

Geometry of Molecules. 3. Iterative Maximum Overlap Calculations of Bond Lengths in Some Conjugated Polyenes and Their Alkylated Derivatives

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Abstract: The geometry of a large number of conjugated aliphatic polyenes and their substituted derivatives was examined by the modified iterative maximum overlap method. The calculated interatomic distances and bond angles are in a good overall agreement with the experimental data and available MINDO/3 or ab initio results. The present calculations show that π -electron delocalization contributes 0.01 Å to the shortening of the C–C central bond in 1,3-butadiene and related molecules. The corresponding resonance contribution to the heat of formation is ~ 5 kcal/mol which is in good accordance with the experimental barrier of rotation around the C–C bond in question. The additivity of the heats of formation in conjugated linear polyenes is rationalized by a high degree of transferability of the local hybrid orbitals. The IMO method results indicate that the changes in hybridization might well describe the most important factor determining bond distances and bond angles in hydrocarbons.

(I) Introduction

An understanding of the molecular architecture is one of the first aims of theoretical chemistry. Interatomic distances and bond angles are important characteristics of covalent chemical bonds and their prediction is a serious test for any valence theory. Conjugated and aromatic hydrocarbons have been particularly extensively studied from both the experimental and theoretical points of view for the last 50 years. In theoretical treatments of large unsaturated systems it is customary to divide electrons into three classes: (a) inner-shell electrons which do not significantly contribute to the formation of covalent bonds, (b) σ electrons engaged in the formation of localized two-center bonds and which exhibit the maximum density along the line joining two adjacent nuclei (with some off-line deviations in the case of bent bonds), and (c) the mobile π electrons whose orbitals are antisymmetric with respect to the plane of a molecule formed by σ bonds. The inner-shell and σ electrons are supposed to have their energies and charge distributions governed solely by the atomic orbitals or pairs of localized two-center orbitals. On the contrary, π electrons are assumed to be spread over the whole conjugated system and described accordingly by appropriate delocalized molecular orbitals. The orbital energies of π electrons are as a rule higher than the energies of the other types of electrons. They are also much more diffuse and consequently more susceptible to external influences. Therefore, it is not surprising that properties of conjugated molecules were usually interpreted in terms of π electrons only (for example, variation of bond lengths via bond order changes). The early quantum-chemical treatments were characterized by complete disregarding of inner-shell and σ electrons and by neglecting explicit computations of the interelectronic interactions.^{2,3} A more refined semiempirical method based on many-electron Hamiltonian was put forward by Pariser, Parr, and Pople,^{4,5} which also rests on the σ - π separability⁶ where σ and π manifolds of orbitals are considered independently. The role of inner-shell and σ electrons together with the atomic nuclei is reduced to the formation of a core producing a field in which π electrons are embedded. This type of approach has long served to provide a qualitative and quantitative understanding of π -electron systems with a remarkable success. However, the method is less suitable for large conjugated molecules involving highly strained rings because the transferability of σ bonds from unstrained to strained rings does not hold. It is, therefore, desirable to develop a method allowing for variations in the σ framework retaining

at the same time the mathematical simplicity of, e.g., the Hückel method.

Previous papers^{7,8} in this series⁹ have described the iterative maximum overlap approximation (IMO) which allows simple and efficient calculations of the geometry of nonconjugated hydrocarbons and their heats of formation with a good accuracy. The results of these calculations agreed with experimental values within 0.01 Å and 2° or better for bond lengths and angles, respectively. The standard deviation of the calculated heats of formation was 3 kcal/mol, which is quite satisfactory because a wide variety of saturated and unsaturated hydrocarbons involving highly strained cyclic and polycyclic systems were included in the correlation.¹⁰ The IMO method is based on the variable hybridization model of covalent bonding which proved very useful in discussing physical and chemical properties of nonconjugated hydrocarbons.⁷⁻¹¹ This model should also be suitable for a treatment of σ skeletons of large conjugated compounds and particularly advantageous for a description of strained fused π systems where the hybrids emanating from juncture carbon atoms significantly deviate from the canonical sp^2 state. In this paper we consider bond lengths and angles in some linear polyenes and their alkylated derivatives. The bond distances are calculated first by the standard IMO procedure. Then, the corrections due to π -electron delocalization are included by the Hückel-type calculations. This type of treatment has an apparent advantage over previous methods because the effect of loosely bound π electrons is taken into account as a perturbation of the almost rigid σ framework. The comparison between calculated bond distances and observed values will shed some light on the relative importance of hybridization, conjugation, and hyperconjugation in determining molecular geometry. An impetus for this work was given by the large body of experimental data provided by Traetteberg, Kuchitsu, and others.¹²

(II) Outline of the Method

(1) The Localized Bond Approach. The iterative maximum overlap method was designed for the calculation of bond lengths in hydrocarbons characterized by localized bonds. The details of the method are published elsewhere.^{7,8} Here we give a brief account. The computations are not directly based on the variational theorem in which an average energy expression involving the molecular Hamiltonian is minimized with respect to a set of adjustable hybridization parameters. Instead, a basis set of local hybrid orbitals was assumed for a given geometry,

and parameters specifying the hybridization were varied to maximize the sum of the weighted bond overlaps. In other words we search for optimal parameters a_i of individual hybrids

$$\psi_i = a_i(2s) + (1 - a_i^2)^{1/2}(2p) \quad (1)$$

which maximize the sum of bond energies

$$E_b = \sum_{CC} E_b(CC) + \sum_{CH} E_b(CH) \quad (2)$$

where the summations are extended over all CC and CH bonds in a molecule. It is plausible to assume that the bond energies are linear functions of the corresponding overlap integrals¹³ $E_{AB} = k_{AB}S_{AB} + l_{AB}$, where k_{AB} and l_{AB} are empirically adjusted parameters. In order to reduce the number of parameters we shall suppose that the weighting factors k_{AB} depend only on the nature of the atoms A and B. They do not vary with the changes in chemical environment of the atoms in question. Then, (2) takes the form

$$E_b = k_{CC} \sum_{CC} S_{CC} + k_{CH} \sum_{CH} S_{CH} + (n_{CC}l_{CC} + n_{CH}l_{CH}) \quad (3)$$

where n_{CC} and n_{CH} are the numbers of CC and CH bonds in a molecule, respectively. The term in parentheses is an additive constant and we can drop it in a process of maximization of the total bond energy, E_b . The weighting factors k_{CC} and k_{CH} were obtained by matching the calculated and experimental bond energies in ethane and methane. If the double ζ STO atomic functions suggested by Clementi¹⁴ are adopted the numerical values of k_{CC} and k_{CH} are 121 and 136 kcal/mol, respectively. The hybridization parameters a_i are subject to orthonormality conditions

$$a_i a_j + (1 - a_i^2)^{1/2}(1 - a_j^2)^{1/2} \cos \theta_{ij} = \delta_{ij} \quad (4)$$

