2. Except for substitution of F, substitution of a π-electron-donating and σ-electron-withdrawing group for H in the 4 position stabilizes the hydrogen bonds in the water–4-R-pyridine dimers relative to the water–pyridine dimer. In contrast, substitution of the σ and π electron-withdrawing groups CHO and CN weakens the hydrogen bonds in the water–4-pyridinecarboxaldehyde and water–4–cyanopyridine dimers.

3. The variation in the hydrogen-bond energies in the series of water–4-R-pyridine dimers is a direct consequence of the primary electronic effects of the substituents. Secondary substituent effects, which include long-range interactions between the substituent and the water molecule and the relative alignment of the dipole-moment vectors of the hydrogen-bonded pair, are not significant factors determining the equilibrium structures or stabilization energies of these dimers.

4. Primary substituent effects influence the electronic environment at the nitrogen, and are evident from the variation in the n-orbital energies of the pyridine bases. A linear correlation exists between the n-orbital energies of both 2- and 4-R-pyridines and the hydrogen-bond energies of the perpendicular water–2-R-pyridine and water–4-R-pyridine dimers, provided that the n orbital is essentially localized at the nitrogen.

5. The hydrogen bond in the equilibrium perpendicular conformation of a water–4-R-pyridine dimer is stronger than that in the corresponding perpendicular water–2-R-pyridine dimer, due primarily to a stronger destabilizing σ withdrawing effect by the substituent in the 2 position. However, since secondary substituent effects may be important in stabilizing planar water–2-R-pyridine dimers, the 2-R-pyridine may form the more stable complex in particular cases.

Acknowledgments. The support of a Camille and Henry Dreyfus Foundation Teacher–Scholar Grant (1974–1979) is gratefully acknowledged. Thanks are also due to the Youngstown State University Computer Center for support and assistance and to the Media Center for preparing the figures.

Pauling "3-Electron Bonds", "Increased-Valence", and 6-Electron 4-Center Bonding

Richard D. Harcourt

Contribution from the Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. Received January 18, 1980

Abstract: The molecular orbital description of the Pauling "3-electron bond" A···B (or $\dot{A}{\cdot}\dot{B}$ according to the Linnett notation) involves two bonding electrons and one antibonding electron. When the antibonding orbitals of $\dot{A}{\cdot}\dot{B}$ and $\dot{C}{\cdot}\dot{D}$ overlap and their electrons are spin-paired, the valence structure

$$\dot{A}\cdot B\!-\!C\cdot\dot{D}$$

(I)

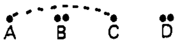
for 6-electron 4-center bonding is generated, which has the following properties: (a) It summarizes resonance between the standard valence-bond structure

$$\ddot{A}\quad B\!-\!C\quad\ddot{D}$$

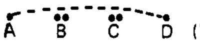
(II)

and the "long-bond" (or spin-paired diradical) structures.

(III)

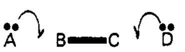


(IV)



(V)

Therefore I is more stable than II, and has a weaker B-C bond. (b) It can involve a total of four electrons in fractional bonding between all pairs of atoms. Therefore relative to the component Lewis–Langmuir structures II–V (each of which has two bonding electrons), I is designated as an "increased-valence" structure. (c) The valencies of atoms B and C can exceed the valencies of unity for these atoms in II. (d) If A and D and B and C are pairs of equivalent atoms, the wave function for I is the covalent component for the lowest energy molecular orbital configuration with three 4-center molecular orbitals doubly occupied. (e) It can be generated from II by delocalizing nonbonding A and D electrons into bonding AB and CD orbitals, i.e.



→ (I)

For the following systems with one or more 6-electron 4-center bonding units, aspects of their electronic structures are illustrated by using "increased-valence" structures: N_2O_4, $C_2O_4^{2-}$, $S_2O_4^{2-}$, N_2O_2, Cl_2O_2, Br_4^{2-}, Ru(II)–N_2–Ru(II), $(RNO)_2$, $(SN)_2$, $Cu_2(CH_3CO_2)_4{,}2H_2O$, Fe(III)–O_2^{2-}–Fe(III) (or $Fe^{II}O_2Fe^{II}$), N_2O_3, and the reaction $Cl + O_3 \rightarrow ClO + O_2$.

Introduction

The molecular orbital description of the Pauling "3-electron bond"[1] A···B (or $\dot{A}{\cdot}\dot{B}$ according to the Linnett notation[2]) involves two bonding electrons and one antibonding electron. When overlap integrals are omitted from normalization constants,[3] the maximum net AB bond order is $^1/_2$; the bonding effect of one of the two bonding electrons is cancelled by that of the antibonding electron. With respect to orbital occupations, it can be deduced quite generally[4] that two bonding electrons and one antibonding electron

---

(1) (a) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367, 3225 (1931); (b) "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, N.Y., Chapter 10.

(2) (a) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961); (b) "The Electronic Structures of Molecules", Methuen, London, 1964, p 57; (c) *Sci. Prog.*, **60**, 1 (1972). Linnett has pointed out that the designation "3-electron bond" is a misnomer because there is effectively only one bonding electron. However, in line with common practice, we shall continue to use this designation, with the adjective "Pauling" to qualify it. But we shall use the Linnett representation $\dot{A}{\cdot}\dot{B}$ rather than A···B as the valence structure, thereby emphasizing the point that the Pauling "3-electron bond" involves one bonding electron and two nonbonding electrons. We remind the reader that $\dot{A}{\cdot}\dot{B} \equiv \ddot{A}\ \dot{B} \leftrightarrow \dot{A}\ \ddot{B}$.

(3) Throughout this paper, we shall for simplicity omit the overlap integrals from the normalizing constants and the orthogonality relationships for molecular orbitals. If overlap is included, the antibonding orbital is more destabilized than is the bonding orbital stabilized. See N. C. Baird, *J. Chem. Educ.*, **54**, 291 (1977); R. D. Harcourt, *Aust. J. Chem.*, **31**, 199 (1978), for discussions of the effect of inclusion of overlap on the energy of a Pauling "3-electron bond".

0002-7863/80/1502-5195$01.00/0

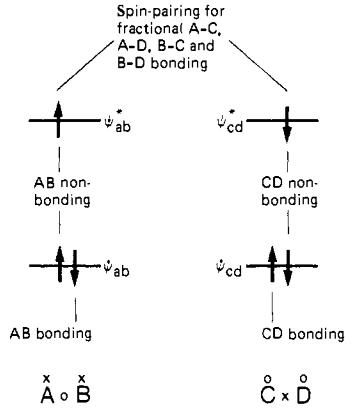
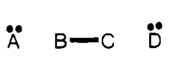
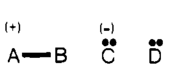


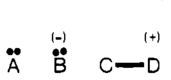
Figure 1. Bonding properties of two Pauling "3-electron bonds" (with overlap integrals omitted from normalizing constants).

are equivalent to two electrons occupying A and B atomic orbitals with parallel spins and one AB bonding electron. (If a and b are the overlapping atomic orbitals and $\psi_{ab} = a + \kappa b$ and $\psi_{ab}^* = \kappa^* a - b$ are the bonding and antibonding molecular orbitals, then the Slater determinant $|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{*\alpha}|$ is equivalent to $-(1 + \kappa\kappa^*)|a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}|$.) Whereas the ψ_{ab} electron with spin opposed to that of the ψ_{ab}^* electron is responsible for the AB bonding, the ψ_{ab}^* electron is available for external bonding with a second atomic or molecular species, if the latter has a singly occupied orbital (atomic or molecular) that overlaps with ψ_{ab}^*. Therefore the Pauling "3-electron bond" may have a maximum valence of 2.[5]

If the antibonding orbitals of two Pauling "3-electron bonds" (designated as $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$) overlap, a total of four electrons can simultaneously participate in bonding when the two antibonding electrons are spin paired. The resulting bonding unit for the molecule (ABCD) involves six electrons distributed amongst four overlapping atomic orbitals (a, b, c and d). For 6-electron 4-center bonding units, familiar examples of Lewis–Langmuir valence structures are of the general types[6] **1–3**, each of which has two


(1)


(2)


(3)

lone pairs of electrons and two bonding electrons shared by a pair of adjacent atoms. Therefore relative to these latter structures, the bonding together of two Pauling "3-electron bonds" must generate "increased-valence" in the sense that four instead of two electrons can participate in bonding. The bonding properties of the molecular orbitals are indicated in Figure 1 for one arrangement of the electron spins.

