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## Maximum Overlap Hybridization in Cyclobutane, Bicyclobutane and Related Highly Strained Systems

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The hybridization in cyclobutane, bicyclobutane, 1,3-dimethylcyclobutane, 1,3-dimethylbicyclobutane, bicyclo(1.1.1)pentane, tricyclo(1.1.0.0<sup>2,4</sup>)butane, cubane and tetracyclo(3.3.1.0<sup>2,8</sup>0<sup>4,6</sup>)nonane is considered applying the method of maximum overlap (Tab. 1). Overlap seems to be a good index of a CC bond: overlaps below 0.6000 are characteristic for molecules containing C<sub>3</sub>-ring ( $\delta \sim 20^\circ$ ), between 0.6000 and 0.6300 for four membered ring ( $\delta \sim 10^\circ$ ), and above 0.6300 for normal or very slightly bent bonds ( $\delta < 5^\circ$ ). Description and details of actual numerical calculations are given.

Die Hybridisierung in Cyclobutan, Bicyclobutan, 1,3-Dimethylcyclobutan, 1,3-Dimethylbicyclobutan, Bicyclo(1.1.1)pentan, Tricyclo(1.1.0.0<sup>2,4</sup>)butan, Kuban und Tetracyclo(3.3.1.0<sup>2,8</sup>0<sup>4,6</sup>)nonan wird mittels des Kriteriums der maximalen Überlappung berechnet (Tab. 1). Die Überlappung scheint ein gutes Unterscheidungsmerkmal für C-C Bindungen zu sein: Überlappungswerte unter 0,6000 sind charakteristisch für Moleküle, die C<sub>3</sub>-Ringe enthalten ( $\delta \sim 20^\circ$ ), zwischen 0,6000 und 0,6300 für Viererringe ( $\delta \sim 10^\circ$ ), während die über 0,6300 normale und sehr wenig gespannte ( $\delta < 5^\circ$ ) Bindungen charakterisieren. Die Beschreibung und die Einzelheiten der durchgeführten Berechnungen werden gegeben.

L'hybridation dans cyclobutane, bicyclobutane, 1,3-diméthylcyclobutane, 1,3-diméthylbicyclobutane, bicyclo(1.1.1)pentane, tricyclo(1.1.0.0<sup>2,4</sup>)butane, cubane et tétracyclo(3.3.1.0<sup>2,8</sup>0<sup>4,6</sup>)nonane est étudiée à l'aide du critère du recouvrement maximum (Tab. 1). Le recouvrement semble bien indiquer la nature de la liaison C-C: Des intégrales de recouvrement sous 0,6 sont caractéristiques pour les cycles triatomiques ( $\delta \sim 20^\circ$ ), entre 0,6 et 0,63 pour les tétraatomiques ( $\delta \sim 10^\circ$ ), et au-dessus de 0,63 pour les liaisons normales ou peu tendues ( $\delta < 5^\circ$ ). Nous décrivons les calculs et donnons des détails numériques.

### Introduction

Several polycyclic compounds containing only three- and (or) four-membered rings have recently been prepared [22, 26]. These compounds are highly strained and it is of considerable interest to examine them theoretically. An important quantum-mechanical treatment of strained molecules was done by COULSON and MOFFITT [4] for the cycloalkanes ( $n = 3, 4, 5$ ). An elaborate valence bond calculation is possible, since, by assuming that these molecules possess planar rings the problem reduces to one of high symmetry. The energy per C-CH<sub>2</sub> group is evaluated as a function of a single hybridization parameter until the minimum is found. Molecules which we have considered, however, lack such symmetry, and the calculations thus depend on too many parameters to be solved completely. We therefore adopted an approximate method of calculating *hybridization* by means of the criterion of maximum overlap. An outline of this method is described in our earlier publications (ref. [20] and [24]) so we need only to mention here the main features.

We assume hybrids of carbon atom of the form

$$\psi_i = a_i s + b_i p_i = sp_i^n \quad \text{with } n = \frac{b_i^2}{a_i^2}$$

where  $s$  and  $p_i$  are Slater  $2s$  and  $2p$  orbitals of carbon. The problem is to find a set of coefficients  $a_i$ ,  $b_i$  such that the total overlap

$$S = k_{CC} \sum S_{CC} + k_{CH} \sum S_{CH}$$

is a maximum. The summation is over all bonds, the partial contributions of which are weighted by  $k_{CC}$  or  $k_{CH}$  in order to compensate for the difference in energies between the two kinds of bond. A result of this maximization procedure is that the hybrids are not generally directed along the straight line joining the atoms which form the bond. The atomic overlap integrals and the weighting factors used are as in ref. [20].

Various strained molecules have already been examined by this or slightly modified methods [5, 20, 24, 25]. For the lower cycloalkanes, it is possible to draw a comparison between maximum overlap and the more elaborate valency-bond calculations; the results from both methods are found to be in good agreement with each other. In this paper we continue with the application of the maximum overlap method to the calculation of the hybridization in highly strained small ring molecules. We will examine in particular cyclobutane, bicyclobutane and some closely related molecules. Because bond overlaps are very sensitive to the angle\* of deviation between the hybrid forming a bond and the straight atom-atom line, and because this angle does not depend strongly on the particular choice of atomic orbitals, or atomic overlap integrals employed, as may be seen by comparing the results on cyclopropane [5, 14, 20] the method of maximum overlap seems suitable for the highly strained systems considered.

