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Valence bond and molecular orbital studies of three N_2O isomers, and valence bond representations for some azide decompositions

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Abstract The results of STO-6G valence bond calculations with Lewis-type valence bond structures are reported for the S=0 spin ground states of the linear NNO ($C_{\infty v}$) and NON ($D_{\infty h}$) isomers of N_2O. It is calculated that the singlet diradical character of the NON isomer is substantially larger than for the NNO isomer. The results of B3LYP/6-31G(d) density functional calculations are also reported for the $C_{\infty v}$ and $D_{\infty h}$ ground states, the single-determinant approximations to the lowest-energy S=1 spin excited states of these two isomers, and for the triangular C_{2v} isomer. The calculated bond lengths are in accord with qualitative valence bond considerations.

Valence bond formulations of mechanisms for $O(N_3)_2 \rightarrow N_2O + 2N_2$ and $C_6(CH_2N_3)_6 \rightarrow 3C_2 + 3H_2 + 6HCN + 6N_2$ decompositions are presented. These formulations exploit the singlet diradical character present in the azide substituents. The results of further molecular orbital calculations for the $O(N_3)_2$ decomposition are also provided.

Keywords Nitrous oxide isomers · Oxygen diazide · Hexa(azidomethyl)benzene · Valence bond · Density functional

Introduction

As well as the $C_{\infty v}$ (linear NNO) isomer of N_2O, higher-energy C_{2v} (isosceles triangle) and $D_{\infty h}$ (linear NON) isomers have been located on the ground-state (singlet, S=0 spin) potential energy surface. [1, 2, 3, 4, 5, 6] A qualitative valence bond (VB) formulation for a $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization mechanism has also been provided. [5] Electron momentum spectroscopy (EMS) studies, together with density functional theory (DFT) molecular orbital (MO) calculations, have revealed the core MO contributions to the N_2O isomerization, [7] and the valence MOs for the $C_{\infty v}$ structure isomer have been similarly examined. [8]

In this paper, we provide additional VB and MO considerations, (a), (b) and (c) here, for these isomers and related systems.

a. For the singlet (S=0) spin ground states of the $C_{\infty v}$ and $D_{\infty h}$ isomers, we report the results of STO-6G VB calculations, and use them to compare qualitative VB descriptions of their electronic structures. Both canonical Lewis structures and increased-valence [9, 10, 11, 12, 13, 14, 15, 16] structures are used for this purpose. It is calculated that each isomer involves appreciable singlet diradical character, but the canonical Lewis structures responsible for this property differ for the two isomers.
b. For each of the three N_2O isomers, we have used the hybrid Hartree–Fock DFT method B3LYP/6-31G(d) to perform MO calculations [17] of the geometries for its S=0 spin ground state, and a single-determinant approximation, via GAUSSIAN 98, [17] to its lowest-energy triplet (S=1 spin) excited state. The results of these calculations are reported, and the bond lengths are shown to be in qualitative accord with those implied by the primary VB structures for these isomers. For the $C_{\infty v}$ and $D_{\infty h}$ isomers, these VB structures are of the increased-valence type. [5, 9, 10, 11, 12, 13, 14, 15, 16]
c. We provide qualitative VB representations for the formation of the C_{2v} and $C_{\infty v}$ isomers of N_2O via the decomposition of the recently characterized [4] $O(N_3)_2$. A qualitative VB representation for the decomposition of the recently prepared [18] $C_6(CH_2N_3)_6$ is also presented. Each of these VB representations exploits the singlet diradical character, which is also present in the azide substituents as well as in NNO.

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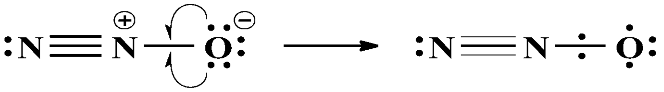
To provide a focus for this paper, we shall initially redescribe the construction of increased-valence structures for the familiar, well-characterized $C_{\infty v}$ isomer.

