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## Hybridization in Several Polycyclic Alkanes by the Method of Maximum Overlap\*

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The hybridization in spiro-pentane, nortricyclene, cubane, tricyclo(1.1.0.0<sup>2,4</sup>)butane, bicyclo(1.1.1)pentane, and tetracyclo(3,3.1<sup>2,8</sup>.0<sup>4,6</sup>)nonane has been determined by the method of maximum overlap. For the atomic functions Clementi Orbitals (ref. 1) have been assumed. A comparison between these results and those, obtained previously, by assuming Slater orbitals indicates the improvements that can be achieved by using more exact wave functions. The overlaps for CC bonds fall into the groups: (1)  $S < 0.61$ , (2)  $0.61 < S < 0.63$  and (3)  $S > 0.64$ . They are characteristic of highly strained three-membered rings, ( $\delta \sim 20^\circ$ ), of four membered rings, ( $\delta \sim 10^\circ$ ), and of normal or very slightly bent bonds, ( $\delta < 5^\circ$ ), respectively.

### INTRODUCTION

In this paper we consider an application of the method of maximum overlap to several polycyclic alkanes. However, we will not use as basic functions the well known Slater orbitals. Instead of we employ a particular linear combination of Slater type orbitals recently suggested for molecular calculations by Clementi<sup>1</sup>. In previous applications of the maximum overlap method to calculations of the hybridization in a number of strained cycloalkanes<sup>2-5</sup> for the form of the atomic radial functions Slater orbitals have been assumed. It is known that these functions do not behave satisfactorily at large distances, which is the region of interest for molecular problems. It is therefore of considerable importance to resort to more accurate functions. But the approximate nature of the maximum overlap method does not require extremely high precision on the wave functions. For example, a precision such as associated with the Hartree-Fock SCF functions. Functions recently recommended by Clementi attain a fair degree of the accuracy, and seem therefore adequate for our purpose. These functions are of the so called »double zeta« type<sup>6</sup>; each Slater orbital is replaced by two Slater-type functions. They form an orthogonal set, the coefficients and exponents are found by minimizing the energy. They are also sufficiently different from Slater orbitals to make it worthwhile to re-evaluate the hybridization in molecules already considered employing the simple Slater orbitals. For example, for the Clementi functions the C—C basic atomic overlap integrals  $(2p, 2p)_\delta$  and  $(2p, 2p)$  are of the same magnitude, while the corresponding integrals for Slater orbitals differ considerably. The calculations of the hybridization

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zation in cases when there already exist similar calculations based on Slater orbitals will therefore provide information as to the extent by which the results of the maximum overlap method depend on the assumed form of the orbitals, and how much they improve by using more realistic functions. Also they will show to what extent the results of the calculations are restricted by inherent limitations of the method itself. The revised values for bond overlaps and hybrids will facilitate comparison with calculations on related molecules based also on Clementi orbitals<sup>7</sup>. Finally the results for cyclopropane, cyclobutane, and cyclopentane indicate that the revised figures obtained by using the Clementi orbitals are generally more satisfactory than the earlier ones obtained by using the Slater orbitals<sup>8</sup>.

Here we consider the following molecules: spiropentane, nortricyclene, cubane, tricyclo(1.1.0.0<sup>2,4</sup>)butane, bicyclo(1.1.1)pentane and tetracyclo(3.3.1.0<sup>2,8</sup>.0<sup>4,6</sup>)nonane, all have been treated by the method of maximum overlap assuming the Slater orbitals<sup>3,9</sup>. Therefore a description of the calculations and the details, concerning the choice of parameters, the relationships between various hybrid coefficients, interorbital angles and the geometry for these molecules will not be repeated here. The basic atomic overlap integrals for Clementi orbitals, for assumed bond lengths: CH = 1.07 Å, and CC = 1.535 Å, are<sup>10</sup>:

$$\begin{array}{ll} (1s_H, 2s_C) = 0.5843 & (2s_C, 2s_C) = 0.3569 \\ (1s_H, 2p_C) = 0.5083 & (2s_C, 2p_C) = 0.4145 \\ & (2p_C, 2p_C)_\sigma = 0.2739 \\ & (2p_C, 2p_C)_\pi = 0.2644 \end{array}$$

The weighting factors, which scale the contributions of CC and CH bonds in order to account for differences in bond energies between the two kinds of bonds become:  $k_{CH} = 135.9$  and  $k_{CC} = 121.2$ .

