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Hybridization in Highly Strained Small Ring Hydrocarbons. II. Methylene Biscyclopropylidene and Dimethylene Biscyclopropylidenes

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The hybridization in methylene biscyclopropylidene, 1,1'-dimethylene biscyclopropylidene, and 1,2-dimethylene biscyclopropylidene is considered by applying the method of maximum overlap. The results show variations in hybrids describing exocyclic double bonds: for ring carbons from $sp^{2.38}$ to $sp^{2.85}$, and for off-ring carbons from $sp^{1.10}$ to $sp^{1.41}$, depending on the immediate surounding. Bond overlaps for C=C consequently vary somewhat, the largest bond overlap being of the central C=C bond connecting two three membered rings. The results of the maximum overlap calculations are compared with available experimental data.

INTRODUCTION

Hybrids of the form sp^n, when n is nonintegral, give a more satisfactory base for a description of molecules, especially strained cyclic and polycyclic hydrocarbons, than the standard *sp*, sp^2, and sp^3 hybrids. We continue with the investigations of maximum overlap hybrids in these systems[1], and in this paper in particular we wish to consider highly strained unsaturated hydrocarbons having small rings related to biscyclopropylidene. We have selected methylene biscyclopropylidene, 1,1'-dimethylene biscyclopropylidene, and 1,2-dimethylene biscyclopropylidene. Three membered rings in these molecules have exocyclic C=C double bonds which introduce interesting structural features which merit detailed examination. Several molecules having exocyclic double bonds have already been investigated[2] by the maximum overlap method. The previous investigations include methylene cyclopropane, dimethylene cyclopropane, and bisethanoallene. The results of that work are summarized by observing that »in cummulenes the double bond as judged by the overlap criterion has considerably larger strength than an exocyclic C=C bond, which is already stronger than a normal C=C bond such as the double bond in ethylene, due to an appreciable withdrawal of *s*-character from the cyclic bent bonds in C_3-systems«. Besides these larger effects, which are characteristic for the kind of C=C bond, smaller variations in the *s*-character of the hybrids constituting a bond occur. In this work we wish to investigate these smaller variations in C=C bond overlaps which are

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caused by the relative positions of two or more methylene substituents. Similar investigations have been reported for methyl substitution on the cyclopropane ring, where it has been demonstrated clearly that systematic variations in hybrids and bond overlaps follow as the number of methyl groups attached to the molecular skeleton is altered[3]. We establish in this paper a similar regularity for methylene substitution of cyclopropane rings.

The method of maximum overlap has been described in details in earlier work, in particular in ref. 1, the first paper in this series of application of the method of maximum overlap to the calculation of hybridization for highly strained small ring systems. We therefore assume that the method and the notation is familiar and will report the results. It should be mentioned only that we assumed the CC single and double bond lengths from 1.54 Å to 1.48 Å, according to their sp^n—sp^m type, CC double bond of 1.34 Å, and C—H bonds of 1.102 Å and 1.086 Å, according to C—H bond type as suggested by Dewar and Schmeising[4]. The basic overlap integrals used are summarized in Table I.

TABLE I

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

	C—C		C=C	
Bond type:	$sp^3 — sp^3$	$sp^3 — sp^2$	$sp^2 — sp^2$	$sp^2 — sp^2$
Bond length (Å)	1.54	1.52	1.48	1.34
$(2s, 2s)$	0.3567	0.3653	0.3827	0.4469
$(2s, 2p)$	0.4154	0.4213	0.4329	0.4695
$(2p, 2p)_\sigma$	0.2750	0.2724	0.2662	0.2326
$(2p, 2p)_\pi$	0.2648	0.2719	0.2865	0.3427
	C—H			
Bond type:	sp^3	sp^2		
Bond length (Å)	1.102	1.086		
$(2s, 1s_H)$	0.5654	0.5736		
$(2p, 1s_H)$	0.5033	0.5056		

