Table IV. Mulliken Gross Carbonyl π Densities in the Ground and Excited States of the H_2CO Monomer and Dimers $ROH\cdots OCH_2$[a]

	O	C
H_2CO	1.085	0.915
	(1.543)	(1.457)
$ROH\cdots OCH_2$		
R = H	1.115	0.885
	(1.557)	(1.443)
CH_3	1.116	0.884
	(1.558)	(1.442)
NH_2	1.123	0.877
	(1.562)	(1.438)
F cis	1.128	0.872
	(1.564)	(1.436)
F trans	1.128	0.872
	(1.564)	(1.436)

[a] Densities in parentheses are for the excited states.

performed on the lowest excited singlet states of the dimers $ROH-H_2CO$ have produced vertical excitation energies which are greater than the vertical n → π^* transition energy obtained for H_2CO. Hence, the experimentally observed blue shift of the n → π^* band upon hydrogen-bond formation is reproduced by the theory. An analysis of the data shows that the magnitude of the blue shift is essentially equal to the strength of the hydrogen bond in the dimer. Such a relationship suggests that the blue shift reflects the additional energy required to break the hydrogen bond in the dimer lowest excited singlet states. This conclusion is also supported by the nature of the intermolecular potential curve as a function of R which was found to be repulsive in the dimer H_2O-H_2CO. No correlation in the series of dimers was found between the CI excitation energies and either the change in the energy of the H_2CO n orbital in the dimers or the virtual excitation energies. The general features of the electron distribution in H_2CO in the dimer excited states are similar to those observed in the excited state of H_2CO itself. Some of the electron density transfered in the dimer ground states from H_2CO to ROH is transfered back to H_2CO in the excited states.

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Comparative Study of Hybridization in Hydrocarbons[1a]

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Abstract: A comparative study of the hybridization in some 30 hydrocarbons was made by using the EHT, IEHT, CNDO/2, and MOA methods. It was found that the hybridization in hydrocarbons is relatively insensitive to the method applied. The MOA method gives slightly better hybrids than other semiempirical methods, as judged from a comparison with available *ab initio* results and $J(^{13}C-H)$ coupling constants. The hybrids obtained by the MOA method might provide a good initial guess for wave functions for *ab initio* SCF calculations employing hybrid basis sets.

There are numerous methods and approaches available for a theoretical study of medium size molecules on the semiempirical level. These methods often differ in their intended or achieved accuracy. Some are designed for a description of a single molecular property; others are quite general in their applicability. Many of these approaches are unfortunately vague about the advantages or disadvantages of the individual approximations. It seems that the present trend is to produce more results for increasing numbers of molecules using the existing methods, rather than examining the underlying assumptions and evaluating the deficiencies. True, the semiempirical methods need to be applied to a large number of molecules in order to test their generality and to avoid a situation where the selected parameters suit only a small group of molecules. However, it also seems that the numerous applications of semiempirical methods have weakened the caution which the underlying assumptions suggest. Some attention has been given to the deficiencies of the diagonal elements,[2] but a particularly troublesome problem seems to be the choice of the off-diagonal elements.[3] It seems, therefore, that the comparative study of several semiempirical methods might be very illuminating, even if it is limited to a de-

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(1) (a) Supported in part by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1184-67 and the National Science Foundation (Grant GP-31373X). (b) Institute "Rudjer Bošković." (c) Harvard University; on leave of absence from the Department of Chemistry, Faculty of Science and Mathematics, University of Zagreb, Croatia, Yugoslavia.

(2) A. Viste and H. B. Gray, *Inorg. Chem.*, **3**, 1113 (1964); F. A. Cotton and G. B. Harris, *ibid.*, **6**, 369, 376 (1967); C. K. Jorgensen, S. M. Horner, W. E. Hatfield, and S. Y. Tyree, Jr., *Int. J. Quantum Chem.*, **1**, 191 (1967).

(3) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **52**, 890 (1964); R. F. Fenske and C. C. Sweeny, *Inorg. Chem.*, **3**, 1105 (1964), and subsequent papers in this journal by Fenske, *et al.*; G. Berthier, G. Del Re, and A. Veillard, *Nuovo Cimento*, **44**, 315 (1966); N. J. Feinberg and K. Ruedenberg, *J. Chem. Phys.*, **54**, 1495 (1971).

tailed comparison of the results of diverse methods for a particular class of molecules. An extensive and detailed comparison of the results of different methods may indicate systematic deviations and thus, without analyzing the underlying assumptions, point to deficiencies in certain approaches and possibly suggest the remedy.

In this paper we will examine by an extensive comparison of the results for hydrocarbons the following well-known semiempirical methods: (1) extended Hückel method (EHT); (2) self-consistent charge method (SCC), a variation of the iterative extended Hückel method; (3) complete neglect of differential overlap method, version 2 (CNDO/2); and (4) maximum overlap approximation (MOA). We shall discuss, in particular, the notion of the hybridization in the framework of the molecular orbital theory. For this purpose we compare the hybrids obtained by different semiempirical methods mentioned above for some 30 hydrocarbons. This comparison involves adoption of the particular localization procedure or an extraction of the s character from delocalized molecular orbitals (*vide infra*). Some variations of the results may be expected when a different procedure is employed. However, if one definition is applied systematically on the certain class of similar molecules and the individual correlations with a selected molecular property are made, the absolute values of the nonphysical parameters are not relevant. They play a role of dummy variables and serve only to predict the values of the experimental quantities of similar molecules. Finally, we compare the semiempirically obtained hybridization in hydrocarbons with some available *ab initio* results.

