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Valency Structures for N_2O_4

Part II

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The energies (i.e. energy expectation values) and weights of various N_2O_4 valency structures are reported. Certain structures that apparently violate the octet rule are of low energy. This is because their wave functions allow for considerable resonance interaction between orthogonal wave functions that represent non-octet violating structures.

Erwartungswerte der Energien und Gewichte verschiedener Valenz-Strukturen des N_2O_4 werden mitgeteilt. Einige scheinbar die Oktett-Regel verletzende Strukturen sind energiearm: es sind Hybridstrukturen nicht die Oktett-Regel verletzender Valenzstrukturen.

Les énergies (espérances mathématiques de l'énergie) et les poids de diverses structures de valence de N_2O_4 sont donnés. Certaines structures qui violent apparemment la regle de l'octet ont une basse énergie. Ceci est dû à ce que leurs fonctions d'ondes permettent une forte interaction de résonance entre fonctions d'onde orthogonales qui représentent des structures respectant la regle de l'octet.

Introduction

In Fig. 1 of [*5*]*, seven types of N_2O_4 valency structures are shown. They differ in their distributions of ten mobile σ-electrons. Of these, VII (or B in this paper) is that with the greatest weight for the N_2O_4 ground-state. B is represented as involving nine electrons in bonding to each nitrogen atom, and therefore apparently violates the octet rule for first-row elements. Its importance is confirmed by the results of energy calculations for the various structures. These energies are reported here, as well as those for two other covalent structures, A and C, and the ionic structure D. Consideration of other types of structures that involve one-electron two-centre bonds [*9*, *10*], such as E, F, and the ionic structures with the different NO_2^+ distributions of G, will be given in another paper.

Method of Calculation

a) Wave functions

The ground state wave function for the ten mobile σ-electrons is called Ψ. For orbital notation and construction of Ψ, see [*5*]. [*1*, *2*, and *3*] display the six AOs and D_{2h} symmetry orbitals for these electrons. Ψ may be expressed as a linear combination of three covalent and three ionic functions [*5*] which are

$$\Phi^0_{\text{cov}}\,,\quad \Phi^2_{\text{cov}}\,,\quad \text{and either}\quad \Phi^1_{\text{cov}}\quad \text{or}\quad \Phi^{1'}_{\text{cov}}\,, \tag{1}$$

$$\Phi^0_{\text{ion}}\,,\quad \Phi^2_{\text{ion}}\,,\quad \text{and either}\quad \Phi^1_{\text{ion}}\quad \text{or}\quad \Phi^{1'}_{\text{ion}}\,. \tag{2}$$

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* Part I of this work.

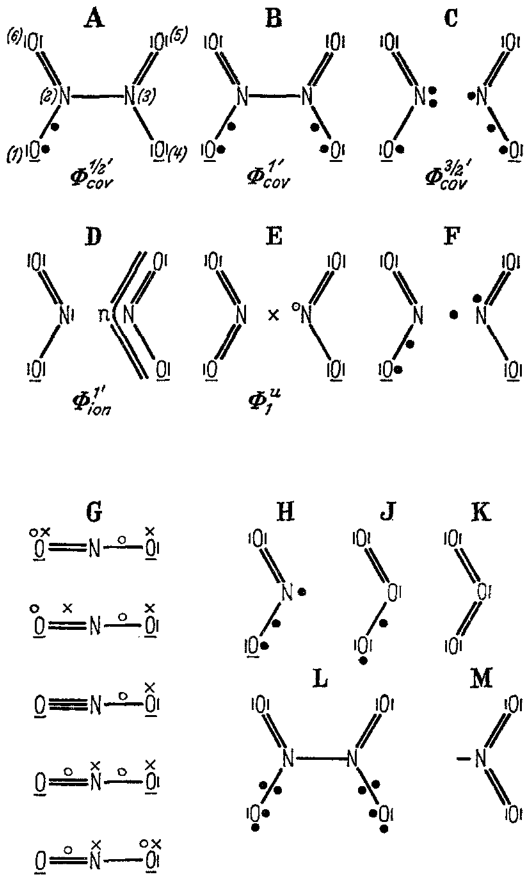

Fig. 1. Valency structures

These eight functions are those for the mobile σ-electrons of the valency structures I, V, III, VII $\equiv$ B, II, VI, IV and D. I—VI are shown in Fig. 1 of [5]. $\Phi^{1'}_{\text{cov}}$ and $\Phi^{1'}_{\text{ion}}$ may be expressed as

$$\Phi^{1'}_{\text{cov}} = \tfrac{1}{2}\,\Phi^{0}_{\text{cov}} + \frac{1}{\sqrt{2}}\Phi^{1}_{\text{cov}} + \tfrac{1}{2}\Phi^{2}_{\text{cov}}\,, \tag{3}$$

$$\Phi^{1'}_{\text{ion}} = \tfrac{1}{2}\,\Phi^{0}_{\text{ion}} + \frac{1}{\sqrt{2}}\Phi^{1}_{\text{ion}} + \tfrac{1}{2}\Phi^{2}_{\text{ion}} \tag{4}$$

and are therefore not orthogonal to the covalent or ionic functions from which they are constructed.

