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Maximum Overlap Hybridization in Cyclopropane and Some Related Molecules

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The hybridization in cyclopropane, spiropentane, nortricyclene and 1,1-dimethyl cyclopropane is calculated applying the criterion of maximum overlap. The *s*-*p* content in the general hybrids is found to be sensitive to changes in the interorbital angle Θ_{ij}. The results give information about the strain associated with bent bonds and its delocalization. The application also allows calculations of skeletal angles, such as $\sphericalangle C_1 C_2 C_3$ in nortricyclene, which determine the geometry of the molecule.

Die Hybridisierung in Cyclopropan, Spiropentan, Nortricyclen und 1,1-Dimethylcyclopropan wird mittels des Kriteriums der maximalen Überlappung berechnet. Dabei findet man eine starke Abhängigkeit des *s*- (*p*-) Anteils von dem von den Orbitalen gebildeten Winkel Θ_{ij}. Daraus lassen sich Aussagen über die Spannung in Systemen mit anomalen Bindungswinkeln gewinnen. Der $C_1 C_2 C_3$-Winkel in Nortricyclen wird bestimmt.

Nous calculons l'hybridation dans cyclopropane, spiropentane, nortricyclène et 1,1-diméthyl-cyclopropane à l'aide du critère de recouvrement maximal. Le rapport *s*/*p* dans les hybrides est sensible aux angles Θ_{ij} entre les orbitales. Les résultats donnent des informations sur la tension dans les liaisons courbées. On peut aussi calculer des angles de squelette, comme $C_1 C_2 C_3$ dans le nortricyclène.

Introduction

The well known *sp*, sp^2 and sp^3 hybrids present a very useful description of valence bonding in molecules, but, however they are still a crude approximation even within the theory of hybridization itself. When the symmetry of a molecule is reduced, more general hybrids with varying *s*-*p* content have to be considered [*6*, *8*, *10*]. Various approaches to ascertain the *s*-*p* content of these more general hybrids are possible. In earlier works, because of computational difficulties the amplitudes, instead of the overlaps of the hybrids, were maximized. When extensive tables of overlap integrals became available [*15*] it became possible to calculate the overlap between hybrids, and the criterion of maximum overlap could then be applied. This criterion is, of course, only approximately correct, and care must sometimes be taken in interpreting the results. In the absence of more rigorous calculations, however, the maximum overlap method may be of considerable use in discussing the bonding and other properties of large molecules. The aim of this paper is to demonstrate the determination of the hybridization in molecules of medium complexity by the maximum overlap method. As a particular example, cyclopropane and some related, less symmetrical, derivatives, all characterized by a large strain associated with bent bonds, are considered. The

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results lead to an insight into the delocalization of the strain in larger molecules and also to an account of a rehybridization in related molecules. For a recent development and some applications of maximum overlap method see literature cited in reference [*18*].

Outline of Calculations

The mixing of s and p orbital produces a directed hybrid of the general form:

$$\psi_i = a_i\,(s) + b_i\,(p_i)$$

where a_i and b_i are subjected to the orthogonality conditions [*13, 21*]

$$a_i\,a_j + b_i\,b_j \cos \Theta_{ij} = \delta_{ij}$$

the subscripts i and j refering to orbitals of the same atom; Θ_{ij} is the interorbital angle. For $a_i = 1/2,\ 1/\sqrt{3},\ 1/\sqrt{2}$ simple sp^3, sp^2 and sp hybrids are obtained. To determine a_i and b_i for a general case, one maximizes the overlap

$$S_{ii'} = \int \psi_i\,\psi_{i'}\,d\tau$$

where ψ_i and $\psi_{i'}$ are orbitals of the two atoms forming the bond.