Estimate of Hybridization in Delocalized Orbitals

There are two distinctive approaches for defining the hybridization in delocalized molecular orbitals: (1) one firstly transforms delocalized orbitals into a set of localized orbitals, for which s/p content is easily deduced; (2) one estimates the s character directly from delocalized orbitals by introducing an adequate definition of s content in terms of the coefficients of the relevant atomic orbitals. Neither of the two approaches secures a unique definition. The former approach was investigated thoroughly and leads to about a dozen localization procedures discussed in the literature.[4] The alternative approach received much less attention and will be briefly presented here, since it was also adopted in this work. A local hybid orbital centered at atom A and directed toward atom B is of the form

$$\psi_{AB} = c_{s(AB)}(2s)_A + c_{x(AB)}(2p_x)_A + c_{y(AB)}(2p_y)_A + c_{z(AB)}(2p_z)_A \qquad (1)$$

In the MOA method we assume that all hybrids placed on the same atom are orthogonal

$$\sum_i^{A} c_{i(AB)}c_{i(AC)} = p_{AB}\delta_{BC} \qquad (2)$$

where p_{AB} is the population of the hybrid ψ_{AB}, which takes the value 1 for all MOA hybrids. In other words, the MOA method deals with perfectly covalent bonds while the other approaches considered in this paper allow for some charge transfer. We shall see later that the local hybrid orbitals obtained by the CNDO/2 and SCC molecular orbital methods are nearly orthogonal. The quantity

$$W_s = c_{s(AB)}^2/(c_{s(AB)}^2 + c_{x(AB)}^2 + c_{y(AB)}^2 + c_{z(AB)}^2) \qquad (3)$$

gives the relative participation of the s orbital charge to be associated with ψ_{AB} and it is called s character. Wiberg[5a] suggested that the s character of the CH bond may well be represented by the square of a bond order called bond index

$$W_s^{CH} = P_{2s_C1s_H}^{\ 2} \qquad (4)$$

where

$$P_{\mu\nu} = 2\sum_{i=1}^{occ} c_{ui}c_{\nu i} \qquad (5)$$

is an element of the bond order–charge density matrix defined analogously to the well-known expression introduced by Coulson in the π-electron theory.[5b] Wiberg found that W_s^{CH} quantities obtained from CNDO/2 molecular orbitals make a good linear correlation with $J(^{13}C\text{–}H)$ spin–spin coupling constants. Trindle and Sinanoğlu[5c] generalized this approach by introducing a relative magnitude of the appropriate bond indices as a definition of the s content

$$W_s^{AB} = W_{s(AB)}/(W_{s(AB)} + W_{x(AB)} + W_{y(AB)} + W_{z(AB)}) \qquad (6)$$

where

$$W_{i(AB)} = (1/2)\sum_{b\in B} P_{ib}^2 \quad (i = s, x, y, z)$$

The summation is confined to the orbitals belonging to the atom **B**. For a well-localized bond[6] the definition of s content of Trindle and Sinanoğlu reduces approximately to that of Wiberg (eq 4). Equation 3 was used for the calculation of hybridization in localized orbitals. The Trindle–Sinanoğlu formula (eq 6) has been applied to the molecular orbitals calculated within the zero-differential overlap (ZDO) approximation in order to extract the corresponding s characters. In MO methods which include overlap integrals, *e.g.*, EHT and SCC, one cannot apply directly eq 6. The hybridization in these methods, however, could be defined in the following way. Let us consider a closed shell molecule with N valence electrons. The normalization condition gives the relationship

$$2\sum_{i=1}^{occ}\int \psi_i^2\, dv = N \qquad (7)$$

where ψ_i is a molecular orbital which, in turn, is a linear combination of atomic orbitals

$$\psi_i = \sum_\mu c_{\mu i}\varphi_\mu \qquad (8)$$

Substituting (8) into (7) we obtain

$$\sum_\mu P_{\mu\mu} + 2\sum\sum_{\mu<\nu} P_{\mu\nu}S_{\mu\nu} = N \qquad (9)$$

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(4) C. Trindle and O. Sinanoğlu, *J. Chem. Phys.*, **49**, 65 (1968).

(5) (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (b) C. A. Coulson, *Proc. Roy. Soc., Ser. A*, **169**, 413 (1939); (c) C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

(6) A bond is well localized if the pair of electrons is to a high extent distributed over the region of the bond in question.

Table I. The Overlap Integrals between the Geminal Hybrids for Methane, Acetylene, and Cyclopropane as Calculated by the CNDO/2 and SCC Methods

Method	Molecule Methane	 Acetylene	 Cyclopropane
CNDO/2	S(CH,CH) = −0.001	S(CC,CH) = 0.033	S(CC,CC) = 0.007 S(CH,CH) = 0.024
SCC	S(CH,CH) = 0.073	S(CC,CH) = 0.002	S(CC,CC) = −0.076 S(CH,CH) = 0.024

where $S_{\mu\nu}$ is the corresponding overlap integral; $S_{\mu\nu} = \int \varphi_\mu \varphi d\nu$, and $P_{\mu\nu}$ is the element of the already mentioned density matrix, eq 5. It was tacitly assumed here that the valence atomic orbitals placed on the same atom were mutually orthogonal. The way of the summation in eq 9 is quite arbitrary. Therefore, we can express a distribution of the electronic density as a sum of atomic and bond contributions

$$\sum_{\mathrm{A}}\sum_{\mu}^{\mathrm{A}} P_{\mu\mu}{}^{\mathrm{A}} + 2\sum\sum_{\mathrm{A}<\mathrm{B}}\sum^{\mathrm{A}}\sum_{\mu<\nu}^{\mathrm{B}} P_{\mu\nu}{}^{\mathrm{AB}} S_{\mu\nu}{}^{\mathrm{AB}} = N \qquad (10)$$

where the summations over A and B are extended on all atoms in a molecule. The first term of eq 10 gives a portion of the charge placed solely on atoms. Therefore, this part of the electron charge is not involved in the covalent bonding. The second term represents the charge distributed along the chemical bonds. It contributes to the covalent bonding and could be termed "active charge," since it provides some measure of the bonding power. We can define a bond index as a part of the "active charge" belonging to the bond in question.

$$W^{\mathrm{AB}} = 2\sum^{\mathrm{A}}\sum_{\mu<\nu}^{\mathrm{B}} P_{\mu\nu}{}^{\mathrm{AB}} S_{\mu\nu}{}^{\mathrm{AB}} \qquad (11)$$

The partitioning of the "active charge" W^{AB} to the constituent atoms A and B is quite arbitrary. There are many definitions of the formal charge of an atom in a molecule available in the literature.[7a] We shall adopt Mulliken's suggestion[7b] which is expected to give quite reliable results for hydrocarbons.[8] According to Mulliken population analysis, the "active charge" W^{AB} should be divided equally among the participitating A and B atoms. Now we can define a part of the "active charge" of the $2s_{\mathrm{A}}$ orbital which is involved in the A–B covalent bond

$$W_{\mathrm{s(AB)}} = \sum_{\nu}^{\mathrm{B}} P_{2s_{\mathrm{A}}\nu}{}^{\mathrm{AB}} S_{2s_{\mathrm{A}}\nu}{}^{\mathrm{AB}} \qquad (12)$$

