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- (37) The sum of inductive and conjugative influences of SO_2 on the $\pi_{C=C}$ orbital of dimethylthiirene 1,1-dioxide amounts to -0.56 eV.⁹ This value is smaller than the corresponding sum of calculated influences of SO_2 on π_1 of 2,3-diphenylthiirene 1,1-dioxide, which is -0.89 eV (cf. Figure 5) because of the higher conjugative effect in the dimethyl derivative.
- (38) The calculated π charge transfer from $\text{PhC}=\text{CPh}$ to M (using the CNDO/S procedure) is (in $10^{-3}e$) for **6** 8.2, for **7** 245.4, for **8** 344.4, for **9** 82.2, and for **10** 81.4.
- (39) The CNDO/S conjugation energies (aromaticities) amount (in kcal/mol) to -4.55 for **6**, -53.76 for **7**, -52.84 for **8**, -22.05 for **9**, and -2.184 for **10**.

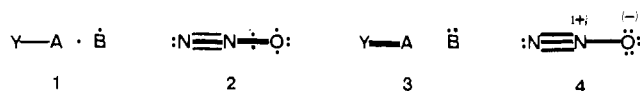
"Increased Valence" When the Octet Rule Is Obeyed. A Reply to a Challenge

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Abstract: Consideration is given to the use of the term "increased valence" when it is applied to the valence structure $\text{Y}-\text{A} \cdot \text{B}$ (I) relative to the standard valence-bond structure $\text{Y}-\text{A} \text{B}$ (II), each structure having a set of four electrons and three overlapping atomic orbitals (y , a , and b). One type of wave function for I is $|\bar{y}\bar{a}\psi_{abb}\rangle + |\bar{y}a\psi_{abb}\rangle$ with $\psi_{ab} = a + kb$ and $0 < k < \infty$. From this wave function, it is deduced that a maximum of three electrons may simultaneously participate in bonding for I, and that for $1 < k < \infty$, the valence for A in I may exceed its value of unity in II. Therefore on at least two counts, I may be designated as an "increased-valence" structure relative to II. This point of view is contrasted with that expressed recently by Halgren et al. (ref 2).

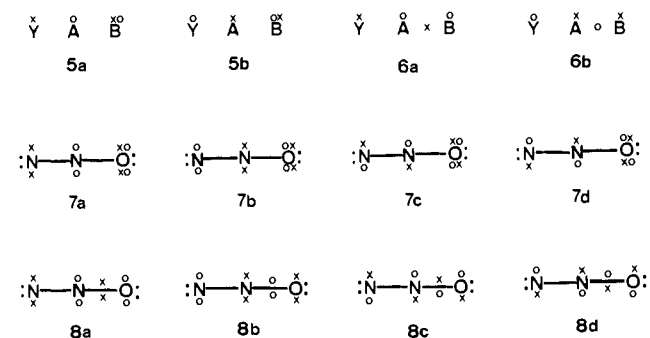
The use of the term "increased valence"¹ when it is applied to the general valence structure **1** has recently been questioned.² This structure may be constructed^{1,3c-e} whenever four electrons are distributed among three overlapping atomic orbitals centered on the three atoms Y, A, and B. For example, each set of four $2p\pi$ and $2p\pi'$ electrons of N_2O has the electron distribution of **1** in the valence structure **2**. Although ten electrons seem somehow to be involved in bonding to the central nitrogen atom, an *apparent*^{3a-d} rather than a real violation of the octet rule occurs in a minimal basis set description of **2**. Here I shall demonstrate that the designation of "increased valence" for valence structures **1** and **2** is appropriate in two senses, namely, (1) that more electrons participate in bonding for **1** and **2** than occur in the Lewis valence-bond structures **3** and **4** with electron-pair bonds, and (2) that the valence of the A atom in **1** and **2** can exceed that of unity and four for the same atom in **3** and **4**.



To demonstrate these propositions, we shall use Heitler-London rather than localized molecular orbital procedures to describe the YA bonding for **1** and **3**, thereby avoiding an effect that is associated⁴ with electron spin and the overutilization

of the A-atom atomic orbital when localized molecular orbitals (or bond orbitals) are used to describe the YA and AB bonding electrons of **1**. From an examination of the Heitler-London type wave function for **1**, Halgren et al.² have attempted to demonstrate the converse of the second proposition.

