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$J(C^{13}$-H) SPIN–SPIN COUPLING CONSTANTS OF SEVERAL UNSATURATED HYDROCARBONS CALCULATED BY THE MAXIMUM OVERLAP METHOD

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Abstract—The hybrids for 3.3-dimethylcyclopropene (I), 1.3.3-trimethylcyclopropene (II), isobutylene (III), 1.1-dimethylallene (IV), and tetramethylallene (V) have been calculated by the maximum overlap method. The obtained hybrid coefficients were used to calculate $J(C^{13}$-H) coupling constants using the Muller–Pritchard relationship (1) and also the modified expression (2) suggested by Maksić, Eckert–Maksić and Randić. The calculated spin–spin coupling constant values were compared with the experimental data. The values obtained with (2) are superior to those obtained with (1). Thus, for example, for the olefinic part of I the following values were obtained: 190·9 cps and 208·3 cps by (1) and (2), respectively, as compared with the experimental value of 220 cps.

INTRODUCTION

Recently carbon–hydrogen and carbon–carbon spin–spin coupling constants have been calculated for various hydrocarbons applying the method of maximum overlap for the construction of carbon hybrid orbitals.[1] It has been shown that the dominant factor in determining the spin–spin coupling constants was the hybridization of the relevant carbon atomic orbital. The following linear relationship which connects the directly bonded carbon–hydrogen coupling constants with the s-character and bond overlaps, was found:

$$J(C^{13}\text{-H}) = 1079a^2/(1 + S^2) - 54{\cdot}9 \tag{1}$$

Here a is the coefficient of the 2s orbital of the relevant CH-bond hybrid and S is the CH-bond overlap as calculated by the maximum overlap method. The above relationship was found to be superior to the well known relationship of Muller and Pritchard[2]

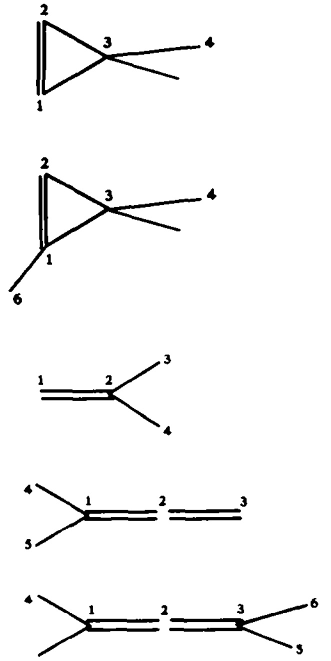
$$J(C^{13}\text{-H}) = 500a^2 \tag{2}$$

However, several small deviations have been observed between the calculated and experimental $J(C^{13}$-H) spin–spin coupling constants. Particularly large deviations were observed for cyclopropane and several molecules having CC double bonds. The deviations are within the estimated error limits for neglected contributions like dipole–dipole interaction between nuclear magnetic moments and electronic magnetic moments. Since they persist in some structurally characteristic groupings it seems desirable to examine them more closely and possibly find their origin. In this work we apply the method of maximum overlap to several molecules with CC double bonds and/or having strained three-membered rings, in order to understand better the origin of these small deviations from the correlation between $J(C^{13}$-H), the hybrid parameters a, and the bond overlap S.

We have selected for examination several methyl derivatives of cyclopropene, allene and ethylene. In particular we shall consider; 3,3-dimethylcyclopropene (I), 1,3,3-trimethylcyclopropene (II), isobutylene (III), 1,1-dimethylallene (IV) and tetramethylallene (V). These molecules have been selected because of available experimental $J(C^{13}\text{-H})$ values. The method of maximum overlap has been described in several papers discussing the hybridization in various hydrocarbons.[3–5] We assume therefore that the method, its basic assumptions and its limitations are known. We will only briefly mention that in this method one searches for optimal hybrid coefficients which will maximize a suitably weighted sum of bond overlaps. For various CC and CH bond types the standard bond lengths suggested by Dewar and Schmeising were assumed.[6] The basic overlap integrals were taken from the tables.[7]