#### RESULTS AND DISCUSSION

Diagrams of the molecules considered are shown in the Figure 1. Carbon atoms are numbered 1—4, depending on the number of neighbouring carbon atoms to which they are bonded. A hybrid orbital designated  $\psi_{ij}$  is directed from carbon atom  $i$  towards carbon atom  $j$ . Hybrids directed towards hydrogen atoms are designed as  $\psi_{iH}$ . In nortricyclene hybrids of the bridge head carbon are marked with a prime. The results are summarized in Table I. Comparison with the results obtained with Slater orbitals indicates that the major change, caused by the increased value of carbon-carbon  $\pi$ -overlap, is a decrease of the p-content of the CC-hybrids, and an increase of the p-content of the CH-hybrids. Because in highly strained systems the CC-hybrids already have a high p-content, and correspondingly the CH-hybrids have a low p-content, a general effect is a smaller deviation of the hybrids from  $sp^3$  hybridization. Thus for example, in spiropentane hybrid  $\psi_{22}$ , describing the external CC bond of C<sub>3</sub>-ring, is  $sp^{4.91}$  for Slater orbitals, and has changed to  $sp^{3.78}$  for Clementi orbitals, while the corresponding CH-hybrids have changed from  $sp^{2.04}$  to  $sp^{2.40}$  respectively. In less strained systems CC-hybrids may further increase their s-content. An extreme case is the hybrid  $\psi_{32} = sp^{2.49}$  in tetracyclononane. The difference between the hybrids describing methylene bridge in this molecule and related

\* The numbering of atoms in ref. 4 is different.

nortricyclene is interesting. In tetracyclononane the bending of the bridge is towards inside and is small ( $\delta_{3,2} = -2^\circ$ ). In nortricyclene the bending is appreciable ( $\delta_{3,2} = 9^\circ$ ). Therefore the hybrid  $\psi_{3,2}$  in nortricyclene prefer a higher p-content, with the result that  $\psi_{3H}$  has a very high s-content:  $sp^{1.93}$ . This is close to an idealized  $sp^2$  hybridization, assumed, for example, in benzene. It is than not suprising that the C—H stretching frequency in infrared spectra of nortricyclene<sup>11</sup> and benzene\* appears at approximately the same place:  $3070\text{ cm}^{-1}$ .

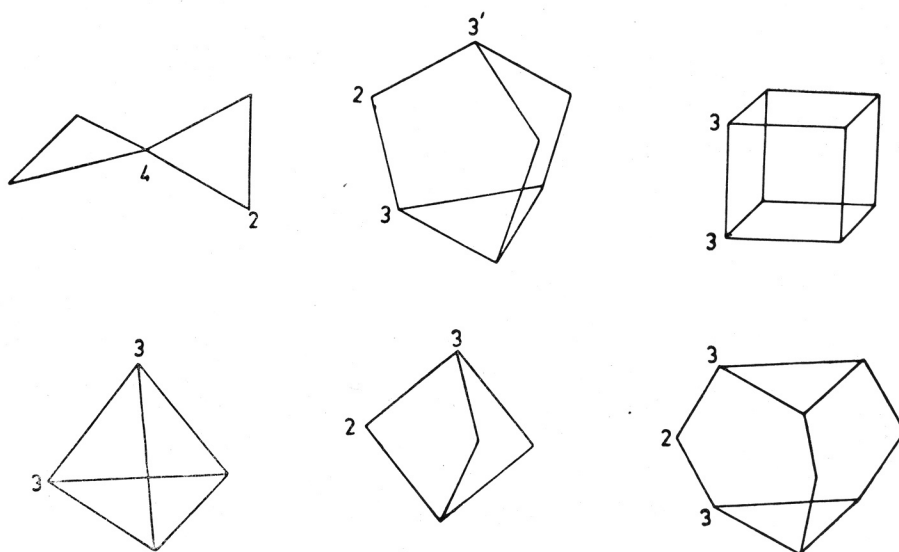


Fig. 1. Schematic diagrams of molecular geometries and numbering of atoms: spiropentane, nortricyclene, cubane, tricyclobutane, bicyclopentane and tetracyclononane.