RESULTS

Methylene biscyclopropylidene (I), 1,1′-dimethylene biscyclopropylidene (II), and 1,2-dimethylene biscyclopropylidene (III), considered in this paper are illustrated in Fig. 1. The various carbon atoms are designated by numbers in such a way that like groupings of atoms retain the same numbering in different molecules, thus facilitating comparisons. A hybrid orbital Φ_{ij} is directed from carbon atom i to carbon atom j, and with another orbital Φ_{ji} contributed to an overlap S_{ij} of a bond C_i—C_j. Hybrids directed towards hydrogens are designated as Φ_{iH}, Φ_{jH}. The Table II summarises the results: the hybrids, bond overlaps, interorbital angles and deviation angles. Biscyclopropylidene, which may be regarded as the parent hybrocarbon, is discussed elsewhere[5], but is included in Table I for the sake of comparison. The local environment of C=C bonds vary in the molecules considered. In biscyclopropylidene we have three membered rings with one exocyclic C=C bond.

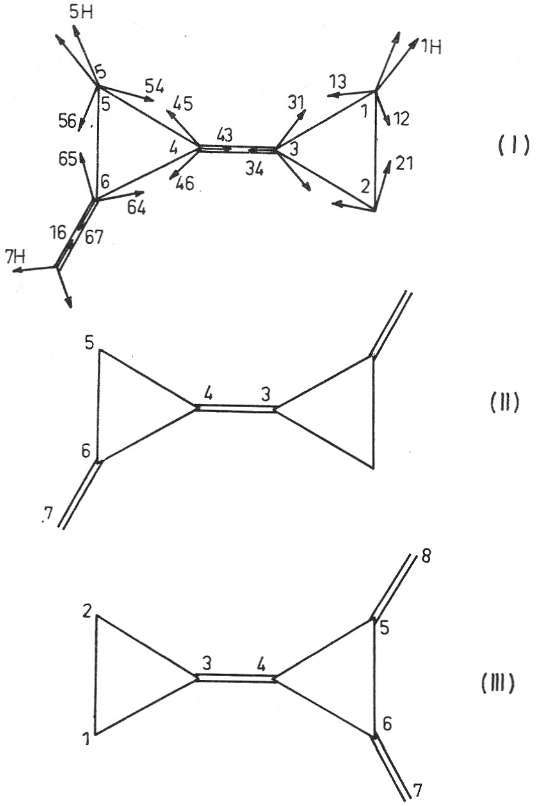

Fig. 1. **Schematic diagrams of molecular geometries and the numbering of atoms for methylene substituted biscyclopropylidenes.**

In methylene biscyclopropylidene and 1,1′-dimethylene biscyclopropylidene there are two exocyclic C=C bonds in C_3 ring, and finally in 1,2-dimethylene biscyclopropylidene we reach the maximal number of three C=C exocyclic bonds attached to a cyclopropane ring. The molecules also possess different symmetry properties, thus (II) has a center of symmetry (point group D_{2h}), while (III) has instead of a plane of symmetry (point group C_{2v}). It has been noticed in several earlier calculations of hybrids that symmetry may constrain hybrids and produce different hybrids in otherwise very similar structural groupings[2]. For that reason the inclusion of methylene biscyclopropylidene, which belongs to point group C_s, having neither a center of inversion nor an additional plane of reflexion, will provide useful information. The different symmetry properties of the molecules (I)—(III) are also reflected in the number of independent parameters which have to be optimized in order to maximize the suitably scaled sum of bond overlap. For the two molecules having higher symmetry there are in all seven independent hybrids, while for methylene-biscyclopropylidene there are ten independent hybrid orbitals, *i. e.*, ten hybrid exponents n to be found.

TABLE II

The Exponents n of sp^n *Hybrids*

Calculated by the maximum overlap method for methylene biscyclopropylidene (I), 1,1′-dimethylene biscyclopropylidene (II), and 1,2-dimethylene biscyclopropylidene. Notation: Hybrid ij is directed from carbon atom i to carbon atom j (for numbering see Fig. 1).