Valence bond structures for the NNO $C_{\infty v}$ isomer

As discussed recently in [5, 9, 10], on many occasions, [11] it has been indicated that the primary VB structure for linear NNO is the increased-valence structure **II** (shown in Scheme 1), with fractional π_x(NN) and π_y(NN) bonds and one-electron π_x(NO) and π_y(NO) bonds (Scheme 1). This VB structure may be constructed from the familiar standard Lewis structure **I** via the one-electron delocalizations of oxygen $2p\pi_x$ and $2p\pi_y$ electrons into π_x(NO) and π_y(NO) bonding MOs, as indicated in **I**. Three less-important increased-valence structures, **IV**, **VI** and **VIII** (shown in Scheme 2), may be constructed from the familiar Lewis structures **III**, **V** and **VII** via one-electron delocalizations, but only the increased-valence structure **II** is needed in order to demonstrate simply the primary features of the electronic reorganization that may occur for $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization via a unimolecular process. [5]

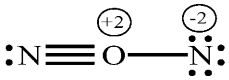
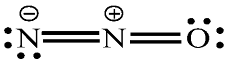
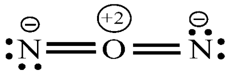
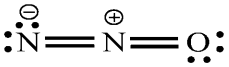
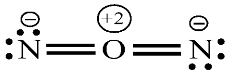
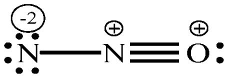
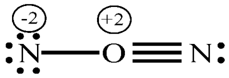
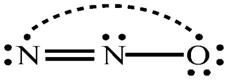
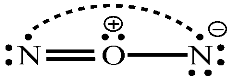
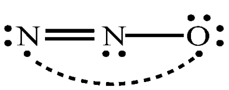
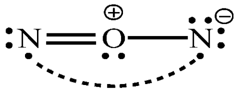
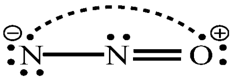
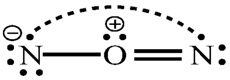
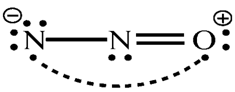
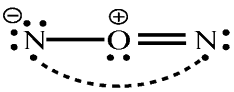
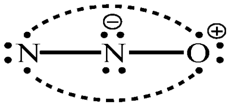
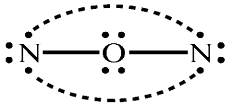
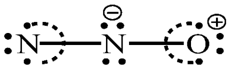


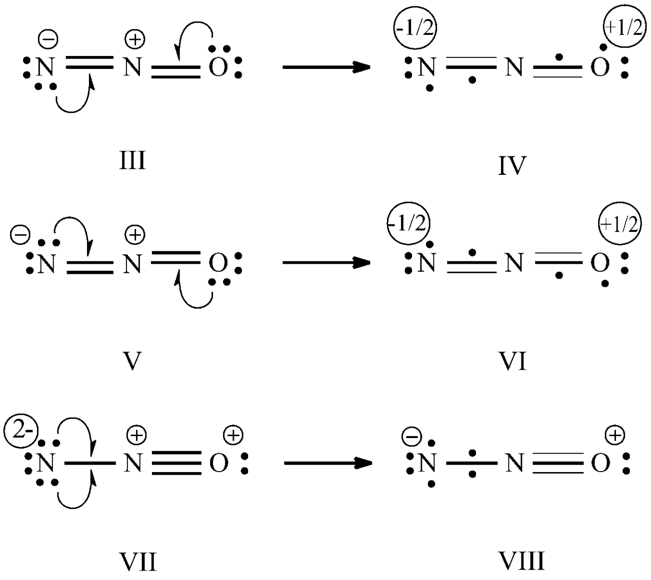
I **II**

Scheme 1 Structures of **I** and **II**

The simplest formulation of the wavefunctions for the fractional π_x(NN) and π_y(NN) bonds of increased-valence structure **II** involves the use of nitrogen $2p\pi_x$ and $2p\pi_y$ AOs to form Heitler–London-type wavefunctions (for example, $a(1)b(2)+b(1)a(2)$ in which a and b are a pair of overlapping $2p\pi_x$ or $2p\pi_y$ AOs). Using this formulation, it has been deduced on numerous occasions [9, 10, 11, 12, 13, 14, 15, 16] that increased-valence struc-

Table 1 (STO-6G) Chirgwin–Coulson [28] structural weights for $C_{\infty v}$ NNO [16] and $D_{\infty h}$ NON isomers, with polarized σ-bonds. For NON, the weights in parentheses have been calculated as $W_i=C_i^2/\Sigma_i C_i^2$ (cf. [29]), thereby ensuring that no negative weights are obtained

1		0.194		0.010 (0.003)
2		0.104		0.028 (0.016)
3		0.104		0.028 (0.016)
4		0.005		0.010 (0.003)
5		0.241		0.131 (0.113)
6		0.241		0.131 (0.113)
7		0.029		0.131 (0.113)
8		0.029		0.131 (0.113)
9		0.052		0.439 (0.476)
10				-0.038 (0.040)