In the case of an atom, which due to the symmetry of the molecule has two or three equivalent hybrids, these can simply be expressed in terms of Θ, the angle between equivalent hybrids:

$$\psi_i = \left(\frac{-\cos\Theta}{1-\cos\Theta}\right)^{\frac{1}{2}}(s) + \left(\frac{1}{1-\cos\Theta}\right)^{\frac{1}{2}}(p_i)\,. \tag{1}$$

In the case where three hybrids are equivalent (local symmetry C_{3v}) the non-equivalent orbital is given by

$$\psi_4 = \left(\frac{1+2\cos\Theta}{1-\cos\Theta}\right)^{\frac{1}{2}}(s) + \left(\frac{-3\cos\Theta}{1-\cos\Theta}\right)^{\frac{1}{2}}(p_4)$$

with $\cos\Theta_{14} = \cos\Theta_{24} = \cos\Theta_{34} = -(1+2\cos\Theta)^{\frac{1}{2}}/\sqrt{3}$. In symmetry C_{2v} two of the equivalent hybrids are given by the above relationship (1), and the other two, also equivalent, as follows:

$$\psi_j = \left(\frac{1+\cos\Theta}{2\,(1-\cos\Theta)}\right)^{\frac{1}{2}}(s) + \left(\frac{1-3\cos\Theta}{2\,(1-\cos\Theta)}\right)^{\frac{1}{2}}(p_j) \qquad j = 3{,}4$$

where Θ is the same as in (1).

It has been mentioned [*21*] that there is no set of four s-p hybrid orbitals with symmetry C_s. This is not true, as we will show later by considering the hybridization in nortricylene. Finally, a case in which all four hybrids are non-equivalent may arise (sym. C_1). Various relationships between all the Θ_{ij} are readily obtained from the orthogonality conditions, and any particular interorbital angle can be obtained from the corresponding coefficients a_i, a_j, b_i, b_j. For example in Tab. 3 ref. [*21*] the explicit values of Θ_{ij} in C_{3v} and C_{2v} symmetries are given, together with the corresponding hybridization ratios (b_i/a_i).

If the orbitals are not directed along the bonds, the overlap can be obtained by decomposing the p_i and $p_{i'}$ orbitals into components along $(p)_{||}$ and perpendicular $(p)_{\perp}$ to the bond. In addition to atomic overlaps (s, s), (s, p) and $(p, p)_\sigma$ therefore, a contribution $(p, p)_\pi$ arises in bent bonds. Varying the coefficients characterizing a single hybrid in order to obtain a better overlap produces a change in the coefficients of the remaining orbitals of the atom considered, since the total *s*-*p* content is normalized. An increase in the *s* character of one hybrid, therefore, will require a decrease in the *s* content of one or more of the other hybrids of the same atom. In this way a change in the hybridization of one bond is transfered to neighbouring bonds.

In the following calculations the well known Slater atomic orbitals [*19*] were used. For all molecules considered, we assumed the following bond distances:

$$\mathrm{CC} = 1.535\ \text{Å} \quad \text{and} \quad \mathrm{CH} = 1.07\ \text{Å}.$$

These values lead to the following atomic overlap integrals [*3*]

$(1s_{\mathrm{H}},\ 2s_{\mathrm{C}}) = 0.5809$

$(1s_{\mathrm{H}},\ 2p_{\mathrm{C}}) = 0.4699$

$(2s_{\mathrm{C}},\ 2s_{\mathrm{C}}) = 0.3447$

$(2s_{\mathrm{C}},\ 2p_{\mathrm{C}}) = 0.3684$

$(2p_{\mathrm{C}},\ 2p_{\mathrm{C}})\sigma = 0.3298$

$(2p_{\mathrm{C}},\ 2p_{\mathrm{C}})\pi = 0.1952$

For molecules having several different bonds, the total overlap has previously been obtained by summing the overlap contributions of the individual bonds. When different bonds are present, e. g. the C-C and C-H bonds of cyclopropane, a simple summation assumes that the given overlap for a C-H bond is equivalent in energy to the same overlap for a C-C bond. This cannot be justified, and an approximate scaling factor has to be introduced. We have followed a suggestion by Prof. COULSON* and have replaced the overlap S_{XY} by the reduced energy $E_{\mathrm{XY}} = (S_{\mathrm{XY}}/S^0{}_{\mathrm{XY}})\,E^0{}_{\mathrm{XY}}$. Here $S^0{}_{\mathrm{XY}}$ is the overlap of a selected standard XY bond having energy E_{XY}. The above suggestion is based on the proportionality $E = kS$. We have selected the following standard bond energies:

$E^0{}_{\mathrm{CC}} = 79.2$ kcal from C_2H_6

$E^0{}_{\mathrm{CH}} = 99.5$ kcal from CH_4 .

