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Bent Bonds in Cis-1,2,3-Tricyanocyclopropane

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The electronic structure of cis-1,2,3-tricyanocyclopropane has been studied by the maximum overlap method, using Clementi atomic orbitals. It is assumed that the bond energies are proportional to the corresponding overlap integrals. Scale factors were checked on the ethylene, vinylcyanide and tetracyanoethylene. Bent bonds in the cis-1,2,3-tricyanocyclopropane ring are confirmed. The possibility of the complex hybridisation in strained molecules is discussed. It is shown that the principle of maximum overlap necessarily leads to real hybridisation and consequently to the bent bonds.

Die Elektronenstruktur von cis-1,2,3-Tricyanocyclopropan wurde mit der Methode der maximalen Überlappung und unter Verwendung von Clementi-Funktionen untersucht. Dabei wurde angenommen, daß die Bindungsenergien proportional zu den entsprechenden Überlappungsintegralen sind. Die entsprechenden Faktoren wurden an Äthylen, Vinylzyanid und Tetrazyanoäthylen getestet. Die Ergebnisse zeigen, daß die Bindungen im cis-1,2,3-Tricyanocyclopropanring gekrümmt sind. In diesem Zusammenhang wurde auch auf die Möglichkeit komplexer Hybride in gespannten Molekülen eingegangen. Es zeigt sich dabei, daß das Prinzip der maximalen Überlappung notwendig zu reellen Hybriden und damit zu gekrümmten Bindungen führt.

La structure électronique du cis-1,2,3, tricyanocyclopropane a été étudiée en utilisant la méthode du recouvrement maximum pour les orbitales atomiques de Clémenti. On suppose que les énergies de liaison sont proportionelles aux intégrales de recouvrement correspondantes. Les facteurs d' ajustement ont été testés sur l'éthylène, le cyanure de vinyle et le tétracyanoéthylène. L'existence de liaisons courbes dans le cycle du cis-1,2,3, tricyanocyclopropane est confirmée. On discute de la possibilité de l'hybridation complexe dans les molécules à tensions internes. Il est montré que le principe du recouvrement maximum conduit nécessairement à une hybridation réelle et par conséquent à des liaisons courbes.

Introduction

It is well established that the chemical bond is accompanied by an increase in the electron density in the region between bonded atoms. An overlap integral $S_{AB} = \int \psi_A \psi_B d\tau$, where ψ_A and ψ_B are bonding electronic wave functions at the atoms A and B respectively, presents a good measure of the increased electronic density, or in other words, a good measure of the bonding strength [1]. It is easy to show that mixing of the "nearly" degenerate s and p orbitals of the carbon atom considerably increases the magnitude of the overlap integral [2]. Thus, we reach the maximum overlap principle, which together with the symmetry constraints and orthonormality conditions enable one to calculate hybridisation parameters [3, 4]. It can be easily seen that the orthogonality requirement for the two equivalent hybrids of the same atom necessarily leads to the bent bond concept, when the corresponding geometrical angle is less than 90°. In such a case the chemical bond is represented by the line passing through the points of the maximum electronic

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density and therefore it differs from the line joining the neighbouring atoms. Since not much is known about the electronic distribution in molecules the bent bonds have been for long the subject of controversy [5–9].

Recently, the bent bonds were experimentally found by X-ray measurements made on 2,5-dimethyl-7,7-dicyanonorcaradiene, and on cis-1,2,3,-tricyanocyclopropane [10, 11]. In this paper we present the results of the maximum overlap calculations performed on cis-1,2,3,-tricyanocyclopropane, ethylene, vinylcyanide and tetracyanoethylene. Complex hybridisation and its application to cyclopropane is discussed.