Hybrid	(I)	(II)	(III)
12	3.726	—	3.730
13	3.706	—	3.712
31	2.640	—	2.632
34	1.220	1.393	1.225
43	1.407	1.393	1.266
45	2.462	2.478	2.580
46	2.382	2.394	—
54	3.738	3.738	2.618
56	3.658	3.660	2.612
64	—	2.796	—
65	2.850	2.850	—
67	1.097	1.097	1.238
76	1.736	1.736	1.726
1H	2.473	—	2.470
5H	2.483	2.482	—
7H	—	2.152	2.159

The CC hybrids given in Table II may be grouped as follows:

(a) $sp^{3.66}$—$sp^{3.74}$: hybrids forming bent bonds of C_3 rings at non-substituted carbons

(b) $sp^{2.38}$—$sp^{2.85}$: hybrids forming bent bonds of C_3 rings at exocyclic C=C carbon

(c) $sp^{1.70}$—$sp^{1.73}$: hybrids forming exocyclic C=C bond at methylene carbon, and

(d) $sp^{1.10}$—$sp^{1.41}$: hybrids forming exocyclic C=C bond at C_3 ring.

The results in group *(a)* are also found for a number of other hydrocarbon compounds, sometimes even with a larger interval for the variations of the hybrid exponent n, than the one found in biscyclopropylidenes considered here. The results in *(b)*—*(d)* point to a considerable spread of hybrid composition for hybrids participating in various C=C bonds. Even within single groups, except for *(c)*, there is a large range of hybrids variation. The reason for this rather large variation is that in these molecules we have two effects supporting one another thus magnifying the range of variation of n. In small rings bent bonds arise. These prefer high *p* content, associated with smaller interorbital angle which thus reduces the amount of deviation of the ring bonds. This makes *s* content available for exocyclic bonds. If now the exocyclic bond is a double CC bond, then there is already a preference for high *s* content, as observed for a large number of unsaturated hydrocarbons. This follows from the fact that the relative magnitude of the basic overlap integrals, *i. e.*, $(2s, 2s)$, $(2s, 2p)$, $(2p, 2p)_\mathrm{s}$ and $(2p, 2p)_\mathrm{p}$, is such that for shorter CC bonds the first two overlaps are dominant. The two effects are in phase, supporting one another giving a high *s* content for exocyclic C=C bonds. In the central C=C bond this becomes especially pronounced since the effects are present at both ends of the double bond.

In Table III are listed carbon-carbon bond overlaps in ascending order illustrating the effects of the methylene substitution at C_3 rings on the magnitude of bond overlap. In several places there should be two or three different bond overlaps associated with same substituents or same bond termini. The difference comes from the presence of a third substituent in the ring, or is due to rings with different substituents. These smaller variations are reflecting the presence of next nearest neighbours. The results in Table III indicate that a methylene substitution, or generally a substitution of an exocyclic C=C, increases C—C overlap in C_3 ring by approximately 0.020, and that this is additive if two sites are substituted. Variations in the magnitudes of $C=C_3$ bonds is smaller, from 0.780 to 0.795, as compared with the variations of bond overlaps within C_3 rings (from 0.600 to 0.650). The cyclopropane ring is therefore considerably strengthen by exocyclic substitutions. This permits speculations on the possibility of relatively stable polycyclic derivatives of biscyclopropylidene consisting of three membered rings joined by CC double bonds. Some of such higher derivatives of biscyclopropylidene would be of considerable theoretical interest, like a system having six C_3 rings connected by exocyclic C=C bonds forming a single large twelve membered ring. Finally, by joining a large number of such units a planar system is obtained, representing an example of a completely cross-conjugated system and having a distant relationship to graphite (same degree of unsaturation and an expected layer structure), but consisting of rings of different size.

