1046. *Maximum Overlap Hybridisation in Methyl Substituted Cyclopropanes*

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The hybridisation in various methyl substituted cyclopropanes is determined by the criterion of maximum overlap. Slater orbitals are used, assuming standard C–C and C–H bond lengths. The main results show that the hybridisation of the CH_3 group is not affected by substitution, that the hybridisation of one carbon atom of the C_3-ring does not affect the hybridisation at the other positions, and that a CH_3 substituent causes a decrease in the *s*-content of the hybrid involved in the substitution. The remaining hybrids at the substitution site, which must therefore increase in *s*-content, do so by approximately equal amounts.

SOME important theoretical work on strained systems is the well known treatment of cycloalkanes ($n = 3$, 4, or 5) by Coulson and Moffitt,[1] in which they show that the strain in these molecules should be associated with the presence of " bent " bonds. Their results, for example, for cyclopropane show that the deviation from a "straight" C–C bond is 22°. Their calculations are based on the minimisation of the energy, and are not suitable for application to large molecules, or molecules with little or no symmetry. Recently it has been shown that essentially the same results are obtained for cyclopropane if the criterion of maximum overlap is applied to determine the form of the hybrids.[2-4] It is not difficult to extend maximum-overlap calculations to more complex molecules, as was recently demonstrated in calculations on spiropentane, nortricyclene, and dimethylcyclopropane.[4] In this Paper we report similar results for several methyl substituted derivatives of cyclopropane.

Outline of Calculations.—To describe the bonding in the hydridisation model, one forms, for every atom, linear combinations of suitable atomic orbitals of that atom called hybrids. For carbon atoms the atomic orbitals used are (2*s*) and (2*p*). Bonds are formed by combining two hybrids, each on a different atom, which are suitably oriented towards one another. Construction of hybrid orbitals has been considered by several people.[5] The result depends on the method used in evaluating the relative contributions of *s*- and *p*-orbitals. The criterion of maximum overlap, which is based on an intuitive assumption that the stronger bonding will result when approaching orbitals have a large overlap, has been generally accepted as satisfactory. Although it lacks theoretical foundation, and consequently care must be taken in interpreting the results, it has been found very useful and provides approximate orbital forms where more accurate calculations are not yet possible.

We can write hybrids and the accompanying orthogonality conditions as:[5a]

$$\psi_i = a_i(s) + b_i(p_i)$$
$$a_i a_j + b_i b_j \cos \theta_{ij} = \delta_{ij}$$

Hybrids generally differ in their *s*–*p* content, which characterises the finer details of their

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[1] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 1949, **40**, 1.

[2] C. A. Coulson and T. H. Goodwin, *J.*, 1962, 2851 (errata 1963, 3161).

[3] A. Veilard and G. del Re, *Theoret. Chim. Acta*, 1964, **2**, 55.

[4] M. Randić and Z. Maksić, *Theoret. Chim. Acta*, 1965, **3**, 59.

[5] (*a*) N. F. Mott and I. N. Sneddon, " Wave Mechanics," Dover Publns., New York, 1963; (*b*) G. E. Kimball, *J. Chem. Phys.*, 1940, **8**, 188; R. Hultgren, *Phys. Rev.*, 1932, **40**, 891; H. Kuhn, *J. Chem. Phys.*, 1948, **16**, 727; G. H. Duffey, several Papers in *J. Chem. Phys.*, 1949—1951, **17**, **18**, and **19**; J. N. Murrell, *J. Chem. Phys.*, 1960, **32**, 767; A. Golebiewski, *Trans. Faraday Soc.*, 1961, **57**, 1849; F. A. Cotton, *J. Chem. Phys.*, 1961, **35**, 228; D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 354; M. Randić, *J. Chem. Phys.*, 1962, **36**, 3278.