In this paper, we shall give consideration to the Pauling "3-electron bond" and "increased-valence" theory for symmetrical 6-electron 4-center bonding units and demonstrate its connection with conventional valence-bond and delocalized molecular orbital theory. The purpose is to generalize previous results obtained largely from N_2O_4 studies[7] and to provide a number of examples of other molecular systems for which 6-electron 4-center bonding and "increased-valence" are appropriate.

In ref 5, the Pauling "3-electron bond" and "increased-valence" theory has been described for 4-electron 3-center bonding units. The extension here to deal with symmetrical 6-electron 4-center bonding units involves some additional points of interest. Perhaps the most important of these is that the primary "covalent"[8] component of the molecular orbital–configuration interaction (MO–CI) wave function corresponds to the wave function for the two Pauling "3-electron bonds" $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$ with their antibonding electrons spin paired in a Heitler–London sense, i.e., as $|...\psi_{ab}{}^{*\alpha}\psi_{cd}{}^{*\beta}| - |...\psi_{ab}{}^{*\beta}\psi_{cd}{}^{*\alpha}|$. Because (as we shall show) this covalent wave function always represents the most important component of the MO–CI wave function for these systems (cf. $C_1|\sigma^{\alpha}\sigma^{\beta}| + C_2|\sigma^{*\alpha}\sigma^{*\beta}| \equiv N(\Psi_{\mathrm{cov}} + \lambda\Psi_{\mathrm{ion}})$ with $|\lambda| < 1$ for the ground state of H_2), the resulting "increased-valence" structure (with two Pauling "3-electron bonds") must represent the most important of the valence structures. In general we shall show that it is possible to use these structures alone to rationalize the nature of the observed bond properties for a number of systems that involve 6-electron 4-center bonding units. However, to account for certain properties (such as the N_2O_4 rotation barrier and the magnetic exchange parameter for $Cu_2(CH_3CO_2)_4{,}2H_2O$) that involve quite small energy terms, calculations from our laboratory indicate that it is also necessary to include small contributions from ionic structures (such as **2** and **3**) in the descriptions of the electronic structure. We shall only indicate briefly how this is done and refer the reader to published papers for fuller details.

It should be noted here that the spin pairing of the antibonding electrons of the two Pauling "3-electron bonds" is formulated within a Heitler–London framework, whereas the 1-electron bonds of these structures are described by using singly occupied bonding molecular orbitals (i.e., ψ_{ab} and ψ_{cd}). This mixture of Heitler–London valence-bond and molecular orbital techniques gives rise to two different definitions of atomic valencies for each atom and permits the atomic valencies to exceed the values of unity that occur in the Lewis–Langmuir structures.

Pauling "3-Electron Bonds" and Valence-Bond Theory

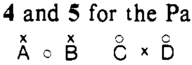
Let $(\psi_{ab})^2(\psi_{ab}{}^*)^1$ and $(\psi_{cd})^2(\psi_{cd}{}^*)^1$ be the molecular orbital configurations for two equivalent Pauling "3-electron bond" structures $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$, with $\psi_{ab} = N(a + \kappa b)$, $\psi_{ab}{}^* = N(\kappa a - b)$, $\psi_{cd} = N(\kappa c + d)$, $\psi_{cd}{}^* = N(\kappa d - c)$ and $N = (1 + \kappa^2)^{-1/2}$. When the $\psi_{ab}{}^*$ and $\psi_{cd}{}^*$ orbitals overlap, the singlet-spin ($S = 0$) "covalent"[8] wave function is given by eq 1, in which the two

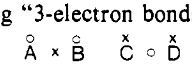
$$\Psi_{\mathrm{cov}} = (|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{*\alpha}\psi_{cd}{}^{*\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}| - |\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{*\beta}\psi_{cd}{}^{*\alpha}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}|)/2^{1/2} \quad (1)$$

antibonding electrons are spin paired in a Heitler–London sense. Some of the orbitals within the Slater determinants of eq 1 may be transformed to give eq 2 for Ψ_{cov}; the Slater determinants of

$$\Psi_{\mathrm{cov}} = (|a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}c^{\beta}\psi_{cd}{}^{\alpha}d^{\beta}| - |\psi_{ab}{}^{\alpha}a^{\beta}b^{\beta}c^{\alpha}d^{\alpha}\psi_{cd}{}^{\beta}|)/2^{1/2} \quad (2)$$

eq 2 generate the spin distributions (α = ×, β = ○) of valence structures **4** and **5** for the Pauling "3-electron bonds".


(4)


(5)

On substituting the LCAO expressions for ψ_{ab} and ψ_{cd} into the determinants of eq 2 and then expanding Ψ_{cov} in terms of atomic orbital configurations, we obtained eq 3 in which Ψ_1 and Ψ_6 –

$$\Psi_{\mathrm{cov}} = \{\Psi_1 + \kappa(\Psi_6 + \Psi_7) + \kappa^2\Psi_8\}/(1 + \kappa^2) \quad (3)$$

Ψ_8 are the bond eigenfunctions[9] for the standard valence-bond structure **1** and the "long-bond" structures **6–8**.

Because the valence structure **1** has a BC electron-pair bond and this bond is absent in each of **6–8**, a fractional BC electron-pair bond must be formed when $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ bonds to $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$. The resulting

---

(4) (a) J. W. Linnett, *J. Chem. Soc.*, 275 (1956); (b) *Sci. Prog.*, 60, 1 (1972). (c) M. Green and J. W. Linnett, *J. Chem. Soc.*, 4959 (1960).

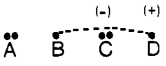
(5) R. D. Harcourt, *J. Am. Chem. Soc.*, **100**, 8060 (1978). The discussion of "increased-valence" presented in this reference may be contrasted with that of T. A. Halgren, L. D. Brown, D. A. Kleier, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **99**, 6793 (1977).

(6) Lewis–Langmuir valence structures such as 1–3 are designated here at "standard valence-bond" structures, because in them, the electron-pair bonds are located only between pairs of adjacent atoms. They may be contrasted with the Lewis–Langmuir structures of 6–8, which have "long-bonds" (- - -) linking nonadjacent atoms.

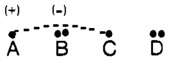
(7) R. D. Harcourt, *Aust. J. Chem.*, **32**, 933 (1979), and ref 8–13 and 20 therein.

(8) The terms "covalent" and "ionic" refer here to the (AB)(CD) and $(AB)^+(CD)^-$ or $(AB)^-(CD)^+$ type valence structures.

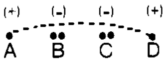
(9) $\Psi_1 = (|a^{\alpha}a^{\beta}b^{\alpha}c^{\beta}d^{\alpha}d^{\beta}| - |a^{\alpha}a^{\beta}b^{\beta}c^{\alpha}d^{\alpha}d^{\beta}|)/2^{1/2}$, etc. The "best" linear combination of Ψ_1, Ψ_6, Ψ_7, and Ψ_8, namely, $N[\Psi_1 + C_6(\Psi_6 + \Psi_7) + C_8\Psi_8]$ with C_6 and C_8 chosen variationally, is equivalent to the two-parameter Pauling "3-electron bond" wave function $N'(|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{*\alpha}\psi_{cd}{}^{*'\beta}\psi_{cd}{}^{'\alpha}\psi_{cd}{}^{'\beta}|) - |\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{*\beta}\psi_{cd}{}^{*'\alpha}\psi_{cd}{}^{'\alpha}\psi_{cd}{}^{'\beta}| + |\psi_{ab}{}^{'\alpha}\psi_{ab}{}^{'\beta}\psi_{ab}{}^{*'\alpha}\psi_{cd}{}^{*\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}| - |\psi_{ab}{}^{'\alpha}\psi_{ab}{}^{'\beta}\psi_{ab}{}^{*'\beta}\psi_{cd}{}^{*\alpha}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}|)$ with the unprimed (ψ and ψ^*) and primed (ψ' and $\psi^{*'}$) orbitals defined in terms of κ and κ' parameters.