Method and Results

The scaled maximum overlap method has been already described [4, 12]. Its main features are as follows: the total overlap of the molecule is

$$S_t = \sum_{\mathrm{AB}} K_{\mathrm{AB}} \times S_{\mathrm{AB}}, \tag{1}$$

where S_{AB} is the overlap integral of the bonding hybrids. The summation is over all bonds, the partial contributions of which are weighted by factors K_{AB} in order to compensate for the difference in energies of different bonds. When the "double zeta" atomic functions of Clementi [13] are used the weighting factors are $K_{\mathrm{CC}} = 121.17$ and $K_{\mathrm{CH}} = 135.86$ for the C–C and C–H bond, respectively [8]. These were justified for a large variety of strained molecules [4, 12, 14], however, their validity has to be proved on the molecules containing C≡N groups. Therefore, a check was made on vinylcyanide, tetracyanoethylene and their parent molecule, ethylene (Fig. 1). In all the calculations we assumed that C–H and C—C≡N bonds are not bent. As a matter of fact, the deviation from the linearity is found only for C—C≡N bonds in cis-1,2,3,-tricyanocyclopropane [11]. However, it is so small that it can be neglected. Further, we assumed that the carbon atom in the C≡N group has the *sp* hybridisation, which is valid, at least, in the first approximation.

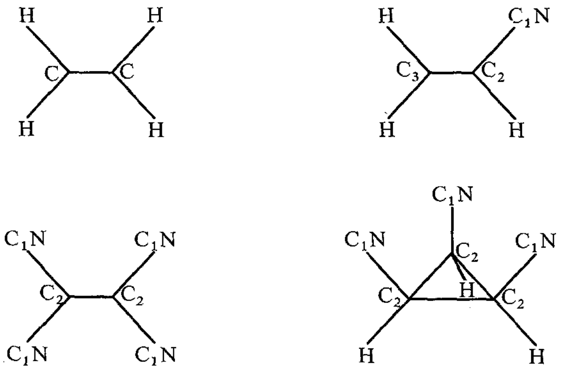

Fig. 1. Schematic diagrams of molecular geometries and numbering of C atoms: ethylene, vinylcyanide, tetracyanoethylene and cis-1,2,3-tricyanocyclopropane

Table. *Calculated maximum overlap hybrids in the shortened sp^n form, bond overlaps, and molecular angles, theoretical and experimental*

Hybrids	Bond overlap	Geometrical angle (in degrees)	
		calc.	exptl.
Ethylene			
$\psi_{CC} = sp^{1.72}$	$S_{CC} = 0.7621$		
$\psi_{CH} = sp^{2.16}$	$S_{CH} = 0.7403$	$\angle \mathrm{HCH} = 117.5$	$\angle \mathrm{HCH} = 117.6 \pm 0.5$[a]
Vinylcyanide			
$\psi_{12} = sp$ (ass.)			
$\psi_{21} = sp^{2.10}$	$S_{12} = 0.7509$		
$\psi_{23} = sp^{1.68}$			
$\psi_{32} = sp^{1.72}$	$S_{23} = 0.7655$	$\angle 321 = 122$	$\angle 321 = 122.6$[b]
$\psi_{2H} = sp^{2.25}$	$S_{2H} = 0.7386$	$\angle 32\mathrm{H} = 120.9$	$\angle 32\mathrm{H} = 121.7$[b]
$\psi_{3H} = sp^{2.16}$	$S_{3H} = 0.7403$	$\angle \mathrm{H3H} = 117.5$	$\angle \mathrm{H3H} = 117.5$[b]
Tetracyancethylene			
$\psi_{22} = sp^{1.66}$	$S_{22} = 0.7711$		
$\psi_{21} = sp^{2.19}$	$S_{12} = 0.7457$	$\angle 212 = 117.1$	$\angle 212 = 117.4$[c]
cis-1,2,3-Tricyanocyclopropane			
$\psi_{21} = sp^{2.68}$	$S_{12} = 0.7320$		
$\psi_{22} = sp^{3.86}$	$S_{22} = 0.6060$		
$\psi_{2H} = sp^{2.19}$	$S_{2H} = 0.7873$	$\angle 12\mathrm{H} = 114.3$	$\angle 12\mathrm{H} = 116.2 \pm 1.1$[d]

[a] Ref. [11]. – [b] Ref. [12]. – [c] Ref. [13]. – [d] Ref. [7].

