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Valence Bond Structures for N_2O and HCNO with Apparently Pentavalent Nitrogen Atoms

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For N_2O, the results of STO-6G calculations indicate that a valence-bond structure **I** with a π electron configuration $R[\pi_x(\mathrm{NO})]^1[\pi_x(\mathrm{O})]^1[\pi_y(\mathrm{NO})]^1[\pi_y(\mathrm{O})]^1$, in which $R = [\pi_x(\mathrm{NN})]^2[\pi_y(\mathrm{NN})]^2$, generates a lower energy than does resonance between two valence-bond structures, **II** and **III**, with π electron configurations $R[\pi_x(\mathrm{NO})]^2[\pi_y(\mathrm{O})]^2$ and $R[\pi_y(\mathrm{NO})]^2[\pi_x(\mathrm{O})]^2$, respectively. In each of these three structures, the central nitrogen atom is *apparently* pentavalent. A similar conclusion is obtained from the results of the corresponding calculations for isoelectronic HCNO, with $R = [\pi_x(\mathrm{CN})]^2[\pi_y(\mathrm{CN})]^2$. Using HCNO + HCCH → isoxazole as the example, valence-bond representations for 1,3-dipolar cycloaddition reactions are compared using the above types of valence-bond structures. For N_2O, the bond orders that are implied by structure **I**, but not those by structures **II** and **III**, are shown to be in qualitative accord with the observed bond lengths. The energy for structure **I** is also calculated to lie below that for a $R[\pi_x(\mathrm{NO})]^2[\pi_y(\mathrm{NO})]^2$ configuration, in which the central nitrogen atom is *apparently* hexavalent.

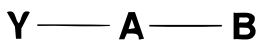
Introduction

Since the 1860's,[1,2,3a,4] the nitrogen atom has sometimes been assigned a valence of five in valence bond (VB) structures for a number of covalent molecules. Structure **1** for linear N_2O is an example of this type of VB structure.


1

As a consequence of conclusions that have been obtained from spin-coupled VB calculations,[4] pentavalent (or quinquevalent) nitrogen atoms have featured prominently in VB structures that have been constructed for N_2O and a number of other 1,3-dipolar molecules. Summaries of attempts to account quantum mechanically for the occurrence of nitrogen pentavalence have been provided in refs 1m and 3a. The essential conclusion[3a] is that unless the nitrogen atom expands its valence shell in a VB structure, for example, via a $2s^12p^33d^1$ configuration,[1d] the pentavalence (and the associated octet violation) is *apparent*, not real. The apparent violation of the Lewis−Langmuir octet rule arises from the inclusion of singlet-diradical (or "long-bond") Lewis structures in an equivalent canonical-structure resonance scheme.[2b−d] Because nitrogen $n = 3$ atomic orbitals (AOs) make only very minor contributions to bonding in the ground states of nitrogen-containing molecules, further consideration will not be given in this paper to the high-energy expanded valence-shell structures.

Linear N_2O has two degenerate 4-electron 3-center bonding units, one for the π_x electrons and one for the π_y electrons. For a 4-electron 3-center bonding unit, we may construct two nonorthogonal localized molecular orbitals (LMOs).[5] Thus, if Y, A, and B are the three atomic centers, and y, a, and b are the associated overlapping AOs, these LMOs may be expressed as $\psi_{ya} = y + ka$ and $\psi_{ba} = b + la$, in which k and l are variationally determined polarity parameters. The four electrons may be accommodated in these MOs, to give the LMO configuration $\Phi(\mathrm{LMO}) = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi_{ba}{}^{\alpha}\psi_{ba}{}^{\beta}|$, in which α and β are the $m_s = +^1/_2$ and $m_s = -^1/_2$ spin wave functions. The associated VB structure may be represented as either **2** or **3**, in which the A atom is *apparently* divalent.[6]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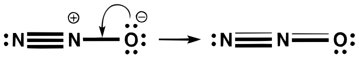
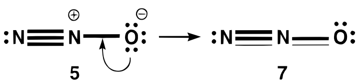
3

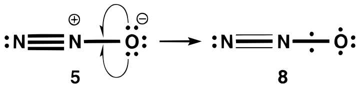

4

These VB structures may be generated[2b,5g,h] from the Lewis VB structure **4** by delocalizing the B electrons into the ψ_{ba} bonding MO, as indicated. When this procedure is applied separately to the π_x electrons and the π_y electrons of the (zwitterionic) Lewis structure **5** for N_2O, we obtain the apparently pentavalent VB structures **6** and **7**. Similar types of


5 **6**


5 **7**

VB structures have been provided previously[2b,c] for CH_2N_2, O_3, and HN_3. An apparent pentavalence is also present in the VB structure **8**, which may be derived[2,3b,9] from the Lewis structure


5 **8**

5 by delocalizing one $2p\pi_x$ and one $2p\pi_y$ electron from the O^- into bonding $\pi_x(\mathrm{ON})$ and $\pi_y(\mathrm{ON})$ LMOs. The latter pair of orbitals are examples of the ψ_{ba} type LMOs.

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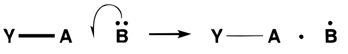
For one 4-electron 3-center bonding unit, the preference of a one-electron delocalization of the type **4** → **9** over the concerted two-electron delocalizations of the type **4** → **2** or **3** has been demonstrated in ref 5h. (By concerted, it is meant that the two electrons occupy the same orbital at all stages.) In this paper we compare the minimal basis set energies of **6** ↔ **7**, with that for structure **8**, to provide further support for this theory. With a minimal basis set, we shall demonstrate that the **4** → **9** type delocalization for each set of π_x and π_y electrons is to be preferred energetically to the concerted **4** → **2** or **3** type delocalizations for either set of π_x or π_y electrons. For isoelectronic HCNO, we also obtain a similar conclusion from the results of the corresponding calculations for VB structures **10**−**12**.



4 **9**

10 **11** **12**

Because only minimal basis sets are used, the VB calculations are certainly modest by current standards. However, the following considerations provide support for the qualitative conclusion obtained from the calculations, namely that the energies for structures **8** and **12** lie below those for **6** ↔ **7** and **10** ↔ **11**, respectively.