(6)

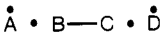


(7)

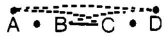


(8)

valence structure is **9**, in which a thin bond line is used to represent the fractional BC bond. Fractional AC, BD, and AD bonds are also generated when $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$ form an extended tetraatomic system. These latter bonds are extremely weak, and therefore we have not indicated their presence in **9**. If they are included, as in **10**, the valence structure contains too much detail. Valence structure **9** (or **10**) with two additional bonding electrons relative to each of **1**–**3** and **6**–**8** is an example of an "increased-valence" structure[10] for a 6-electron 4-center bonding unit. By virtue of eq 3, this structure summarizes resonance between the standard valence-bond structure **1** and the "long-bond" structures **6**–**8**. Therefore if κ is chosen variationally, "increased-valence" structure **9** is stabilized relative to the standard valence-bond structure **1**.



(9)



(10)

"Increased-valence" structure **9** has been generated by bonding together the two Pauling "3-electron bond" structures $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$. It may also be constructed from the standard valence-bond structure **1** by delocalizing nonbonding A and D electrons into the adjacent AB and CD bond regions,[10] as is shown in **11**. The delocalized electrons then occupy the AB and CD bonding orbitals ψ_{ab} and ψ_{cd}.

(11) (9)

In the next section, we shall identify the Ψ_{cov} for valence structure **9** with the covalent component for the delocalized (4-center) molecular orbital configuration.

Pauling "3-Electron Bonds" and 4-Center Molecular Orbitals

For the extended (and symmetrical) 6-electron 4-center bonding unit, the delocalized molecular orbitals are given by eq 4 with the

$$\begin{aligned}\psi_1 &= [a+d+\lambda(b+c)]/[2(1+\lambda^2)]^{1/2} \equiv (\psi_{ad}+\lambda\psi_{bc})/(1+\lambda^2)^{1/2} \equiv (\psi_{ab}{}^{(\lambda)}+\psi_{cd}{}^{(\lambda)})/2^{1/2}\\ \psi_2 &= [a-d+\mu(b-c)]/[2(1+\mu^2)]^{1/2} \equiv (\psi_{ad}{}^*+\mu\psi_{bc}{}^*)/(1+\mu^2)^{1/2} \equiv (\psi_{ab}-\psi_{cd})/2^{1/2}\\ \psi_3 &= [\lambda(a+d)-(b+c)]/[2(1+\lambda^2)]^{1/2} \equiv (\lambda\psi_{ad}-\psi_{bc})/(1+\lambda^2)^{1/2} \equiv (\psi_{ab}{}^{*(\lambda)}+\psi_{cd}{}^{*(\lambda)})/2^{1/2}\\ \psi_4 &= [\mu(a-d)-(b-c)]/[2(1+\mu^2)]^{1/2} \equiv (\mu\psi_{ad}{}^*-\psi_{bc}{}^*)/(1+\mu^2)^{1/2} \equiv (\psi_{ab}{}^*-\psi_{cd}{}^*)/2^{1/2} \quad (4)\end{aligned}$$

parameters λ and μ both finite and >0. The molecular orbital ψ_4 is antibonding with respect to each pair of adjacent atoms, and therefore it is vacant in the lowest energy configuration Φ_1 of eq 5. The orbitals for this configuration may be transformed (cf. N_2O_4)[7,10b] to generate eq 6 for Φ_1, in which the $\Psi_{\text{cov}}{}^{\mu}$ is given by eq 1 with μ replacing κ in the ψ_{ab}, $\psi_{ab}{}^*$, ψ_{cd}, and $\psi_{cd}{}^*$. Therefore the covalent component of the molecular orbital configuration corresponds to the wave function for the "increased valence" structure **9**. The ionic $[(AB)^+(CD)^-$ and $(AB)^-(CD)^+]$ components are given by eq 7.

$$\Phi_1 = |\psi_1{}^{\alpha}\psi_1{}^{\beta}\psi_2{}^{\alpha}\psi_2{}^{\beta}\psi_3{}^{\alpha}\psi_3{}^{\beta}| \quad (5)$$

$$\equiv |\psi_{ad}{}^{\alpha}\psi_{ad}{}^{\beta}\psi_2{}^{\alpha}\psi_2{}^{\beta}\psi_{bc}{}^{\alpha}\psi_{bc}{}^{\beta}|$$

$$\equiv \left|\frac{(\psi_{ad}+\mu\psi_{bc})^{\alpha}}{(1+\mu^2)^{1/2}}\,\frac{(\psi_{ad}+\mu\psi_{bc})^{\beta}}{(1+\mu^2)^{1/2}}\,\psi_2{}^{\alpha}\psi_2{}^{\beta}\,\frac{(\mu\psi_{ad}-\psi_{bc})^{\alpha}}{(1+\mu^2)^{1/2}}\,\frac{(\mu\psi_{ad}-\psi_{bc})^{\beta}}{(1+\mu^2)^{1/2}}\right|$$

$$\equiv \left|\frac{(\psi_{ab}+\psi_{cd})^{\alpha}}{2^{1/2}}\,\frac{(\psi_{ab}+\psi_{cd})^{\beta}}{2^{1/2}}\,\psi_2{}^{\alpha}\psi_2{}^{\beta}\,\frac{(\psi_{ab}{}^*+\psi_{cd}{}^*)^{\alpha}}{2^{1/2}}\,\frac{(\psi_{ab}{}^*+\psi_{cd}{}^*)^{\beta}}{2^{1/2}}\right|$$

$$\equiv \left|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}\,\frac{(\psi_{ab}{}^*+\psi_{cd}{}^*)^{\alpha}}{2^{1/2}}\,\frac{(\psi_{ab}{}^*+\psi_{cd}{}^*)^{\beta}}{2^{1/2}}\right|$$

$$= (\Psi_{\text{cov}}{}^{\mu}+\Psi_{\text{ion}}{}^{\mu})/2^{1/2} \quad (6)$$

$$\Psi_{\text{ion}}{}^{\mu} = (|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}\psi_{cd}{}^{*\alpha}\psi_{cd}{}^{*\beta}| + |\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{*\alpha}\psi_{ab}{}^{*\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}|)/2^{1/2} \quad (7)$$

Altogether there are five excited $S = 0$ configurations with the same symmetry that may be linearly combined with the lowest energy configuration Φ_1. The most important of these is the lowest energy doubly excited configuration Φ_2 of eq 8, which involves

$$\Phi_2 = |\psi_1{}^{\alpha}\psi_1{}^{\beta}\psi_2{}^{\alpha}\psi_2{}^{\beta}\psi_4{}^{\alpha}\psi_4{}^{\beta}| \quad (8)$$

the excitation of two electrons from molecular orbital ψ_3 into the vacant orbital ψ_4. To demonstrate that $\Psi_{\text{cov}}{}^{\mu}$ is the primary component of the lower energy linear combination $\Psi = C_1\Phi_1 + C_2\Phi_2$ (with $|C_1| > |C_2|$ and $C_1 > 0$ when $C_2 < 0$),[7] it is necessary to express the ψ_1 of eq 8 in terms of the orbitals $\psi_1{}^{(\mu)}$ and $\psi_3{}^{(\mu)}$ in which the latter orbitals correspond to the ψ_1 and ψ_3 of eq 4 with μ replacing λ. When this is done, we obtain eq 9. With

$$\psi_1 = [(1+\lambda\mu)\psi_1{}^{(\mu)} + (\mu-\lambda)\psi_3{}^{(\mu)}]/[(1+\mu^2)(1+\lambda^2)]^{1/2} \equiv x\psi_1{}^{(\mu)} + y\psi_3{}^{(\mu)} \quad (9)$$

use of procedures similar to those used to obtain eq 6 from eq 5, Φ_2 of eq 8 may be transformed[7] to generate eq 10, in which the

$$\Phi_2 = [x^2(-\Psi_{\text{cov}}{}^{\mu} + \Psi_{\text{ion}}{}^{\mu}) + 2^{1/2}xy(-\Psi_{\text{cov}}{}^{*\mu} + \Psi_{\text{ion}}{}^{*\mu}) + y^2(-\Psi_{\text{cov}}{}^{**\mu} + \Psi_{\text{ion}}{}^{**\mu})]/2^{1/2} \quad (10)$$