"shape." Two hybrids forming a C–C bond in cyclic systems are generally not directed along the straight lines joining the atoms. To calculate the bond overlap in such a case, the *p*-orbitals of both hybrids are separated into components along and perpendicular to the bond:

$$\psi_i = a_i(s) + b_i[\cos \delta_i(p_{\parallel}) + \sin \delta_i(p_{\perp})]$$

Here, δ_i is the angle of deviation of the hybrid from the direction of the other atom making the bond, $p_{\parallel}$ and $p_{\perp}$ are *p*-orbitals directed along and perpendicular to the bond, respectively. The overlap of two hybrids with the same deviation angle $\delta_i = \delta_j$ is, for example:

$$S_{ij} = a_i a_j(s,s) + (a_i b_j + b_i a_j) \cos \delta\, (s,p) + b_i b_j[\cos^2 \delta\, (p,p)_\sigma + \sin^2 \delta\, (p_{\perp} p)_\pi]$$

where (s,s), (s,p), $(p,p)_\sigma$, and $(p,p)_\pi$ are atomic overlap integrals.[6] The C–H and C–CH_3 bonds are assumed to be "straight." The problem is to find all coefficients *a* and *b* that will maximise the total overlap:

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

The summations are over all C–C and C–H bonds, the partial contributions of which are weighted by k_{CC} or k_{CH}, in order to take into account differences in energy between the two kinds of bonds.[7] The following atomic overlap integrals and the weighting factors were used:[2,4] $(1s_H,2s_C) = 0{\cdot}5809$, $(1s_H,2p_C) = 0{\cdot}4699$, $(k_{CH} = 142{\cdot}67)$; $(2s_C,2s_C) = 0{\cdot}3447$, $(2s_C,2p_C) = 0{\cdot}3684$, $(2p_C,2p_C)_\sigma = 0{\cdot}3298$, $(2p_C,2p_C)_\pi = 0{\cdot}1942$, $(k_{CC} = 121{\cdot}37)$. First, the total overlap is calculated for an assumed hybridisation, taking advantage of the results for a similar or related molecule. The maximum is found by a systematic variation of independent parameters. Usually those selected are δ, deviations angles, and θ_{ij} the angle between two hybrids ψ_i,ψ_j of the same atom, rather than ratios of coefficients b/a.

This numerical approach is found to be sufficiently practical and speedy, even when the number of independent parameters is quite large, because the optimum values do not frequently depend too much on the assumed trial values of other parameters. To simplify the calculation it is assumed that the two hybrids of a carbon atom in the C_3-ring describing the C–C bonds are equivalent (but different for different carbon atoms), and the corresponding δ's are the same. This is justified by the work on spiropentane and related molecules [4] where more details of the procedure can be found.

Results.—Before presenting the results for different substituted cyclopropanes, we wish to discuss in some detail the C–C bonding in the cyclopropyl ring. We consider cyclopropane and spiropentane, since the data for these molecules are less sensitive to a particular choice of atomic overlap integrals. In cyclopropane the CC and CH hybrids are:[4]

$$\psi_{CC} = 0{\cdot}4114\ (s) + 0{\cdot}9114\ (p) \text{ approx. } sp^5$$

$$\psi_{CH} = 0{\cdot}5752\ (s) + 0{\cdot}8180\ (p) \text{ approx. } sp^2$$

There are two factors that govern the magnitude of the *s* to *p* ratio of CC-hybrids in these molecules: (1) the large difference in the C–H atomic overlap integrals $(1s_H,2s_C) > (1s_H,2p_C)$, compared with small differences between C–C atomic overlaps, will cause the C–H bonds to be rich in *s*-content; (2) the bent bonds of the C_3-ring will compete for *s*-character since the overlap is greater for hybrids than for pure *p*-orbitals. Hybrids ψ_{CC} and ψ_{CH} in spiropentane happen to be of the same *s–p* composition as those in cyclopropane,[4] except for the central carbon atom which has four equivalent C–C bonds and is hence sp^3-hybridised. Because of this additional constraint, one might expect spiropentane to be more strained than cyclopropane. For example, the tetrahedral angle in C_5H_8 is larger by approximately 8°