The active charge of all four orbitals of atom A distributed along the A–B bond is $(1/2)W^{\mathrm{AB}}$. The s character of the ψ_{AB} hybrid is the properly normalized $W_{\mathrm{s(AB)}}$ quantity

$$W_{\mathrm{s}}{}^{\mathrm{AB}} = W_{\mathrm{s(AB)}}/(^1/_2)W^{\mathrm{AB}} \qquad (13)$$

This equation is completely analogous to 6, which holds within the ZDO approximation. One easily finds out that the s characters defined by eq 13 are rotationally invariant. It can be shown that the expression like (13) should to be applied in methods which employ overlap integrals. Namely, by neglecting the overlap contributions, the s characters of the CH hybrids for ethane, ethylene, and acetylene, as calculted by the SCC method, are 11.6, 170, and 31.5%, respectively. The modified approach by using formula 13 gives 27.8, 32.5, and 42.2%, respectively, which is close to the results obtained by other semiempirical methods and quite close to the values of 25.0, 33.3, and 50% which correspond to idealized sp^3, sp^2, and sp hybridizations. Finally, a comment about the orthogonality conditions 2 should be made at this point. They are adopted in the MOA method as a postulate which is based on the following simple picture; the local hybrid orbitals represent perturbed atomic orbitals which satisfy the local symmetry requirements. According to Hund's rule their spins are parallel and consequently their spatial wave functions avoid each other as much as possible due to the Pauli principle. On the other hand, it can be easily calculated that the hybrids obtained by the semiempirical MO methods are practically orthogonal. The local hybrid orbital calculated by eq 6 or 13 is of the form

$$\psi_{\mathrm{AB}} = \sqrt{W_{\mathrm{s(AB)}}}(2\mathrm{s})_{\mathrm{A}} + \sqrt{W_{x(\mathrm{AB})}}(2\mathrm{p}_x)_{\mathrm{A}} + \sqrt{W_{y(\mathrm{AB})}}(2\mathrm{p}_y)_{\mathrm{A}} + \sqrt{W_{z(\mathrm{AB})}}(2\mathrm{p}_z)_{\mathrm{A}} \qquad (14)$$

The overlap integral between two geminal hybrids ψ_{AB} and ψ_{AC} placed on the same atom A is given by eq 15. The overlap integrals between the hybrids

$$\int \psi_{\mathrm{AB}}\psi_{\mathrm{AC}}\, dv = \sqrt{W_{\mathrm{s(AB)}}W_{\mathrm{s(AC)}}} + \sqrt{W_{x(\mathrm{AB})}W_{x(\mathrm{AC})}} + \sqrt{W_{y(\mathrm{AB})}W_{y(\mathrm{AC})}} + \sqrt{W_{z(\mathrm{AB})}W_{z(\mathrm{AC})}} \qquad (15)$$

obtained by the CNDO/2 and SCC methods for methane, acetylene, and cyclopropane are shown in the Table I. The deviations from the orthogonality are very small and the hybrids obtained by the semiempirical MO methods can be directly compared with the corresponding hybrids calculated by the MOA approach. It is interesting to point out that the overlap between the ψ_{CC} hybrids describing he cyclopropane ring is also negligible.

Description of the Methods Examined

The extended Hückel method is described in a number of publications.[9] For a number of molecules listed in Tables I and II, the results were not available and therefore have been evaluated for the present comparative study. The self-consistent charge method

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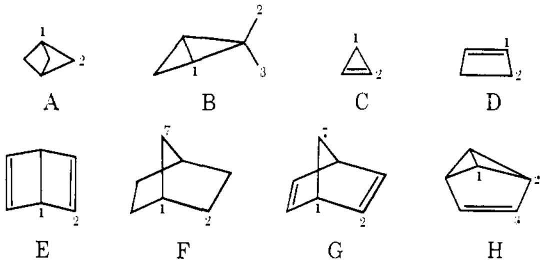
[7] (a) See for instance R. E. Christoffersen and K. A. Baker, *Chem. Phys. Lett.*, **8**, 4 (1971), and the references cited therein; (b) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

[8] G. De Alti and V. Galasso, *Chem. Phys. Lett.*, **8**, 223 (1971), have shown that several widely diverse recipes for orbital population analysis give qualitatively the same results.

[9] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962).

Table II. Comparison between s Character of C–H Hybrids Obtained by Different Semiempirical Methods (in Percentage)



Molecule	Bond	EHT[a]	SCC[b]	CNDO/ 2[a]	MOA[c]	Em- pirical
Methane		27.5[b]	27.8	25.0	25.0	25.0
Ethane		29.3	25.6	24.6	25.4	25.0
Cyclobutane		32.2		26.1	27.4	26.8
Ethylene		34.5	32.5	30.8	31.5	31.3
Benzene		34.8	32.5	28.8	31.5	31.8
Cubane			35.6	30.6	32.1	32.0
Cyclopropane		34.9	33.4	30.3	28.6	32.2
Acetylene		45.0	42.2	44.5	44.5	49.7
Primazane		38.3[b]	38.8	34.8	34.1	
A	C_1–H	38.3[b]	38.9	34.2	32.1	32.8
	C_2–H	31.8[b]	32.0	27.5	28.9	28.8
B	C_1–H	40.2[b]	41.0	35.0[b]	38.6	40.6
	C_2–H	32.4[b]	32.8	32.1[b]	33.0	30.4
C	C_3–H	33.0[b]	33.3	38.6[b]	33.0	34.0
	C_1–H	33.7[b]	34.1	32.8[b]	30.0	
	C_2–H	41.8[b]	42.6	38.7[b]	39.1	44.0
D	C_1–H	36.3[b]	37.0	33.3[b]	35.4	34.0
	C_2–H	31.0[b]	31.3	26.5[b]	27.9	28.0
E	C_1–H	34.1[b]	34.4	28.6[b]	31.0	
	C_2–H	37.2[b]	37.4	34.1	35.4	
F	C_1–H	31.9[b]	32.1	25.1	28.7	27.8
	C_2–H^{exo}	29.4[b]	29.6	24.2	25.9	26.0
	C_7–H	30.6[b]	30.8	25.3	27.4	26.0
G	C_1–H	31.6[b]	31.8	25.5	28.3	29.2
	C_2–H	35.5[b]	36.1	31.6	33.4	34.5
	C_7–H	30.7[b]	30.9	24.9	27.4	27.1
H	C_1–H	38.8[b]	39.6	33.1[b]	35.8	
	C_2–H	36.9[b]	37.1	35.3[b]	34.0	
	C_3–H	33.6[b]	34.1	32.0[b]	33.3	

[a] Taken from ref 12, if not otherwise stated. [b] This paper. [c] Taken from M. Randić and Z. B. Maksić, *Chem. Rev.*, **72,** 43 (1972), and the references cited therein.

was applied as developed by Drago, *et al.*,[10] while for some molecules listed in the tables, the results of CNDO/2-MO calculations of the form introduced by Pople, *et al.*,[11] were available.[12,13] For the remaining molecules, we performed the MO calculations. The maximum overlap method is described in a number of publications of the present authors.[14] We give a concise statement about the MOA method and a brief discussion on the underlying assumptions.