Scheme 2 Structures of **III**–**VIII**

Table 2 B3LYP/6-31G(d) [17] estimates of bond lengths and angles (r and θ), energies (E), dipole moments (μ) and atomic net charges (Q) for singlet-spin ground state and single-determinant approximation to the first triplet-spin excited state for the three N_2O isomers

Property	Singlet	Triplet
N–N'–O ($C_{\infty v}$)		
r(NN') (Å)	1.134	1.267
r(NO) (Å)	1.193	1.226
E (a.u.)	–184.660273	–184.482421
μ (Debye)	–0.02	0.55
Q(N) (a.u.)	0.62	0.38
Q(N') (a.u.)	–0.12	–0.07
Q(O) (a.u.)	–0.50	–0.31
N–O–N (triangular) (C_{2v})		
r(NN) (Å)	1.185	1.434
r(NO) (Å)	1.532	1.386
θ(NNO) (°)	45.50	62.29
E (a.u.)	–184.551165	–184.499011
μ (Debye)	–1.00	–0.05
Q(N) (a.u.)	0.14	0.06
Q(O) (a.u.)	–0.28	–0.12
N–O–N ($D_{\infty h}$)		
r(NO) (Å)	1.190	1.277
E (a.u.)	–184.478611	–184.410552
μ (Debye)	0.0	0.0
Q(N) (a.u.)	–0.07	0.03
Q(O) (a.u.)	0.14	–0.06

ture **II** is equivalent to resonance between the (S=0 spin) canonical Lewis structures **1**, **5**, **6** and **9** of Table 1, each of which has two singly-occupied $2p\pi_x$ and two singly-occupied $2p\pi_y$ AOs. Structures **5**, **6** and **9** have either one or two "long" or formal bonds (—) with negligible strengths, and when these types of bond-lines are not indicated, such structures are designated as "singlet diradical" structures. There are five other canonical Lewis structures with two singly-occupied $2p\pi_x$ and two singly-occupied $2p\pi_y$ AOs (Table 1), and the results of both semiempirical [15] and ab initio VB calculations [16] (cf. Table 1 here also) show that structures **1**, **5** and **6** are the primary canonical Lewis structures, with the familiar canonical structures **2** and **3** also making substantial contributions to the ground-state resonance scheme.

Increased-valence structure **II** will participate in resonance with increased-valence structures **IV**, **VI** and **VIII**. However the N–N and N–O bond orders that are implied by increased-valence structure **II**, with a fractional N–N triple bond and an N–O double bond, are in qualitative accord with experimental [19] and/or calculated (Table 2) estimates for the N–N and N–O bond lengths, namely 1.13 Å and 1.19 Å (cf. an STO-6G estimate 1.07 Å for an N–N triple bond with the same AO hybridization, [20] and 1.20 Å for an N–O double-bond [21]).

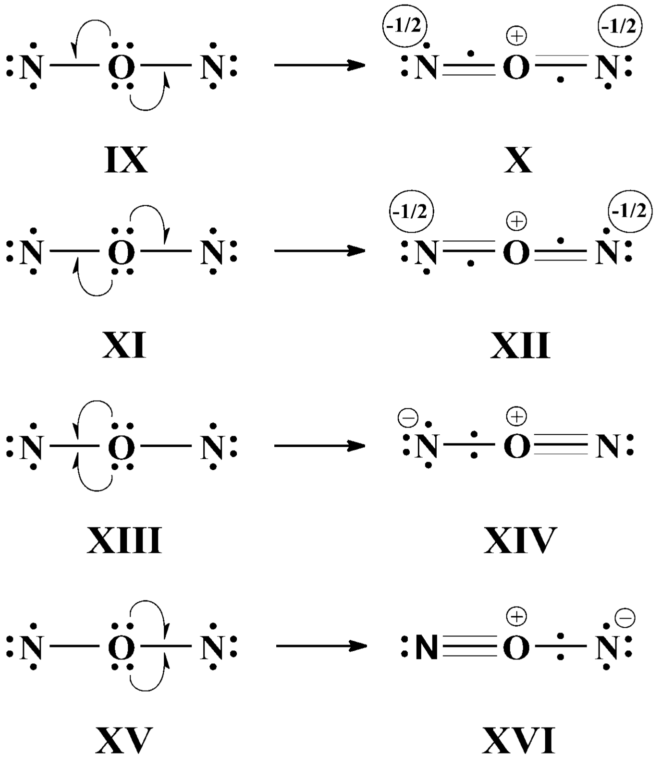
Valence bond structures for the NON $D_{\infty h}$ isomer

