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Valence Bond Studies of the N-N Bonds of ONNO, $ONNO_2$, O_2NNO_2 and CH_2NNCH_2*

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The results of some STO-5G valence bond calculations are presented for a *cis* ONNO component of each of $ONNO_2$ and O_2NNO_2, and the CNNC component of *trans* CH_2NNCH_2. These studies provide support for the hypothesis that the –NO nitrogen atomic orbital, which is involved in the formation of the (fractional) N–N σ bond of $ONNO_2$, is primarily $2p$ in character, and oriented at right angles to the N–O internuclear axis, rather than along the N–N internuclear axis. Whereas delocalization of oxygen lone-pair electrons into the atomic orbitals of the N–N σ bond is responsible for the N–N bond lengthening for N_2O_4 relative to that of N_2H_4, the orientation and $2p$ character of the –NO nitrogen atomic orbital, as well as some delocalization of the oxygen lone-pair electrons, leads to the lengthening of the N–N bond of $ONNO_2$. It has been shown previously (*J. Mol. Struct. (Theochem)* **206** (1990) 253) that repulsions between nitrogen lone-pair electrons, together with the nitrogen atomic orbital hybridization and orientation, are associated with the existence of a very long N–N bond in *cis* N_2O_2. These factors are calculated to operate in a different manner for the *trans* CNNC component of CH_2NNCH_2, for which the measured N–N bond length is essentially that of an N–N single bond.

Consideration is given to the construction and properties of increased-valence structures for ONON, $ONONO_2$, two NO_3 isomers, OSSO and S_4, as well as for ONNO, $ONNO_2$ and O_2NNO_2.

INTRODUCTION

Very often, inspection of valence bond (VB) structures can provide realistic qualitative information about the nature of bond properties, provided that one knows how to construct the primary structure(s) and interpret them. This point of view has always been a feature of much of Pauling's work. Here, VB descriptions of N_2O_4, N_2O_3, N_2O_2, NO_3, CR_2N–NCR_2, S_2O_2 and S_4 will be presented, to help provide a partial up-

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* Dedicated to Professor Linus Pauling on the occasion of his 90th birthday.

date in the understanding of the origin of variations in the N–N and S–S bond lengths that are observed to occur in these systems. Attention will be given initially to the N–N bonds in the nitrogen oxides.

Various explanations for the observed differences in the N–N bond lengths of N_2H_4, sym N_2O_4, asym N_2O_3 and *cis* N_2O_2 (1.45, 1.78, 1.84 and 2.24 Å)[1-6] have been proposed on numerous occasions over the last forty or so years.[7] Each of these molecules has an N–N single bond in its standard Lewis structures (*cf.* VB structures of types (I)-(III) for N_2O_4, N_2O_3 and N_2O_2, in resonance with structures that differ in the locations of the N=O bonds). It is now well-recognized that delocalization of oxygen lone-pair electrons[8-11] into the atomic orbitals (AOs) of the N–N σ bond of (I) is responsible for the lengthening of the N–N bond of N_2O_4 relative to that of N_2H_4. Although this type of delocalization will also occur for N_2O_3 and N_2O_2, the results of *ab initio* (STO-5G) VB calculations show that the extent of the delocalization is insufficient to account for the existence of the extraordinarily long N–N bond in N_2O_2.[12] Here, the results of these and other VB calculations for various electronic states of N_2O_2 are reported and used as models to illustrate the factors that could be responsible for the N–N bond-length variations in these molecules. These factors, which involve concepts that have been used extensively by Pauling in other contexts, include[12]

(i) The nature of the hybridization for the nitrogen AOs.
(ii) The orientation of the nitrogen AOs.
(iii) The delocalization of the oxygen lone-pair electrons in the Lewis structures (I)-(III).
(iv) The presence of nitrogen lone-pair electrons in the Lewis structure for N_2O_2.

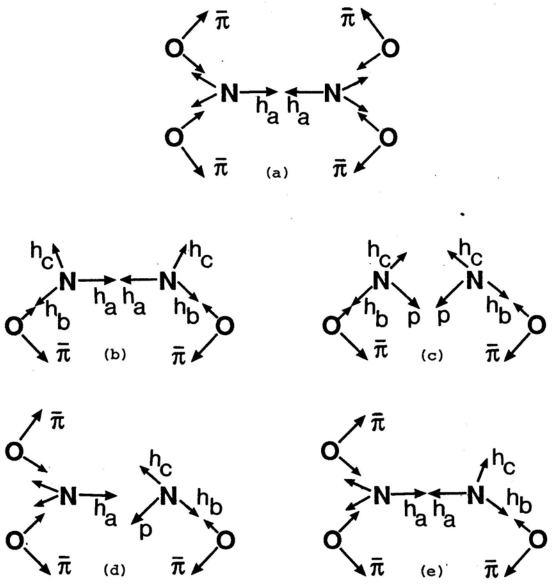


Figure 1. Orientations for some of the valence shell AOs for N_2O_4, N_2O_2 and N_2O_3. In (c) and (d), $p = \bar{\pi}_N$. The $\bar{\pi}$ and h_a or p type AOs are the mobile σ electron AOs.[8-12]

INCREASED-VALENCE STRUCTURES

In Figure 1, the h_a or p AOs of the N–N σ bond and the $\bar{\pi}_O$ AOs have been designated as »mobile σ electron« AOs.[8-12]