In the maximum overlap method one searches for optimal hybrid parameters *c* of the individual hybrids, eq 1, subjected to the orthogonality requirement 2, so that a suitably weighted sum of bond overlaps

$$S_{\text{total}} = k_{\text{CH}} \sum_{\text{C–H}} S_{\text{CH}} + k_{\text{CC}} \sum_{\text{C–C}} S_{\text{CC}} \qquad (16)$$

has a maximum value. Here S_{CC} and S_{CH} represent bond overlaps of CC and CH bonds, respectively. The weighting factors $k_{\text{CH}} = 135.9$ and $k_{\text{CC}} = 121.2$ kcal mol^{-1} take into account the difference in energy of different bonds. In cyclic systems, hybrids generally deviate from the internuclear lines. In these cases p orbitals are decomposed into the parallel and the perpendicular to the bond components

$$p = \cos \delta(p_{\parallel}) + \sin \delta(p_{\perp})$$

Here δ denotes the deviation of the hybrid from the internuclear vector. It should be pointed out that double and triple bonds are treated within the σ–π approximation in the MOA approach.

The maximum of the expression for S_{total} is found by a numerical trial and error procedure. One starts with assumed initial hybrid compositions, *e.g.*, sp^3, sp^2, or sp hybrids, and then by a systematic variation of all independent parameters approaches the optimal values. A simultaneous variation of all these parameters would be time consuming. However, the hybrids at a single atom do not strongly depend on the assumed hybridization in the neighboring atoms. Consequently, the parameters can be varied successively. In practice each of the independent parameters (hybrid exponent n in sp^n notation) to be optimized is varied in steps of 0.02 (sometimes 0.01) over the range of plausible values. This usually means about 1000 individual calculations of the total overlap for optimization per one independent parameter. Thus, it is not likely that the resulting calculated hybrids are due to local maximum or due to saddle points. In some cases hybrids on the same atom are strongly influencing results (like in the case of fused rings of highly strained bonds), and in such cases it is desirable to vary two or more hybrids simultaneously to secure that the orthogonality conditions do not restrict the results to a local solution. The optimizing procedure used has resemblance with a rather sophisticated subroutine, known as VAO4, written by M. J. Powell and available through the Quantum Chemistry Program Exchange.[15]

The experimental bond lengths were used in MOA calculations whenever they were available. If they were not known, the standard bond lengths of Dewar and Schmeising,[16] which differentiate various sp^n–sp^m and sp^n–s$_{\text{H}}$ bond types (n and m are integers), were employed. This is not a serious inconsistency as already discussed in a previous paper.[17] Namely, it was shown that the hybrids obtained by using experimental bond lengths give only slightly better agreement with experimental quantities. The method of calculation of hybrids assumes that all hybrids in acyclic molecules or the noncyclic part of cyclic and polycyclic systems follow perfectly the corresponding bond directions.

(10) P. C. van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88,** 3255 (1966); W. O. White and R. S. Drago, *J. Chem. Phys.*, **52,** 4717 (1970).

(11) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43,** S 129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43,** S 136 (1965); **44,** 3289 (1966).

(12) F. Jordan, Dissertation, University of Pennsylvania, 1967.

(13) G. E. Maciel, J. W. McIver, N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92,** 1 (1970).

(14) M. Randić and Z. B. Maksić, *Theor. Chim. Acta*, **3.** 59 (1965); Z. B. Maksić, L. Klasinc, and M. Randić, *J. Chem. Soc. A*, 755 (1966), and subsequent papers in *J. Chem. Soc.*, *Theor. Chim. Acta*, and *Croat. Chem. Acta.*

(15) The subroutine VAO4 search for optimal parameters minimizes a function of several variables in a very efficient way, since the changes of the variable are varied during the process of optimization. In our programs the change of a variable is constant and can be altered through the input information at the beginning of the calculation.

(16) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5,** 166 (1959); 11, 96 (1960).

(17) Z. B. Maksić and M. Eckert-Maksić, *Croat. Chem. Acta*, **42.** 4433 (1970).

In particular this means that the perfect following of the C–H bonds is assumed according to the criterion of maximum overlapping. Quite considerable bending of ψ_{CH} hybrids is possible without a significant loss of orbital overlap, as discussed by Bartell.[18] However, this is not very likely for two reasons. First of all, the bond angles calculated by the maximum overlap method are, as a rule, in very good agreement with the experiment.[17,19,20] Secondly, there are more elaborate calculations which show that bending of ψ_{CH} hybrids is actually very small. It has been calculated, for example, that the CH orbitals for ethane lie slightly inside (less than 0.5°) the pyramide formed by the CH_3 group. Similarly, the results show small departure of the ψ_{CH} hybrids ($\sim$1°) outside of the HCH angle.[21] It has to be mentioned that MOA calculations in the present form neglect the nonbonded interactions. For instance, the nonequivalent geminal CH bonds are not distinguished; *i.e.*, the corresponding ψ_{CH} hybrids are assumed to be equal. This is the case, for example, of exo and endo CH bonds in bicyclo[1.1.0]butane and norbornane, axial and equatorial CH bonds in cyclic molecules, and cis and trans CH bonds in various conformers. These nonequivalent CH bonds differ somewhat in their physical and chemical properties which are not reproduced by the MOA calculations. We would like to point out first that the maximum overlap method was not designed for a description of the long range interaction in molecules. The aim of local hybrid orbitals is to correlate gross molecular properties like bond energies,[20,22] bond lengths,[23] spin–spin coupling constants across one bond,[24,25] etc., which depend mainly on the nature of the nearest neighbor atoms. They proved very useful in this respect. The effect of nonbonded repulsions to gross properties is actually very small at least in hydrocarbons. For example, CNDO/2 and MINDO/3 calculations have shown that their contribution to heats of atomization is negligible.[26,27] Second, it seems that the influence of nonbonded interactions on hybridization as such is very small too. There are available *ab initio* SCF molecular orbitals for eclipsed and staggered propylene and for cis and trans butadiene isomers. They were analyzed and transformed to a set of strictly localized orbitals.[28] It has been found that the difference in the s/p content between the corresponding cis and trans hybrids in butadiene is less than 1% while in the case of eclipsed and staggered propylene this difference is even below 0.3%. The bicyclo[1.1.1]pentane is an example of a molecule where the nonbonded sites are very close. Yet the MOA hybrids[29] describing C_1C_2, C_2C_1, C_1H, and C_2H bonds are $sp^{3.38}$, $sp^{3.51}$, $sp^{2.17}$, and $sp^{2.59}$ and can be favorably compared with more elaborate *ab initio* calculations of Newton and Schulman,[30] which give for the corresponding hybridization $sp^{3.46}$, $sp^{3.64}$, $sp^{2.22}$, and $sp^{2.62}$, respectively. The resemblance is remarkable indeed and provides some justification that the nonbonded interactions can be neglected in the first approximation.

