Theoret. chim. Acta (Berl.) 3, 194—201 (1965)

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Valency Structures for Oxalate and Dithionite Anions, and Dimers of Nitrosoalkanes

By

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Using molecular orbital theory and experimental bond orders, valency structures for $C_2O_4^{2-}$, $S_2O_4^{2-}$ and cis $(CH_3NO)_2$ are deduced. For the latter system, the wave function for a structure that violates the octet rule for the first row elements is contrasted with that pertaining to the double quartet hypothesis [*14*].

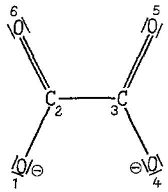
Valenzstrukturen für $C_2O_4^{2-}$, $S_2O_4^{2-}$ und cis $(CH_3NO)_2$ werden mit Hilfe der MO-Theorie und experimenteller Werte für die Bindungsordnungen abgeleitet. Für das letzte der aufgezählten Systeme wird die Wellenfunktion für eine Struktur, welche die Oktettregel für die Elemente der ersten Reihe des Periodensystems verletzt, verglichen mit einer Funktion, die der Doppel-Quartett-Hypothese [*14*] gehorcht.

A l'aide de la théorie des orbitales moléculaires et des ordres de liaison expérimentaux, on déduit des structures électroniques, au cadre des formules mésomères, pour $C_2O_4^{2-}$, $S_2O_4^{2-}$ et cis-$(CH_3NO)_2$. Au dernier cas, la fonction d'onde correspondant à une formule qui manque à la règle d'octet pour la première période, est confrontée à celle d'après l'hypothèse du «quartet double» [*14*].

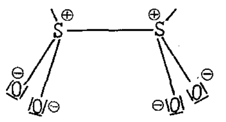
A determinantal wave function involving the orthonormal orbitals χ_a and χ_b and of the form

$$\Phi = \left| \dots \left(\frac{\chi_a + \mu \chi_b}{\sqrt{1+\mu^2}} \right)^2 \right|$$

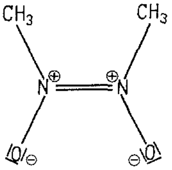
may be expanded as a linear combination of either orthogonal or non-orthogonal basis functions [*10*]. Such expansions have been previously used [*10*] to obtain wave functions representing two sets of valency structures for N_2O_4. The weights of these structures depended on μ. The χ_a and χ_b were oxygen and nitrogen symmetry orbitals for the mobile σ-electrons. In the present paper, the most significant covalent valency structures for the A_2Y_4 and A_2Y_2 systems $C_2O_4^{2-}$ (which is isoelectronic with N_2O_4), $S_2O_4^{2-}$ and cis $(CH_3NO)_2$ will be obtained by consideration of experimental bond orders and the extent of delocalization of Y-atom lone-pair electrons into an antibonding AA orbital. For these systems, the classical valency structures which involve no such delocalization, are of the types (a), (b) and (c).



a



b



c

The adjacent charge rule for positive charges [*5*] suggests that such charges should induce considerable delocalization of oxygen lone-pair electrons for (b) and (c). The experimental geometries are consistent with this.

Method of Calculation of Weights from Experimental Bond Orders

The procedure to be used is that described in the last section of reference [*10*]. Only a brief summary will be given here to show how μ (which governs the extent of delocalization of the Y-atom lone-pair electrons) may be related to the AA bond order.

In order to obtain a "good" wave function for the mobile σ-electrons of N_2O_4 (and for other A_2Y_4 systems with D_{2h} symmetry), it has been shown necessary to construct [*10*] a wavefunction of the form

$$\Psi = C_1\Phi_1 + C_2\Phi_2 .$$

Φ_1 is the lowest energy molecular orbital configuration. Φ_2 arises by raising two mobile σ-electrons from the frontier σ-orbital to the vacant σ-orbital of lowest energy. The AA σ-bond order* (P^{σ}_{23}) for Ψ is calculated from equ. (21) of reference [*10*]. However, because a doubly excited configuration such as Φ_2 usually lies many e.v. above Φ_1 (i.e. $|C_1| \gg |C_2|$), it should be a reasonable approximation to assume that $\Psi = \Phi_1$, and that Φ_1 gives a fair estimate of the AA σ-bond order. Equ. (21) of reference [*10*] then reduces to

