

Hybridization in Methylene-cyclopropane and Related Molecules Having Exocyclic Double Bonds

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The hybridization in methylenecyclopropane, dimethylenecyclopropane, bisethanoallene, and related molecules containing double bonds externally attached to a cyclopropane ring is considered by applying the method of maximum overlap. The results show that the bond overlap of an exocyclic double bond is larger than the bond overlap of a normal C=C bond, and double bonds in allenes have even larger overlap than an exocyclic C=C bond. The results of the calculations are correlated with some available experimental data.

Die vorliegende Arbeit behandelt die Hybridisierung in Methylene-cyclopropan, Dimethylene-cyclopropan, Bisäthanoallen und verwandten Molekülen, die alle einen Cyclopropanring mit exocyclischen Doppelbindungen enthalten. Den Berechnungen liegt die Methode der maximalen Überlappung zugrunde. Wie die Ergebnisse zeigen, ist die Überlappung in diesen exocyclischen Doppelbindungen größer als in gewöhnlichen C=C-Bindungen. Die Doppelbindungen in den bearbeiteten Allenen besitzen eine bedeutend größere Überlappung als die exocyclischen C=C-Bindungen. Die theoretisch ermittelten Werte werden mit einigen verfügbaren experimentell gefundenen Werten verglichen.

Le principe du recouvrement maximum est appliqué à l'étude de l'hybridation dans le méthylène-cyclopropane, le diméthylène-cyclopropane, le biséthanollène et des molécules voisines contenant des doubles liaisons attachées extérieurement à un cyclopropane. Les résultats montrent que le recouvrement de liaison d'une double liaison exocyclique est plus élevé que celui d'une liaison C=C normale, et que les doubles liaisons des allènes ont un recouvrement encore plus grand. Les résultats de calcul sont corrélés à certaines données expérimentales disponibles.

Introduction

The method of maximum overlap has recently been applied to calculations of hybridization in several highly strained three- and four-membered rings [13, 19, 24]. We consider in this paper some related molecules: methylenecyclopropane, dimethylenecyclopropane, bisethanoallene, and similar systems containing double bonds externally attached to a cyclopropane ring, and some of their methyl substituted derivatives. The results may lead to information regarding the role of exocyclic double bonds in the rehybridization and stability of a cyclopropane ring.

The criterion of maximum overlap has been repeatedly used in qualitative discussions of bonding in molecules. However, since there are tables of overlap integrals [17] and auxiliary functions [12] available it is possible to calculate the hybrids which give the optimum overlap. In this way we can examine to what extent the empirical approach of maximum overlap is useful and adequate in the discussions of bonds and bond strengths on a quantitative level. The method of

Table 1. The basic atomic overlap integrals for Clementi orbitals

C-H: 1.07 Å	C-C: 1.535 Å	C=C: 1.337 Å
$(1s_H, 2s_C) = 0.5843$	$(2s_C, 2s_C) = 0.3569$	$(2s_C, 2s_C) = 0.4470$
$(1s_H, 2p_C) = 0.5083$	$(2s_C, 2p_C) = 0.4145$	$(2s_C, 2p_C) = 0.4686$
	$(2p_C, 2p_C)_\sigma = 0.2739$	$(2p_C, 2p_C)_\sigma = 0.2322$
	$(2p_C, 2p_C)_\pi = 0.2644$	$(2p_C, 2p_C)_\pi = 0.3641$

maximum overlap which has been so widely and frequently used in a qualitative form deserves some quantitative examination before it is judged, modified or abandoned. We hope that this paper, together with other published calculations, will help to achieve an appraisal of the method.

The method of calculation has been described in many papers (see for example [13, 14, 19], and [24] and references therein). It shall be mentioned here only that an idealized geometry of the molecules is taken as basis, i.e. we neglect the fact that similar bond lengths vary by a few percent, that overlap integrals of the so called double zeta type AO's [21] calculated by CLEMENTI [4] are used (see Tab. 1), and that the scaling factor of CC single and double bonds has been given the same value [see 18]. As variable parameters it is convenient to select: θ_i^{jk} , the angle between two hybrids ψ_{ij} and ψ_{ik} of the same atom i , and δ_{ij} , the deviation angle of the hybrid ψ_{ij} from the straight line joining the atoms i, j .

