lithium aluminum deuteride was used and this converted 2.2 mol of cyclohexene oxide, whereas in a previous experiment lithium aluminum hydride converted 2.6 mol of cyclohexene oxide. The product, obtained in 90% yield based on converted cyclohexene oxide, and with only 1.2% dideuteration, had mass spectrum (12 eV) *m/e* (rel intensity) 101 (10), 84 (7.9), 83 (100), and 82 (4.9).

cis-1,2-Dibromocyclohexane, mp 10-10.5° (lit.[25] mp 9.7-10.5°), prepared as previously described,[1] had mass spectrum in the M^+ region (12 eV) *m/e* (rel abundance) 245 (5), 244 (52.5), 243 (10), 242 (100), 241 (5), 240 (55); normal mass spectrum (12 eV) *m/e* (rel intensity) 244 (8), 242 (15), 240 (8), 163 (25), 161 (24), 82 (15), and 81 (100).

cis-1,2-Dibromocyclohexane-*1-d* (2.3% d_2, 84.0% d_1, 13.7% d_0) was prepared from 1-bromocyclohexene-*2-d*, which could not be prepared straightforwardly from a 1-metallo-2-bromocyclohexene because of the instability of this type of intermediate; *e.g.*, 1-lithio-2-bromocyclohexene loses lithium bromide so rapidly that it cannot be carboxylated with CO_2 even at −120°.[26] Alternatively, 1,2-dibromocyclohexene (24 g, 0.1 mol) was treated with zinc (20 g, 0.3 mol, twice preequilibrated with D_2O) in a refluxing solution of D_2O (30 g, 1.5 mol) and acetic acid-d_1 sufficient to dissolve the 1,2-dibromocyclohexene (*ca.* 70 ml) for 24 hr to yield 1-bromocyclohexene-*2-d* (2.5% d_2, 83.8% d_1, 13.7% d_0), 8 g (50%). The purification was simplified by freezing out the relatively high-melting starting material. Identical results (including label) were obtained in the absence of D_2O, though the reaction may have been slower. The product had the following nmr spectrum (CCl_4), δ 1.5-2.5 (m, 8 H), 5.8 m, 0.12 H), consistent with the mass spectrum (12 eV) *m/e* (rel intensity) 164 (9.2), 163 (98.2), 162 (23.8), 161 (100), 160 (16), 83 (8), 82 (69), and 81 (13). The 1-bromocyclohexene-*2-d* was converted to *cis*-1,2-dibromocyclohexane-*1-d*, mp 10-10.5°, by photolytic addition of hydrogen bromide as for the undeuterated compound. The product had nmr spectrum (CCl_4) δ 1.2-2.4 (m, 8 H) and 4.28 (m, 1 H); detailed mass spectrum of the M^+ region (12 eV) *m/e* (rel intensity) 246 (6.5), 245 (49), 244 (16.5), 243 (100), 242 (20), 241 (51.8), 240 (7.5); normal mass spectrum (12 eV) *m/e* (rel intensity) 245 (15), 244 (5), 243 (31), 242 (7), 241 (15), 164 (42), 163 (16), 162 (43), 161 (14), 83 (29), 82 (100), and 81 (31).

cis-2-Bromocyclohexyl cyanide-*1-d* (0.5% d_2, 93.0% d_1, 6.5% d_0) was prepared from cyclohexenyl cyanide by addition of DBr, but differing from the method for cyclohexyl-*trans-2-d* bromide in that inhibitor concentrations were doubled, a time period of 2.5 hr was used, and the deuterium bromide was led directly from the generator through a cold trap (−40°) to the reaction vessel under a Dry Ice condenser. The acetyl bromide used to generate deuterium bromide was twice distilled from dimethylaniline. The product, obtained in 30% yield, had mp 26-27°; nmr spectrum (CCl_4) δ 1.73 (m, 5 H), 2.1 (m, 3 H) and 4.2 (5, 1.0 H, $J = 8$ Hz), and no peak at δ 3.18; detailed mass spectrum of the M^+ region (14 eV) *m/e* (rel intensity) 191 (8.8), 190 (97.9), 189 (15.2), 188 (100.0), 187 (7.2); normal mass spectrum (14 eV) *m/e* (rel intensity) 190 (8), 188 (7), 110 (7), 109 (100), and 108 (11).