$$P^{\sigma}_{23} = \frac{1}{1+\mu^2} .$$

This type of expression also obtains for the relevant mobile σ-electrons of $C_2O_4^{2-}$, $S_2O_4^{2-}$ and $(CH_3NO)_2$, and for the π-electrons of the latter system. Therefore μ may be approximately determined from the experimental AA σ-bond order. The weights of the various types of valency structures may then be calculated from the formulae of Tab. 3 in reference [*10*]. For Φ_1, these formulae obtain for the corresponding ionic structures as well as for the covalent structures. We may calculate the weights from Φ_1 alone, and know that configuration interaction will not affect the qualitative conclusions concerning the most significant covalent structures except to increase the weights of some of them at the expense of the ionic

Table 1. *Weights of* N_2O_4 *Covalent Valency Structures.*
(The most significant structures are underlined; see ref. [*10*] for details of calculation).

	Orthogonal Expansion						Non-orthogonal Expansion					
	$\Psi = \Phi_1$			$\Psi = C_1\Phi_1 + C_2\Phi_2$			$\Psi = \Phi_1$			$\Psi = C_1\Phi_1 + C_2\Phi_2$		
	I	III	V	I	III	V	I	VII	V	I	VII	V
i $\mu = 1$	0.125	$\underline{0.25}$	0.125	0.14	0.32	0.23	0.0	$\underline{0.5}$	0.0	−0.03	$\underline{0.65}$	0.07
ii $\mu = 1$	0.215	$\underline{0.25}$	0.125	0.15	$\underline{0.36}$	0.26	0.0	$\underline{0.5}$	0.0	−0.03	$\underline{0.73}$	0.08
iii $\mu = 1.22$	0.08	$\underline{0.24}$	$\underline{0.18}$	0.14	$\underline{0.46}$	$\underline{0.40}$	−0.04	$\underline{0.48}$	0.06	−0.10	$\underline{0.93}$	0.17
iv $\mu = 0.70$	$\underline{0.23}$	$\underline{0.22}$	0.05	$\underline{0.23}$	$\underline{0.25}$	0.08	0.12	$\underline{0.44}$	−0.06	0.11	$\underline{0.49}$	−0.03

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* The numbering of the atoms, atomic orbitals, and the A_2Y_4 symmetry orbitals are as given in references [*5*] and [*10*]. Where helpful for $S_2O^{2-}_4$ and $(CH_3NO)_2$, the symmetry orbitals and μ are given the extra designations σ- or π. For each system, the valency structures resembling I – VII of N_2O_4 are designated here by the same Roman numbers.

structures. This is verified by calculations i, ii, iii, and iv for N_2O_4 [*10*], as shown in Tab. 1. To calculate the weights from the more exact expression for Ψ requires values for a second parameter λ and for C_1/C_2. These are difficult to estimate from experimental data.

The following bond lengths [*18*] have been used to construct bond-order bond-length curves:

NN bonds: $\mathrm{N{\equiv}N}$ 1.10 Å; $\mathrm{N=N}$ 1.24 Å; $\mathrm{N-N}$ 1.48 Å;
NO bonds: $\mathrm{N{\equiv}O}$ 1.06 Å; $\mathrm{N=O}$ 1.20 Å; $\mathrm{N-O}$ 1.44 Å;
CC bonds: $\mathrm{C=C}$ 1.334 Å; $\mathrm{C} \dot{-} \mathrm{C}$ 1.397Å ; $\mathrm{C-C}$ 1.504 Å.

Our conclusions do not depend on the exact magnitudes of the bond orders.