(a) The degree of electron charge correlation is larger in structures **8** and **12**.

(b) The presence of radical-like character in structures **8** and **12** is indicated explicitly. This radical character helps N_2O and HCNO to react with certain radicals and to participate in 1,3-dipolar cycloaddition reactions.

(c) The bond orders that can be associated with structures **8** and **12** are in better accord with the experimental bond lengths than are those for **6** ↔ **7** and **10** ↔ **11**.

Aspects of these considerations will be described later in the paper. In Appendix 1, some comments are provided with regard to the use of double-ζ basis sets.

Method

Ab initio VB calculations were performed using Roso's program.[10] An STO-6G basis with carbon, nitrogen, and oxygen "best-atom" exponents[11] and the experimental geometries,[12] were assumed. (The hydrogen atom of HCNO was assigned an exponent of 1.2 for its 1s AO.) The closed-shell σ electron core was treated (see Appendix 1) as described in ref 2d, and the π electrons were treated initially in the following manner, which we describe for N_2O:

For structures **6** and **7**, LMOs for the π electrons are defined according to eqs 1 and 2, in which y, a, and b are the $2p\pi_x$ AOs, and y′, a′, and b′ are the $2p\pi_y$ AOs. The resulting ($S = 0$ spin) wave functions for the π electrons of these structures are given by eqs 3 and 4. Each of these degenerate configurations possesses three variational parameters, k, k', and l.

$$\pi_x(\mathrm{NN}) \equiv \psi_{\mathrm{ya}} = \mathrm{y} + k\mathrm{a} \qquad \pi'_{\mathrm{y}}(\mathrm{NN}) \equiv \psi'_{\mathrm{y'a'}} = \mathrm{y'} + k'\mathrm{a'} \qquad \pi_x(\mathrm{ON}) \equiv \psi_{\mathrm{ba}} = \mathrm{b} + l\mathrm{a} \quad (1)$$

$$\pi'_x(\mathrm{NN}) \equiv \psi'_{\mathrm{ya}} = \mathrm{y} + k'\mathrm{a} \qquad \pi_{\mathrm{y}}(\mathrm{NN}) \equiv \psi_{\mathrm{y'a'}} = \mathrm{y'} + k\mathrm{a'} \qquad \pi_{\mathrm{y}}(\mathrm{ON}) \equiv \psi_{\mathrm{b'a'}} = \mathrm{b'} + l\mathrm{a'} \quad (2)$$

$$\Phi_6(\mathrm{LMO}) = |\psi_{\mathrm{ya}}{}^{\alpha}\psi_{\mathrm{ya}}{}^{\beta}\psi_{\mathrm{ba}}{}^{\alpha}\psi_{\mathrm{ba}}{}^{\beta}\psi'_{\mathrm{y'a'}}{}^{\alpha}\psi'_{\mathrm{y'a'}}{}^{\beta}\mathrm{b'}^{\alpha}\mathrm{b'}^{\beta}| \quad (3)$$

$$\Phi_7(\mathrm{LMO}) = |\psi_{\mathrm{y'a'}}{}^{\alpha}\psi_{\mathrm{y'a'}}{}^{\beta}\psi_{\mathrm{b'a'}}{}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\beta}\psi'_{\mathrm{ya}}{}^{\alpha}\psi'_{\mathrm{ya}}{}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}| \quad (4)$$

Two degenerate, three-parameter π electron wave functions for VB structure **8** may be constructed from the LMOs of eqs 5 and 6. With four singly occupied orbitals, namely, ψ_{ba}, b, $\psi_{\mathrm{b'a'}}$, and b′, two $S = 0$ spin Rumer-type wave functions may be constructed[2d,3c,9f] for structure **8**, namely, those of eqs 7 and 8, in which R is either $\psi_{\mathrm{ya}}{}^{\alpha}\psi_{\mathrm{ya}}{}^{\beta}\psi'_{\mathrm{y'a'}}{}^{\alpha}\psi'_{\mathrm{y'a'}}{}^{\beta}$ or $\psi'_{\mathrm{ya}}{}^{\alpha}\psi'_{\mathrm{ya}}{}^{\beta}\psi_{\mathrm{y'a'}}{}^{\alpha}\psi_{\mathrm{y'a'}}{}^{\beta}$.

$$\pi_x(\mathrm{NN}) \equiv \psi_{\mathrm{ya}} = \mathrm{y} + k\mathrm{a} \qquad \pi_x(\mathrm{ON}) \equiv \psi_{\mathrm{ba}} = \mathrm{b} + l\mathrm{a}$$

$$\pi'_y(\mathrm{NN}) \equiv \psi'_{\mathrm{y'a'}} = \mathrm{y'} + k'\mathrm{a'} \qquad \pi_y(\mathrm{ON}) \equiv \psi_{\mathrm{b'a'}} = \mathrm{b'} + l\mathrm{a'} \quad (5)$$

$$\pi'_x(\mathrm{NN}) \equiv \psi'_{\mathrm{ya}} = \mathrm{y} + k'\mathrm{a} \qquad \pi_x(\mathrm{ON}) \equiv \psi_{\mathrm{ba}} = \mathrm{b} + l\mathrm{a}$$

$$\pi_y(\mathrm{NN}) \equiv \psi_{\mathrm{y'a'}} = \mathrm{y'} + k\mathrm{a'} \qquad \pi_y(\mathrm{ON}) \equiv \psi_{\mathrm{b'a'}} = \mathrm{b'} + l\mathrm{a'} \quad (6)$$

$$\begin{aligned}\Phi_8(\psi_{\mathrm{ba}}{-}\mathrm{b},\psi_{\mathrm{b'a'}}{-}\mathrm{b'}) = {} & |R\psi_{\mathrm{ba}}{}^{\alpha}\mathrm{b}^{\beta}\psi_{\mathrm{b'a'}}{}^{\alpha}\mathrm{b'}^{\beta}| + |R\psi_{\mathrm{ba}}{}^{\beta}\mathrm{b}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\beta}\mathrm{b'}^{\alpha}| - |R\psi_{\mathrm{ba}}{}^{\alpha}\mathrm{b}^{\beta}\psi_{\mathrm{b'a'}}{}^{\beta}\mathrm{b'}^{\alpha}| - \\ & |R\psi_{\mathrm{ba}}{}^{\beta}\mathrm{b}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\alpha}\mathrm{b'}^{\beta}| \quad (7)\end{aligned}$$