Results and Discussion

The molecules considered in this paper are: methylenecyclopropane (I), dimethylenecyclopropane (II), trimethylenecyclopropane (3-radialene) (III), diisopropylidenecyclopropane (IV), 1,1-dimethyl - diisopropylidenecyclopropane (V), methylene-ethylenecyclopropane (VI), ethylenewisopropylidenecyclopropane (VII), bisethanoallene (VIII), 1,1'-dimethylbisethanoallene (IX), 1,1,1',1'-tetramethylbisethanoallene (X), illustrated in Fig. 1. The various carbon atoms are designated by letters in such a way that like groupings of atoms retain the same notation in the different molecules, thus facilitating comparison. A hybrid orbital ψ_{ab} is directed from carbon atom a to b , and with another orbital ψ_{ba} contributes to an overlap S_{ab} of the bond C_a-C_b . The hybrids directed towards hydrogens are designated ψ_{aH} , ψ_{bH} etc. Methylenecyclopropane, which may be considered the parent hydrocarbon, is discussed in some detail, and the remaining molecules are described and discussed jointly.

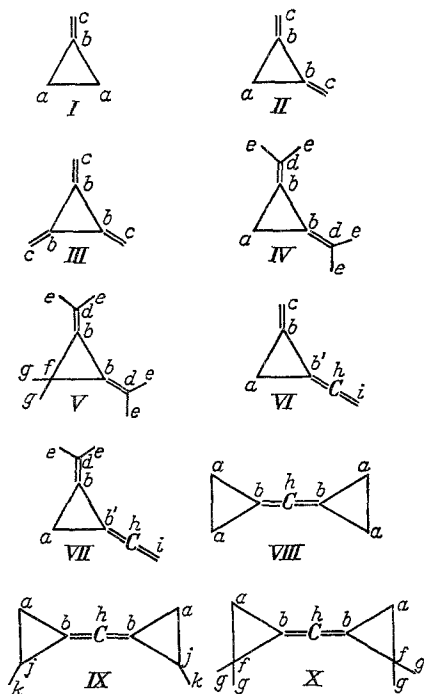


Fig. 1. Cyclopropanes

Methylenecyclopropene

This molecule has three nonequivalent carbon atoms (designated as a , b , c), and it requires the following hybrids for a complete description of the C-C bonds: ψ_{aa} , ψ_{ab} , ψ_{ba} , ψ_{bc} and ψ_{cb} . Once these five hybrids are known the remaining hybrids ψ_{aH} and ψ_{cH} , which characterize the C-H bonds, are uniquely determined from the orthogonality conditions. At the beginning of the search for the optimum parameters we assumed: 1) $\psi_{aa} = \psi_{ab}$, i.e. no asymmetry between the two non-equivalent hybrids at carbon atom a , and 2) that these hybrids are the same as those in cyclopropane, i.e. we assumed $\theta_a^{ab} = 105^\circ$. We then attempted to find the best values for the remaining interorbital angles, θ_b^{aa} and θ_c^{HH} , which are associated with the exocyclic double bond, since we have no previous experience concerning the hybridization in a double bond exocyclic to a cyclopropene ring and hence no knowledge as to the approximate values for these interorbital angles.