$\Psi_{\text{cov}}{}^{\mu}$ and $\Psi_{\text{ion}}{}^{\mu}$ are those of eq 6, and the Ψ^* and Ψ^{**} configurations involve single and double excitations of electrons from the ψ_{ab} and ψ_{cd} orbitals[11] of $\Psi_{\text{cov}}{}^{\mu}$ and $\Psi_{\text{ion}}{}^{\mu}$. Because λ and μ are both >0 and $C_1 > 0$ when $C_2 < 0$, $\Psi_{\text{cov}}{}^{\mu}$ is the primary contributor to the lower energy linear combination of Φ_1 with Φ_2. The coefficients of $\Psi_{\text{cov}}{}^{\mu}$ and $\Psi_{\text{ion}}{}^{\mu}$ in this linear combination are $(C_1 - C_2x^2)/2^{1/2}$ and $(C_1 + C_2x^2)/2^{1/2}$, respectively.

When the BC internuclear separation for the 6-electron 4-center system ABCD is infinite, $\lambda = \mu \equiv \kappa_0$. Therefore $x = 1$ and $y = 0$ in eq 9 and 10. The configurations Φ_1 and Φ_2 are degenerate for this distance[7] and therefore $C_1 = -C_2 = 2^{-1/2}$. Consequently the lower energy linear combination of Φ_1 with Φ_2 generates the Pauling "3-electron bond" structures $\dot{\mathrm{A}}\cdot\dot{\mathrm{B}}$ and $\dot{\mathrm{C}}\cdot\dot{\mathrm{D}}$ as dissociation products.

The relevance of this configuration interaction theory for the calculation of ionization potentials for N_2O_4, and magnetic exchange parameters for Cu(II) carboxylate dimers, is described in ref 7 and 13b,c–15. From the photoelectron ionization potential studies, an estimate of 0.90 has been obtained[7] for the μ parameter for N_2O_4. This parameter gives a measure of the extent of delocalization of the A and D lone-pair electrons of **1** into the BC antibonding orbital, according to the ψ_2 of eq 4.

Atomic Valencies for Pauling "3-Electron Bonds"

In the Introduction, it was deduced that four electrons are available for bonding when two Pauling "3-electron bond" structures are bonded together. For the resulting valence structure **9**, we shall now demonstrate that the B and C atom valencies can exceed the values of unity that occur for them in the Lewis–Langmuir structure **1**.

By squaring the coefficient of Ψ_1 in eq 3, we obtained the weight (W_1 of eq 11) for valence-bond structure **1**. Because **9** ≡ **1** ↔

---

(10) (a) R. D. Harcourt, *J. Mol. Struct.*, **8**, 11 (1971); (b) *ibid.*, **9**, 221 (1971); (c) *ibid.*, **21**, 111 (1974).

(11) Relative to either $\Psi_{\text{cov}}{}^{\mu}$ and $\Psi_{\text{ion}}{}^{\mu}$, the relevant excitations are the following: $\Psi_{\text{cov}}{}^{*\mu}$ and $\Psi_{\text{ion}}{}^{*\mu}$, $\psi_{ab} \to \psi_{ab}{}^*$ or $\psi_{cd} \to \psi_{cd}{}^*$; $\Psi_{\text{cov}}{}^{**\mu}$, $\psi_{ab} \to \psi_{ab}{}^*$ and $\psi_{cd} \to \psi_{cd}{}^*$; $\Psi_{\text{ion}}{}^{**\mu}$, $(\psi_{ab})^2 \to (\psi_{ab}{}^*)^2$ or $(\psi_{cd})^2 \to (\psi_{cd}{}^*)^2$.

(12) R. D. Harcourt, *Chem. Phys. Lett.*, **61**, 25 (1979); **64**, 194 (1979).

(13) (a) Reference 7, and ref 8 and 11 therein; (b) R. D. Harcourt in "Methods and Structure of Quantum Science", J.-L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn, Eds., Plenum Press, New York, 1976, p 105. (c) *Aust. J. Chem.*, **27**, 2065 (1974).

(14) R. D. Harcourt and G. E. Martin, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1 (1977).

(15) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).

$$W_1 = 1/(1 + \kappa^2)^2 \equiv N(b,c) \equiv V_{bc} \equiv P_{bc}{}^2(\mu = \kappa) \qquad (11)$$

6 ↔ **7** ↔ **8**, this weight corresponds to the BC bond number[7,16] ($N(b,c)$) for "increased-valence" structure **9**; it is equivalent to the Wiberg bond index[17] ($P_{bc}{}^2$ with P_{bc} = Coulson bond order) for the BC bond of molecular orbital configuration Φ_1 (eq 5) when $\mu = \kappa$. The bond number represents the number of pairs of electrons that form a fractional electron-pair bond, and therefore it also represents the valence for B (V_{bc}) when the B electron participates in (fractional) BC bonding. Similarly the weights for structures **6**–**8** (eq 12 and 13) give the valencies V_{bd}, V_{ac}, and

$$W_6 = W_7 \equiv V_{bd} \equiv V_{ac} = \kappa^2/(1 + \kappa^2)^2 \qquad (12)$$

$$W_8 \equiv V_{ad} = \kappa^4/(1 + \kappa^2)^2 \qquad (13)$$

V_{ad} for the "increased-valence" structures **9**. When V_{bc} and V_{bd} are added, the B atom odd-electron charge ($c_b{}^{*2}$ of eq 14) for the

$$V_{bc} + V_{bd} = 1/(1 + \kappa^2) \equiv c_b{}^{*2} \equiv P_{bc}(\mu = \kappa) \qquad (14)$$

Pauling "3-electron bond" configuration $(\psi_{ab})^2(\psi_{ab}{}^*)^1$ is obtained. This result shows how the fractional odd-electron charge of the B atom is used for both BC and BD bonding. The odd-electron charge also corresponds to the Coulson bond order P_{bc} for eq 5 when $\mu = \kappa$.

Within the Pauling "3-electron bond" $\dot{\mathrm{A}}{\cdot}\dot{\mathrm{B}}$ it may be deduced[5,18] that the A and B valencies (V_{ab} and V_{ba}) are equal to $2P_{ab}{}^2$, in which $P_{ab} \equiv \kappa/(1 + \kappa^2)$ is the Coulson bond order for $(\psi_{ab})^2(\psi_{ab}{}^*)^1$. Therefore the total B atom valence is given by eq 15, which has

$$V_{\mathrm{B}} \equiv V_{ba} + (V_{bc} + V_{bd}) \equiv V_{\mathrm{C}} = 2\kappa^2/(1 + \kappa^2)^2 + 1/(1 + \kappa^2) \qquad (15)$$

a maximum value of 1.125 when $\kappa = 3^{-1/2}$; i.e., the B atom valence for "increased-valence" structure **9** can exceed the value of unity that occurs in either of the Lewis structures **1** and **6**. An identical expression obtains for V_{C} ($\equiv V_{ca} + V_{cb} + V_{cd}$). The total A atom and D atom valencies are given by eq 16. The total valence for

$$V_{\mathrm{A}} = V_{ab} + (V_{ac} + V_{ad}) \equiv V_{\mathrm{D}} = 2\kappa^2/(1 + \kappa^2)^2 + \kappa^2/(1 + \kappa^2) \qquad (16)$$

"increased-valence" structure **9** ($V_{\mathrm{A}} + V_{\mathrm{B}} + V_{\mathrm{C}} + V_{\mathrm{D}}$) has a maximum value of **9** when $\kappa = 1$.

It may also be noted that the Coulson AB and CD bond orders for $\Psi_{\mathrm{cov}}{}^{\mu}$ of eq 6 (namely, $P_{ab} = P_{cd} = \mu/(1 + \mu^2)$) are also the Coulson bond orders for the molecular orbital configuration Φ_1 of eq 5.