RESULTS

The molecules (I–V) are illustrated in Fig. 1. The various carbon atoms are designated by numbers in such a way that similar groupings of atoms retain the same numbering in different molecules, thus facilitating comparisons. A hybrid orbital ϕ_{ij} is directed from the carbon atom i to the carbon atom j and with another orbital ϕ_{ji} contributes to the overlap S_{ij} for the bond C_i—C_j. The hybrids directed towards the hydrogens are designated as ϕ_{iH} and ϕ_{jH}. In Table I the results of the maximum overlap calculation are summarized for molecules I–V: the hybrids, the bond overlaps, the interorbital angles, and also (in the case of cyclopropene derivatives) the deviation angles. Throughout the calculation the deviation angles of hybrids of individual carbons in the C_3-



(I) 3,3-dimethylcyclopropene

(II) 1,3,3-trimethylcyclopropene

(III) isobutylene

(IV) 1,1-dimethylallene

(V) tetramethylallene

FIG 1. Schematic diagrams and numbering of atoms for the molecules considered.

ring are assumed equal. *i.e.* $d_{12} = d_{13}$. $d_{21} = d_{23}$. but $d_{12} \neq d_{21}$ unless required by symmetry. No assumptions were made on the equalities of hybrids above those required by symmetry. The results lead to several interesting conclusions. A comparison of the hybrids in 3.3-dimethylcyclopropene and 1.3.3-trimethylcyclopropene

TABLE 1.

3.3-*Dimethylcyclopropene* (I)

Hybrid[a]	*a*	n[b]	*S*
12	0·5961	1·81	0·73179
13	0·5126	2·81	0·61381
31	0·4607	3·71	
34	0·5365	2·47	0·66033
43	0·4838	3·27	
1H	0·6180	1·62	0·75200
4H	0·5053	2·92	0·71998

Interorbital angles[c]:
$\theta_1^{2,3} = 116{\cdot}31°$. $\theta_3^{2,1} = 105{\cdot}63°$
Deviation angles[d]:
$d_{12} = d_{13} = 25{\cdot}86°$. $d_{31} = d_{32} = 27{\cdot}41°$

1.3.3-*Trimethylcyclopropene* (II)

Hybrid	*a*	n	*S*
12	0·5953	1·82	0·73094
21	0·5951	1·82	
13	0·5129	2·80	0·61436
31	0·4613	3·70	
23	0·5130	2·80	0·61440
34	0·5359	2·48	0·66017
43	0·4837	3·27	
16	0·6187	1·61	0·68556
61	0·4861	3·23	
2H	0·6186	1·61	0·75211
4H	0·5053	2·92	0·71999
6H	0·5046	2·93	0·71978

Interorbital angles:
$\theta_1^{2,3}$ 116·27°. $\theta_2^{1,3}$ 116·26°. $\theta_3^{1,2}$ 105·68°
Deviation Angles:
$d_{12} = d_{13} = 25{\cdot}99°$. $d_{21} = d_{23} = 25{\cdot}93°$. d_{31}
$d_{31} = d_{32} = 27{\cdot}13°$

Isobutylene (III)

Hybrid	*a*	n	*S*
12	0·6163	1·63	0·77778
21	0·6234	1·57	
23	0·5529	2·27	0·67126
32	0·4851	3·25	
1H	0·5569	2·22	0·73940
3H	0·5049	2·92	0·72606

Interorbital angles:
$\theta_2^{3,4} = 116{\cdot}13°$. $\theta_1^{H,H} = 116{\cdot}71°$

1.1-*Dimethylallene* (IV)

Hybrid	*a*	n	*S*
12	0·6160	1·64	0·79773
21	0·7066	1·003	
23	0·7076	0·997	0·79618
32	0·6097	1·69	
14	0·5570	2·22	0·67226
41	0·4850	3·25	
3H	0·5605	2·18	0·74024
4H	0·5049	2·92	0·72607