The hybrids at carbon atom b are of particular interest. Simple sp^2 hybridization predicts interorbital angles of 120° , however a smaller value is expected for θ_b^{aa} , in order to reduce somewhat the very large deviation of the hybrids ψ_{ba} . The results of the calculation show an increase in p -character of the hybrids ψ_{ba} forming the ring, and this is in accordance with expectations. The angle is found to be $111^\circ 45'$, so that the angle of deviation of the bond is about 26° , compared with a value of 22° found in cyclopropane. Although the angle of deviation increases by several degrees the corresponding C-C bond overlap does not decrease: $S_{ba} = 0.6151$, and is appreciably larger than the overlap $S_{aa} = 0.6016$ associated with $\delta_{aa} = 22^\circ$. This is due to the larger s -contribution in the hybrids ψ_{ba} which secures a larger overlap, since the basic atomic overlap ($2s_C$, $2s_C$) is larger than ($2p_C$, $2p_C$). A similar situation occurs in spiropentane [19, 24], where the hybrids on the central atom are symmetry forced into sp^3 , and thus makes the overlaps of the central C-C bonds larger than those of the external C-C bonds, which are described by sp^{3-86} hybrids. Because the bond overlap is an index of the bond strength, we may conclude that the bond C_a-C_b is stronger than C_a-C_a , and, on the whole, that the C_3 -ring in methylenecyclopropane is relatively stronger than that in cyclopropane i.e. that *the exocyclic double bond has a stabilizing effect with respect to bond strength in the C_3 -ring.*

The hybrids at atom c will also differ from the idealized sp^2 case, although a smaller change is expected here since there are no strained or bent bonds associated with this part of the molecule. We found the valence angle HCH to be 118° . The hybrid ψ_{cb} therefore which is involved in the formation of the double bond shows (relative to the remaining hybrids of this atom which are involved in C-H bond formation) a slight preference for s -character. Since the other hybrid involved in the formation of the double bond is very rich in s -content we have, as a result, a *considerable participation of s -orbital and s -character in the constitution of the exocyclic C=C bond.*

The whole calculation is now repeated with these preliminary values of the interorbital angles θ_b^{aa} and θ_c^{HH} so obtained in order to find the best hybrids ψ_{aa} , ψ_{ab} and the angle θ_a^{ab} which were previously restricted. The angle θ_a^{ab} remains at 105° , while a slightly better overlap is obtained when ψ_{aa} and ψ_{ab} are assumed to be different. The results are listed in Tab. 2 which contains the hybrids, the interorbital angles and the bond overlaps. Throughout the calculations we assumed that the deviation angles δ_{aa} and δ_{ab} at the same atom are equal. A check was made to see whether, if assumed different, a significant increase in the total overlap would be obtained. The best values found were: $\delta_{aa} = 22.35$ and $\delta_{ab} = 22.65$, a deviation of only 0.15° from their average value. Such a small change has hardly any meaning at all and is neglected with full justification.

Table 2

Calculated maximum overlap hybrids, bond overlaps, and angles between the directions of hybrids

(I) Methylenecyclopropane

$$\begin{aligned} \psi_{aa} &= sp^{3.781} & S_{aa} &= 0.6017 \\ \psi_{ab} &= sp^{3.950} & S_{ab} &= 0.6119 \\ \psi_{ba} &= sp^{2.699} & & \\ \psi_{bc} &= sp^{1.177} & S_{bc} &= 0.7794 \\ \psi_{cb} &= sp^{1.770} & & \\ \psi_{aH} &= sp^{2.397} & S_{aH} &= 0.7440 \\ \psi_{cH} &= sp^{2.130} & S_{cH} &= 0.7496 \end{aligned}$$

$$\theta_a^{ab} = 105^\circ, \theta_b^{aa} = 111^\circ 45', \theta_c^{HH} = 118^\circ$$

(II) Dimethylenecyclopropane

$$\begin{aligned} \psi_{ba} &= sp^{2.674} & S_{ab} &= 0.6137 \\ \psi_{bb} &= sp^{2.784} & S_{bb} &= 0.6238 \\ \psi_{bc} &= sp^{1.157} & S_{bc} &= 0.7801 \end{aligned}$$

other hybrids and overlaps as in (I)

$$\theta_b^{ab} = 111^\circ 30'$$

(III) Trimethylenecyclopropane

$$\begin{aligned} \psi_{bc} &= sp^{1.157} \\ \psi_{bb} &= sp^{2.729} & S_{bb} &= 0.6257 \end{aligned}$$

other hybrids and overlaps as in (I)