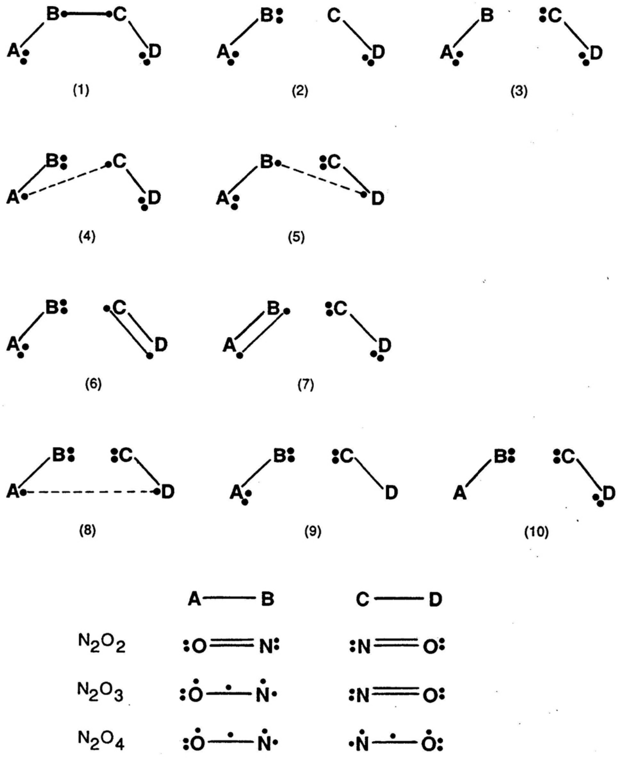
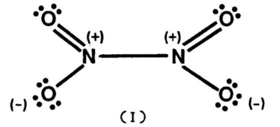
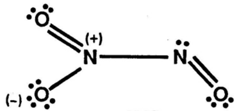


Figure 2. Lewis (S = 0 spin) VB structures for distributions of six electrons amongst four mobile σ electron AOs.

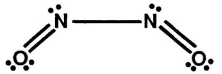
To establish a framework for the VB calculations, it is helpful, initially, to give consideration to increased-valence structures (VII)-(IX) for these systems. They may be derived from the standard Lewis structures of types (I)-(III) by delocalizing π_O and $\bar{\pi}_O$ electrons into bonding N–O MOs, as it is indicated in (IV)-(VI). Each of the increased-valence structures is equivalent to resonance between one of the Lewis structures (I)-(III), and numerous »long-bond« (or singlet diradical) Lewis structures.[9-12] For a given π electron distribution, the resulting increased-valence structure that arises from the delocalization of the $\bar{\pi}_O$ electrons is equivalent to resonance between four covalent (AB-CD) structures, namely the standard Lewis structure (1) and the long-bond structures (4), (5) and (8) of Figure 2. The remaining six structures of Figure 2 are the ionic partners ($(AB)^+(CD)^-$ and $(AB)^-(CD)^+$) for the covalent structures. Here, we focus at-



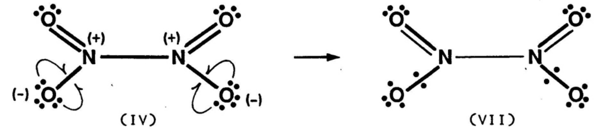
(I)



(II)

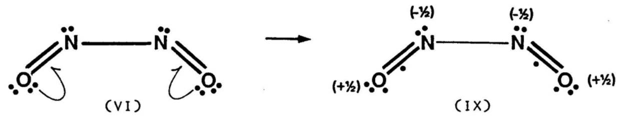


(III)

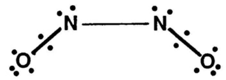


(IV) (VII)

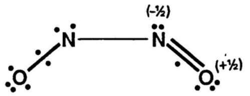
(V) (VIII)



(VI) (IX)



(X)



(XI)

tention on VB calculations for resonance between these ten types of structures for each of the three nitrogen oxides. However, to simplify the calculations for N_2O_4 and N_2O_3, we have omitted the neutral $=O$ oxygen atoms of (VII) and (VIII), to give the *cis* N_2O_2 pseudo excited states (X) and (XI) as the relevant N_2O_2 components* for N_2O_4 and N_2O_3.

The NO moieties of structures (IX), (X) and (XI) involve either of the two electronic states. One of them is the ground-state, whose VB structure is (XII) with a Pauling three-electron bond configuration, $(\pi_{NO})^2(\pi^*_{NO})^1 = (\pi_N)^1(\pi_{NO})^1(\pi_O)^1$, for one set of π electrons.[13] The other state is an excited state, whose VB structure is (XIV). It is obtained by exciting a nitrogen lone-pair electron of (XII) into the other antibonding π^*_{NO} MO, which is vacant in this structure. The excitation is indicated in (XIII), with the label »a« used to designate that electron transfer is antibonding in its effect. (The

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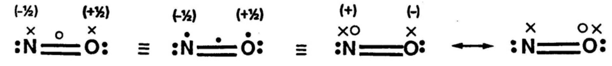
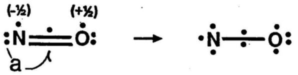
* Of course, *trans* N2O2 structures analogous to (X) and (XI) may also be written down for N2O3 and N2O4. However, because the basic principles that are involved in rationalizing the origin of N–N bond-length variations should not depend on the choice of isomer used in the calculations, we have restricted our attention here to studies of the *cis* isomers.