($i, j = 1, \dots, 4$)

where θ_{ij} is the angle between the directions of hybrids ψ_i and ψ_j sharing the same carbon nucleus. The orthogonality requirements in (4) were justified by the analysis of hybrid orbitals extracted from the semiempirical molecular orbitals.¹⁵ During the calculations the hybrid orbitals are allowed to follow the directions of the straight lines passing through the directly bonded nuclei freely, except in cyclic molecules (e.g., cyclooctatetraene, cyclopentadiene, fulvene, and their methylated derivatives) where bent bonds in the ring appear.¹⁶ The salient feature of the IMOA procedure is the use of the empirical bond length-bond overlap linear relations of the form¹⁷

$$d(C-C) = -1.166S_{CC} + 2.298 \text{ \AA} \quad (5)$$

$$d(C=C) = -0.677S_{C=C} + 2.087 \text{ \AA} \quad (6)$$

$$d(C-H) = -0.869S_{CH} + 1.726 \text{ \AA} \quad (7)$$

In the first iterative step the initial bond lengths are selected and the independent hybridization parameters a_i are varied until the maximum of (2) is reached. The search for the maximum is performed by the Simplex method.¹⁸ The choice of the starting set of bond distances is quite arbitrary but the use of Dewar and Schmeising values¹⁹ for standard C-C bonds, which are classified roughly by the corresponding canonical hybridization states sp^n-sp^m ($n, m = 1, 2, 3$), is advantageous. After the optimization of the hybridization parameters in the first cycle of the calculation, the new set of better bond lengths is deduced from correlations 5-7. The whole procedure is then repeated until a consistency between input and output bond lengths is achieved. Thus in the IMOA method the hybridization parameters are optimized in the sense of the maximum

overlap criterion satisfying at the same time the constraints 4-7. The use of the relations 5-7 in the IMOA method is of crucial importance because the hybridization, generally speaking, depends on the bond lengths via the basic overlap integrals between ($2s_C$), ($2p_C$), and ($1s_H$) orbitals. If bond distances other than the experimental ones are employed (e.g., the standard bond lengths), then a certain arbitrariness in the "optimal" composition of hybrids is introduced. This type of inaccuracy is reduced to a minimum in the IMOA approach because the resulting bond lengths are as a rule very close to the observed values. The IMOA method was devised for a prediction of the geometries of molecules possessing localized bonds. The following section deals with a refinement of the method in order to allow for the π -electron delocalization effect.

(2) π -Electron Delocalization Correction. According to Lykos and Schmeising²⁰ the maximum overlap molecular orbitals (MOMO) are the eigenvectors of the metric matrix formed by the overlap integrals of the nonorthogonal basis set functions. Let us denote a basis set of real atomic orbitals by ϕ_i ($i = 1, \dots, n$) which are normalized and linearly independent but not orthogonal. The desired MOMO's are of the form

$$\psi = \sum_{j=1}^n c_j \phi_j \quad (8)$$

where the coefficients c_j are the real numbers. They are determined by a requirement that the sum s of the squares of the projections of the molecular orbital ψ in eq 8 on the basis set functions ϕ_i ($i = 1, \dots, n$) is a maximum

$$s = \sum_i \langle \phi_i | \psi \rangle^2 = \max \quad (9)$$

After substituting (8) into (9) and performing some algebra one obtains

$$s = \sum_{jk} c_j c_k (\mathbf{S}^2)_{jk} \quad (10)$$

where \mathbf{S} is the overlap matrix with elements $S_{jk} = \langle \phi_j | \phi_k \rangle$. The sum s in (9) should be the extremum for coefficients c_j which ought to satisfy the normalization condition of the molecular orbital ψ

$$\langle \psi | \psi \rangle = \sum_{jk} c_j c_k S_{jk} = 1 \quad (11)$$

By using the conventional method of Lagrange multiplier λ , the problem is reduced to finding the absolute extremum of the expression s'

$$s' = \sum_{jk} c_j c_k (\mathbf{S}^2)_{jk} - \lambda \sum_{jk} c_j c_k S_{jk} \quad (12)$$

The conditions $(\partial s' / \partial c_i) = 0$ ($i = 1, \dots, n$) yield a set of linear homogeneous equations

$$\sum_k c_k ((\mathbf{S}^2)_{ik} - \lambda S_{ik}) = 0 \quad (13)$$

which has a nontrivial solution if the corresponding determinant vanishes

$$|\mathbf{S}^2 - \lambda \mathbf{S}| = 0 \quad (14)$$

Since the \mathbf{S} matrix is nonsingular, (14) is reduced to

$$|\mathbf{S} - \lambda \mathbf{I}| = 0 \quad (15)$$

where \mathbf{I} is the unit matrix. Thus we have to solve the eigenvalue problem of the overlap matrix \mathbf{S} . The coefficients $c_i^{(m)}$ which correspond to the largest eigenvalue λ_m form the molecular orbital ψ_m which has maximum projections to the initial basis

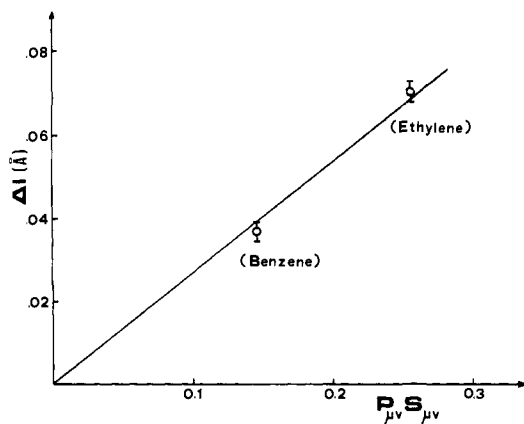


Figure 1. Linear relation between the π -electron active charge and the CC bond length changes due to π -electron delocalization.

set. Imposing additional constraint for the next molecular orbital ψ_{m-1}

$$\langle \psi_{m-1} | \psi_m \rangle = 0$$

and applying the maximum overlap criterion, one obtains that ψ_{m-1} is given by $c_i^{(m-1)}$ which belong to the second highest eigenvalue λ_{m-1} . By an obvious extension of the argument it is concluded that the eigenvectors of the overlap matrix ordered according to the magnitude of the corresponding eigenvalues represent the maximum overlap molecular orbitals. Since the overlap matrix reflects the symmetry of a molecule, the MOMO's surely contain a certain degree of similarity with true wave functions. Lykos and Schmeising have shown that they are equivalent to Hückel molecular orbitals. The eigenvalues of the overlap matrix are identical with Hückel MO energies if a proper scale and choice of their origin is made. Furthermore, a test calculation on the sample molecule naphthalene has shown that MOMO's are very close to SCF π -electron molecular orbitals.²⁰ The method of Lykos and Schmeising was recently thoroughly examined and discussed by Bartlett and Öhrn.²¹ Their calculations indicate that MOMO charge densities and dipole moments are quite reliable for predominantly covalent molecules where the intramolecular charge transfer is not highly pronounced. Then the overlap and Hartree-Fock matrices **S** and **F** nearly commute and consequently their eigenvectors are similar. Rein et al.²² found out that molecular higher moments calculated by MOMO's are in reasonable agreement with the experimental values. Whitehead and Zeiss²³ have conclusively shown that the constrained maximum overlap molecular orbitals are significantly better than other constrained nonempirical and semiempirical SCF wave functions. Thus the Lykos-Schmeising method provides molecular orbitals which give reliable information about molecular charge distributions being in the same time very simple and feasible for large systems.