### Calculations and Results

The calculation of the hybridization is described for each molecule separately, and the results are collected in Tab. 1. For most of the molecules considered, the expressions relating the different angles in space are rather cumbersome (see the appendix). By comparing the results for some related molecules one can start with a set of parameters which is close to the optimum set. Thus, for example, calculations on 1,3-dimethyl bicyclobutane, have been considerably reduced by taking as initial parameters those of bicyclobutane. If there are no available data for comparison, one can start with tetrahedral hybridization and vary each parameter individually. Except for those parameters which characterize the hybrids of the same atom, they usually do not depend strongly on each other and can be individually optimized. When two (or more) parameters are coupled, a two-dimensional search for the parameters is necessary. Such is the case for the hybrids of the  $\text{CH}_2$  bridge in nortricyclene (see Tab. 2 in ref. [20]).

#### *Cyclobutane*

For a description of the C—C bonds in cyclobutane,  $\text{C}_4\text{H}_8$ , we require only two distinct hybrids:  $\psi_{CC}$  directed towards another carbon atom and  $\psi_{CH}$  directed

\*  $\delta$  deviation angle for bending in suitably selected plane,  $\epsilon$  deviation angle describing bending perpendicular to that plane.

Table 1. *Maximum overlap hybrids and bond overlaps*

Bond	Hybrid	Bond overlap	Bond	Hybrid	Bond overlap
Cyclobutane			1,3-dimethyl bicyclobutane		
C - C	$\psi_{22} = sp^{4.28}$	0.6177		$\psi_{41} = sp^{4.22}$	0.5952
C - H	$\psi_{2H} = sp^{3.88}$	0.7139		$\psi_{1H} = sp^{2.64}$	0.7046
			C - H	$\psi_{2H} = sp^{2.03}$	0.7184
1,3-dimethyl cyclobutane			Bicyclo(1.1.1)pentane		
C - C	$\psi_{23} = sp^{4.28}$	0.6220	C - C	$\psi_{23} = sp^{4.45}$	0.6027
	$\psi_{32} = sp^{3.86}$			$\psi_{32} = sp^{4.72}$	
	$\psi_{31} = sp^{3.17}$			$\psi_{2H} = sp^{2.16}$	
	$\psi_{13} = sp^{4.68}$	0.6304	C - H	$\psi_{3H} = sp^{1.10}$	0.7153
C - H	$\psi_{1H} = sp^{2.64}$	0.7046			0.7409
	$\psi_{2H} = sp^{2.22}$	0.7139	Tricyclo(1.1.0.0 <sup>2.4</sup> )butane		
	$\psi_{3H} = sp^{1.87}$	0.7223	C - C	$\psi_{33} = sp^{4.50}$	0.5542
Bicyclobutane			C - H	$\psi_{3H} = sp^{1.20}$	0.7387
C - C	$\psi_{23} = sp^{4.89}$	0.5914	Cubane		
	$\psi_{32} = sp^{3.66}$			C - C	$\psi_{33} = sp^{3.90}$
	$\psi_{33} = sp^{4.39}$	0.5917	C - H	$\psi_{3H} = sp^{1.58}$	0.7294
C - H	$\psi_{2H} = sp^{2.03}$	0.7184	Tetracyclo(3.3.1.0 <sup>2,5</sup> .0 <sup>4,6</sup> )nonane		
	$\psi_{3H} = sp^{1.59}$	0.7291	C - C	$\psi_{23} = sp^{2.74}$	0.6435
1,3-dimethyl bicyclobutane				$\psi_{32} = sp^{2.85}$	
C - C	$\psi_{14} = sp^{4.68}$	0.6456		$\psi_{33} = sp^{4.13}$	0.5881
	$\psi_{41} = sp^{2.11}$			C - H	$\psi_{2H} = sp^{2.46}$
	$\psi_{24} = sp^{4.89}$	0.5960		$\psi_{3H} = sp^{1.85}$	0.7226
	$\psi_{42} = sp^{3.11}$				

towards the hydrogen atom (Fig. 1). The molecule is non-planar (symmetry point group  $D_{2d}$ ), the experimental dihedral angle being  $\gamma = 160^\circ$  [7]. The maximum overlap method cannot account for non-planarity of the carbon rings since the angle between the two  $\psi_{CC}$  hybrids on the same atom is still too small compared with the corresponding angle in the strain free system (acyclic molecule). Similarly, the simple hybridization model cannot distinguish between the axial and equatorial CH bonds. In Tab. 1 are given the results of maximum overlap calculations obtained for a planar model, and the results for an assumed non-planar ( $\gamma = 160^\circ$ ) model are given in Tab. 2. The difference between the bond overlaps of the planar and a non-planar model is very small: CC-overlap has slightly decreased while CH-overlap has increased by approximately a same amount. The overall change in (scaled) overlap per C-CH<sub>2</sub> group is therefore almost zero, in spite that a departure from planarity is considerable, about  $20^\circ$ . This clearly indicates that other

Table 2. *Hybrids and bond overlaps for cyclobutane and bicyclobutane for experimentally observed geometries*

Bond	Hybrid	Bond overlap
Cyclobutane ( $\gamma = 160^\circ$ )		
C - C	$\psi_{CC} = sp^{4.35}$	0.6161
C - H	$\psi_{CH} = sp^{2.19}$	0.7145
Bicyclobutane ( $\gamma = 126^\circ$ )		
C - C	$\psi_{23} = sp^{4.86}$	0.5901
	$\psi_{32} = sp^{3.84}$	
	$\psi_{33} = sp^{4.55}$	
C - H	$\psi_{2H} = sp^{2.04}$	0.7182
	$\psi_{3H} = sp^{1.46}$	0.7324

interactions (even if small), must be dominant in causing non-planarity of the molecule. Non-bonded repulsions make a dominant contribution in determining conformations in acyclic and larger cyclic systems (e. g. ethane, cyclohexane), and they favour staggered arrangements of CH-bonds. In a planar model of cyclobutane all hydrogen atoms are in eclipsed positions, this is a cause of addi-

