair (II)	O_3	0.220	0.856	0.419	0.0	5.08 ($\sim$p)	4.35
	N_2	−0.021	0.163	0.018	0.0	1.59 ($\sim$p)	
	N_1	0.018	0.116	0.023	0.0	2.33 ($\sim$p)	
N_2−O_2 σ bond	N_2	0.547	0.148	0.521	0.0	50.47 ($sp^{0.98}$)	1.26
	O_2	0.198	−0.256	−0.538	0.0	9.91 ($sp^{9.09}$)	
O_2 lone pair (III)	O_2	0.191	0.886	−0.355	0.0	5.61 ($\sim$p)	5.27
	N_2	−0.027	0.179	−0.005	0.0	2.27 ($\sim$p)	
	N_1	0.019	0.131	0.023	0.0	2.04 ($\sim$p)	
O_3 lone pair (III)	O_3	0.0	0.0	0.0	0.902	0.0 (p)	18.58
	N_2	0.0	0.0	0.0	0.417	0.0 (p)	
	O_2	0.0	0.0	0.0	−0.108	0.0 (p)	
N_1−N_2 σ bond	N_1	0.087	0.619	0.104	0.0	1.89 ($\sim$p)	3.96
	N_2	0.397	−0.634	−0.011	0.0	28.15 ($sp^{2.55}$)	
	O_2	−0.028	0.081	0.088	0.0	5.32 ($\sim$p)	
	O_3	−0.029	0.091	−0.093	0.0	4.73 ($\sim$p)	

[a] Refer to Figure 3 for the numbering of the atoms and for the coordinate axes.

Table IV. Bond Orders,[a] Dipole Moments, and Binding Energies for N_2O_4, N_2O_2 and N_2O_3

Molecule	Bond orders			Dipole moment, D	Binding energies, kcal mol⁻¹	
	(N–N)[b]	(N–N)[c]	N–O[d]		Theor	Exptl[e]
N_2O_4	0.515	0.873	1.446	0.0	408 (425)[g]	455
N_2O_2	0.600	0.962	2.109	0.397 (0.63)[f]	263 (301)	
N_2O_3	0.587	0.896	N_1–O_1 2.121 N_2–O_2 1.466 N_2–O_3 1.374	2.572 (2.12)[g]	351 (386)	380

[a] Bond order index due to Wiberg = $\Sigma_a \Sigma_b (2\Sigma_i{}^{occ} C_{ia} C_{ib})^2$,[27,28] where a and b are AO's of the two atoms and i is summed over the MO's. [b] Total N–N bond order. [c] N–N bond order calculated exclusively from the N–N bond TLMO. [d] For the numbering of atoms in N_2O_3, refer to Figure 3a. [e] From thermochemical measurements, ref 35. [f] From ab initio calculation, ref 29. [g] From microwave spectrocopy, ref 2 and 5. [h] Binding energies for the geometry optimized structures; see text.

Conclusion

N_2O_2, N_2O_3, and N_2O_4 have only nitrogen–nitrogen σ bonds weakened by oxygen lone-pair delocalization and no N–N π-bonding. The small nitroso angle and large nitro angle are described by hybridization effects and bent bonds.

The localized molecular orbitals described in this paper give a conventional chemical description of the molecules. Properties such as the MO energy levels, atomic charges, and dipole moments calculated by the present semiempirical method agree fairly well with those from the more laborious ab initio calculations. This suggests the wave functions by the two methods are close and would give similar LMO's. However, localization of an ab initio wave function would be comparatively very expensive; moreover, multideterminantal (CI) wave functions cannot be easily localized as they do not have the invariance property of a single determinantal function. These higher level wave functions are also very difficult to analyze in terms of chemical ideas such as bonds, lone pairs, hybridization, etc. In contrasting the two procedures, it is well to remember that the ab initio method too has many aspects of arbitrariness such as the size and nature of the basis set, orbital exponents, types of configurations included, etc. As discussed above for nitrogen oxides, these factors can lead to even quantitatively different answers. Our aim in this paper has been to treat the rather difficult problem of the bonding in nitrogen oxides by a single easy, yet carefully parameterized and reliable semiempirical method. These remarks are not intended as a critique of ab initio vs. semiempirical methods, but to show that each has its own usefulness and limitations.[40,41] When very accurate numbers (but not necessarily agreeing with experiment) are required, or when effects such as those due to electron correlation are to be studied, the ab initio method should be employed, time and money permitting. But when simple and easily interpretable answers to chemical problems for which stringent accuracy of the numbers is irrelevant are desired, a carefully parameterized semiempirical method is adequate. It is an instructive commentary on the state of the art of quantum chemistry that neither the ab initio nor the semiempirical method, within or beyond the Hartree—Fock limit, is capable of predicting quantities, such as dissociation energies and rotational barriers of the order of a few kcal mol⁻¹, which are of great chemical significance as in the present case of the nitrogen oxides.[42]

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(42) These general remarks were prompted by the criticism of the semiempirical methods by one of the referees who calls them "simplistic". Our view is that the two methods are complementary, and one or the other or both may be chosen according to the investigator's requirements.[40,41]

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Configuration Interaction Studies on the Ground and Lower Excited States of N-Methylcarbazole

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Abstract: Ab initio calculations on N-methylcarbazole have been carried out using a basis set obtained from the molecular fragment technique. A self-consistent field calculation was done on the ground state, and configuration interaction studies were carried out subsequently on the ground state plus other low-lying singlet and triplet states. Several electronic structural features were derived from these studies, including ionization potentials, Franck–Condon transition energies, oscillator strengths, charge distributions, and dipole moments. The first ionization potential was found to be lowered in N-methylcarbazole compared to carbazole with other ionization potentials not affected greatly. The ordering of the molecular states is found to be the same as observed experimentally, and the calculated transition energies are found to be linearly related to the observed transition energies. Analysis of the changes in molecular orbital energies and charge distribution are also found to provide a satisfactory rationale for both the red shift in the absorption spectrum observed when carbazole is methylated and the changes in dipole moment in the various states.

I. Introduction

Several experimental spectral studies[1-3] previously have shown the effect of various N-alkyl substituents on the electronic spectra of carbazole. This effect primarily is a major red shift in transitions to the first and third excited singlet states. These results have generated interest in possible causes of the red shift, and the apparently related[4] loss of nitrogen lone pair density in the red-shifted transitions. This study was undertaken to attempt to reproduce theoretically the experimentally observed red shifts and to find a mechanism for their occur-

rence, based on observed changes in the calculated spectrum and electron distribution in the various states of the N-alkylated molecule.

A number of spectral studies have been done to characterize the low-lying excited states and π-charge densities of the ground state of carbazole and its N-alkyl derivatives. Witanowski et al.[3] have characterized these molecules using nitrogen-14 NMR and the linear relationship found between the observed chemical shifts and SCF-PPP-MO π-electron densities at the nitrogen in the ground states of carbazole and N-methylcarbazole. Johnson[1] has studied the spectra of car-