The changes in bond distances caused by the π -electron delocalization are estimated by using their well known dependence on bond orders.²⁴ Since the overlap integrals in the Lykos-Schmeising method are retained, the changes in bond lengths are actually related to π -electron active charge distributed along the bond in question,^{15,25} which provides some measure of the bonding power

$$W^{AB} = 2P_{\mu\nu}^{AB} S_{\mu\nu}^{AB} \quad (16)$$

where

$$P = \sum_{i=1}^{\text{occ}} c_{i\mu} c_{i\nu}$$

is the element of the bond order and charge density matrix. The

directly bonded atoms, contributing one π electron each, are denoted by A and B, respectively. The overlap integral between the corresponding p_π orbitals $\int \phi_\mu^A \phi_\nu^B dv$ is designated by $S_{\mu\nu}^{AB}$. The calibration curve for the bond lengths correction was obtained by choosing specimen molecules (ethylene and benzene) which have $P_{\mu\nu}$ matrix elements determined by the symmetry alone. The effect of π electrons is then found by taking a difference Δl between the calculated bond lengths using σ overlaps only (eq 5) and the experimental values. It appears that the corrections Δl are linearly related to the corresponding active charges (Figure 1). The straight line

$$\Delta l = 0.266 P_{\mu\nu} S_{\mu\nu} \quad (17)$$

passes through the origin of the coordinate system as it should because the π -electron correction is zero if the overlap integral between π -orbital $S_{\mu\nu}$ values vanishes. Results obtained in this modified IMO method are presented in the next section.

(III) Results and Discussion

(1) **Hybrid Orbitals.** The optimal hybridization ratios n_i ($n_i = a_i^2 / (1 - a_i^2)$) and the relevant overlap integrals are listed in Table I. One notices that deviations of hybrid orbitals from the canonical states are small but significant. The variable hybridization model, where n_i changes continuously, is more flexible to conform to the local symmetry of an atom in a molecule. By the local symmetry of an atom we mean the symmetry of the field produced by its nearest neighbors. It should be pointed out that symmetries of the molecules considered in this paper are not imposed as constraints but they are results of the calculations which constitute additional checking of the algorithm used here. The inadequacy of the canonical hybridization and the flexibility of the variable n_i model will be illustrated on ethylene. Three equivalent sp^2 hybrid orbitals, which are customarily used for the description of its σ skeleton, assume the D_{3h} local symmetry of the carbon atom. There is, however, no reason whatsoever why the two C-H bonds should be equivalent to the CC σ bond. On the contrary, one could expect on the intuitive grounds that the local symmetry of the carbon atoms is D_{2h} that the HCC and HCH bond angles differ by 120° . Indeed, the experiment reveals that the HCH angle is 117.6° . The deviation from the "ideal" value is small but conceptually very important. The calculated ψ_{CH} hybrid orbitals are of the $sp^{2.17}$ composition forming the mutual angle of 117.5° , which is in good agreement with experiment. Another interesting observation is that hybrid orbitals describing similar structural environments are almost identical. The characteristic hybridization ratios for molecules studied in this paper are: 2.9 and 2.2 for methyl and olefinic C-H bonds, respectively, 1.7 for the σ part of the C=C double bond, and 3.2 and 2.2 for the C-C bond linking saturated and unsaturated carbon atoms, respectively. By using these values one can easily describe the σ skeletons of long chain polyenes in the local hybrid orbital approximation. Thus hybrid orbitals provide a useful basis for the interpretation of bond additive schemes which hold for many molecular properties. The calculated hybrids can be used as starting wave functions for more sophisticated and ambitious calculations particularly for large molecules which are still out of range of the rigorous ab initio SCF methods. Namely, the aforementioned transferability of hybrids describing similar chemical environments enables the construction of local orbitals for a large molecule by considering separately its constituent fragments. The elements of the Hartree-Fock matrix are then also transferable providing a basis of simple and efficient simulated ab initio techniques.²⁶ The calculated hybridization parameters are related to a number of local physical and chemical molecular properties like CC and CH spin-spin coupling constants, CH stretching frequencies, proton thermodynamic

Table I. The Calculated Hybridization Parameters and the Corresponding Overlap Integrals for the Molecules Considered in This Paper