(XII)



(XIII) (XIV)

reader is referred to refs. 11 and 14 for discussions of the antibonding MO terminology when Heitler-London type wave-functions are used to describe covalent electron-pair bonds.) Three singly-occupied orbitals are now present in (XIV). To obtain VB structure (XI), the π^*_{NO} electron of (XII) is spin-paired in a σ manner with the corresponding π^*_{NO} electron of (XIV). Increased-valence structure (X) involves two NO moieties of type (XIV), whereas the NO moieties of (IX) are both of type (XII).

For N_2O_2 and the N_2O_2 moieties of N_2O_3 and N_2O_4, the A-B and C-D valence-shell cores for the mobile σ electrons are displayed in Figure 2. Inspection of them, and also VB structures (IX)-(XI), reveals that the latter structures have four, six and five (out-of-plane) π electrons, respectively.

ATOMIC ORBITAL ORIENTATIONS

Orientations for some of the AOs used in the VB calculations[12,15] are displayed in Figure 1. Those of Figure 1(a) are obtained for N_2O_4 as $O_2N{-}NO_2$; the nitrogen AOs that form the (fractional) N–N σ bond are directed along the N–N internuclear axis. For N_2O_2 as *cis* ON–NO, two sets of orientations need to be considered, namely those of Figures 1(b) and 1(c). The results of VB calculation[12] show that Figure 1(c) is to be preferred for this molecule. The preferred AO orientations for asym N_2O_3 should then be those of Figure 1(d) rather than Figure 1(e), and this assumption is supported by the results of the VB calculations that are described below.

VB CALCULATIONS

As indicated in ref. 12, the eight electrons that form the localized A-B and C-D σ and π bonds for the N_2O_2 ground-state are accommodated in homopolar bonding molecular orbitals (MOs), in order to simplify the electron spin theory for each of the VB structures. The one or two additional π electrons for N_2O_3 and N_2O_4 are located in homopolar antibonding π^*_{NO} MOs (which are orthogonal to the π_{NO} MOs). The techniques for determining the nature of the hybridization for the nitrogen AOs are described in ref. 12 for the –NO substituents of N_2O_2 and N_2O_3, and in refs. 16 for the $-NO_2$ substituents of N_2O_3 and N_2O_4. The $S = 0$ spin wavefunctions for the VB structures involve either one or two Slater determinants according to whether or not there are zero or two mobile σ electron AOs that are singly occupied in these structures.[12,15,17,18] In each of the Slater determinants for the VB structures for N_2O_4, the singly-occupied h_c and π^*_{NO} orbitals of the left-hand and right-hand moieties were assigned α and β spins, respectively, thereby preventing the occurrence of any N–N bonding that would arise from h_c-h_c and π^*_{NO}-π^*_{NO} overlap. All electrons have been included in the calculations, which were performed for various N–N lengths using Roso's program.[15,17,18] The results of the calculations for N_2O_2 have been reported previously[12], and are redescribed in (a) below.

RESULTS

(a) N_2O_2

For the AO orientations of Figure 1(b), the optimum value of the hybridization parameter λ_a (in $h_a = s + \lambda_a p$) for the AOs of the N–N bond is 3.0. The resulting energy minimum occurs when r(NN)) = 1.75 Å. For the orientations of Figure 1(c), the N–N bond arises from p orbital overlap, and the minimum energy occurs when r(NN) is near 2.24 Å, whether or not the remaining non-π nitrogen valence AOs are s-p hybridized. Inclusion of only structures (1)-(3) in the VB calculations, *i.e.* omitting the structures that arise from $\bar{\pi}_O$ electron delocalization, produces only a small shortening of the N–N bond to either 1.70 Å (Figure 1(b)) or 2.10 Å (Figure 1(c)). However, very substantial shortening does occur when the nitrogen lone-pair electrons are omitted. With no s-p hybridization and the AO orientations of Figure 1(c), these electrons are 2s electrons, and exclusion of them reduces the N–N bond length to 1.65 Å. Thus, the non-bonded repulsion between the nitrogen lone-pair electrons, when their AOs are oriented as in Figure 1(c), are calculated to be primarily responsible for the existence of a very long N–N bond in N_2O_2. It may be noted that this effect is less substantial for the AO orientations of Figure 1(b). This is due to the smaller overlap that occurs between the nitrogen lone-pair AOs. When r(NN) = 1.45 Å, the overlap integrals for pairs of these AOs have values of 0.100 (Figure 1(b)) and 0.267 (Figure 1(c)).

(b) N_2O_4

The nitrogen hybridization was determined from some *ab initio* studies of NO_2,[16] which gave $\lambda_a = 1.5$ for the AOs of the N–N σ bond. Due to the N–N σ bond formation, this NO_2 estimate of λ_a would of course change for N_2O_4. However, use of this value is adequate in order to illustrate the effects of $\bar{\pi}_O$ electron delocalization on the calculated lengths of the N–N bonds for both N_2O_4 and N_2O_3. When ten structures are included in the VB calculations, the equilibrium N–N length of N_2O_4 is calculated to occur at 1.61 Å (Table I). Exclusion of the structures that correspond to (4)-(10) for N_2O_2, *i.e.* the structures arise from the $\bar{\pi}_O$ electron delocalization, shortens the bond to 1.38 Å. Therefore, the delocalization of the $\bar{\pi}_O$ electrons is calculated to be responsible for the N–N bond lengthening for this molecule, *via* the reduction in the N–N σ bond order and the associated N–N σ antibonding destabilization when the overlap between the AOs of this bond is appreciable. The latter effect is associated primarily with the contribution of structures (8)-(10) to the resonance scheme; double occupation of the h_a AOs in these structures generates strong non-bonded repulsions. When structures (8)-(10) are omitted from the calculations, the N–N bond length is reduced from 1.61 Å to 1.55 Å (Table I).