The wave functions for the mobile σ-electrons of A and C have not been previously reported. They are

$$\begin{aligned}\Phi^{1/2'}_{\text{cov}} &= \frac{1}{\sqrt{6}}\,(\,|\,\bar{\pi}_1^2\,\bar{\pi}_6^2\,h_2^{\beta}\,a_R^{*\alpha}\,n_R^{*2}\,a_R^2\,| - |\,\bar{\pi}_1^2\,\bar{\pi}_6^2\,h_2^{\alpha}\,a_R^{*\beta}\,n_R^{*2}\,a_R^2\,| + \\ &\qquad + |\,\bar{\pi}_4^2\,\bar{\pi}_5^2\,h_3^{\beta}\,a_L^{*\alpha}\,n_L^{*2}\,a_L^2\,| - |\,\bar{\pi}_4^2\,\bar{\pi}_5^2\,h_3^{\alpha}\,a_L^{*\beta}\,n_L^{*2}\,a_L^2\,|\,) \\ &= \frac{1}{\sqrt{3}}\,(\sqrt{2}\,\Phi^{0}_{\text{cov}} + \Phi^{1}_{\text{cov}})\,,\end{aligned} \tag{5}$$

$$\Phi^{3/2'}_{\mathrm{cov}} = \frac{1}{\sqrt{6}} \left(\left| a_L^2\, n_L^{*2}\, a_L^{*\alpha}\, h_3^2\, \bar{\pi}_4^{\beta}\, \bar{\pi}_5^{\beta}\, n_R^{*\alpha} \right| - \left| n_L^{*\beta}\, \bar{\pi}_1^{\alpha}\, \bar{\pi}_6^{\alpha}\, h_2^2\, a_R^{*\beta}\, n_R^{*2}\, a_R^2 \right| + \right.$$
$$\left. + \left| a_R^2\, n_R^{*2}\, a_R^{*\alpha}\, h_2^2\, \bar{\pi}_1^{\beta}\, \bar{\pi}_6^{\beta}\, n_L^{*\alpha} \right| - \left| n_R^{*\beta}\, \bar{\pi}_4^{\alpha}\, \bar{\pi}_5^{\alpha}\, h_3^2\, a_L^{*\beta}\, n_L^{*2}\, a_L^{*2} \right| \right)$$
$$= \frac{1}{\sqrt{3}} (\Phi^1_{\mathrm{cov}} + \sqrt{2}\, \Phi^2_{\mathrm{cov}}) \,. \tag{6}$$

b) *Energies*

The energies of the functions of (1) and (2) are conveniently calculated relative to that for the function

$$\Phi_1^{\mu=0} = \left| (s_1)^2 (s_3)^2 (s_4)^2 (s_5)^2 (s_6)^2 \right| = \frac{1}{\sqrt{2}} (\Phi^0_{\mathrm{cov}} + \Phi^0_{\mathrm{ion}}) \,. \tag{7}$$

This is because other functions given in appendix 4 of [*5*] are derivable from it by one or two electron singlet-singlet excitations, and Eqs. (26—28) and (34) of [*5*] connect them to the structure functions of (1) and (2). The excitations that produce the functions of appendix 4, Φ_1 and Φ_2 (the two MO configurations given by (18) and (19) of [*5*]), are*

$$\Phi_1^{\mu=1} : (s_4)^2 \to \left(\frac{s_4 + s_2}{\sqrt{2}}\right)^2 \;;\; \Phi_1^{\mu=\infty} : (s_4)^2 \to (s_2)^2 \,. \tag{8}$$

$$\Phi_2^{\lambda=0} : (s_1)^2 \to (s_2)^2 \;;\; \Phi_2^{\lambda=1} : \left(\frac{s_3 - s_1}{\sqrt{2}}\right)^2 \to (s_2)^2 ; \Phi_2^{\lambda=\infty} : (s_3)^2 \to (s_2)^2 \,. \tag{9}$$

$$\Phi_1^{\mu} : s_4 \to s_2 \;;\; \Phi_2^{\lambda} : s_1 s_3 \to (s_2)^2 \,. \tag{10}$$

$$\Phi_1 : (s_4)^2 \to (\sigma_2(b_{1u}))^2 \;;\; \Phi_2 : (\sigma_5(a_g))^2 \to (s_2)^2 \,. \tag{11}$$