The corresponding overlaps, assuming carbon sp^3 hybrids and hydrogen ($1s$) orbitals are: $S^0{}_{\mathrm{CC}} = 0.6526$, $S^0{}_{\mathrm{CH}} = 0.6974$. This gives for the scaling factors $k_{\mathrm{CC}} = 121.37$ and $k_{\mathrm{CH}} = 142.67$ respectively.

In the calculations the hybrid composition was varied in a suitable region and the corresponding overlaps were then calculated until the maximum value was found. This was found much more practicable than attempting to differentiate cumbersome expressions for the total overlap which was possible in cases of high symmetry, e. g. for cyclopropane [*3*]. Some approximations were also introduced in order to reduce the numerical work and are discussed later.

Cyclopropane

Cyclopropane is the simplest molecule possessing bent bonds, and has been investigated by several authors [*3*, *4*, *22*]. We have included it by means of comparison with other related molecules. The hybridization in cyclopropane is determined by a single parameter. We have selected Θ, the angle between the two hybrids describing the bent bonds of the C_3 ring. The quantity $k_{\mathrm{CC}}\,S_{\mathrm{CC}} + 2\,k_{\mathrm{CH}}\,S_{\mathrm{CH}} = 1/3\,S$ is plotted in Fig. 1, as a function of Θ, illustrating a sensitivity of the overlap to the hybrid composition. The final bond overlap integrals and hybridization ratios are listed in Tab. 1. The maxium is obtained for $\Theta = 101° \, 3/4$, the

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* Private communication.

deviation from a straight bond being $\omega = 21°$. This is in very good agreement with $\omega = 22°$ obtained by Coulson and Moffitt [*4*] by minimizing the energy, and also with $\omega = 21° 1/2$ obtained by Coulson and Goodwin [*3*] by maximizing the overlap but neglecting the energy difference of the CC and CH bonds. The HCH angle in all these calculations is about 119°, in good agreement with the experimental value [1] of 118.2°. It should be mentioned however that cyclopropane itself does not present a good example for comparing the various computations with experiment since ω is very large and therefore not very sensitive to any particular choice of parameters employed in the calculations.

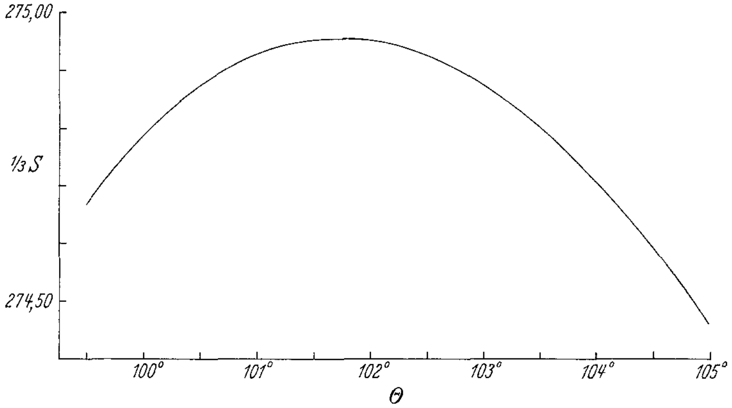

Fig. 1. Dependence of 1/3 of the total overlap on the parameter Θ for cyclopropane

Spiropentane

For a description of the C-C bonds in spiropentane we require three distinct hybrids (Fig. 2). However, the central carbon atom has four equivalent bonds and it must be described by sp^3 hybridization, thus reducing the number of hybrid coefficients to be calculated. The two hybrids of the external atom one directed towards the central atom and the other towards another external carbon atom remain to be determined by the maximizing procedure; the hybrid composition of the C-H bonds is then fixed. Some preliminary calculations have shown that bond overlaps are sensitive to the interorbital angle Θ_{ij}, but are little affected if both angles of inclinations of the two hybrids, δ_i and δ_j, are varied separately so that Θ_{ij} remains constant. This justifies the assumption that $\delta_i = \delta_{i'}$, $\delta_j = \delta_{j'}$, which reduces the number of combinations to be considered. The best hybrid orbitals and the corresponding bond overlaps are listed