TABLE I

N_2O_4 energies (a.u.) for resonance between: (a) structures (1) — (10); E_{min} = *—256.7393 a.u. at* r(*NN*) = *1.61 Å. (b) structures (1) — (3);* E_{min} = *—256.6175 a.u. at* r(*NN*) = *1.38 Å. (c) structures (1) — (7);* E_{min} = *—256.7289 a.u. at* r(*NN*) = *1.55 Å.*

r(NN)/Å	1.40	1.55	1.70	1.80
$E + 256.0^a$	–0.72083	–0.73815	–0.73738	–0.73329
$E + 256.0^b$	–0.61723	–0.59447	–0.54992	–0.51752
$E + 256.0^c$	–0.7166	–0.72886	–0.71985	–0.70853

(c) N_2O_3

The nitrogen hybridizations for N_2O_2 and NO_2, namely[12,16] $\lambda_b(NO) = 3.1$ and $\lambda_a(NO_2) = 1.5$, were used for the –NO and $-NO_2$ substituents of N_2O_3, in calculations with the AO orientations of Figure 1(d). When ten VB structures are included in the calculations, an energy minimum occurs when $r(NN) = 1.77$ Å (Table II). The length shortens to 1.59 Å when only structures of types (1)-(3) are included.

For calculations with the AO orientations of Figure 1(e), the nitrogen hybridization for the –NO moiety was determined *via* energy optimization at various N–N distances (Table III). With ten structures included in the calculations, the energy minimum occurs at 1.59 Å. Its value of –256.911 a.u. is higher than the –256.936 a.u. at $r(NN) = 1.77$ Å for Figure 1(d). (The latter energy would decrease if the nitrogen hybridization for the –NO moiety were energy optimized for N_2O_3 rather than for N_2O_2). Therefore, the orientations of Figure 1(d) are preferred for N_2O_3, and, as a consequence, the N–N bond is calculated to be somewhat longer than that calculated for N_2O_4 (1.61 Å). Thus, the N–N bond lengthening for N_2O_3 relative to both N_2H_4 and N_2O_4 is due primarily to the nature of the orientation and hybridization of the

TABLE II

N_2O_3 energies (a.u.) for resonance between (a) structures (1)-(10); $E_{min} = -256.9362$ a.u. at $r(NN) = 1.77$ Å. (b) structures (1)-(3); $E_{min} = -256.8328$ a.u. at $r(NN) = 1.59$ Å. The calculations involve the AO orientations of Figure 1(d), with $\lambda_b = 3.0$ for the right-hand N=O moiety

r(NN)/Å	1.40	1.55	1.70	1.80	1.95
$E + 256.0^{(a)}$	–0.87680	–0.92027	–0.93411	–0.93554	–0.89979
$E + 256.0^{(b)}$	–0.80749	–0.83266	–0.82745	–0.81583	–0.75663

TABLE III

N_2O_3 energies ($E+256.0$ a.u.) for resonance between structures (1)-(10), with AO orientations of Figure 1(e), and variable values for λ_a for the right-hand N=O moiety
$E_{min} = -256.9114$ a.u. at $r(NN) = 1.59$ Å for $\lambda_a = 2.47$

	r(NN)/Å			
λ_a	1.40	1.55	1.70	1.80
2.0	–0.88032	–0.89970	–0.89274	–0.88273
2.5	–0.88306	–0.91015	–0.90525	–0.89019
3.0	–0.87299	–0.89583	–0.89108	–0.88184
	Three point interpolation			
λ_a	2.36	2.46	2.48	2.49
E + 256.0	–0.88359	–0.91022	–0.90527	–0.89108

TABLE IV

N_2O_3 energies (a.u.) for resonance between structures (1)-(3) with AO orientations of Figure 1(e) and $\lambda_a = 2.5$ for right-hand N=O moiety. $E_{min} = -256.8209$ a.u. at $r(NN) = 1.48$ Å

r(NN)/Å	1.40	1.55	1.70	1.80
E + 256.0	–0.81526	–0.81671	–0.78891	–0.76391

nitrogen AOs, but the $\bar{\pi}_O$ electron delocalization lengthens the bond from 1.59 Å to 1.77 Å when the orbital orientations of Figure 1(d) are used. When the AO orientations of Figure 1(e) are used, and $\bar{\pi}_O$ electron delocalization is not permitted to occur, the N–N bond-length shortens from 1.59 Å to 1.48 Å (Table IV).

(d) N_2O_4, N_2O_3 and N_2O_2

In Table V, weights for the VB structures are reported for N–N distances that are close to the calculated equilibrium values. The sum of the weights for structures with mobile σ electron distributions of types (4)-(10) shows that the extent of delocalization of the $\bar{\pi}_O$ electrons is larger for N_2O_4 than it is for N_2O_3 and N_2O_2, even though N_2O_4 has the shortest N–N length.