To give an example of how to calculate an energy, we shall evaluate

$$E^0_{\mathrm{cov}} = \langle \Phi^0_{\mathrm{cov}} \,|\, \mathscr{H} \,|\, \Phi^0_{\mathrm{cov}} \rangle \,.$$

From Eq. (26) of [*5*], we have

$$\Phi^0_{\mathrm{cov}} = \frac{1}{\sqrt{2}} (\Phi_2^{\lambda=0} - \Phi_1^{\mu=0})$$

and therefore

$$E^0_{\mathrm{cov}} = \tfrac{1}{2} (E_2^{\lambda=0} + E_1^{\mu=0}) - \langle \Phi_1^{\mu=0} \,|\, \mathscr{H} \,|\, \Phi_2^{\lambda=0} \rangle \,. \tag{12}$$

$\Phi_2^{\lambda=0}$ is derived from $\Phi_1^{\mu=0}$ by the $(s_1)^2 \to (s_2)^2$ excitations. It requires the energy (relative to $E_1^{\mu=0}$) [*12*]

$$E_2^{\lambda=0} = 2\varepsilon_2 - 2\varepsilon_1 - 4J_{12} + J_{11} + J_{22} + 2K_{12} \,. \tag{13}$$

The ε_i, J_{ij}, and K_{ij} are the energies, coulomb and exchange integrals** for the symmetry orbitals (s_i). In terms of integrals involving AOs, they may be expressed as

$$\varepsilon_1 = F_{22} + F_{13} \,, \qquad \varepsilon_2 = F_{22} - F_{23} \,; \tag{14}$$

$$J_{11} = J_{12} = J_{22} = \tfrac{1}{2}(\gamma_{22} + \gamma_{23}) \,, \qquad K_{12} = \tfrac{1}{2} (\gamma_{22} - \gamma_{23}) \,. \tag{15}$$

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* Because Ψ may be expressed either as $C_1 \Phi_1 + C_2 \Phi_2$ or in terms of the functions of (1) and (2), a check on the energy calculations has been obtained by evaluating $E(\Psi) = \langle \Psi \,|\, \mathscr{H} \,|\, \Psi \rangle$ from both types of expansions.

** The subscripts should not be confused with those of Eq. (22) of [*5*], where they refer to the MOs (σ_i). The $\mathscr{F}$ which generates these MOs (for Φ_1) is also different from that of $\Phi_1^{\mu=0}$. When calculating the $F_{\mu\mu}$ or $F_{\mu\nu}$ for either function, the valence-state ionization potentials, resonance and repulsion integrals of Φ_1 are used.

The $F_{\mu\mu} = \langle \chi_\mu \mid \mathscr{F} \mid \chi_\mu \rangle$ and $F_{\mu\nu} = \langle \chi_\mu \mid \mathscr{F} \mid \chi_\nu \rangle$ (with $\chi = \bar{\pi}$ or h AOs) to be used in (14) and (19—21) involve the Roothaan LCAO hamiltonian operator $\mathscr{F}$ that obtains to $\Phi_1^{\mu=0}$. This function generates the following mobile σ-electron charge densities (P_μ^σ) and non-zero bond orders ($P_{\mu\nu}^\sigma$):

$$P_O^\sigma = 2, \qquad P_N^\sigma = 1, \qquad P_{23}^\sigma = 1. \tag{16}$$

Using these, the $F_{\mu\mu}$ and $F_{\mu\nu}$ are calculated from Eqs. (5) and (6) of [*2*]. Here, we only require

$$F_{23} = \beta_{23} - \tfrac{1}{2}\gamma_{23} \,. \tag{17}$$

The $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ of (15—24) are the "σ-peel" resonance integrals and mobile σ-electron atomic repulsion integrals [*3*, *5*]. We thus obtain for (13),

$$E_2^{\lambda=0} = -4\beta_{23} \,.$$

In (12) the interaction matrix element is equal to K_{12} of (15), $\Phi_1^{\mu=0}$ and $\Phi_2^{\lambda=0}$ differing by two spin orbitals.