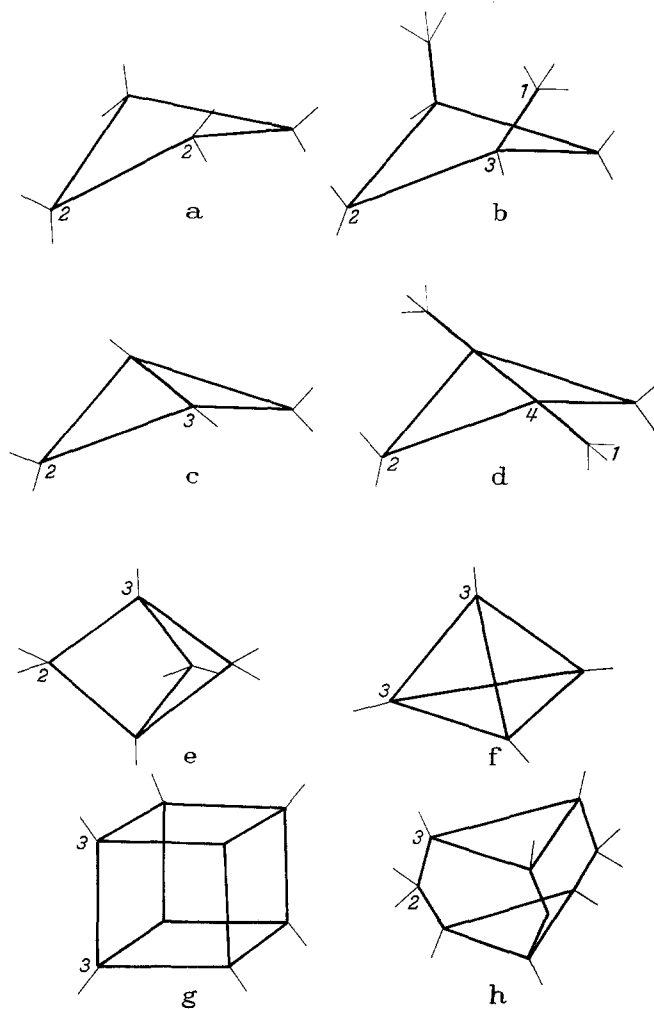


Fig. 1. Schematic diagrams of molecular geometries and numbering of atoms: a) cyclobutane, b) 1,3-dimethylcyclobutane, c) bicyclobutane, d) 1,3-dimethylbicyclobutane, e) bicyclo(1.1.1)pentane, f) tricyclo(1.1.0.0<sup>2,4</sup>)butane, g) cubane, h) tetracyclo(3.3.1.0<sup>2,8</sup>)nonane

tional strain and is energetically less favourable. A relieve is obtained by bending the skeleton of the molecule, since the CH bonds are then approaching a staggered conformation. A compromise is reached for an intermediale geometry, (here  $\gamma = 160^\circ$ ), in a complete analogy with the similar situation in biphenyl and related molecules where direct non-bonded H . . . . . H repulsions are opposed by a decrease of the  $\pi$ -electron overlap.

### 1,3 Dimethyl Cyclobutane

There are three nonequivalent carbon atoms in 1,3-dimethyl cyclobutane (Fig. 1 b), and if we assume that the hybrids describing the CC bonds are known, it remains only to determine the hybridization ratios of the remaining C—H bonds.

Assuming a planar model the following parameters to be varied were chosen: 1. the angle  $\Theta_1$  characterizing the hybridization within the methyl groups, 2. the angle  $t$  giving the orientation of the methyl group relative to the plane of the ring, 3. the angle  $\delta_{23}^*$ , giving bent hybrids of the non-substituted carbons, 4. the angle  $\delta_{32}$  describing bending of the hybrids of the methyl substituted carbons, and 5. the angle  $\Phi_2$  which describes small changes in the geometry of the  $C_4$  ring in order to obtain some insight into effects of the possible deformations of the square. Commencing with parameters which are based on the results for cyclobutane and for the methyl group in substituted cyclopropane  $\Theta_1 = 113^\circ$ ,  $t = 120^\circ$  and  $\delta_{23} = \delta_{32} = 6^\circ$  the optimum is obtained when:  $\Theta_1 = 112^\circ 1/4$ ,  $t = 116^\circ$ ,  $\delta_{23} = 7^\circ 1/4$  and  $\delta_{32} = 7^\circ$ . The hybrid composition and bond overlaps are given in Tab. 1. The optimum values of all parameters considered are to a large degree, independent of each other, except, to some extent, for  $t$  and  $\delta_{32}$  what should be expected since both describe hybrids on the same atom. Once the best hybrids were obtained the angle  $\Phi_2$  was changed, and a slight increase in the total (scaled) overlap was found when  $\Phi_2 = 91^\circ$ .

### Bicyclobutane

Bicyclobutane consists of two fused three-membered rings for which a high degree of strain could be expected. By comparing its vibrational spectra and molecular structure investigations [11] with those of cyclopropane differences in the details of their bondings are expected. For example, attempted normal coordinate calculations show that the transfer of force constants from cyclopropane is not possible. We therefore expect larger differences of the hybrid composition between the corresponding hybrids in cyclopropane and bicyclobutane. The molecule is also related to cyclobutane, but however, its lower symmetry ( $C_{2v}$ ) permits deviations of the  $\psi_{CC}$ -hybrids from reflection planes, adding to the complexity of the calculations. There are three different CC-hybrids in this molecule, the  $s$ - $p$  content of which determines uniquely the hybridization of the remaining CH-hybrids. We start by assuming that all C—C hybrids are in the planes of their respective  $C_3$ -rings, except for the pair forming the C—C bridge, which, because of the symmetry of the system has to be in the vertical plane containing the  $C_2$  rotational axis (Fig. 2). The parameters which are varied are the deviation angles  $\delta_{23}$  and  $\delta_{32}$  which determine the hybrids  $\psi_{23}$  and  $\psi_{32}$ . The maximum overlap for  $\gamma = 126^\circ$  (experimental value) is obtained when  $\Theta_2 = 102^\circ$ , with  $\delta_{23} = 7^\circ$  and  $\delta_{33} = 38^\circ$ . The hybrids and bond overlaps are:

$$\begin{aligned} \psi_{23} &= sp^{4.78}, & \psi_{32} &= sp^{2.89}; & S_{23} &= 0.6082 \\ \psi_{33} &= sp^{10}; & S_{33} &= 0.4595. \end{aligned}$$