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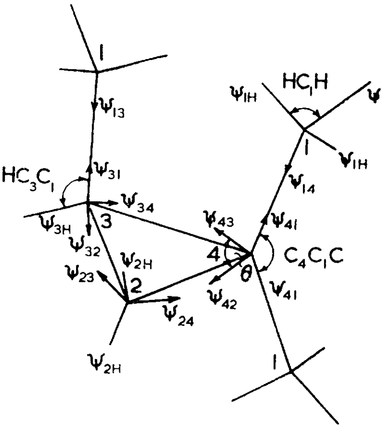
[6] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

[7] C. A. Coulson, personal communication.

than the corresponding angle in cyclopropane. However, the symmetry "forced" sp^3-hybridisation in C_5H_8 (or the lack of hydrogen atoms which "drain" the *s*-content) preserves the *s*-content of the tetrahedral hybrids, resulting in considerably greater overlap with the other ψ_{CC} hybrids. This compensates for the increase in interhybrid angle. Thus, the C–C bond overlap in cyclopropane is 0·5762, considerably less than that of the central C–C bonds of spiropentane, 0·5908. This result is in agreement with the fact that the observed C–C bond distances in C_5H_8 (1·48 and 1·51 Å for the central and the external bonds, respectively [8]) are shorter than in C_3H_6 (1·535 Å).[9]

The results for methyl substituted cyclopropanes are given in the Table. In the Figure is illustrated 1,2,2-trimethylcyclopropane, which contains all the local groupings that are present in the other molecules considered. The carbon atoms are numbered 1—4, depending on the number of neighbouring carbon atoms to which they are bonded. A hybrid orbital designated ψ_{ij} is directed from carbon atom i towards carbon atom j. Hybrids directed towards hydrogen atoms are designed as ψ_{iH}. Such a notation is convenient, as it facilitates comparisons between related molecules.*

The main features of the numerical data contained in the Table may be summarised as follows. (1) The hybridisation within the methyl group is only slightly affected by substitution. This is in agreement with the empirically established observation that the hybridisation of CH_3 is independent of its surroundings. (2) The re-hybridisation of one carbon atom of the cyclopropyl ring causes only a slight change in the hybridisation at the other positions. (3) The optimum values for a number of variational parameters are almost independent of the choice of the other parameters. It is thus possible to transfer bond overlaps or *b*/*a* ratios between related parts of a molecule, or between two molecules. (4) The substitution of H by CH_3 removes some *s*-character from the substituted bond, and this is then redistributed amongst the other bonds, resulting in an overall increase in their *s*–*p* character by approximately equal amounts. (5) Successive methyl substitution results in an additional stabilisation of the C_3-ring (negelecting steric factors which may interfere). Thus, for example the CC hybrids of the C_3-ring of cyclopropane, methyl cyclopropane, and 1,1-dimethylcyclopropane are approximately sp^5, sp^4, and $sp^{3\cdot7}$, respectively. The corresponding bond overlaps are 0·5762, 0·5816, and 0·5853. There is a further increase for tri- and tetra-substituted cyclopropanes: 0·5906 and 0·5943, respectively.



The systematic variations of the hybrids, in the procedure of maximisation, were performed by changing the angles between the hybrids on the same atom in ½° steps. Within this precision, and the limits inherent in the method, all CC and CH hybrids form groups as follows: CC hybrids sp^5 $\psi_{22},\psi_{23},\psi_{24}$, $sp^{4\cdot7}$ ψ_{14},ψ_{13}, sp^4 ψ_{32},ψ_{34}, $sp^{3\cdot7}$ ψ_{42},ψ_{43}, sp^3 ψ_{31}, $sp^{2\cdot4}$ ψ_{41}; CH hybrids $sp^{2\cdot6}$ ψ_{1H}, sp^2 ψ_{2H}, $sp^{1\cdot7}$ ψ_{3H}. By varying the coefficients characterising a single hybrid, in order to obtain a better overlap, a change in the coefficients also occurs for the remaining hybrids of the same atom. An increase in the *s* content of one hybrid, therefore, will cause a decrease in the *s* content of one or more of the remaining hybrids of the same atom, and in this way a change in hybridisation of one bond is transferred to neighbouring bonds. However, in the substituted cyclopropanes, although the C–C bond overlap is sensitive to a choice of hybrids forming the bond, a change of one

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* The numbering of carbon atoms in ref. 4 where some related molecules have been discussed is arbitrary.