References to numerous MO and VB studies of N_2O_2 and N_2O_4 are provided in refs. 12 and 19. Those for N_2O_3 are provided in refs. 20-23. In ref. 21, consideration is given to the nature of the hybridization of the nitrogen AOs. The (CNDO) canonical MOs for each of the three species in ref. 21 were transformed to give localized MOs. It was found that the h_a-type AOs of the present study involved substantial s–p mixing for the $-NO_2$ substituents of N_2O_4 and N_2O_3, but were almost entirely 2p in character for the –NO substituents of N_2O_2 and N_2O_3. These findings are in general accord with those obtained from the present VB studies. However, the orientation of the h_a AO of the –NO substituents was directed along the N–N internuclear axis, as in Figures 1(b) and 1(e), rather than at right angles to the N–O bond axis, as in Figures 1(c) and 1(d). Perhaps, the inability of all but very detailed MO calculations to generate a very long N–N bond length for N_2O_2 is due in part to the nature of the orientations of the AOs basis sets that have been used in the calculations.

In ref. 7(c), the lengthening of the N–N bonds of N_2O_3 and N_2O_2 relative to that of N_2O_4 has been associated with the presence of one and two sets of geminal sp^2 lone-pair electrons on the –NO nitrogen atoms of N_2O_3 and N_2O_2. These lone-pair electrons can be delocalized into the antibonding σ^*_{NN} MO which is vacant in structures of types (II) and (III). To some extent, this effect has been explored *via* VB calculations for

TABLE V

Chirgwin-Coulson weights (W_i) and N—N σ bond order (n(NN)) at N—N distances that are either near or equal to calculated equilibrium distances

	N_2O_2 (2.24 Å)	N_2O_3 (1.80 Å)	N_2O_4 (1.61 Å)[a]	N_2O_4 (1.55 Å)
W_1	0.715	0.455	0.358	0.421
W_2	0.021	0.127	0.066	0.081
W_3	0.021	0.026	0.066	0.081
W_4	0.105	0.205	0.146	0.124
W_5	0.105	0.069	0.146	0.124
W_6	0.009	0.057	0.091	0.084
W_7	0.009	0.038	0.091	0.084
W_8	0.013	0.022	0.031	
W_9	0.0001	0.001	0.002	
W_{10}	0.0001	0.001	0.002	
n(NN)	0.757	0.608	0.490	0.583

[a] Interpolated from weights at 1.40, 1.55, 1.70 and 1.80 Å.

N_2O_2. Little interaction* is calculated to occur between structure (III) with a $(h_c)^2(h_a)^1 (h'_c)^2(h'_a)^1$ configuration for the six relevant electrons, and two structures with $(h_c)^1 (h_a)^2(h'_c)^2(h'_a)^1$ and $(h_c)^2(h_a)^1(h'_c)^1(h'_a)^2$ configurations for the six relevant electrons. (The h'_c and h'_a refer to the right-hand NO moiety). In any case, the N–N lengthening due to geminal interactions in HN=N–N=NH, which is isoelectronic with N_2O_2, is calculated[7c] to be much smaller than that needed to produce a bond length which exceeds 2 Å. As it has been indicated above and also in ref. 12, the results of the VB studies make clear that the orientation and hybridization of the nitrogen AOs of the –NO moieties of N_2O_2 and N_2O_3 are the primary factors that determine the lengths of the N–N bonds.

INCREASED-VALENCE STRUCTURES: SOME FURTHER EXAMPLES

(a) N–O Bond-Lengths for NO, NO_2, N_2O_4, N_2O_3 and N_2O_2

The N–O bond-lengths for the NO_2 monomer and the –NO_2 substituents of N_2O_4 and N_2O_3 are 1.19, 1.19 and 1.21 (av.) Å, respectively. Those for the NO substituents of N_2O_3 and N_2O_2, and free NO[24] are 1.14, 1.16 and 1.15 Å. Inspection of the increased-valence structures (VII)-(IX) makes it clear that the lengths of the N–O bonds of the –NO_2 substituents and the NO_2 monomer (with the increased-valence structures of (XV)) should be longer than those for the –NO substituents, which in turn are similar to those for free NO as (XII). But only in the case of N_2O_4 is the fractionality of the N–N σ bond *primarily* responsible for the N–N bond lengthening relative to a »normal« N–N single bond.

(b) ONON, ONONO and $ONONO_2$

The ONON isomer of N_2O_2 was characterized,[25] in 1978 and the results of MO calculations[26] show that the ONON isomer has a $^3A''$ *trans* ground state. To construct an appropriate VB structure for the (S = 1 spin) ground-state, we spin-pair in a σ manner the π^*_{NO} electron of the VB structures (XII) with one of the π^*_{NO} electrons of (XVI). (The latter structure is the $S = M_S = 3/2$ spin component of (XIV)). The resulting VB structure (XVII) has two singly-occupied orbitals in the right-hand ON moiety, with parallel spins for the electrons. Alternatively, we may commence with VB structure (XV) for NO_2, and spin-pair its unpaired-electron in a σ manner with an unpaired electron of a ^4S (ground-state) nitrogen atom. Electronic reorganization in the resulting increased-valence structure (XVIII), *via* the one-electron delocalizations that are indicated in (XIX) and (XX), generates the increased-valence structure (XVII). A set of calculated bond lengths[26] for $O_aN_aO_bN_b$, namely $r(O_aN_a)$ = 1.17 Å, $r(N_aO_b)$ = 1.44 Å and $r(O_bN_b)$ = 1.38 Å implies that there is little development of the two Pauling three-electron bonds in the O_bN_b moiety of (XVII).

It may be noted that when proceeding from (XX) to (XVII), it is necessary to change the locations in the VB structures of some of the electrons. This is also the case for the conversion of (XXVII) into (XXVI) in the next section.