Thus, the C≡N group is left out from the variation procedure. Experimental bond distances and the values of basic overlap integrals are taken from papers already published [15–18]. The extremum of the expression (1) is found by a numerical procedure, performing a calculation for an assumed initial hybrid composition and a systematic variation of the independent parameters. The maximum overlap hybrids (in the shortened sp^n form) and molecular angles are given in the Table. There is a good agreement between calculated and experimental molecular angles, what supports previous assumptions. The same procedure was applied to cis-1,2,3,-tricyanocyclopropane taking the experimental bond distances obtained by Hartman and Hirshfeld [11]. The results are summarised in the Table.

Discussion

It is well known that orbital hybridisation has a significant effect on the molecular properties. It has been found that there is a good correlation between spin-spin coupling constants, bond lengths, inductive constants and the hybridisation ratio [19–21]. A good quantitative agreement between experimental molecular angles and angles obtained by the maximum overlap method, previously reported [4, 12, 14] has been confirmed by the present results. All angles with the exception of the H–C–C≡N angle of cis-1,2,3,-tricyanocyclopropane are within the experimental error. The deviation of the later from the experimental value is about 2°. The bond lengths are also compatible with the obtained hybridisation contents. For instance, the exocyclic C–C bond length of tricyanocyclopropane, C—C = 1.449 Å, is between the values characteristic for an $sp-sp^2$ and an $sp-sp^3$ hybridisation [22]. This is in good agreement with the $sp-sp^{2.7}$ hybridisation obtained by the maximum overlap method. The hybridisation in the C–H bond of the same molecule is of the $sp^{2.2}$ type, which compared with the $sp^{2.4}$ hybridisation found in cyclopropane [12], shows an increase in the s character. Since a larger s content means a shorter covalent bond, the change in s character explains to some extent the shortening of the C–H bond. Hartman and Hirshfeld found that the maximum of the electronic density of the highly strained endocyclic C–C bond in cis-1,2,3,-tricyanocyclopropane is displaced from the internuclear vector. The line joining the carbon atom and the point of the maximum electronic density, makes an angle of 22° with the straight line connecting neighbouring carbon atoms. The deviation of our maximum overlap hybrids is 22.5°. Since the symmetry axis of the real hybrid coincides with the line passing through the maximum density of the hybrid, the above deviation is in a fairly good accordance with the experimental data as well as with the results of the calculations performed on cyclopropane [5, 12]. In order to be more precise, it should be pointed out that the agreement with the experiment is only of a qualitative nature, since the maximum density curve is certainly closer to the straight line connecting neighbouring nuclei.

Trying to retain the advantage of the well defined bond lengths and valence angles Mårtensson and Öhrn [23] introduced the complex hybrids. These are discussed here in some detail with special emphasis to their application to cyclopropane. The complex hybrids proposed by these authors are of the form:

$$h_k = a_{k1}(s) + f(r)\left[a_{k2}\frac{x}{r} + a_{k3}\frac{y}{r} + a_{k4}\frac{z}{r}\right] \tag{2}$$

where $a_{ki}(i = 1 \dots 4)$ are the elements of the k-th row of the unitary matrix $\boldsymbol{a}$. Since the phases of the hybrids are arbitrary, they were chosen so that the first column of the matrix $\boldsymbol{a}$ was real. The direction of the hybrid is defined as the direction of the line connecting the carbon nucleus and the center of the hybrid density. The direction cosines of the hybrid center are:

$$\gamma_{k\mu} = \frac{\langle h_k|\mu|h_k\rangle}{\left[\sum\limits_{\nu=x,y,z} \langle h_k|\nu|h_k\rangle^2\right]^{1/2}}, \tag{3}$$

where the Greek indices represent the coordinates x, y, and z. It can be easily shown that the phase convention mentioned above gives the direction cosines of the form:

