Hybridization in Highly Strained Small Ring Hydrocarbons.
I. Tricyclo- and Tetracyclopropylidene

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The hybridization in tricyclopropylidene and tetracyclopropylidene has been calculated by the method of maximum overlap. The results show that the hybrids describing the central ring have more s character than those in cyclopropane and cyclobutane: $sp^{3.02}$ and $sp^{3.31}$ as compared to $sp^{3.86}$ and $sp^{3.47}$ respectively. Consequently the central bonds in the two molecules investigated are stabilized by the cyclopropyl substitutions. An interesting comparison between the maximum overlap hybridization and hybridization based on more elaborated calculations is made.

INTRODUCTION

There is considerable evidence in the literature to indicate that the approximate description of molecules by hybrids when the hybridization is restricted to the special cases: sp, sp^2 and sp^3 is not adequate. Within the hybridization model the hybrids of the form sp^n, when n is non-integer, give a more general base for a description of molecules, and are expected to be more useful for establishing empirical correlations, providing methods are available for determining the exponents n which characterize them. The principle, or more correctly the criterion of maximum overlapping, originally suggested by Slater and Pauling, has served as the basis for the determination of approximate hybrids. Several papers considered the problem of the construction of non-equivalent hybrids[1-3], and discussed the application[4-6]. There has been an extensive application of a particular form of the maximum overlap method[6] to strained hydrocarbons which leads to useful correlations between hybridization parameters and various experimental quantities, such as ^{13}C—H spin-spin coupling constants[7], bond energies[8] or chemical shifts[9]. The application to less strained hydrocarbons similarly leads to correlations with CC and CH bond length[10] and the acidities in non-conjugated hydrocarbons[11].

In the present paper and the following in this series we investigate the hybridization in highly strained systems containing three-membered rings with the aim of finding the hybrids for various structural groupings which arise in such molecules. The method of maximum overlap has been already applied to several molecules containing three membered rings such as cyclopropane[12] and methyl substituted cyclopropanes[13], cyclopropene[8], spiropentane, nortricyclene and tetrahedrane[14], methylene cyclopropane and related molecules having exocyclic double bonds[15], but this is far from exhausting the

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abudance of molecules having three-membered rings in various structurally interesting environments.

In this paper in particular we consider tetracyclopropylidene and related hypothetical tricyclopropylidene (Fig. 1) in which cyclopropane rings are attached to a cyclobutane and cyclopropane skeleton respectively.
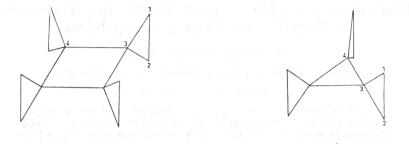

Fig. 1. Schematic diagrams of molecular geometries and the numbering of atoms for (a) tetracyclopropylidene and (b) tricyclopropylidene.

OUTLINE OF THE METHOD

The method of calculation has been described in several earlier papers (see for example refs. 6., 12.). It should be mentioned only that we assumed the CC bond lengths of 1.54 Å and CH bond lengths of 1.08 Å as suggested by Dewar and Schmeising[16]. The atomic orbitals of double zeta type, given by Clementi[17], have been assumed for which the basic overlap integrals are available[18] (Table I). The aim of the calculations is to find the coefficients

TABLE I

The Basic Overlap Integrals for Carbon-Carbon and Carbon-Hydrogen Bonds Used in the Calculation

$(2s, 1s_H)$	0.5654
$(2p, 1s_H)$	0.5033
$(2s, 2s)$	0.3567
$(2s, 2p)$	0.4154
$(2p, 2p)_\sigma$	0.2750
$(2p, 2p)_\pi$	0.2648

a and b for all hybrids $\psi_{ij} = a\,(s) + b\,(p) \equiv sp^n$, directed from atom i towards atom j, (here $n = (b/a)^2$) so that a suitably weighted sum of bond overlaps:

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

attains the maximum. Here S_{CC} and S_{CH} are bond overlaps for various CC and CH bonds in the molecule, the sum is extended over all bonds, while $k_{CC} = 121.17$ and $k_{CH} = 135.86$ take into account the fact that the same overlap in different bonds corresponds to different energy. The coefficients a, b of the hybrids belonging to the same carbon atom are subject to the orthogonality relationship

$$a_i a_k + b_i b_k \cos \Theta_{ik} = \delta_{ik}$$

Here Θ_{ik} is the angle between the directions of hybrids ψ_{ij} and ψ_{kj}. In cyclic systems the hybrids are generally not alined along the bond direction. The search for the best hybrids, *i. e.* those which give maximum sum of weighted bond overlaps, is made numerically by a systematic variation of independent hybrid parameters in the appropriate regions. The calculation is considerably reduced when the initial hybridization assumed in the calculation is carefully selected and here the results available for structurally similar molecules are very useful. As the search of the optimal hybridization involves numerous repetitions of the calculation, the method is suitable for programming on small computers.

