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A Parametrized Valence-Bond Study of the Origin of the Long, Weak N−N Bond of *asym*-N_2O_3

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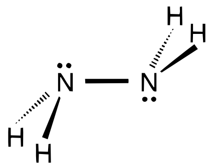
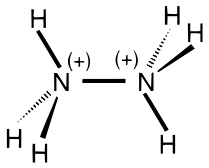
The results of an all-electron STO-6G valence-bond study of the origin of the long, weak N−N bond of *asym*-N_2O_3 are reported. Attention is given to the valence-bond structures which differ in the locations of eight electrons among five overlapping nitrogen and oxygen atomic orbitals, designated as $\bar{\pi}_1$, h_2, and $\bar{\pi}_3$ for NO_2, and h_4 and $\bar{\pi}_5$ for NO. These orbitals accommodate the electrons of the N−N σ-bond and oxygen lone-pair electrons prior to any delocalization of the latter electrons. The calculations are parametrized so that UHF/cc-pVQZ estimates of the atomic spin densities for NO_2 and NO are approximately reproduced when their odd electrons are assumed to occupy these overlapping atomic orbitals. The origin of the N−N bond lengthening is thereby shown to be associated with (a) the orientation of the h_4 atomic orbital, and (b) some delocalization of oxygen $\bar{\pi}$ electrons into the nitrogen h_2 and h_4 atomic orbitals when the latter orbitals are initially singly occupied. Covalent−ionic resonance ($O_2N{-}NO \leftrightarrow O_2N^{-}NO^{+} \leftrightarrow O_2N^{+}NO^{-}$) is calculated to be needed in order to stabilize the N_2O_3 relative to the NO_2 and NO dissociation products.

Introduction

The N−N bond-length[1] of 1.864 Å for *asym*-N_2O_3 (hereafter, N_2O_3) is substantially longer than experimental estimates of the lengths[2,3] of 1.445 Å and 1.438 Å for the N−N bonds of N_2H_4 and $N_2H_6^{2+}$. The primary Lewis-type valence bond (VB) structures for the latter two systems, **I** and **II**, involve electron-pair N−N σ-bonds. The same type of N−N bond is present in each of the familiar Lewis VB structures **III** and **IV** for N_2O_3.



I



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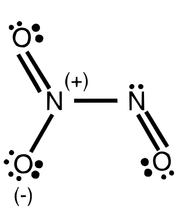

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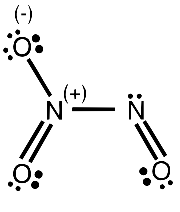
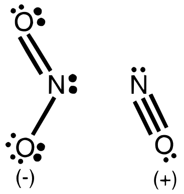
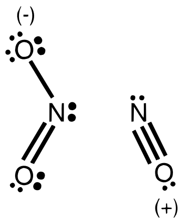


IV

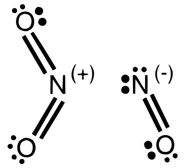
Obvious Lewis-type VB rationalizations for the origin of the substantial bond lengthening in N_2O_3 relative to those of N_2H_4 and $N_2H_6^{2+}$ would involve the "no-bond single-bond" resonance between these structures and either the ionic $O_2N^{-}NO^{+}$ structures **V** and **VI** or the ionic $O_2N^{+}NO^{-}$ structures **VII** and **VIII**.



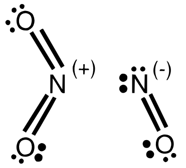
V



VI



VII



VIII

The primary (active space) AOs that are involved in the covalent−ionic resonance are the oxygen $\bar{\pi}_1$, $\bar{\pi}_3$, and $\bar{\pi}_5$ AOs and the nitrogen h_2 and h_4 AOs of Figure 1a. When singly occupied AOs are used to formulate the (Heitler−London type) wave functions for the active-space electron-pair bonds, both of the VB structures **III** and **IV** involve the $(\bar{\pi}_1)^2(h_2)^1(\bar{\pi}_3)^2(h_4)^1(\bar{\pi}_5)^2$ AO configuration, the $(\bar{\pi}_1)^2(h_2)^2(\bar{\pi}_3)^2(\bar{\pi}_5)^1(h_4)^1$ configuration pertains to each of the structures **V** and **VI,** and structures **VII** and **VIII** involve the $(\bar{\pi}_1)^1(h_2)^1(\bar{\pi}_3)^2(h_4)^2(\bar{\pi}_5)^2$ and $(\bar{\pi}_1)^2(h_2)^1(\bar{\pi}_3)^1(h_4)^2(\bar{\pi}_5)^2$ configurations, respectively.