For comparison with the NNO $C_{\infty v}$ isomer, we have also performed some STO-6G ab initio VB calculations for the NON $D_{\infty h}$ isomer, with ten canonical Lewis structures included in the resonance scheme (Table 1). Structure **9** of Table 1 has four singly-occupied oxygen $2p\pi_x$ and $2p\pi_y$ AOs. Because this structure is calculated to be an important structure for NON in a nine-structure calculation, we have also included structure **10** with the second allowed Rumer-type spin-pairing scheme. [13c] The VB computational procedure, with allowance made for polarization of the N–O σ bonds, is described in [16]. Although the calculations use a very modest basis set, they are good enough to enable a comparison to be made of the primary qualitative VB features of the electronic structures of NNO and NON, each in its ground state.

The results of the calculations for NON (Table 1) show that the primary canonical structures are the singlet diradical structures **5**–**9**. As is the case for the NNO isomer, [15, 16] the (STO-6G) primary canonical structures are those that involve either zero atomic formal charges or a pair of (+) and (–) formal charges located on adjacent atoms. (N.B. In VB structures, atomic formal charges are assigned on the assumption that bonding electrons are shared equally by pairs of adjacent atoms. Such formal charges are of course not the variationally best formal charges.) From structure **9**, we can construct increased-valence structures **X, XII**, **XIV** and **XVI** as indicated in **IX**→**X**, **XI**→**XII**, **XIII**→**XIV** and **XV**→**XVI** (shown in Scheme 3). Formal charges considerations indicate that structures **X** and **XII** are the primary increased-valence structures.

With Heitler–London formulations of the wavefunctions for the fractional π_x(NO) and π_y(NO) bonds, resonance between increased-valence structures **X** and **XII** is equivalent to resonance between the important (Table 1) canonical Lewis structures **2**, **3** and **5**–**9**.

The ab initio MP2/6-311++G(d), CCSD(T)/ANO and BD(T)/cc-pVTZ MO estimates of the N–O bond length for the S=0 spin $D_{\infty h}$ isomer are 1.34 Å [4] and 1.20 Å, [5, 6] respectively. The B3LYP/6-31G(d) estimate in the present work (Table 2) is 1.19 Å. Each of these lengths is substantially shorter than the estimate of 1.44 Å [22] for a “normal” N–O single bond, and resonance between increased-valence structures **X** and **XII** reflects the presence of double-bond character.



