

On the Use of Complex Hybridization in Stereochemical Investigations*

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Complex hybrids are used to describe the tetrahedral P_4 molecule and the triangular molecules: C_3H_6 (cyclopropane), C_2H_5N (ethylene imine), C_2H_4O (ethylene oxide), and C_2H_4S (ethylene sulphide). Overlap integrals are calculated and the choice of the atomic orbitals and the concept of strain energy are discussed.

I. INTRODUCTION

The concept of directed valences is of essential importance for the understanding of stereochemistry. It is based on the existence of localized molecular orbitals and on the criterion of maximum overlap.¹ The idea of hybridization has been of great aid in the search for these orbitals. Recently Mårtensson and Öhrn² proposed the use of complex hybridization in order to treat bond angles less than 90° ³ with the intention of retaining the useful idea of directed classical valence.

In the present work we make use of this proposal in a treatment of the tetrahedral P_4 molecule and the four triangular molecules C_3H_6 (cyclopropane), C_2H_5N (ethylene imine), C_2H_4O (ethylene oxide), and C_2H_4S (ethylene sulphide).

In accordance with the criterion of maximal overlap we restrict ourselves to calculations of overlap integrals. The choice of the atomic orbitals is discussed.

II. COMPLEX HYBRIDIZATION

In the following we consider only hybrids formed by one s - and three p -orbitals

$$h_k = \sum_{\mu=1}^4 a_{k\mu} \Phi_{\mu} \quad (1)$$

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with $\Phi_1=s$, $\Phi_2=p_x$, $\Phi_3=p_y$, and $\Phi_4=p_z$. The coefficients $a_{k\mu}$ can be complex numbers. The coefficient matrix should be unitary in order to keep the hybrids on one center orthogonal to each other

$$\mathbf{a}^+ \mathbf{a} = \mathbf{a} \mathbf{a}^+ = \mathbf{1} \quad (2)$$

The direction of a hybrid (valence) is defined as the direction from the atomic nucleus to the center of gravity of the hybrid density $|h_k|^2$.² The cosine of the valence angle between two hybrids h_k and h_l is then²

$$\cos \theta_{kl} = \frac{\sum_{\mu} \operatorname{Re}\{a_{k\mu} a_{l\mu}^*\} \operatorname{Re}\{a_{l\mu} a_{k\mu}^*\}}{[\sum_{\nu} (\operatorname{Re}\{a_{k\nu} a_{k\nu}^*\})^2 \sum_{\mu} (\operatorname{Re}\{a_{l\mu} a_{l\mu}^*\})^2]^{\frac{1}{2}}} \quad (3)$$

i) *Tetrahedral phosphorus* (P_4). The coefficient matrix which fulfills the angular and unitary conditions and which has equivalent hybrids with respect to the s -orbital content is found to be

$$\mathbf{a} = \begin{pmatrix} \frac{1}{2} & \sqrt{3}/2 & 0 & 0 \\ \frac{1}{2} & -\sqrt{3}/6 & 0 & \sqrt{6}/3 e^{i\kappa} \\ \frac{1}{2} & -\sqrt{3}/6 & \sqrt{2}/2 e^{i\kappa} & -\sqrt{6}/6 e^{i\kappa} \\ \frac{1}{2} & -\sqrt{3}/6 & -\sqrt{2}/2 e^{i\kappa} & -\sqrt{6}/6 e^{i\kappa} \end{pmatrix} \quad (4)$$

where κ is a phase factor at our disposal. The lone pair is chosen to correspond to h_1 (along the x -axis) (Fig. 1). From (3) we get the angle between the other three hybrids

$$\cos \theta_{23} = \frac{1 - 4 \cos^2 \kappa}{1 + 8 \cos^2 \kappa} \quad (5)$$

If κ is varied the angle θ_{23} goes through all values in the interval $(0^\circ, 109.47^\circ)$. For $\cos \kappa = 0.25$ the experimental value⁴ $\theta_{23} = 60^\circ$ is obtained.

ii) *Cyclopropane* ($\text{CH}_2\text{CH}_2\text{CH}_2$). The molecules CH_2NHCH_2 , CH_2OCH_2

and CH_2SCH_2 are treated in the same way.

The coefficient matrix with the properties as in i) is found to be

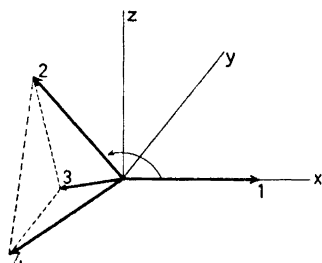


Fig. 1. Hybrids in the phosphorus molecule.