Therefore,

$$E_{\text{cov}}^0 = -2\beta_{23} - \tfrac{1}{2}(\gamma_{22} - \gamma_{23}) = E_{\text{ion}}^0 - 2K_{12} \,. \tag{18}$$

The expressions for the other energies are

$$E_{\text{cov}}^1 = F_{22} - F_{11} - 2\beta_{23} - \gamma_{12} + \tfrac{1}{2}\gamma_{23} = E_{\text{ion}}^1 - 2\langle s_1 s_2 \mid s_3 s_4 \rangle \,, \tag{19}$$

$$E_{\text{cov}}^2 = 2(F_{22} - F_{11}) - 2\beta_{23} - 2(\gamma_{12} + \gamma_{13}) + \tfrac{1}{2}(\gamma_{22} + 3\gamma_{23} + \gamma_{14} + \gamma_{15}) = E_{\text{ion}}^2 - 2K_{34}, \tag{20}$$

$$E_{\text{cov}}^{1'} = F_{22} - F_{11} - 2\beta_{23} - \gamma_{12} - \tfrac{1}{2}\gamma_{13} + \tfrac{3}{4}\gamma_{23} + \tfrac{1}{8}(\gamma_{14} + \gamma_{15}) + 2\sqrt{2}\beta_{12} \tag{21}$$

$$= E_{\text{ion}}^{1'} - 2\left(\tfrac{1}{4}K_{12} + \tfrac{1}{2}\langle s_1 s_2 \mid s_3 s_4 \rangle + \tfrac{1}{4}K_{34}\right) . \tag{22}$$

In (19), (20), and (22),

$$\langle s_1 s_2 \mid s_3 s_4 \rangle \equiv \langle \Phi_1^\mu \mid \mathscr{H} \mid \Phi_2^\lambda \rangle = \tfrac{1}{2}(\gamma_{12} - \gamma_{13}) \,,$$

$$K_{34} = \langle \Phi_1^{\mu=\infty} \mid \mathscr{H} \mid \Phi_2^{\lambda=\infty} \rangle = \tfrac{1}{4}(\gamma_{11} - \gamma_{14} - \gamma_{15} + \gamma_{16}) \,.$$

Non-zero matrix interaction elements between the orthogonal or non-orthogonal functions of (1) and (2) are

$$\langle \Phi_{\text{cov}}^0 \mid \mathscr{H} \mid \Phi_{\text{cov}}^1 \rangle = \langle \Phi_{\text{cov}}^1 \mid \mathscr{H} \mid \Phi_{\text{cov}}^2 \rangle = \langle \Phi_{\text{ion}}^0 \mid \mathscr{H} \mid \Phi_{\text{ion}}^1 \rangle = \langle \Phi_{\text{ion}}^1 \mid \mathscr{H} \mid \Phi_{\text{ion}}^2 \rangle = 2\beta_{12}, \tag{23}$$

$$\langle \Phi_{\text{cov}}^0 \mid \mathscr{H} \mid \Phi_{\text{ion}}^0 \rangle = 2\beta_{23}; \quad \langle \Phi_{\text{cov}}^1 \mid \mathscr{H} \mid \Phi_{\text{ion}}^1 \rangle = \langle \Phi_{\text{cov}}^{1'} \mid \mathscr{H} \mid \Phi_{\text{ion}}^{1'} \rangle = \beta_{23} \,. \tag{24}$$

The energies of $\Phi_{\text{cov}}^{1/2'}$ and $\Phi_{\text{cov}}^{3/2'}$ may be derived from (18), (19), (20), and (23).

The orthogonal wave function Φ_{ion}^2 involves two types of ionic structures that are shown in Fig. 1 of [*5*]. One has the two oxygen mobile σ-electrons on different atoms of the NO_2^+ moiety; the other has them on the same atom. We shall distinguish these structures by the labels* VIc and VIi, with wavefunctions Φ_{ion}^{2c} and Φ_{ion}^{2i}. Relative to E_{ion}^2, their energies are

$$E_{\text{ion}}^{2c} = -\tfrac{1}{2}(\gamma_{11} - \gamma_{16}) = E_{\text{ion}}^{2i} - (\gamma_{11} - \gamma_{16}) \,.$$

c) Structural weights

The weight for structure i has been calculated from $(\Psi)^2$ using the formula [*20*]

$$c_i\Big(c_i + \sum_{j \neq i} c_j \langle \Phi_i \mid \Phi_j \rangle\Big) \,. \tag{25}$$

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* The "*c*" and "*i*" indicate that these two oxygen electrons are distributed covalently and onically with respect to the two oxygen atoms of NO_2^+.