TABLE I

Maximum overlap hybrids, bond overlaps, and scaled overlaps and various angles.  $\Theta_{ijk}$  is the angle at atom  $i$ , between hybrids directed towards atoms  $j$  and  $k$ .  $\Phi_{ijk}$  is the geometrical angle between bonds  $C_i-C_j$  and  $C_i-C_k$ .  $\delta_{ij}$  is the deviation angle of hybrid  $\psi_{ij}$  from the bond  $C_i-C_j$ .

Hybrid	(b/a) <sup>2</sup>	Bond overlap	Scaled overlap
<b>Spiropentane</b>			
$\psi_{4,2} = 0.5000(s) + 0.8660(p)$	$sp^{3.00}$		
$\psi_{2,4} = 0.4516(s) + 0.8922(p)$	$sp^{3.90}$	$S_{2,4} = 0.6089$	73.79
$\psi_{2,2} = 0.4553(s) + 0.8904(p)$	$sp^{3.82}$	$S_{2,2} = 0.6005$	72.76
$\psi_{2H} = 0.5426(s) + 0.8400(p)$	$sp^{2.40}$	$S_{2H} = 0.7440$	101.08
$\Theta_2^{2,4} = 105^\circ$ , $\Theta_4^{2,2} = 109^\circ 28'$ , $\Theta_2^{HH} = 114^\circ 33'$ .			
$\delta_{2,2} = \delta_{2,4} = 22^\circ 30'$ , $\delta_{4,2} = 24^\circ 44'$ .			

\* An average of several CH stretching frequencies.