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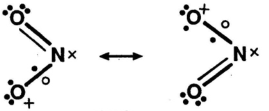
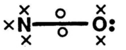
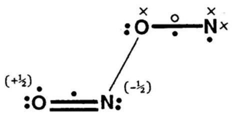
* For r(NN) = 1.75 Å, *i.e.* for the energy minimum for Figure 1(b)[12], resonance between these three structures, designated as 1, 2 and 3 here, give the following energies (a.u.) and coefficients for calculations with the AO orientations of Figures 1(b) and 1(c):
Figure 1(b), $\lambda_a = 3.0^{12}$: $E = -257.0443$, $E_1 = -256.9503$, $C_1 = 1.209$, $C_2 = C_3 = 0.337$.
Figure 1(c), $\lambda_b = 3.1^{12}$: $E = -257.1061$, $E_1 = -257.0905$, $C_1 = 0.956$, $C_2 = C_3 = 0.122$.


(XV)


(XVI)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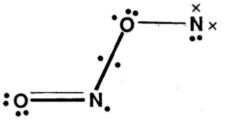
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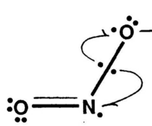
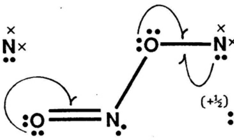
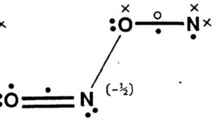
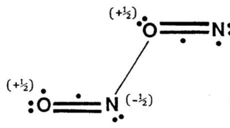
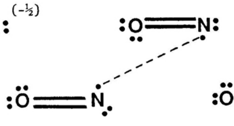
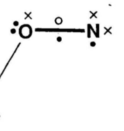

(XIX)


(XX)


(XVII)

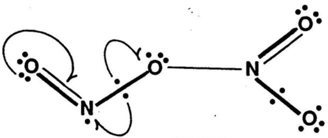

(XXI)


(XXII)

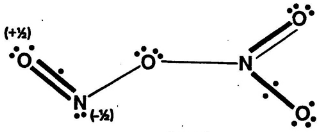

(XXIII)

Appeal to the electroneutrality principle[27] provides a possible explanation as to why the ground-state of ONON has an $S = 1$ rather than an $S = 0$ spin state. For the latter state, the increased-valence structure (XXI) may be constructed[9] by spin-pairing in a σ manner the π^*_{NO} electrons of two ground-state NO monomers, each with a VB structure of type (XII), but with a spin for its π^*_{NO} electron which is opposed to that of the other monomer. Presumably the preference for (XVII) is due to the presence of less formal charge separation in this structure relative to what occurs in (XXI). The formal charge separation in (XXI) cannot be reduced to zero unless the N_a–O_b σ bond is broken, to form the long-bond structure (XXII), whereas little reduction in bonding need occur to generate the $S = 1$ spin structure (XXIII) with zero formal charges.

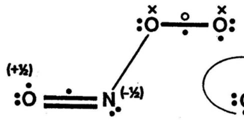
Increased-valence structures of type (XXV) are obtained for the $ONONO_2$ isomer of N_2O_4 *via* the electronic reorganization indicated in (XXIV), which is constructed by spin-pairing the odd electrons of the NO_2 monomers with the VB structures of (XV) to form a fractional intermolecular N–O σ bond. In ref. 9, the bond properties associated with the observed N–O stretching frequencies are shown to be in accord with those implied by increased-valence structures of type (XXV). For sym N_2O_3, the bond properties implied by the Lewis structure O=N–O–N=O are in qualitative accord with those obtained from spectroscopic and theoretical studies.[22] Increased-valence structures of type (XXV) may also be obtained[9] by spin-pairing in a σ manner the odd electrons of NO_3 and NO with VB structures of types (XXIX) (see below) and (XII) for these species.



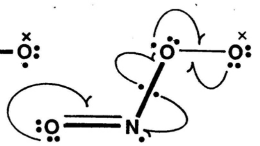
(XXIV)



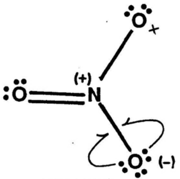
(XXV)



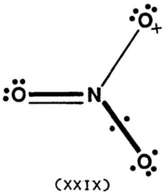
(XXVI)



(XXVII)



(XXVIII)

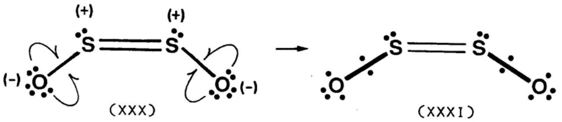


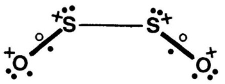
(XXIX)

(c) NO_3: ONOO and O–NO_2

VB structures for the ONOO and O–NO_2 (with either C_{2v} or D_{3h} symmetry) isomers will be considered here. The VB structure for the $^3\Sigma_g$-ground state of O_2 is: $:\overset{\times}{\underset{\times}{O}}\,\overset{\circ}{\underset{\circ}{-}}\,\overset{\times}{\underset{\times}{O}}:$ when the M_S spin quantum number is +1. On spin-pairing in a σ manner one of the π^*_{OO} electrons of O_2 with the π^*_{NO} electron of ground-state NO, increased-valence structure (XXVI) is obtained for ONOO. This VB structure may also be constructed from the increased valence structure (XXVII) *via* the one-electron delocalizations that are indicated in this structure. Structure (XXVII) is obtained *via* the formation of a (fractional) O–O σ bond between ONO and an O atom, by spin-pairing in a σ manner of an unpaired electron of a ^3P oxygen atom with the unpaired electron of NO_2, when the VB structure for the latter species is of type (XV).