A separate program for each molecule is written in Fortran IV. As input particular values of the exponents n of hybrids ψ_{12}, ψ_{13} and ψ_{31} are assumed, and the coefficients of all hybrids are expressed by them. For example $a_{12} = (1/(1 + n_{12}))^{1/2}$, $b_{12} = (n_{12}/(1 + n_{12}))^{1/2}$, $a_{1H} = (0.5 - 0.5/(1 + n_{12}) - 0.5/(1 + n_{13}))^{1/2}$ *etc.* Each of the assumed hybrid exponents n_{ij} is varied in the interval ± 0.06 from the initially assumed value, in steps of 0.002. When the maximum of the sum of scaled overlaps was found, the whole procedure is repeated assuming now as input the output of the previous calculation. When the input and output exponents are the same on four significant figures the calculation is stopped. For example, in tetracyclopropylidene we started the calculation assuming $n_{12} = 3.800$, $n_{13} = 3.800$ and $n_{31} = 3.300$, the values which are based on the results available for related three and four membered hydrocarbons. Since this is a very good estimate of the hybridization, after as few as four iterations we obtained for the final values $n_{12} = 3.721$, $n_{13} = 3.757$ and $n_{31} = 3.309$ which are identical to the input of the fourth iteration.

RESULTS AND DISCUSSION

Tetracyclopropylidene (I) and tricyclopropylidene (II) are the first members of the series of structurally related molecules for which the trivial name rotanes was suggested[19,20]. The hybridization of the spiro-carbon atoms is of special interest. The magnitude of CC bond overlaps gives some information on the strain in these molecules and the relative stability of the central bonds when compared with CC bond overlaps in other molecules having cyclobutane and cyclopropane rings. This is particularly interesting in the case of tricyclopropylidene which up to this moment has not been synthetized.

In Table II are summarized the hybrids, the bond overlaps, the interorbital angles and the deviations of hybrids from the bond directions for the molecules considered. As expected the hybrids describing the substituted cyclopropane parts in the two molecules are very similar. There are small differences between hybrids ψ_{12} and ψ_{13} of the two molecules. Firstly we notice that $\psi_{12} \neq \psi_{13}$, *i. e.* there is some differentiation or »asymmetry« between the hybrid directed to the central ring and the one directed to a peripheral carbon. A similar »asymmetry« was observed earlier, for example in methylene cyclopropane and spiropentane, between the hybrid directed towards non-equivalent carbons, and it is a regular feature of such structural environments. Although the difference between ψ_{12} and ψ_{13} is more pronounced in tricyclopropylidene it has little effect on the magnitudes of the respective bond overlap integrals S_{12} and S_{13}. The difference between the two integrals for tetracyclo and tricyclopropylidene is mainly determined by the large difference in the hybrid ψ_{31} of the two molecules, which is for the latter

The Maximum Overlap Hybrids, the Bond Overlaps, the Interorbital Angles and the Angles of Deviation of Hybrids from the Bond Directions for Tetracyclopropylidene and Tricyclopropylidene

Tetracyclopropylidene

Hybrids		Overlap
$\psi_{12} = 0.4602$ (s) $+ 0.8878$ (p)	$sp^{3.722}$	$S_{12} = 0.6041$
$\psi_{13} = 0.4584$ (s) $+ 0.8887$ (p)	$sp^{3.758}$	$S_{13} = 0.6084$
$\psi_{31} = 0.4817$ (s) $+ 0.8763$ (p)	$sp^{3.310}$	
$\psi_{34} = 0.5177$ (s) $+ 0.8556$ (p)	$sp^{2.732}$	$S_{34} = 0.6582$
$\psi_{1H} = 0.5376$ (s) $+ 0.8432$ (p)	$sp^{2.460}$	$S_{1H} = 0.7283$

Interorbital angles

$$\Theta_1^{2,3} = 105^0\,20' \qquad \Theta_3^{1,2} = 106^0\,50' \qquad \Theta_5^{4,5} = 110^0\,50'$$

Deviation angles

$$\delta_{12} = 22^0\,30' \qquad \delta_{31} = 23^0\,30' \qquad \delta_{34} = 10^0\,30'$$