In ref 4, an alternative explanation for the bond-lengthening was provided. Using model four-atom VB calculations (with atoms 1, 2, 4, and 5 of Figure 1, and 24 electrons), it was

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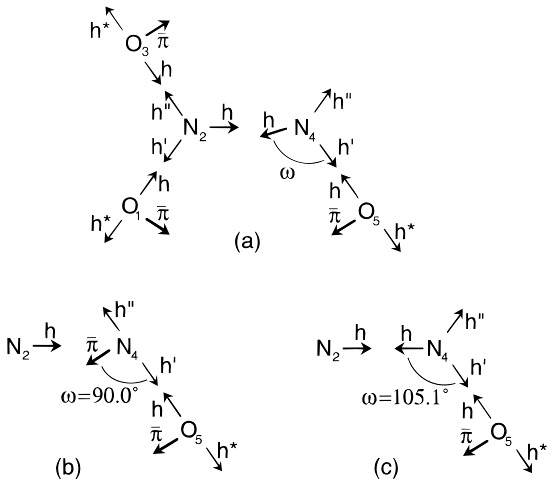
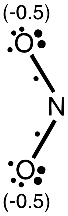


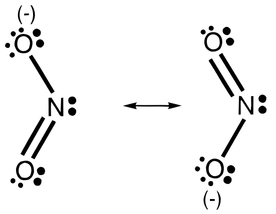
Figure 1. Orientation of the valence shell σ AOs for (a) different values of the hybridation angle ω, (b) $\omega = 90.0°$, and (c) $\omega = 105.1°$, respectively.

demonstrated that the orientation and hybridization of the h_4 AO of Figure 1b is preferred to that of Figure 1c, and that some delocalization of the oxygen $\bar{\pi}_1$ electrons of structure **III** into the h_2 AO is needed in order to lengthen the N−N bond appreciably. Here, we provide further support for this hypothesis by including all atoms and electrons in STO-6G VB calculations, which we parametrize with regard to the distributions of the odd electrons of free NO_2 and NO. Although the primary interaction which is involved in the formation of the N−N bond involves the spin-pairing of the odd electrons of the NO_2 and NO moieties, we shall also show some covalent−ionic resonance is needed in order to stabilize the covalent O_2N−NO structures relative to the NO_2 and NO dissociation products.

Numerous molecular orbital (MO) determinations of the geometry of N_2O_3 have been reported,[7−14] and in accord with the experimental determination, each generates a long N−N bond. For a fixed geometry, some earlier MO studies have been reported in refs 15−19. Qualitative VB representations of the electronic structure of N_2O_3 have been provided using double quartet structures[1] (several of which involve the NO_2 π-electron distribution of structure **IX**), and increased-valence structures,[4,6,20,21] which we shall describe again later in this paper. Each of the component Lewis VB structures that contributes to either of these VB representations for N_2O_3 involves either an electron-pair N−N bond or no N−N bonding electrons. Therefore, resonance between the contributing Lewis structures generates an N−N bond-order which is less than unity, to account for the lengthening and weakening of the N−N bond.



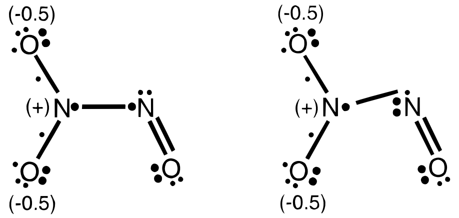
IX



X **XI**

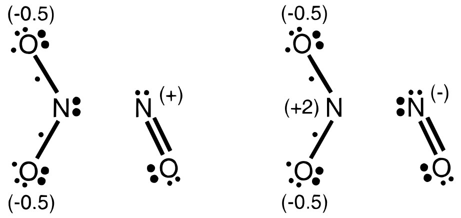
Method

We have used Roso's ab initio program,[22] with "best atom" AO exponents[23] to perform the STO-6G VB calculations. We have idealized slightly the geometry of the NO_2 moiety by using the NO_2 bond length of 1.19 Å, and the NO_2 bond angle of 135° rather than the values reported for N_2O_3. However, the −NO moiety bond length and the $N_2N_4O_5$ bond angle were set at the N_2O_3 equilibrium values of 1.14 Å and 105.1°, respectively. Calculations were performed for different values of the N−N internuclear separation r(NN).



1 **1a**

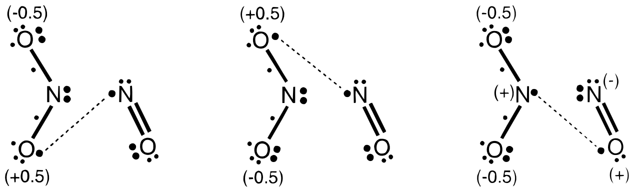
Covalent (O_2N)(NO)



2 **3**

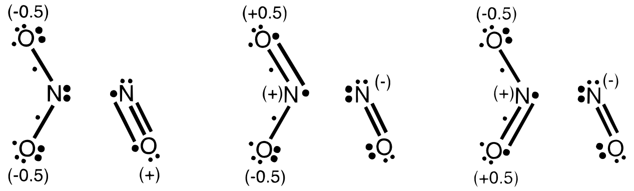
Ionic (O_2N^-)(NO^+) and (O_2N^+)(NO^-)

Figure 2. Valence-bond structures with no delocalization of the $\bar{\pi}_o$ electrons.