One could imagine an alternative maximum overlap method which employs the experimental CH bond angles. This could take into account the nonbonded interaction to the same extent, since the exo and endo hybrids would then be different. However, in this case the CH and CC hybrids would not be treated on the same footing. Namely, the latter would be completely determined by the CH hybrids *via* the orthogonality relationship. Furthermore, this variation of the MOA would be confined only to the molecules with experimentally known geometry, which is certainly not a desirable feature of any method. The present form of the maximum overlap method is able to predict the geometry of hydrocarbons by using the available bond length–bond overlap correlation in an iterative fashion.[31] To conclude our discussion about the MOA method we mention that Clementi double ζ atomic functions[32] are used in the calculations, since they are somewhat more flexible than Slater orbitals. The basic overlap integrals are available.[33]

Discussion on the Hybridization in Hydrocarbons

It is interesting that the results of the four different and independent approaches are so similar when the s characters of the hybrids are considered in spite of the diversity of approximations employed. This indicates that the definition of Trindle and Sinanoğlu and eq 13 extracts the s characters from molecular orbitals which are in good overall agreement with the results of the intuitive approach characterizing the maximum overlap method (Table II). The comparison between the s characters obtained by the EHT and SCC methods is very useful. The EHT method does not include repulsion between the electrons while in the SCC method it is simulated by the charge dependence of the off-diagonal matrix elements. It was concluded on the basis of the calculation of a large number of molecular quadrupoles that the SCC method mimic electronic Coulomb repulsions in a quite satisfactory way.[34] If we compare the s characters obtained by these two methods we observe that they differ numerically in some cases, but they are quite similar if the qualitative features are concerned. For that matter, CNDO/2 calculations give essentially the same results for the hybrid s/p contents. This is very important since the CNDO/2 method is apparently superior when the quantum mechanical foundations of the methods applied are considered.

(18) L. S. Bartell, *Tetrahedron*, 17, 177 (1962).

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The reported hybrids show deviations from the idealized canonical cases: sp, sp^2, and sp^3. The deviations are, however, not excessive when the bonds of less strained molecules are examined. This may be contrasted with the results in highly strained small ring compounds. The deviations show trends which were already observed by the numerous applications of the maximum overlap method. For example, the σ parts of C=C and C≡C bonds require increased s contents as it is seen in ethylene and acetylene. The ψ_{CH} hybrids describing CH bonds of the strained parts of the molecules also have the increased s characters compatible with several experimental observations.[35]

When details of the hybrids are examined, the results of the four methods differ. If one has to evaluate the reliability of the calculated hybrids one needs an additional standard, which is beyond the limits of accuracy of the methods applied. Ideally, one could use the results of the highly accurate *ab initio* calculations. However, they are not available for most of the molecules considered here (a few cases will be discussed in the next section). Therefore, we have to resort to empirical regularities. Among the experimental quantities we selected the $J(^{13}C\text{–}H)$ spin–spin coupling constant, which is widely accepted as a measure of the s characters of the corresponding hybrids. This choice is not free from criticism since the Muller–Pritchard formula $J(^{13}C\text{–}H) = 5(s\%)_{CH}$ is based on several simplifying assumptions.[36] One of them is "average energy approximation" where the difference between the excited states and the ground state energy, appearing in the second order perturbation sum, is replaced by the average excitation energy. This cannot always be justified since Cyr and Cyr have shown that variations in average energy do account for changes in $J(^{13}C\text{–}H)$ coupling constants in halomethanes.[37] However, this is not likely to be the case in pure hydrocarbons where the properties of CH bonds do not change dramatically from molecule to molecule. For instance, the difference in C–H bond lengths between methane and acetylene is only 0.05 Å while bond energies differ approximately 11 kcal/mol.[16] We conclude that the $J(^{13}C\text{–}H)$ constant provides approximate but reliable criterion of hybridization. Some care has to be taken into account when CH bonds of the highly strained parts of molecules are discussed, *e.g.*, strained double bonds, etc. More serious objection, however, can be made that each semiempirical method needs its own correlation with $J(^{13}C\text{–}H)$ coupling constants, and the quality of the results has to be judged, for instance, by the magnitude of the standard deviations. Namely, it was shown[24] that MOA gives better agreement with experiment than the simple Muller–Pritchard formula if the normalization constant of the VB function describing the C–H fragment is taken into account

$$J(^{13}C\text{–}H) = 10.8(s\%)_{CH}/(1 + S_{CH}^2) - 54.9 \text{ cps} \quad (17)$$

where S_{CH} is the corresponding overlap integral and $S_{CH} = \int \psi_{CH}(1s)_H dv$. The linear relationship, based on the data presented in ref 24, $J(^{13}C\text{–}H) = 6.3(s\%)_{CH} - 34$ cps, is also superior to the Muller–Pritchard direct proportionality between $J(^{13}C\text{–}H)$ and $(s\%)_{CH}$. In spite of the fact that each semiempirical method should be evaluated within its own correlation, we shall compare the calculated hybridizations with empirical ones obtained by the formula $(s\%)_{CH}^{emp} = 0.2J(^{13}C\text{–}H)$ where $J(^{13}C\text{–}H)$ is the experimental coupling constant. This comparison will reveal the major deviations and the larger systematic shifts which suffice for a qualitative discussion. We observe from Figure 1 that for large values of s% all four semiempirical methods give the results which are below the values predicted by the empirical relationship. So either all four methods have a systematic error or the empirical relationship needs some correction for larger values of s%. It is also apparent from Figure 1 that more general linear relationships of the form $(s\%)_{CH}^{calcd} = K(s\%)_{CH}^{emp} + L$ would give a better description of the empirical results. In particular this seems to be important for EHT and SCC methods. The points corresponding to these two methods are grouped above the $(s\%) = 0.2J(^{13}C\text{–}H)$ line for smaller and medium values of s character. The results of the maximum overlap and CNDO/2 methods appear to be more evenly distributed around the values predicted by the empirical approach; the latter method shows the larger deviations though. It might prove useful to examine more carefully the individual cases which do not show agreement with the empirical relationship. Such investigations may lead to improvements of the methods concerned if these discrepancies are not purely of statistical nature. For this purpose we plot the difference between the empirical and the calculated s characters in Figure 2 for each of the methods discussed in this paper. If the deviations have a systematic component this will manifest itself in an asymmetrically shaped and displaced distribution of the number of molecules *vs.* the difference $\Delta = (s\%)_{CH}^{calcd} - (s\%)_{CH}^{emp}$. Unfortunately, 24 of the calculated s characters is still a small number for a complete statistical analysis from