Peters [17] has pointed out that it is generally arbitrary how the overlap terms in $(\Psi)^2$ are to be divided up among the two structures corresponding to Φ_i and Φ_j. Using (25) divides them equally. In previous papers [5, 6], if Φ_i were Φ^0_{cov} or Φ^2_{cov}, and Φ_j were $\Phi^{1'}_{\mathrm{cov}}$, the overlap terms were given to I and V only. The resulting weights for I, B, and V were $c^0_{\mathrm{cov}}(c^0_{\mathrm{cov}} + 2c^{1'}_{\mathrm{cov}} \langle \Phi^0_{\mathrm{cov}} \,|\, \Phi^{1'}_{\mathrm{cov}} \rangle)$, $(c^{1'}_{\mathrm{cov}})^2$, and $c^2_{\mathrm{cov}}(c^2_{\mathrm{cov}} + 2c^{1'}_{\mathrm{cov}} \langle \Phi^2_{\mathrm{cov}} \,|\, \Phi^{1'}_{\mathrm{cov}} \rangle)$. Their numerical values therefore differ slightly from those reported here in Tab. 3.

On substituting from (5) or (6), we may introduce $\Phi^{1/2'}_{\mathrm{cov}}$ or $\Phi^{3/2'}_{\mathrm{cov}}$ into Ψ. For N_2O_4, it is better to do this by substituting for Φ^0_{cov} or Φ^2_{cov} instead of Φ^1_{cov}, and so avoid negative weights of appreciable magnitude for structures I or V.

Discussion

For molecules composed of nitrogen and oxygen atoms, valency structures of low energy should be those with [14]

i. a large number of covalent bonds,

ii. small rather than large formal charges on the constituent atoms.

The energies and formal charges of Tab. 1 and 2 may be shown to meet these requirements.

Table 1. *Energies of* N_2O_4 *valency structures (in* eV*).* P^{σ}_{23} *is the* NN *σ-bond order for* Ψ

	Valency Structure	i. $P^{\sigma}_{23} = 0.47$	ii. $P^{\sigma}_{23} = 0.43$	iii. $P^{\sigma}_{23} = 0.01$	iv. $P^{\sigma}_{23} = 0.66$
E^0_{cov}	I	6.07	2.48	− 3.52	12.97
E^0_{ion}	II	12.41	8.68	2.64	19.27
E^1_{cov}	III	0.32	− 1.48	− 7.42	8.90
E^1_{ion}	IV	1.61	− 0.19	− 6.14	10.19
E^2_{cov}	V	− 2.97	− 3.00	− 8.90	7.28
E^2_{ion}	VI	2.98	2.99	− 2.90	13.24
E^{2c}_{ion}	VIc	− 2.05	− 2.07	− 7.97	8.20
E^{2i}_{ion}	VIi	8.00	8.05	2.17	18.27
$E^{1/2'}_{\mathrm{cov}}$	A	− 3.16	− 6.10	−12.10	4.41
$E^{1'}_{\mathrm{cov}}$	B	−10.04	−11.76	−17.73	− 1.29
$E^{3/2'}_{\mathrm{cov}}$	C	− 9.19	− 9.75	−15.68	0.62
$E^{1'}_{\mathrm{ion}}$	D	− 6.32	− 8.07	−14.05	2.42
$E(\Psi)$		−13.22	−13.28	−17.96	− 8.51

Orthogonal covalent structures I, III, *and* V

Each of these structures has one mobile σ-electron bond*. Their energies decrease in the order I > III > V. So do the magnitudes of the formal charges. I is the valency structure for the N_2O_4 ground state given in many books. Weight and energy show that it is a poor approximation.

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* There are six other covalent bonds that are the same for all structures. In III, V, and VIc, the mobile σ-electron bond is formed between O_1–N_3, O_1–O_4 and O_4–O_5 sets of atoms in Fig. 1 of [5]. Similarly, for *B* and *C*, extra bonds may be formed between the O_1–O_4, and either the O_1–O_4 or the O_1–N_3 atoms respectively.

Table 2. *Oxygen and nitrogen formal charges, Q_O and Q_N*

Calc.	Φ^0_{cov} I	Φ^1_{cov} III	Φ^2_{cov} V	Φ^0_{ion} II	Φ^1_{ion} IV	Φ^{2c}_{ion} VIc	Φ^{2i}_{ion} VIi	$\Phi^{1/2'}_{cov}$ A	$\Phi^{1'}_{cov}$ B	$\Phi^{3/2'}_{cov}$ C
i. $P^\sigma_{23} = 0.47$										
Q_O	−0.5	−0.25	0	−0.5	0	+0.5	+0.5	−0.375	−0.25	−0.125
Q_N	+1.0	+0.5	0	+2.0	+1.0	0	0	+0.75	+0.5	+0.25
ii. $P^\sigma_{23} = 0.43$										
Q_O	−0.432	−0.182	+0.068	−0.432	+0.068	+0.568	+0.568	−0.307	−0.182	−0.057
Q_N	+0.863	+0.363	−0.137	+1.863	+0.863	−0.137	−0.137	+0.613	+0.363	+0.113
iii. $P^\sigma_{23} = 0.01$										
Q_O	−0.455	−0.205	+0.045	−0.455	+0.045	+0.545	+0.545	−0.330	−0.305	−0.080
Q_N	+0.910	+0.410	−0.090	+1.910	+0.910	−0.090	−0.090	+0.660	+0.410	+0.160
iv. $P^\sigma_{23} = 0.66$										
Q_O	−0.393	−0.143	+0.107	−0.393	+0.107	+0.607	+0.607	−0.268	−0.143	−0.018
Q_N	+0.787	+0.287	−0.213	+1.787	+0.787	−0.213	−0.213	+0.537	+0.287	+0.037