$$\theta_b^{bb} = 111^\circ 30'$$

(IV) Diisopropylidenecyclopropane

$$\begin{aligned} \psi_{ea} &= sp^{3.507} & S_{ae} &= 0.6597 \\ \psi_{da} &= sp^{2.241} & & \\ \psi_{ab} &= sp^{1.611} & S_{ba} &= 0.7349 \\ \psi_{eH} &= sp^{2.855} & S_{eH} &= 0.7350 \end{aligned}$$

other hybrids and overlaps as in (II)

$$\theta_e^{HH} = 110^\circ 30', \theta_a^{ee} = 116^\circ 30'$$

(V) 1,1-Dimethyldiisopropylidenecyclopropane

$$\begin{aligned} \psi_{fb} &= sp^{3.623} & S_{bf} &= 0.6163 \\ \psi_{fg} &= sp^{2.522} & S_{fg} &= 0.6541 \end{aligned}$$

other hybrids and overlaps as in (IV)

$$\theta_f^{bb} = 106^\circ, \theta_g^{HH} = \theta_e^{HH} = 110^\circ 30'$$

(VI) Methyleneethylenecyclopropane

$$\begin{aligned} \psi_{ih} &= sp^{1.797} & S_{hi} &= 0.7843 \\ \psi_{hi} &= \psi_{hb'} = sp & S_{b'h} &= 0.8025 \\ \psi_{b'h} &= sp^{1.385} & & \end{aligned}$$

$$\psi_{ba'} = sp^{2.642} \quad S_{ab'} = 0.6150$$

$$\psi_{b'b} = sp^{2.698} \quad S_{b'b} = 0.6249$$

$$\psi_{ab'} = sp^{3.713}$$

$$\psi_{ab} = sp^{3.950} \quad S_{ab} = 0.6125$$

other hybrids and overlaps are as in (II)

$$\theta_i^{HH} = 118^\circ 15', \theta_b^{ab} = 112^\circ, \theta_b^{b'b} = 111^\circ 30'$$

(VII) Ethenyleneisopropylidenecyclopropane

all hybrids and overlaps as in (IV) and (VI)

(VIII) Bisethanoallene

$$\psi_{ba} = sp^{2.61} \quad S_{ab} = 0.6129$$

$$\psi_{bh} = sp^{1.24}$$

$$\psi_{hb} = sp \quad S_{bh} = 0.8013$$

other hybrids and overlaps as in (I)

$$\theta_b^{aa} = 112^\circ 30'$$

(IX) 1,1'-Dimethylbisethanoallene

$$\psi_{aj} = sp^{3.78}$$

$$\psi_{ja} = sp^{3.68} \quad S_{aj} = 0.6028$$

$$\psi_{bj} = sp^{2.61}$$

$$\psi_{jb} = sp^{3.61} \quad S_{bj} = 0.6145$$

$$\psi_{kj} = sp^{3.51}$$

$$\psi_{jk} = sp^{2.64} \quad S_{kj} = 0.6518$$

$$\psi_{jH} = sp^{2.29} \quad S_{jH} = 0.7462$$

$$\psi_{kH} = sp^{2.86} \quad S_{kH} = 0.7350$$

other hybrids and overlaps are as in (VIII)

$$\theta_k^{HH} = 110^\circ 30', \theta_j^{ab} = 105^\circ 30',$$

$$\theta_a^{bj} = 105^\circ, \theta_b^{aj} = 112^\circ 30'$$

(X) 1,1,1',1'-Tetramethylbisethanoallene

$$\psi_{af} = sp^{3.82}$$

$$\psi_{fa} = sp^{3.55} \quad S_{af} = 0.6037$$

$$\psi_{ab} = sp^{3.90} \quad S_{ab} = 0.6135$$

$$\psi_{fg} = sp^{2.52}$$

$$\psi_{gf} = sp^{3.51} \quad S_{fg} = 0.6541$$

$$\psi_{fb} = sp^{3.71}$$

$$\psi_{bf} = sp^{2.61} \quad S_{bf} = 0.6155$$

$$\psi_{gH} = sp^{2.86} \quad S_{gH} = 0.7350$$

other hybrids and overlaps are as in (VIII)