Oxalate Anion

The most precise determination of the $C_2O_4^{2-}$ geometry is that for the lithium salt [*3*]. The CC bond length of 1.561 ± 0.0040 Å is about 0.08 Å longer than that of the central bond of butadiene (1.483 ± 0.01 Å, 1.476 ± 0.010 Å) [*2, 15*]. If it is assumed that the effect of CC π-bonding on the CC bond length is similar in the two systems (V.E.S.C.F. molecular orbital estimates [*4*] of their π bond orders are both small: 0.1 for $C_2O_4^{2-}$ and 0.2 for C_4H_6), the longer CC bond of $C_2O_4^{2-}$ may be attributed to oxygen $\bar{\pi}$-electron delocalization into the antibonding CC σ-orbital. Approximate V.E.S.C.F. molecular orbital calculations [*5*] suggest that such delocalization can occur to a not insignificant extent. Using the CC bond-order — bond length relation*, a CC bond order of 0.75 may be calculated, which corresponds to $\mu \approx 0.6$. The types of valency structures to be considered are identical with those for N_2O_4 (see I — VII of ref. [*10*]. The resulting weights for such structures for $C_2O_4^{2-}$ are given in Tab. 2.

Table 2. *Weights of* $C_2O_4^{2-}$, $S_2O_4^{2-}$ *and cis* $(CH_3NO)_2$ *Valency Structures*

	Covalent				Ionic		
	I	III	V	VII	II	IV	VI
			$C_2O_4^{2-}$				
Orthog.	0.32	0.16	0.02		0.32	0.16	0.02
Non-orthog.	0.24		−0.06	0.32	0.32	0.16	0.02
			$S_2O_4^{2-}$				
Orthog.	0.08	0.24	0.18		0.08	0.24	0.18
Non-orthog.	−0.04		0.06	0.48	0.08	0.24	0.18
			$(CH_3NO)_2$				
Orthog. (σ)	0.44	0.06	0.00		0.44	0.06	0.0
Non-orthog. (σ)	0.41		−0.03	0.11	0.44	0.06	0.0
Orthog. (π)	0.22	0.22	0.06		0.22	0.22	0.06
Non-orthog. (π)	0.11		−0.05	0.45	0.22	0.22	0.06

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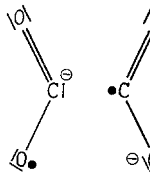
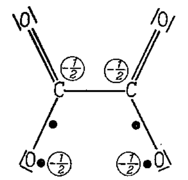
* The C—C bond of butadiene is 0.02 Å shorter than that of 1.504 Å for a single bond. This may be attributed to the CC π-bonding. If it is assumed that the CC π-bonding of $C_2O_4^{2-}$ also shortens its CC bond by 0.02 Å, then the length of the CC σ-bond is 1.58 Å. This value has been used to calculate μ.

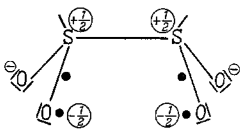
Both expansions predict two significant types of covalent structures — I [i.e. (a) in this paper] and either III or VII.



III

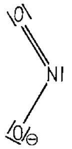


VII



VII

A hybrid of I and VII stresses that the OCO bond angles should be intermediate between those [*19*] of NO_2^- (115.4°) and NO_2 (134° 25′). The OCO angle of $C_2O_4^{2-}$ (127.3° ± 0.3°) [*3*] is similar to that of approximately 128° [*17*] for CO_2^-. The C odd electron density of CO_2^- is 0.64 [*17*], and generates weights of 0.18, 0.92 and —0.10 for structures of types (f), (g) and (h).



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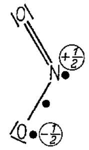

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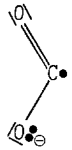

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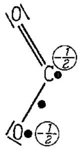

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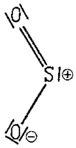

i

Dithionite Anion

The SS bond length of $S_2O_4^{2-}$ is 2.389 Å [*7*] and corresponds to a bond order of 0.36 [*1*]. $S_2O_4^{2-}$ is non-planar and so the distinction between σ- and π-electrons is lost. (However, the planar configuration designations for orbitals and electrons will continue to be used here.) The oxygen π- and $\bar{\pi}$-electrons can delocalize into the antibonding orbital $\frac{1}{\sqrt{2}}(h_2 - h_3)$ between the S atoms. Such combined delocalization has been referred to as "$\pi\bar{\pi}$"-delocalization previously [*5*]. The π-electron orbitals $\frac{1}{\sqrt{2}}(\pi_2 + \pi_3)$ and $\frac{1}{\sqrt{2}}(\pi_2 - \pi_3)$ must each be doubly filled forming non-bonding lone-pairs on the S atoms, because $S_2O_4^{2-}$ is non-planar. If it is assumed that the oxygen π- and $\bar{\pi}$-electrons are degenerate (a very reasonable, but not always exact assumption — however, it is quite satisfactory for the present purpose), then the ground-state configuration for the mobile electrons may be expressed as