Comparing the C—C bond overlaps one notes a considerable decrease in the magnitude of that of the C—C bridge. This indicates that the assumptions

\* The indices are referred to primary, secondary and tertiary carbon atoms. The orbitals are directed from the atom named by the first index to that named by the second.

employed need revising, namely, the results have been constrained by forcing the  $\psi_{CC}$  hybrids to lie in the planes of the corresponding cyclopropyl rings, which, in fact, restricts  $\psi_{33}$  to unnecessary high values. That this is the case is demonstrated by the results obtained when this restriction is lifted. By letting the  $\psi_{CC}$  hybrids deviate from the cyclopropyl plane we obtain *twisted* bonds, i.e. bonds bent not in a plane, but in space. The numerical calculations are now considerably

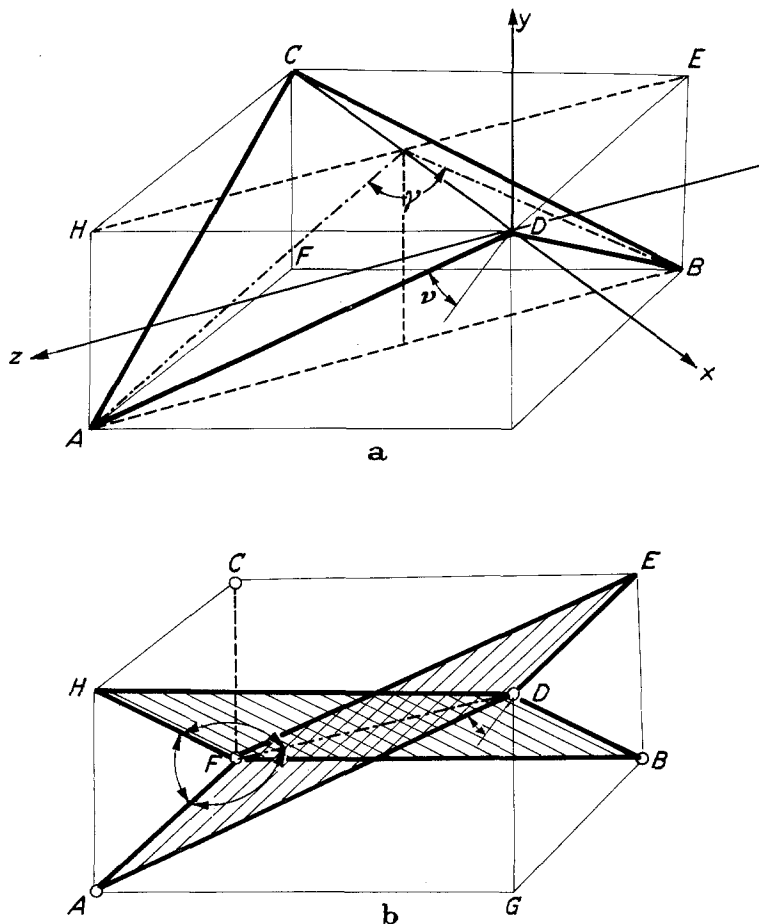


Fig. 2. a) cyclobutane skeleton imbedded in a square prism, b) the two reflection planes which contain hybrids

complicated, not only because of the increased number of parameters, but also by rather complex relations between them (details are given in the appendix). By rotating the hybrids at carbon atom  $D$  about an axis passing through  $D$  and parallel to  $AB$  (Fig. 2 a) the overlap ( $\psi_{23}$ ,  $\psi_{32}$ ) will slightly decrease (since it is at a maximum for the non-rotated case), while the overlap ( $\psi_{33}$ ,  $\psi_{33}$ ) will considerably increase, thus leading to a greater total overlap. For the observed geometry of the molecule ( $\gamma = 126^\circ$ ) the angle of rotation,  $\varphi = 25^\circ$ , increases the total overlap from 969.04 to 976.74. The deviation angle  $\delta_{33}$  is then  $(44^\circ - 25^\circ) = 19^\circ$ , which is close to those values found in other three-membered ring molecules. In Tab. 3

Table 3. *Optimum parameters and bond overlaps for different geometries of bicyclobutane*

$\gamma$	$\nu$	$\kappa$	$\varphi$	$\epsilon_{23}$	overlap $S(C_3 - C_3)$	$S(C_2 - C_3)$	$S(C_3 - H)$	$S_{Total}$
126° (experi- mental)	3°	44°	25°	2½°	0.5885	0.5901	0.7324	976.14
130½°	1°23'	46°15'	27°15'	2¾°	0.5915	0.5912	0.7296	976.91
131°	1°15'	46°30'	27°30'	3°	0.5917	0.5914	0.7291	

$S(C_2 - H) = 0.7182$ ;  $\kappa - \varphi = \delta_{33} = 19^\circ$  and  $\delta_{23} = 21^\circ$   
practically do not depend on dihedral angle  $\gamma$ .

are given the optimum parameters and bond overlaps for a geometry with the observed dihedral angle ( $\gamma = 126^\circ$ ), and for a geometry which give the best total overlap. The maximum is reached at  $\gamma = 130^\circ 1/2$  to  $131^\circ$ , as a results of the competition between the opposing contributions of the C—C and C—H overlaps at the tertiary carbon atom.