Appropriate VB structures of type (XXIX) for O–NO_2 may be constructed either from standard Lewis VB structures of type (XXVIII) *via* the delocalizations that are indicated, or by the formation of a (fractional) O–N σ bond between O_2N and a ^3P


(XXX) (XXXI)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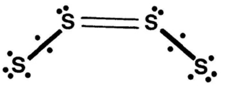
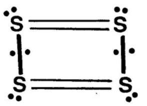
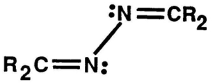
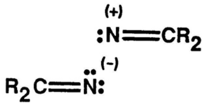
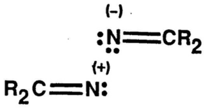
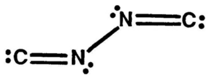

(XXXIII)


(XXXIV)


(XXXV)


(XXXVI)


(XXXVII)


(XXXVIII)

oxygen atom, using an NO_2 VB structure of (XV). In (XXIX), the odd electron is assumed to occupy an in-plane $\bar{\pi}_O$ AO, in accord with the results of MO calculations.[28]

Some recent MO-estimates[28,29] of the bond-lengths for the two isomers are indicated in Figure 3. These lengths are in qualitative accord with those that may be deduced from inspection of the increased-valence structures, if it is assumed that some of the N–O_b multiple bonding which is present in (XXVII) for $O_aNO_bO_c$ is retained in (XXVI).

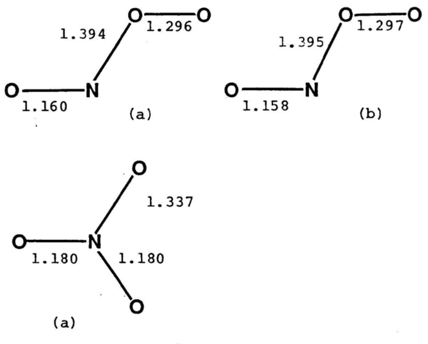


Figure 3. Calculated bond lengths (Å) for NO_3 isomers. (a) Ref. 28. (b) Ref. 29.

(d) S_2O_2 and S_4

For the C_{2v} isomer of S_2O_2, the corresponding increased-valence structure is (XXXI), which may be derived from the standard Lewis structure (XXX) by means of the π_O and $\bar{\pi}_O$ electron delocalizations that are indicated in the latter structure.[30] Inspection of the increased-valence structure (XXXI) indicates immediately that the central S–S bond should be longer than those of standard S–S double bonds, and that the S–O bond lengths should be similar to those of the SO monomer as $:\overset{x}{\underset{x}{\mathrm{S}}}\overset{o}{\underset{o}{\text{——}}}\overset{x}{\underset{x}{\mathrm{O}}}:$. Each of these expectations is in accord with what has been observed[24,31] namely $r(\mathrm{SS}) = 2.02$ and 1.89 Å for S_2O_2 and S_2, and $r(\mathrm{SO}) = 1.47$ and 1.48 Å for S_2O_2 and SO. It may be noted also that in the $S = 1$ spin state for S_2O_2, with VB structure (XXXII), the S–S π bond of (XXXI) has been broken. However the S–S σ bond is fractional, and therefore it is not surprising that the length of this bond is calculated[32] to be 0.14 Å longer than the S–S single bond of H_2S_2.

For S_4, increased-valence structures for the *cis* and rectangular isomers with C_{2v} and D_{2h} symmetries are (XXXIII) and (XXXIV). As yet no experimental structural data has been reported for S_4, but it may be noted that the σ and π bond-numbers for the S=S bonds in (XXXIV) are each 0.25 and, therefore, these bonds should be rather longer than that for (XXXI) for S_2O_2. In the latter system, the S–S–O bond angles of 112°[31] are substantially larger than the 99.6° for N_2O_2; this suggests that the AO orientations similar to those of Figure 1(b) could be the appropriate types. As it will be discussed below, the nitrogen AO orientations of Figure 1(b) should also be appropriate for CR_2NNCR_2 with R = H, Br, F, and $CH_3CH{=}N{-}N{-}CHCH_3$, whose C–N–N bond angles (110–115°)[33,34] are also close to 112°. Very recently, the results of TCSCF/SDCI calculations[35] for S_4 indicate that the ground-state of S_4 has C_{2v} symmetry, with S–S bond-lengths of 1.85, 2.04 and 1.85 Å. These lengths are in accord with those implied by the increased-valence structure (XXXIII), for which the central S–S bond has a bond-number rather less than 2 (*cf.* structure (XXXI) and the bond lengths for S_2O_2).