$$\theta_g^{HH} = 110^\circ 30', \theta_f^{ab} = 106^\circ,$$

$$\theta_a^{bf} = 105^\circ, \theta_b^{af} = 112^\circ 30'$$

Other molecules

The results (i.e. the hybrids, the interorbital angles and the bond overlaps) for the other molecules considered are listed in Tab. 2. Because the hybridization in same groupings of atoms in different molecules is frequently the same, such data are included in the table only where a particular grouping of atoms first appears, unless, of course, there is a change in the hybridization. The main features of the numerical results contained in Tab. 2 may be summarized as follows:

(1) The hybridization of the methyl group is constant. This is in agreement with an empirically established rule that the properties of methyl groups are independent of their surroundings, and is also in agreement with similar findings in methyl substituted cyclopropanes [20, 24].

(2) A change in hybridization of a carbon atom forming the cyclopropyl ring due to substitution causes only a very slight effect on the hybridization at other positions, although the relevant bond overlaps may change appreciably. (Compare, for example, bond overlaps in compounds IV and V: after a dimethyl substitution at position *a* there is no change in the hybrids at atom *b*, but the corresponding C-C bond overlaps differ: $S_{ab} = 0.6137$ and $S_{fb} = 0.6163$).

(3) The optimum values of many parameters depend only on the local groupings of atoms and may be transferred to similar parts of another molecule. However, the symmetry of a molecule may introduce some constraints, therefore restricting the *s* or *p*-content of some hybrids. Thus, for example, hybrids ψ_{ab} in methylenecyclopropane and dimethylenecyclopropane are different.

(4) A C-H bond has a tendency, when adjacent to a C-C bond, to increase its *s*-content to some extent when compared with idealized sp^3 hybridization, and to decrease its *s*-content somewhat when adjacent to a C=C bond when compared with idealized sp^2 hybridization. Therefore in an " $sp^3 \rightarrow sp^2$ "-rehybridization a loss of only about 0.7 *p*-character is involved.

(5) Another regularity to be noticed is a fairly constant increase in the C-C bond overlap of the C_3 -ring by methyl substitution. This is apparent from the list of C-C bond overlaps given in Tab. 3 in ascending order. The data for methylcyclopropanes are also included. The increase is about 0.0015. A substitution of hydrogens by a methylene group produces a ten times larger increase. A further methyl substitution results in isopropylencyclopropane and produces only a small change in the C-C overlap of the C_3 -ring as is expected, since the two sites are not nearest neighbours.

Symmetry constraints, as mentioned above, may produce some larger changes in the hybrids which would otherwise be similar. Thus in methylenecyclopropane $\psi_{ab} \neq \psi_{aa}$, and in dimethylenecyclopropane $\psi_{ba} \neq \psi_{bb}$. If we compare hybrids ψ_{ab} in the two molecules, (or similarly the hybrids ψ_{ba}) we find that they are different, whereas the average of ψ_{aa} and ψ_{ab} in methylenecyclopropane, (or put it another way, if we assume $\psi_{aa} = \psi_{ab}$) has the same *s-p*-composition as ψ_{ab} in dimethylenecyclopropane. Similarly, if we take the average of ψ_{ba} and ψ_{bb} of dimethylenecyclopropane we will obtain ψ_{ba} of the parent hydrocarbon.