$$\Phi_1 = \left| (s_1^\sigma)^2 (s_3^\sigma)^2 (s_5^\sigma)^2 (s_6^\sigma)^2 (s_9^\pi)^2 (s_{11}^\pi)^2 (s_{12}^\pi)^2 \left(\sqrt{\frac{s_{10}^\pi - \nu s_4^\sigma}{1+\nu^2}} \right)^2 \left(\frac{\sqrt{\frac{\nu s_{10}^\pi + s_4^\sigma}{1+\nu^2}} + \mu s_2^\sigma}{\sqrt{1+\mu^2}} \right)^2 \right| .$$

The relative extent of delocalization of the π- and $\bar{\pi}$-electrons is governed by ν, which may be related to the bond angles $2\varphi = \sphericalangle$ OSO and $\omega = \sphericalangle$ SSO through the overlap integrals. These integrals involving the π_1-, $\bar{\pi}_1$- and h_2 atomic orbitals may be expressed as [*5*]:

$$\int \pi_1 h_2 \, d\tau = -\tfrac{1}{2} N_2 \lambda_2 \cos\theta \int \pi_1 \pi_2 \, d\tau$$
$$\int \bar{\pi}_1 h_2 \, d\tau = -\tfrac{1}{2} N_2 \lambda_2 \sin\varphi \sin\theta \int \pi_1 \pi_2 \, d\tau$$

in which, neglecting d-orbitals, $h_2 = N_2 (s_2 + \lambda_2 p_2)$, $\int \pi_1 \pi_2 \, d\tau = \pi$-electron overlap integral for a planar system, and $\theta = \sin^{-1}(-\cos\omega/\cos\varphi)$. Therefore ν may be expressed as cosec φ cot θ with $\lim_{\omega\to\pi/2} \nu = \infty$. For tetrahedral dispositions of the four S hybrid atomic orbitals (forming three bonds and one lone-pair), $\nu = 1.7$, whereas for the $S_2O_4^{2-}$ geometry ($2\varphi = 108° 11'$, $\omega = 98° 1'$, $99° 23'$), $\nu = 4.5$.

The expansion of Φ_1 in terms of valency structure functions is more complicated than for A_2Y_4 systems with 34 valence-electrons. In order that the molecular orbitals remain ortho-normal, Φ_1 cannot be transformed in such a manner that the π- and $\bar{\pi}$-electron delocalizations are separated. Therefore a complete expansion of Φ_1 would generate many types of valency structures. To simplify the problem, it may be concluded that since $\nu = 4.5$, π-electron delocalization must be considerably more extensive than is the $\bar{\pi}$-electron delocalization. Therefore it should be reasonable to neglect the delocalization of the latter electrons. Φ_1 may then be expressed as

$$\Phi_1 = \left| \bar{\pi}_1^2\, \bar{\pi}_4^2\, \bar{\pi}_5^2\, \bar{\pi}_6^2\, (s_1^\sigma)^2\, (s_9^\pi)^2\, (s_{11}^\pi)^2\, (s_{12}^\pi)^2 \left(\frac{s_{10}^\pi + \mu^\pi s_2^\sigma}{1 + (\mu^\pi)^2} \right)^2 \right|$$

and expanded as described above for N_2O_4 and $C_2O_4^{2-}$. With $\mu^\pi = 1.2$, the weights of Tab. 2 have been calculated.