cis-2-Bromocyclohexyl cyanide similarly prepared had mp 26-26.5°; nmr spectrum (CCl_4) δ 1.73 (m, 5 H), 2.1 (m, 3 H), 3.18 (q, 1.0 H), and 4.2 (m, 1.0 H) (*Anal.* Calcd for $C_7H_{10}BrN$: C, 44.70; H, 5.36; N, 7.45. Found: C, 44.49; H, 5.45; N, 7.56); detailed mass spectrum of the M^+ region (14 eV) *m/e* (rel abundance) 190 (8.5), 189 (95.5), 188 (8), 187 (100); normal mass spectrum (14 eV) *m/e* (rel intensity) 189 (8), 187 (8), 109 (8), 108 (100), and 107 (13).

It is interesting that the small, strongly electron-withdrawing cyano group does not strongly retard the rate of addition of HBr. This is consistent with a synchronous hydrogen bromide addition reaction mechanism, rather than a two-step protonation mechanism.

Registry No. IV, 1085-94-5; V, 49676-86-0; VI, 49676-87-1; XI, 49676-88-2; XII, 49676-89-3; $C_6H_{11}OTs$, 953-91-3; $C_6H_{11}Br$, 108-85-0; cyclohexanol-*trans-2-d*, 49676-90-6; *cis*-1,2-dibromocyclohexane, 19246-38-9; 1-bromocyclohexene-*2-d*, 49676-91-7; 1,2-dibromocyclohexene, 49676-92-8.

References and Notes

(1) Part V: P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2240 (1972).

(2) G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **94**, 2234 (1072).

(3) D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, **34**, 1985 (1969).

(4) D. N. Kevill, G. H. Coppens, and N. H. Cromwell, *J. Amer. Chem. Soc.*, **86**, 1553 (1964).

(5) W. H. Saunders, Jr., *Surv. Progr. Chem.*, **3**, 109 (1966).

(6) A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972).

(7) W. H. Saunders, Jr., in "Investigation of Rates and Mechanisms of Reactions," Vol. 8, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 389.

(8) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962).

(9) D. Muir and A. J. Parker, unpublished work.

(10) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(11) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 4735 (1971); D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5029 (1970).

(12) R. A. More O'Ferrall, *J. Chem. Soc. B*, 274, 785 (1970).

(13) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(14) A. F. Cockerill, *J. Chem. Soc. B*, 964 (1967); A. F. Cockerill and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **89**, 4985 (1967).

(15) K. T. Finley and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **89**, 898 (1967).

(16) D. Cook, M. R. J. Dack, R. E. J. Hutchinson, and A. J. Parker, unpublished work.

(17) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

(18) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966); R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970).

(19) We have pK_a values for the bases HB in dimethylformamide, but not in acetone. We have noted, however, that pK_a values are linearly related in a variety of dipolar aprotic solvents and therefore assume $\Delta pK_a\ (HB - HBr)_{DMF} = \Delta pK_a\ (HB - HBr)_{acetone}$: B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966); A. J. Parker, unpublished work.

(20) A. J. Parker and D. J. Lloyd, *Tetrahedron Lett.*, 5183 (1968).

(21) D. Cook, A. J. Parker, and M. Ruane, *Tetrahedron Lett.*, 5715 (1968).

(22) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2228 (1972).

(23) G. S. Hammond and J. Warkentin, *J. Amer. Chem. Soc.*, **83**, 2554 (1961).

(24) R. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).

(25) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Amer. Chem. Soc.*, **74**, 3588 (1952).

(26) G. Wittig and W. Mayer, *Ber.*, **96**, 329 (1963).

Calculation of Bond Lengths and Angles of Hydrocarbons by the Iterative MOA Method

K. Kovačević and Z. B. Maksić*

Institute "Ruder Bošković," 41001 Zagreb, Croatia, Yugoslavia

Received July 26, 1973

The bond lengths and angles of some characteristic strained cyclic and polycyclic alkanes and alkenes were calculated by the iterative maximum overlap approximation (IMOA) procedure. The agreement with experimental bond lengths and angles is satisfactory indicating that IMOA method might be useful for a semiquantitative prediction of the geometry of hydrocarbons.