[8] J. Donohue, G. L. Humphrey, and V. Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 332.

[9] O. Bastiansen and O. Hassel, *Tidsskr. Kjemi Bergvesen Met.* 1946, **6**, 71.

Molecule	Hybrid	b/a	$(b/a)^2$	Bond overlap	Scaled overlap	Inter-orbital angle
Cyclopropane	$\psi_{22} = 0{\cdot}4114(s) + 0{\cdot}9114(p)$	2·216	sp^5	$S_{22} = 0{\cdot}5762$	69·93	101° 45′
	$\psi_{2H} = 0{\cdot}5752(s) + 0{\cdot}8180(p)$	1·422	sp^2	$S_{2H} = 0{\cdot}7185$	102·51	119° 37′
Methylcyclopropane	$\psi_{32} = 0{\cdot}4382(s) + 0{\cdot}8989(p)$	2·051	sp^4	$S_{32} = 0{\cdot}5816$	70·59	103° 45′
	$\psi_{3H} = 0{\cdot}6066(s) + 0{\cdot}7951(p)$	1·311	$sp^{1{\cdot}7}$	$S_{3H} = 0{\cdot}7289$	103·56	
	$\psi_{31} = 0{\cdot}4980(s) + 0{\cdot}8679(p)$	1·742	sp^3	$S_{31} = 0{\cdot}6322$	76·73	
	$\psi_{22} = 0{\cdot}4114(s) + 0{\cdot}9114(p)$	2·216	sp^5	$S_{22} = 0{\cdot}5762$	69·93	101° 45′
	$\psi_{2H} = 0{\cdot}5752(s) + 0{\cdot}8180(p)$	1·422	sp^2	$S_{2H} = 0{\cdot}7182$	102·51	119° 37′
	$\psi_{1H} = 0{\cdot}5241(s) + 0{\cdot}8517(p)$	1·625	$sp^{2{\cdot}6}$	$S_{1H} = 0{\cdot}7046$	100·46	112° 15′
	$\psi_{13} = 0{\cdot}4149(s) + 0{\cdot}9078(p)$	2·164	$sp^{4{\cdot}7}$			
1,1-Dimethylcyclopropane	$\psi_{42} = 0{\cdot}4593(s) + 0{\cdot}8883(p)$	1·934	$sp^{3{\cdot}7}$	$S_{42} = 0{\cdot}5853$	71·03	105° 30′
	$\psi_{41} = 0{\cdot}5377(s) + 0{\cdot}8432(p)$	1·586	$sp^{2{\cdot}4}$	$S_{41} = 0{\cdot}6403$	77·73	114°
	$\psi_{22} = 0{\cdot}4114(s) + 0{\cdot}9114(p)$	2·216	sp^5	$S_{22} = 0{\cdot}5762$	69·93	101° 45′
	$\psi_{2H} = 0{\cdot}5751(s) + 0{\cdot}8181(p)$	1·422	sp^2	$S_{2H} = 0{\cdot}7185$	102·51	119° 37′
	$\psi_{1H} = 0{\cdot}5241(s) + 0{\cdot}8517(p)$	1·625	$sp^{2{\cdot}6}$	$S_{1H} = 0{\cdot}7046$	100·53	112° 15′
	$\psi_{14} = 0{\cdot}4195(s) + 0{\cdot}9078(p)$	2·164	$sp^{4{\cdot}7}$			
1,1,2-Trimethylcyclopropane	$\psi_{43} = 0{\cdot}4593(s) + 0{\cdot}8883(p)$	1·934	$sp^{3{\cdot}7}$	$S_{43} = 0{\cdot}5906$	71·58	105° 30′
	$\psi_{41} = 0{\cdot}5377(s) + 0{\cdot}8432(p)$	1·586	$sp^{2{\cdot}4}$	$S_{41} = 0{\cdot}6403$	77·73	114°
	$\psi_{34} = 0{\cdot}4382(s) + 0{\cdot}8989(p)$	2·051	sp^4	$S_{32} = 0{\cdot}5816$	70·59	103° 45′
	$\psi_{3H} = 0{\cdot}6066(s) + 0{\cdot}7951(p)$	1·311	$sp^{1{\cdot}7}$	$S_{3H} = 0{\cdot}7289$	103·56	
	$\psi_{31} = 0{\cdot}4980(s) + 0{\cdot}8672(p)$	1·742	sp^3	$S_{31} = 0{\cdot}6322$	76·73	
	$\psi_{24} = 0{\cdot}4114(s) + 0{\cdot}9114(p)$	2·216	sp^5	$S_{24} = 0{\cdot}5853$	71·73	101° 45′
	$\psi_{2H} = 0{\cdot}5751(s) + 0{\cdot}8181(p)$	1·422	sp^2	$S_{2H} = 0{\cdot}7185$	102·51	119° 37′
	$\psi_{1H} = 0{\cdot}5241(s) + 0{\cdot}8517(p)$	1·625	$sp^{2{\cdot}6}$	$S_{1H} = 0{\cdot}7046$	100·53	112° 15′
	$\psi_{14} = 0{\cdot}4195(s) + 0{\cdot}9078(p)$	2·164	$sp^{4{\cdot}7}$			
1,1,2,2-Tetramethylcyclopropane	$\psi_{43} = 0{\cdot}4593(s) + 0{\cdot}8813(p)$	1·934	$sp^{3{\cdot}7}$	$S_{44} = 0{\cdot}5943$	72·13	105° 30′
	$\psi_{41} = 0{\cdot}5377(s) + 0{\cdot}8432(p)$	1·586	$sp^{2{\cdot}4}$	$S_{41} = 0{\cdot}6403$	77·73	114°
	$\psi_{24} = 0{\cdot}4114(s) + 0{\cdot}9114(p)$	2·216	sp^5	$S_{24} = 0{\cdot}5853$	71·03	101° 45′
	$\psi_{2H} = 0{\cdot}5751(s) + 0{\cdot}8181(p)$	1·422	sp^2	$S_{2H} = 0{\cdot}7185$	102·51	119° 37′
	$\psi_{1H} = 0{\cdot}5241(s) + 0{\cdot}8517(p)$	1·625	$sp^{2{\cdot}6}$	$S_{1H} = 0{\cdot}7046$	100·53	112° 15′
	$\psi_{14} = 0{\cdot}4195(s) + 0{\cdot}9078(p)$	2·164	$sp^{4{\cdot}7}$			