For valence structures **3** and **1**, the $S = 0$ wave functions are given by^{5,6} eq 1 and 2, respectively, in which y , a , and b are the overlapping atomic orbitals centered on the Y, A, and B atoms, and $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$ is the AB bonding molecular orbital that accommodates the electron of the AB bond of **1**. The Slater determinants of eq 1 and 2 generate the electron spin distributions ($x \equiv s_z = +1/2$, $o \equiv s_z = -1/2$) of **5** and **6** for



3 and 1, respectively. The corresponding electron spin distributions for the N₂O structures 4 and 2 are those of 7 and 8, respectively.⁷

$$\Psi(\text{Y}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) = (|y\bar{a}b\bar{b}| + |\bar{y}a\bar{b}b|)/2^{1/2} \quad (1)$$

$$\Psi(\text{Y}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) = (|y\bar{a}\psi_{ab}\bar{b}| + |\bar{y}a\bar{\psi}_{ab}b|)/2^{1/2} \quad (2)$$

To demonstrate the validity of proposition 1, it is helpful to invoke a unitary transformation of the *a* and *b* orbitals within each of the Slater determinants of eq 2, thereby obtaining eq 3, which is equivalent to eq 2. The $\psi_{ab}^* \equiv (ka - b)/(1 + k^2)^{1/2}$ of eq 3 is the AB antibonding molecular orbital which is orthogonal to the bonding molecular orbital ψ_{ab} .

$$\Psi(\text{Y}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) = (|y\bar{\psi}_{ab}^*\psi_{ab}\bar{b}| + |\bar{y}\psi_{ab}^*\bar{\psi}_{ab}b|)/2^{1/2} \quad (3)$$

Inspection of eq 3 reveals that the *y* and ψ_{ab}^* electrons are spin paired in a Heitler-London manner. Because the orbitals overlap, these two electrons must therefore be involved in (fractional) YA and YB bonding. A third electron in each of the Slater determinants of eq 3 is also involved in AB bonding, namely, the ψ_{ab} electron whose spin is opposed to that of the ψ_{ab}^* electron. (It is this ψ_{ab} electron that forms the one-electron AB bond of 1, 6a, and 6b.) Therefore in valence structure 1, a total of three electrons simultaneously participate in YA, YB, and AB bonding, whereas 3 has only two bonding electrons, namely, those that form the YA bond. Similarly for the N₂O valence structures 2 and 4, it is easy to deduce that a total of ten and eight electrons, respectively, participate in bonding. Therefore, with respect to proposition 1, valence structures 1 and 3 qualify to be designated as "increased-valence" structures, and they shall be referred to as such in the following discussions.

Inspection of "increased-valence" structure 1, and more particularly the electron spins for it in 6a and 6b, suggests that proposition 2 may also be valid,⁸ because three spin orbitals (and hence three electrons) are somehow involved in bonding to A, whereas there are only two spin orbitals and electrons similarly involved in 3. However, a comparison of the valence for A in 1 and 3 requires quantification. Halgren et al. have pointed out that whether or not an increase in atomic valence does occur depends on how valence is defined.² In the present context, the valence for A is that which pertains for the AB Pauling "three-electron bond" configurations that occur in the Slater determinants of eq 3, namely, those of eq 4. For each of these configurations, there are two components to the valence of A. These arise from the two electrons that occupy the ψ_{ab}^* orbital and the ψ_{ab} orbital with spin opposed to that of ψ_{ab}^* and (as we shall now show) represent the valence of A when it is involved in YA and AB bonding, respectively. Because the YA and AB bonding of eq 2 is described using Heitler-London and molecular orbital procedures, respectively, two different definitions of A-atom valence are required.

$$|\bar{\psi}_{ab}^*\psi_{ab}\bar{b}| \equiv |\bar{a}\psi_{ab}\bar{b}|, |\psi_{ab}^*\bar{\psi}_{ab}b| \equiv |\bar{a}\bar{\psi}_{ab}b| \quad (4)$$

The ψ_{ab}^* electron generates an odd-electron charge of $k^2/(1 + k^2)$ for atom A. This "free valence" can spin pair with a corresponding fraction of the odd-electron charge of the Y atom of 1 (or 6a + 6b) to generate a fractional YA bond in 1. With respect to this bond, the A-atom valence V_{AY} is therefore equal to $k^2/(1 + k^2)$. For the one-electron AB bond of 1, the valence of A (V_{AB}) is one-half of the valence for A when it is involved in the formation of an electron-pair bond and the molecular orbital configuration (ψ_{ab})² is used to describe the latter bond. Following Halgren et al.,² we may use the Armstrong et al.⁹ formula $2P_{aa} - P_{aa}^2 \equiv P_{ab}^2$ (with $P_{aa} = 2/(1 + k^2)$ and $P_{ab} = 2k/(1 + k^2)$) to calculate the valence of A for the (ψ_{ab})² configuration. We thereby obtain $V_{AB} =$

