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Hybridization in Cyclopropane, Cyclobutane and Cubane

By

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The general procedure derived by DEL RE [6] for determining the hybrid orbitals of a molecule from the overlap matrix has been applied to cyclopropane, cyclobutane and cubane, for which the concept of hybridization is of a peculiar interest. The results are in good agreement with experimental facts and results of other theoretical procedures. The approximation which describes these molecules just in terms of localized bonds appears to be rather limited and such a phenomenon seems general for methylenic compounds. The problem of bent bonds is equally discussed.

La méthode générale proposée par DEL RE [6] pour déterminer les orbitales hybrides d'une molécule à partir de la matrice des intégrales de recouvrement a été appliquée au cyclopropane, au cyclobutane et au cubane, pour lesquels le concept d'hybridation présente un intérêt particulier. Les résultats sont en bon accord avec les faits expérimentaux et avec les conclusions auxquelles conduisent les autres méthodes théoriques. L'approximation qui consiste à décrire ces molécules en termes de liaisons localisées entre orbitales atomiques hybrides paraît limitée et ce phénomène semble général pour les composés à groupements méthylènes. Le problème des liaisons courbes est également discuté.

Die von DEL RE [6] vorgeschlagene, von der Matrix der Überlappungsintegrale ausgehende Methode zur Bestimmung der Hybrid-Orbitale eines Moleküls wurde auf Cyclopropan, Cyclobutan und Cuban angewandt. Bei diesen Molekülen beansprucht die Frage der Hybridisierung besonderes Interesse. Die Ergebnisse stimmen gut mit den experimentellen Befunden und den Schlußfolgerungen anderer Theorien überein. Die Beschreibung dieser Moleküle durch lokalisierte Bindungen zwischen atomaren Hybrid-Orbitalen ist nur eine grobe Näherung; das scheint allgemein für Verbindungen mit Methylengruppen zu gelten. Das Problem der gekrümmten Bindungen wird diskutiert.

Introduction

The concept of hybridization has been used for a long time as a powerful auxiliary in the description of molecules in terms of atomic orbitals. Some physical effects which are possibly related directly to the *s* characters of hybrid orbitals have been recently discovered [2], thus providing a more physical basis for this concept. However, from a theoretical point of view, the concept of hybridization is not clearly and uniquely defined. In particular, what definitions are given are often not applicable in practice to large molecules. In order to overcome this difficulty, one of us re-examined the problem of hybridization in the frame of the simple MO-LCAO method, and proposed that the "best" hybrid orbitals should be those providing the highest localization of the MO-LCAO Overlap matrix, under the condition that they be atomic orbitals orthonormal to each other for every given atom [6]. (By "localization" we mean here an approximate factorization of the Hamiltonian matrix into blocks; these blocks will be 2×2 blocks to a certain degree of approximation, unless they happen to have more than two off diagonal elements equal to each other, in which case they will be larger, and will correspond to many-centre bonds).

The hybrid orbitals corresponding to the above definition are unique, and can be easily obtained even for molecules with large numbers of different atoms. The procedure leading to them also corresponds to a special form of the Criterion of Maximum Overlap: in fact, by requiring that the whole overlap matrix between the eight orbitals of two atoms be brought as close as possible to a form where only one off diagonal element is non-vanishing, it requires essentially that the orbitals which form a bond overlap as much as is consistent with the orthonormality conditions imposed to the hybrids of each atom. However, this is not equivalent to imposing that the total overlap be maximum, as would be necessary if the hybrids were to satisfy the criterion of Maximum Overlap as used by many authors. Therefore, a comparison of the procedure of Ref. [*6*] with the latter form of the Criterion of Maximum Overlap may be most illuminating. Such a comparison has been made possible by a recent study of the cycloparaffins published by Goodwin and Coulson [*5*]. The present paper is devoted to a report on this comparison. In addition to presenting a practical example of the procedure of Ref. [*6*], we shall thus be able to discuss the general significance of the hybrids obtained in connection with bent bonds and lone pairs.