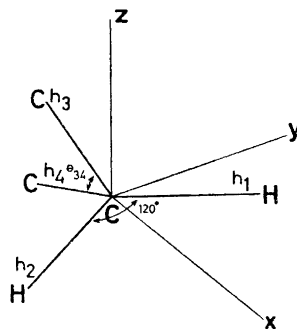


Fig. 2. Hybrids in cyclopropane.

$$\mathbf{a} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2}(\sqrt{6}/3+i\sqrt{3}/3) & \sqrt{2}/2 & 0 \\ \frac{1}{2} & \frac{1}{2}(\sqrt{6}/3+i\sqrt{3}/3) & -\sqrt{2}/2 & 0 \\ \frac{1}{2} & -\frac{1}{2}(\sqrt{6}/3+i\sqrt{3}/3) & 0 & \sqrt{2}/2 e^{i\kappa} \\ \frac{1}{2} & -\frac{1}{2}(\sqrt{6}/3+i\sqrt{3}/3) & 0 & -\sqrt{2}/2 e^{i\kappa} \end{pmatrix} \quad (6)$$

where h_3 and h_4 correspond to the two CC bonds and h_1 and h_2 to the two CH bonds with a fixed valence angle of 120° ⁴ (Fig. 2). This angle could be varied by introducing a second phase factor in (6).

The angle between h_3 and h_4 is found to be

$$\cos \theta_{34} = \frac{1-3 \cos^2 \kappa}{1+3 \cos^2 \kappa} \quad (7)$$

The allowed range for θ_{34} is then (0° , 120°). For $\cos \kappa = \frac{1}{3}$ the value $\theta_{34} = 60^\circ$ is obtained.

III. INVARIANCE PROPERTIES

Consider two atoms A and B with hybridization matrices \mathbf{a}^A and \mathbf{a}^B . The bonding overlap between two hybrids is defined as

$$S_{kl} = \frac{1}{2} \{ \langle h_k^A | h_l^B \rangle + \langle h_l^B | h_k^A \rangle \} \quad (8)$$

and the total bonding overlap between A and B as

$$S = \sum_{k,l} S_{kl} \quad (9)$$

Table 1. Overlap integrals between hybrids; Slater orbitals with fixed c (eqn. 12).^a

Bond Angle ^b	CC ^d R=1.52	CC ^e R=1.49	CC ^f R=1.47	CN ^g R=1.49	CO ^f R=1.44	CS ^e R=1.82	PP ^h R=2.21
normal bond ^c	0.656	0.670	0.679	0.563	0.490	0.423	0.645
109.°47	0.555	0.568	0.577	0.477	0.416	0.351	0.539
60°	0.484	0.496	0.504	0.418	0.366	0.303	0.384

^a Internuclear distance R in Å (Ref. 4).

^b Angle between the hybrids (eqns. 5 and 7).

^c Two sp^3 hybrids directed along the internuclear axis.

^d $\text{CH}_2\text{CH}_2\text{CH}_2$ (cyclopropane).

^e CH_2SCH_2 (ethylene sulphide); $R_{\text{CC}}=1.48$ in CH_2NHCH_2 .

^f CH_2OCH_2 (ethylene oxide).

^g CH_2NHCH_2 (ethylene imine).

^h P_4 .

i) Case $\mathbf{a}^A = \mathbf{a}^B$. This occurs, *e.g.*, in P_4 and between the atoms C, N, O, and S in the other molecules considered here. By use of the unitary properties of \mathbf{a} and the fact that the hybrids are equivalent with respect to their *s*-orbital content we find

$$S = \frac{1}{2} \sum_{k,l} \sum_{\mu,\nu} \{a_{k\mu}^* a_{l\nu} + a_{l\mu}^* a_{k\nu}\} \langle \Phi_{\mu}^A | \Phi_{\nu}^B \rangle = 4 \langle \Phi_1^A | \Phi_1^B \rangle \quad (10)$$

The total overlap S is thus independent of the type of hybridization used, unless the atomic orbitals have a dependence on the phase factor κ (bond angle θ). In Table 1 and Fig. 3 we report the values for S_{kl} for "fixed" atomic orbitals and for some θ -values of interest. The hybrids h_k^A and h_l^B are those directed towards A and B, respectively.