Interorbital angles:
$\theta_1^{4,5} = 116{\cdot}73°$. $\theta_3^{H,H} = 117{\cdot}25°$

Tetramethylallene (V)

Hybrid	*a*	n	*S*
23	0·7071	1·00	0·79788
32	0·6162	1·63	
36	0·5569	2·22	0·67220
63	0·4848	3·25	
6H	0·5050	2·92	0·72608

Interorbital angle:
$\theta_3^{6,5} = 116{\cdot}72°$

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[a] The first number indicates the atom on which the hybrid is based; the second number the atom towards which it points.

[b] In the formulation sp^n.

[c] $\theta_i^{j,k}$ is the angle at atom *i* between the hybrids *ij* and *ik*.

[d] d_{ij} is the angle between bond *ij* and the direction of the *ij* hybrid.

shows that local environments are not much perturbed by a distant Me substitution. Thus to a large extent the hybrids of similar parts of structurally related molecules are transferable. The deviations from simple sp^2 and sp^3 hybrids are appreciable even in molecules or parts of the molecules without strain. The use of sp, sp^2 and sp^3 hybrids, still perpetuated in discussions of bonding in molecules among many organic chemists, is demonstrated to be inadequate. An increase of p-character in the hybrids participating in the highly strained three-membered ring is expected. We obtain, for example, in molecules I and II for $\phi_{31} \sim sp^{3.70}$. A similar s–p content has been found for hybrids in many different molecules having three-membered rings.[5]

In the cyclopropene ring the situation is complicated by a tendency of CC double bond to favour hybrids with increased s-character. As already noticed in the calculation on cyclopropene,[8] the balance between the two opposing tendencies is achieved with ϕ_{12} and ϕ_{13} considerably different: $sp^{1.80}$ and $sp^{2.80}$, respectively. This indicates an interesting feature of the cyclopropene ring and other less symmetrical highly strained small rings, which is generally overlooked. Namely, in these systems not only are there bent bonds present but also the hybrids describing them may be considerably different. Thus the hybrids ϕ_{12} of cyclopropene derivatives are at first sight paradoxical: instead of increasing the p-content, characteristic for small rings, the maximum overlap calculation leads to hybrids with increased s-content. However, the mean value of the p-content for CC hybrids ϕ_{12} and ϕ_{13} has increased somewhat, as expected.

The hybrids in isobutylene (III), 1,1-dimethylallene (IV) and tetramethylallene (V) again confirm the transferability of local hybridization between similar parts of different molecules. This is especially true for molecules IV and V. In nonsymmetrical 1,1-dimethylallene (IV) the hybrids of the central carbon need not be sp, since the two CC double bonds are not strictly equivalent. The calculations give slightly different hybrids, the difference being too small to be of importance, but it does indicate that the method of maximum overlap is capable of registering even such small effects due to distant Me substituents.

COMPARISON WITH EXPERIMENTAL DATA

The hybridization parameters calculated by the method of maximum overlap, in particular the s-content (alternatively the exponent n in sp^n) or the magnitude of bond overlaps, give useful correlations with several experimental quantities including bond lengths,[9] bond energy,[8, 10] proton acidity,[11] chemical shifts[12] and spin–spin coupling constants.[1] We are particularly interested in spin–spin coupling constants, and we wish to examine the deviations which such empirical correlations give for some molecules. As mentioned in the introduction, small but persistent deviations are found for computed values of $J(C^{13}\text{–}H)$ in highly strained small rings, and also in some unsaturated acyclic molecules. The origin of this is not understood, but some possible sources for the discrepancy will be mentioned later. In Table II we list the calculated $J(C^{13}\text{–}H)$ values for the molecules investigated. The two values correspond to $J(C^{13}\text{–}H)$ calculated using the Muller and Pritchard relationship (1) and the modified expression (2) which takes into account the variations in CC bond overlaps. We obtain a somewhat better agreement with experiment when the modified expression is used. Thus in 3,3-dimethylcyclopropene for olefinic hydrogens Muller–Pritchard's relationship gives 191 cps, while the modified expression 208 cps, as compared to the experimental value of 220 cps. Thus taking into account bond overlap

TABLE 2.