It will be useful to mention explicitly the following differences between our calculations on the cycloparaffins and those of Ref. [*5*]. Goodwin and Coulson, aided by the symmetry of the molecules under study, expressed the total overlap between the bonding hybrids as a function of a single parameter, letting the hydrogen atoms always follow the corresponding carbon orbitals, so that the CH bonds be straight; then they maximized the total overlap and derived the geometries of the molecules under study from the directions of the hybrids corresponding to the latter situation. We, on the other hand, assumed fixed positions of all the nuclei, and determined the hybrids corresponding to them; only for the sake of a comparison we consider different geometries, so as to be able to obtain by interpolation the configuration for which the CH bonds will be straight. This difference is due to the nature of our procedure, which is not expected to take advantage of special symmetries, but rather is designed to work along the same lines for any molecule.

From this point of view, situation is much simpler in cubane C_8H_8, which can be considered as the three dimensional homologous of cyclobutane (the octaphenyl derivative has been recently invoked [*8*]): the symmetry of the molecule determines the location of the hydrogen atoms.

Calculations and results

We studied the molecules of cyclopropane, cyclobutane and cubane. The bond distances have been taken equal to 1.53 Å for the $C - C$ bond and 1.08 Å for the $C - H$ bond in the first two compounds [*9*], and to 1.54 Å for $C - C$ and 1.09 Å for $C - H$ (which are the corresponding values in paraffins [*9*]) in cubane.

In order to study the dependence of our results on the assumed geometry, we have studied cyclopropane with two different values of the HCH angle (118° and 110°); cyclobutane has been assumed to be planar in one case, non-planar with a dihedral angle of 20° in the second case, the HCH angle being the same (118°) in both cases. (An additional calculation for cyclobutane has been carried out, as will be mentioned, with an HCH angle of 110°, but its results are not reported *in extenso*).

The overlap integrals have been calculated for Slater orbitals by means of Roothaan's formulas [*12*]. Their values, for adjacent atoms, are the following:

$$\begin{aligned}
&S\,[2s\,(C_1), && 2s\;\;(C_2)] &&= 0.3451\\
&S\,[2s\,(C_1), && 2p\sigma\,(C_2)] &&= 0.3687\\
&S\,[2p\sigma\,(C_1), && 2p\sigma\,(C_2)] &&= 0.3298\\
&S\,[2p\pi\,(C_1), && 2p\pi\,(C_2)] &&= 0.1955\\
&S\,[2s\,(C), && 1s\;\;(H)] &&= 0.5759\\
&\mathrm{S}\,[2p\sigma\,(C), && 1s\;\;(H)] &&= 0.4681.
\end{aligned}$$

A straightforward application of the method of Ref. [*6*] then leads to the various hybrid orbitals. For this, a numbering of the various atoms and a suitable choice of the coordinate axes are necessary. These are shown in Fig. 1 (for non-planar cyclobutane, atoms 1 and 7 are supposed to lie in the $x0y$ plane, atoms 4 and 10 are above this plane).

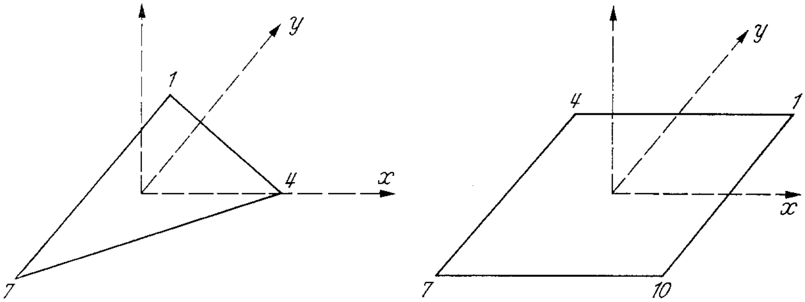

Fig. 1. Co-ordinate axes

The calculations were performed with an IBM 704 computer, using a program provisionally limited to 16 atoms with 1 or 4 orbitals per atom.*

Table 1**

	Cyclopropane		Cyclobutane		Cubane
	$H—C—H = 118°$	$H—C—H = 110°$	planar***	non planar	
a	0,4182	0,4284	0,4397	C_1 0,4382 C_4 0,4397	0,450
α	118° 48′	117° 36′	116° 16′	C_1 116° 16′ C_4 116° 16′	104° 40′
ω	21° 7′	21° 30′	6° 56′	C_1 7° 44′ C_4 6° 56′	11° 20′
S	6,0156	5,8761	8,1501	8,1476	13,1453

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* This program is available for distribution.