Average formal charges have been calculated over all equivalent structures. The NO_2^- structure is the same for II, IV, VIc and VIi [*5*]. Therefore the formal charges for these structures obtain to their NO_2^+ moieties.

Table 3. *Weights of* N_2O_4 *covalent structures*

Calc.	Φ^0_{cov} I	Φ^1_{cov} III	Φ^2_{cov} V	$\Phi^{1/2'}_{\text{cov}}$ A	$\Phi^{1'}_{\text{cov}}$ B	$\Phi^{3/2'}_{\text{cov}}$ C
i. $P^{\sigma}_{23} = 0.47$						
(*a*)	0.14	0.32	0.23			
(*b*)		0.18	0.23	0.28		
(*c*)	−0.01		0.04		0.67	
(*d*)	0.14	0.13				0.43
ii. $P^{\sigma}_{23} = 0.43$						
(*a*)	0.15	0.36	0.26			
(*b*)		0.20	0.26	0.31		
(*c*)	−0.02		0.04		0.74	
(*d*)	0.15	0.15				0.47
iii. $P^{\sigma}_{23} = 0.01$						
(*a*)	0.14	0.46	0.40			
(*b*)		0.29	0.40	0.31		
(*c*)	−0.04		0.09		0.94	
(*d*)	0.14	0.16				0.70
iv. $P^{\sigma}_{23} = 0.66$						
(*a*)	0.23	0.25	0.08			
(*b*)		0.08	0.08	0.40		
(*c*)	0.06		−0.02		0.52	
(*d*)	0.23	0.14				0.19

(*a*) orthogonal structures.
(*b*), (*c*), and (*d*) include A, B, and C respectively.

Orthogonal ionic structures II, IV, VIc and VIi

The ionic structures differ in their distributions of the four mobile σ-electrons for the NO_2^+ moiety. They produce one mobile σ-electron bond for IV and VIc, but no such bond for II and VIi. The energy order is $E^0_{\text{ion}} > E^{2i}_{\text{ion}} > E^1_{\text{ion}} > E^{2c}_{\text{ion}}$. E^1_{ion} would be expected to be greater than E^{2c}_{ion} because the formal positive charge is localized on the nitrogen atom of IV, but may be carried by either oxygen atom of VIc. Formal charge considerations also suggest that E^0_{ion} should be greater than E^1_{ion}.

Non-orthogonal covalent structures A, B, and C

When a linear combination of interacting functions is made, resonance or interaction energy is generated. This energy, if negative and of appreciable magnitude, may reduce the energy of the linear combination below that of any of the interacting functions. For A, B, and C, the interaction energies are

$$\text{A and C}: \frac{2\sqrt{2}}{3}\langle\Phi^0_{\text{cov}}\,|\,\mathscr{H}\,|\,\Phi^1_{\text{cov}}\rangle = \frac{2\sqrt{2}}{3}\langle\Phi^1_{\text{cov}}\,|\,\mathscr{H}\,|\,\Phi^2_{\text{cov}}\rangle = \frac{4\sqrt{2}}{3}\beta_{12}$$

$$\text{B}: \frac{1}{\sqrt{2}}\left\{\langle\Phi^0_{\text{cov}}\,|\,\mathscr{H}\,|\,\Phi^1_{\text{cov}}\rangle + \langle\Phi^1_{\text{cov}}\,|\,\mathscr{H}\,|\,\Phi^2_{\text{cov}}\rangle\right\} = 2\sqrt{2}\,\beta_{12}\,.$$

(That for ionic structure D is also $2\sqrt{2}\,\beta_{12}$). β_{12} is negative (-3.8 to -3.9 eV [*3*, *5*]), and so these interactions are negative. Their magnitudes are sufficiently large to reduce the energies of A, B, and C below that of any of the orthogonal structures from which they are derived.