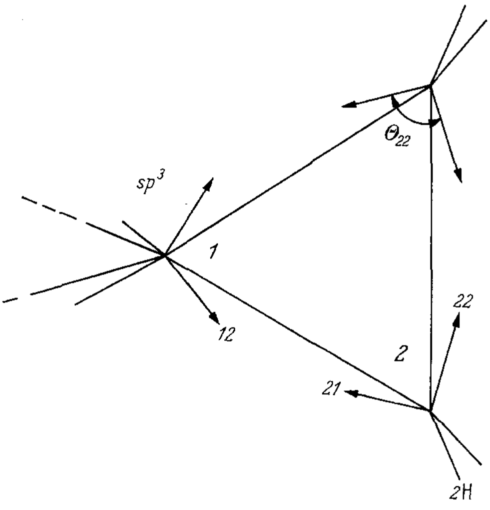

Fig. 2. Spiropentane

Table 1

Bond	Hybrid	Ratio b/a	Approx. $(b/a)^2$*	Bond Overlap	Scaled Overlap**	Interorbital Angle
		Cyclopropane				
C – C	$\psi_{CC} = 0.4113\,(s) + 0.9115\,(p)$	2.216	sp^5	0.5762	69.93	101° 3/4
C – H	$\psi_{CH} = 0.5752\,(s) + 0.8180\,(p)$	1.422	sp^2	0.7185	102.51	119° 38′
		Spiropentane				
$C_1 - C_2$	$\psi_{12} = 0.5000\,(s) + 0.8660\,(p)$ $\psi_{21} = 0.4113\,(s) + 0.9115\,(p)$	1.732 2.216	sp^3 sp^5	0.5908	71.71	$\Theta_{11} = 109° 28'$
$C_2 - C_2$	$\psi_{22} = 0.4113\,(s) + 0.9115\,(p)$	2.216	sp^5	0.5762	69.93	$\Theta_{22} = 101° 45'$
$C_2 - H$	$\psi_{2H} = 0.5752\,(s) + 0.8180\,(p)$	1.429	sp^2	0.7185	102.51	$\Theta_{2H} = 119° 38'$
		Nortricyclene				
$C_1 - C_2$	$\psi_{12} = 0.4722\,(s) + 0.8815\,(p)$ $\psi_{21} = 0.4414\,(s) + 0.8973\,(p)$	1.867 2.033	$sp^{3.5}$ sp^4	0.6314	76.63	
$C_2 - C_3$	$\psi_{23} = 0.4414\,(s) + 0.8973\,(p)$ $\psi_{32} = 0.4731\,(s) + 0.8810\,(p)$	2.033 1.862	sp^4 $sp^{3.5}$	0.6304	76.51	
$C_3 - C_3$	$\psi_{33} = 0.4285\,(s) + 0.9036\,(p)$	2.109	$sp^{4.5}$	0.5832	70.78	$\Theta_{33} = 103$
$C_1 - H$	$\psi_{1H} = 0.5754\,(s) + 0.8179\,(p)$	1.421	sp^2	0.7186	102.52	
$C_2 - H$	$\psi_{2H} = 0.5525\,(s) + 0.8335\,(p)$	1.509	$sp^2 - sp^{2.5}$	0.7126	101.67	
$C_3 - H$	$\psi_{3H} = 0.6396\,(s) + 0.7687\,(p)$	1.202	$sp^{1.5}$	0.7328	104.55	
		1,1 Dimethyl Cyclopropane				
$C_1 - C_2$	$\psi_{12} = 0.4196\,(s) + 0.9077\,(p)$ $\psi_{21} = 0.5377\,(s) + 0.8431\,(p)$	2.163 1.568	$sp^{4.5} - sp^5$ $sp^{2.5}$	0.6403	77.71	$\Theta_{22} = 105° 30'$
$C_3 - C_2$	$\psi_{23} = 0.4592\,(s) + 0.8883\,(p)$ $\psi_{32} = 0.4113\,(s) + 0.9115\,(p)$	1.934 2.216	$sp^{3.5} - sp^4$ sp^5	0.5852	71.03	$\Theta_{33} = 101° 45'$
$C_3 - C_3$	$\psi_{33} = 0.4113\,(s) + 0.9115\,(p)$	2.216	sp^5	0.5762	69.93	
$C_1 - H$	$\psi_{1H} = 0.5241\,(s) + 0.8517\,(p)$	1.625	$sp^{2.5}$	0.7046	100.53	$\Theta_{11} = 112° 15'$
$C_3 - H$	$\psi_{3H} = 0.5752\,(s) + 0.8180\,(p)$	1.422	sp^2	0.7185	102.51	

* Approximate ratio $(b/a)^2$ may be used as an extension of the sp, sp^2, sp^3 notation, representing the exponent "n" in the general form sp^n. This form is useful for qualitative discussion. Because of an approximate nature of the hybridization theory, it is thought sufficient to retain only integer and half integer exponents. Other examples are refered as in between cases, thus for example $sp^{2.5} - sp^3$ stands for approximately $2.65 < (b/a)^2 < 2.85$.