Hybrid	(b/a) <sup>2</sup>	Bond	Scaled
<b>Nortricyclene</b>			
$\psi'_{32} = 0.4889(s) + 0.8723(p)$	sp <sup>3.18</sup>	$s'_{23} = 0.6442$	78.05
$\psi_{23} = 0.4808(s) + 0.8768(p)$	sp <sup>3.33</sup>	$s_{23} = 0.6428$	77.88
$\psi_{23} = 0.4808(s) + 0.8768(p)$	sp <sup>3.33</sup>	$s_{33} = 0.5994$	72.63
$\psi_{32} = 0.4971(s) + 0.8677(p)$	sp <sup>3.05</sup>	$s_{2H} = 0.7376$	100.21
$\psi_{33} = 0.4534(s) + 0.8913(p)$	sp <sup>3.86</sup>	$s'_{3H} = 0.7411$	100.69
$\psi_{2H} = 0.5185(s) + 0.8551(p)$	sp <sup>2.72</sup>	$s_{3H} = 0.7514$	102.08
$\psi'_{3H} = 0.5316(s) + 0.8470(p)$	sp <sup>2.54</sup>		
$\psi_{3H} = 0.5730(s) + 0.8196(p)$	sp <sup>2.05</sup>		
$\Theta_2^{33} = 107^\circ 30'$ , $\Theta_3^{33} = 105^\circ$ , $\Theta_2^{HH} = 111^\circ 34'f$			
$\delta_{3,2} = 3^\circ 30'$ , $\delta_{23} = 4^\circ$ , $\delta_{23} = 9^\circ$ , $\delta_{32} = 10^\circ$ , $\delta_{33} = 22^\circ 30'$ .			
<b>Tetracyclononane</b>			
$\psi_{33} = 0.4592(s) + 0.8883(p)$	sp <sup>3.74</sup>	$s_{33} = 0.6022$	72.96
$\psi_{32} = 0.5272(s) + 0.8497(p)$	sp <sup>2.60</sup>	$s_{32} = 0.6568$	79.58
$\psi_{23} = 0.4859(s) + 0.8740(p)$	sp <sup>3.24</sup>	$s_{2H} = 0.7363$	100.03
$\psi_{2H} = 0.5137(s) + 0.8580(p)$	sp <sup>2.79</sup>	$s_{3H} = 0.7454$	101.27
$\psi_{3H} = 0.5480(s) + 0.8365(p)$	sp <sup>2.33</sup>		
$\Phi_2^{33} = 112^\circ$ , $\Theta_2^{33} = 108^\circ$ , $\Theta_3^{33} = 105^\circ 30'$ , $\Theta_2^{HH} = 111^\circ$			
$\delta_{32} = \delta_{23} = 2^\circ$ , $\delta_{33} = 22^\circ 45'$ , $t = 122^\circ$ .			
<b>Bicyclopentane</b>			
$\psi_{32} = 0.4756(s) + 0.8797(p)$	sp <sup>3.42</sup>	$s_{23} = 0.6216$	75.32
$\psi_{32} = 0.4592(s) + 0.8883(p)$	sp <sup>3.74</sup>	$s_{2H} = 0.7428$	100.91
$\psi_{2H} = 0.5377(s) + 0.8431(p)$	sp <sup>2.46</sup>	$s_{3H} = 0.7500$	101.89
$\psi_{3H} = 0.5669(s) + 0.8238(p)$	sp <sup>2.11</sup>		
$\Phi_2 = 74^\circ$ , $\Theta_2^{33} = 105^\circ 30'$ , $\Theta_3^{22} = 107^\circ$ , $\Theta_2^{HH} = 114^\circ$ .			
$\delta_{23} = 15^\circ 45'$ , $\delta_{32} = 15^\circ 10'$ .			
<b>Cubane</b>			
$\psi_{33} = 0.4756(s) + 0.8797(p)$	sp <sup>3.42</sup>	$s_{33} = 0.6297$	76.30
$\psi_{3H} = 0.5669(s) + 0.8238(p)$	sp <sup>2.11</sup>	$s_{3H} = 0.7500$	101.89
$\Theta_3^{33} = 107^\circ$ , $\delta_{33} = 13^\circ 25'$ .			
<b>Tricyclobutane</b>			
$\psi_{33} = 0.4534(s) + 0.8913(p)$	sp <sup>3.86</sup>	$s_{33} = 0.5759$	69.78
$\psi_{3H} = 0.6190(s) + 0.7854(p)$	sp <sup>1.61</sup>	$s_{3H} = 0.7609$	103.38
$\Theta_3^{33} = 105^\circ$ , $\delta_{33} = 31^\circ 05'$ .			

On the other hand, in tetracyclononane s-p content of the hybrids  $\psi_{32}$  and  $\psi_{3H}$  is more even, the hybrids are:  $sp^{2.49}$  and  $sp^{2.31}$  respectively.

A list of CC bond overlaps for the molecules considered is given in Table II. The CC bond overlaps form three distinct groups: overlaps below 0.6100 appear in three-membered rings, those between 0.6100 and approximately 0.6400 are characteristic of four-membered rings, and the CC bond overlaps above 0.6400 signify normal CC bonds, or CC bonds with a very small deviation angle  $\delta$ . It is pleasing to observe that the revised figures leave the relative order of bond overlaps, obtained for Slater and Clementi orbitals, unaffected. The magnitudes have increased however, by approximately 0.01. The results based on Clementi orbitals also differ from those based on Slater orbitals in that the optimum values of the variable parameters (interorbital angles  $\Theta_i^{j/h}$  and angles deviation  $\delta_{ij}$ ) have changed. For example, the CCC interorbital angle of the methylene group in nortricyclene has shifted from its old value of  $104^\circ$  to the more reasonable value  $107\ 1/2^\circ$ .

TABLE II  
Bond overlaps and hybrids for several cycloalkanes.