Molecule	Bond	Hybridization ratios n_i-n_j	σ overlap	Molecule	Bond	Hybridization ratios n_i-n_j	σ overlap
	C=C	1.72-1.72	$S_{CC} = 0.7643$		C ₁ =C ₂	1.68-1.67	$S_{12} = 0.7683$
	C-H	2.17	$S_{CH} = 0.7403$		C ₂ -C ₃	2.21-2.20	$S_{23} = 0.7046$
	C ₁ =C ₂	1.72-1.68	$S_{12} = 0.7657$		C ₃ =C ₄	1.68-1.66	$S_{34} = 0.7690$
	C ₂ -C ₃	2.18-3.01	$S_{23} = 0.6847$		C ₄ -C ₅	2.27-3.17	$S_{45} = 0.6740$
	C ₁ -H	2.17	$S_{1H} = 0.7403$		C ₁ -H	2.19	$S_{1H} = 0.7422$
	C ₂ -H	2.20	$S_{2H} = 0.7399$		C ₅ -H	2.95	$S_{5H} = 0.7202$
	C ₃ -H	2.93	$S_{3H} = 0.7205$				
	C ₁ =C ₂	1.72-1.64	$S_{12} = 0.7672$		C ₁ -C ₂	3.17-2.27	$S_{12} = 0.6740$
	C ₂ -C ₃	2.22-3.22	$S_{23} = 0.6755$		C ₂ =C ₃	1.66-1.65	$S_{23} = 0.7692$
	C ₁ -H	2.17	$S_{1H} = 0.7403$		C ₃ -C ₄	2.17-2.17	$S_{34} = 0.7069$
	C ₃ -H	2.93	$S_{3H} = 0.7205$		C ₃ -C ₅	2.25-3.17	$S_{38} = 0.6744$
					C ₁ -H	2.95	$S_{1H} = 0.7202$
					C ₂ -H	2.15	$S_{2H} = 0.7432$
	C ₁ -C ₂	3.22-2.27	$S_{12} = 0.6725$		C ₁ =C ₂	1.69-1.69	$S_{12} = 0.7675$
	C ₂ =C ₃	1.65-1.65	$S_{23} = 0.7705$		C ₂ -C ₃	2.18-2.17	$S_{23} = 0.7064$
	C ₁ -H	2.93	$S_{1H} = 0.7210$		C ₃ -C ₄	1.70-1.70	$S_{34} = 0.7668$
	C ₂ -H	2.16	$S_{2H} = 0.7424$		C ₁ -H	2.19	$S_{1H} = 0.7422$
					C ₂ -H	2.19	$S_{2H} = 0.7422$
	C ₁ -C ₂	3.18-2.27	$S_{12} = 0.6733$		C ₁ =C ₂	1.69-1.69	$S_{12} = 0.7675$
	C ₂ =C ₃	1.65-1.63	$S_{23} = 0.7712$		C ₂ -C ₃	2.18-2.17	$S_{23} = 0.7064$
	C ₃ -C ₄	2.23-3.17	$S_{34} = 0.6749$		C ₃ =C ₄	1.70-1.70	$S_{34} = 0.7668$
	C ₁ -H	2.94	$S_{1H} = 0.7204$		C ₄ -C ₅	2.17-2.17	$S_{45} = 0.7069$
	C ₂ -H	2.15	$S_{2H} = 0.7431$		C ₅ -C ₇	2.25-3.17	$S_{57} = 0.6744$
	C ₄ -H	2.94	$S_{4H} = 0.7204$		C ₁ -H	2.19	$S_{1H} = 0.7422$
					C ₂ -H	2.19	$S_{2H} = 0.7422$
	C ₁ -C ₂	3.19-2.23	$S_{12} = 0.6746$		C ₇ -H	2.95	$S_{7H} = 0.7202$
	C ₂ =C ₃	1.63-1.63	$S_{23} = 0.7720$				
	C ₁ -H	2.94	$S_{1H} = 0.7204$				
	C ₁ -C ₂	3.16-2.27	$S_{12} = 0.6743$		C ₁ =C ₂	1.66-1.00	$S_{12} = 0.7972$
	C ₂ =C ₃	1.66-1.63	$S_{23} = 0.7710$		C-H	2.20	$S_{CH} = 0.7394$
	C ₃ -C ₄	2.22-3.05	$S_{34} = 0.6783$				
	C ₄ -C ₅	3.23-3.28	$S_{35} = 0.6452$		C ₁ =C ₂	1.66-1.00	$S_{12} = 0.7972$
	C ₃ -C ₆	2.23-3.16	$S_{36} = 0.6754$		C ₂ =C ₃	1.00-1.00	$S_{23} = 0.8255$
	C ₁ -H	2.95	$S_{1H} = 0.7201$		C-H	2.20	$S_{1H} = 0.7394$
	C ₂ -H	2.15	$S_{2H} = 0.7431$				
	C ₄ -H	2.87	$S_{4H} = 0.7222$		C ₁ =C ₂	1.69-1.00	$S_{12} = 0.7972$
	C ₅ -H	2.91	$S_{5H} = 0.7209$		C ₂ =C ₃	1.00-1.69	$S_{23} = 0.7972$
					C ₃ -C ₄	2.17-2.17	$S_{34} = 0.7065$
	C ₁ =C ₂	1.69-1.67	$S_{12} = 0.7680$		C ₁ -H	2.19	$S_{1H} = 0.7411$
	C ₂ -C ₃	2.22-2.22	$S_{23} = 0.7034$		C ₃ -H	2.20	$S_{3H} = 0.7409$
	C ₁ -H	2.19	$S_{1H} = 0.7421$				
	C ₂ -H	2.17	$S_{2H} = 0.7425$				
	C ₁ =C ₂	1.69-1.66	$S_{12} = 0.7688$		C ₁ -C ₂	1.69-1.69	$S_{12} = 0.7677$
	C ₂ -C ₃	2.16-2.20	$S_{23} = 0.7060$		C ₂ -C ₃	2.18-2.18	$S_{23} = 0.7060$
	C ₂ -C ₅	2.26-3.16	$S_{25} = 0.6744$		C ₁ -H	2.19	$S_{CH} = 0.7411$
	C ₁ -H	2.19	$S_{1H} = 0.7421$				
	C ₃ -H	2.18	$S_{3H} = 0.7422$		C ₁ =C ₂	1.65-1.65	$S_{12} = 0.7709$
	C ₄ -H	2.19	$S_{4H} = 0.7421$		C ₂ -C ₃	2.15-2.15	$S_{23} = 0.7083$
	C ₅ -H	2.95	$S_{5H} = 0.7201$		C ₂ -C ₄	2.28-3.18	$S_{24} = 0.6732$
					C ₄ -H	2.94	$S_{4H} = 0.7206$
	C ₁ =C ₂	1.69-1.65	$S_{12} = 0.7688$		C ₁ -C ₂	1.66-1.66	$S_{12} = 0.7683$
	C ₂ -C ₃	2.17-2.17	$S_{23} = 0.7069$		C ₂ -C ₃	2.16-2.19	$S_{23} = 0.7069$
	C ₂ -C ₅	2.25-3.17	$S_{25} = 0.6744$		C ₂ -C ₄	2.25-3.17	$S_{24} = 0.7412$
	C ₁ -H	2.19	$S_{1H} = 0.7422$		C ₄ -H	2.95	$S_{4H} = 0.7202$
	C ₅ -H	2.95	$S_{5H} = 0.7202$				

acidities,¹¹ etc., which can be qualitatively predicted by using available correlations. This was discussed in considerable length earlier^{10,11,27} and needs not be repeated here. However, we would like to comment on the use of the standard bond lengths in the maximum overlap method because it may well have some significance for other more advanced semiempirical methods. During our studies we have observed that heats of formation of molecules and strain energies were strongly dependent on the bond lengths assumed in the calculations.²⁸ The reasonable results were obtained only for the equilibrium interatomic distances. Apparently, the use of the latter is a prerequisite for the best hybrid orbitals calculated within the maximum overlap approximation. This is the main reason behind our use of the IMOA method which provides self-consistent geometries via the empirical correlations relating overlap integrals and interatomic distances. The so obtained

geometries are as a rule quite close to the experimental ones thus decreasing the arbitrariness in the choice of the initial bond lengths and/or angles. A much less satisfactory alternative is the use of standard bond lengths which were classified according to sp^n-sp^m hybridization states, where $n, m = 1, 2, 3$ for carbon atoms and $m = 0$ for hydrogen.¹⁹ These values were recommended for acyclic CC bonds and they do not hold for highly strained small-ring compounds because the bond lengths between carbon atoms in these molecules are widely different. On the other hand, it appears that the hybridization parameters are very sensitive to geometry in small polycyclic systems particularly at the spiro junction carbon atoms. Consequently the use of standard bond distances for this type of molecule is unjustified and the hybridization parameters calculated by Randić and Kumar²⁹ for a large number of spiro hydrocarbons should be considered with a due cation.