Another example of symmetry constraints may be observed in bisethanoallene and related symmetrically methyl substituted compounds. Here, the hybrids of the central atom are forced into *sp*. This will have an effect on the *s-p*-composition

Table 3. Bond overlaps and hybrids for various C-C and C=C bonds in ascending order, illustrating the effects of substitution

bond overlap	<i>p</i> -character of the hybrids		substitut. at C ₍₁₎ substitut. at C ₍₂₎	
	hybrid on C ₍₁₎	hybrid on C ₍₂₎		
	C ₃ ring bonds		substitution at the C ₃ ring	
0.6017	3.78	3.78	—	—
0.6028	3.78	3.68	—	methyl
0.6037	3.82	3.55	—	dimethyl
0.6119—0.6137	{ 3.95	{ 2.70	—	methylene
	{ 3.95	{ 2.67		
0.6129—0.6150	{ 3.95	{ 2.61	—	ethenylene
	{ 3.72	{ 2.64		
0.6145	3.81	2.61	methyl	ethenylene
0.6155	3.71	2.61	dimethyl	methylene
0.6163	3.63	2.67	dimethyl	isopropylidene
0.6238—0.6257	{ 2.78	{ 2.78	methylene	methylene
	{ 2.73	{ 2.73		
0.6249	2.79	2.70	methylene	ethenylene
	C ₃ -C bonds		bond termini	
0.6518	3.51	2.64	ring	methyl
0.6541—0.6547	{ 3.51	{ 2.57	ring	dimethyl
	{ 3.51	{ 2.52		
	C-C bond			
0.6597	3.51	2.24	dimethylene	methyl
	C ₃ =C bonds			
0.7794—0.7801	{ 1.18	{ 1.77	ring	methylene
	{ 1.16	{ 1.77		
0.7849	1.16	1.61	ring	dimethylene
0.8013—0.8025	{ 1.24	{ 1.00	ring	allene
	{ 1.39	{ 1.00		

of the hybrids of atom *b*, and, as a result, the interorbital angle θ_b^{aa} slightly increases. To what extent, therefore, does the symmetry contribute to the particular strain to be associated with such "forced" hybridization? To answer the above question we will compare the corresponding bond overlaps in two related molecules of different symmetry. For example, the C=C bond overlaps in bisethanoallene and methylenecyclopropane are 0.8005 and 0.7775 respectively. This is quite a large increase in the C=C bond overlap, indicating that *in cumulenes 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 the C₃-system.

Comparison with Experimental Data

The hybridization model is a crude approximation in itself, and calculations of hybrid coefficients by the maximum overlap procedure is an additional approximation. Concepts such as hybrids (orbitals) have no direct physical meaning, but

have proved to be very useful for computational and theoretical analysis, and within these frameworks may permit some comparison with experimental quantities.

Most useful in our case are the data from NMR and IR spectra. In the first case, the C^{13} -H spin-spin coupling constants, according to some theoretical interpretations, may be correlated with the *s*-character of the hybrid describing the C-H bond [9, 11]. Although there are some useful correlations [15, 16, 23] there have recently been raised some doubts and critical remarks, and the problem is not yet settled [7, 10].

On the other hand, the infrared frequencies may also give some indication about the *s-p*-character of a bond. Intuitively one would expect that if a C-H bond possesses larger overlap, due to a larger *s*-orbital participation, the bond will be stronger and consequently its IR absorption band will be at higher frequency. Some theoretical work on the connection between force constants and hybrid composition has very recently been initiated: SCROCCO [22] has obtained a relationship between the stretching force constant and the overlap integral valid for simple tetrahedral molecules. Since the variation in the stretching force constant (K_r) parallels the variation in $J(C^{13}\text{-H})$, BROWN and PUCKET [3] have searched in more detail for a quantitative relationship between the two variables. They found that the variation of the fractional *s* character in the carbon orbital directed to hydrogen does not in itself, lead to a significant variation in K_r . The force constant increases with increasing ionic character in the C-H bond, rather than as a result of hybridization changes. This finding is in support of the work of GRANT and LITCHMAN [7] who argued that the variation in the effective nuclear charge Z_{eff} of carbon experienced by the electrons in the C-H bonds is a function of the electron withdrawing properties of adjacent substituents.