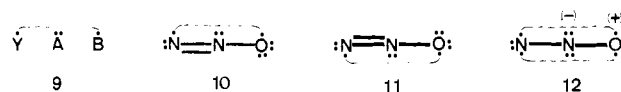
$2k^2/(1 + k^2)^2$ as the valence of A for the one-electron bond of 1. If we assume that V_{AY} and V_{AB} are additive, then the total valence for atom A in the "three-electron bond" configurations of eq 4, and hence for "increased-valence" structure 1, is given by $V_A \equiv V_{AY} + V_{AB} = k^2/(1 + k^2) + 2k^2/(1 + k^2)^2$. For $1 < k^2 < \infty$, $V_A > 1$, i.e., according to this procedure for calculating atomic valence, the valence of A in 1 may be increased relative to its value of unity in 3. A similar conclusion was reached in earlier papers by summing the YA bond number ($N(y,a) = k^2/(1 + k^2)$) and the AB bond order ($k/(1 + k^2)$) for 1,¹⁰ although the use of bond orders to deduce "increased valence" is considered to be less satisfactory.² For "increased-valence" structure 2, the A-atom valence of $2 + 2\{k^2/(1 + k^2) + 2k^2/(1 + k^2)^2\}$ has a maximum value of 4.25 when $k^2 = 3$, thereby exceeding the valence of four for the same atom in the Lewis structure 4.

A similar procedure may be used to calculate the valence for atom B in 1, namely, $V_B \equiv V_{BY} + V_{BA} = 1/(1 + k^2) + 2k^2/(1 + k^2)^2$. With $V_Y \equiv V_{YA} + V_{YB} = 1$, the sum of the three atomic valencies ($V_Y + V_A + V_B = 2 + 4k^2/(1 + k^2)^2$) has a maximum value of 3 when $k = 1$. This number is in accord with the deduction from eq 3 that a maximum of three electrons may participate in bonding in "increased-valence" structure 1.

The fractionality for the YA and YB bonding of "increased-valence" structure 1 may also be demonstrated by expanding eq 2 in terms of the valence-bond wave functions of eq 5. The resulting weights for the valence-bond structures 3 and 9, namely, $k^2/(1 + k^2)$ and $1/(1 + k^2)$, give the YA and YB bond numbers.¹⁰ They correspond to the fractional valencies V_{YA} and V_{YB} . Halgren et al.² also remark that the YA bond of eq 2 is a partial bond, although it is not fractional in the sense that they have defined the term (i.e., as in ref 4). The fractionality for eq 2 arises because the odd electron of the $\overset{\cdot}{\text{A}}\overset{\cdot}{\text{B}}$ component of 1 (or 6a and 6b) is distributed over two atomic centers, and therefore less than one electron is available for the A atom to form a complete YA electron-pair bond.

$$\Psi(\text{Y}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) = \left\{ k(|y\bar{a}b\bar{b}| + |\bar{y}a\bar{b}b|) + (|y\bar{a}\bar{a}b| + |\bar{y}a\bar{a}b|) \right\} / \left\{ 2(1 + k^2) \right\}^{1/2} \quad (5)$$

$$\equiv \left\{ k\Psi(\text{Y}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) + \Psi(\overset{\cdot}{\text{Y}}-\overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}}) \right\} / (1 + k^2)^{1/2}$$



For a number of electron-rich molecules, the results of valence-bond calculations¹¹ support the hypothesis^{3d} that certain "long-bond" structures of the general type 9 (for example, 10-12) may often have appreciable ground-state weights. Inspection of eq 5 shows that "increased-valence" structures summarize resonance between standard valence-bond structures (such as 3 and 4) and "long-bond" structures. With this type of wave function, the octet rule is obeyed by the "long-bond" structure(s) if it is obeyed by the standard structure.^{3d}

The additional stability of "increased-valence" structures relative to the standard valence-bond structures has been discussed on numerous occasions elsewhere.^{1,3d,7}

Acknowledgments. I thank Professor T. A. Halgren for stimulating discussions, the University of Melbourne for study leave, and Professor R. Hoffmann for the use of the facilities of his department at Cornell University.