** The values obtained for the carbon 4 of cyclobutane are the same for the two geometries, whereas those for the carbon 1 are different. This is due to the fact that in both cases the local geometry around carbon 4 remains the same (the angle $C_1 — C_4 — C_7$ is 90°), and that around carbon 1 changes, the $C_{10} — C_1 — C_4$ angle becoming smaller that 90° in the non-planar molecule. The value of α remains practically constant, which indicates that α varies only slowly with the geometry of the molecule.

*** These results are not greatly altered for a $C—C$ bond length of 1.55 Å [*14*, *15*]: $a = 0{,}4354$; $\alpha = 116°46'$; $\omega = 6°46'$; $\delta = 8{,}1151$.

The most important results are assembled in Tab. 1, where the various symbols have the following meanings:

a is the coefficient of the pure s orbital of the hybrid of a carbon atom pointing towards another carbon atom;

α is the angle between the two orbitals of a carbon atom that point towards the two hydrogen atoms linked to it;

ω is the angle between the hybrid orbital pointing from a carbon atom towards a carbon atom linked to it, and the corresponding $C-C$ line;

S is the sum of the overlap integrals corresponding to the localized bonds obtained through the procedure in question (these bonds are those of the chemical formula). S is the half sum of the non-diagonal elements of the blocks corresponding to the bonds (Ref. [*6*] and Tab. 3), and to the total overlap of Ref. [*5*].

Discussion

The values of the total overlaps S are practically the same as those corresponding to the maximum overlap according to the procedure of Ref. [*5*]. (Our result for the total overlap is practically the same as that which can be obtained by the procedure of Ref. [*5*], using our values of the individual overlap integrals, namely, 6.0163; the difference with respect to the values of Ref. [*5*] is to be traced back to the different bond distances used).

The two calculations for cyclopropane allow us to verify that the angle α found by the present procedure is not necessarily equal to the value assumed for the *HCH* angle; if, as it seems likely, the *CH* bonds are supposed to be straight, one finds (by extrapolation of the above results) that the value of α and *HCH* must be close to 119°. This is in very good agreement with the experimental values of 118° in cyclopropane [*9*] and 117° 35′ in 1,1-dichlorocyclopropane [*7*], as well as with the theoretical value of 116° derived by COULSON and MOFFITT [*4*]. The same holds for cyclobutane, where our calculations allow us to predict for the *HCH* angle a value close to 116°, whereas the experimental results are 114° ± 8° in cyclobutane [*9*], 109° and 111° in bromocyclobutane [*13*], the theoretical calculation by COULSON and MOFFITT [*4*] leading to a value of 111°. These results are in agreement with the idea that the *HCH* angle should be smaller in cyclobutane than in cyclopropane. The values obtained for the angle ω are practically the same as those of COULSON and MOFFITT, 22° for cyclopropane and 9° for cyclobutane.

The results for cubane are summarized in Tab. 1. This compound is a striking example of bent bonds. In the assumption of straight bonds, the $C-C$ bonds should be built from pure p_x, p_y, p_z atomic orbitals. In fact, from the present calculation, the coefficient a for the s orbital in the corresponding hybrid is 0.450 and the angle β, between the two orbitals of a carbon atom that point towards two carbon atoms linked to it, is 104° 40′ (instead of 90° for straight bonds). The value of angle ω is 11° 20′.