$$\begin{aligned}\Phi_8(\psi_{\mathrm{ba}}{-}\mathrm{b'},\psi_{\mathrm{b'a'}}{-}\mathrm{b}) = {} & |R\psi_{\mathrm{ba}}{}^{\alpha}\mathrm{b}^{\beta}\psi_{\mathrm{b'a'}}{}^{\alpha}\mathrm{b'}^{\beta}| + |R\psi_{\mathrm{ba}}{}^{\beta}\mathrm{b}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\beta}\mathrm{b'}^{\alpha}| - |R\psi_{\mathrm{ba}}{}^{\alpha}\mathrm{b}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\beta}\mathrm{b'}^{\beta}| - \\ & |R\psi_{\mathrm{ba}}{}^{\beta}\mathrm{b}^{\beta}\psi_{\mathrm{b'a'}}{}^{\alpha}\mathrm{b'}^{\alpha}| \quad (8)\end{aligned}$$

Because $\Phi_8(\psi_{\mathrm{ba}}{-}\mathrm{b},\psi_{\mathrm{b'a'}}{-}\mathrm{b'})$ of eq 7 involves opposed spins for the π_x-type ψ_{ba} and b electrons, and for the π_y-type $\psi_{\mathrm{b'a'}}$ and b′ electrons, this wave function must be the dominant Rumer-type wave function. The $\Phi_8(\psi_{\mathrm{ba}}{-}\mathrm{b'},\psi_{\mathrm{b'a'}}{-}\mathrm{b})$ of eq 8, with $\psi_{\mathrm{ba}}{-}\mathrm{b'}$ and $\psi_{\mathrm{b'a'}}{-}\mathrm{b}$ spin-pairings for their associated electrons, will therefore be omitted from the subsequent treatment, and the $\Phi_8(\psi_{\mathrm{ba}}{-}\mathrm{b},\psi_{\mathrm{b'a'}}{-}\mathrm{b'})$ will be subsequently designated as Φ_8.

For the corresponding calculations with VB structures **10**−**12** for isoelectronic HCNO, we have assumed that the carbon and nitrogen atoms use equivalent sp hybrid AOs for H−C, C−N, and N−O σ bond formation.

Results

For the wave functions described via eqs 1−7, the energy-optimized π electron parameters for N_2O and HCNO and their associated energies are reported in Tables 1 and 2. Similar types of results are obtained for both molecules. Thus, for N_2O, either a two-parameter or a three-parameter calculation for increased-valence structure **8** generates a substantially lower energy than does resonance between **6** and **7**, with three variational parameters. However eq 7 for structure **8** accommodates the two N−O π bonding electrons in separate LMOs (the ψ_{ba} and $\psi_{\mathrm{b'a'}}$ of eqs 5 and 6), whereas in each of eqs 3 and 4 for structures **6** and **7**, the two N−O π bonding electrons occupy the same LMO (either the ψ_{ba} or the $\psi_{\mathrm{b'a'}}$ of eqs 3 and 4). Therefore, the two N−O π bonding electrons are better correlated spatially in structure **8** than they are in structures **6** and **7**. To introduce some N−O π electron correlation into structures **6** and **7**, we have proceeded as follows.

The $\psi_{\mathrm{ba}}{}^{\alpha}\psi_{\mathrm{ba}}{}^{\beta}$ of eq 3 and the $\psi_{\mathrm{b'a'}}{}^{\alpha}\psi_{\mathrm{b'a'}}{}^{\beta}$ of eq 4 are replaced with[13] $\psi'_{\mathrm{ba}}{}^{\alpha}\psi''_{\mathrm{ba}}{}^{\beta} + \psi''_{\mathrm{ba}}{}^{\alpha}\psi'_{\mathrm{ba}}{}^{\beta}$ and $\psi'_{\mathrm{b'a'}}{}^{\alpha}\psi''_{\mathrm{b'a'}}{}^{\beta} + \psi''_{\mathrm{b'a'}}{}^{\alpha}\psi'_{\mathrm{b'a'}}{}^{\beta}$, respectively, in which the LMOs are defined according to eq 9.

$$\psi'_{\mathrm{ba}} = \mathrm{b} + l'\mathrm{a} \qquad \psi''_{\mathrm{ba}} = \mathrm{b} + l''\mathrm{a} \qquad \psi'_{\mathrm{b'a'}} = \mathrm{b'} + l'\mathrm{a'} \qquad \psi''_{\mathrm{b'a'}} = \mathrm{b'} + l''\mathrm{a'} \quad (9)$$

TABLE 1: N_2O Energies (E, kcal mol^{-1}) Relative to Three-Parameter Structure 8 and π electron Polarity Parameters (Eqs 1, 2, 5, and 6) for VB Structures 6 ↔ 7 and 8

	E	k	k'	l
8	0.0	0.643	2.179	0.483
8	5.6	1.198	1.198	0.497
6 ↔ 7	44.2	0.743	1.585	0.881

TABLE 2: HCNO Energies (E, kcal mol^{-1}) Relative to the Three-Parameter Structure 12 and π electron Polarity Parameters (Eqs 1, 2, 5, and 6) for VB Structures 10 ↔ 11 and 12

	E	k	k'	l
12	0.0	0.648	2.227	0.477
12	5.0	1.208	1.208	0.500
10 ↔ 11	42.5	0.785	1.590	0.855

TABLE 3: N_2O Energies (E, kcal mol^{-1}) Relative to Three-Parameter Structure 8 of Table 1 and π electron Polarity Parameters (Eqs 9−11) for VB Structures 6 ↔ 7 and 8

	E	k	k'	l'	l''
8	0.0	0.643	2.179	0.483	0.483
8	−17.1	1.230	1.230	0.145	1.999
6 ↔ 7	−5.3	1.21	1.21	0.15	6.00
6 ↔ 7	−6.2	1.14	1.26	0.15	6.15

TABLE 4: HCNO Energies (E, kcal mol^{-1}) Relative to Three-Parameter Structure 12 of Table 2 and π electron Polarity Parameters (Eqs 9−11) for VB Structures 10 ↔ 11 and 12