References and Notes

- (1) (a) R. D. Harcourt and W. Roso, *Can. J. Chem.*, **56**, 1093 (1978), and ref 1, 3, 4, 20, and 21 therein. See also (b) R. D. Harcourt, *Aust. J. Chem.*, **31**, 199 (1978); (c) *ibid.*, **31**, 1635 (1978); (d) *Tetrahedron*, in press.
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- (3) (a) R. D. Harcourt, *Theor. Chim. Acta*, **2**, 437 (1964); **4**, 202 (1966); (b) *ibid.*, **6**, 131 (1966); (c) *J. Chem. Educ.*, **45**, 779 (1968); **46**, 856 (1969); (d) *J. Mol. Struct.*, **9**, 221 (1971). In the latter sections of ref 3b the adjective "apparent" was omitted because continuous use of it seemed unnecessary. The reasons for apparent octet violation that are described by Halgren et al.² correspond to those that have also been advanced in some of these references; see in particular ref 3a, pp 439, 440, and 437.
- (4) This effect, namely, that "as a result of the Pauli exclusion principle, self cancellations occur when the LCAO expansions for fractional localized (YA and AB) molecular orbitals are inserted into the determinantal wave functions and multiplied out",² is discussed in both ref 2 and by us: *Aust. J. Chem.*, **22**, 279 (1969).
- (5) The y , a , ψ_{ab} , and b orbitals that we use here and in the earlier papers^{1,3} correspond to the l , c , π_{cr} , and r orbitals of ref 2. We have ignored all overlap integrals in any normalization constant, and in the orthogonality relationship for the AB molecular orbitals. The same simplifications have been made by Halgren et al.² for the calculation of their bond indices. It is to be understood that YA-type overlap integrals need to be included if the YA binding energy for either 1 or 3 were to be calculated from eq 2 and 1.
- (6) Halgren et al.² comment that the Heitler-London wave function for 1 should be formulated as $\psi'(\text{VHL}) = |(y\bar{a} + a\bar{y})\psi_{ab}b| + |(y\bar{a} - a\bar{y})b\psi_{ab}|$. This wave function may be expressed as $\psi'(\text{VHL}) = |y\bar{a}ab| + |a\bar{y}b\bar{a}| + 2k(|y\bar{a}bb| + |a\bar{y}bb|)$, which is equivalent to eq 2 (with k replacing $2k$) when the latter is expanded to give eq 5.
- (7) R. D. Harcourt and J. F. Sillitoe, *Aust. J. Chem.*, **27**, 691 (1974). If the order of spatial orbitals for the four π and four π' electrons is $y, a, \psi_{ab}, b, y', a', \psi'_{ab}$, and b' within a Slater determinant, then the $S = 0 \pi + \pi'$ wave function for 2 is $|\alpha\beta\alpha\beta\alpha\beta\alpha\beta| + |\beta\alpha\beta\alpha\beta\alpha\beta\alpha| - |\alpha\beta\alpha\beta\beta\alpha\beta\alpha| - |\beta\alpha\beta\alpha\alpha\beta\alpha\beta|$. These four Slater determinants generate the spin distributions of 8a-d.
- (8) The arguments that have been advanced against this proposition by Halgren et al.² are easily refuted. Firstly, Halgren et al.² claim that only two electrons (those occupying \bar{a} and ψ_{ab} or a and ψ_{ab}) are involved in bonding to atom A in eq 2. Therefore, two A-atom spin orbitals participate in bonding. For eq 1 for valence-bond structure 3, only one A atom spin orbital (a or \bar{a}) participates in bonding. Therefore, qualitatively at least, the A atom may increase its valence when 1 is generated from 3 by delocalizing a non-bonding B electron into the AB orbital. Further, if the atomic spin orbitals a or \bar{a} of eq 2 are involved in bonding, they need to overlap with another atomic spin orbital. Spin requirements indicate that the latter orbitals can only be the \bar{y} or y orbitals of eq 2. Halgren et al. seem to reject this possibility early in their footnote, but concede it later by referring to the partial YA bonding of "increased-valence" structure 1.
- (9) D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 838 (1973); eq 7 of ref 2. The formula $V_{AB} = 2k^2/(1 + k^2)^2$ for a one-electron bond may also be derived using either of the following procedures: (a) For the one-electron structures (A B), (A-B), and (A B) with wave functions $a, (a + b)/2, 1/2$ and b , the A atom valencies (V_{AB}) and atomic orbital charges (P_{aa}) are 0, $1/2$, and 0, and 0, $1/2$, and 0, respectively, in which we have assumed that the A-atom valence is $1/2$ for the "homopolar" one-electron bond (A-B). The V_{AB} is related to the P_{aa} through the expression $V_{AB} = 2P_{aa}(1 - P_{aa}) (\equiv 2k^2/(1 + k^2)^2$ when $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$ for the one-electron bond). Because the bond order P_{ab} is $k/(1 + k^2)$, the identity $P_{aa}(1 - P_{aa}) = P_{ab}^2$ pertains. (b) A similar approach for the three-electron structures (A B), (A-B), and (A B) gives the relationship $V_{AB} = -2(2 - P_{aa})(1 - P_{aa}) (\equiv 2k^2/(1 + k^2)^2$ when $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$ and $\psi'_{ab} = (ka - b)/(1 + k^2)^{1/2}$). The identity $(P_{aa} - 2)(1 - P_{aa}) = P_{ab}^2$ follows. See also K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
- (10) (a) R. D. Harcourt, ref 3c; (b) *J. Mol. Struct.*, **8**, 11 (1971); (c) *Int. J. Quantum Chem.*, **5**, 479 (1971).
- (11) (a) Reference 1a and ref 4-19 therein and ref 7; (b) P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.*, **100**, 2012 (1978); (c) R. D. Harcourt and G. E. Martin, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1 (1977).