(2) Bond Lengths and Angles. The bond lengths and angles obtained by the modified IMO method are summarized in Table II. We added also some molecules employed earlier for the parametrization of correlation 6 for the sake of completeness. There are several experimental methods now in use for the molecular structure determination which can be roughly divided into spectroscopic (abbreviated as SP) and electron diffraction (ED) ones. Concomitantly one can find in current literature a large number of different definitions of the equilibrium and average molecular structures.^{30,31} If the interatomic distances of the particular bond in question in different molecules are to be compared, then the same method and the same definition should be employed. The use of such a self-consistent set of data obtained preferably by the combined application of SP and ED methods^{31,32} would be highly desirable. Unfortunately, an extensive set of experimental bond lengths of this kind encompassing characteristic CC bonds is not available. Therefore we used r_s distances or, if they were lacking, r_g structures of SP and ED techniques, respectively. These geometries provide meaningful and reliable interatomic distances and bond angles. Whenever it was possible we included ED-SP data which probably are the most accurate ones.^{31,32} It should be pointed out that r_s and r_g structures are not identical. The r_g values are as a rule larger, the difference being $+0.01 \pm 0.02 \text{ \AA}$ (in most cases it is $+0.006 \pm 0.008 \text{ \AA}$) for CC bonds, and it is even larger for CH distances.³³ The origin of these differences is mainly in the process of averaging over the zero-point vibrations which is not the same in both methods. An additional obstacle arises from the fact that sometimes there are discrepancies for the same structure measured in different ED laboratories. Therefore, the experimental data presented in Table II are not, strictly speaking, compatible. Furthermore, the empirical relationships 5-7 were obtained by using predominantly SP bond distances and consequently the IMO results correspond to SP values. However, in spite of these inconsistencies the emerging general picture is quite clear and we can draw several interesting conclusions. A survey of the results shows that the shapes and sizes of the studied molecules are fairly well reproduced. The calculated bond lengths can be favorably compared with the results of the MINDO/3 method³⁴ giving sometimes even better agreement with experiment (particularly for bond angles). We shall now focus our attention on structural characteristics of methyl-substituted ethylenes. The average SP-ED geometries for this series of molecules were determined by Kuchitsu et al.³³ It was found that the C=C bond is the largest in tetramethylethylene while the shortest one is that in ethylene, the difference being 0.016 \AA . In other words, the C=C bond length increases by increasing the number of substituted CH_3 groups. Similarly, the C-C bond distances increase slightly in the same manner along the series. The difference between propene and tetramethylethylene in the C-C bond length is 0.005 \AA . It is interesting to note that the hybridization theory inherent in the IMO method predicts a slight decrease of the C=C bond lengths (by 0.008 \AA) contrary to the experimental observations. Since the hyperconjugative effect can be excluded on the grounds that both types of CC bonds increase their interatomic distances at the same time, we conclude that the observed trend for double bonds has to be explained in terms of steric interactions. The hyperconjugative and hybridization effects are overwhelmed in tetramethylethylene by steric repulsions which are responsible for the increase of at least 0.024 \AA in C=C bond distance relative to the corresponding value in ethylene. Comparison of the bond distances for 1,3-butadiene, cyclooctatetraene, and their methyl derivatives is very instructive. The deviation of the calculated IMO bond lengths from the experimental data for 1,3-butadiene indicates the scope and the limitation of the local bond model. The calculated C=C double bond was shorter (by 0.008 \AA) and the C-C single bond

longer (by 0.015 \AA) than the experimental values indicating that the conjugative effect is of some importance here. Indeed, the corrections due to π -electron delocalization calculated by (16) yield the shortening of the C-C bond by 0.008 \AA and lengthening of the double bond by 0.007 \AA fully in line with theoretical expectation and experimental observation. Our estimate of resonance shortening of the C-C central bond in 1,3-butadiene can be compared with the Dewar and Schmeising¹⁹ estimate (0.01 \AA or smaller) and recent ab initio results³⁵ (0.02 \AA). It is in any case smaller than Mulliken's prediction³⁶ that about 40% of the C-C shortening in this molecule relative to ethane is due to conjugation ($\sim 0.03 \text{ \AA}$). There is quite a different situation in cyclooctatetraene and similar molecules because the conjugation is to a large extent reduced by the unfavorable angle between the π orbitals of the double bonds ($\sim 67^\circ$). The local orbital model operating via overlap integrals now gives geometries in fine agreement with experiment. The resonance shortening of the single bonds is 0.002 \AA while the accompanied lengthening of the double bonds is 0.003 \AA . It is interesting to mention that the experimental C-C bond lengths in 1,3-butadiene and cyclooctatetraene are the same. Our calculations indicate that the decreased s character of the hybrids describing the C-C bond in 1,3-butadiene (Table I) is compensated by the increase in the π -electron active charge. The calculated CC bond lengths in cyclopentadiene, fulvene, and 6,6-dimethylfulvene were considerably improved by inclusion of the π -delocalization correction (Table II) demonstrating thus the utility of the modified IMO technique.

The calculated C-H bond lengths are as a rule significantly shorter than the experimental values. This is not surprising because the IMO results correspond to SP bond distances while a large body of experimental data belongs to values provided by the ED technique. It should be pointed out that the ED C-H bond lengths are particularly inaccurate since the hydrogen atom is a poor scatterer of electrons and has also very large vibrational amplitudes. One has to mention that the IMO method always distinguishes quite clearly between aliphatic and olefinic C-H bond lengths. Its predictive power is best illustrated on fulvene where our calculated methylene C-H bond length was in complete disagreement with the old experimental value of 1.13 \AA .³⁷ However, the more recent microwave measurements on 6-deuteriofulvene gave 1.083 \AA for the CH bond in question³⁸ which agrees nicely with our theoretical estimate. The other calculated C-H bond distances are also in very good agreement with precise SP microwave data (Table II). The bond angles in acyclic parts of the studied polyolefins were calculated by using the complete orbital following assumption. It was found by Bartell³⁹ that in ethylene it is about fivefold less costly in loss of overlap to fix the hybridization at an optimum value and bend the C-H bonds (i.e., change HCH angle by moving H atoms) than it is to vary the carbon hybrid orbitals to follow the angular displacements. In other words, the CH bonds might fall in the category of bent bonds. However, the ab initio study of ethane⁴⁰ has shown that bending of ψ_{CH} hybrids is very small. The hybrid orbitals lie slightly inside (0.5°) the pyramid formed by the CH_3 group. Similarly, the results show small departure of the ψ_{CH} hybrids (1°) outside of the HCH angle in ethylene.⁴⁰ Therefore, the orbital following approximation seems to be justified. If we adopt this approximation, the deviations of the calculated bond angles from the observed ones should be ascribed to the influence of steric factors. A word of caution is needed here because the interatomic angles as determined by the ED method are sometimes very inaccurate due to the shrinkage effect.³¹ Thus the bond angles do not provide a reliable measure of the nonbonded interference in a molecule if ED data are employed. Our calculated bond angles are in fair agreement with experiment, the average absolute error being 1.9° . The serious dis-

Table II. Comparison between the Geometries of Mono- and Polyolefins and Their Alkylated Derivatives as Calculated by the IMOA Method, MINDO/3 Method, and the Available Observed Values