Only one important type of covalent structure obtains for the non-orthogonal expansion, i. e. VII. Such a structure stresses that the SO bonds for $S_2O_4^{2-}$ should be longer than those for SO_2 ($S_2O_4^{2-}$ 1.496 Å, 1.515 Å; SO_2 1.4308 ± 0.0002 Å) [*7*, *16*] because of a smaller value for the SO bond order. It is also consistent with the OSO angles being narrower than for SO_2, (i) (or reference [*18*] p. 329), but wider than the HNH angles of N_2H_4 ($S_2O_4^{2-}$ 108° 11'; SO_2 119° 19' ± 2'; N_2H_4 106° 0') [*7*, *16*, *11*].

The SO bond lengths of $S_2O_4^{2-}$ and SO_2 are near or similar to that of 1.40 Å for SO double bonds [*9*]. The above valency structures for these systems do not suggest this, and it is presumably necessary to include *d*-orbitals of sulphur to account for the lengths. Such a more elaborate description of $S_2O_4^{2-}$ may possibly modify our conclusions concerning the nature of its SS bond. The present calculation is based on the assumption that the "$\pi\,\bar{\pi}$"-delocalisation is responsible for its lengthening.

Cis Dimer of Nitrosomethane

The NN bond length of cis $(CH_3NO)_2$ is 1.31 ± 0.02 Å [*8*] which corresponds to an NN bond order (P_{23}) of ~1.6. The valency structure (c) involves an NN double bond. The reduction in bond order could arise from delocalization of oxygen π- and $\bar{\pi}$-electrons into the antibonding π- and σ-electron orbitals between the nitrogen atoms. As remarked earlier in this paper, such delocalizations should be facilitated by the nitrogen positive charges. Two μ parameters, μ^π and μ^σ, determine the extent of these delocalizations. It is necessary to also use the NO bond length in order to empirically determine these parameters. The NO length of 1.31 Å corresponds to a NO bond order of ~1.5*. Assuming no configuration

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* Using molecular orbital theory, LEROY et al. [*13*] have calculated NO and NN bond orders of 1.425 and 1.237 for cis $(CH_3NO)_2$, and 1.466 and 1.320 for trans $(CH_3NO)_2$. These correspond to NO lengths of 1.32 Å and 1.31 Å, and NN lengths of 1.41 Å and 1.38 Å. Earlier LEROY [*12*] had calculated NO and NN bond orders of 1.441 and 1.736 for the trans system which imply bond lengths of 1.32 Å and 1.29 Å. SMITH's [*20*] simple Hückel calculations give NN and NO bond orders of (i) 1.725 and 1.448 (ii) 1.927 and 1.354.

interaction, the total NN and NO bond orders may be expressed as

$$P_{23} = \frac{1}{1+(\mu^{\sigma})^2} + \frac{1}{1+(\mu^{\pi})^2}\,; \quad P_{12} = 1 + \frac{1}{\sqrt{2}}\left[\frac{\mu^{\sigma}}{1+(\mu^{\sigma})^2} + \frac{\mu^{\pi}}{1+(\mu^{\pi})^2}\right].$$

Using the experimental bond orders, values of either $\mu^{\sigma} = 0.25$ and $\mu^{\pi} = 0.72$ or $\mu^{\pi} = 0.25$ and $\mu^{\sigma} = 0.72$ have been obtained. Overlap considerations suggest that the former set of parameters should be preferred, i. e. only the π-electrons should appreciably delocalize.

The ground-state σ- and π-electron configurations are

$$\Phi_1^{\sigma} = \left|(s_1^{\sigma})^2\,(s_3^{\sigma})^2\left[\frac{s_4^{\sigma}+\mu^{\sigma}\,s_2^{\sigma}}{\sqrt{1+(\mu^{\sigma})^2}}\right]^2\right|\;;\quad \Phi_1^{\pi} = \left|(s_1^{\pi})^2\,(s_3^{\pi})^2\left[\frac{s_4^{\pi}+\mu^{\pi}\,s_2^{\pi}}{\sqrt{1+(\mu^{\pi})^2}}\right]^2\right|.$$