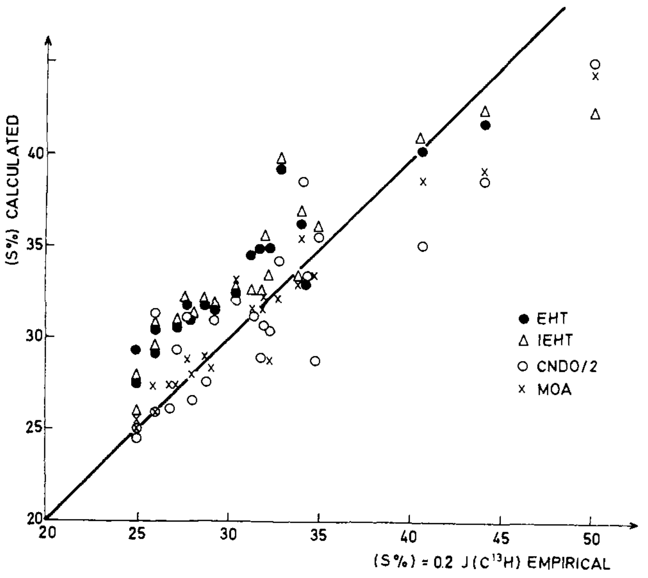

Figure 1. Comparison between the calculated s characters by the EHT, IEHT, CNDO/2, and MOA methods and the corresponding "experimental" hybridization.

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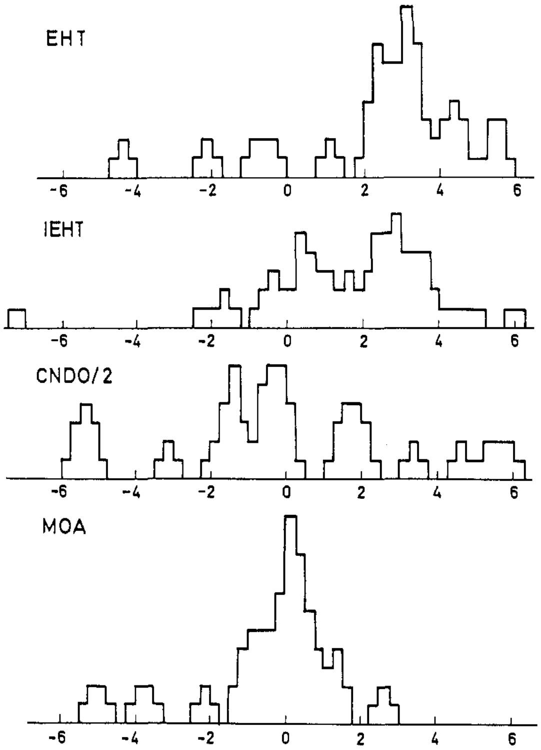

Figure 2. Distribution of the number of molecules *vs.* $\Delta = (s\%)_{CH}^{calcd} - (s\%)_{CH}^{emp}$ as calculated by the semiempirical methods considered in this paper.

which finer forms and distortions of this distribution could be revealed. Nevertheless, some qualitative conclusions can be drawn from Figure 2. We see that EHT and IEHT methods are predominantly asymmetrically placed with respect to the origin and both show a wide range of the values of Δ. The results of the CNDO/2 and MOA methods are centered close to the $\Delta = 0$ value; *i.e.*, they are more symmetrically distributed with respect to the origin. However, only the results of the latter method show a sufficiently sharp accumulation of the points about the center, which indicates a possible Gaussian distribution (if we ignore the tail $\Delta < -3$). The slight asymmetry shows that a linear relationship between $J(^{13}C–H)$ and $(s\%)_{CH}$ would be more appropriate as it was already discussed earlier (*vide supra*). Figure 2 confirms that the results of the MOA method are somewhat superior to the hybrids obtained by the other three methods as far as the $J(^{13}C–H)$ constants are concerned. When the individual molecules are considered we see that there are cases where all methods fail. Notably, this is the case for acetylene and cyclopropene where the calculated s contents are lower for all four approaches. This indicates that some of the approximations involved in these semiempirical methods are not very well balanced. These two molecules do possess some special features indeed, the C≡C triple bond and a C=C double bond, which is a part of a strained ring, which probably have to be parameterized separately.

It is also apparent that the MOA method seems suitable for the description of CH bonds of the bicyclic molecules where CNDO/2 gives widely scattered results. This indicates that the CNDO/2 method should be adjusted for strained molecules by altering the existing parameters or perhaps by critical examination of the basic assumptions. For instance, the Coulomb repulsions between the electrons are spherically averaged in order to maintain the rotational invariance of the local coordinate axes, which is a drastic simplification. It can be observed that the s characters extracted from the molecular orbitals are generally somewhat higher than the corresponding quantities obtained by the MOA method, where a perfect localization[38] is assumed and the intermolecular charge transfer is completely neglected. The reason is a very simple one. The $2s_c$ orbital has lower energy and consequently its orbital population is greater than 1, while the $2p_c$ orbital is relatively unaffected. Methane is a good example to illustrate this point. The SCC method gives 1.169 and 0.955 for $2s_c$ and $2p_c$ orbital populations, respectively. Therefore, the sum of (s%) characters for the same carbon atom is greater than 100%. The C–H bond overlap populations, $W_{2s(CH)} + W_{2p_x(CH)} + W_{2p_y(CH)} + W_{2p_z(CH)}$ as calculated by the CNDO/2 method, are practically constant for different CH bonds. Therefore, the bond index criterion of Wiberg and that of Trindle and Sinanoğlu give the same or very similar results in hydrocarbons.

