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Some Remarks on the Use of Experimental Bond Lengths in the Maximum Overlap Method

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The hybridization in norbornane, ethane, acetylene, cyclopropane, cyclobutane and cyclopentane has been reexamined by the maximum overlap calculations based on experimental bond lengths. The irregularity in the variations of the C—C bond lengths in small ring hydrocarbons is discussed and a qualitative agreement with the experimental bond lengths has been found. The results also indicate that the use of experimental molecular geometry is advantageous for the maximum overlap method.

The maximum overlap method was recently applied to a large number of cyclic and polycyclic hydrocarbons[1-4]. It has been found that the hybrids so obtained are very useful in discussing the bonding in these molecules and several empirical correlations between the hybridization parameters and various physical and chemical bond properties were established. However, most of the calculations so far reported were based on standard bond lengths: d (C—C) = 1.535 Å and d (C—H) = 1.07 Å for the CC and CH bonds respectively. Some most recent results on correlations of CC and CH bond lengths with corresponding bond overlaps indicate that better quantitative agreement with experimental data is possible if experimental bond lengths are involved in the maximum overlap procedure[5]. Therefore, it seems worthwhile to reevaluate the hybridization in some interesting molecules by adopting experimental molecular geometries.

In this paper we consider in particular the hybridization obtained by the maximum overlap method for norbornane, ethane, acetylene, cyclopropane, cyclobutane and cyclopentane for which fairly accurate bond lengths are available. The details of the maximum overlap procedure have already been reported[1,2]. Briefly, coefficients of the hybrids $\psi_{ij} = a_{ij}\,(2\,s) + (1 - a_{ij}^2)^{1/2}\,(2\,p)$ are varied in order to obtain the maximum of the sum of the suitably weighted bond overlap integrals

$$S = k_{CH}\,\Sigma\,S_{CH} + k_{CC}\,\Sigma\,S_{CC} \tag{1}$$

where the weighting factors k_{CH} and k_{CC} take into accoount the difference in energies of the CC and CH bonds. The weighting factors depend on the nature of the atomic functions employed in the calculations. For the radial parts of the orbitals we adopted Clementi double zeta atomic functions[6]. Then the weighting factors are: k_{CH} = 135.9 kcal mole^{-1} and k_{CC} = 121.2 kcal mole^{-1}. The basic overlap integrals were taken from the available tables[7]. The hybrids of the same carbon atom are mutually orthogonal since the interaction between the adjacent bonds is neglected in our scheme. This leads to the following relationship between the coefficients of mixing a_{ij} and a_{ik} and the interhybrid angle ϑ_{jk}:

$$a_{ij}\, a_{ik} + (1 - a_{ij}^2)^{1/2} (1 - a_{ik}^2)^{1/2} \cos \vartheta_{jk} = \begin{cases} 1 \text{ if } j = k \\ 0 \text{ if } j \neq k \end{cases} \qquad (2)$$

The interbond angles in cyclic systems are frequently different from the interhybrid angles, *i. e.* the hybrids are inclined to the internuclear line by the bending angles δ_{ij}. The actual search for the optimum parameters is a numerical one assuming the initial set of parameters and varying them until the maximum of expression (1) is achieved.

RESULTS

The results of the application of the maximum overlap method on norbornane, ethane, acetylene, cyclopropane, cyclobutane and cyclopentane are summarized in the Table. The hybrids are presented in the shorthand sp^n notation where n is a noninteger defined by the relation $n = (1 - a^2)/a^2$. Earlier obtained results are given in parentheses for comparison.