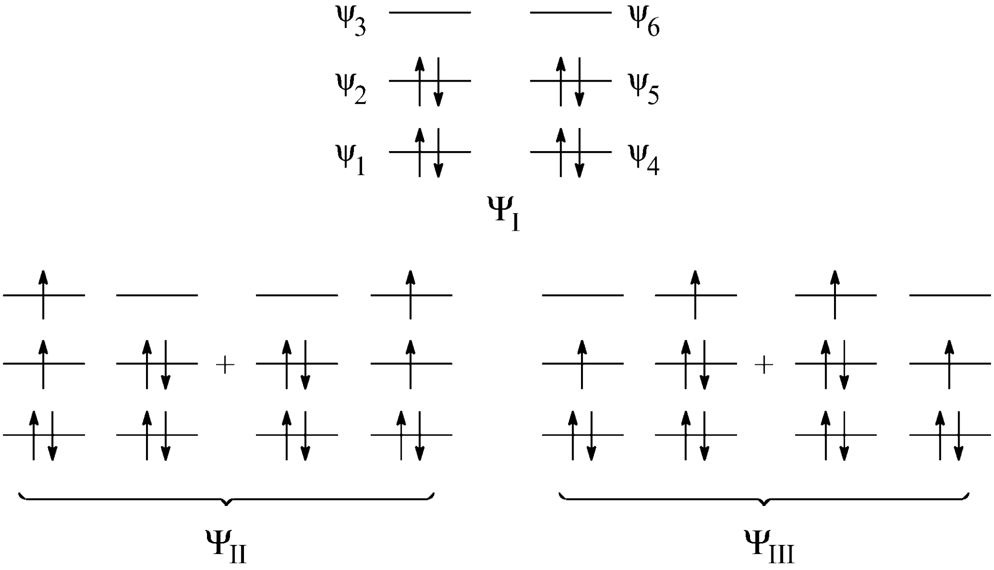
Scheme 3 Structures of **IX**–**XVI**

For a fixed σ-electron core, 36 S=0 spin canonical Lewis structures [15] can be constructed for each of the linear NNO and NON isomers with four $2p\pi_x$ and four $2p\pi_y$ electrons. The spin-pairings occur within rather than between each set of four electrons. If localized MOs (LMO) instead of Heitler–London AO-type wavefunctions are used to accommodate the electrons that form the fractional π_x(NN) and π_y(NN) bonds in VB structure **II**, then this structure is equivalent to resonance between 25 canonical Lewis structures of this type. [9, 20] Canonical structure **10** of Table 1 involves two sets of spin-pairings between the $2p\pi_x$ and $2p\pi_y$ electrons. There are eight additional structures of this type. However, because these structures involve the breaking of N–N and/or N–O π bonds in structures **1**–**8** of Table 1, these structures will only make small contributions to the ground-state resonance schemes. Therefore they have been excluded from the calculations.

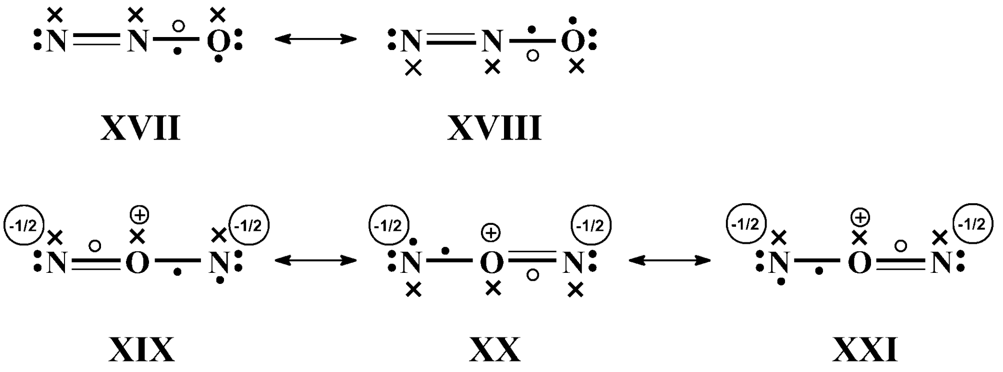
B3LYP/6-31G(d) MO characterizations of the S=0 and S=1 spin states for the $C_{\infty v}$, C_{2v} and $D_{\infty h}$ isomers

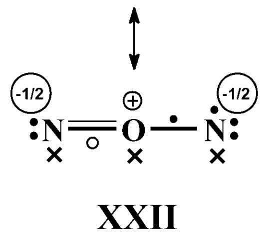
In Table 2, we report the DFT B3LYP/6-31G(d) [17] estimates of the energies (a.u.), bond lengths (Å), dipole moments (Debye) and atomic net charges (a.u.) for the lowest-energy S=0 and S=1 spin states for the three N_2O isomers. Each of the calculations involves a single determinantal wavefunction. This type of formulation is satisfactory for the S=0 spin ground state of each isomer, with a $\Psi_I=(\psi_1)^2(\psi_2)^2(\psi_4)^2(\psi_5)^2$ π-electron configuration (cf. Fig. 1). However, low-energy S=1 spin states for the $C_{\infty v}$ and $D_{\infty h}$ isomers, Ψ_{II} and Ψ_{III} of Fig. 1, involve linear combinations of two degenerate configurations. As a consequence, our single-determinant calculations are unable to indicate the symmetries of the degenerate configurations from the resulting wavefunctions. In the Appendix, it is deduced that the energy of Ψ_{II} lies below that of

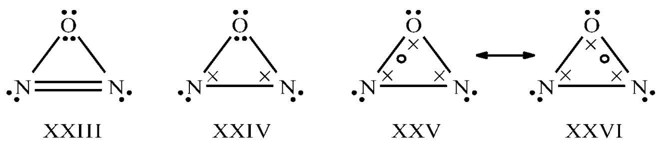
Fig. 1 π_x and π_y electron MO configurations for the S=0 spin ground state (Ψ_I) and two S=1 spin excited states (Ψ_{II} and Ψ_{III}) of the linear NNO and NON isomers