### 1,3-Dimethyl Bicyclobutane

Among the several derivatives of bicyclo(1.1.0)butane recently synthesized, 1,3-dimethyl bicyclo(1.1.0)butane (Fig. 1d) is of special interest in view of the unusual reactivity exhibited by its central 1,3 carbon-carbon bond [6]. The strain energy is one of the molecule's most significant properties, and a calculation of its hybridization is of particular interest. Besides the three different CC hybrids of bicyclobutane, an additional parameter is necessary to characterize the hybrids of the CC bonds at positions 1 and 4. These four hybrids then determine uniquely the *s-p* content of the remaining CH-hybrids. The numerical calculations proceeded similarly as for bicyclobutane, since the hybridization of the methyl groups does

Table 4. *Optimum parameters and bond overlaps for 1,3-dimethylbicyclobutane*

$\gamma$	$\nu$	$\kappa$	$\varphi$	$S(C_2 - C_4)$	$S(C_4 - C_4)$	$S(C_4 - C_1)$	$S_{Total}$
135½°	1°26'	50°4'	31°4'	0.5960	0.5952	0.6456	1531.43

The following parameters do not depend on  $\gamma$  (in the interval  $132^\circ < \gamma < 137^\circ$ ):  $\delta_{21} = 21^\circ$ ,  $\epsilon_{24} = 3^\circ$ ,  $\Theta_2 = 112^\circ 1/4'$ ,  $S(C_2 - H) = 0.7184$ ,  $S(C_1 - H) = 0.7046$

not depend strongly on their surroundings. The dihedral angle  $\gamma$  was assumed to be between  $132^\circ$  and  $137^\circ$ , since the experimental value of  $\gamma$  is not known. The maximum in total overlap is obtained for the geometry with  $\gamma = 135^\circ 1/2$ . The optimum parameters and bond overlaps are listed in Tab. 4. Again, the CC bonds in the cyclobutane ring are twisted. The angle of twist  $\tau$  can be obtained from  $\delta$  and  $\varphi$  using relationships between the angles and the sides of a spherical triangle (see appendix).

It is interesting to compare the results for bicyclobutane and 1,3 dimethyl bicyclobutane (cf. Tab. 1). As expected, hybrids at secondary carbon atom remain the same. A rather surprising result is that  $\psi_{33}$  and  $\psi_{44}$  differ only very little, i.e., the effect of the dimethyl substitution at the bridge carbon atom produces the same increase in the *s* content of all the CC bonds. In actual fact, *all* the hybrids

at the substitution site appear to take a similar amount of the available *s*-content. Although the bridge and the ring bond orbitals are so close in magnitude for both bicyclobutane and dimethyl bicyclobutane there is a significant difference in the *s*-content of the bridge and ring hybrids at the bridge head, the bridge hybrids having a smaller *s* contribution. This comparison is made for the different geometries, the dihedral angle being  $131^\circ$  and  $135^\circ 1/2$  for bicyclobutane and dimethyl bicyclobutane respectively. When a comparison for the same dihedral angle is made, the difference between  $\psi_{44}$  and  $\psi_{33}$  is slightly increased as is also that between  $\psi_{42}$  and  $\psi_{32}$ . If bond overlap is taken as an approximate index of bond strength then the results in Tab. 1 indicate that all C—C bonds in bicyclobutane are approximately of similar strength, and similarly (but with a slightly greater bond strength) are those in dimethyl bicyclobutane.

#### *Tricyclobutane and Cubane*

Tricyclo(1.1.0.0<sup>2,4</sup>)butane is possibly the most highly strained system which can be built from fused three membered rings, and is only a hypothetical structure, not yet synthesized. Nevertheless, it is of interest to find the hybridization

Table 5. *Bond overlaps for tricyclobutane*

$\delta$	$\Theta_3$	$S_{CC}$	$S_{CH}$	$S_{Total}$
$29 \frac{1}{2}^\circ$	$103^\circ 8'$	0.5551	0.7375	825,10

Table 6. *Bond overlaps for cubane*

$\delta$	$\Theta_3$	$S_{CC}$	$S_{CH}$	$\frac{1}{4} S_{Total}$
$11 \frac{1}{2}^\circ$	$104^\circ 52'$	0.6196	0.7294	433,72

parameters for this structure as they present the limit for molecules containing cyclopropyl groups. Similarly, cubane [pentacyclo-(4.2.0.0.2,<sup>5,0</sup>,3,<sup>8,0</sup>,7)octane], built from fused cyclobutane rings is expected to be highly strained. Recently, a few cubane derivatives have been synthesized [8], as well as cubane itself [9, 10]. The results are useful for comparing cyclobutane-containing molecules. Tricyclobutane and cubane possess high symmetry, belonging to  $T_d$  and  $O_h$  point groups respectively. All CC and CH bonds are equivalent, so only a single variational parameter is needed for the description of their hybridizations. The calculation is simple and the results are given in Tab. 1. The angle describing the deviation of a CC bond from a straight CC line is  $29 \frac{1}{2}^\circ$  and  $11 \frac{1}{2}^\circ$  for tricyclobutane and cubane respectively. This is indeed greater than calculated  $\delta$  for other three and four membered carbon rings. Similarly CC bond overlaps are smaller than in cyclopropane and cyclobutane, indicating an additional decrease in the CC bond energies due to greater strain in the former. It is somewhat surprising that the difference between cyclobutane and cubane is not greater.