DISCUSSION

Norbornane

The geometry of norbornane and structurally related compounds was thoroughly investigated by different experimental methods[8]. However, the bond lengths in norbornane are still the subject of controversy since there is a long CC bond [d (C—C) = 1.57 Å] which is not uniquely assigned in this molecule. Thus, Morino *et al.*[9] ascribed the long CC bond to the bridge bond while Dallinga and Toneman[8] attributed it to the wing part of the molecule. Earlier maximum overlap calculations based on the assumption that all CC bonds are equal (1.54 Å) have shown that the C_1—C_7 bridge bond has the smallest overlap[3]. Since the smaller overlap means the larger bond length[5] we accepted in this paper the geometry of norbornane skeleton as proposed by Morino *et al.*[9]. The resulting hybridization parameters show some interesting changes as compared with earlier results. The *p* characters of the hybrid orbitals forming the CC bonds of the wings are decreased being still larger than in the sp^3 hybridization state. This is in accordance with the unusual reactivity evidence of the norbornylbenzenes[10]. The *s* character of the $\psi_{1\cdot\cdot} \equiv \psi_{1\cdot}$ hydrids is transferred to the neighbouring C_1—H bond which is described by the $\psi_{14} = sp^{2.48}$ hybrid being thus intermediate between the sp^3 and sp^2 states. This hybrid exhibited the largest change illustrating at the same time that the noninteger hybrids sometimes deviate considerably from the ideal hybridization states. The bonds of the norbornane bridge increased the *p* character thus contributing to the weakening of these bonds. The hybrids ψ_{17} and ψ_{71} and the corresponding bending angles are similar to those found in the cyclobutane ring. This is not suprising since *(a)* the $C_1C_7C_4$ angle is very close to the right angle and *(b)* the hybrids forming the bond tend to have the same hybridization parameter. If we neglect, as a first approximation, the relatively small deviations of the hybrids participating in the CC bonds, we can apply the formulae which correlate the bond lengths with the bond overlaps

$$d(C-C) = -1.166\, S_{CC} + 2.298 \tag{3}$$

and

$$d(C-H) = -0.869\, S_{CH} + 1.726 \tag{4}$$

for the CC and CH bonds respectively[5]. The results obtained are cited in the last column of the Table. A very close agreement between the calculated and the experimental bond lengths provided by electron diffraction measurements of Morino *et al.*[9] supports their claim that the C_1—C_7 bond is particularly long.

Ethane and Acetylene

The hybridization in ethane remains unaltered since the new CC and CH bond lengths are similarly decreased resulting in almost parallel change of the basic overlap integrals. This confirms at the same time an earlier conclusion that the hybridization in the methyl group is practically constant and unaffected by its environment[11].

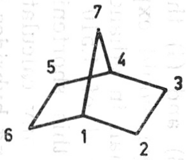
Acetylene is quoted in most textbooks as a typical example of the *sp* hybridization. However, the CC and CH bonds are of different kind and consequently there is no reason for the *sp* hybridization. We found that the CC and CH bonds are described by $\psi_{CC} = sp^{0.80}$ and $\psi_{HC} = sp^{1.25}$ hybrids. There is only a slight difference between the obtained hybrids and those calculated earlier[12]. If the Muller-Pritchard[13] relationship $J_{C^{13}-H} = 5$ (s %) is applied to acetylene assuming the ideal *sp* hybridization, the calculated $J_{C^{13}-H}$ value of 250 cps is in surprisingly good agreement with the experimental value of 248.7 cps[14]. The *sp* hybridization is only a crude approximation and if the more reliable hybridization $sp^{1.25}$ obtained by the maximum overlap method is used the Muller-Pritchard formula fails to give a satisfactory result: $J_{C^{13}-H}$ calculated is only 222.6 cps. However, the Muller-Pritchard correlation can be modified and improved by the inclusion of the bond overlap integral arising from the normalization constant of the localized orbital describing the C—H fragment[15]. Then the calculated $J_{C^{13}-H}$ spin-spin coupling constant is 247.8 cps what is in excellent agreement with the experimental value.