Molecule	Calc. (Muller–Pritchard). ref. 2	Calc. (Maksić *et al.*). ref. 1	Exptl.
3.3-Dimethylcyclopropene	190·9 olefinic	208·3	220[a]
	127·7 methyl	126·5	123[a]
1.3.3-Trimethylcyclopropene	191·3 olefinic	208·8	218[a]
	127·7 methyl	126·5	123[a]
	127·3 allylic	125·7	128[a]
Isobutylene	155·1 olefinic	161·4	—
	127·5 methyl	125·2	126[b]
1.1-Dimethylallene	157·1 olefinic	164·1	166[c]
	127·5 methyl	125·2	—
Tetramethylallene	127·5 methyl	125·3	126[d]

[a] G. L. Closs. *Proc. Chem. Soc.* 152 (1962); G. L. Closs and R. B. Larrabee. *Tetrahedron Letters* 287 (1965)
[b] C. Juan and H. S. Gutowsky. *J. Chem. Phys.* 37. 2198 (1962)
[c] E. I. Snyder and J. D. Roberts. *J. Am. Chem. Soc.* **84**. 1584 (1962)
[d] R. M. Lynden-Bell and N. Sheppard. *Proc. Roy. Soc.* **A269**. 389 (1962)

a considerable improvement results. but still the calculated value is low. In acyclic unsaturated hydrocarbons (III. V) a very good agreement is obtained for Me protons by both relationships. However. for methylene protons the use of Muller–Pritchard's expression gives definitely inferior results as compared to those based on the modified relationship. as illustrated in 1.1-dimethylallene (IV) when we compute the values 157·1 cps and 164·1 cps. respectively. while the experimental value is 166 cps. The deviations from the experimental values are considerably smaller in these systems than in those with three-membered rings.

Before concluding it is worthwhile to point out the differences between the Muller–Pritchard expression and the modified expression introduced by Maksić *et al.*[1] The former expression is used to deduce the s-character of hybrids. while the latter is used to compute $J(C^{13}$–H) values from the calculated hybrid s–p content and bond overlap as obtained by the maximum overlap method. Both relationships are empirical but while Muller and Pritchard assume proportionality. the modified expression presents a more general relationship. The improvement is therefore not only because variations of bond overlaps were taken into account but also because a general linear expression is more suitable for correlations than the line passing through the origin. The presence of the constant term. −54·9 cps. in the modified expression may be attributed to contributions from ionic components in the V.B. wave function for a CH bond.[1] Since the modified expression contains two variables the coefficients a^2 measuring the s-character and the CH bond overlap S, it cannot be used in the simpler manner to deduce hybridization from the experimentally obtained $J(C^{13}$–H) values as is frequently done by using the Muller–Pritchard relationship. However. if we assume for the CH bond overlap a typical value found in some other molecules the modified expression is reduced to a simpler form. For example. if we assume $S_{CH} = 0{\cdot}740$ we have: $700a^2$–55. an expression which can be used to deduce a from the experimental $J(C^{13}\text{-}H)$ values. The coefficient a obtained in this way should now be used to calculate a better value for S_{CH}. which can be simply accomplished by using the tables of basic overlap integrals.[7] This gives a better expression for finding a^2. and the process is continued until selfconsistency is reached: the assumed CH bond overlap and the deduced a^2 are such that the bond overlap calculated using the percentage of s-character of a hybrid is in agreement with the assumed value. The variation of bond lengths with bond overlap. ignored here. may be taken into account by the use of the mentioned bond length–bond overlap correlation.[9]