In connection with the s character of *CH* hybrids, we note that MULLER and PRITCHARD [*10*] have found practically the same spin-spin coupling constants $J_{C^{13}-H}$ in cyclopropane and benzene, (161 and 159 $\sec^{-1}$, respectively). This suggests, according to the well-known interpretation of the spin-spin coupling constants [*10*], that the s character of the *CH* bond in either compound is approximately the same. This is in agreement with the fact that we find 0.570 as a coefficient for the s orbital in the hybrid of the *CH* bond, close to the value of 0.588 obtained by the same method for benzene.

The results found above indicate that, in the case of the cycloparaffins, the procedure of Ref. [*6*] leads to a good agreement between the experimental and the theoretical results, as well as between the latter and those of Refs. [*5*] and [*4*]. As to the nature of the hybrids and to the validity of the approximation which, in the frame of the MO-LCAO method, treats the cycloparaffins as being formed by localized bonds, the following remarks are important. As has been mentioned, the method used leads to an optimal description of a given molecule in terms of localized bonds. One obtains this description by building atomic orbitals such that the corresponding overlap matrix will be as close as possible to a matrix factorized in blocks, (i. e. where all the non-vanishing elements belong to blocks along the main diagonal), and by neglecting all the elements lying outside these blocks.* The smaller will the latter elements be, the better the description in question. In the case of cyclopropane, one can see from Tab. 3 that the factorization is but partially obtained: consequently, the approximation which describes the molecule just in terms of localized bonds between hybrid atomic orbitals appears to be rather limited: the ratio between the highest term outside the diagonal blocks and the smallest term within those blocks is close to 50%. The approximation appears to be definitely worse than in the NF_3 molecule [*6*], as a consequence of the smaller values of the effective charges in cyclopropane. One could expect the approxima-

Table 2

Planar cyclobutane — Elements of the overlap matrix. t_1, t_2, t_3, t_4 *are the hybrid orbitals of carbon*

		H_2	H_3	C_4				H_5	H_6	C_7			H_8	H_9
				t_1	t_2	t_3	t_4			t_1	t_2	t_3		
	t_1	.709	.141	.131	.127	—.068	—.032	.099	—.001	.003	.027	—.032	.018	—.010
C_1	t_3	.120	.120	.620	.131	.131	.143	.203	.203	.198	.003	.003	.056	.056
	t_4	.120	.120	.143	—.032	—.032	.191	.025	.025	.140	.003	.003	.056	.056
H_2		1	.260	.203	.099	—.001	.025	.148	.063	.056	.018	—.010	.041	.020

Table 3. *Overlap matrix of cyclopropane*

t_{11} t_{12} t_{13} t_{14} *are the hybrid orbitals of Carbon* C_1, h_2 *of hydrogen* H_2, *etc... Any other matrix element is equal to a given one by symmetry*

	t_{11}	h_2	t_{12}	h_3	t_{13}	t_{41}	t_{14}	t_{71}	t_{42}	h_5
t_{11}	1	.713	0	.145	0	.117	0	.117	.109	.080
h_2	.713	1	.145	.260	.103	.183	.103	.183	.080	.118
t_{12}			1	.713	0	.117	0	.117	—.086	—.010
h_3			.713	1	.103	.183	.103	.183	—.010	.062
t_{13}					1	.579	0	.194	.117	.183
t_{41}					.579	1	.194	.268	0	.103
t_{14}							1	.579	.002	.062
t_{71}							.579	1	.002	.062
t_{42}									1	.713
h_5									.713	1

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* An example of the overlap matrix obtained after the procedure of Ref. [*6*] has been applied is given in Tab. 2, where part of this matrix for cyclobutane is given. The total matrix for cyclopropane given in Tab. 3 has been rewritten so that the blocks corresponding to the bonds are on the main diagonal.

tion to be better in cyclobutane than in cyclopropane, as the highest term in the non-diagonal blocks corresponds, in cyclopropane, to the overlap of two orbitals pointing one towards the other, whereas the corresponding hybrids of cyclobutane point away from each other (Fig. 2). In fact, the overlap between the hybrids in question is smaller in cyclobutane than in cyclopropane; but the interaction element between the two geminal hydrogen atoms (linked to one carbon atom), which was very slightly different from the highest term in cyclopropane, remains the same in the four-membered ring. This suggests that in most methylenic compounds the approximation will not be better than in cyclobutane. In particular, these results seem to indicate that the methylene group cannot be treated as consisting of two *CH* bonds, if the form of the atomic orbitals here used, and hence the overlap integrals, are indeed the most suited for the description of molecules in terms of atomic orbitals.