The experimental bond lengths and angles give some insight into the nature of chemical bonding in molecules. Unfortunately, there are available only a very few *ab initio* studies since the geometry variation is very time consuming and hence it is too expensive. The available *ab initio* calculations were usually confined either to the small triatomic molecules in connection with discussion of Walsh empirical diagrams[1] or to the medium size molecules like, for instance, ammonia borane.[2] The semiempirical methods based on the CNDO (complete neglect of the differential overlap) approximation are capable to predict molecular geometry. However, the results are not quite satisfactory presumably due to the spherically averaged treatment of the two-center electron repulsion integrals, and consequently the directional properties of the covalent bonds are not adequately described.[3] Much more successful in this respect is Dewar's MINDO/2 method where the bond lengths are included into the parametrization scheme.[4] However, the C–H bond lengths are found to be systematically too long by 0.1 Å. Although this is not a serious flaw from the chemical point of view, since the C–H bonds do not affect the overall geometry, it precludes the potential use of the method in assigning the experimental C–H bond lengths, which is particularly troublesome for the electron diffraction technique. On the other hand, it would be interesting to know what is the driving force in determining the molecular geometry. For this purpose chemistry has developed several heuristic but more or less purely empirical pictorial models, the most important being hybridization, nonbonded repulsions, conjugation, and hyperconjugation. In spite of the fact that these concepts are not, strictly speaking, observable, they proved useful in discussing the properties of the chemical bond. The most extensive experimental studies were so far performed on C–C bond lengths. It was observed that C–C bond length for a given bond environment is remarkably constant in different molecules. On the other hand, the bond lengths increase linearly with an increase in the number of adjacent bonds or adjacent atoms.[5] This experimental fact was explained by the changes in hybridization and its influence on the covalent radius of the carbon atom.[6,7] However, Bartell pointed out that nonbonded interactions might well be the dominant factor in governing the changes in bond lengths accompanying changes in environment. For example, the observed shortening of a single C–C bond when it is adjacent to double bond(s) could be a consequence of a decrease of the nonbonded interference across the central bond since there are a fewer number of atoms attached to carbon nuclei in question.[8] Alternative interpretation of the same experimental finding was given by Mulliken, *et al.*,[9] in terms of conjugation and hyperconjugation. Since all these concepts are empirical in nature, neither of these approaches can claim that it is more reliable than the others. Furthermore, it is very likely that all effects are present at the same time. Keeping in mind that hybridization, nonbonded repulsions, conjugation, and hyperconjugation effects might be interlocked, we shall use the maximum overlap approximation approach[10] in an iterative fashion (*vide infra*) for the calculation of bond lengths in some cyclic and polycyclic hydrocarbons. The bond lengths in this approach are determined by the magnitude of the corresponding overlap integrals, and thus they indirectly depend on the hybridization.

Outline of the IMOA Method. We give here a brief statement on the MOA (maximum overlap approximation) method and discuss in some detail its iterative (IMOA) version. It is well known that the bond energy is only a small fraction of the total energy of a molecule. Furthermore, electron density maps obtained by the rigorous *ab initio* calculations show that the electron distribution is only slightly changed by the formation of molecules.[11] It is therefore plausible to assume that atoms retain their identity in a molecule and that the atomic functions are only perturbed by the influence of the neighbors. This idea is also supported by the additivity of many physical and chemical properties like bond energy,[6] dipole and quadrupole moments,[12] diamagnetic susceptibility,[12,13] etc. The perturbed atomic wave functions must satisfy the symmetry of the local perturbation that can be obtained by mixing of s and p orbitals. The general form of the local hybrid oribital is