	E	k	k'	l'	l''
12	0.0	0.648	2.227	0.477	0.477
12	−15.7	1.250	1.250	0.145	1.940
10 ↔ 11	−4.3	1.22	1.22	0.15	5.82
10 ↔ 11	−4.5	1.15	1.28	0.15	5.98

The resulting wave function for resonance between structures **6** and **7** involves four Slater determinants and four variational parameters (k, k', l', and l''). With these parameters chosen variationally, the energy for the **6** ↔ **7** resonance now lies 6.2 kcal mol^{-1} below the three-parameter energy for structure **8** (Table 3). However, a better three-parameter wave function for VB structures of type **8** is obtained by using either $\psi'_{ba} = b + l'a$ and $\psi''_{b'a'} = b' + l''a'$ or $\psi''_{ba} = b + l''a$ and $\psi'_{b'a'} = b' + l'a'$ instead of $\psi_{ba} = b + la$ and $\psi_{b'a'} = b' + la'$ in eq 7, together with $k = k'$ in ψ_{ya} and $\psi_{y'a'}$.The resulting wave functions for structure **8** are given by eqs 10 and 11, in which $R = \psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi_{y'a'}{}^{\alpha}\psi_{y'a'}{}^{\beta}$.

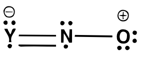
$$\Phi_8(1) = |R\psi'_{ba}{}^{\alpha}b^{\beta}\psi''_{b'a'}{}^{\alpha}b'^{\beta}| + |R\psi'_{ba}{}^{\beta}b^{\alpha}\psi''_{b'a'}{}^{\beta}b'^{\alpha}| - |R\psi'_{ba}{}^{\alpha}b^{\beta}\psi''_{b'a'}{}^{\beta}b'^{\alpha}| - |R\psi'_{ba}{}^{\beta}b^{\alpha}\psi''_{b'a'}{}^{\alpha}b'^{\beta}| \quad (10)$$

$$\Phi_8(2) = |R\psi''_{ba}{}^{\alpha}b^{\beta}\psi'_{b'a'}{}^{\alpha}b'^{\beta}| + |R\psi''_{ba}{}^{\beta}b^{\alpha}\psi'_{b'a'}{}^{\beta}b'^{\alpha}| - |R\psi''_{ba}{}^{\alpha}b^{\beta}\psi'_{b'a'}{}^{\beta}b'^{\alpha}| - |R\psi''_{ba}{}^{\beta}b^{\alpha}\psi'_{b'a'}{}^{\alpha}b'^{\beta}| \quad (11)$$

When the polarity parameters k, l', and l'' for $\Phi_8 = \Phi_8(1) + \Phi_8(2)$ are energy-optimized, the resulting energy for structure **8** (Table 3) now lies 11.9 kcal^{-1} below that for the **6** ↔ **7** resonance, with four variational parameters. Similar types of results are obtained for the analagous calculations for the HCNO structures **10**−**12** (Table 4). Therefore, according to these calculations, **8** and **12** provide better VB representations of electronic structure for N_2O and HCNO than do **6** ↔ **7** and **10** ↔ **11**.

Further Comments on Valence Bond Structures

In ref 2c, it is indicated that resonance between VB structures of types **6** and **7**, or **10** and **11**, is equivalent to resonance between 27 canonical Lewis structures, whereas VB structures of type **8** or **12** are equivalent to resonance between 25 canonical Lewis structures. Except for the canonical structures **13**−**18** for the **6** ↔ **7** or **10** ↔ **11** resonances, and **19**−**22** for **8** or **12**, with Y equivalent to either :N or H−C, the remaining canonical structures contribute to both types of resonance schemes. In the singlet diradical structures **19**−**21**, each of which involves either one or two "long" or formal bond π bonds, and in structure **22** with two N−O π bonds, the electrons of these bonds are better correlated spatially than are the corresponding π electrons in structures **13**−**18**. These charge-correlation considerations imply that structures **19**−**22** should make a larger contribution to the Lewis canonical structure resonance scheme for the ground state than do structures **13**−**18**. This conclusion is supported by the results of both semiempirical and ab initio VB calculations.[2d,9h,14,15] Therefore, for the same AO basis set, it is not surprising that VB structures of the type **8** or **12** generate a lower energy than do the **6** ↔ **7** or **10** ↔ **11** resonances.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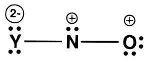
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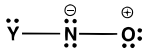
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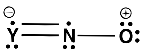
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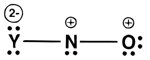
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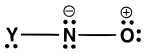
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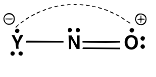
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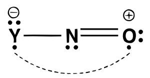
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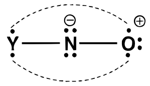
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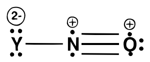
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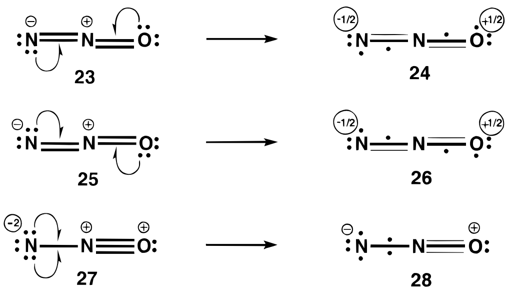
Increased-valence structures **24**, **26**, and **28**, which can participate in resonance with increased-valence structure **8**, may be constructed[2a,b,d,e] from the standard Lewis structures **23**, **25**, and **27**, respectively, via the one-electron delocalizations that are indicated in the latter three structures. Formal charge considerations and the results of some VB calculations[2d,9i] indicate that **8** is the primary increased-valence structure, and therefore we shall use this structure in the subsequent discussions.