4 **5** **6**

Covalent (O_2N)(NO)



7 **8** **9**

Ionic (O_2N^-)(NO^+) and (O_2N^+)(NO^-)

Figure 3. Valence-bond structures with delocalization of one $\bar{\pi}_o$ electron.

The $\bar{\pi}_1$, h_2, $\bar{\pi}_3$, h_4, and $\bar{\pi}_5$ AOs accommodate the eight active-space electrons. With a fixed distribution for the remaining electrons, 15 $S = 0$ spin VB structures of the Lewis type may be constructed that differ in the AO occupancies for these electrons These structures are displayed in Figures 2−4 for the π-electron distribution of VB structure **IX** for NO_2^-. Structures **1**−**3**, **4**−**9**, and **10**−**15** of these figures arise from the delocalization of zero, one, and two oxygen $\bar{\pi}$ electrons into the nitrogen h_2 and h_4 AOs, respectively. Structures **1**, **4**, **5**, **10**, and **11** are covalent (O_2N−NO) structures, and the remaining

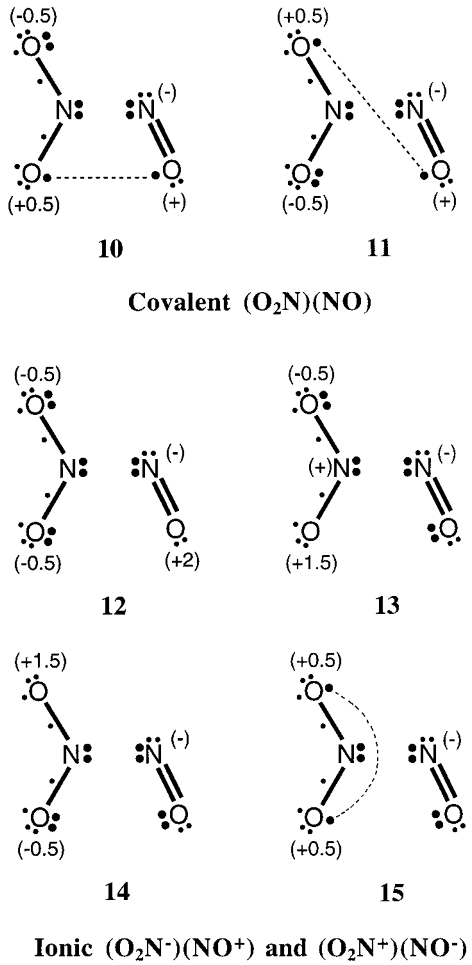


Figure 4. Valence-bond structures with delocalization of two $\bar{\pi}_o$ electrons.

nine structures are ionic ($O_2N^-NO^+$ or $O_2N^+NO^-$) structures. With regard to these distributions of the eight active-space electrons, these VB structures are canonical structures.

Structure **IX** for NO_2^- provides an average for the π-electron distributions of structures **X** and **XI** that arise in structures **III** and **IV** for the NO_2 moiety of the latter structures, and the structure **IX**-type representation for the π-electrons is used in each of the VB structures of Figures 2−4. However, for the purpose of calculation, it is simpler to locate the four $-NO_2$ π-electrons for each VB structure in two three-center MOs of the form $b_1 = \pi_1 + k\pi_2 + \pi_3$ and $a_2 = \pi_1 - \pi_3$, to give the $(b_1)^2(a_2)^2$ configuration for these electrons. (We have used these C_{2v} symmetry MOs at all internuclear separations.) The two π-electrons for the $-N{=}O$ moiety are located in the bonding MO $\phi_1 = \pi_4 + l\pi_5$.

The π-electron parameters k and l were chosen so that VB calculations for NO_2 and NO, with the geometries cited above, reproduced approximately UHF/cc-pVQZ[24] MO estimates[25] of 0.5094 and 0.7976 for the nitrogen odd-electron spin densities for these species. We thereby obtain $k = 2.2$ and $l = 1.2$, which give values of 0.51 and 0.80 for the spin densities. These values for k and l were used at all internuclear separations.

In ref 26, the lengthening of the N−N bond of N_2O_3 relative to that of N_2O_4 has been associated with some delocalization of the nitrogen h''_4 lone-pair electrons into the N−N σ-bond region. This effect would manifest itself in each of the Lewis structures that does not involve a $(h_2)^2(h_4)^2(h''_4)^2$ configuration, i.e., in VB structures **1**−**9**. The Chirgwin−Coulson VB structural weights[27] that are obtained from calculations with 15 structures (cf. Table 5 below) indicate that structure **1** of Figure 2, with a $(h_2)^1(h_4)^1(h''_4)^2$ configuration, is the primary structure of this type. An $h''_4 \rightarrow h_4$ electron transfer generates Lewis structure **1a** of Figure 2, with an $(h_2)^1(h_4)^2(h''_4)^1$ configuration. This structure was also included in some of the VB calculations. Symmetry precludes it from contributing to the ground-state resonance scheme of the NO_2 + NO dissociation products. Structures that arise from an $h''_4 \rightarrow h_4$ electron transfer for each of the (less-important) Lewis structures **2**−**9** were omitted.