The theoretical interpretation is awaiting some additional clarifications and more experimental data sufficiently analysed to be able to settle this problem. There are very little data available (analysed NMR and IR spectra) on molecules which we have considered in our present work. However the infrared spectra of 2,3-bis-(isopropylidene)-1,1-dimethylcyclopropane have been reported [2] to have a band at 1810 cm^{-1} ($5.52\ \mu$) which is assigned to the exocyclic double bond. This should be compared with a band at about 1670 cm^{-1} , which is characteristic of a normal C=C bond [1]. A shift to higher frequencies, which is not small, indicates that the exocyclic bond is considerably stronger than the normal bond, and this is in general accordance with the overlap calculations.

Some infrared frequencies have been reported for trimethylenecyclopropane [5, 25], and the spectra show a band at 1750 cm^{-1} characteristic of a carbon-carbon double bond stretch. A band is also reported at 2950 cm^{-1} , which seems to be too low for a =C-H vibration. However this may be explained by the fact, that S_{cH} has a rather low value.

There is some data on the alkenylidene cyclopropanes. All these compounds exhibit the characteristic allenic infrared absorption at $2020 \pm 20\text{ cm}^{-1}$ [8], the region which is at slightly higher frequencies than the frequency range normally cited for allenes: $1960\text{--}1980\text{ cm}^{-1}$ [1]. As is discussed by HARTZLER [8], it is generally true that force constants of double bonds attached to a cyclopropane ring are increased above their acyclic values. Thus a shift to higher frequency has been

observed for the double bond stretching frequency of methylenecyclopropane [6]. HARTZLER qualitatively explains the different magnitude of the shift in the C=C absorption of alkenylidenecyclopropane and methylenecyclopropane as follows: the frequency shift should not be as large for the allenes, since the stretching vibration of the allenic group mainly involves the motion of the central atom. As a consequence, the compression of the bond angles should not be as large for the alkenylidenecyclopropanes as for alkylidenecyclopropanes. The shift above acyclic values is seen to be about 40 cm^{-1} in the case of allene, as compared with a shift of 100 cm^{-1} for the olefins. This different behaviour can easily be understood by observing the magnitudes and the changes of the C=C overlap integrals in these molecules. Due to the large strain accompanying the bent bonds of the C_3 -ring, the C=C bond in methylenecyclopropane is rich in *s*-character, as discussed on p. 242, and has consequently a large overlap: 0.7794 (only the sigma component). This value should be compared with a value for an idealised sp^2 - sp^2 C=C double bond: 0.7174. The difference between the two values is large. On the other hand we should compare similar overlaps in alkenylidenecyclopropane. We find: $S_{bn} = 0.8025$ as compared with $S_{hi} = 0.7843$ (or with the overlap of an idealised sp - sp^2 bond: 0.7785). The difference is, in this case, considerably smaller and this is in agreement with expectations. The main cause for the different behaviour should be associated (as we propose from our calculations) with the fact that the overlap of an sp^2 - sp^2 double bond is more sensitive to a change of hybridization than that of an sp^2 - sp double bond which is closer to the maximum (saturation) point.

To conclude, we may say that the hybrids calculated by the maximum overlap method seem to provide a plausible quantitative picture of the bonding for molecules of medium complexity, such as the systems which we have considered in this paper. The hybrids so obtained are not too sensitive to the effects of their surroundings, so that for similar local groupings in different molecules, similar results are obtained. Therefore we may construct with considerable confidence the results for some molecules which are built of the same local groups of atoms without making the full calculations. For example, the hybrids of isopropylidenecyclopropane may be deduced from those of the compound IV, and similarly the hybrids of non-symmetrically substituted trimethylbisethanoallene may be deduced from those of the compounds IX and X.

Conjugation. Finally a comment has to be made regarding the presence of several conjugated bonds in some of the molecules considered. We have assumed same parameters (bond lengths or basic bond overlaps) for all molecules disregarding the possibility of delocalization and its consequence: shortening of C-C single bonds and lengthening of C=C double bonds. According to HEILBRONNER [8a] electronic spectra of *n*-radialenes are in good agreement with the calculations based on SIMPSON'S "independent system approach" [22a] which assumes *n* double bonds which do not interact in the electronic ground state of the system. The gross structure of the electronic spectra is deduced by taking into account only the energy delocalization in the excited states.

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