Valence Bond Structures and Concerted 1,3-Dipolar Cycloaddition Reactions

Increased-valence structure **8** for N_2O has been used to show succinctly how electronic reorganization can proceed for the

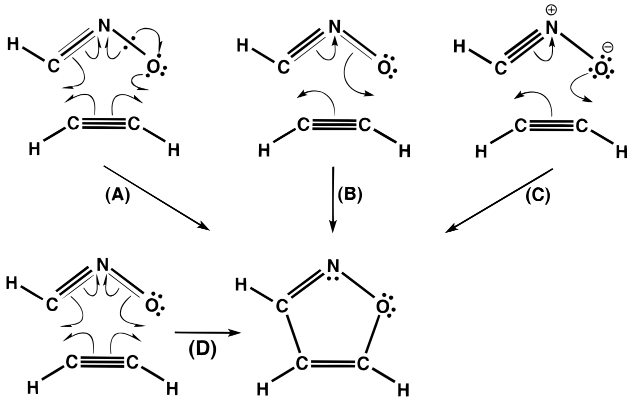


Figure 1. VB representation for fulminic acid + ethyne → isoxazole cycloaddition.

following types of gas-phase reactions: (a) thermal decomposition to generate $N_2 + O^*$,[2d,8,18] (b) radical transfer, for example, $N_2O + H \rightarrow N_2 + OH$,[2d,8,19] (c) $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization of N_2O,[20a] (d) 1,3-dipolar cycloaddition, for example,[2d,8] the formation of a cyclointermediate in the reaction $N_2O + RR'C{=}CH_2 \rightarrow CH_2N_2 + RR'C{=}O$, and (e) the reactions[9g,20b] $NO + NCO \rightarrow N_2O + CO$ and $F_2 + N_2O \rightarrow F_2NO$. Increased-valence formulations of electronic reorganization for gas-phase 1,3-dipolar (or zwitterionic diradical hybrid[2b,d,21]) cycloaddition reactions, have been provided on a variety of occasions.[2b,d,3d,9c,10a,21] Here, we shall use the fulminic acid + ethyne → isoxazole cycloaddition to compare this type of formulation with that provided by Cooper et al.[4e]

Using increased-valence structure **12** to represent HCNO, the electronic reorganization proceeds according to Scheme A of Figure 1. In contrast, Cooper et al.[4e] have performed spin-coupled VB calculations for HCNO and concluded that the HCNO analogue of structure **1**, which we assume here corresponds to the **10** ↔ **11** resonance, should be the primary VB structure for the ground state of this molecule. (Cooper et al. did not give consideration to structure **12**.) These workers have formulated the cyloaddition according to Scheme B of Figure 1, in which we have used structure **11** rather than the HCNO analogue of structure **1**. Three problems are associated with Scheme B. First, the results of our calculations show that the energy of structure **12** is lower than that obtained via the **10** ↔ **11** resonance. Second, Scheme B, as well as Scheme C, involves charge transfer between the reactants. With a 6-31G(d,p) basis set, we have used GAUSSIAN 94 [22] to calculate[23] the atomic net charges (NBO analysis) for the transition state of the HCNO + HCCH cycloaddition (B3LYP geometry).

Summing these net charges gives total net charges of −0.009e and +0.009e on the HCNO and HCCH moieties. These values indicate that little net charge transfer occurs between these species. Therefore, charge-transfer VB structures must contribute only slightly to the VB resonance scheme.[24] Third, Cooper et al. prefer Scheme B to Scheme C. However the energy required to activate the two π_x(ON) bonding electrons in Scheme B must be larger than the energy needed to activate either the oxygen lone-pair $2p\pi_x$ electrons for charge transfer in Scheme C, or the oxygen $2p\pi_x$ electron for pairing with a carbon $2p\pi$ electron of ethyne in Scheme A. It is noted also that because the increased-valence structure for HCNO in Scheme A has a lower energy than has the Lewis structure of Scheme C, Scheme A is preferred to Scheme C.

Scheme D of Figure 1 also uses VB structure **11** and does not involve charge transfer between the reactants. However, structure **12** of Scheme A is to be preferred to structure **11**, and the activation of the oxygen $2p\pi_x$ electron of **12** to form the intermolecular O−C bond of Scheme A must require less energy than that needed to activate the π_x(ON) bonding electrons in Scheme D to form the same intermolecular bond.

N−N and N−O Bond Lengths

Estimates of the lengths of "normal" N−N and N−O double and triple bonds are[3e] 1.24 Å ($CH_3N{=}NCH_3$), 1.10 Å (N_2), 1.21 Å ($CH_3N{=}O$), and 1.06 Å (NO^+). Therefore, the N−N and N−O bond lengths[12a] of 1.13 and 1.19 Å for N_2O are respectively only slightly longer than the N−N triple bond of N_2 and similar to an N−O double bond. Increased-valence structure **8** involves an N−O double bond with a $[\sigma(NO)]^2[\pi_x(NO)]^1[\pi_y(NO)]^1$ configuration, and a fractional N−N triple bond that consists of an electron-pair σ bond and fractional electron-pair π_x and π_y bonds. We shall now demonstrate that the resulting values of two and less-than-three for the simplest type of N−O and N−N bond orders, namely Coulson-type bond orders,[26] which omit AO overlap integrals, are in qualitative accord with the observed bond lengths for N_2O.

For the AOs that are involved in N−N σ bonding for N_2O, we note initially that a hybridization difference exists between the AOs of the central nitrogen atom of N_2O (s + p) and each nitrogen atom of N_2 ($\sim$p + 0.35s)[2c]. The results of STO-6G VB calculations[2c] indicate that the N−N bond of N_2, with p + 0.35s hybridization for both nitrogen atoms is $\sim$0.03 Å longer than a hypothetical N_2 with p + 0.35s hybridization for one atom and p + s hybridization for the other atom. With this estimate for a hybridization correction, the N−N bond length of 1.13 Å is 0.06 Å longer than an N−N triple bond with the same AO hybridization. Using $r(2) = 1.24$ Å and $r(3) = 1.07$ Å, the Pauling-type bond-order (n)−bond-length $r(n)$ relationship[25] $r(n) = 1.24 - 0.565 \log(n - 1)$ gives an N−N bond order of 2.57 for N_2O.