** $E = kS$ is called scaled overlap, rather than energy, thus indicating that in fact overlap, not the energy was calculated.

in Tab. 1. It should be noted that the equivalence of the two hybrids, ψ_{21} and ψ_{22}, of the external carbon atom describing the C-C bonds is a result of the maximizing procedure and has not been assumed. When the coefficients of the *s* orbital are changed by more than 0.005, a decrease in the total overlap from its maximum value can be noted, indicating the sensitivity of the calculated coefficients.

Nortricyclene

The symmetry of this molecule is C_{3v} (see Fig. 3). Five different *s-p* hybrids are required for the description of the C-C molecular skeleton, and the hybrids describing the C-H bonds are uniquely determined from these. Two problems of interest arise:

1. To establish to what extent the angular strain of the cyclopropyl ring is spread out over the whole molecule. The geometry of this molecule does not necessarily require bent bonds outside the C_3-ring. However, a better overlap can be expected by introducing bent bonds throughout the molecule. The reduced overlap due to bending may be compensated by a larger contribution to the overlap from hybrids richer in *s* content.

2. To calculate the skeletal angle C_1 C_2 C_3. The maximum overlap procedure *does not require* the knowledge of the bond angles, therefore by calculating the overlap for structures with differing C_1 C_2 C_3 angles, we can find the angle which leads to the overall maximum of the overlap for all models considered.

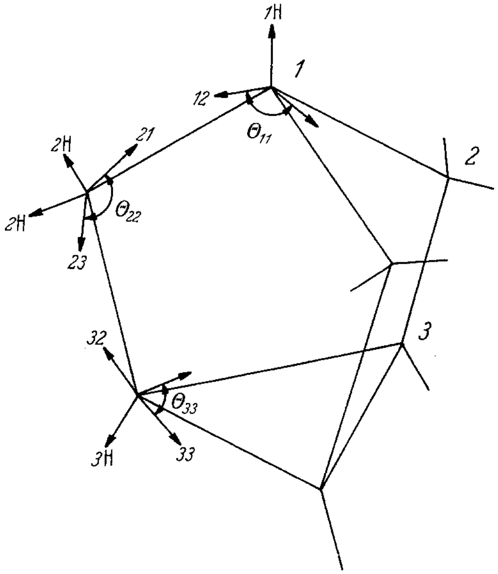

Fig. 3. Nortricyclene

The number of independent parameters needed to define the hybridization in nortricyclene is fairly large, and so to simplify the calculations we assumed the following: *a*) the C-C hybrids of carbon atom 2 are equivalent; this being justified by the results obtained for spiropentane, *b*) the angles δ_i and $\delta_{i'}$, describing the bending of a bond C_i-$C_{i'}$, are equal. Again this is justified by preliminary calculations which have shown that a small reorientation of ψ_i and ψ_j, which keeps Θ_{ij} constant but changes δ_i and δ_j, does not affect the overlap to any great extent. The numerical work proceeded as follows: Firstly we assumed that the hybridization in the C_3 ring is the same as that in cyclopropane. Then, for a given angle C_1 C_2 C_3, varying δ_{12} and δ_{23} independently, a maximum overlap was found. This was repeated for different C_1 C_2 C_3 angles in the interval 94° – 98°. The maximum overlap was found in all cases for $\delta_{12} \sim 3°$, $\delta_{23} \sim 5°$, and the absolute maximum was obtained for C_1 C_2 $C_3 = 96°$. In Tab. 2 one third of the total overlaps for an assumed angle C_1 C_2 C_3 of 96° are given for different values of δ_{12} and δ_{23}, Θ remaining between 102° and 106°. The table indicates the sensitivity of the total overlap towards δ_{12} and δ_{23}. Finally the hybridization within the C_3 ring was varied to see if a better overlap could be obtained. The low sensitivity in the total overlap to changes in C_3-hybridization is evident from Tab. 3. A very small increase in the overlap for the bent hybrids of the C_3 ring is obtained when Θ_{33} is increased from 102° (value for cyclopropane) to 103° (value for the best hybridization).