Molecule ^z	Bond	Bond lengths, Å			Bond angles, deg				
		IMOA	MINDO/3 ^a	Exptl	Angle	IMOA	MINDO/3	Exptl	
*C=C	C=C C-H	1.338 1.085	1.308 1.098	1.337 ^b 1.086	CCH	121.3	124.8	121.2	
*C ₃ -C=C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₁ -H C ₂ -H C ₃ -H	1.335 1.500 1.085 1.083 1.102	1.333 1.480 1.101 1.114 1.114	1.342 ^c 1.506 1.085 1.098	1.336 ^d 1.501	CCC HC ₁ C ₂ HC ₂ C ₃ HC ₃ H	121.5 121.2 117.2 110.0	128.9 123.4 111.4 106.0	124.3 ^c
*C ₄ -C=C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₁ -H C ₃ -H	1.336 1.508 1.082 1.100	1.339 1.498 1.101 1.112	1.342 ^c 1.508 1.072 1.095	1.330 ^e	CCC HC ₁ C ₂ HC ₃ C ₂	116.8 121.3 110.0	116.6	116 ^{c,e}
C ₄ -C=C ₁	C ₁ -C ₂ C ₂ =C ₃ C ₁ -H C ₂ -H	1.514 1.331 1.099 1.081	1.473 1.339 1.111 1.112	1.508 ^c 1.347 1.11	1.506 ^f	C ₁ C ₂ C ₃ C ₁ C ₂ H C ₂ C ₁ H	121.2 116.9 109.0	134.3 110.9 113.0	125.4 120.1 110.6
C ₄ -C ₃ =C ₁	C ₁ -C ₂ C ₂ -C ₃ C ₁ -H C ₂ -H	1.514 1.331 1.099 1.081	1.464 1.346 1.111 1.103	1.510 ^c 1.348	1.508 ^f 1.347	C ₁ C ₂ C ₃ C ₁ C ₂ H C ₂ C ₁ H	121.2 116.9 109.0	129.2 112.5 114.3	123.8 114.7 109.0
C ₅ -C ₃ =C ₁	C ₁ -C ₂ C ₂ =C ₃ C ₃ -C ₄ C ₁ -H C ₂ -H C ₄ -H	1.513 1.330 1.511 1.100 1.080 1.100				C ₁ C ₂ C ₃ C ₃ C ₂ H C ₂ C ₁ H C ₂ C ₃ C ₄	121.1 122.0 109.1 121.7		
C ₄ -C ₃ =C ₂	C ₁ -C ₂ C ₂ =C ₃ C-H	1.512 1.330 1.100		1.511 ^g 1.351 1.111		C ₁ C ₂ C ₃ C ₂ C ₁ H	121.7 109.1		
C ₅ -C ₄ -C ₃ =C ₁	C ₁ -C ₂ C ₂ =C ₃ C ₃ -C ₄ C ₄ -C ₅ C ₃ -C ₆ C ₁ -H C ₂ -H C ₄ -H C ₅ -H C ₆ -H	1.512 1.330 1.507 1.546 1.511 1.100 1.080 1.098 1.100 1.100		1.511 ^h 1.349 ± 0.004 1.511 ± 0.007 1.551 1.511 1.116		C ₁ C ₂ C ₃ C ₂ C ₃ C ₄ C ₂ C ₃ C ₆ C ₃ C ₄ C ₅ C ₃ C ₂ H C ₂ C ₁ H HC ₄ H C ₄ C ₂ H C ₅ C ₄ H	121.1 121.7 121.6 108.6 122 109.1 110.4 108.9 109.2		127.2 121.8 ± 2 121.8 ± 2 111.8 ± 1.4
C ₄ =C ₁ -C ₂ =C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₁ -H C ₂ -H	1.340 1.470 1.081 1.081	1.330 1.464 1.099 1.099	1.341 ⁱ ± 0.002 1.463 ± 0.003 1.090 ± 0.004 1.090 ± 0.004		C ₂ C ₁ H HC ₁ H C ₁ C ₂ C ₃ C ₁ C ₂ H	121.4 117.2 121.3 121.6	131.0	120.9 118.2 123.6 120.9
C ₄ =C ₃ -C ₂ =C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₂ -C ₅ C ₃ =C ₄ C ₁ -H C ₃ -H C ₄ -H C ₅ -H	1.339 1.467 1.512 1.340 1.081 1.081 1.081 1.100		1.338 ^j ± 0.005 1.470 ± 0.005 1.510 ± 0.005 1.338 ± 0.005 1.068 ± 0.01 1.068 ± 0.01 1.068 ± 0.01 1.122 ± 0.01		HC ₁ H C ₁ C ₂ C ₃ C ₂ C ₁ C ₅ C ₂ C ₃ H C ₄ C ₃ H C ₄ C ₃ C ₂ HC ₄ H	117.2 121.9 116.9 109.1 118.3 121.4 117.2		115.5 120 ± 1 120 ± 2 110.5 122.4 ± 2
C ₅ -C ₃ =C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₂ -C ₅ C ₁ -H C ₅ -H	1.339 1.466 1.512 1.081 1.100	1.350 1.515 1.500	1.349 ^k 1.491 1.511 1.093 1.123		C ₁ C ₂ C ₃ C ₂ C ₃ C ₆ C ₂ C ₁ H C ₂ C ₅ H	121.9 116.9 121.4 109.1	119.6	122 117.9 120.4 110.4
C ₅ -C ₄ =C ₃ -C ₂ =C ₁	C ₁ =C ₂ C ₂ -C ₃ C ₃ =C ₄ C ₄ -C ₅ C(sp ²)-H C(sp ³)-H	1.340 1.468 1.339 1.512 1.081 1.100		1.337 ^l 1.476 1.337 1.501 1.09 (ass) 1.09 (ass)		C ₁ C ₂ C ₃ HC ₁ H C ₁ C ₂ H C ₂ C ₃ C ₄ C ₄ C ₃ H C ₄ C ₃ H	121.4 117.2 121.5 121.3 117.2 109.1		122.9 118 119 122.9 119 111
C ₆ -C ₅ =C ₄ -C ₃ =C ₂ -C ₁	C ₁ -C ₂ C ₂ =C ₃ C ₃ -C ₄ C ₄ -C ₅ C ₅ -C ₆ C ₄ -C ₇ C(sp ²)-H C(sp ³)-H	1.512 1.340 1.466 1.332 1.512 1.513 1.082 1.100		1.521 ^m 1.350 1.473 1.521 1.087 1.117		C ₁ C ₂ C ₃ C ₂ C ₃ C ₄ C ₃ C ₄ C ₇ C ₂ C ₁ H C ₃ C ₂ H	121.9 121.5 121.6 109.1 121.2		126.6 122.6 122.3 109.6 119.1

Table II (Continued)