$$\psi_{Ai} = a_{Ai}(2s) + (1 - a_{Ai}^2)^{1/2}(2p)_{Ai} \qquad (1)$$

where A denotes the nucleus A and i refers to the direction in space of the $(2p)_{Ai}$ orbital. The hybrids placed on the same atom are constrained to be orthogonal. This is a very natural assumption since the nonorthogonality of the hybrid wave functions would cause the deviation from the colinearity of their spins. As pointed out by Van Vleck[14] the easiest way of seeing it is to pass to the limiting case in which the nonorthogonal spatial wave functions are identical. In that case the spins would be antiparallel and their valencies would be internally saturated. The orthogonality conditions provide a set of relationships of the form

$$a_{Ai}a_{Aj} + (1 - a_{Ai}^2)^{1/2}(1 - a_{Aj}^2)^{1/2} \cos \theta_{ij} = 0 \qquad (2)$$

where θ_{ij} represents the angle between the axes of the hybrids ψ_{Ai} and ψ_{Aj}. The hybridization parameters a_{Ai} are determined by the maximum overlap criterion. The sum of all bond overlap integrals is maximized by the variation of a_{Ai}'s

$$E_b = k_{CC}\sum_{C-C} S_{CC} + k_{CH}\sum_{C-H} S_{CH} \qquad (3)$$

where $S_{AB} = \int \psi_A \psi_B dv$ is the overlap integral and k_{CC} and k_{CH} are the proportionality constants between the bond energy and bond overlaps. It is worth mentioning that k_{CC} and k_{CH} constants are the same for all kinds of C–C and C–H bonds, respectively. In fact we maximize the sum of all bond energies in a molecule. We employ Clementi "double ζ" atomic wave functions[15] and the bond energy weighting factors k_{CC} = 121.2 and k_{CH} = 135.9 kcal/mol.[10] During the calculations, the bond angles were allowed to follow the directions of hybrids freely except in cyclic systems where necessarily bend bonds appear. Namely, it is easily seen from the relation 2 that two real and equivalent hybrids make an angle greater than 90°. In order to circumvent the bending of the ψ hybrids in cyclopropane, Mårtensson and Öhrn[16] introduced the complex hybridization. However, it was subsequently shown that the complex hybrids have poor overlap and that the principle of maximum overlapping leads straightforwardly to the bent bonds.[17] The latter are experimentally confirmed by the X-ray measurements on cyclopropyl ring.[18] We admit that the assumption of the perfect ψ_{CH} hybrids' following the C–H internuclear lines is open to criticism. Namely, the small displacement of hydrogen atoms off the hybrids' symmetry axes will decrease the bond overlaps almost negligibly. Therefore, the bent bonds might appear even in C–H bonds. However, our assumption that C–H bonds are the straight ones is justified by the *a posteriori* good agreement with HCH experimental angles. We found that there is a very good linear relationship between the S_{CC} and S_{CH} bond overlaps and the corresponding C–C and C–H bond lengths.[19] The linear least-squares fit method gave the following correlations

$$d(\text{C–C}) = -1.166 S_{CC} + 2.298 \text{ Å} \qquad (4)$$

$$d(\text{C–H}) = -0.869 S_{CH} + 1.726 \text{ Å} \qquad (5)$$

The greater overlap gives the smaller bond length, reproducing the well-known fact that the stronger bond has the shorter bond distance. The established relations 4 and 5

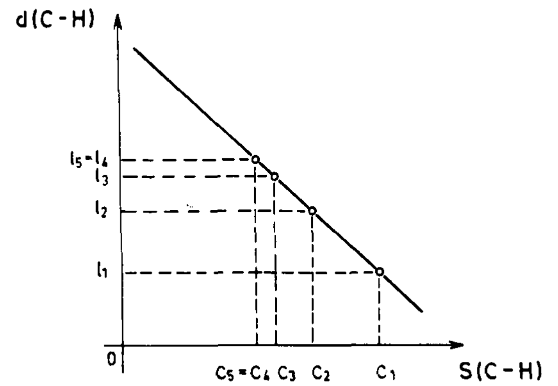


Figure 1. Schematic illustration of the iterative procedure used for the calculation of the bond lengths. The C-H bond is chosen as an example. One starts the calculation with the assumed bond lengths l_1 and optimizes the hybridization parameters accordingly. Generally, a new S(C-H) overlap integral is obtained (denoted here by C_2) and the subsequent bond length l_2 is read from the linear relationship providing the necessary information for the second cycle C_2, etc.