Table 2. *Nortricyclene*

$\gamma = 96°$	$\delta = 1°$	$\delta = 2°$	$\delta = 3°$	$\delta = 4°$	$\delta = 5°$
$\delta' = 4°$	$\Theta = 101°$ 565.36	$\Theta = 102°$ 565.71	$\Theta = 103°$ 565.84	$\Theta = 104°$ 565.80	$\Theta = 105°$ 565.58
$\delta' = 5°$	$\Theta = 102°$ 565.81	$\Theta = 103°$ 565.90	$\Theta = 104°$ 565.95	$\Theta = 105°$ 565.82	$\Theta = 106°$ 565.54
$\delta' = 6°$	$\Theta = 103°$ 565.78	$\Theta = 104°$ 565.93	$\Theta = 105°$ 565.89	$\Theta = 106°$ 565.69	$\Theta = 107°$ 565.33
$\delta' = 7°$	$\Theta = 104°$ 565.75	$\Theta = 105°$ 565.81	$\Theta = 106°$ 565.70	$\Theta = 107°$ 565.43	$\Theta = 108°$ 565.02

$\Theta = \gamma + \delta + \delta'$ $\delta \equiv \delta_{21}$ $\delta' \equiv \delta_{23}$

Table 3. *Nortricyclene*

Θ_{33}	$\gamma = 95° 1/2$	$\gamma = 96°$	$\gamma = 96° 1/2$
101°	565.77	565.79	565.76
101° 1/2	565.86	565.88	565.86
102°	565.94	565.95	565.92
102° 1/2	565.96	565.97	565.95
103°	565.97	565.98	565.95
103° 1/2	565.96	565.96	565.93
104°	565.92	565.93	565.89
104° 1/2	565.86	565.87	565.83
105°	565.79	565.79	565.75

Total is 1/3 of scaled molecular overlaps.

It is worth stressing the good agreement between the calculated value of $C_1 C_2 C_3 = 96°$ and the experimental value of $C_1 C_2 C_3 = 97°$ (obtained by electron diffraction measurements [7]). Although one cannot hope for the approximate theory of hybridization to lead to such a close agreement, at least some insight into the origin of such an unusual angle is obtained.

1,1-Dimethyl Cyclopropane

As a further example of the application of the maximum overlap criterion we have examined the hybridization in 1,1-dimethyl cyclopropane, which gives us some information as to the rehybridization within the cyclopropane ring. As independent orbitals we selected the five hybrids describing the different C-C bonds. This determines the hybridization ratios in the remaining C-H bonds. The following parameters were varied: 1. the angle Θ_{11} characterizing the hybridization within the methyl groups, 2. the angle Θ_{22} defining the C-C hybrids of the substituted cyclopropyl carbon atom, 3. the angle Θ_{33} defining the C-C hybrids of the two remaining cyclopropyl carbon atoms.