Examples

A number of systems will now be considered, whose "increased-valence" structures involve two Pauling "3-electron bonds" with their antibonding electrons spin paired. The nature of the properties of certain bonds follows immediately from inspection of the "increased-valence" structures.

(a) N_2O_4. For the D_{2h} isomer of N_2O_4, "increased-valence" structures, which are obtained by dimerization of Pauling "3-electron bond" structures for NO_2, have now been described on numerous occasions.[7] In Figure 2, the relevant types of valence structures a and b are displayed together with the standard valence-bond structures of c for N_2O_4. (Equivalent mirror-image structures are usually not included in this and other Figures.) The relevant 6-electron 4-center bonding unit for N_2O_4 consists of the six electrons that occupy two O^- $\bar{\pi}$ orbitals and the two nitrogen hybrid orbitals (h_{N}) that form the NN σ bond of c, as in d. The structures of c may be used to generate those of b by delocalizing a nonbonding $\bar{\pi}_{\mathrm{O}}$ electron from each of the O^- into a bonding NO orbital $\psi_{\mathrm{NO}} = \bar{\pi}_{\mathrm{O}} + \kappa h_{\mathrm{N}}$. For b, the NN bond number is less than unity, which is in accord with the existence of a long NN bond (1.782 Å, cf. 1.45 Å for the single bond of N_2H_4)[19,20] in N_2O_4.

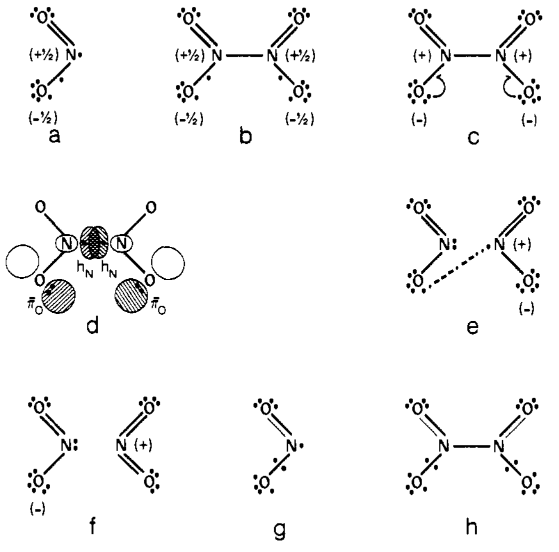


Figure 2. NO_2 and N_2O_4. (In this and subsequent Figures, atomic formal charges are assigned by assuming that bonding electrons are shared equally by pairs of adjacent atoms.)

Using the formula $r(n) = r(1) - 0.6 \log n$, with $r(1)$ = 1.47 Å and $r(n)$ = 1.75 Å, Pauling[21] has calculated a value of 0.34 for the NN bond number (n) of N_2O_4. More recent estimates of 1.45 and 1.78 Å for $r(1)$ and $r(n)$ give n = 0.28. For the molecular orbital configuration Φ_1 of eq 5 (with full D_{2h} symmetry for the molecular orbitals), an estimate of 0.55 for the NN σ-bond order (P_{bc}) has been obtained from photoelectron studies.[12] Because $P_{bc}{}^2 = N(b,c)$ (eq 11), this bond order gives an NN bond number of 0.30 for the NN bond of the "increased-valence" structures of b. The NN bond number that may be calculated from the CI wave function [7] of eq 10 is 0.23–0.25.

It might be thought that the fractional "long bond" which exists between the cis $O^{-1/2}$ atoms of b (cf. structure **10**) is responsible for the cis OO overlap contribution to the barrier to rotation around the NN bond (8–12 kJ mol^{-1})[22] for N_2O_4. However this cis OO bond is calculated to be much too weak.[23] It has been calculated[23] that resonance between the covalent and ionic structures of types e and f (which are of general types **6** and **3**) must be primarily responsible for the cis OO overlap stabilization of the planar conformation. Therefore it is necessary to include ionic structures of type f as well as the "increased-valence" structure b in order to account for the planarity as well as the length of the NN bond.

Because $\dot{\mathrm{O}}\ddot{\mathrm{O}}^- \leftrightarrow {}^-\ddot{\mathrm{O}}\dot{\mathrm{O}}$ is equivalent to ${}^{-1/2}\dot{\mathrm{O}}{\cdot}\dot{\mathrm{O}}^{-1/2}$, resonance between e and f is equivalent to the development of a Pauling "3-electron bond" between the cis oxygen atoms.[23]

Delocalization of a π electron from each of the $O^{-1/2}$ of a and b into a bonding NO π orbital generates "increased valence" structures[10a,b] of types g and h of Figure 2 for NO_2 and N_2O_4. The NO bond properties that are implied by inspection of the latter

---

(16) (a) R. D. Harcourt, *Int. J. Quantum Chem.*, **4**, 173 (1970); (b) ref 10a. An alternative derivation of these results is the following. The antibonding $\psi_{ab}{}^*$ and $\psi_{cd}{}^*$ molecular orbitals generate odd-electron charges of $c_a{}^{*2} = c_d{}^{*2} = \kappa^2/(1 + \kappa^2)$ and $c_b{}^{*2} = c_c{}^{*2} = 1/(1 + \kappa^2)$. The A and B atoms share fractions x and $1 - x$ of their odd-electron charges with the C and D atoms. Therefore two alternative expressions exist for each of the AC and BD bond numbers, namely, $x\kappa^2/(1 + \kappa^2)$ and $(1 - x)/(1 + \kappa^2)$. In order that these bond numbers be equal (due to symmetry), $x = 1/(1 + \kappa^2)$ is required. The bond numbers or weights of eqs 11–13 are thereby obtained.

(17) K. B. Wiberg, *Tetrahedron*, **24**, 1043 (1968).

(18) For the valence structures $\ddot{\mathrm{A}}\,\dot{\mathrm{B}}$, $\dot{\mathrm{A}}{\cdot}\dot{\mathrm{B}}$, and $\dot{\mathrm{A}}\,\ddot{\mathrm{B}}$ with $\kappa = 0$, 1, and ∞ in the molecular orbitals of $(\psi_{ab})^2(\psi_{ab}{}^*)^1$, the (internal) B atom valence V_{ba} and atomic orbital charge P_{bb} are equal to 0, $^1/_2$, and 0 and 2, 1.5 and 1, respectively. The V_{ba} is then related to P_{bb} through the expression $V_{ba} = -2(1 - P_{bb})(2 - P_{bb})$. For any value of κ, $P_{bb} = 1 + \kappa^2/(1 + \kappa^2)$ and $P_{ab} = (\equiv P_{ba}) = \kappa/(1 + \kappa^2)$, from which it follows that $V_{ba} = 2P_{ab}{}^2$.

(19) B. W. McClelland, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, **56**, 4541 (1972).

(20) Y. Morino, T. Iijima, and Y, Murata, *Bull. Chem. Soc. Jpn.*, **33**, 46 (1960).

(21) Reference 1b, p 350.

(22) C. H. Bibart and G. E. Ewing, *J. Chem. Phys.*, 61, 1282 (1974).

(23) R. D. Harcourt, *Aust. J. Chem.*, **31**, 1635 (1978).

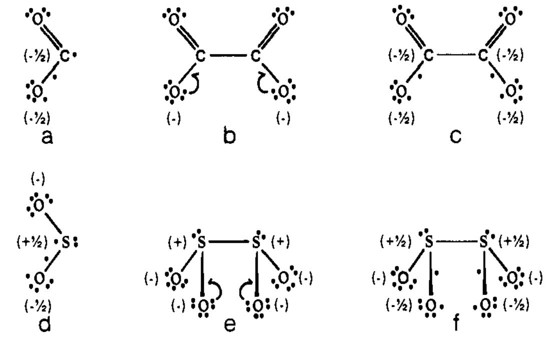


Figure 3. CO_2^-, SO_2^-, $C_2O_4^{2-}$, and $S_2O_4^{2-}$.

structures are in better accord than a and b with the observation that the NO bond lengths for both systems (1.19 Å)[19] are similar to those of double bonds (1.20 Å).[24] For each NO_2 linkage, there is a 4-electron 3-center bonding unit for the π electrons. When we discuss the bonding for N_2O_3, we shall use "increased-valence" structures of type g for the NO_2 components.