Scheme 4 Structures of **XVII–XXII**





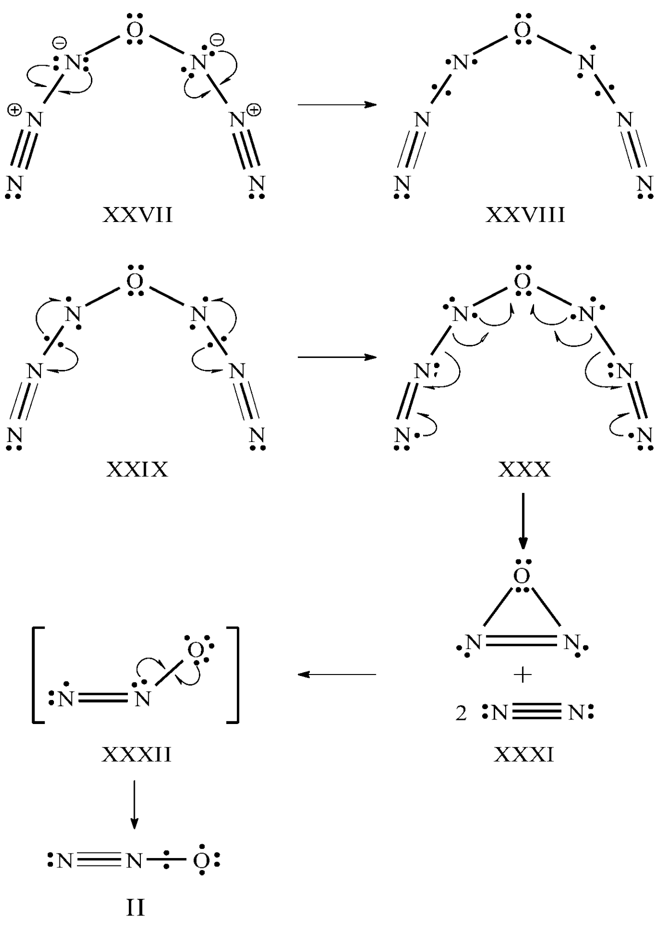


Scheme 5 Structures of **XXIII–XXVI**

Ψ_{III}. Therefore we shall assume that the geometries obtained from the single determinant calculations for the S=1 spin states for the linear isomers are associated with those that obtain for a Ψ_{II}-type symmetry wavefunction.

As indicated above, the calculated (Table 2) bond lengths for the (S=0 spin) $C_{\infty v}$ isomer are in good accord with experimental estimates for these quantities. For the $C_{\infty v}$ and C_{2v} isomers, the S=1 spin N–N bond lengths are respectively 0.133 Å and 0.249 Å longer than the S=0 spin N–N bond lengths (Table 2). Relative to the N–O bond lengths for the S=0 spin isomers, the N–O bond lengths for the S=1 spin N–O isomers increase by 0.033 Å for the $C_{\infty v}$ isomer and 0.087 Å for the $D_{\infty h}$ isomer, whereas they are reduced by 0.146 Å for the C_{2v} isomer. These changes in the calculated bond lengths for the S=1 spin excited states relative to the S=0 spin ground states are in accord with what is expected for excitation of an electron. The associated VB structures for the S=1 spin states of the $C_{\infty v}$ and $D_{\infty h}$ isomers **XVII–XXII** (shown in Scheme 4 with x=m_s=+1/2 spin, ○=m_s=−1/2 spin) are obtained via an S=0→S=1 excitation for one of the fractional electron-pair π bonds of the increased-valence structures **II**, **X** and **XII**.

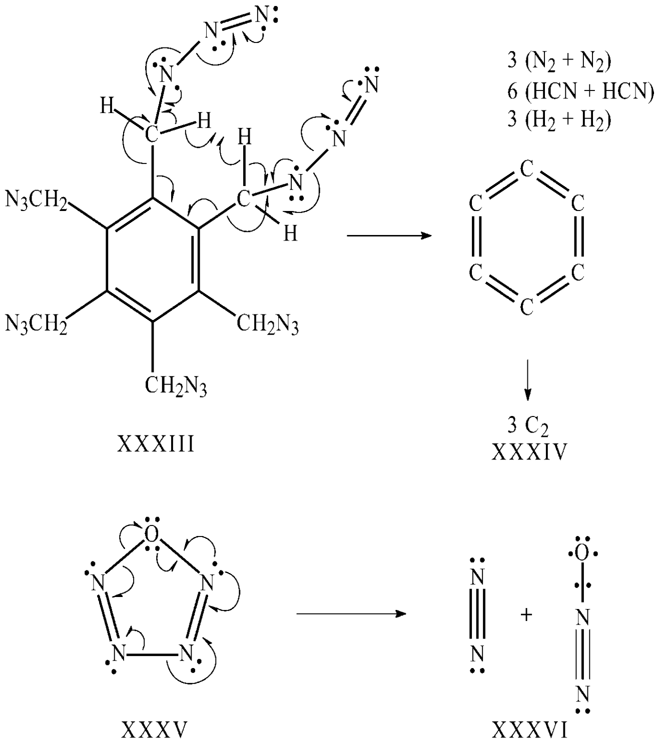
For the C_{2v} isomers, the bond lengths that are implied by VB structures **XXIII** and **XXV**↔**XXVI** (Scheme 5) are in qualitative accord with the calculated bond lengths reported in Table 2. Structures **XXV** and **XXVI** are obtained via one-electron delocalizations of the oxygen $2p\pi$ electrons, with consequent stabilization of the S=1 structure **XXIV**.