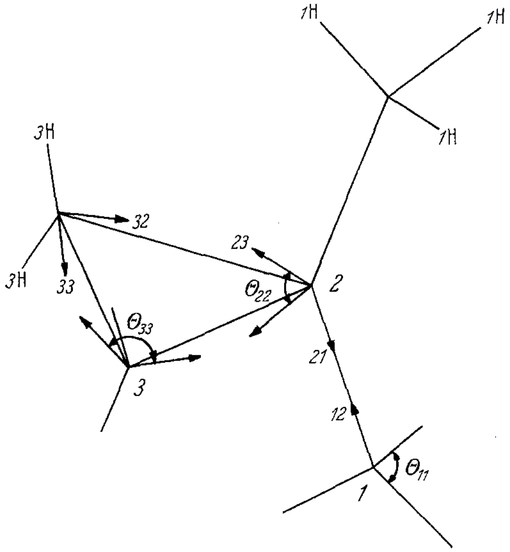

Fig. 4. 1,1-dimenthyl cyclopropane

In order to find the approximate value of Θ_{22}, the first stages were carried out by assuming the following: *a*) $\Theta_{33} = 102°$ (as in cyclopropane) *b*) the methyl group is tetrahedral. Varying Θ_{22} from 103° – 108° the maximum at 105° 1/2 was found. Still keeping $\Theta_{33} = 102°$ and varying both Θ_{11} and Θ_{22} in the regions 111° – 114° and 104° – 107° respectively, the maximum was calculated for $\Theta_{11} = 112° 1/2$ and $\Theta_{22} = 109° 1/2$. Finally Θ_{33} was varied with Θ_{11} and Θ_{22} kept at their optimum values and the maximum was obtained for $\Theta_{33} = 101° 3/4$. The best hybrids and their bond overlaps are included in Tab. 1. The results indicate that there is a drift in the *s*-*p* content of the cyclopropyl carbons towards tetrahedral hybridization, dimethyl cyclopropane being, in this respect, intermediate between spiropentane and cyclopropane.

Discussion

A comparison of the hybrids of different molecules, presented in Tab. 1, indicates some regularities within the structurally related units. Thus, for example, the hybridization ratios and bond overlaps of the C-H bonds for a strain-free carbon atom (CH_3 in dimethyl cyclopropane) and in cases of small strain (CH_2, and bridge head CH of nortricyclene) are comparable. The C-H bonds of cyclopropyl have larger overlap, being rich in *s*-character, and the largest C-H bond overlap occurs in nortricyclene for which $b/a = 1.20$, approximately half way between *sp* and sp^2 hybridization. The CH bond overlaps for all the molecules that we have considered lie between 0.6400 and 0.5760 for normal and bent bonds respectively. Substitution in the cyclopropyl ring may result in larger C-C overlap, as is the case in 1,1-dimethyl cyclopropane, and would therefore indicate the way in which the C_3-ring is stabilized. However, in the above case the difference is not significant as a small variation in the bond lengths, or a choice of different atomic overlaps may reverse the result.

The calculations show also that hybridization in one part of the molecule is frequently independent of that in another, thus a transfer of local hybridization is sometimes possible. The parameters used in the calculations tend to be, to a large extent, unconnected, and can be approximately separated by evaluating the optimum values independently.

The number of molecules examined is insufficient to attempt a more detailed correlation between the calculated hybridization content and bond overlaps, and various experimental quantities, and therefore only the more predominant effects should be considered at this stage. For example, the C-H stretching frequencies of cyclopropane and the *n*-paraffins are at about [*9*] 3050 cm^{-1} and 2950 cm^{-1}. This is in agreement with the larger *s*-orbital content of the C-H bonds of cyclopropane. Similarly a band at about 3070 cm^{-1}, characterizing the nortricyclenes, is consistent with the above data [*12, 16*]. The NMR spectra provide additional data which can be rationalized by the hybridization theory; a larger proton chemical shift in the cycloparaffins (4.5 ppm) compared with the methyl proton in the paraffins (4.1 ppm, ref. [*17*]) indicates a better shielding by orbitals richer in *s*-character. Similarly the spin-spin coupling constant in cyclopropane suggests, according to theoretical interpretation, a higher *s*-content [*14*]. In addition, one may compare the acidity of cyclopropane and the *n*-paraffins. Thus, although all these properties are qualitatively understood, the application of the maximum overlap criterion at least makes a quantitative comparison between experimental observations and hybridization possible.

Also available for comparison with experiment are the calculated bond angles. The agreement for cyclopropane (118° exp., [*1*] 119° theor.) and spiropentane (120° exp., [*5*] and 119° theor.) is good. The bond angles of 1,1-dimethyl cyclopropane have not been experimentally determined but data for 1,1, 2, 2-tetramethyl cyclopropane are available [*11*] for which molecule only a small effect due to successive methyl substitution is expected. The experimental value for the $C_1 C_2 C_3$ angle at the dimethyl substituted carbon is 114° ± 6°, whilst the calculated value is 112°. The most striking result is the agreement obtained for the $C_1 C_2 C_3$ angle in nortricyclene (calc. 96°, obs. 97°), which defines the geometry of the molecular carbon atom skeleton. This result may be useful in choosing between the alternative experimental angles of 97° and 107°, both consistent with diffraction measurements without resulting to calculations on strain energy, as was carried out by HEILBRONNER and SCHOMAKER [*7*].

Future applications may or may not support this rather empirical approach. However, in the absence of more rigorous calculations for larger molecules, the theory of hybridization combined with the criterion of maximum overlap at least makes it possible to compare the bondings in molecules such as we have considered.

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