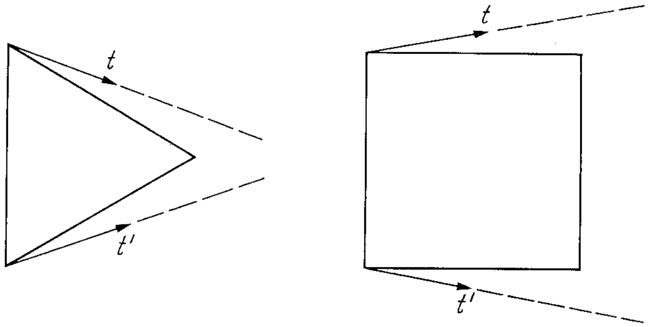

Fig. 2. Direction of hybrid orbitals

Another fact appears in the results given in Table 1 and in the other calculations we have carried out, namely that the hybrids we find are not very sensitive to slight changes in geometry.

Conclusion

The preceding discussion indicates that the hybrids obtained according to Ref. [*6*] are practically the same as those obtained by other methods, at least in the case of the cycloparaffins. It also shows that the use of the procedure of Ref. [*6*] gives some significant information concerning the extent to which, using a certain type of atomic orbitals, certain groups of atoms can be treated as being formed by two-centre bonds.

A more general conclusion could be drawn at first sight from the fact that the *HCH* angles in the cycloparaffins appear to be very close to the corresponding orbital-orbital angles: namely, the conclusion that bonds tend to be straight whenever the geometry of a molecule allows them to be so. Actually, the agreement we and others have found in this connection is probably fortuitous, as far as regards a generalization to bonds other than carbon-hydrogen bonds. In fact, an application of our procedure or of that of GOODWIN and COULSON to oxygen containing molecules, *e. g.* to water, leads to bent bonds for these molecules. The angles between the bonding hybrids of oxygen are much larger than the corresponding bond angles. The results for several molecules containing oxygen bridges will be given in a subsequent paper; here we illustrate this remark only for the case of water, according to the Criterion of Maximum Total Overlap of Ref. [*5*]. If τ is the tangent of half the bond angle of water, and ϱ is the ratio between the $[1s\ (H)\ 2s\ (O)]$ and the $[1s\ (H)\ 2p\ \sigma\ (O)]$ overlap integral, the maximum overlap hybrids will be directed along the bonds only if

$$\varrho = \frac{\tau^2 - 1}{\tau^2 + 1} \tag{1}$$

This condition is obviously not satisfied if the usual Slater orbitals are used, as τ is 1.29 and ϱ is 1.47. We note that the values of τ and ϱ are so far from satisfying Eq. 1 that, even if the effective charges assigned to hydrogen and oxygen are changed by large amounts, the bonds still appear to be bent.

One may wonder if this conclusion means that there is indeed no direct connection between orbital-orbital and bond angles, or just that the rough scheme within which we have introduced our procedure is far too rough. We are inclined to think that the more radical point of view is correct, for the following reasons. First, our own results for several molecules indicate that bent bonds are the rule, and not the exception; moreover, as we have already mentioned, even serious changes in the effective charges and/or in the assumed geometry do not lead to straight bonds, unless these changes are so large as to be hardly justifiable. Second, other authors, following completely different procedures, have reached similar conclusions. Among the most recent studies, we mention that of PETERS [*11*], who has analyzed hybridization in *SCF* wave functions of linear molecules, and has found, following the idea that hybridization is related to localization, that his hybrid orbitals often point in the wrong directions, *i. e.* away from the bond to which they relate: this is equivalent to a difference of 180° between the bond angles and the orbital-orbital angles. BLUKIS *et al.* [*3*], in a microwave study of dimethylether, have come to the conclusion that the bonds in this molecule are bent, the oxygen hybrids pointing outwards with respect to the $O - C$ bonds. Finally, BADER and JONES [*1*], using a particular procedure to determine the electron density distribution in water, again find bent bonds, although their hybrids point inwards with respect to the $O - H$ bonds and form an angle of about 60°.*