Molecule ^z	Bond lengths, Å				Bond angles, deg			
	Bond	IMO	MINDO/3 ^a	Exptl	Angle	IMO	MINDO/3	Exptl
	C ₁ =C ₂	1.339	1.330	1.347 ⁿ	C ₁ C ₂ C ₃	121.4	130.9	121.7
	C ₂ -C ₃	1.456	1.462	1.458	C ₂ C ₃ C ₄	121.4	130.8	124.4
	C ₃ =C ₄	1.345	1.346	1.347	C ₂ C ₁ H	121.3		120.5
	C ₁ -H	1.081	1.100	1.104	C ₃ C ₄ H	121.3		115
	C ₂ -H	1.081	1.100	1.104				
	C ₃ -H	1.081	1.100	1.104				
	C ₁ =C ₂	1.339		1.348 ^o	C ₁ C ₂ C ₃	121.4		124.5
	C ₂ -C ₃	1.456		1.456	C ₂ C ₃ C ₄	121.4		124.5
	C ₃ -C ₄	1.349		1.348	C ₂ C ₁ H	121.3		122
	C ₅ -C ₇	1.512		1.510	C ₅ C ₇ H	109.1		110.5
	C(sp ²)-H	1.080		1.094				
	C(sp ³)-H	1.100		1.104				
C=C=C	C=C	1.306	1.311	1.308 ^p	CCH	121.5	118.4	118.2
	C-H	1.083	1.099	1.087				
C ₄ =C ₃ =C ₂ =C ₁	C ₁ =C ₂	1.307	1.312	1.318 ^q	CCH	121.5	124.7	
	C ₂ =C ₃	1.279	1.295	1.283				
	C-H	1.083	1.100					
	C ₁ =C ₂	1.305		1.312 ^r	C ₂ C ₃ C ₄	121.5		124
	C ₂ =C ₃	1.312		1.312	C ₂ C ₁ H	121.4		120
	C ₃ -C ₄	1.466		1.466	C ₂ C ₃ H	121.3		118
	C ₁ -H	1.082		1.104				
	C ₃ -H	1.082		1.104				
	C=C	1.336	1.344	1.344 ^s	C=C-C	121.4		126.4
	C-C	1.464	1.466	1.462	C=C-H	121.4		118.3 ± 6
	C-H	1.087	1.109	1.090	C-C-H	117.2		
					C=C-C=C	68.1		
	C=C	1.334		1.326 ^t	C=C-C ring	121.9		122.2
	C-C ring	1.470		1.483	C-C-C	116.9		
	C-C exo	1.513		1.513	C=C-C exo	121		123
	C-H	1.100			C-C-H	109.1		
					C=C-C=C	67.2		66.6
	C=C	1.336		1.330 ^u	C=C-C ring	121.4		124.7
	C-C ring	1.472		1.481	C-C-C	117		113.6
	C-C exo	1.512		1.516	C=C-C exo	121.1		121.6
	C(sp ²)-H	1.082			C=C-H	121.4		
	C(sp ³)-H	1.100			C-C-H methyl	109.1		
	C ₁ -C ₂	1.508	1.515 ^v	1.506 ^w	HC ₁ H	110.3		106.3 ^w
	C ₂ =C ₃	1.341	1.352	1.345	HC ₂ C ₁	122.3		123.6
	C ₃ -C ₄	1.466	1.492	1.468	HC ₃ C ₂	127.5		126.0
	C ₁ -H	1.100	1.116	1.099	C ₂ C ₁ C ₅	102.8	103.6	102.9
	C ₂ -H	1.081	1.103	1.078	C ₁ C ₂ C ₃	109.2		109.2
	C ₃ -H	1.081	1.102	1.080	C ₂ C ₃ C ₄	109.4	109.2	109.3
	C ₁ -C ₂	1.472	1.509 ^v	1.470 ^x	HC ₆ H	117.3	114.9	117 ^x
	C ₂ =C ₃	1.354	1.353	1.355	HC ₂ C ₁	123.3		124.7
	C ₃ -C ₄	1.468		1.476	HC ₃ C ₂	128.0	127.6	126.4
	C ₁ =C ₆	1.342	1.339	1.349	C ₂ C ₁ C ₅	105.7	104.5	106.6
	C ₂ -H	1.075	1.103	1.078	C ₁ C ₂ C ₃	107.7	107.9	107.7
	C ₃ -H	1.076	1.092	1.080	C ₂ C ₃ C ₄	108.9		109.9
	C ₆ -H	1.081	1.107	1.083				
	C ₁ -C ₂	1.472	1.510 ^v	1.476 ^y	HC ₇ C ₆	109.2		108.0 ^y
	C ₂ =C ₃	1.354	1.359	1.340	C ₇ C ₆ C ₈	117.0		116.0
	C ₃ -C ₄	1.468	1.477	1.462	C ₂ C ₁ C ₅	105.9	101.8	106.0
	C ₁ =C ₆	1.339	1.374	1.347	C ₃ C ₂ C ₁	107.6		108.0
	C ₆ -C ₇	1.509	1.499	1.510	C ₂ C ₃ C ₄	109.3	108.6	109.0
	C ₇ -H	1.100	(1.100) _{av}		HC ₃ C ₄	123		131.0
	C ₂ -H	1.075						
	C ₃ -H	1.075						

^a Reference 34. ^b L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965); K. Kuchitsu, *ibid.*, **44**, 906 (1966). ^c Reference 33. ^d S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968). ^e L. H. Sharpin and V. W. Laurie, *J. Chem. Phys.*, **39**, 1732 (1963). ^f A. Almeningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970). ^g J. L. Carlos, Jr., and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2*, **70**, 171 (1974). ^h F. J. Geise, F. C. Mijehoff, G. Renes, and F. M. A. Rumens, *J. Mol. Struct.*, **17**, 37 (1973). ⁱ K. Kuchitsu, T. Fukuyama, and Y. Morino, *ibid.*, **1**, 463 (1967-8). ^j L. V. Vilkov and N. I. Sadova, *Zh. Strukt. Khim.*, **8**, 398 (1967). ^k C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968). ^l S. L. Hsu and W. H. Flygare, *J. Chem. Phys.*, **52**, 1053 (1970). ^m M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970). ⁿ M. Traetteberg, *ibid.*, **22**, 628 (1968). ^o M. Traetteberg and G. Paulen, *Acta Chem. Scand., Ser. A*, **28**, 1150 (1974). ^p A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965). ^q B. P. Stoicheff, *Can. J. Phys.*, **35**, 837 (1957). ^r M. Traetteberg, G. Paulen, and H. Hopf, *Acta Chem. Scand.*, **27**, 2227 (1973). ^s O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957). ^t J. Bordner, R. G. Parker, and R. H. Standord, Jr., *Acta Crystallogr., Sect. B*, **28**, 1069 (1972). ^u G. Avitabile, P. Ganis, and V. Petraccone, *J. Phys. Chem.*, **73**, 2378 (1969). ^v R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975). ^w D. Damiani, L. Ferretti, and E. Gallinella, *Chem. Phys. Lett.*, **37**, 265 (1976). ^x R. D. Suernam and M. D. Harmony, *J. Chem. Phys.*, **58**, 5842 (1973). ^y J. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 26 (1970). ^z The molecules denoted by the asterisks were used for parametrization of eq 6, see ref 8.

crepancy was found in 3-methyl-2-pentene where the $C_1C_2C_3$ angle is off by 6° .