$$\gamma_{k\mu} = \frac{\mathrm{Re}\{a_k n(\mu)\}}{\left[\sum\limits_{m=2}^{4} (\mathrm{Re}\{a_{km}\})^2\right]^{1/2}}, \tag{4}$$

where $n(x) = 2$, $n(y) = 3$, and $n(z) = 4$. It follows that the direction cosines are completely defined by the real parts of p orbitals. This definition is not entirely free of criticism, and one could define the hybrid direction as a direction of the straight line joining the carbon atom and the point of the maximum hybrid density. However, if the directional properties of the hybrids are defined by Eqs. (3) and (4), then the complex hybrids are more flexible than the real ones. Namely, the unitary matrix $\boldsymbol{a}$ of order four with a real first column has twelve real parameters. Eight parameters are determined by the direction cosines of the four nonequivalent hybrids, so there are four real parameters left. Let us consider the complex hybrids of cyclopropane. Since the hybrids are of the C_{2v} local symmetry, we have only two independent parameters. If the coordinate system is chosen as suggested by Mårtensson and Öhrn [5], the matrix $\boldsymbol{a}$ in general form is as follows:

$$\boldsymbol{a} = \begin{pmatrix} \mathrm{Re}\{a_{11}\} & a_{12} & a_{13} & 0 \\ \mathrm{Re}\{a_{11}\} & a_{12} & -a_{13} & 0 \\ \mathrm{Re}\{a_{31}\} & a_{32} & 0 & a_{34} \\ \mathrm{Re}\{a_{31}\} & a_{32} & 0 & a_{34} \end{pmatrix}. \tag{5}$$

The first two rows present the hybrids of the C–H bonds and the last two rows are the hybrids of the cyclopropane ring. Taking into account the direction cosines and fixing independent parameters, it is possible to construct hybrids which lie along the C–C bonds. Mårtensson and Öhrn [23] postulated that all elements of the first column are equal to 1/2 and that $\mathrm{Im}\{a_{13}\} = 0$. The resulting hybrids were all of the sp^3 type. We defined the overlap of the bonding hybrids as the absolute value of the corresponding overlap integral. A simple calculation shows that complex hybrids obtained by Mårtensson and Öhrn [23] have a smaller overlap than real hybrids obtained by the scaled maximum overlap method [12]. Therefore, we have attempted to determine the complex hybrids with maximum overlapping. The first step was to take matrix $\boldsymbol{a}$ (5) in its simplest form. Since the C–H bonds make an angle larger than 90°, their hybrids do not need the imaginary parts. Therefore, we could state that $\mathrm{Im}\{a_{12}\} = \mathrm{Im}\{a_{13}\} = 0$. The complex coefficients were retained only for C–C bonds. Under these conditions overlap integrals were real entities. The matrix elements a_{ki} are functions of the hybrid directions (Eq. (4)) and we have to determine directions of hybrids which correspond to the maximum overlap. Using Clementi atomic functions and standard weighting factors for S_{CC} and S_{CH} overlaps, we found that the best hybrids are of the form:

$$\begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \end{pmatrix} = \begin{pmatrix} 0.542 & 0.455 & 0.707 & 0 \\ 0.542 & 0.455 & -0.707 & 0 \\ 0.455 & -0.542 & 0 & 0.707 \\ 0.455 & -0.542 & 0 & 0.707 \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix}. \tag{6}$$

The HCH angle, obtained by the scaled maximum overlap method is 114° what is in good agreement with the experimental value of 113.6° ± 2° [24] and with earlier theoretical results [5, 12]. The bending of the hybrids describing C–C bonds is 22.5°, this value being equal to the result already obtained on cis-1,2,3,-tricyanocyclopropane. This is not a surprising result because a real function is the best variational function for the real Hamiltonian [25]. In other words, real hybrids obtained by the scaled maximum overlap method describe bent chemical bonds better than the complex hybrids do.

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