A, B, and C reflect competition between resonance and formal charge considerations. The formal charges suggest that the order of energies should be $E_{\text{cov}}^{1/2'} > E_{\text{cov}}^{1'} > E_{\text{cov}}^{3/2'}$ instead of $E_{\text{cov}}^{1/2'} > E_{\text{cov}}^{3/2'} > E_{\text{cov}}^{1'}$ as in Tab. 1. However, the magnitude of the resonance energy for B is rather larger than that for C, and is able to outweigh the disadvantage of including the high energy structure I in B*. Alternatively, we might say that B has three mobile σ-electron bonds, whereas A and C each only has $1\frac{1}{2}$. The extra bonds help B to overcome its less favourable distribution of formal charge compared with that for C.

The weights of Tab. 3, and the overlaps between the non-orthogonal covalent functions and Ψ of Tab. 4, also suggest that B is the "best" single type of covalent structure for N_2O_4.

Table 4. *Overlap integrals for non-orthogonal basis functions with* Ψ

Calc.	$\langle \Phi_{\text{cov}}^{1/2'} \mid \Psi \rangle$	$\langle \Phi_{\text{cov}}^{1'} \mid \Psi \rangle$	$\langle \Phi_{\text{cov}}^{3/2'} \mid \Psi \rangle$
i. $P_{23}^{\sigma} = 0.47$	0.63	0.83	0.72
ii. $P_{23}^{\sigma} = 0.43$	0.66	0.87	0.76
iii. $P_{23}^{\sigma} = 0.01$	0.69	0.98	0.91
iv. $P_{23}^{\sigma} = 0.66$	0.68	0.74	0.52

Valency structures of types A, B, or C imply long weak NN bonds. For B, a reason for this was given in terms of the extent of delocalization of oxygen lone-pair electrons into the antibonding NN s_2-symmetry orbital [*5*]. An alternative (and better) explanation runs as follows:

The nitrogen odd-electron density for the NO_2 valency structures of type H (or VIII of [*5*]) is 0.5 e. B for N_2O_4 is formed by the spin-pairing of the nitrogen unpaired electrons of two such monomers. This spin-coupling must result in a NN bond number of 0.5. Therefore the NN bond is longer than a single bond**. (Such an explanation is essentially Pauling's reason [*16*] for the long bond. He calculated a NN bond number of 0.42 from an experimental estimate of the nitrogen odd-electron density of NO_2.) Similarly, it may be deduced that the other mobile σ-electron bonds of A, B, and C have bond numbers less than unity. That for the NN bond for VII of $(CH_3NO)_2$ [*6*, *7*] is 1.5.

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* By squaring $\Phi_{\text{cov}}^{1/2'}$, $\Phi_{\text{cov}}^{1'}$, and $\Phi_{\text{cov}}^{3/2'}$ of (3), (5), and (6), we obtain $A = \frac{1}{3}(2\text{I} + \text{III})$, $B = \frac{1}{4}\text{I} + \frac{1}{2}\text{III} + \frac{1}{4}\text{V}$, and $C = \frac{1}{3}(\text{III} + 2\text{V})$.

** The wave function for B (see Eq. (10) of [*5*]) may be expressed as

$$\Phi_{\text{cov}}^{1'} = 1/\sqrt{2}\,(\,|\,a_L^{\beta}\,n_L^{*\beta}\,\bar{\pi}_6^{\alpha}\,\bar{\pi}_1^{\alpha}\,h_2^{\alpha}\,h_3^{\beta}\,\bar{\pi}_4^{\beta}\,\bar{\pi}_5^{\beta}\,n_R^{*\alpha}\,a_R^{\alpha}\,| + |\,a_R^{\beta}\,n_R^{*\beta}\,\bar{\pi}_5^{\alpha}\,\bar{\pi}_4^{\alpha}\,h_3^{\alpha}\,h_2^{\beta}\,\bar{\pi}_1^{\beta}\,\bar{\pi}_6^{\beta}\,n_L^{*\alpha}\,a_L^{\alpha}\,|\,)\,.$$

The $1/\sqrt{2}\,(\,|\ldots h_2^{\alpha}\,h_3^{\beta}\ldots| + |\ldots h_3^{\alpha}\,h_2^{\beta}\ldots|\,)$ implies that the nitrogen atoms of B should be represented as bonded together [*6*].

Charge transfer

Tab. 1 suggests that the $\Phi^{1'}_{\text{cov}}$ for i, ii, and iv must require combination with other functions to obtain an energy which is near to that of the ground-state function Ψ. These other functions must be for the ionic structures, because the weights of the covalent structures I and V are very small after their contributions to B have been removed (s. Tab. 3, or Tab. 2 of [*5*]). Therefore, when NO_2 dimerizes, charge-transfer should be energetically important, as has been suggested by McEwen[*] [*11*].