Scheme 6 Structures of **XXVII–XXXI**

Valence bond representations for $O(N_3)_2$ and $C_6(CH_2N_3)_6$ decompositions

The preparation of $O(N_3)_2$ has been reported recently, [4] and it has been postulated [4] that its decomposition



Scheme 7 Structures of **XXXIII**–XXXVI

leads to the formation of the cyclic C_{2v} isomer of N_2O. Here we give consideration to VB representations for this process, and for the $C_{2v} \rightarrow C_{\infty v}$ decomposition.

From the standard Lewis structure **XXVII** (shown in Scheme 6) we may generate increased-valence structure **XXVIII** via the one-electron delocalizations that are indicated in **XXVII**. The increased-valence structure **XXVIII** implies that the O–N bond lengths (connectivity N_6–N_4–N_2–O–N_3–N_5–N_7) should be similar to that for a single bond (1.44 Å [22]), the N_2–N_4 and N_3–N_5 bond lengths should be similar to that for an N–N double bond (1.24 Å [21]) and the N_4–N_6 and N_5–N_7 bond lengths should be longer than an N–N triple bond (1.07–1.10 Å [20]). The bond lengths that have been calculated [4] using MP2, B3LYP and CCD/D95 V(d) procedures are in accord with those implied by **XXVIII**.

To our knowledge, there has been only one experimental study directed at the formation and decomposition of $O(N_3)_2$. [4] In this study, the decomposition products which were observed experimentally following the formation of $O(N_3)_2$ were N_2 and $C_{\infty v}$ N_2O. The decomposition mechanism of eqs. (1) and (2) has been suggested. [4]

$$O(N_3)_2\ (C_2) \rightarrow \text{cyclic } N_2O\ (C_{2v}) + 2N_2 \tag{1}$$

$$\text{cyclic } N_2O\ (C_{2v}) \rightarrow \text{linear } N_2O\ (C_{\infty v}) \tag{2}$$

VB representations for these processes are indicated in **XXIX→XXX→XXXI** and **XXXI→XXXII→II**, respectively. A VB formulation of the recently prepared $C_6(CH_2N_3)_6$ is also provided in **XXXIII→XXXIV** (Scheme 7), in which we have displayed the decompositions of two of the six CH_2–N_3 substituents. (The increased-valence precursor to structure **XXXIII**, cf. **XXIX→XXX** for $O(N_3)_2$, is not displayed.) The VB formulations for the $O(N_3)_2$ and $C_6(CH_2N_3)_6$ decompositions exploit the singlet diradical character which is present in 1,3-dipolar molecules, such as the azide substituents. [20]

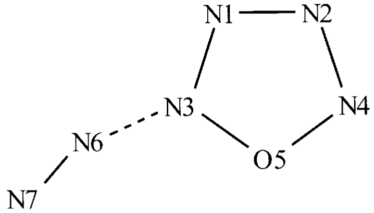


Fig. 2 MP2/6-31G(d) estimate of the geometry for a cyclic ON_4 and N_2 adduct

We now also consider the cleavage of only one N_2 molecule of $O(N_3)_2$, according to eq. (3).

$$O(N_3)_2\ (C_2) \rightarrow N_2 + NO\text{–}N_3 \tag{3}$$

The resulting NO–N_3 would represent a structural isomer of the experimentally known [23, 24, 25, 26, 27] ON–N_3. However at MP2/6-31G(d) level of theory, neither the *S*=0 nor the *S*=1 spin states of lowest energy for NO–N_3 were found to be stable with respect to dissociation into the NO and N_3 radicals (eq. (4)).

