

Theory of the NonTetrahedral Carbon Atom

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Olmer have been combined with the constants of Table II to ascertain if the pressures calculated from Eq. (4) fell within the ranges cited by these authors.

The author feels that the qualitative agree-

ment in six of the seven cases in Table III tends to support the present simple adsorption theory but that more reliable confirmation must await additional experimental results of the type given in Table II.

Theory of the Non-Tetrahedral Carbon Atom

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The hybridization of s and p orbitals to give non-tetrahedral orbitals is discussed. The results are applied to cyclic hydrocarbons. For cyclopentane the theory yields an H-C-H angle of $111^\circ 1'$, and for cyclobutane an H-C-H angle of 180° .

THE method of directed valence bonds as developed by Pauling¹ is based on the following postulates. A single bond arises from the interaction of two unpaired electrons of opposite spin derived from different atoms. Of two orbitals in an atom the one which can overlap more with the orbital of another atom will form the stronger bond with that atom. The direction of this bond will be that direction in which the orbital wave functions of the two atoms overlap as much as possible. In applying these postulates to the carbon atom Pauling assumed that orbitals were formed from a combination or hybridization of s and p orbitals. The hybridization was made in such a way as to yield the maximum bond strengths.

HYBRIDIZATION IN THE NON-TETRAHEDRAL CARBON ATOM

Let us now consider how this theory is to be altered if we specify one of the valence angles of the carbon atom. Such a restriction is present in compounds such as cyclopropane, cyclobutane, and cyclopentane. It will be assumed that a certain amount of symmetry exists. Thus numbering the bonds of carbon as 1, 2, 3, and 4, it will be assumed that bonds 1 and 2 are equivalent and that bonds 3 and 4 are equivalent.

¹L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931). See also W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927); J. C. Slater, Phys. Rev. **37**, 481 (1931).

It is assumed that the radial parts of the wave functions $\psi_s, \psi_{px}, \psi_{py}, \psi_{pz}$ are so similar that their differences are negligible. The angular parts, normalized to 4π , are given by the equations

$$s = 1, \quad (1)$$

$$p_x = \sqrt{3} \sin \vartheta \cos \varphi, \quad (2)$$

$$p_y = \sqrt{3} \sin \vartheta \sin \varphi, \quad (3)$$

$$p_z = \sqrt{3} \cos \vartheta, \quad (4)$$

where ϑ and φ are the angles used in polar coordinates.

The angular part of each of the bond-forming eigenfunctions is approximated by functions of the form

$$f_i = a_i s + b_i p_x + c_i p_y + d_i p_z, \quad (5)$$

where i is 1, 2, 3, or 4. The coefficients a_i, b_i, c_i , and d_i are determined by the normalization condition

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1, \quad (6)$$

and by the orthogonality condition

$$a_i a_j + b_i b_j + c_i c_j + d_i d_j = 0, \quad i \neq j. \quad (7)$$

The direction of the maximum of the first bond eigenfunction is arbitrary. It is chosen to lie along the x axis. Hence

$$f_1 = a_1 s + (1 - a_1^2)^{1/2} p_x, \quad (8)$$

where b_1 has been replaced by $(1 - a_1^2)^{1/2}$ so that Eq. (6) might be satisfied.

The direction of the maximum of the second bond eigenfunction can without loss of generality be chosen to lie in the xz plane. Thus

$$f_2 = a_2 s + b_2 p_x + d_2 p_z. \quad (9)$$

From Eq. (6)

$$a_2^2 + b_2^2 + d_2^2 = 1. \quad (10)$$

From Eq. (7)

$$a_1 a_2 + b_1 b_2 = 0. \quad (11)$$

Since bonds 1 and 2 are assumed to be equivalent bonds

$$a_2 = a_1. \quad (12)$$

Hence

$$b_2 = -[a_1^2/(1-a_1^2)]^{1/2}, \quad (13)$$

and

$$d_2 = [(1-2a_1^2)/(1-a_1^2)]^{1/2}. \quad (14)$$

In a similar way it is found that

$$a_3 = a_4 = (\frac{1}{2} - a_1^2)^{1/2}, \quad (15)$$

$$b_3 = b_4 = -a_1 \{ [(1-2a_1^2)/(2(1-a_1^2))]^{1/2} \}, \quad (16)$$

$$c_3 = -c_4 = 1/\sqrt{2}, \quad (17)$$

$$d_3 = d_4 = -a_1/[2(1-a_1^2)]^{1/2}. \quad (18)$$

Now let us relate the direction of the maximum of the second bond eigenfunction to the value of a_1 . First substitute Eqs. (1), (2), (4), (12), (13), and (14) in Eq. (9). Then let $\varphi = 180^\circ$ and differentiate f_2 with respect to ϑ . Setting this derivative equal to zero then gives the result

$$\tan \vartheta = a_1^2/(1-2a_1^2)^{1/2}. \quad (19)$$

Since the direction of the maximum of the first bond eigenfunction lies along the x axis, the angle between the two maxima equals $90^\circ + \vartheta$.

CYCLOPENTANE

It is assumed that all the carbon atoms in cyclopentane lie in a plane and form a symmetrical ring. Also it is assumed that the directions of the bonds coincide with the directions of the maxima of the bond eigenfunctions. Consider one carbon atom in the ring and choose the coordinate axes so that f_1 and f_2 represent the angular part of the eigenfunctions which

form the bonds with the neighboring carbon atoms. The value of a_1 can be obtained using Eq. (19) and taking $\vartheta = 18^\circ$. The value of a_3 is then calculated using Eq. (15). Now consider the axes rotated so that the direction of the x axis coincides with the direction of a C-H bond. The new value of a_1 is equal to the value of a_3 in the old coordinate system. The value of the H-C-H angle can now be calculated using Eq. (19). The final result is

$$\angle \text{HCH} = 111^\circ 1'. \quad (20)$$

It is evident that this value differs appreciably from the tetrahedral angle $109^\circ 28'$.

CYCLOBUTANE

If a_1 is taken equal to zero, it is found by Eq. (19) that ϑ equals zero and hence the angle between the directions of the maxima of f_1 and f_2 equals 90° . Proceeding as before one obtains

$$\angle \text{HCH} = 180^\circ. \quad (21)$$

CYCLOPROPANE

The calculations of Herzberg² seem to support the view that the HCH angle in cyclopropane is a straight angle. This indicates an electronic structure similar to that described for cyclobutane. However now the directions of the maxima of f_1 and f_2 would not coincide with the C-C bond directions. Instead there would be a difference of 15° between each C-C bond and the maximum of f_1 and f_2 , respectively.

DISCUSSION

The results obtained are to be regarded as rough approximations. The principal effect neglected is probably the repulsion between different groups in the molecule. In the case of cyclobutane the HCH angle is probably altered considerably by the repulsion between the hydrogen atoms and the neighboring carbon atoms.

² G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).