(b) $C_2O_4^{2-}$ and $S_2O_4^{2-}$. Similar Pauling "3-electron bond" theories for other A_2Y_4 systems such as $C_2O_4^{2-}$ and $S_2O_4^{2-}$ may also be developed. The CC and SS bond lengths[25,26] of 1.57 and 2.39 Å for these anions are respectively longer than lengths of 1.52 Å for an (sp^2 hybridized) CC single bond[27] and 2.08 Å for an SS single bond.[28] Relevant monomer and dimer valence structures are displayed in Figure 3. The CC and SS bond numbers for "increased-valence" structures c and f are less than unity, which reflect the observed lengthenings of the bonds relative to single bonds. Due to electronegativity differences between C and N^+ or S^+, the extent of delocalization of O^- $\bar{\pi}$ electrons for the $C_2O_4^{2-}$ standard valence-bond structure b must be rather less than that for either N_2O_4 (Figure 2c) or $S_2O_4^{2-}$ (e); i.e., the CC bond number is appreciably larger than the NN and SS bond numbers.

Lengthenings of the AA bonds of the above species may also be described by using molecular orbital theory, with emphasis given to the extent of delocalization of $\bar{\pi}_O$ electrons into antibonding AA σ^* orbitals.[29,30] The present treatment corresponds to a consideration of the covalent component (Ψ_{cov}^{μ}) of the molecular orbital configuration (cf. eq 6). All-electron or all-valence-electron molecular orbital treatments[31] also lay emphasis on the delocalization of oxygen lone-pair electrons into the antibonding AA σ^* orbital for some of these species—in particular N_2O_4.

(c) Cl_2O_2, N_2O_2, and Br_4^{2-}. Cl_2O_2, N_2O_2, and Br_4^{2-} are representative A_2Y_2 species whose AA bond properties follow immediately from inspection of their "increased-valence" structures a–c of Figure 4, which are obtained by dimerization of the Pauling "3-electron bond" structures d–f for ClO, NO, and Br_2^-. The NN bond of N_2O_2 is well-known to be longer and weaker than a single bond,[32,33] and IR studies[34,35] show that ClO forms weakly bonded dimers. The BrBr bonds of Br_4^{2-} (AB = CD = 2.94 Å, BC = 2.34 Å) are longer[36] than the single-bond length[28] of 2.28 Å. In each of a–c, the AA bond number is less than unity. For Cl_2O_2 and N_2O_2, the 6-electron 4-center bonding units utilize chlorine and oxygen $\bar{\pi}$ orbitals and oxygen (or chlorine) and nitrogen hybrid orbitals, whereas the same type of bonding unit for linear Br_4^{2-} involves four $4p\sigma$-atomic orbitals.

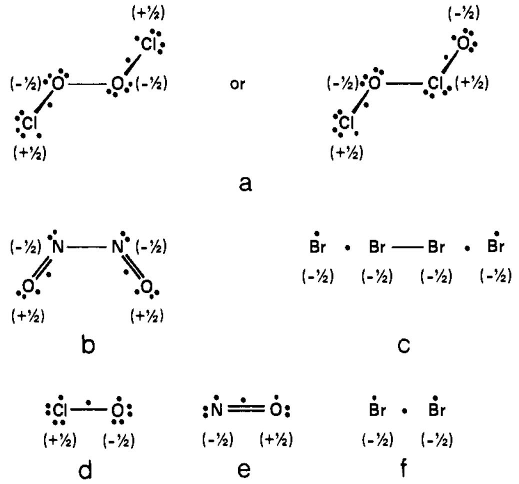


Figure 4. Cl_2O_2, N_2O_2, Br_4^{2-}, and monomers.

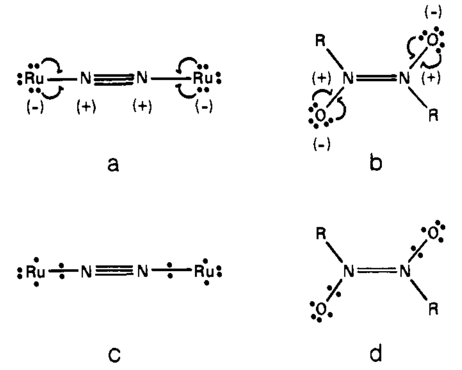


Figure 5. Ru(II)-N_2-Ru(II) and $(RNO)_2$. (For a and c, the Ru formal charges are relative to Ru(II) when it is not coordinated to the N_2.)

(d) Ru(II)-N_2-Ru(II) and $(RNO)_2$. For the Ru(II)-N_2-Ru(II) linkage of $[Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+}$ and the dimers of nitroso alkanes $(RNO)_2$, there are two sets of 6-electron 4-center bonding units in the standard valence-bond structures (**a**) and (**b**) of Figure 5. For the dinitrogen complex, each of these bonding units is of π type and involves a $4d_{xz}$ or $4d_{yz}$ orbital from each Ru(II) and the $2p_x$ or $2p_y$ orbitals of the N_2. The relevant atomic orbitals for $(RNO)_2$ consist of a set of four $2p\pi$ orbitals and a set of two $\bar{\pi}_O$ and two nitrogen hybrid orbitals (as in N_2O_4). From the standard valence-bond structures, "increased-valence" structures c and d may be generated by delocalizing $4d_{xz}$ and $4d_{yz}$ electrons of Ru(II), and π and $\bar{\pi}$ electrons of the O^-, into bonding RuN and NO orbitals. The "increased-valence" structures have NN bond numbers less than 3 and 2, respectively, thereby reflecting the observed lengthening of the NN bonds for the two compounds[37,38] (1.13 and 1.30 Å) relative to the standard triple- and double-bond lengths[39] of 1.10 and 1.24 Å. For $(RNO)_2$, overlap considerations for the NN σ and π bonds indicate that the delocalization of $\bar{\pi}_O$ lone-pair electrons is less extensive than is that

---

(24) Reference 1b, p 344.

(25) H. Küppers, *Acta Crystallogr., Sect B*, **29**, 318 (1973).

(26) J. D. Dunitz, *Acta Crystallogr.*, **9**, 579 (1956).

(27) I. Fischer-Hjalmars, *Pure Appl. Chem.*, **11**, 571 (1966).

(28) Reference 1b, p 224.

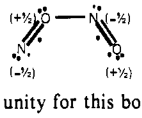
(29) (a) R. D. Brown and R. D. Harcourt, *Proc. Chem. Soc.*, 216 (1961); (b) *Aust. J. Chem.*, **16**, 737 (1963); (c) *ibid.*, **18**, 1118 (1965).

(30) R. D. Harcourt, *Theor. Chim. Acta*, **3**, 191 (1965); **4**, 202 (1966).

(31) B. M. Gimarc, S. A. Khan, and M. C. Kohn, *J. Am. Chem. Soc.*, **100**, 1996 (1978). See ref 1–5 and 18 of ref 7 for ab initio and recent CNDO studies of N_2O_4.

(32) W. N. Lipscomb, F. E. Wang, W. R. May, and E. L. Lippert, *Acta Crystallogr.*, **14**, 1101 (1961). J. Mason, *J. Chem. Educ.*, **52**, 445 (1975).

(33) C. E. Dinerman and G. E. Ewing, *J. Chem. Phys.*, **53**, 626 (1970). For the cis and trans dimers, NN bond lengths of 1.768 and 1.689 Å have been calculated (S. Skaarup, P. N. Skancke, and J. E. Boggs, *J. Am. Chem. Soc.*, **98**, 6106 (1976)). An asymmetric ONON dimer has also been reported (J. R. Ohlsen and J. Laane, *ibid.*, **100**, 6948 (1978)). The N–O bond that links the NO moieties is weak, and the "increased valence" structure



has a bond number less than unity for this bond.

(34) (a) R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, **88**, 2394 (1966); (b) M. M. Richkind and G. C. Pimentel, *J. Chem. Phys.*, **46**, 4481 (1967); **48**, 2372 (1968).

(35) F. K. Chi and L. Andrews, *J. Phy. Chem.*, **77**, 3062 (1973).