The symmetry orbitals $s_1^{\sigma} \ldots s_4^{\sigma}$ and $s_1^{\pi} \ldots s_4^{\pi}$ are defined as

$$s_1^{\sigma} = \frac{1}{\sqrt{2}}(h_2+h_3);\; s_2^{\sigma} = \frac{1}{\sqrt{2}}(h_2-h_3);\; s_3^{\sigma} = \frac{1}{\sqrt{2}}(\overline{\pi}_1+\overline{\pi}_4);\; s_4^{\sigma} = \frac{1}{\sqrt{2}}(\overline{\pi}_1-\overline{\pi}_4)\,.$$

$$s_1^{\pi} = \frac{1}{\sqrt{2}}(\pi_2+\pi_3);\; s_2^{\pi} = \frac{1}{\sqrt{2}}(\pi_2-\pi_3);\; s_3^{\pi} = \frac{1}{\sqrt{2}}(\pi_1+\pi_4);\; s_4^{\pi} = \frac{1}{\sqrt{2}}(\pi_1-\pi_4)\,.$$

The orthogonal basis functions for the expansions of Φ_1^{σ} or Φ_1^{π} may be expressed as linear combinations of the following structure functions:

$$\Phi_{\text{cov}}^{0} = \frac{1}{\sqrt{2}}\left(|\varphi_1^2\varphi_2^{\alpha}\varphi_3^{\beta}\varphi_4^2| - |\varphi_1^2\varphi_2^{\beta}\varphi_3^{\alpha}\varphi_4^2|\right) \tag{1}$$

$$\Phi_{\text{ion}}^{0} = \frac{1}{\sqrt{2}}\left(|\varphi_1^2\varphi_2^2\varphi_4^2| + |\varphi_1^2\varphi_3^2\varphi_4^2|\right) \tag{2}$$

$$\Phi_{\text{cov}}^{2} = \frac{1}{\sqrt{2}}\left(|\varphi_1^{\alpha}\varphi_2^2\varphi_3^2\varphi_4^{\beta}| - |\varphi_1^{\beta}\varphi_2^2\varphi_3^2\varphi_4^{\alpha}|\right) \tag{3}$$

$$\Phi_{\text{ion}}^{2} = \frac{1}{\sqrt{2}}\left(|\varphi_1^2\varphi_2^2\varphi_3^2| + |\varphi_2^2\varphi_3^2\varphi_4^2|\right) \tag{4}$$

$$\Phi_{\text{cov}}^{1} = \frac{1}{2}\left(|\varphi_1^2\varphi_2^{\beta}\varphi_3^2\varphi_4^{\alpha}| - |\varphi_1^2\varphi_2^{\alpha}\varphi_3^2\varphi_4^{\beta}| + |\varphi_1^{\beta}\varphi_2^2\varphi_3^{\alpha}\varphi_4^2| - |\varphi_1^{\alpha}\varphi_2^2\varphi_3^{\beta}\varphi_4^2|\right) \tag{5}$$

$$\Phi_{\text{ion}}^{1} = \frac{1}{2}\left(|\varphi_1^{\alpha}\varphi_2^{\beta}\varphi_3^2\varphi_4^2| - |\varphi_1^{\beta}\varphi_2^{\alpha}\varphi_3^2\varphi_4^2| + |\varphi_1^2\varphi_2^2\varphi_3^{\alpha}\varphi_4^{\beta}| - |\varphi_1^2\varphi_2^2\varphi_3^{\beta}\varphi_4^{\alpha}|\right)\,. \tag{6}$$

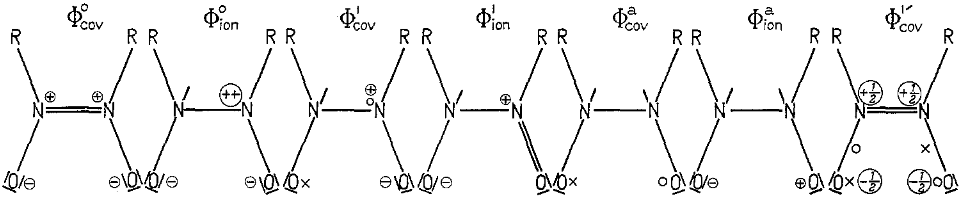
In these, $\varphi_{\nu} = \overline{\pi}_{\nu}$ or h_{ν} for the σ-electrons, and π_{ν} for the π-electrons.