#### *Bicyclo(1.1.1)pentane.*

Bicyclopentane (Fig. 1e) is another member of the bicyclic small ring compounds synthesized in recent years, and is of some interest for the interpre-



tation of the effects of bond angle deformation on the properties of these compounds [28]. The molecule belongs to the  $D_{3h}$  point group, although the exact geometry of the skeleton is not known. We assumed therefore that angle  $\Phi_2$  was in the region  $70^\circ - 100^\circ$  and varied  $\delta_{23}$  and  $\delta_{32}$  until the maximum was obtained. It is interesting that maximum overlap always occurs (irrespective of the assumed value of  $\Phi_2$ ) with  $\Theta_3 = 102^\circ$  and  $\Theta_2 = 103^\circ$ , and only  $\delta_{23}$  and  $\delta_{32}$  depend strongly on  $\Phi$ . When  $\Phi = 78^\circ$  (the geometry with overall maximum overlap)  $\delta_{23}$  and  $\delta_{32}$  become very similar in magnitude, but with  $\Phi_2 = 90^\circ$ , they differ considerably:  $\delta_{23} = 7^\circ$  and  $\delta_{32} = 19^\circ$ . So it appears therefore that on increasing the overlap (by varying  $\Phi_2$ ) there is a tendency for the angles of deformation for bent bond hybrids to approach the same value. This, together with the fact that the maximum is always obtained for  $\Theta_2 \approx 103^\circ$  (providing one uses Slater orbitals in the calculations) may considerably reduce the work as it permits a fairly close initial estimate of other parameters.

*Tetracyclo(3.3.1.0.2,80.4,6)nonane.*

Tetracyclononane,  $C_9H_{12}$ , (also called asterane, [1]) consists of two cyclopropane rings bridged by methylene groups. The molecule belongs to symmetry  $D_{3h}$ , with two non-equivalent CC and CH bonds. The exact geometry of the molecule (bond angles and bond lengths) however, is not known. The maximum overlap hybrids are calculated for various geometrical angles, covering a wide range:  $95^\circ < \Phi_2 < 120^\circ$ . As in nortrycyclene [20], which is related to this molecule, it is difficult to assume any particular value for  $\Phi_2$ , since the methylene  $CH_2$  bridge is expected to be described by bent bonds. The maximum was found for a geometry  $\Phi_2 = 114\ 1/2^\circ$  and the deviation angles  $\delta_{32}$  and  $\delta_{23}$  are approximately *minus*  $4\ 1/2^\circ$ . The interorbital angle  $\Theta_2$  is then  $105\ 1/2^\circ$ , a value not far from those usually obtained at the maximum for other molecules. It is rather surprising that optimum value for  $\Theta_2$  differ so little in very dissimilar structures (cf. nortrycyclene:  $\Theta_2 = 104^\circ$ ,  $\Phi_2 = 96^\circ$ ,  $\delta_{23} = 3^\circ$  and  $\delta'_{23} = 5^\circ$ ). The methylene CC bonds in  $C_9H_{12}$  are therefore bent towards the center of the molecule, the bending being small but significant. A similar situation (with negative  $\delta$ ) arises in some other molecules, such as the planar model for cyclopentane [5], and adamantane [13], although in these cases the angle is smaller and less significant. That is to say, the hybrids depend to some extent on the choice of orbitals used in the overlap calculation, and it is likely that another choice will affect bond overlaps and  $\delta$ -angles. In the calculations on cycloalkanes based on double-zeta orbitals recommended by CLEMENTI [2] one sees a decrease of negative  $\delta$  for cyclopentane [14].

### Discussion

The results in Tab. 1 and Tab. 2 together with those for cyclopropane and related molecules [20, 24] give the calculated hybridization and bond overlaps for more than fifteen highly strained molecules. We can try therefore by comparison to find some trends and regularities in the hybridizations of these molecules. Bond overlaps seem to be a good index when comparing C—C bonds in such different environments as cyclopropyl and cyclobutyl, or bicyclic groups. In the following table a list of bond overlaps for the highly strained molecules is given:

Table 7. *Bond Overlaps and hybrids for several highly strained molecules*

Bond Overlap	Molecule	Hybrids
0.5542	tricyclobutane	$sp^{4.5} - sp^{4.5}$
0.5762	cyclopropane, spiropentane	$sp^5 - sp^5$
0.5832	nortricyclene	$sp^{4.5} - sp^{4.5}$
0.5852	dimethylcyclopropane	$sp^{3.7} - sp^5$
0.5908	spiropentane	$sp^3 - sp^5$
0.5914	bicyclobutane, (bridge)	$sp^{4.9} - sp^{3.7}$
0.5917	bicyclobutane, (ring)	$sp^{4.4} - sp^{4.4}$
0.5952	dimethylbicyclobutane, (bridge)	$sp^{4.2} - sp^{4.2}$
0.5960	dimethylbicyclobutane, (ring)	$sp^{4.9} - sp^{3.1}$
0.6027	bicyclopentane	$sp^{4.5} - sp^{4.7}$
0.6177	cyclobutane	$sp^{4.3} - sp^{4.3}$
0.6196	cubane	$sp^{3.9} - sp^{3.9}$
0.6220	dimethylcyclobutane, (ring)	$sp^{4.3} - sp^{3.9}$
0.6304	dimethylcyclobutane, (methyl)	$sp^{3.2} - sp^{4.7}$
0.6314	nortricyclene	$sp^{3.5} - sp^4$
0.6403	dimethylcyclopropane	$sp^{4.7} - sp^{2.5}$
0.6435	tetracyclononane	$sp^{3.7} - sp^{2.9}$
0.6456	dimethylcyclobutane	$sp^{4.7} - sp^{2.1}$

The smaller the overlap the larger strain is to be associated with bent bonds. A glance at the above list reveals a rather surprising fact that cubane, as far as the overlap criterion is concerned, contains approximately as much strain as cyclobutane (of course, other factors besides "bending" of bonds contribute to the total strain energy, such as H . . . . . H repulsion etc., and this will have different contributions in cyclobutane and cubane). The most strained four-membered ring molecule is clearly bicyclopentane, the bond overlap being close to 0.6000 as compared with a value 0.6400 for a normal acyclic C — C bond. The C — C bond overlaps below 0.6000 characterize three-membered ring molecules, falling to 0.5760 (cyclopropane), those for tricyclobutane being exceptionally low. Bicyclobutanes have slightly higher C — C overlaps, close in magnitude to methyl substituted cyclopropanes. The bond overlaps above 0.6300 signify normal C — C bonds. Not too much weight should be given to these numbers, however, as the results depend to some extent on the assumed forms of the atomic orbitals employed. We used Slater orbitals, which are an approximate set of functions, and by changing to a better set the above figures will be revised. However, one hopes that the trends will remain.