(36) V. R. Siepmann and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **357**, 289 (1968).

(37) I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 5612 (1969).

(38) F. P. Boer and J. W. Turley, *J. Am. Chem. Soc.*, **91**, 1371 (1969).

(39) Reference 1b, p 228.

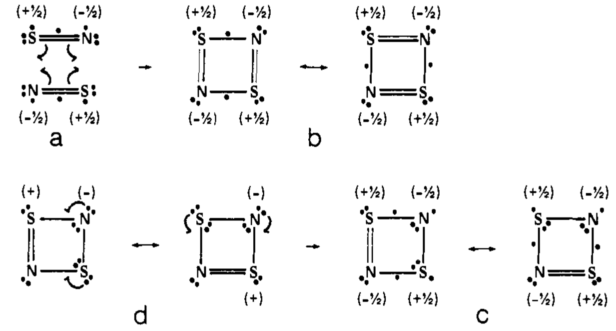
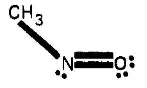


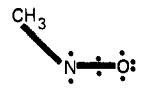
Figure 6. SN and S_2N_2.

for the π_O electrons; i.e., the NN σ-bond number of d is larger than the NN π-bond number.

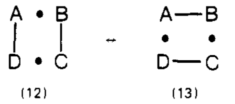
The ground state of the RNO monomer does not involve a Pauling "3-electron bond". (The CN and NO bond lengths[40] of 1.48 and 1.21 Å for CH_3NO are essentially those of single and double bonds, respectively, and therefore, the Lewis structure



provides an adequate qualitative description of the electronic structure.) The valence state for the dimer, with two unpaired electrons, is obtained by exciting an antibonding NO electron from the doubly occupied $\bar{\pi}_O - \mu h_N$ molecular orbital into the vacant π_{NO}^* antibonding molecular orbital. Two Pauling "3-electron bonds" are thereby developed in the valence state; the resulting valence structure (with randomized electron spins) is



(e) S_4^{2+}, Se_4^{2+}, Te_4^{2+}, and $(SN)_2$. Cyclic dimers of S_2^+, Se_2^+, Te_2^+, and SN have been characterized.[41,42] Each of these monomers has 11 valence-shell electrons and a Pauling "3-electron bond" (cf. NO). The dimers are square planar and have a 6-electron 4-center π-electron system. The dimerization process must involve some electronic excitation, namely, the unpairing of the electron spins of the two π electrons that form an electron-pair π bond of the monomer. These electrons form electron-pair σ bonds between the monomers (cf. $2C_2H_4 \rightarrow C_4H_8$). The Pauling "3-electron" π bonds of the monomers generate the six π electrons of the dimer. Thus with use of $2SN \rightarrow S_2N_2$ as the example,[43] the dimerization process may be represented according to a → b of Figure 6. Due to symmetry requirements, two ("increased-valence") structures for the dimer participate in resonance with equal weights. The "increased-valence" structures can also be generated from the standard valence-bond structures of c by delocalizing nonbonding π electrons from N^- and S into bonding SN π orbitals and then spin pairing the unpaired electron charges that remain on these atoms in d. In each of the structures of b, there is a cyclic "increased-valence" structure of the general type **12** or **13** for the six π electrons. The (fractional) AD



(12) (13)

"long-bond" that is present in the extended "increased-valence" structure **9** becomes a fractional bond between adjacent atoms in **12**. When $\kappa = 1$ in each of the molecular orbitals for the Pauling "3-electron bond" configurations of **12** and **13**, a total of three electrons participate in nearest-neighbor bonding, i.e., $V_{ab} + V_{bc} + V_{cd} + V_{da} = 1.5$ for each of these "increased-valence" structures.

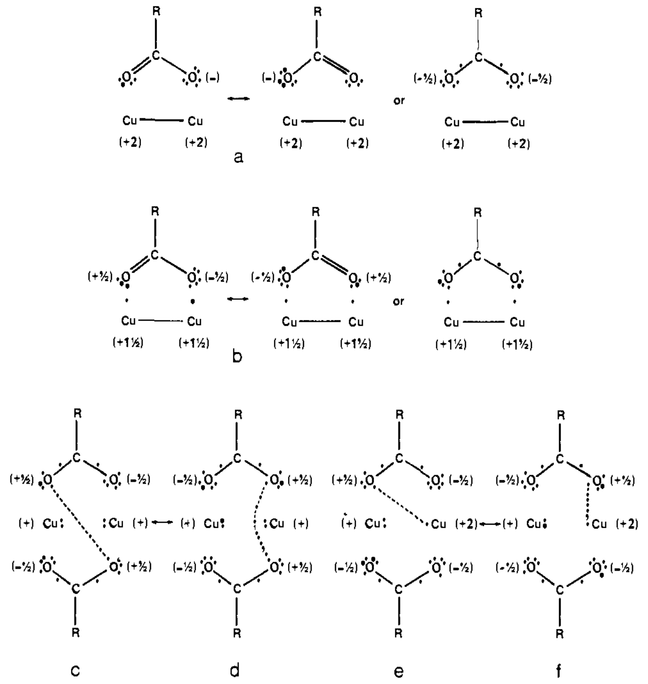


Figure 7. Cu(II) carboxylate dimers, $Cu_2(RCO_2)_4$.

(f) Cu(II) Carboxylate Dimers. For Cu(II) carboxylate dimers (e.g., $Cu_2(CH_3CO_2)_4{,}2H_2O$), the singly occupied $d_{x^2-y^2}$ orbital of each Cu^{2+} ion can overlap[13b,c,14,44] with a doubly occupied lone-pair orbital located on an adjacent oxygen atom of each carboxylate ligand. Within the carboxylate ligand, these lone-pair orbitals overlap with each other. A 6-electron 4-center bonding unit is thereby generated for the Cu(II)–RCO_2^-–Cu(II) linkage, for which the standard valence-bond structures are displayed in Figure 7a. In these structures, the singly occupied $d_{x^2-y^2}$ orbitals overlap weakly to form a Cu–Cu δ bond. The strength of this bond is considered to be insufficient to account for the magnitude of the magnetic exchange parameter J $(\equiv {}^1/_2\{E(S = 0) - E(S = 1)\})$, whose values[45] are $\simeq -50$ to -250 cm^{-1}. Delocalization of the oxygen lone-pair electrons into bonding Cu–O orbitals generates the "increased-valence" structure b, thereby forming a fractional "long-bond" between the oxygen atoms. The results of molecular orbital studies[14] indicate that overlap between the cis oxygen orbitals is more effective for stabilizing the $S = 0$ state than that which exists between the copper orbitals. It might be thought that the fractional OO "long-bond" of b is primarily responsible for the antiferromagnetism, but its strength is also too small. A stronger resonance stabilization for the $S = 0$ ground state is obtained[14] from resonance between c and d which is equivalent to the development of a Pauling "3-electron bond" between the oxygen atoms. Resonance between e and f will produce the same effect. This latter type of resonance is similar to that described above for N_2O_4 to account for aspects of the origin of the rotation barrier.

(g) Fe^{III}–O_2^{2-}–Fe^{III} Decomposition. Numerous Fe(II) porphyrin complexes are oxidized irreversibly by molecular O_2 to form oxo-bridged dimers.[46,47] One step in the mechanism is assumed to involve the decomposition of the Fe(III)–O_2^{2-}–Fe(III) complex

---

[40] P. H. Turner and A. P. Cox, *Chem. Phys. Lett.*, **39**, 585 (1976).

[41] R. J. Gillespie and P. Passmore, *Acc. Chem. Res.*, **4**, 413 (1971).

[42] C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975).

[43] R. D. Harcourt, *J. Inorg. Nucl. Chem.*, **39**, 237 (1977). See also R. D. Harcourt and H. M. Hügel, *J. Inorg. Nucl. Chem.*, in press, for "increased-valence" structures for cyclic S–N compounds. Some of these involve 6-electron 5-center and 10-electron 7-center bonding units.

[44] K. Yokata and A. Kawamori, *Solid State Commun.*, **21**, 61 (1977).

[45] R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton, Trans.*, 428 (1972).