CH_2NNCH_2

The N–N bond length[33] of 1.42 Å for *trans* CH_2NNCH_2 (which is isoelectronic with N_2O_2) is similar to the 1.45 Å for N_2H_4. With each of these species, there are no vicinal lone-pair electrons that correspond to the oxygen $\bar{\pi}_O$ electrons of the standard Lewis structure (III) for N_2O_2. Therefore, to study the properties of the N–N σ bonds for these systems, it is only necessary to consider the covalent and ionic Lewis structures (XXXV)-(XXXVII). To simplify the *ab initio* VB calculations, the CR_2 substituents were replaced by :C, as in structure (XXXVIII), with sp^2 hybridization for the carbon AOs that are involved in C–N σ bonding. Non-polar C–N σ and π bonding has been assumed, with doubly-occupied C–N bonding MOs used to describe these bonds. The optimized nitrogen hybridization was determined for the orientations of each of Figures 4(a) and (b). It was found that the preferred orientations of the nitrogen AOs were those of Figure 4(a), for which an energy minimum occurs at $r(\mathrm{NN}) = 1.51$ Å (Table VI). If the orientations of Figure 4(b) are assumed, the energy minimum is calculated to occur at a rather longer N–N bond length – 2.01 Å (Table VI). This energy lies above the energy minimum for the AO orientations of Figure 4(a). Therefore, the orientations and hybridization of the nitrogen AOs differ from those for *cis* N_2O_2, and because of this, the N–N bonds of the CR_2NNCR_2 type molecules behave more like »normal« N–N single bonds than does the N–N bond of *cis* N_2O_2.

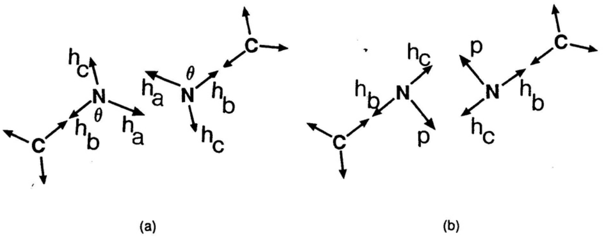


Figure 4. AO orientations for the CNNC component of CH_2NNCH_2. In (a) and (b), $\theta = \sphericalangle h_aNh_b$ and $p = \bar{\pi}_N$, respectively.

TABLE VI

NCCN energies (a.u.) for resonance between structures (XXXVI) — (XXXVIII)

$r(NN)$/Å	1.418	1.50	1.60	1.80	2.00	2.24
E +183.0[(a)]	–0.48064	–0.48772	–0.48207	–0.44827	–0.40890	–0.37307
E +183.0[(b)]	–0.38435	–0.41889	–0.44536	–0.46885	–0.47390	–0.47233

[(a)] Figure 4(a). $\theta = 99^\circ$, $\lambda_a = 2.5$. $E_{min} = -183.4877$ a.u. at $r(NN) = 1.51$ Å.
[(b)] Figure 4(b). $\lambda_b = 4.2$. $E_{min} = -183.4739$ a.u. at $r(NN) = 2.01$ Å.

At the time of writing, the optimum orientations of the nitrogen hybrid AOs have not been determined for the NO substituents of *cis* N_2O_2 and $ONNO_2$ in the way that it has been done for the CNNC component of CH_2NNCH_2 (Table VI). However, because the O–N–N bond angles of 99.6° for *cis* N_2O_2 are close to the near-optimum value of 99° for the $\theta = \sphericalangle h_b\text{–N–}h_a$ angles of CH_2NNCH_2, it is probable the AO orientations of Figure 1(c) are near optimum. It may be noted also that the energy minimum of –257.1564 a.u. for Figure 1(b) occurs when $r(NN) = 1.75$ Å[12], but for this distance, the energy for Figure 1(c) is rather less, namely –257.2105 a.u. for $\lambda_a = 3.1$. In contrast, when $r(NN) = 1.50$ Å, *i.e.* near the energy minimum for Figure 4(a), the energy of –183.4418 a.u. for Figure 4(a) with $\lambda_a = 2.5$ and $\theta = \sphericalangle CNN = 111.4^\circ$ (*cf.* Figure 1(b) for N_2O_2) is less than the –183.4189 a.u. for Figure 4(b) (*cf.* Figure 1(c) for N_2O_2).

The N–N and CH–CH lengths of 1.42 and 1.46 Å[33,36] for isoelectronic CH_2NNCH_2 and $CH_2CHCHCH_2$ are shorter than the 1.45 and 1.54 Å [1,37] for the lengths of these bonds in isoelectronic N_2H_4 and C_2H_6. It is probable that these shortenings arise from both the presence of some N–N π bonding in the former compounds, and differences in the nature of the AO hybridization in the two sets of molecules.

CONCLUSIONS

Although they are certainly crude by modern standards, the above model VB calculations show up macro effects in an unambiguous manner. Therefore, it is probable that similar conclusions concerning the origin of the N–N bond length variations will be obtained from better VB calculations. The importance of AO hybridization and orientation in helping to determine differences in the lengths of the N–N bonds of N_2O_2, N_2O_3 and N_2O_4 has usually been underplayed relative to the effect on these bonds of delocalization of oxygen lone-pair electrons. Although these delocalizations do occur to different extents for all three molecules, it is only for N_2O_4 that N–N bond-lengthening relative to that of N_2H_4 is associated entirely with the delocalizations.

Acknowledgements. – I am indebted to and thank, Dr. W. Roso for making his *ab initio* VB program available to me, and Dr. F. L. Skrezenek for installing it.

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SAŽETAK

Istraživanje svojstava N-N veza u molekulama ONNO, $ONNO_2$, O_2NNO_2 i CH_2NNCH_2 primjenom metode valentnih struktura

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Duljina N-N veza u molekulama ONNO, $ONNO_2$, O_2NNO_2 i CH_2NNCH_2 interpretirana je pomoću koncepcije hibridizacije atomskih orbitala atoma dušika, njihove orijentacije i delokalizacije orbitala osamljenih parova atoma kisika.