A comparison with experimental data is possible for some of the molecules considered. According to the theoretical interpretation of spin-spin coupling constants in high resolution *NMR* spectra [17]  $J$  should be proportional to the fractional  $s$  character. In the following table we list  $J$  (cps), the fractional  $s$ -character and the CH bond overlaps for three and four carbon atom ring systems.

It is seen that the molecules form groups with secondary and tertiary cyclopropane and cyclobutane carbons which are characterized by different experimental  $J$  constants and with corresponding  $s\%$  or CH overlap. The CH overlaps increase with  $J$  as expected [29].

Table 8.  $C^{13}$ -H *Spin-spin coupling constants,  $s\%$  and CH bond overlaps*

Molecule		$J$ (cps)**	$s\%$	CH overlap
cyclopropane	secondary	161	33.1	0.7185
bicyclo(1.1.0)butane	carbon	161*	33.0	0.7184
bicyclo(1.1.0)butane	tertiary carbon	202	38.6	0.7291
cyclobutane	secondary	134	31.1	0.7139
bicyclo(1.1.1)pentane	carbon	144	31.6	0.7153
cubane	tertiary	160	38.8	0.7294
bicyclo(1.1.1)pentane	carbon	164	47.6	0.7409

\* Average of axial and equatorial coupling constants

\*\* Ref. [22] and [29].

Other experimental data are very scarce and are in general less direct in their interpretations. Thus for example chemical shifts for bicyclopentane: 8.16 ppm and 7.55 ppm indicate much higher  $s$ -content than in cyclopropane (4.5 ppm) or methane (4.1 ppm), which agrees with the data in Tab. 1. However, factors other than carbon hybridization determine the chemical shifts of cyclopropyl hydrogens, as a comparison between the chemical shifts of 1,1-dimethyl cyclopropane, spirohexane and spiro-pentane indicates [18]: as the external C—C—C bond angle is decreased, the resonance is shifted to lower field, despite the fact that the theoretical models indicate the opposite.

Comparison with more accurate calculations is instructive as it indicates the limitations of this and other methods more clearly. There are several calculations of hybridization for highly strained molecules. Besides those of COULSON and MOFFITT for the cycloalkanes  $(CH_2)_n$  ( $n = 3, 4, 5$ ), there is the equally ambitious work on "acetylenic" strained hydrocarbons (i.e. tricyclobutane and cubane) by WELTNER [27]. When our results are compared with his (Tab. 4 in ref. [27]) a consistently higher  $s\%$  is found in our calculations. A better agreement could be expected with Clementi or some other more realistic wavefunctions. HOFFMANN considered among many acyclic hydrocarbons a few cyclic systems, for which an extended Hückel-type calculation [12] was employed, in which overlap integrals and all interactions are included. With the same parameters for over 60 saturated or unsaturated molecules considered, he calculated, among other things, the resistance to internal rotation, ring conformations and geometrical isomerism. Although he could not predict strain energies, the geometries of the molecules appear to be reliably predictable. For cyclobutane the most stable conformation found was planar, albeit the potential curve was quite flat for bent forms with a dihedral angle up to  $15^\circ$ . This is then in agreement with our results, where similarly a slow change in energy on puckering was noted. There are a few other methods, such as that of SANDORFY and KLOPMAN [21, 15] or the MO method of POPLÉ and SANTRY [19], which have so far only been applied to paraffins and acyclic systems.

To conclude we wish to emphasize that the results of maximum overlap calculations provide hybrids, interorbital angles, deviations of "bent" bonds,

bond overlaps, and even provide information on "twisted" bonds for many molecules, for which more accurate methods, (such as the above mentioned semitheoretical methods or even more sophisticated approaches) may not easily yield results. More reliable results will be probably obtained with more realistic wave functions, but there is a limit to the method as such, and it cannot be successively improved as it lacks a correct fundamental basis. So do several other very useful empirical approaches such as the free-electron model and the Hückel theory.

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### Appendix

Trigonometric relationships between various angles in the cyclobutane and bicyclobutane skeletons are given. The angle ( $\xi$ ) between two symmetrical planes (ABD and ACD) in cyclobutane is related to the geometry by:

$$\sin \frac{\xi}{2} = \sqrt{\frac{\sin(s - \Phi_{HD}) \cdot \sin(s - \Phi_{AD})}{\sin \Phi_{HD} \cdot \sin \Phi_{AD}}}$$

Here  $2s = \Phi_{HD} + \Phi_{AD} + \Phi_{AH}$ , where  $\Phi_{HD}$ ,  $\Phi_{AD}$  and  $\Phi_{AH}$  are defined as:

$$\cos \Phi_{HD} = \frac{HF}{DF}, \quad \cos \Phi_{AD} = \frac{AF}{DF}, \quad \cos \Phi_{AH} = \frac{AF}{HF}.$$