The non-orthogonal expansion of Φ_1^{σ} or Φ_1^{π} involve (1) — (4) together with

$$\begin{aligned}
\Phi_{\text{cov}}^{1'} &= \frac{1}{\sqrt{2}}\left[\left|\varphi_1^{\alpha}\left(\frac{\varphi_1+\varphi_2}{\sqrt{2}}\right)^{\beta}\varphi_2^{\alpha}\,\varphi_3^{\beta}\left(\frac{\varphi_3+\varphi_4}{\sqrt{2}}\right)^{\alpha}\varphi_4^{\beta}\right| + \right.\\
&\quad \left. + \left|\varphi_4^{\alpha}\left(\frac{\varphi_3+\varphi_4}{\sqrt{2}}\right)^{\beta}\varphi_3^{\alpha}\,\varphi_3^{\beta}\left(\frac{1}{\sqrt{2}}\right)^{\alpha}\varphi_1^{\beta}\right|\right]\\
&= \frac{1}{2}\Phi_{\text{cov}}^{0} + \frac{1}{\sqrt{2}}\Phi_{\text{cov}}^{1} + \frac{1}{2}\Phi_{\text{cov}}^{2}
\end{aligned} \tag{7}$$

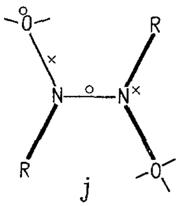
$$\begin{aligned}
\Phi_{\text{ion}}^{1'} &= \frac{1}{\sqrt{2}}\left[\left|\left(\frac{\varphi_1+\varphi_2}{\sqrt{2}}\right)^{2}\varphi_3^2\varphi_4^2\right| + \left|\varphi_1^2\varphi_2^2\left(\frac{\varphi_3+\varphi_4}{\sqrt{2}}\right)^{2}\right|\right]\\
&= \frac{1}{2}\Phi_{\text{ion}}^{0} + \frac{1}{\sqrt{2}}\Phi_{\text{ion}}^{1} + \frac{1}{2}\Phi_{\text{ion}}^{2}\,.
\end{aligned}$$

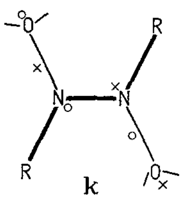
Functions (1) — (7) are those for the mobile σ- or π-electrons of the valency structures of types (I) — (VII). For these structures, it is possible to be more explicit concerning electron spin designations than for A_2Y_4 systems. In (I) — (VII) a × or o represents an electron with $s_z = +\frac{1}{2}$ or $-\frac{1}{2}$. The weights of these structures for Φ_1^σ and Φ_1^π are given in Tab. 2.



I II III IV V VI VII

The most significant covalent structures are type I for the σ-electrons and type VII for the π-electrons. Therefore it may be deduced that a structure of type VII best represents the total electron distribution. Such a structure implies NN and NO bond orders of 1.5 which are similar to the above experimental estimates. Linnett [*14*] has suggested that a hybrid of (j) (and its mirror image) and (k) could perhaps provide a reasonable description for trans $(BrC_6H_4NO)_2$. Such a description would not be adequate for cis $(CH_3NO)_2$ because it must imply (whatever the weights of each) that either the NN or the NO bond order is significantly smaller than the experimental value. (k) is similar to VII but avoids violation of the octet rule by not representing as a bonding pair the unpaired electrons with opposite spins on the N atoms. A reason for this will now be given.





The two-electron bond wave functions for VII (and all other structures in the present type of treatment) are of the Heitler—London valence bond type, i. e. result from the pairing of two electrons with opposite spins in atomic orbitals on adjacent atoms. For example, the wave functions for the two bonds joining the N atoms of VII are

$$\frac{1}{\sqrt{2}}\left(|h_2^\alpha h_3^\beta| + |h_3^\alpha h_2^\beta|\right) \quad \text{and} \quad \frac{1}{\sqrt{2}}\left(|\pi_2^\alpha \pi_3^\beta| + |\pi_3^\alpha \pi_2^\beta|\right).$$

In (k), the wave functions for bonds indicated by heavy lines between atoms are doubly occupied bond orbitals — for example in L. C. A. O. theory the NN σ-bond wave function is $\left|\left(\frac{h_2 + h_3}{\sqrt{2}}\right)^\alpha \left(\frac{h_2 + h_3}{\sqrt{2}}\right)^\beta\right|$. The light lines represent two electrons with opposite spins occupying different spatial orbitals.