For increased-valence structure **9**, with a $(y + la)^2(a + kb)^1(b)^1$ orbital configuration, we may use eqs 31 and 32 of ref 5g, with $l' = 1/l'' = l$ in these formulas, to calculate the Coulson-type Y−A and A−B bond orders P_{ya} and P_{ab}. The simplest π electron formulation for increased-valence structure **8** involves $(y + la)^2(a + kb)^1(b)^1$ and $(y' + la')^2(a' + kb')^1(b')^1$ configurations. With $n(NN) = 1 + P_{ya} + P_{y'a'} = 2.57$, we obtain $P_{ya} = P_{y'a'} = 0.785$. When an N−O bond order of 2 is assigned to structure **8**, $n(NO) = 1 + P_{ab} + P_{a'b'}$ gives $P_{ab} = P_{a'b'} = 0.5$. The resulting values for k and l are 0.58_2 and 0.98_0, respectively. Therefore, increased-valence structure **8** accommodates the Coulson bond orders that can be associated with the experimental bond lengths of N_2O. In refs 27 and 28, the use of Wiberg bond indices to discuss bond lengths is considered.

A fractional N−N triple bond is also present in either of the VB structures **6** and **7**. However the N−O bonds of these structures are fractional double bonds, i.e., $n(NO) < 2$. Therefore, VB structures **6** and **7** imply that the N−O bond length for N_2O should be longer than an N−O double bond. The expanded valence-shell structure **1** involves $n(NN) = 3$, rather than a fractional triple bond. Consequently, with regard to bond lengths, VB structure **8** provides a better representation of electronic structure than do structures **1**, **6**, and **7**.

Similar types of considerations apply to the C−N and N−O bond lengths that are implied by VB structures **10**−**12** for HCNO.

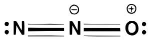
TABLE 5: Hartree−Fock Wiberg and NLMO Bond Orders

	STO-6G		3-21G		6-31G(d)		6-311+G(3df)	
	Wiberg	NLMO	Wiberg	NLMO	Wiberg	NLMO	Wiberg	NLMO
Individual Bond Orders								
N1−N2	2.39	2.44	2.47	2.51	2.54	2.57	2.53	2.58
N2−O3	1.46	1.11	1.45	1.19	1.47	1.24	1.47	1.22
N1−O3	0.58	−0.32	0.53	−0.29	0.49	−0.28	0.49	−0.26
Total Bond Orders								
(a) Without 1−3[a] Interaction								
N1	2.39	2.44	2.47	2.51	2.54	2.57	2.53	2.58
N2	3.84	3.55	3.93	3.70	4.01	3.81	4.00	3.81
O3	1.46	1.11	1.45	1.19	1.47	1.24	1.47	1.22
(b) With 1−3[a] Interaction								
N1	2.97	2.11	3.01	2.22	3.03	2.29	3.02	2.32
N2	3.84	3.55	3.92	3.70	4.01	3.81	4.00	3.81
O3	2.03	0.79	1.98	0.90	1.97	0.96	1.96	0.96

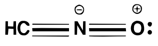
[a] In the Wiberg scheme, the N1−O3 interaction is a positive quantity as no distinction is made between bonding and antibonding interactions; however, a negative bond order is obtained when using the NLMO procedure.

Apparently Hexavalent Nitrogen

In ref 2b, VB structures **29** and **30** are also provided for N_2O and HCNO. In these structure, the central nitrogen atom is apparently hexavalent. However, with the Wiberg definition of



29



30

valence,[7] it may be demonstrated[2b,5g] that the maximum valence for this atom must be four for any of the configurations of eqs 12−15 below. Using the usual assumption that atomic net charges displayed in a VB structure are those that arise when bonding electrons are shared equally by a pair of adjacent atoms, the net charges displayed in **29** and **30** are counterintuitive. This is not the case for VB structures **6**−**8** and **10**−**12**, with apparent pentavalence for the central nitrogen atoms. As indicated in refs 2b,c and 9g, the apparent violation of the Lewis−Langmuir octet rule arises because singlet-diradical Lewis structures contribute significantly to the equivalent resonance schemes with canonical Lewis structures.

We have also performed some three-parameter calculations for the N_2O structure **29**, using the configurations of eqs 12−15:

$$\Phi_{29}(1) = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi'_{ba}{}^{\alpha}\psi'_{ba}{}^{\beta}\psi_{y'a'}{}^{\alpha}\psi_{y'a'}{}^{\beta}\psi'_{b'a'}{}^{\alpha}\psi'_{b'a'}{}^{\beta}| \quad (12)$$

$$\Phi_{29}(2) = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi'_{ba}{}^{\alpha}\psi'_{ba}{}^{\beta}\psi_{y'a'}{}^{\alpha}\psi_{y'a'}{}^{\beta}\psi''_{b'a'}{}^{\alpha}\psi''_{b'a'}{}^{\beta}| \quad (13)$$

$$\Phi_{29}(3) = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi''_{ba}{}^{\alpha}\psi''_{ba}{}^{\beta}\psi_{y'a'}{}^{\alpha}\psi_{y'a'}{}^{\beta}\psi'_{b'a'}{}^{\alpha}\psi'_{b'a'}{}^{\beta}| \quad (14)$$

$$\Phi_{29}(4) = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi''_{ba}{}^{\alpha}\psi''_{ba}{}^{\beta}\psi_{y'a'}{}^{\alpha}\psi_{y'a'}{}^{\beta}\psi''_{b'a'}{}^{\alpha}\psi''_{b'a'}{}^{\beta}| \quad (15)$$

in which the LMOs are given by eqs 16 and 17. The energy-optimized values for the parameters k, l', and l'' for $\Phi_{\mathbf{29}} = C(1)\Phi_{29}(1) + C(2)[\Phi_{29}(2) - \Phi_{29}(3)] + C(4)\Phi_{29}(4)$ are 1.2_2, 0.5_1, and 0.5_9, respectively. The corresponding calculation for

$$\psi_{ya} = \mathrm{y} + k\mathrm{a},\ \psi'_{ba} = \mathrm{b} + l'\mathrm{a},\ \psi''_{ba} = \mathrm{b} + l''\mathrm{a} \quad (16)$$

$$\psi_{y'a'} = \mathrm{y}' + k\mathrm{a}',\ \psi'_{b'a'} = \mathrm{b}' + l'\mathrm{a}',\ \psi''_{b'a'} = \mathrm{b}' + l''\mathrm{a}' \quad (17)$$

structure **8** (cf. Table 3, for $k = 1.230$, $l' = 0.145$, and $l'' = 1.999$) involves the linear combination $\Phi_8 = \Phi_8(1) + \Phi_8(2)$ with $\Phi_8(1)$ and $\Phi_8(2)$ given by eqs 10 and 11. The energy for structure **29** is thereby calculated to lie 11.7 kcal mol^{-1} above that for structure **8**. The results of these calculations indicate that the two one-electron delocalizations that are used to obtain structure **8** from structure **5** generate a lower energy than do two *concerted* electron-pair delocalizations that are needed to obtain structure **29** from structure **5**. We have already indicated that the **4** → **9** one-electron delocalization is preferred energetically to the concerted **4** → **3** delocalization for a pair of electrons.