The above remarks do not imply that our results would not be changed if some refinements were introduced. For instance, changes in the form of the atomic orbitals used, or even just of the effective charges assigned to the various atoms, would change the directions of the hybrids calculated according to our procedure: but these changes would be minor ones, as we have repeatedly mentioned.

In conclusion, our procedure gives satisfactory results in comparison with other methods and experimental data, but leads to some results which are not fully in agreement with previous ideas on the meaning and uses of the concept of hybridization. This is by no means surprising, no matter how disagreeable it may be, for the hybrids were never more than useful mathematical fictions, and correspond to an arbitrary decomposition of a total wave function. This consideration must be borne in mind also in connection with attempts to correlate hybridization with experimental facts: it is not yet clear if it is really hybridization that is

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* The latter result is obviously impossible in any calculation requiring the hybrids of the same atom to be orthogonal.

related to the experimental data or some more physically acceptable quantity which, in the MO-LCAO scheme, does indeed correspond to hybridization because of some mathematical equalities.

Therefore the best use one can make of the hybrids derived according to any procedure, and in particular to ours, is that of determining a new basis for the MO-LCAO method where some features, like localization, are introduced in a more direct way since the beginning. In this sense hybridization is certainly important, as in general a correct choice of the coordinate system in any physical problem is extremely helpful for the interpretation of the results and their analysis. But, as the existence of a most suitable coordinate system does not imply that this coordinate system is in itself a physical entity, so hybridization cannot be assigned a physical reality, at least if the definition to which it corresponds is that of a particular choice of the basis functions. And this is true, naturally, even if one accepts as a working hypothesis the statement that the MO-LCAO scheme leads to results essentially correct.

Bibliography

[*1*] BADER, R., and G. JONES: Can. J. Chem. **41**, 586 (1963).
[*2*] BENT, H. A.: Chem. Rev. **61**, 275 (1961).
[*3*] BLUKIS, U., P. H. KASAI, and R. J. MYERS: J. chem. Physics **38**, 2753 (1963).
[*4*] COULSON, C. A., and W. E. MOFFITT: Phil. Mag., 7. Ser. **40**, 1 (1949).
[*5*] —, and T. H. GOODWIN: J. chem. Soc. **1962**, 2851, **1963**, 3161.
[*6*] DEL RE, G.: Theoret. chim. Acta **1**, 197 (1963).
[*7*] FLYGARE, W. H., A. NARATH, and W. D. GWINN: J. chem. Physics **36**, 200 (1962).
[*8*] FREEDMAN, H. H., and R. S. GOHLKE: Proc. chem. Soc. **1963**, 249.
[*9*] "Interatomic distances", The Chemical Society, Special Publ. 11, London 1958.
[*10*] MULLER, N., and D. E. PRITCHARD: J. chem. Physics **31**, 768 (1959).
[*11*] PETERS, D.: J. chem. Soc. **1963**, 2003, 4017.
[*12*] ROOTHAAN, C. C. J.: J. chem. Physics **19**, 1445 (1951).
[*13*] ROTHSCHILD, W. G., and B. P. DAILEY: J. chem. Physics **36**, 2931 (1962).
[*14*] SKANCKE, P. N., A. ALMENNINGEN, and O. BASTIANSEN: Acta chem. Scandin. **15**, 711 (1961).
[*15*] STOICHEFF, B. P., and R. C. LORD, Canad. J. Physics **40**, 725 (1962).

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Note added in proof. Table 1: For cubane, α is the angle between the two orbitals of a carbon atom that point towards the two carbon atoms linked to it.