TABLE 1: Energies at Various NN Internuclear Separations, *r*(NN), for 15 and 16 Structure Calculations with the Limiting Values of the Hybridization Angle, *ω* (In all Tables, the Units for Energy, *E*, and *r*(NN) Are au and Å, Respectively.)

	15		16	
r(NN)	*ω* = 90.0°	*ω* = 105.1°	*ω* = 90.0°	*ω* = 105.1°
1.6	−331.70446	−331.61706	-	−331.68046
1.7	−331.71951	−331.61860	−331.72122	−331.68605
1.8	−331.72668	−331.61442	−331.72747	−331.68526
1.9	−331.72931	−331.60758	−331.72963	−331.68137
2.0	−331.72909	−331.59951	−331.72919	−331.67591
2.1	−331.72781	−331.59184	−331.72783	−331.67053
∞			−331.71899	

For the $-NO_2$ moiety, an O−N−O bond angle of 134° was used to determine the nature of the (valence-shell) s−p hybridization for the orthogonal hybrid AOs h_2, h'_2, and h''_2 of Figure 1. For NO, the h'_4 AO was assigned the form $h'_4 = (2s_4) + 3(2p'_4)$ (cf. ref 4). The resulting hybrid forms for h_4 and h''_4 were then determined via orthogonality requirements and the value of the h_4−N−h'_4 angle (ω). In Figures 1b and 1c, this angle is equal to 90° and 105.1°, respectively. For $\omega = 90°$, the h_4 AO is equivalent to the $\bar{\pi}_4$ AO.

The pairs of electrons that form the localized N−O σ bonds in each of the VB structures of Figure 2−4 were accommodated in the homopolar, localized MOs $\sigma_{12} = h_1 + h'_2$, $\sigma_{32} = h_3 + h''_2$, and $\sigma_{54} = h_5 + h'_4$, for which the oxygen hybrid AOs h_1, h_3, and h_5 were assigned the hybridization reported elsewhere[22c] for NO_2, namely, $h_O = 0.25(2s_O) + (2p_O)$. On each oxygen atom, there is a (nonactive-space) lone-pair of valence-shell electrons.These electrons were accommodated in a hybrid AO of the form $h^*_O = 0.25(2p_O) - (2s_O)$, which is orthogonal to h_O.

The resulting $S = 0$ spin wave function for each of the VB structures involves either one or two Slater determinants, according to whether there are either zero or two singly occupied “active space” AOs.

Results and Discussion

For the AO orientations of Figures 1b and 1c, i.e., for $\omega = 90°$ and 105.1°, the energies for calculations with structures **1**−**15** and **1a** included are reported in Table 1. They give minimum energies of −331.72970 and −331.68630 au for equilibrium N−N internuclear separations (r_e(NN)) of 1.925 and 1.730 Å, respectively. Therefore, in accord with the results of the four-atom calculations reported in ref 4, the h_4 orientation of Figure 1a is preferred to that of Figure 1b, and the (fractional) N−N σ-bond may be described as a bent bond. When structure **1a** is omitted (Table 3), the N−N bond lengthens slightly to 1.937 Å when $\omega = 90°$. However, there is substantial shortening to 1.667 Å when $\omega = 105.1°$.

To obtain the optimum orientation for the h_4 AO (cf. Figure 1a), we have performed additional calculations with $\omega = 91.89°$, 93°, and 96° at various N−N distances and then interpolated to find minimum energies. The results are reported in Table 2.

TABLE 2: Optimum Energies, *E*, and (a) r_e(NN) for Fixed Hybridization Angle, and (b) Hybridization Angle for Fixed *r*(NN), for 16 VB Structure Calculations

(a)	ω (deg)	r_e(NN)	*E*
	90.0	1.925	−331.72970
	91.89	1.886	−331.73310
	93.0	1.866	−331.73299
	96.0	1.821	−331.72609
	105.0	1.730	−331.68630
	92.36	1.877	−331.73323

(b)	*r*(NN)	ω	*E*
	1.7	93.13	−331.72745
	1.8	92.68	−331.73229
	1.9	92.26	−331.73316
	2.0	91.88	−331.73165
	2.1	91.53	−331.72945
	1.877	92.36	−331.73323

TABLE 3: Optimum Energies, *E*, and (a) r_e(NN) for Fixed Hybridization Angle, and (b) Hybridization Angle for Fixed *r*(NN), for 15 VB Structure Calculations