Tricyclopropylidene

Hybrids		Overlap
$\psi_{12} = 0.4609$ (s) $+ 0.8875$ (p)	$sp^{3.708}$	$S_{12} = 0.6045$
$\psi_{13} = 0.4572$ (s) $+ 0.8894$ (p)	$sp^{3.784}$	$S_{13} = 0.6119$
$\psi_{31} = 0.5010$ (s) $+ 0.8654$ (p)	$sp^{2.984}$	
$\psi_{34} = 0.4990$ (s) $+ 0.8666$ (p)	$sp^{3.016}$	$S_{34} = 0.6205$
$\psi_{14} = 0.5379$ (s) $+ 0.8430$ (p)	$sp^{2.457}$	$S_{1H} = 0.7284$

Interorbital angles

$$\Theta_1^{2,3} = 105^0\,20' \qquad \Theta_3^{1,2} = 109^0\,15' \qquad \Theta_3^{4,5} = 108^0\,50'$$

Deviation angles

$$\delta_{12} = 22^0\,30' \qquad \delta_{31} = 24^0\,30' \qquad \delta_{34} = 24^0\,20'$$

molecule very close to the sp^3 type. The overlap S_{13} is somewhat larger than S_{12} for the two molecules, in agreement with the same results found for example in spiropentane. This is the consequence of the higher s-content of the hybrids ψ_{31} compared to ψ_{13} and ψ_{12}. However, it is more important to observe that overlap S_{34} of the central ring is considerably larger than S_{13} or S_{12} of the substituted cyclopropyl rings. The corresponding hybrids forming the central ring in tricyclopropylidene are very close to idealized sp^3 type. One may expect therefore that the ring would be much more strained than a normal cyclopropane ring since CC bonds in cyclopropane involve hybrids with higher p-character, *i. e.*, smaller interorbital and deviation angle, and this may be more favourable than having sp^3 hybridization[21]. But on the contrary the central ring in tricyclopropylidene is less strained than those in spiropentane and cyclopropane since the correct amount of the skeletal strain should be obtained from the magnitude of CC bond overlaps and not from the magnitude of the deviation angles which may sometimes be misleading. Thus the stabilizing effect of the substituted cyclopropyl group on the skeletal strain is evident. Since the nonbonded repulsions in tricyclopropylidene will make a smaller opposing contribution than in tetracyclopropylidene we may expect that tricyclopropylidene is relatively stable.

There are few experimental data on tetracyclopropylidene available to facilitate a comparison with the results of the maximum overlap calculation. Conia and Denis[19] report several IR bands, maxima of UV absorptions and the position of a single peak in NMR, which indicates that the central cyclo-

butane skeleton is either planar (as we assumed in our calculations) or effectively planar. The frequency at 3056 cm^{-1} is in the region characteristic for cyclopropanes and is consistent with a high s-content of CH hybrids. However, it is not easy to establish a quantitative correlation between IR stretching frequencies and hybridization, as discussed by Scrocco[22]. Spin-spin coupling constants J (^{13}C—H) are currently assumed to depend mainly on the percentage of s-character in the bonds[23], and when available can indicate the degree of hybridization. In particular for several cyclic and polycyclic hydrocarbons it has been found that there is an excellent agreement between the hybridization parameters calculated by the method of maximum overlap and the experimental values deduced from Muller and Pritchard's empirical relationship J = 500 a^2. (Here a is the coefficient of the hybrid describing CH bond in question. See ref. 7, 24—26.) However, there is no J (^{13}C—H) coupling constant for tetracyclopropylidene, but a value J = 160 Hz has been reported for related pentacyclopropylidene[20]. This value is very close to reported values for several cyclopropane derivatives (summarized in Table I of ref. 27) which indicates little variations of J value in various cyclopropane rings, and so we expect a value close to 160 Hz also in tetracyclopropylidene. When J (^{13}C—H) is calculated for the cyclopropane ring from the hybrids for CH bonds, which are similar in their s-p composition in different cyclopropane derivatives, the value J = 145 Hz is obtained which is too low. The agreement between the calculated (by maximum overlap method) and experimental (from J = 500 a^2) values for less strained four, five membered and acyclic hydrocarbons is within 1—2%, not 10% as in molecules having three-membered cyclopropane ring. Several factors besides the hybridization are of importance in determining the magnitudes of spin-spin coupling constants[28-30], but Juan and Gutowsky[31] have derived linear relationship between s character and the corresponding J (C^{13}—H) coupling constant not invoking other contributions. They employed a valence bond formalism and an »average excitation energy« approximation in the perturbation expression for J. The calculated values of J which deviate from the experimental J values by a large amount may originate from partial delocalisation accompaned by an unusual value for an »average excitation energy«. This may make an important contribution in three-membered rings and account for difficulties in the J — s character correlation in three membered rings.