Table III. Comparison between *ab Initio* and Semiempirical Hybridization in Various Hydrocarbons (W_{2s} Quantities Are Shown)

Molecule	Hy-brid	*Ab initio*[a]	Semiempirical *b*	Semiempirical *c*	MOA[d]
Methane	CH	27.4	26.0	24.9	25.0
Ethane	CH	26.9	24.8	24.6	25.4
	CC	34.0	24.2	26.0	23.8
Ethylene	CH	35.1[e]	28.8	31.0	31.5
	CC	36.5[e]	37.8	37.8	36.8
Acetylene	CH	49.8[e]		47.2[f]	44.4
	CC	49.8[e]		52.8[f]	55.6
$H_3C_aC_b{\equiv}C_cH$	C_aH	28.2		25.8[f]	25.0
	C_cH	45.9		47.2[f]	43.5
	C_aC_b	27.6		31.7[f]	24.9
	C_bC_a	46.5		38.6[f]	45.6
	C_cC_b	14.3		26.4[f]	18.8
	C_bC_c	15.1		26.6[f]	18.0
$H_2C_aC_b(C_cH_3)$	C_aH		33.7	30.8	31.5
	C_cH		25.5	24.9	25.4
	C_aC_b		38.7	37.9	36.8
	C_bC_a		35.6	37.2	37.9
	C_cC_b		25.3	25.2	23.7
	C_bC_c		32.4	30.1	31.1
Cyclopropane	CH	32.9	33.2	30.5	28.6
	CC	20.8	18.0	19.7	21.4
Benzene	CH	34.8[e]		38.7[f]	31.5
	CC	36.6[e]		36.5[f]	34.3
$H_2C_a{=}C_bHC_bH{=}C_aH_2$	C_aH	34.3		32.2[f]	31.5[f]
	C_bH	33.4		32.2[f]	31.3[f]
	C_aC_b	17.2		13.9[f]	18.5[f]
	C_bC_a	17.9		13.6[f]	18.5[f]
	C_bC_b	35.5		34.4[f]	31.7[f]

[a] *Ab initio* hybrids are taken from ref 7b and 9. [b] Hybrids taken from ref 5c and refer to localized orbitals. [c] Hybrids taken from ref 5c and refer to delocalized orbitals. [d] Hybrids taken from sources given in M. Randić and Z. B. Maksić, *Chem. Rev.*, **72**, 43 (1972), if not otherwise stated. [e] Hybrids calculated within σ–π approximation. [f] This paper.

Comparison with the Results of Some *ab Initio* Calculations

We compare the hybrids obtained by the semiempirical methods with some *ab initio* calculations em-

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[38] The electrons are perfectly localized if each atomic or hybrid orbital contains exactly one electron.

ploying minimal basis sets (Table III). These calculations carefully optimize the exponents of the Slater orbitals used in the variational procedure. We have selected the results of Newton, *et al.*,[39] and Newton and Switkes,[40] since their calculations cover some molecules already considered in Table I. These authors adopted a localization procedure in which the self-repulsion energy of localized orbitals is maximized, or what is equivalent, which minimizes their exchange energy. The localized orbitals are then broken up into the hybrid orbitals which turn out not to be orthogonal. However, Newton, *et al.*,[39] have shown that geminal hybrids are nearly orthogonal since their mutual overlap never exceeds 0.15. Therefore, a comparison of their hybrids with the localized hybrids obtained by the maximum overlap method can be made directly. We also include the results of CNDO/2 calculations of Trindle and Sinanağlu[5c] obtained by using two sets of s characters. One set is obtained by direct calculation of s content from delocalized MO's while the other is obtained from localized orbitals calculated by the Trindle and Sinanoğlu semiempirical scheme.[4] Different localization procedures could lead to different results, since they are very sensitive on the criteria involved in the localization requirements.[41] Thus, one could expect that different localization techniques[41,42] would produce somewhat different s characters of the local hybrid orbitals.[43] However, all these procedures have the same legality and should be judged within their own frameworks by correlating the physical or chemical property in question. Unfortunately, there are available only a few *ab initio* calculations of this type. Consequently, we can compare their hybrids with the corresponding semiempirical ones in order to draw some conclusions, but one should keep in mind that they are only tentative. It is seen from Table III that there is apparent similarity between the hybridization obtained by the methods discussed characterized by different levels of sophistication. The most striking discrepancy is found in ethane where the *ab initio* calculation predicts high s character (34%) of the CC bond, a value expected for ethylene. The same finding was made earlier by Pitzer.[44] This indicates that C–C and C–H bonds are not very well balanced in the semiempirical methods, since ethane has no special structural features. This effect is expected to be large in ethane since the ratio of CC and CH bonds is one to six. The *ab initio* hybrids of Newton, *et al.*,[39] show the characteristic decrease in s character from ethane to methylacetylene in agreement with the Bent empirical rule,[45] which states that the more electronegative substituent requires more p character in the neighboring hybrid. Thus, a hybrid directed to the C≡C triple bond in methylacetylene (which is a more electronegative group than a methyl group) has decreased s character to 27.6% as compared with 34% in ethane. The semiempirical calculations do not show this trend. The *ab initio* hybrids for CH and the σ part of the C≡C bond appear to be equivalent and a difference in hybridization could be anticipated. This nonequivalence is reflected in all semiempirical approaches, the ψ_{CC} hybrids being richer in s content. It is worthwhile to discuss the results for cyclopropane, since this molecule is a specimen for the highly strained hydrocarbons. The MOA method underestimates the s character of the C–H bonds as judged by the results of the *ab initio* calculation and $J(^{13}C\text{–}H)$ coupling constants, as discussed earlier.[24] The source of this error is not quite clear, but it seems that σ and π interaction of the cyclopropane ring should be parametrized separately. The present version of the MOA method employs only one k_{CC} weighting factor, eq 16. On the other hand, the calculated H–C–H angle by the MOA method[46] is in excellent agreement with the experimental value.[47] Furthermore, the bending of the ψ_{CC} hybrids describing the cyclopropyl ring in *cis*-1,2,3-tricyanocyclopropane[19] is in fair agreement with X-ray measurements, where the maximum of the electronic density is found to be 0.32 Å away from the straight line connecting the carbon atoms.[48] The incompatibility of the two experimental quantities, *i.e.*, the HCH angle and the $J(^{13}C\text{–}H)$ coupling constant for cyclopropane, indicates perhaps the limitations of the localized orbitals concept. The orthogonality requirements of the valence bond two-center orbitals may be more appropriate and could possibly lead to a better maximum overlap method.[49] It seems, however, that the orthogonality between the hybrids placed on the same atom is to a large extent responsible for a success of the MOA method as evidenced by the result presented in Table I. This conclusion is supported also by the CNDO/2 calculations on cyclopropane based on the "self-consistent hybrids"[50] which were constrained to be orthogonal. Namely, the CNDO/2 method in its original form failed to give a reasonable HCH angle (the minimum was not found for a variation of this angle between 102 and 122°) in cyclopropane. The inclusion of the hybridization by using a formula which is a special case of eq 6 reproduced the experimental HCH angle very nicely. Since the inclusion of the self-consistent hybrids in the semiempirical methods employing ZDO approximation might lead to a better variation of these methods, at least as far as the geometry of molecules is concerned, we shall consider them in some detail. For this purpose we write eq 14 in a somewhat modified form