(a)	ω (deg)	r_e(NN)	*E*
	90.0	1.937	−331.72949
	91.89	1.871	−331.73230
	93.0	1.839	−331.73016
	96.0	1.770	−331.71252
	105.0	1.667	−331.61895
	91.58	1.881	−331.73241

(b)	*r*(NN)	ω (deg)	*E*
	1.6	92.78	−331.71476
	1.7	92.30	−331.72664
	1.8	91.88	−331.73145
	1.9	91.50	−331.73237
	2.0	91.18	−331.73095
	2.1	90.90	−331.72888
	1.881	91.58	−331.73242

TABLE 4: Chirgwin−Coulson Estimates of the Weights and Coefficients of Normalized Wave Functions for the 16 VB Structures of N_2O_3 (cf. Figures 2−4) for ω = 92.36° and r_e(NN) = 1.877 Å[a]

structure	weight	coefficient	structure	weight	coefficient
1	0.429	0.542	**9**	0.022	0.095
2	0.085	0.184	**10**	0.019	0.089
3	0.025	0.073	**11**	0.021	0.096
4	0.117	0.271	**12**	0.001	0.013
5	0.114	0.267	**13**	0.001	0.010
6	0.092	0.211	**14**	0.000_4	0.009
7	0.050	0.158	**15**	0.004	0.043
8	0.021	0.091	**1a**	−0.002	0.048

[a] With these values of ω and r_e(NN), the calculated energy (−331.73314 au) for this Table differs slightly from the interpolated energy of Table 2.

TABLE 5: Chirgwin−Coulson Estimates of the Weights and Coefficients of Normalized Wavefunctions for 15 VB Structures of N_2O_3 (cf. Figures 2−4) for ω = 91.58° and r_e(NN) = 1.881 Å[a]

structure	weight	coefficient	structure	weight	coefficient
1	0.428	0.541	**9**	0.023	0.097
2	0.082	0.183	**10**	0.019	0.089
3	0.024	0.070	**11**	0.021	0.097
4	0.119	0.273	**12**	0.001	0.013
5	0.115	0.289	**13**	0.001	0.010
6	0.093	0.212	**14**	0.000_4	0.009
7	0.049	0.156	**15**	0.004	−0.043
8	0.021	0.092	**1a**		

[a] With these values of ω and r_e(NN), the calculated energy (−331.73228 au) for this Table differs slightly from the interpolated energy of Table 3.

The minimum energy (−331.73323 au) occurs for ω = 92.36° and r_e(NN) = 1.877 Å, to give a dissociation energy (D_e) of 37.24 kJ mol^{-1}. An approximate estimate of 0.34 kJ mol^{-1} for the zero-point energy for N−N vibration is obtained from the observed wavenumber[28] ν_6 = 241 cm^{-1} for N_2O_3, which has been identified[29] primarily (85%) with the N−N stretching mode of vibration. The resulting estimate for the chemical dissociation energy, D_o, is 36.9 kJ mol^{-1}. Allowance for a basis set superposition error (BSSE, see Appendix) changes the estimates for r_e(NN) and D_o slightly to 1.876 Å and 35.0 kJ mol^{-1}, respectively. The calculated values for r_e(NN) and D_o, with or without BSSE correction, are in reasonable accord with experimental estimates[1,30] of 1.864 Å and 39.7 kJ mol^{-1} for these quantities. Because inclusion of the BSSE correction hardly affects the bond length in this 16-structure calculation, we will not report BSSE-corrected values for the calculations with smaller numbers of structures.

In Table 4, we report the magnitudes of the coefficents for the normalized wave functions for structures **1**−**15** and **1a** when ω = 92.36° and r_e(NN) = 1.877 Å, together with the Chirgwin−Coulson[27] estimates of the structural weights. The primary structure is **1**, with an N−N bond. The covalent ($O_2N{-}NO$) structures **4**−**6**, and the ionic ($O_2N^-NO^+$) structures **2** and **7** also make appreciable contributions to the ground-state resonance scheme. These results are in general accord with qualitative expectations based on formal charge considerations. Omission of structure **1a**, (Tables 3 and 5), affects only slightly the length and strength of the N−N bond.

We now describe the results of calculations (Table 6) with smaller numbers of VB structures.

(a) If no delocalization of oxygen lone-pair electrons occurs, the relevant VB structures are **1**−**3** and **1a** of Figure 2. Resonance between structures **1**−**3** generates a minimum energy at r_e(NN) = 1.619 Å for ω = 92.4°. When ω = 90° and 105.1°, energy minima occur at r_e(NN) = 1.658 and 1.485 Å, respectively. The latter length is in reasonable accord with the length of a "normal" N−N σ-bond (1.43−1.45 Å),[2,3] for which the h_2 and h_3 AOs are oriented along the N−N internuclear axis. When structure **1a** is included, the minimum energy occurs at r_e(NN) = 1.624 Å for ω = 93.39°. With structures **1**−**3** and **1a**, ω = 90° and 105.1° give energy minima at 1.631 and 1.589 Å. Thus, allowance for $\bar{\pi}_O$ electron delocalization, via the inclusion of structures **4**−**15**, lengthens the N−N bond to 1.925, 1.877, and 1.730 Å when ω = 90°, 92.36°, and 105.1°, respectively (Table 2). Similar types of optimum N−N bond lengths and angles are obtained when structure **1a** is omitted from the calculations with sixteen structures (Table 3).