Ab Initio Studies on the Electronic Structure of ONF (Nitrosyl Fluoride) and NOF (Nitrogen Hypofluorite)

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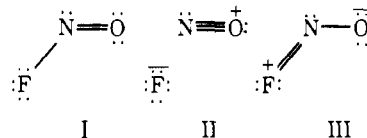
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Abstract: Using ab initio Gaussian self-consistent field (SCF) and configuration-interaction (CI) methods, the geometry, binding energy, and dipole moment are obtained for ONF and NOF. It is found that only CI methods lead to agreement with the experimental NF bond distance of ONF. The optimized geometry for NOF is 1.07 Å for the N-O and 1.76 Å for the O-F bond distance, with a bond angle of 112.3°. Basis sets with polarization functions are required to obtain a positive atomization energy for ONF. Population analysis data show both molecules to be of polar structure. The molecular orbital and natural orbital contributions to the N-F bond of ONF (and O-F bond of NOF) are studied.

Introduction

The chemical bonding in nitrosyl fluoride (ONF) has been a matter of considerable interest. In Table I experimental bond distances, bond dissociation energies, infrared data, and dipole moments are given for N-O, N-F, and O-F bonded molecules.¹⁻⁴⁵ It is seen that the N-O bond distance of ONF (1.136 Å) is smaller than that of NO (1.15 Å), indicating a slight positive charge in the N-O region (compare the NO⁺ distance of 1.06 Å). The N-O stretching frequency is the same as in NO. No other molecules, with the possible exception of ONF₂⁺ and NOF, have such a short N-O bond distance or high N-O stretching frequency. Similarly, comparing ONF with other N-F bonded molecules, one finds from Table I that the N-F bond distance of ONF is much longer (1.512 Å) than for other N-F bonded molecules, and that the N-F stretching frequency is unusually low. The dipole moment is rather large.

Pauling⁴⁶ explained the bonding in ONF by utilizing three contributing resonance structures with weights of 25, 50, and 25%, respectively. Owing to the high proportion of structure II, the NF distance is explained to be very long and the N-O



distance shorter than for the NO molecule. Pauling concluded that the nitrosyl group is less electronegative than either nitrogen or oxygen, owing to the high stability of the N≡O triple bond (79 kcal/mol). Linnett⁴⁷ considered the N-F bond in ONF to be a one-electron bond, thereby accounting for its unusual bond distance. In his scheme, the atoms assume formal charges of $1/2$ for O and $-1/2$ for F.

Spratley and Pimentel⁴⁸ used a molecular orbital approach to describe the bonding and some physical properties of a series of molecules XNO (X = H, F, Cl, Br, Li, etc.). In this scheme, the X-N bonding is due to the overlap of the lone p electron of X (s for H, Li, etc.) with the singly occupied π^* orbital of NO. Changes in the N-O bond length, stretching frequency, and force constant are attributed to the electronegativity of the X group. Strongly electronegative X groups should withdraw