$$\psi_{AB} = \sqrt{W_{2s(AB)}}(2s)_A + \sqrt{W_{2p(AB)}}(2p)_{A-B} \quad (18)$$

where $(2p)_{A-B}$ is the 2p orbital oriented along the

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(43) For an excellent review article on localized molecular orbitals see: H. Weinstein and R. Pauncz, "Advances in Atomic and Molecular Physics," Vol. 7, Academic Press, New York, N. Y., 1971, pp 97–140.

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A–B bond and $W_{2p(AB)}$ is its population by the active charge: $W_{2p(AB)} = W_{2p_x(AB)} + W_{2p_y(AB)} + W_{2p_z(AB)}$. If we now denote two equivalent and mutually orthogonal hybrid orbitals by ψ_{AB} and ψ_{AC}, one can easily find out that the interhybrid angle BAC satisfies eq 19.

$$\cos \vartheta_{BAC} = -W_{2s(AB)}/W_{2p(AB)} \qquad (19)$$

For two equivalent C–H bonds, eq 19 takes the form

$$\cos \vartheta_{HCH} = -P_{2s(CH)}{}^2/P_{2p(CH)}{}^2 \qquad (20)$$

By using the arguments of Meyer[50] one obtains

$$P_{2s(CH)}{}^2 + P_{2p(CH)}{}^2 = 1$$

which by substitution into formula 20 gives

$$\cos \vartheta_{HCH} = -P_{2s(CH)}{}^2/(1 - P_{2s(CH)}{}^2) \qquad (21)$$

To obtain internally consistent s characters one starts with a trial $P_{2s(CH)}$ and calculates the corresponding HCH angle by using eq 21. Then the CNDO/2 method is applied and the new $P_{\mu\nu}$ matrix elements are found. This procedure is repeated until input and output $P_{2s(CH)}$ matrix elements are the same. It is interesting to compare the CNDO/2 self-consisting hybrids for cyclopropane $(s\%)_{CH} = 28.7\%$ and $(s\%)_{CC} = 21.3\%$ with the corresponding MOA s characters[46] $(s\%)_{CH} = 28.6\%$ and $(s\%)_{CC} = 21.4\%$ for the CH and CC bonds, respectively. The results are practically identical and provide additional justification of the orthogonality conditions employed in the MOA method introduced on the basis of the intuitive argument that the electrons of the same spin should avoid each other as much as possible.

Conclusions

In view of the widespread interest and numerous applications of the various semiempirical methods, it is useful to have comparative studies which may help to establish relative merits of the individual approaches. One way to do this is the calculation of the various molecular properties which are very sensitive on the quality of the calculated wave functions and a comparison with the corresponding experimental results.[34] The other possibility is the critical examination of the basic assumptions and approximations involved in the semiempirical methods in question. This is usually not so straightforward since a number of the semiempirical methods only simulate the fundamental laws and first principles and lean heavily on the intuitive picture of bonding and qualitative concepts. In this paper we discussed the notion of the hybridization and compared the hybrids obtained by the *ab initio* minimum basis set and those calculated by the four semiempirical methods: EHT, SCC, CNDO/2, and MOA. Newton, *et al.*,[39] have shown that the hybrids are highly insensitive on the choice of the basis set in the *ab initio* approach. The present analysis shows that the calculated hybridization is not too sensitive even on the method employed for its calculation. Namely, in spite of the fact that so diverse methods were used, characterized by the different levels of sophistication, the calculated hybrids are qualitatively the same. It was also observed that the hybrids describing similar structural units are also similar to a high degree and indeed one may consider that the localized orbitals based on hybrids are transferable. This is in agreement with the empirical observations and eliminates the calculation of hybrids in trivial substituted molecules. The MOA hybrids are the most consistent with the empirical or "experimental" hybridization obtained by the Muller–Pritchard formula $(s\%)_{CH} = 0.2J(^{13}C\text{–}H)$. Taking into account many other linear correlations with various other physical and chemical properties like bond lengths,[23] bond energies,[20,22] CH stretching frequencies,[51] proton acidities of nonconjugated hydrocarbons,[52a] heats of formation,[52b] etc., we can say that the concept of noninteger sp^n hybrids offers a very simple and useful model describing covalent bonding. Furthermore, the compatibility of the MOA hybrids with the results obtained by using much more elaborate methods provides some *a posteriori* justification of the maximum overlap criterion. This conclusion is consistent with findings of Bartlett and Öhrn[53] who recently pointed out that it is possible to obtain the same resulting wave functions by using the maximum overlap criterion and by minimization of the energy of the molecule if the corresponding operators commute. This is approximately the case for the predominantly covalent systems. It would also be very useful to include the MOA hybrids in the SCF calculations, since it was shown that the hybrid orbitals significantly improve the convergency of the iterative procedure.[54]

As already mentioned, all four semiempirical methods give very close results as far as the hybridization is concerned. The choice of the particular method for the investigation of gross molecular properties of hydrocarbons is a matter of personal taste. We should like to mention that the MOA approach is the most pictorial one and the simplest one. Its simplicity is reflected *inter alia* in the number of parameters used in the calculations. For instance, the CNDO/2 method requires five parameters for hydrocarbons, EHT employs four parameters, while MOA uses only two parameters. The number of parameters could be easily increased in EHT and MOA methods without any danger of overparametrization. This could improve the aforementioned methods when the highly strained molecules are concerned. The inclusion of different weighting factors in the MOA method for σ and π interactions in strained rings gives quite promising results.[55]

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