For ω = 92.36°, the (fractional) N−N bond is a bent bond.[4] We note however that the Lagrangian of the electron charge-density distribution of ref 13, which was obtained using MO procedures, does not appear to involve this type of bond.

(b) In Table 6, the results of the calculations with (i) structures **6**, **7**, and **10**−**12** omitted and (ii) structures **4**, **5**, **8**−**11**, and **13**−**15** omitted show that delocalization of the $\bar{\pi}_1$ and $\bar{\pi}_3$ electrons of the $-NO_2$ moiety leads to a greater N−N bond lengthening (1.781 Å, ω = 92.72°) than does delocalization of the $\bar{\pi}_5$ electrons of the −NO moiety (1.721 Å, 93.15°). This result is in accord with the following considerations. For the dissociation products of calculation (i), the NO_2 and NO nitrogen odd-electron spin densities are 0.51 and 1.0, whereas they are 1.0 and 0.8 for calculation (ii). The resulting N−N bond numbers are 0.2601 and 0.64 for the (i) and (ii) calculations, respectively. These bond numbers imply that calculation (i) should generate a longer N−N bond.

(c) The primary process which occurs for the $NO_2 + NO \rightarrow N_2O_3$ reaction involves the spin-pairing in a σ-manner of the odd electrons of the reactants. The VB structures that participate in this process are the covalent structures **1**, **4**−**6**, **10**, and **11** of

TABLE 6: Energies, E, Equilibrium Internuclear Separations, r_e(NN), and Hybridization Angles, ω, for Resonance between Selected VB Structures. For a−e; See Text

		best			$\omega = 90°$		$\omega = 105.1°$	
	resonance	ω	r_e(NN)	$E + 331.0$	$r_{e(NN)}$	$E + 331.0$	r_e(NN)	$E + 331.0$
(a)	**1 ↔ 2**	92.48°	1.645	−0.56903	1.703	−0.55894	1.483	−0.44418
	1 ↔ 2 ↔ 3	92.42°	1.619	−0.58204	1.658	−0.57300	1.485	−0.46817
	1 ↔ 2 ↔ 1a	93.02°	1.650	−0.56937	1.656	−0.56390	1.616	−0.53835
	1 ↔ 2 ↔ 3 ↔ 1a	93.39°	1.624	−0.58275	1.631	−0.57671	1.589	−0.55585
(b)	**1 ↔ 2 ↔ 3 ↔ 4 ↔ 5 ↔ 8 ↔ 9 ↔ 13 ↔ 14 ↔ 15 ↔ 1a**	92.72°	1.781	−0.67871	1.825	−0.67407	1.651	−0.63720
	1 ↔ 2 ↔ 3 ↔ 6 ↔ 7 ↔ 12 ↔ 1a	93.15°	1.721	−0.64612	1.734	−0.63963	1.680	−0.61173
(c)	**1 ↔ 2 ↔ 4 ↔ 5 ↔ 6 ↔ 7 ↔ 10 ↔ 11 ↔ 1a**	90.86°	2.140	−0.71936	2.770	−0.71927	1.880	−0.65848
	1 ↔ 2 ↔ 3 ↔ 4 ↔ 5 ↔ 6 ↔ 7 ↔ 8 ↔ 9 ↔ 10 ↔ 11 ↔ 1a	92.33°	1.881	−0.73129	1.931	−0.72789	1.727	−0.68370
(d)	**1 ↔ 2 ↔ 4 ↔ 5 ↔ 6 ↔ 7**	91.49°	1.905	−0.70111	1.968	−0.69813	1.627	−0.56012
	1 ↔ 2 ↔ 4 ↔ 5 ↔ 6 ↔ 7 ↔ 1a	92.22°	1.902	−0.70196	1.957	−0.69830	1.749	−0.64451
(e)	**1 ↔ 2 ↔ 7 ↔ 8 ↔ 9**	93.98°	1.624	−0.62696	1.676	−0.61285	1.492	−0.52188
	1 ↔ 2 ↔ 7 ↔ 8 ↔ 9 ↔ 1a	93.69°	1.632	−0.62741	1.633	−0.61926	1.573	−0.59961

Figures 2−4. The present type of VB calculations for the covalent structures alone (together with structure **1a**, which does not contribute when r(NN) $= \infty$) generates no stabilization of N_2O_3 relative to the infinitely separated dissociation products. Therefore, covalent−ionic resonance is needed to generate the stabilization. In Table 4, the primary ionic structures are **2** and **7**, and when these structures are included in the resonance scheme together with the seven covalent structures (Table 6), a minimum energy is obtained when $\omega = 90.86°$ with r_e(NN) = 2.140 Å. With this set of structures, a further shortening to 1.880 Å is calculated to occur when $\omega = 105.1°$. When only the unimportant ionic structures **12**−**15** of Tables 4 and 5 are excluded, the energy-optimized N−N bond-length of 1.881 Å is similar to the 1.877 Å obtained for the 16 structure calculation of Table 2.