CONCLUSION

If we use the modified expression for correlating the calculated hybrid s-character and CH bond overlap with the experimental $J(C^{13}\text{-}H)$ spin–spin coupling constants. no deviations for olefinic and allylic proton spin–spin coupling constants are observed (Table II). Therefore the deviations found in some molecules having two or more CC double bonds are likely to be due to other specific interactions. Some specific interactions have been discussed in the literature. such as delocalization of the electrons in the CC double bonds separated by the insulating atom (homoconjugation). or delocalization of the electrons in the carbon–carbon σ-bonds. particularly in highly strained small rings. to a suitably oriented π-system of the other part of the molecule.[13] Some disagreement may also be due to the use of approximate geometrical parameters in some calculations.[1] The origin of the deviations in the three-membered rings is not quite clear. Several factors could be responsible. and we can group them into (a) those caused by defficiencies of the maximum overlap method, and (b) those due to inadequacy of the assumption that only changes of hybridization affecting the Fermi contact contribution are responsible for changes in J. Factors of possible importance in determining spin–spin coupling constants beside changes in hybridization have been extensively discussed in the literature. These include orbital electronegativities. effective nuclear charge. bond polarity. excitation energies. and criticism of some concepts usually tacitly assumed. like adequacy of the localized picture and correctness of the average energy approximation. Frequently opposite views have been advocated and the problem cannot be considered to be settled. Fortunately. in hydrocarbons the above mentioned factors are expected not to vary sharply from molecule to molecule. Before discussing the modifications of the present form of the maximum overlap method we would like briefly to mention other theoretical work in which hybrids are determined.

The most frequently adopted criteria for determining optimum functions. beside using alternative maximum overlap approaches.[14] is that giving the best reproduction of results given by SCF calculations.[15] In several instances. when a comparison between the maximum overlap hybrids and those obtained from more ambitious calculations have been made. agreement has been satisfactory.[16, 17] Thus the maximum overlap hybrids in cyclopropane and methylene–cyclopropane are in very good agreement with the results of Trindle and Sinanoglu obtained in their CNDO/2-SCF calculation.[16] Such an agreement may not hold generally. as indicated by results for the central CC bond in highly strained bicyclobutane. inferred to be of extremely high p-character (sp 24·3) from an *ab initio* SCF calculation by Newton and Schulman.[18] This may suggest that the maximum overlap criteria may not always be satisfactory for highly strained rings, or may reflect limitations of some currently used LCAO–MO methods when applied to highly strained rings.

The present form of the maximum overlap method can also be improved. For example by: (1) modifying the weighting procedure. (2) adopting the screened (1s) orbitals for hydrogen. (3) possibly considering some other functions for carbons, (4) using the bond orthogonality relationship. and (5) allowing for some ionic contributions to the V.B. wave function. *i.e.* allowing small charges on carbons and hydrogens.

No doubt that all these factors play some role and need to be examined. But we expect that their individual effects will be reduced to a large extent by a subsequent scaling procedure in the maximum overlap method. The most important therefore seems to be an examination of the weighting factors and their modification. After all, they have been determined by attempting to reproduce bond energies. and the alternative may be to select them so as to reproduce better experimental spin–spin coupling constants. Such a procedure is not new in empirical and semiempirical calculations, as it is well known from calculations on π-electron systems.[19] Also, it is possible to consider the dependence of the weighting factors K_{CC} and K_{CH} on the bond overlap,[20] or some other bond parameters like bond energies or deviation angles. However. such investigations are outside the scope of the present work. They require examination of a larger number of molecules and have been mentioned here only to indicate that the method of maximum overlap. although found very useful as applied in this work. need not be considered as final. One of the possible modifications is the inclusion of bond overlap-bond length dependence[21] so that the calculation produces a set of hybrids giving bond overlap consistent with the assumed geometry. The present work confirms, however. that hybrids calculated by the current version of the maximum overlap method give a satisfactory account of carbon–hydrogen spin–spin coupling constants in hydrocarbons.

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