TABLE III

Bond Overlaps and the Exponents of the Corresponding Hybrids for Various C—C and C=C Bonds in ascending order illustrating the effects of substitution

Bond Overlap	Hybrids		Substituents	
	C_3 ring bonds		C_1	C_2
0.603	3.73	3.73	—	—
0.621	3.66	2.85	—	$=CH_2$
0.623	3.71	2.64	—	$=C_3$
0.624	3.74	2.47		
0.648	2.61	2.61	$=CH_2$	$=CH_2$
0.649	2.58	2.62	$=C_3$	$=CH_2$
0.652	2.39	2.80		
	$C_3=C$ bonds		bond termini	
0.780	1.24	1.73	ring	methylene
0.784	1.10	1.74		
0.785	1.39	1.39	ring	ring
0.790	1.22	1.41		
0.795	1.23	1.27		

Before discussing and comparing the calculated and the experimental quantities we have to comment on the possibility of some delocalization in these cross conjugated molecules. The presence of alternation of single and double CC bonds does not necessarily lead to extensive delocalization. The assumption in our calculations that C=C bonds do not interact is supported for example by work on n-radialenes[6] and on fulvene and related systems[7]. The electronic spectra of these molecules have been interpreted without invoking conjugation of C=C bonds in the ground electronic state with which we are concerned. In the excited electronic states however C=C bonds can no longer be assumed as non interacting.

COMPARISON WITH EXPERIMENTAL DATA

It has been found that hybridization parameters, in particular *s*-content and the magnitudes of CC bond overlaps, may be correlated with several experimental quantities. Thus besides the well known empirical correlation of NMR spin-spin coupling constants and *s*-character of C^{13}—H an C^{13}—C^{13} bonds[8-10] for which maximum overlap hybrids may also be well used[11], quantitative correlations were reported for proton acidity and *s* character of maximum overlap hybrids[12]. Another correlation is found between CC and CH bond overlaps and the corresponding bond lengths[13], and between CC bond overlaps and bond energies[14,15]. Finally a linear relationship between the exponent n of sp^n hybrids and the magnitude of chemical shifts is found for a large family of hydrocarbons, although it lacks theoretical justification[16]. Qualitative comparisons beetwen hybrids *s/p* content and the magnitudes of vibrational frequencies, specifically bond stretching frequencies, have occasionally been raised, but no useful correlation has been established in spite of some theoretical examinations of the problem[17]. It is difficult to estimate the role of several factors influencing the force constants, but nevertheless some comparison between the C—H, C—C and C=C stretching frequencies and bond overlaps for selected closely related molecules will indicate to which extent the differencies in the stretching frequencies for a given bond type can be accounted for by variations in the hybrid compositions.

For molecules considered here there are no reported spin-spin coupling constants J (C^{13}—H) or J (C^{13}—C^{13}), proton acidities, or precise bond lenghts and bond energies. However, there are values of several infrared and Raman frequencies and a number of chemical shifts for biscyclopropylidenes and some molecules which are related, and for which a similar if not the same hybridization can be assumed. As has been said above, infrared frequencies and chemical shifts are the least suitable for detalied correlations and comparisons, but some trends in the hybridization in the molecules considered may become more obvious. Thus while the normal C=C bond has a band at 1670cm.$^{-1}$, bands in the range 1700—1820 cm.$^{-1}$ have been reported for small rings with exocyclic double bonds. In 1,1′-dimethylene biscyclopropylidene thus exocyclic C=C absorbs at 1750 cm.$^{-1}$ (IR), 1793 cm.$^{-1}$ and 1820 cm.$^{-1}$ (Raman)[18]. If we assign to asymmetric and symmetric exocyclic C=C stretching the frequencies at 1750 cm.$^{-1}$ and 1793 cm.$^{-1}$ respectively, for the mean C=C stretching frequency we obtain about 1770 cm.$^{-1}$ This is close to the value found in methylenecyclopropane (1780 cm.$^{-1}$)[19] and trimethylenecyclopropane (1773 cm.$^{-1}$)[19]. The band at 1820 cm.$^{-1}$ is then due to the central C=C bond, which is consistant with it being Raman active. The difference of approximately 50 cm.$^{-1}$ between the mean exocyclic C=C frequency and the frequency of the central C=C is too big to be attributed solely to kinetic and geometrical factors which are included through the matrix. Thus the two different C=C bonds have to be described with different force constant. From Table III we see that the two C=C bonds are characterized by different hybrids and have appreciably different bond overlaps: the central C=C bond overlap is 0.790 as compared with the exocyclic terminal C=C which is 0.780. The difference indicates that the former bond is stronger, which is in agreement with the observed vibrational frequencies.