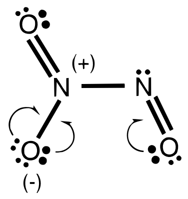
(d) The structural weights reported in Tables 4 and 5 show that the primary structures are **1**, **2**, and **4**−**7**. Resonance between these structures generates an energy-optimized N−N bond-length of 1.905 Å when $\omega = 91.49°$. These structures have the most-favorable distributions of atomic formal charges. Inclusion of structure **1a** shortens the bond slightly to 1.902 Å for $\omega = 92.22°$.

(e) In the Introduction, it was indicated that a conventional type of VB rationalization for the origin of the N−N bond lengthening would involve resonance between VB structures **III**−**VIII**. Because of the nature of the assumed π-electron distribution, i.e., that of **IX** rather than **X** ↔ **XI**, we have not tested directly this hypothesis. However, with regard to the distribution of the active-space electrons that occupy the h_2, h_4, and three $\bar{\pi}_O$ AOs, the corresponding structures here are **1** and **7**−**9**. We have included these structures in calculations, together with the important ionic structure **2**, which involves no delocalization of $\bar{\pi}_O$ electrons. Resonance between these five structures generates a minimum energy at r_e(NN) = 1.624 Å for $\omega = 93.98°$; with structures **7**−**9** omitted, the minimum energy occurs at 1.645 Å for $\omega = 92.48°$. Inclusion of structure **1a** lengthens the N−N bond only slightly, viz. r_e(NN) = 1.632 Å when $\omega = 93.69°$. Thus, with regard to the distribution of the eight active-space electrons, a resonance scheme that resembles the **III** ↔ **IV** ↔ **V** ↔ **VI** ↔ **VII** ↔ **VIII** resonance does not lead to a lengthening of the N−N bond when the hybridization angle ω is energy optimized. However, when the h_4 AO is oriented along the N−N internuclear separation, i.e., $\omega = 105.1°$, r_e(NN) increases from 1.492 to 1.573 Å when structure **1a** is included.

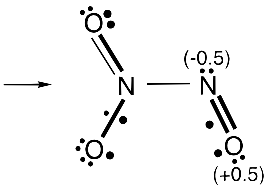
(f) Structure **1a**, which does not contribute when the reactants are infinitely separated, affects significantly the length of the N−N bond only when this bond is relatively short (~1.5 Å) and ω is near 105.1° (cf. the **1** ↔ **2** ↔ **3** and **1** ↔ **2** ↔ **3** ↔ **1a** resonances, for which no $\bar{\pi}_O$ electron delocalizations occur, and the resonances discussed in the previous paragraph). These conditions permit the singly occupied h_2 and h_4'' AOs of structure **1a** to overlap appreciably.

Increased-Valence Structures

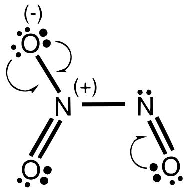
On several occasions,[4,6,20,21] it has been indicated that the Lewis-type VB structures **III** and **IV** may be stabilized via the one-electron delocalizations of oxygen $\bar{\pi}$ and π electrons, as is indicated in **XII** → **XIII** and **XIV** → **XV**.