$$NO\text{–}N_3 \rightarrow NO + N_3 \tag{4}$$

Since decomposition of the experimentally known ON–N_3 [23] has been shown by several research groups [24, 25, 26, 27] to occur most likely via cyclic ON_4 (with C_{2v} symmetry), we also calculated the decomposition of $O(N_3)_2$ yielding N_2 and cyclic ON_4 (eq.(5))

$$O(N_3)_2 \rightarrow N_2 + \text{cyclic } ON_4 \tag{5}$$

All attempts to shorten the distance between the terminal nitrogen atom of one azide group of $O(N_3)_2$ and the oxygen-bound nitrogen atom in the other azide group caused the molecule to dissociate into two equivalents of N_2 and N_2O ($C_{\infty v}$) (MP2/6-31G(d)).

Finally, we computed the structure (cf. Fig. 2) of the very weak adduct formed between cyclic ON_4 and N_2. At MP2/6-31G(d) level of theory, this species lies 95.8 kcal mol^{-1} above $O(N_3)_2$. This species already resembles the more stable decomposition products, i.e. N_2, N_3 and NO.

Therefore we conclude that the mechanism of eqs. (1) and (2) is the most likely mechanism for the decomposition of $O(N_3)_2$.

In [25], VB representations for the decomposition of cyclic ON_4 are provided. Here, the diradical formulation is provided again as **XXXV→XXXVI** (Scheme 7).

Conclusions

The results of VB calculations show that the ground state of NON is primarily singlet diradical in character. The singlet diradical character that is also present in the 1,3-dipolar azide species has been exploited to develop qualitative VB mechanisms for several decomposition processes that involve azide derivatives as reactants. The bond lengths implied by VB structures for the first (S=1 spin) excited state of each of the three N_2O isomers are in qualitative accord with those obtained from single-determinant DFT MO calculations.

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Appendix: Lowest-energy S=1 spin states for the $C_{\infty v}$ and $D_{\infty h}$ isomers

With the three π_x and three π_y MOs designated as ψ_1, ψ_2 and ψ_3, and ψ_4, ψ_5 and ψ_6 respectively, two types of low-energy S=1 spin configurations (cf. Fig. 1) arise from the excitation of either a ψ_2 electron or a ψ_5 electron of the ground-state S=0 spin configuration (Ψ_I) for the π-electrons, namely $\psi_2 \rightarrow \psi_3$ and $\psi_5 \rightarrow \psi_6$, and $\psi_2 \rightarrow \psi_6$ and $\psi_5 \rightarrow \psi_3$. The resulting ($S=M_S$=1 spin) wavefunctions are then given by eqs. (A1) and (A2).

$$\begin{aligned} \Psi\mathrm{II} \quad = \quad & |\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_3^\alpha \psi_4^\alpha \psi_4^\beta \psi_5^\alpha \psi_5^\beta| \\ & + |\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_2^\beta \psi_4^\alpha \psi_4^\beta \psi_5^\alpha \psi_6^\alpha| \end{aligned} \tag{A1}$$

$$\begin{aligned} \Psi_{\mathrm{III}} \quad = \quad & |\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_6^\alpha \psi_4^\alpha \psi_4^\beta \psi_5^\alpha \psi_5^\beta| \\ & + |\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_2^\beta \psi_4^\alpha \psi_4^\beta \psi_5^\alpha \psi_3^\alpha| \end{aligned} \tag{A2}$$

The excitation energies to obtain Ψ_{II} and Ψ_{III} are given by eqs. (A3) and (A4):

$$E_{\mathrm{II}}\text{-}E_{\mathrm{I}}=e_3\text{-}e_2\text{-}(22|33)\text{-}(36|25) \tag{A3}$$

$$E_{\mathrm{III}}\text{-}E_{\mathrm{I}}=e_6\text{-}e_2\text{-}(22|66)\text{-}(36|25) \tag{A4}$$

in which the $e_2=e_5$ and $e_3=e_6$ are the Hartree–Fock MO energies for the π-electron MOs of Ψ_I, and $(ij|kl)=\langle\psi_i(1)\psi_k(2)|1/r_{12}|\psi_j(1)\psi_l(2)\rangle$. Because (22|33)>(22|66), it follows that $E_{\mathrm{II}}\text{-}E_{\mathrm{I}}<E_{\mathrm{III}}\text{-}E_{\mathrm{I}}$.

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