[46] J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).

[47] R. D. Harcourt, *J. Inorg. Nucl. Chem.*, **39**, 243 (1977). In this reference, the $Fe^{II}O_2Fe^{II}$ formulation (with ground-state O_2 and intermediate-spin Fe(II)) is used to construct the mechanism. It represents a more general formulation of the electronic structure, and includes Fe(III)–O_2^{2-}–Fe(III) (with O_2^{2-} coordinated to low-spin Fe(III)) as a special case.

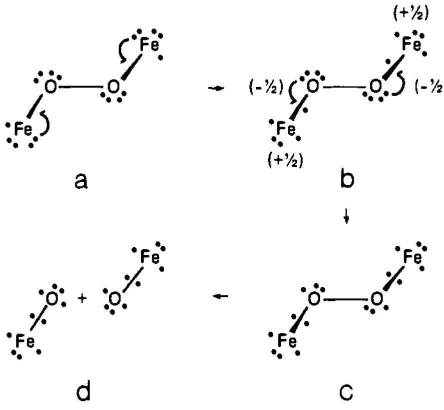


Figure 8. Fe(III)-O_2^{2-}-Fe(III) → $2(FeO)^{2+}$. (In b the Fe formal charges are relative to those of Fe(III) of a.)

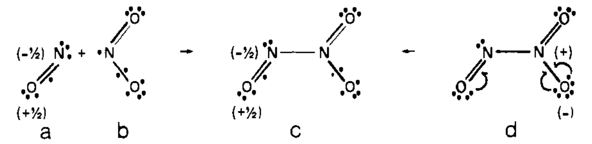


Figure 9. NO, NO_2, and N_2O_3.

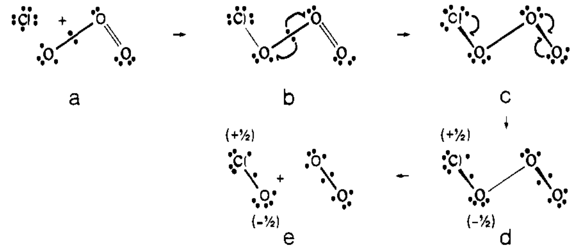


Figure 10. Cl + O_3 → ClO + O_2.

which is formed by (the stepwise) reaction of O_2 with 2 mol of Fe(II). It is possible to formulate the decomposition of this complex so that it involves the development of an "increased-valence" structure for a 6-electron 4-center bonding unit.[47] This is displayed in Figure 8. A Pauling "3-electron bond" may be formed for each of the FeO moieties of b to maintain approximate constancy in the magnitudes of the formal charges. In both b and c, the OO bond number is less than unity and therefore the OO bond is weak. The 6-electron 4-center bonding unit utilizes the oxygen atomic orbitals that form the OO σ bond and a t_{2g} orbital from each of the metal ions.

(h) Nonequivalent Pauling "3-Electron Bonds". In each of Figures 2–8, the two Pauling "3-electron bond" components of the "increased-valence" structures are equivalent. For nonequivalent Pauling "3-electron bonds", the κ parameters for the configuration $(\psi_{ab})^2(\psi_{ab}^*)^1$ and $(\psi_{cd})^2(\psi_{cd}^*)^1$ will differ. This is the case for N_2O_3, for which suitable valence structures (Figure 9) are obtained by spin pairing the unpaired electrons of the Pauling "3-electron bond" structures for NO_2 and NO (Figures 2g and 3b). The NO bond lengths[48] (nitroso, 1.142 Å, nitro, 1.202 and 1.207 Å) are similar to those[49,19] of free NO and NO_2 (1.153 and 1.19 Å), as are the NO stretching frequencies[50,51] (nitroso, 1832 cm^{-1}; nitro, 1652 cm^{-1}; NO, 1876 cm^{-1}; NO_2, 1616 cm^{-1}); these observations are in accord with the bond properties that would be deduced by comparing the NO, NO_2, and N_2O_3 valence structures of Figure 9. The "increased-valence" structure c for N_2O_3 involves an NN bond number less than unity; the observed bond length[48] of 1.864 Å is 0.41 Å longer than the single bond of N_2H_4.

Reactions of the type X + O_3 → XO + O_2 (X = NO, Cl) provide another illustration of the development of an "increased-valence" structure with two nonequivalent Pauling "3-electron bonds". A mechanism for X = NO is presented in ref 52; a similar mechanism with X = Cl is displayed in Figure 10. An "increased-valence" structure of type **9** is present for six electrons in the ClOOO valence structure d. The O_2 of e is predicted[52] to be generated as the S = 1 ground state, with two (orthogonal) Pauling "3-electron bonds" for the π electrons. The ClO valence structure of e corresponds to d of Figure 4.

Conclusions

The above examples provide some feel for the relevance of Pauling "3-electron bonds" for qualitative discussions of bonding for molecules that involve 6-electron 4-center bonding units. At an elementary level, the techniques that have been described are easily related to conventional valence-bond and molecular orbital theory. Fairly obviously, it is possible to extend the number of Pauling "3-electron bonds" that are bonded together; $(SN)_x$ provides an obvious example.[43] And of course if an atomic orbital of an adjacent atom is singly occupied, its electron may be spin paired with the antibonding electron of a Pauling "3-electron bond" if the orbitals overlap. This latter possibility always exists for 4-electron 3-center bonding units.[5,52]

We may conclude by reemphasizing what we have indicated elsewhere,[52,53] namely, that in contrast to what is usually thought, the Pauling "3-electron bond" is an extremely useful structure and its relevance for descriptions of the electronic structures of diamagnetic as well as paramagnetic electron-rich molecules is very considerable. This is because "increased-valence" structures, with Pauling "3-electron bonds" as components, summarize resonance between standard Lewis structures and "long-bond" (or spin-paired diradical) Lewis structures. The "long-bond" structures are usually omitted from elementary valence-bond descriptions of bonding for electron-rich molecules, but the results of recent semiempirical[7,14,54] and ab initio[55-57] valence-bond calculations show that they can make very substantial contributions to the ground-state resonance. Use of "increased-valence" structures (with Pauling "3-electron bonds" as components) to represent the electronic structures provides an economical way to ensure that only a few valence structures need be written down,[57a] i.e., that a rather cumbersome valence-bond description is not developed.

Acknowledgments. I thank Ms. Suzie Boxshall of the Educational Technology Services, Melbourne University, for preparing the diagrams.

---

(47)

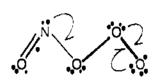
(48) A. H. Brittain, A. P. Cox, and R. L. Kuczkowski, *Trans. Faraday Soc.*, **65**, 1963 (1969).

(49) J. H. Shaw, *J. Chem. Phys.*, **24**, 399 (1956).

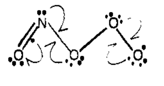
(50) G. E. Moore, *J. Opt. Soc. Am.*, **43**, 1045 (1953).

(51) C. H. Bibart and G. E. Ewing, *J. Chem. Phys.*, **61**, 1293 (1974).

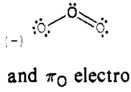
(52) R. D. Harcourt, *J. Mol. Struct.*, **12**, 1 (1972); **18**, 515 (1973). In this reference, the electronic reorganization of ONOOO has been represented as



If it is formulated as



then NO_2 with the electronic structure of Figure 2f will be generated. The "increased-valence" structure of Figure 10a for O_3 may be generated from the standard valence-bond structure



by delocalizing nonbonding $\bar{\pi}_O$ and π_O electrons from the O^- into adjacent bonding OO orbitals.

(53) R. D. Harcourt, *Biopolymers*, **11**, 1551 (1972).

(54) R. D. Harcourt and J. F. Sillitoe, *Aust. J. Chem.*, **27**, 691 (1974).

(55) S. P. Walch and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 5319 (1975).

(56) P. C. Hiberty and C. Le Forestier, *J. Am. Chem. Soc.*, **100**, 2012 (1978).

(57) (a) R. D. Harcourt and W. Roso, *Can. J. Chem.*, **56**, 1093 (1978), and ref 4–19 therein; (b) *Int. J. Quantum Chem.*, **16**, 1033 (1979).