Tab. 5 gives the charge-transfer stabilization obtained by interaction of $\Phi^{1'}_{\text{cov}}$ with each of the four ionic functions of Tab. 1. That for $\Phi^{1'}_{\text{ion}}$ representing structure D is greatest. D involves a two-electron three-centre bond (using Linnett's et al. [*4*, *8*] representation for a wave function of the form $|\, a_L^2\, n_L^{*2} \,|$ or $|\, a_R^2\, n_R^{*2} \,|$). Its weights for the four $(\Psi)^2$ are (i) 0.31, (ii) 0.23, (iii) 0.00, and (iv) 0.39. Except for (iii), for which no ionic structure makes much contribution, these weights are considerably greater than those for the other three ionic structures [*5*].

Table 5. *Resonance or charge-transfer stabilization energy (in* eV*) obtained by interaction of* $\Phi^{1'}_{\text{cov}}$ *with ionic functions*

Ionic Function	i. $P^{\sigma}_{23} = 0.47$	ii. $P^{\sigma}_{23} = 0.43$	iii. $P^{\sigma}_{23} = 0.01$	iv. $P^{\sigma}_{\text{ion}} = 0.66$
Φ^{0}_{ion}	−0.91	−0.37	−0.002	−2.78
Φ^{1}_{ion}	−0.85	−0.33	−0.004	−2.35
Φ^{2}_{ion}	0	0	0	0
$\Phi^{1'}_{\text{ion}}$	−3.12	−1.50	−0.013	−6.23

Some other octet-violating considerations

Samuel [*18*, *19*] has advanced experimental and quantum mechanical reasons for the existence of a pentacovalent nitrogen atom, e.g. in $-N\equiv N=O=$. They have been criticized by Wheland [*21*]. Pauling [*15*] doubts the wisdom of the use of such a structure for N_2O. However, by use of non-orthogonal basis functions similar to the procedure that has been described for N_2O_4, an apparent pentacovalency could of course occur, and $-N\equiv N \div O-$ may be an important structure. Such a structure may be shown to arise from the delocalizations of one π- and one $\bar{\pi}$-electron from the (terminal) nitrogen atom into the anti-bonding π- and $\bar{\pi}$-NO orbitals of $\equiv \overset{--}{N} - \overset{+}{N} \equiv \overset{+}{O} -$. (Structure E for N_2O_4, with wave function Φ^{μ}_{1}, is similar, because one oxygen $\bar{\pi}$-electron has delocalized into the antibonding s_2 orbital).

Octet violation is also possible for any system that could involve valence-bond resonance of the type A—B $\ddot{Y} \longleftrightarrow \ddot{A}$ B—Y. For example, J may be an important type of O_3 structure. (Samuel suggested K, but this is not in accord with the

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[*] Her description, although approximately correct, ignores "local excitations" [*13*] that manifest themselves in the small contributions of Φ^{0}_{cov} and Φ^{2}_{cov} to Ψ, in addition to that of $\Phi^{1'}_{\text{cov}}$. Such functions can only slightly stabilize the $\Phi^{1'}_{\text{cov}}$. The molecular orbital description of N_2O_4 takes "local excitations" into account by means of the h^{σ}_{N} and k^{σ}_{NN} parameters of Eqs. (16) and (17) of [*5*]. It is hoped to further elaborate this theme.

bond properties, e.g. length, strength, which indicate less than double bond character for the OO bonds). Transition metal complexes, for which the possibility exists of delocalization of metal electrons into antibonding ligand orbitals, appear to lend themselves particularly well to such octet violating considerations.

Similary, we may formulate the generalized S_{N2} displacement reaction as

$$\ddot{X} + R - Y \rightarrow [X - R \cdot \dot{Y}] \rightarrow X - R + \ddot{Y}$$

Here, the transition state arises from the transfer of one electron from the Lewis base X to the antibonding orbital between Y and the atom of R that is bonded to Y in the substrate. (The real extent of charge transfer will, of course, be a function of the XR and RY distances). Octet violation (or doublet violation if R = H) may therefore occur in the transition state.

For N_2O_4, the structural representation for the π-electrons most probably requires reconsideration. (We have so far contented ourselves with studying the mobile σ-electron distributions of the valency structures, because these electrons are responsible for the anomalous NN bond properties [*1*, *2*, *3*, *5*]). It is possible that a structure such as L may take better account of the π-electrons than does B. The nitro groups of L are similar to M suggested by Samuel, i.e. in both cases, the nitrogen atoms are apparently pentacovalent.

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