Several highly strained small-ring systems have been recently investigated by more elaborate methods and it is of interest to compare the results. Sinanoğlu and Trindle[32] have examined cyclopropane and a few polycyclic systems such as cubane, tetrahedrane, prismane, etc.[33] with the aim of establishing the importance of hybridization changes vs. hyperconjugation in the qualitative description of the bonding. In their calculation they set up completely localized bond orbitals with variable hybridization indices. These indices are adjusted until a maximum in repulsion self-energies of orbitals or minimum of exchange is achieved.* Their results and ours (which are based on the maximum overlap method) are not very different, as a comparison between hybrids in cyclopropene (Table III) shows. The coefficients of s orbital, for example, differ about 2% (the exponents n = (b/a)^2 are more sensitive, as the coefficients a and b change in the opposite directions). On

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* Trindle and Sinanoğlu method of localization from which hybridization is also extracted is given in ref. 34.

TABLE III

A Comparison Between Hybrids Obtained by the Maximum Overlap Approximation
and Hybrids Obtained by Adopting Wiberg's Bond Index Definition (ref. 44)
and Del Re Procedure (ref. 36).

Cyclopropane

Trindle and Sinanoğlu (ref. 32) (Wiberg's bond index)		Maximum overlap approximation (ref. 8)	
	n		n
$\psi \sigma'_C = 0.438$ (s) $+ 0.899$ (p)	4.20	0.448 (s) $+ 0.894$ (p)	3.99
$\psi_{C'H} = 0.564$ (s) $+ 0.826$ (p)	2.15	0.548 (s) $+ 0.837$ (p)	2.34
$\psi \sigma'_C = 0.494$ (s) $+ 0.869$ (p)	3.10	0.510 (s) $+ 0.860$ (p)	2.85
$\psi_{CC} = 0.579$ (s) $+ 0.815$ (p)	1.98	0.591 (s) $+ 0.807$ (p)	1.86
$\psi_{CH} = 0.614$ (s) $+ 0.789$ (p)	1.65	0.625 (s) $+ 0.781$ (p)	1.56

Methylene cyclopropane

Del Re procedure (Jordan, Gilbert, Malreau and Pincelli (ref. 34).		Maximum overlap approximation (ref. 15)
$C(1) — C(2)$	$sp^{4.26}$	$sp^{3.78}$
$C(1) — C(3)$	$sp^{4.26}$	$sp^{3.95}$
$C(3) — C(1)$	$sp^{3.13}$	$sp^{2.70}$
$C(3) — C(4)$	$sp^{0.94}$	$sp^{1.18}$
$C(4) — C(3)$	$sp^{1.58}$	$sp^{1.77}$
$C(1) — H$	$sp^{2.23}$	$sp^{2.40}$
$C(4) — H$	$sp^{2.27}$	$sp^{2.13}$

the other hand Malreau et al.[35] proposed to build a fully localized determinant using bond orbitals and expressed the energy by a perturbation expansion and in the case of several small strained molecules analyzed the influence of the assumed hybridization state on the ground state energy. They found for hybrids obtained by Del Re's process[36,37] in which the overlap in each bond is maximized and then the orbitals are orthogonalized by a local transformation allowing variations in the directional properties of the hybrids according to the relative values of the initial bond overlaps, a beter energy than for hybrids following from the maximum overlap method which we have used, in which Clementi orbitals are assumed for carbon atoms and hydrogen 1 s-orbital with $\zeta = 1.00$ is used. (A comparison of hybrids obtained by the two procedures for methylene cyclopropane is given in Table III to illustrate the differences between the results obtained by the two methods.) We observe that when Slater instead of Clementi orbitals are used in the maximum overlap method on cyclopropane hybrids similar to those of Del Re's method are obtained, which then give satisfactory values for J (^{13}C—H) coupling constants for C_3-rings, but poor results for less strained systems. All this indicates that in three-membered rings some features are present the origin of which is not at the moment fully understood. However, there are several very recent non-empirical calculations on cyclopropane, cyclopropene and related small rings[38-43], which will help to improve the present semiempirical and approximate treatments and help to formulate the necessary modifications so that their future application may have a better success.

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IZVOD

Hibridizacija jako napregnutih malih prstena ugljikovodika I. Triciklo- i tetraciklopropiliden

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Metodom maksimalnog prekrivanja izračunata je hibridizacija za triciklopropiliden i tetraciklopropiliden. Rezultati pokazuju da hibridi koji opisuju središnji prsten u promatranim molekulama imaju veći s-karakter nego odgovarajući hibridi ciklopropana i ciklobutana: $sp^{3.02}$ i $sp^{3.31}$ u usporedbi sa $sp^{3.86}$ i $sp^{3.47}$. Dosljedno tomu, središnji prsten triciklopropana i tetraciklobutana su stabilizirani ciklopropilnom zamjenom. U radu se razmatra za nekoliko strukturno srodnih molekula zanimljiva usporedba među rezultatima metode maksimalnog prekrivanja i nekih razrađenijih metoda.

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