Cycloalkanes

The main feature of the present calculation in the series cyclopropane, cyclobutane and cyclopentane is the increase in the *s* character of the carbon-hydrogen bonds; it is most pronounced in cyclopropane. The CH bond lengths calculated by means of eqn. (4) are in excellent agreement with the experimental ones. The carbon-carbon bond lengths in cyclopropane and cyclobutane deserve some more comments. It is evident from the Table that the CC bond overlaps in strained rings are smaller than, for instance, in ethane. This is the result of the hybrid deviations which necessarily appear in small rings. It follows from eqns. (3) and (4) that the smaller overlap means the longer CC bond. Therefore we would expect that the CC bond in cyclopropane is considerably longer than in ethane. This, however, is not the case since the cyclopropane CC bond of 1.510 Å is unusually short. Coulson and Moffitt[16] tried to explain this shortening by the π-character of the CC bond, but they did not make any calculations. In order to settle this point let us consider two neighbouring hybrides inclined by the angle δ

TABLE

Maximum Overlap Hybrids, Corresponding Deviation Angles, Bond Overlaps and Experimental and Calculated Bond Lengths

Molecule	Hybridization	Bending	Overlap	Bond Lengths (exp.)	Bond Lengths (calcd.)
	$\psi_{12} = sp^{3.14}$ $(sp^{3.29})$	$\delta_{12} = 2.8^0$ (5^0)	$S_{12} = 0.650$ (0.643)	1.539 ± 0.015^8 (1.54)	1.540
	$\psi_{21} = sp^{3.15}$ $(sp^{3.26})$ $\psi_{23} = \psi_{21}$	$\delta_{21} = 2.5^0$ (1.5^0) $\delta_{23} = \delta_{21}$	$S_{23} = 0.650$ (0.645)	1.539 ± 0.025 (1.54)	1.540
	$\psi_{17} = sp^{3.36}$ $(sp^{3.35})$	$\delta_{17} = 6.5^0$ (8^0)	$S_{17} = 0.631$ (0.639)	1.568 ± 0.016 (1.54)	1.562
	$\psi_{71} = sp^{3.42}$ $(sp^{3.36})$ $\psi_{1H} = sp^{2.48}$ $(sp^{2.29})$ $\psi_{2H} = sp^{2.86}$ $(sp^{2.77})$	$\delta_{71} = 7.5^0$ (4.5^0)	$S_{1H} = 0.725$ (0.746) $S_{2H} = 0.718$ (0.737)	1.114 ± 0.012 av (1.07)	1.096 1.102
	$\psi_{7H} = sp^{2.65}$ $(sp^{2.69})$		$S_{7H} = 0.722$ (0.738)		1.099
Ethane	$\psi_{CH} = sp^{2.94}$ $(sp^{2.94})$ $\psi_{CC} = sp^{3.20}$ $(sp^{3.20})$		$S_{CH} = 0.722$ (0.720) $S_{CC} = 0.650$ (0.648)	1.096^a (1.102) 1.534 (1.543)	1.099 1.540
Acetylene	$\psi_{CH} = sp^{1.25}$ $(sp^{1.29})$ $\psi_{CC} = sp^{0.80}$ $(sp^{0.77})$		$S_{CH} = 0.771$ (0.769) $S_{CC} = 0.858$ (0.861)	1.059 (1.063) 1.205^b (1.201)	1.056
Cyclopropane	$\psi_{CH} = sp^{2.50}$ $(sp^{2.40})$ $\psi_{CC} = sp^{3.67}$ $(sp^{3.86})$	$\delta = 22.9^0$ (22.5^0)	$S_{CH} = 0.733$ (0.744) $S_{CC} = 0.613$ (0.599)	1.089^c (1.07) 1.510 (1.535)	1.089 1.491*
Cyclobutane	$\psi_{CH} = sp^{2.65}$ $(sp^{2.62})$ $\psi_{CC} = sp^{3.42}$ $(sp^{3.47})$	$\delta = 8.5^0$ (8.4^0)	$S_{CH} = 0.729$ (0.739) $S_{CC} = 0.635$ (0.636)	1.092^d (1.07) 1.548 (1.535)	1.092 1.528*
Cyclopentane	$\psi_{CH} = sp^{2.82}$ $(sp^{2.75})$ $\psi_{CC} = sp^{3.20}$ $(sp^{3.28})$	$\delta = 0.1^0$ (-0.1^0)	$S_{CH} = 0.724$ (0.736) $S_{CC} = 0.649$ (0.646)	1.095^d (1.07) 1.538 (1.535)	1.097 1.534*