Note Added in Proof. Of course variationally determined nonconcerted electron-pair delocalizations will lower the energies of structures **29** and **30** relative to structures **8** and **12**, in each of which a b electron and a b′ electron remain localized on the oxygen atom. However, the extent of delocalization of the latter electrons should be small (cf. values of l' and l'' in Tables 3 and 4 for **6** ↔ **7** and **10** ↔ **11**), and therefore structures **8** and **12** should be good approximations to the counterintuitive structures **29** and **30**.

Conclusions

For each of N_2O and HCNO, we have demonstrated that, with minimal basis sets, one-electron delocalizations of oxygen $2p\pi_x$ and $2p\pi_y$ electrons into bonding $\pi_x(\mathrm{ON})$ and $\pi_y(\mathrm{ON})$ LMOs are preferred energetically to electron-pair $(2p\pi_x)^2 \rightarrow [\pi_x(\mathrm{ON})]^2$ and $(2p\pi_y)^2 \rightarrow [\pi_y(\mathrm{ON})]^2$ (or $(2p\pi_x)^2 \rightarrow [\pi'_x(\mathrm{ON})]^1[\pi''_x(\mathrm{ON})]^1$ and $(2p\pi_y)^2 \rightarrow [\pi'_y(\mathrm{ON})]^1[\pi''_y(\mathrm{ON})]^1$) delocalizations. Therefore, structures **8** and **12** provide lower-energy primary VB representations of electronic structure than do **6** ↔ **7** and **10** ↔ 11. This result is shown to be in accord with electron correlation and bond-length considerations. By exploiting their explicit singlet diradical character, structures **8** and **12** can be used[2d,8,9f,20] to indicate succinctly how the primary features of electronic reorganization could proceed for a variety of gas-phase reactions that involve these molecules and related[2b,3,21] 1,3-dipolar molecules.

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Appendix 1: Treatment of the Valence-Shell σ Electron Core and Basis Sets

For N_2O, the nitrogen and oxygen lone-pair AOs and the N−N and NO σ bond LMOs are defined in eqs 2−4 of ref 2d, but with the simplifying assumption the central nitrogen uses equivalent sp hybrid AOs; i.e., the hybridization parameter μ

TABLE 6: CISD(fc):Wiberg and NLMO Bond Orders

	STO-6G		3-21G		6-31G(d)	
	Wiberg	NLMO	Wiberg	NLMO	Wiberg	NLMO
	Individual Bond Orders					
N1−N2	2.12	2.35	2.25	2.44	2.31	2.50
N2−O3	1.44	1.18	1.43	1.25	1.44	1.29
N1−O3	0.56	−0.38	0.54	−0.34	0.51	−0.33
	Total Bond Orders					
	(a) Without 1−3[a] Interaction					
N1	2.12	2.35	2.25	2.44	2.31	2.50
N2	3.56	3.54	3.67	3.69	3.75	3.79
O3	1.44	1.18	1.43	1.25	1.44	1.29
	(b) With 1−3[a] Interaction					
N1	2.68	1.97	2.79	2.10	2.82	2.18
N2	3.56	3.54	3.67	3.69	3.75	3.79
O3	2.00	0.80	1.97	0.91	1.95	0.96

*See Table 5.

has been set equal to unity in eqs 3 and 4 of ref 2d. The polarity parameters for these bonds (k and κ of eqs 3 and 4 of ref 2d), were chosen variationally, with nine canonical Lewis structures included in the VB resonance scheme. Their values are 1.61 and 1.29. For HCNO, the C−H σ bond replaces the terminal nitrogen lone-pair electrons. We have assumed that carbon uses equivalent sp hybrid AOs for σ bonding, with $\sigma(\mathrm{CH}) = (\mathrm{sp})_\mathrm{C} + \gamma 1\mathrm{sH}$ and $\sigma(\mathrm{CN}) = (\mathrm{sp})_\mathrm{C} + k(\mathrm{sp})_\mathrm{N}$. The energy-optimized values for γ, k, and κ are 0.620, 1.75, and 1.27.

Use of double-ζ instead of single-ζ AO basis sets increases dramatically the number of $S = 0$ spin configurations (and associated Slater determinants) that are needed for the VB calculation. For example if the oxygen $2p\pi_x$ and $2p\pi_y$ AOs (b and b′) are replaced by b_1 and b_2, and b'_1 and b'_2, respectively, the *dominant* N−O π bond configurations with two polarity parameters (l_1 and l_2) are those that contribute to eqs 18 and 19.

$$\begin{aligned}\Phi_{\mathbf{6\leftrightarrow7}} = {} & C_1[(\mathrm{a} + l_1\mathrm{b}_1)^2(\mathrm{b}'_1)^1(\mathrm{b}'_2)^1 + (\mathrm{a}' + l_1\mathrm{b}'_1)^2(\mathrm{b}_1)^1(\mathrm{b}_2)^1] + \\ & C_2[(\mathrm{a} + l_2\mathrm{b}_2)^2(\mathrm{b}'_1)^1(\mathrm{b}'_2)^1 + (\mathrm{a}' + l_2\mathrm{b}'_2)^2(\mathrm{b}_1)^1(\mathrm{b}_2)^1] \quad (18)\end{aligned}$$

$$\begin{aligned}\Phi_{\mathbf{8}} = {} & C_1(\mathrm{a} + l_1\mathrm{b}_1)^1(\mathrm{b}_2)^1(\mathrm{a}' + l_1\mathrm{b}'_1)^1(\mathrm{b}'_2)^1 + \\ & C_2(\mathrm{a} + l_2\mathrm{b}_2)^1(\mathrm{b}_1)^1(\mathrm{a}' + l_2\mathrm{b}'_2)^1(\mathrm{b}'_1)^1 + \\ & C_3[(\mathrm{a} + l_2\mathrm{b}_2)^1(\mathrm{b}_1)^1(\mathrm{a}' + l_1\mathrm{b}'_1)^1(\mathrm{b}'_2)^1 + \\ & (\mathrm{a} + l_1\mathrm{b}_1)^1(\mathrm{b}_2)^1(\mathrm{a}' + l_2\mathrm{b}'_2)^1(\mathrm{b}'_1)^1] \quad (19)\end{aligned}$$