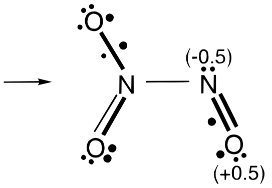
XII



XIII



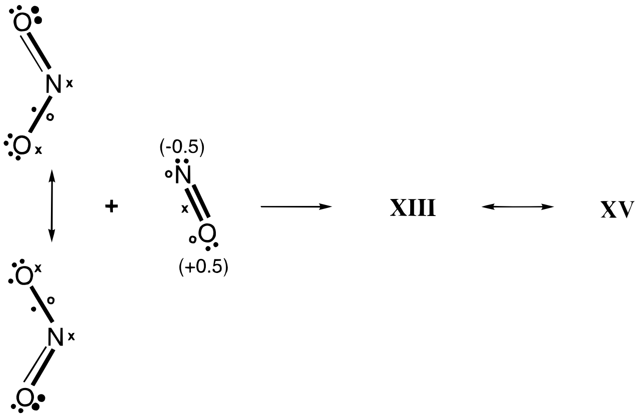
XIV



XV

These VB structures, which are examples of increased-valence structures,[4,6,20,21] may also be obtained by spin-pairing[4,6,20,21] of the (delocalized) odd-electrons of NO_2 and NO of **XVI**, whose VB structures involve a Pauling three-electron bond for three of the active space σ-electrons. (Crosses and circles, × and ○, represent electrons with m_s spin quantum numbers of $+^1/_2$ and $-^1/_2$, respectively.) With regard to the distribution of the eight active-space electrons, resonance between the increased-valence structures **XIII** and **XV** is equivalent to resonance between the covalent structures **1**, **4**−**6**, **10**, and **11** of Figures 2−4. It is also equivalent[22c] to use of the moiety-MO configuration $(a_1)^2(b_2)^2(a_1^*)^1(a)^2(b)^1$, with $a_1 = \bar{\pi}_1 + \kappa h_2 + \bar{\pi}_3$, $b_2 = \bar{\pi}_1 - \bar{\pi}_3$, $a_1^* = \bar{\pi}_1 - \kappa^* h_2 + \bar{\pi}_3$, $a = h_4 + \lambda\bar{\pi}_5$, and $b = h_4 - \lambda^*\bar{\pi}_5$ to accommodate these electrons. Ionic-type configurations may then be obtained via $b \rightarrow a_1^*$ and $a_1^* \rightarrow b$ electron transfers. The structural weights reported in Tables 4 and 5 indicate that the primary ionic structures are **2** and **7**, and these are of the $(O_2N^-)(NO^+)$ type, thereby indicating that the extent to which $b \rightarrow a_1^*$ electron-transfer occurs is greater than it is for $a_1^* \rightarrow b$ electron transfer.

In refs 22c and 31, other types of VB representations for NO_2 are provided, and these may be applied to the $-NO_2$ substituent of N_2O_3. We shall not consider them here. We note also that



XVI

the double-quartet structures **IV** and **V** of ref 1 become increased-valence structures when a (fractional) N−N bond-line is located between the unpaired electrons on the nitrogen atoms of each of these structures (cf., **XVI** → **XIII** ↔ **XV** here and ref 32 for N_2O_4).

Conclusions

The results of the parametrized VB calculations reported here, with all electrons included, provide further support for the hypothesis[4] that the lengthening and weakening of the N−N bond of N_2O_3 is associated primarily with the nature of the hybridization of the NO-moiety nitrogen AOs, and the delocalization of the odd electron of the NO_2 moiety. It has been demonstrated elsewhere[4,33] that the former effect, coupled with associated nonbonded repulsions between lone pairs on the nitrogen atoms, is responsible for the existence of a very long N−N bond (2.24 Å) for C_{2v} N_2O_2, whereas the latter effect lengthens the N−N bond of D_{2h} N_2O_4 from 1.4 to 1.5 Å, to 1.78 Å. However, to stabilize the N_2O_3 relative to the NO_2 and NO dissociation products, it is calculated that it is necessary to allow for some charge transfer to occur between the two radicals, primarily from NO to NO_2.

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Appendix: Basis Set Superposition Error

We have used the counterpoise method[34] to estimate values for the BSSE for N−N internuclear separations of 1.7, 1.8, 1.877, 2.0, and 2.1 Å. For each of these distances, this procedure involves the calculation of the energies for NO_2, with NO AOs included, and NO with NO_2 AOs included. The following nine and eight VB configurations (with either 18 NO_2 or 12 NO core electrons also included) are needed for these two sets of calculations.

(a) The NO_2 configurations, $(\bar{\pi}_1)^1(h_2)^2(\bar{\pi}_3)^2$, $(\bar{\pi}_1)^2(h_2)^1(\bar{\pi}_3)^2$ and $(\bar{\pi}_1)^2(h_2)^2(\bar{\pi}_3)^1$, together with six $(NO_2^+)(\phi_{NO})^1$ configurations, in which the NO_2^+ is obtained by removing the odd $\bar{\pi}_1$, h_2, or $\bar{\pi}_3$ electron and locating it in either of the h_4 or $\bar{\pi}_5$ AOs (ϕ_{NO}) of NO.

(b) The NO configurations, $(h_4)^1(\bar{\pi}_5)^2$ and $(h_4)^2(\bar{\pi}_5)^1$, together with six $(NO^+)(\phi_{NO_2})^1$ configurations, in which the NO^+ is obtained by removing the odd h_4 or $\bar{\pi}_5$ electron and locating it in one of the $\bar{\pi}_1$, h_2, or $\bar{\pi}_3$ AOs (ϕ_{NO_2}) of NO_2.

At infinite separation between the NO_2 and NO, the hybridization angle ω of Figure 1 is equal to 90°, and this angle was retained for the BSSE calculations. For N−N internuclear separations of 1.7, 1.8, 1.877, 2.0, and 2.1 Å, the resulting values for the BSSE ($\times 10^4$) are 5.58, 6.69, 7.14, 7.02, and 6.50 au, respectively.

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