Several chemical shifts have been reported for molecules here considered. However the difficulty in directly using and correlating the chemical shifts is due to some inherent complications when three membered rings are present. Here several factors not fully understood obscure the simple proportionality established for hydrocarbons which relates the chemical shift and the exponent n.

CONCLUSIONS

In spite of limited comparisons between the experimental and theoretical quantities discussed here, due to lack of additional experimental data, hybrids calculated by the maximum overlap method have been found useful in correlating some molecular properties. The results are also useful in discussing structural features and bonding as has been demonstrated in Table III. Such constructed hybrids differentiate between the same structural or functional groups in slightly different environments. This makes the maximum overlap method and the maximum overlap hybrids of potential use in discussing finer details of the chemistry of these and similar molecules, and of hydrocarbons in general. However, it should be mentioned that it is possible to use hybrids determined by methods other than the maximum overlap method used here. These other methods have been discussed in the literature[21,22], and the most frequently criteria for determining optimum hybrid functions, besides using alternative maximum overlap approaches[21], is the best reproduction of the results given by SCF calculations[22]. The maximum overlap method is only one of several, and it cannot be proved that it is the best for the problem under the study. But in several instances when a comparison between the maximum overlap hybrids and those obtained from more ambitious calculations was made the agreement is quite satisfactory. Thus the maximum overlap hybrids in cyclopropane and methylenecyclopropane, which are structurally very closely related to the molecules studied here, are in very good agreement with the results of Trindle and Sinanoğlu obtained in their CNDO/2-SCF calculation[23]. There are minor differences characterizing any diverse theoretical approach, the origin and the significance of which should be investigated. In another paper such a discussion relevant to comparison of the maximum overlap method and other available methods will be presented[24]. What is important however, is that one should not use only the standard hybrids, that the use of general hybrids may be more appropriate, and that a detailed description of hybridization is a powerful tool for the interpretation of molecular properties.

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IZVOD

Hibridizacija jako napregnutih malih prstena ugljikovodika. II. Metilen bis ciklopropiliden i dimetilen bis ciklopropilideni

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Korištenjem metode maksimalnog prekrivanja razmatrana je hibridizacija slijedećih molekula: metilen bis ciklopropilidena, 1,1′-dimetilen bis ciklopropilidena, i 1,2-dimetilen bis ciklopropilidena. Rezultati pokazuju promjene kod hibrida koji opisuju eksocikličnu dvostruku vezu: u slučaju ugljikovih atoma prstena od $sp^{2.38}$ do $sp^{2.85}$, a za ostale ugljikove atome od $sp^{1.10}$ do $sp^{1.41}$ u ovisnosti o neposrednoj okolini. Integrali prekrivanja za pojedine C=C veze, kao posljedica ovih varijacija, također primaju različite vrijednosti; najveću vrijednost imaju za centralnu C=C vezu koja spaja dva tročlana prstena. Rezultati ovih računa metodom maksimalnog prekrivanja uspoređuju se s eksperimentalnim podacima, posebno s vrijednostima frekvencija istezanja C=C veze.

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