[a] K. Kuchitsu, J. Chem. Phys. 49 (1968) 4456.

to the internuclear line (Fig. 1). Since they form a bent bond the maximum electronic density curve is displaced from the internuclear vector. We shall assume that a parabola, which approaches points A and B the hybrids being its tangents, describes approximately this line. A calculation shows that

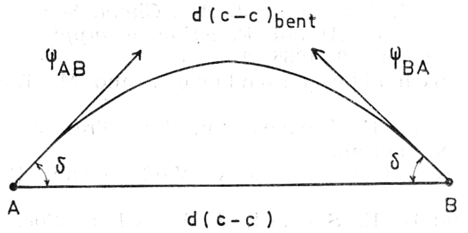


Fig. 1. Schematic Presentation of the Bent Bond.

the distance between the vertex of this parabola in cyclopropane and the internuclear line is 0.319 Å; it is in full agreement with the displacement of 0.32 Å of the maximum electronic density point found by X-ray measurements in *cis*-1,2,3-tricyanocyclopropane[17]. It can be easily found that

$$d\,(C - C) = K\,(\delta)\,d\,(C - C)_{\text{bent}} \tag{5}$$

where $d\,(C—C)_{\text{bent}}$ is the length of the parabola between the points A and B while $K\,(\delta) = 2\,\text{tg}\,\delta/[\text{tg}\,\delta\,(1 + \text{tg}^2\,\delta)^{1/2} + \ln\,(\text{tg}\,\delta + (1 + \text{tg}^2\,\delta)^{1/2})]$. In order to get some insight into the shortening of the CC bonds in strained rings we have to replace $d\,(C—C)_{\text{bent}}$ by a reference straight CC bond length. We adopted the value of 1.534 Å, appearing in ethane, as the standard CC bond length. Then by the following eqn.

$$d\,(C - C) = 1.534\,K\,(\delta)\ \text{Å} \tag{6}$$

quantitative estimates of the CC bond lengths in strained hydrocarbons can be obtained. The results of the applications of eqn. (6) on the series cyclopropane, cyclobutane and cyclopentane are presented in the Table. The calculated bond lengths are in good accordance with the experimental ones but their magnitudes are consistently low. However, it has to be recalled that our reference bond length corresponds to the $sp^{3.2}$—$sp^{3.2}$ hybridization and that the hybrids describing the CC bonds in cyclopropane and cyclobutane are $sp^{3.67}$ and $sp^{3.42}$ respectively. It is likely that the increased *p*-character in the latter molecules would lengthen the bonds, thus improving the agreement with the experimental bond lengths.

Finally, we can say that the use of experimental bond lengths in maximum overlap calculations does not alter the qualitative conclusions obtained with standard bond lengths. However, quantitative agreement with the experimental data is generally better when experimental bond lengths are used in the calculations. Thus we can recommend their use in further applications of the maximum overlap method.

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IZVOD

Primjedbe na primjenu eksperimentalnih dužina veza u metodi maksimalnog prekrivanja

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Ponovo je primjenom metode maksimalnog prekrivanja, te uzimanjem u obzir eksperimentalnih dužina veza ispitana hibridizacija u norbornanu, etanu, acetilenu, ciklopropanu, ciklobutanu i ciklopentanu. Rezultati idu u prilog daljnje upotrebe eksperimentalne molekularne geometrije u računima maksimalnog prekrivanja. Diskutirane su dužine C—C veza u malim prstenastim ugljikovodicima, i postignuto je dobro kvalitativno slaganje s eksperimentalnim podacima.

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