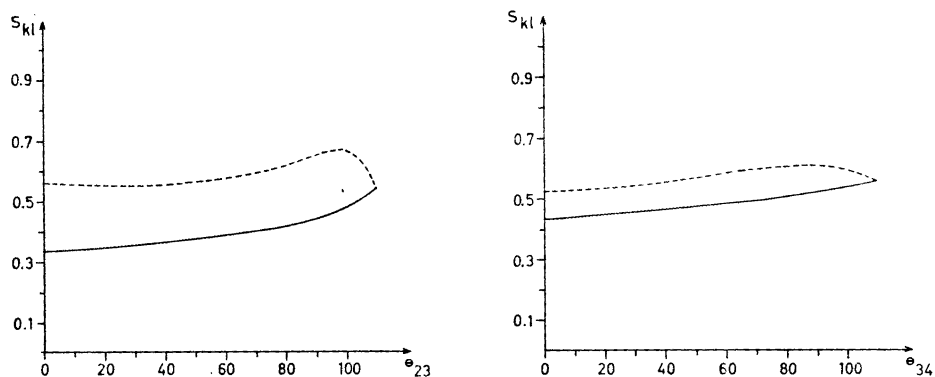


Fig. 3. Overlap integrals (eqn. 8) as function of the valence angle.

- fixed c (eqn. 13)
 - - - - variable c (eqn. 13).
 a) P_4 .
 b) cyclopropane (C—C bond).

ii) Case $\mathbf{a}^A \neq \mathbf{a}^B$. This is the situation for the CH-bonds and in that case we get

$$S = \frac{1}{2} \sum_{k=1}^4 \{ \langle s_H | h_k \rangle + \langle h_k | s_H \rangle \} = \sum_{k,\mu} \text{Re} \{ a_{k\mu} \} \langle s_H | \Phi_{\mu} \rangle = 2 \langle s_H | \Phi_1 \rangle \quad (11)$$

For "fixed" atomic orbitals the largest S_{kH} -value occurs for the real case (sp^3 -case) if h_k is directed towards the H-atom.

IV. THE CHOICE OF THE ATOMIC ORBITALS

In view of the results above it seems natural to let the atomic orbitals Φ_p depend on the valence angle θ through the phase factor κ . A first simple attempt in this direction would be to assume proportionality between the covalent radius of the atom and the distance to the gravity point of $|\hbar_k|^2$.

If Slater type orbitals⁵

$$\Phi_{nlm}(r\theta\varphi) = N_{nl}r^{n-1}e^{-(c/n)r}Y_{lm}(\theta,\varphi) \quad (12)$$

are used and the conventional sp^3 -hybridization is taken as norm we find⁶

$$c_k = c_{sp^3} \frac{R_{sp^3}}{R_k} \cdot \frac{\sqrt{3}/2}{[\sum_{\mu \neq 1} a_{k\mu}^2 \cdot \cos^2 \kappa_{k\mu}]^{1/2}} \quad (13)$$

where the coefficients $a_{k\mu}' = a_{k\mu} \cdot \exp(i\kappa_{k\mu})$ and c_k and c_{sp^3} are the effective nuclear charges for hybridization k and sp^3 , respectively. R_k and R_{sp^3} are the corresponding covalent radii. c_{sp^3} is determined by Slaters rules.⁵ Results by use of this method are shown in Fig. 3.

A more satisfactory way of determining the c -values would be by use of the criterion of maximal overlap. At the present time this, however, seems to destroy the simple and intuitive picture given here.

V. THE STRAIN ENERGY

Complex hybridization with fixed c -values makes it possible to approach the concept of strain energy⁷ for molecules of the type considered here in a new way. The strain energy in a bond could be defined as the difference between the bond energy in sp^3 -hybridization and the energy in the hybridization corresponding to the experimental bond angles, if the energies are calculated for the same overall geometry. If we then confine to the approximation of localized bonds the total strain energy will be the sum of the strain energies in the bonds. In case c in (12) depends on κ the concept of strain energy is meaningless.

The main advantages of the concepts discussed in this paper lie on the conceptual side. However, considerations along the lines indicated can also be of great help in problems concerning the stability of transition states in chemical reactions.

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REFERENCES

1. Slater, J. C. *Phys. Rev.* **38** (1931) 1109; Mulliken, R. S. *Phys. Rev.* **41** (1932) 67; Pauling, L. *J. Am. Chem. Soc.* **53** (1937) 1367.
2. Mårtensson, O. and Öhrn, Y. *Theoret. Chim. Acta* **9** (1967) 133.

3. The "bent bond" model for angles less than 90° is treated in, *e.g.*, Coulson, C. A. *Valence*, University Press, Oxford 1952, p. 104 ff; Del Re, G., Esposito, U. and Carpentieri, M. *Theoret. Chim. Acta* **6** (1966) 36; Veillard, A. and Del Re, G. *Theoret. Chim. Acta* **2** (1964) 55; Flygare, W. H. *Science* **140** (1963) 1179.
4. Sutton, L. D., (Ed.), *Tables of internuclear distances* (London Chem. Soc. 1958).
5. Slater, J. C. *Phys. Rev.* **36** (1930) 57.
6. Mårtensson, O. *Unpublished*.
7. See, *e.g.* Wheland, G. W. *Resonance in organic chemistry*, Wiley, New York 1955.

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