CC bond overlap	Molecule	Bond	Hybrids
0.5759	Tricyclobutane	3—3	$sp^{3.86}$ — $sp^{3.86}$
0.5994	Nortricyclene	3—3	$sp^{3.86}$ — $sp^{3.86}$
0.6005	Spiropentane	2—2	$sp^{3.82}$ — $sp^{3.82}$
0.6056	Tetracyclononane	3—3	$sp^{3.86}$ — $sp^{3.86}$
0.6089	Spiropentane	4—2	$sp^{3.00}$ — $sp^{3.90}$
0.6225	Bicyclopentane	2—3	$sp^{3.63}$ — $sp^{3.47}$
0.6297	Cubane	3—3	$sp^{3.42}$ — $sp^{2.42}$
0.6423	Nortricyclene	2—3	$sp^{3.33}$ — $sp^{3.05}$
0.6442	Nortricyclene	2—3'	$sp^{3.33}$ — $sp^{3.18}$
0.6589	Tetracyclononane	2—3	$sp^{3.24}$ — $sp^{2.49}$

In calculating the hybridization in spiropentane the condition that  $\psi_{22}$  and  $\psi_{24}$  are equivalent in their s-p content assumed in previous calculation<sup>4</sup> is examined in more details. The results indicate there is a small difference between the two hybrids. When equivalent  $\psi_{22} = \psi_{24} = sp^{3.86}$ , but when this restriction is removed  $\psi_{22} = sp^{3.82}$  and  $\psi_{24} = sp^{3.90}$ . The s-p content is altered in such a way that the difference between the bond overlaps  $S_{24}$  and  $S_{22}$  is less pronounced. This is expected if the larger overlap is to be obtained. Another restriction:  $\delta_{ij} = \delta_{ji}$  employed for bridged CC bonds in the original calculation on nortricyclene<sup>4</sup> is also lifted. Even so the results show that the two deviation angles  $\delta_{ij}$ , and  $\delta_{ji}$ , now differ by only one degree.

An elaborate calculation of hybridization for the »acetylenic« strained hydrocarbons, *i. e.* tricyclobutane and cubane, similar to that of Coulson and Moffitt<sup>12</sup> for cycloalkanes, when the energy per C—CH<sub>2</sub> group is minimized, is

made by Weltner<sup>10</sup>. A comparison of these results and those obtained by the maximum overlap method based on Slater orbitals indicate a consistently higher s-character for CH hybrids obtained by the latter method. Now, employing Clementi orbitals, the calculated  $s^0$  for CH hybrids is in fair agreement with that obtained by Weltner. Similarly a better agreement with the more exact calculation is found for cycloalkanes<sup>8</sup>, when the Clementi orbitals are used.

#### CONCLUSION

It seem therefore desirable to continue with the use of Clementi orbitals in future application of the method of maximum overlap. It still remain to evaluate the degree to which the method of maximum overlap is adequate for approximate description of hybridization in various molecular systems. We have to postpone the judgement until more results of the calculation of hybridization in different molecules and local environments are available for a comparison with relevant experimental data. At this stage at least we may trace and eliminate some of the deficiencies which are not inherent to the method itself, but are due to the use of crude functions in the calculations.

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#### IZVOD

#### Hibridizacija u nekim policikličkim alkanima metodom maksimalnog prekrivanja

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Metodom maksimalnog prekrivanja izračunavana je hibridizacija u više policikličkih alkana. Za atomske orbitale su pri tome korištene Clementi-eve funkcije (ref. 1). Upoređenje ovih rezultata sa rezultatima ranije izračunatih na osnovu Slater-ovih funkcija pokazuju poboljšanja postignuta upotrebom točnijih valnih funkcija. Vrijednosti prekrivanja CC veza, koje predstavljaju izvjesni indeks veze, možemo podijeliti u tri grupe: (1) vrijednosti ispod 0.61 su karakteristične za jako napregnute tročlane prstenove ( $\delta \sim 20^\circ$ ), (2) vrijednosti između 0.61 i 0.64 su karakteristične za četveročlane prstenove ( $\delta \sim 10^\circ$ ), i (3) vrijednosti iznad 0.64 su karakteristične za normalne veze, ili za neznatno »svinute« veze ( $\delta < 5^\circ$ ).