These equations, with 8 and 16 Slater determinants, respectively, involve three and four independent variational parameters for a given set of AO exponents. Therefore, greater variational flexibility exists with $\Phi_{\mathbf{8}}$ than with $\Phi_{\mathbf{6\leftrightarrow7}}$. Consequently, use of eqs 18 and 19 instead of single-ζ formulations should lead to further stabilization of structure **8** relative to **6 ↔ 7.**

Appendix 2: Some ab Initio MO Estimates of Wiberg Bond Indices and Natural Localized MO Bond Orders

In Tables 5 and 6, some ab initio MO estimates of Wiberg bond indices and NLMO/NPA[29] bond orders are reported. The Wiberg-type estimates of the atomic valencies are mostly in qualitative accord with those that obtain to increased-valence structure **8**. However, if the elementary VB concepts of double and triple bonds are used to describe bond character, neither the NLMO bond orders nor the Wiberg bond indices for the N−O bond reflect the essentially double-bond character of the N−O bond. In other words, inspection of increased-valence structure **8** provides a simpler qualitative picture of the electronic structure of N_2O than do the ab initio MO results reported.

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(6) Because the ψ_ya and ψ_ab LMOs are not orthogonal, the Y−A and A−B bonds of VB structure are fractional; i.e., their bond orders are less than unity. Thin bond lines[2,3,5c,e−h] are used to represent fractional electron-pair bonds in VB structures **2**, **6−12**, **24**, **26**, **28−30**, and Figure 1. With $(\psi_\mathrm{ya})^2(\psi_\mathrm{ab})^2$ and $(\psi_\mathrm{ya})^2(\psi_\mathrm{ab})^1(\mathrm{b})^1$ configurations for VB structures **2** and **9**, it has been demonstrated[5g] that, when the Wiberg definition of valence[7] is used to estimate valence, the A-atom valence cannot exceed unity[5g] in each of the VB structures **2** and **4**, but it can exceed unity[5g,8] in structure **9**, with a maximum value of 1.21 when $k = 1.32$ and $l = 1.45$. For this reason, and others, VB structure **9** is an example of an "increased-valence" structure for a 4-electron 3-center bonding unit.

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(15) As indicated in ref 16 below, an MO three-center bond index has been introduced by Giambiagi, de Giambiagi, and co-workers.[1l,17] These workers have calculated values of this index (I_{AC}, with A and C as terminal atoms), for a variety of systems that involve four-electron three-center bonding units and have concluded that three-center bonding indices have appreciable values if and only if there exists a "long" or secondary bond between a pair of nonadjacent atoms. Thus the (STO-6G) value[11] of 0.5812 for the I_{AC} of the 1,3-dipolar molecule N_2O is appreciable; this result is in accord with the existence of substantial contributions by "long-bond" (i.e., singlet-diradical) Lewis structures to the ground-state resonance scheme for this molecule.

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(23) For another recent study of the transition state, see, for example: Nguyen, M. T.; Chandra, A. K.; Sakai, S.; Morokuma, K. *J. Org. Chem.* **1999**, *64*, 65.

(24) In ref 21a, it is demonstrated that, if charge transfer between the reactants is appreciable, then a two-step (gas-phase) mechanism can obtain.

(25) When proceeding from nitrogen sp^2 to nitrogen sp, we have not applied a small hybridization correction to the estimate of 1.24 Å for the length of an N−O double bond.

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(27) A referee has suggested that Wiberg bond indices[7] rather than the bond orders should be correlated with the bond lengths. If this is done, we have $W_{ya} = W_{y'a'} = 0.785$ and $W_{ab} = W_{a'b'} = 0.5$ instead of $P_{ya} = P_{y'a'} = 0.785$ and $P_{ab} = P_{a'b'} = 0.5$ in order that $n(NN) = 2.57$ and $n(NO) = 2.0$. The total Wiberg valence for the central nitrogen atom is then 4.57, which exceeds the maximum allowed value[7] of 4.42. With $P_{ya} = P_{y'a'} = 0.785$ and $P_{ab} = P_{a'b'} = 0.5$, we obtain $W_{ya} = W_{y'a'} = 0.616$ and $W_{ab} = W_{a'b'} = 0.5$. The resulting valence of the central nitrogen atom is 4.23, which is allowed. In Tables 5 and 6 of Appendix 2, ab initio MO[22] estimates of bond orders and bond indices are reported for N_2O.

(28) The Coulson bond order for each C−C bond of C_6H_6 is $1 + {}^{2}/_{3}$. The resulting Wiberg bond index is $1 + {}^{4}/_{9}$. When a Pauling-type relationship, $r(n) = r(1) - 0.637 \log n$ is assumed, with $r(1) = 1.528$ Å for sp^2-hybridized C−C single[26b] bonds, $n = {}^{5}/_{3}$ and ${}^{13}/_{9}$ give bond lengths of 1.387 and 1.426 Å, respectively. The observed C−C bond length of 1.397 Å is closer to the Coulson bond-order estimate. It may also be noted that the Wiberg bond index is smaller than the simplest estimate of 1.5 for the degree of C−C bonding, which is obtained by averaging the C−C bond numbers (2 or 1) of the two Kekulé structures. These considerations, and those of ref 27, suggest that the Coulson bond order rather than the Wiberg bond index is the more appropriate quantity to be associated with the bond lengths that are implied by increased-valence structure **8**.

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