hybrid will hardly affect the others. For example, although ψ_{41} differ from ψ_{31}, the hybrids ψ_{14} and ψ_{13} for methyl and dimethyl substituents are the same. Consequently, the overlaps S_{14} and S_{13} differ only slightly.

The atomic integrals we have used, and which were used in other calculations,[2-4,10] are based on Slater orbitals and Slater rules for the effective nuclear charges. They do not give good agreement with experimental HCH angles for the methyl group. Better agreement could be obtained by adopting an empirical set of atomic integrals. We have not attempted to modify the calculations by adjusting atomic overlaps. To be useful such an approach should be examined by selecting the new parameters for a large number of molecules. In addition, other approximations incorporated in the method should then be examined. For example, the scaling relationship $E = kS$ could be replaced by $E = kS^2$, or an attempt to take into account the differences in the promotional energies of atomic orbitals could be made.

Although the hybridisation within the methyl group is sensitive to a choice of atomic overlap parameters, there is no doubt that the main features of the hybridisation for methyl substituted cyclopropanes, summarised in (1)—(5), above, will remain valid even if a different set of atomic overlap integrals are introduced.

The only experimental valence angle available for comparison is that of 1,1,2,2-tetramethylcyclopropane.[11] The angle CCC at the dimethyl substituted carbon atom is 114° (±6°).

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[11] H. P. Lemaire and R. L. Livingston, *Acta Cryst.*, 1952, **5**, 817.