An orbital wave function for the N and O valence electrons of (k) for cis $(CH_3NO)_2$ (but neglecting the electrons involved in bonding to the CH_3 groups) may be obtained by transforming the following function:*

---

* In (8) and (9), the h_2' and h_3' are N hybrid atomic orbitals directed towards the O_1 and O_4 atoms. The σ_1- and σ_2- are the O $2p\sigma$ atomic orbitals directed towards the N_2 and N_3 atoms. In (9) the transformations of the O non-bonding s-, $\bar{\pi}$- and π-atomic orbitals have not been indicated. These could be of the types $\frac{1}{\sqrt{3}}(s + \bar{\pi} + \pi)^\alpha$, $\frac{1}{\sqrt{6}}(2s - \bar{\pi} - \pi)^\alpha$, $\frac{1}{\sqrt{2}}(\pi - \bar{\pi})^\alpha$, $\frac{1}{\sqrt{2}}(s + \bar{\pi})^\beta$ and $\frac{1}{\sqrt{2}}(s - \bar{\pi})^\beta$.

$$\left| s_1^2\, \bar{\pi}_1^2\, \pi_1^\alpha \left(\frac{\sigma_1 + h_2'}{\sqrt{2}}\right)^2 \left(\frac{\pi_1 + \pi_2}{\sqrt{2}}\right)^\beta \pi_2^\alpha \left(\frac{h_2 + h_3}{\sqrt{2}}\right)^2 \pi_3^\beta \left(\frac{\pi_3 + \pi_4}{\sqrt{2}}\right)^\alpha \left(\frac{h_3' + \sigma_4}{\sqrt{2}}\right)^2 \pi_4^\beta \bar{\pi}_4^2 s_4^2 \right| . \tag{8}$$

On writing $\sigma_{\mu\nu} = \frac{1}{\sqrt{2}} (\sigma_\mu + h_\nu')$, $\pi_{\mu\nu} = \frac{1}{\sqrt{2}} (\pi_\mu + \pi_\nu)$ and $\sigma_{23} = \frac{1}{\sqrt{2}} (h_2 + h_3)$, (8) can be transformed to

$$\left| s_1^2\, \bar{\pi}_1^2\, \pi_1^\alpha\, \sigma_{12}^\alpha \left(\frac{\sigma_{12} + \pi_{12}}{\sqrt{2}}\right)^\beta \left(\frac{\pi_{12} - \sigma_{12}}{\sqrt{2}}\right)^\beta \pi_2^\alpha\, \sigma_{23}^2\, \pi_3^\beta \left(\frac{\sigma_{34} + \pi_{34}}{\sqrt{2}}\right)^\alpha \left(\frac{\pi_{34} - \sigma_{34}}{\sqrt{2}}\right)^\alpha \sigma_{34}^\beta \pi_4^\beta \bar{\pi}_4^2\, s_4^2 \right| , \tag{9}$$

which represents (k). This shows why the two unpaired electrons on the N atoms of (k) are not indicated as bond-forming in this structure, because they are not contained in bond orbitals.

The geometry of trans $(CH_3NO)_2$ ($R_{NN} = 1.22$ Å, $R_{NO} = 1.25$ Å) [*21*] seems to be incompatable with the present delocalization theory because it implies complex values for μ^σ and μ^π. The condition that they shall be real is that

$$P_{12} \leqslant 1 + \sqrt{P_{23} - \tfrac{1}{2} P_{23}^2} .$$

The standard deviations of the bond lengths of trans $[(CH_3)_2CHCH_2NO]_2$ ($R_{NN} = 1.27 \pm 0.02$ Å, $R_{NO} = 1.30 \pm 0.02$ Å) [*6*] do not preclude them from satisfying this condition.

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(Received February 7, 1965)