The problem of bond distances in hydrocarbons has been a subject for a longstanding controversy.⁴¹⁻⁴⁶ The experimentally well established environmental dependence of CC bond distances^{47,48} was rationalized by several simple models of covalent bonding. Among them the hybridization of atomic orbitals was one of the most important concepts. It was put forward by Walsh as early as 1947 and elaborated later by many others.⁴²⁻⁴⁴

Dewar and Schmeising gave in their classical papers¹⁹ impressive evidence that not only the bond lengths but also the bond energies are almost completely determined by the changes in hybridization of the participating atoms. This point of view was questioned recently by Miyazaki et al.⁴⁹ It was concluded on the basis of the CNDO/2 and INDO model calculations performed on ethane, ethylene, and acetylene that the C-C bond lengths are very little affected by the hybridization states of the carbon atoms in question. This conclusion is vitiated by the fact that the total electronic energy in the CNDO/2 and INDO methods is invariant to hybridization and so is its derivative against the internuclear distance. In addition it is well known that directional properties of covalent bonds are not adequately described by these methods. The rotational and hybridization invariance is achieved at the expense of accuracy. For example, the electronic Coulomb interaction integrals are calculated by the spherical averaging of the atomic charge distributions⁵⁰ which is a rough approximation. It should be mentioned that the hybridization invariance in the CNDO/2 and INDO methods is an artificial requirement which is not dictated by the physical nature of the problem. In fact, the widely accepted zero-differential overlap approximation is justified in all valence electron methods only if the symmetrically orthogonalized hybrid orbital basis sets are employed.⁵¹

Our variable hybridization model coupled with the empirical bond length-bond overlap correlations satisfactorily accounts for the main features of molecular geometries in hydrocarbons. The present results indicate that the hybridization is the driving force determining C-C, C=C, and C-H bond distances and angles. An additional check of the reliability of the IMOA method was provided by 4-31G ab initio calculations performed by Schulman and Venanzi⁵² which confirmed the geometry of tetrahedrane predicted earlier by the IMOA method.⁷ The IMOA values for CC and CH bond lengths 1.491 (1.482 Å) and 1.065 Å (1.054 Å) are in good agreement with ab initio ones given in parentheses. The recent STO-3G ab initio results of Hehre and Pople,⁵³ 1.473 and 1.069 Å for CC and CH bond distances, respectively, are in fair agreement with precedent calculations. It seems paradoxical that the hybridization model works so well even in conjugated polyenes if it is known that π -bond orders successfully predict the CC bond distances in aromatic and benzenoid hydrocarbons.²⁴ A careful examination of the bond order-bond length correlation made by Popov and Kogan⁵⁴ is very illuminating in this respect. By using the relation between C-C bond distances and the corresponding force constants, Popov and Kogan have shown that bond orders within the interval 0.4-0.9 strongly affect C-C bond shortening. The bond orders in benzenoid hydrocarbons fall in this range. Since the carbon atoms in these molecules are roughly characterized by hybridization which deviates very little from the sp^2 state, the changes in bond distances are entirely determined by the magnitude of bond orders. On the contrary, the bond orders in the intervals 0-0.4 and 0.9-2.0 have no influence on the bond lengths. In this class of molecules the changes in hybridization become decisive. The results of this analysis are in full accordance with our modified IMOA calculations.

(3) **Heats of Formation.** The heats of formation provide

Table III. Comparison between the Calculated Heats of Formation by IMOA and MINDO/3 Methods for Some Olefins and the Available Experimental Data

Molecule	IMOA	MINDO/3	Obsd
$C=C$	13.2	19.2	12.4
$C=C$	5.8	6.5	4.9
$C=C$	-2.0	-6.3	-3.0
$C=C$	-2.0	-5.7	-1.9
$C=C$	-1.9	2.5	-4.3
$C=C$	-9.6		-10.2
$C=C$	-15.7		-16.7
$C=C$	30.8	31.9	26.1
$C=C$	23.2	19.2	18.1
$C=C$	23.0		18.1
$C=C$	15.5	30.6	10.8
$C-C$	0.5	1.0	-0.03
$C-C$	-6.8		-7.6
$C-C$	-14.6		-15.1
$C=C=C$	39.2	42.0	45.9
$C=C=C=C$	66.1	64.3	
Cyclopentadiene	36.2	41.7	32.2

another piece of information about the electronic structure of the studied molecules. The IMOA values were obtained by using bond energy-local hybrids' overlap empirical relations.²⁸ They are summarized in Table III and compared with MINDO/3 values and available experimental data. Our method gives a slightly better agreement with experiment. A very interesting discrepancy was found in 1,3-butadiene where the observed heat of formation is lower by ~ 5 kcal/mol than the IMOA value. The additional stability of 1,3-butadiene could be ascribed to π -electron delocalization energy. It is in excellent agreement with the experimental rotational barrier around the central CC bond (5 kcal/mol) and the ab initio result of Boggs et al.³⁵ (5.68 kcal/mol). The same amount of increased stabilization was found in all molecules possessing the butadiene structural unit, i.e., two conjugated double bonds. If this resonance energy is taken into account, the agreement between the IMOA heats of formation and the observed values becomes remarkable indeed. Our results support the conclusion of Dewar and Gleicher⁵⁵ that linear polyenes are satisfactorily described by classical valence bond structures and that their heats of formation are additive.

(IV) Conclusion

The interatomic distances and bond angles calculated by the modified IMO method for a large number of conjugated polyenes, cycloalkenes, and their methylated derivatives are in good agreement with experimental data and the available MINDO/3 or ab initio results. It is found that the shortening of the central C-C bond in 1,3-butadiene and related molecules is roughly 0.01 Å due to π -electron delocalization. The estimated π -electron resonance energy in this molecule is ~ 5 kcal/mol in good agreement with the experimental barrier of rotation around the central bond. The additivity of the heats of formation in polyenes was rationalized by the transferability of local hybrid orbitals. The present results indicate that the variable hybridization model reflects faithfully the gross effects which determine interatomic distances and bond angles in hydrocarbons. The π -electron delocalization effect and steric interactions are to be regarded as perturbations imposed on the σ skeleton. They are responsible only for finer details of the molecular structures. The hybrid orbitals can serve as convenient starting wave functions for various simulated ab initio techniques due to a high degree of their transferability between the similar structural units. They provide also a useful tool for tackling the convergence problems of the iterative SCF procedures.⁵⁶ Summarizing our earlier work and present results we can say that the variable hybridization model offers a fair description of covalent bonding. It is simple, pictorial, and intuitively appealing because it corresponds to the idea of the chemical bond formed by a pair of electrons. The hybrid orbitals possess the desired directional properties and reflect one of the most important features of chemical bonding: migration of the electron density in the region between nuclei. In addition, the variable hybridization enables semiquantitative prediction of a large number of local physical and chemical properties via the empirically established correlations.

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