The angle  $\Theta_{CC}$ , between two hybrids which deviate from a straight CC line by  $\delta$ , is given by:

$$\sin \frac{\Theta_{CC}}{2} = \sin \left( \frac{\pi - \xi}{2} \right) \sin (\Phi_{AF} + \delta)$$

where

$$\cos \Phi_{AF} = \frac{AD}{FD}.$$

Using

$$\sin \frac{\xi}{2} = \left[ 2 \left( 1 + 2 \tan^2 \frac{\gamma}{2} \right) \right]^{-\frac{1}{2}}$$

the relationship between  $\Theta_{CC}$ ,  $\gamma$  and  $\delta$  is obtained:

$$\sin \frac{\Theta_{CC}}{2} = \frac{\sin \frac{\gamma}{2}}{\sqrt{1 + \sin^2 \frac{\gamma}{2}}} \cos \delta + \frac{1}{\sqrt{2}} \sin \delta.$$

In bicyclobutane the situation is more complicated in so far as  $AB \neq CD$ . Hybrids  $\psi_{33}$  and  $\psi_{32}$  with the interorbital angle  $\Theta'_{CC}$  are related through:

$$\left( \frac{a}{b} \right)_{33} \cdot \left( \frac{a}{b} \right)_{32} = \cos \frac{\Theta'_{CC}}{2} \cos (\lambda + \kappa)$$

where

$$\sin \frac{\Theta'_{CC}}{2} = \sin \frac{\gamma}{2} \cdot \sin (60^\circ + \delta_{32}),$$

$\lambda$  is the angle between the plane formed by two  $\psi_{32}$  hybrids and  $C_3 - C_3$  bond, and  $\kappa$  is the angle between  $\psi_{33}$  and the  $C_3 - C_3$  bond:

$$\tan \lambda = \left( 1 + \sin^2 \frac{\gamma}{2} \right)^{\frac{1}{2}} \cdot \tan (60^\circ + \delta_{32}).$$

To obtain the angle of twist of a  $C_2 - C_3$  bond (by rotating the hybrids  $\psi_{33}$  and  $\psi_{32}$  at  $D$  by angle  $\varphi$ ), and to calculate the  $\pi - \pi$  overlap for twisted bonds, additional relations are needed. These can be obtained from the known components of the unit vectors: 1. along the  $C_2 - C_3$  bond:

$$\left( -\frac{1}{2}, -\frac{\sqrt{3}}{2} \cos \frac{\gamma}{2}, \frac{\sqrt{3}}{2} \sin \frac{\gamma}{2} \right);$$

2. along hybrid  $\psi_{32}$ :

$$\left[ \sin (\delta_{32} - 30^\circ), -\cos (\delta_{32} - 30^\circ) \cos \frac{\gamma}{2}, \sin \frac{\Theta}{2} \right]$$

where  $\Theta$  is the interorbital angle  $\sphericalangle \psi_{32}, \psi_{33}$ ; and 3. along the hybrid  $\psi_{32}$  after rotation by an angle  $\varphi$  about the  $z$ -axis. These later are obtained with the help of the rotation matrix:

$$\begin{pmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{pmatrix} .$$

The coordinate system is oriented as in Fig. 2. If  $\omega_{32}$  is the angle between the hybrid  $\psi'_{32}$  and the line joining atoms  $C_2, C_3$ , then:

$$\begin{aligned} \cos \omega_{32} = & -\frac{1}{2} \left[ \cos \varphi \sin (\delta_{32} - 30^\circ) + \sin \varphi \cos (\delta_{32} - 30^\circ) \cos \frac{\gamma}{2} \right] - \\ & - \frac{\sqrt{3}}{2} \cos \frac{\gamma}{2} \left[ \sin \varphi \sin (\delta_{32} - 30^\circ) - \cos \varphi \cos (\delta_{32} - 30^\circ) \cos \frac{\gamma}{2} \right] + \\ & + \frac{\sqrt{3}}{2} \sin \frac{\gamma}{2} \sin \frac{\Theta}{2} . \end{aligned}$$

Similarly from the components of a unit vector perpendicular to  $C_2 - C_3$ , but in the plane  $AFE$ :

$$\left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \cos \frac{\gamma}{2}, \frac{1}{2} \sin \frac{\gamma}{2} \right)$$

and the components of  $\psi'_{32}$  ( $\psi_{32}$  after the rotation by  $\varphi$ ) we obtain for the angle  $\pi_{32}$ , the angle between them:

$$\begin{aligned} \cos \pi_{32} = & \frac{\sqrt{3}}{2} \left[ \cos \varphi \sin (\delta_{32} - 30^\circ) + \sin \varphi \cos (\delta_{32} - 30^\circ) \cos \frac{\gamma}{2} \right] - \\ & - \frac{1}{2} \cos \frac{\gamma}{2} \left[ \sin \varphi \sin (\delta_{32} - 30^\circ) - \cos \varphi \cos (\delta_{32} - 30^\circ) \cos \frac{\gamma}{2} \right] + \\ & + \frac{1}{2} \sin \frac{\gamma}{2} \sin \frac{\Theta}{2} . \end{aligned}$$

The angle of "twist" can be obtained from the difference

$$\tau = \alpha_3 - \alpha_2$$

where

$$\cos \alpha_2 = \frac{\cos \pi_{32}}{\sin \omega_{32}}, \quad \cos \alpha_3 = \frac{\cos \pi_{23}}{\sin \omega_{23}} .$$

Alternatively  $\tau$  can be obtained from the known values of  $\varepsilon, \delta$  and  $\omega$  as the difference

$$\tau = \chi_{32} - \chi_{23}$$

where  $\chi_{ik}$  are the angles between the plane containing the bond  $C_i - C_k$  and the hybrid  $\psi_{ik}$ , and a reference plane (for example the plane of  $C_3$ -ring ( $AFE$ )):

$$\cos \chi_{ik} = \frac{\cos \varepsilon_{ik} - \cos \delta_{ik} \cos \omega_{ik}}{\sin \delta_{ik} \sin \omega_{ik}} .$$

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