enable the prediction of bond lengths in an iterative fashion providing a basis for the IMOA (iterative maximum overlap approximation) method. One starts the calculation assuming certain C-C and C-H bond lengths and performs the maximum overlap approximation procedure. The resulting S_{CC} and S_{CH} overlap integrals are substituted into eq 4 and 5 and the new bond lengths are deduced. The whole cycle is repeated and continued until the self-consistency between the input and output bond lengths is achieved. The calculation of the C-H bond lengths is schematically shown in Figure 1 where consistency is obtained after five cycles. The similar pattern holds for C-C bonds and usually the four or five iterations will suffice to obtain consistency. In order to illustrate this procedure we applied IMOA method to dimethylacetylene, a molecule which is not used for the derivation of the relations 4 and 5. The C≡C triple bond is practically independent of the environment so that we can accept the experimental value of 1.214 Å. The IMOA method gave after four cycles the following bond lengths: d(C-C) = 1.460 Å, d(C-H) = 1.106 Å. These results can be favorably compared with the experimental results of 1.468 Å and 1.116 Å for the C-C and C-H bond, respectively.[20] The calculated HCC bond angle of 109.6° is also in good agreement with experimental value of 110.7°. It was also found that for the C=C double bond there is the following linear relation[21]

$$d(\mathrm{C{=}C}) = -0.677(S_{CC}^{\sigma} + S_{CC}^{\pi}) + 2.087\ \text{Å} \qquad (6)$$

It should be stressed that the eq 4-6 work only for bonds where the hybrid bending is absent. For small ring compounds eq 4 and 6 should be generalized to allow for a difference between σ and π interactions. This will be discussed in the next section.

Correlated and experimental carbon-carbon bond lengths are represented graphically in Figure 2.

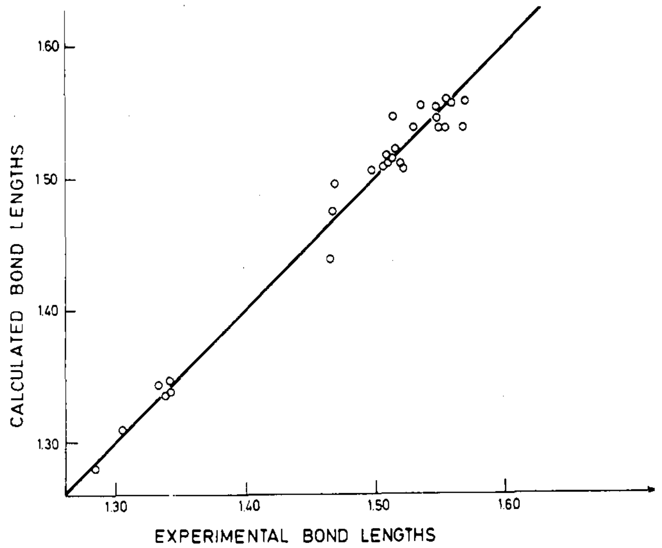


Figure 2. Graphical representation of the correlated and experimental carbon-carbon bond lengths. The straight line bisecting the coordinate axes denotes a full agreement between the experiment and the theory. The discrepancies at 1.47 Å are due to the central bond in spiropentane (upper dot) and exo bond in cyclopropylacetylene (lower dot).

Results and Discussion

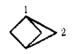
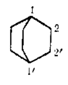
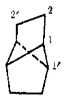
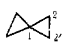
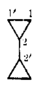
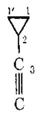
There is an intrinsic difficulty in defining the bond lengths in a strained molecule. Is the bond length the shortest path between the two neighboring nuclei or perhaps a line passing through the points of the maximum electronic density?[22-24] Since the former is much more easily experimentally measured, we shall keep it as a definition of the bond length. If this definition is adopted, then there is a puzzling feature in changing of C-C bond lengths along the series cyclopropane, cyclobutane, and cyclopentane. The C-C bond in cyclobutane is longer than the corresponding bond in ethane as expected since the hybrids are bent in the former molecule and consequently have smaller overlap than the same hybrids without bending. However, the C-C bond distance in cyclopropane is unusually short, 1.510 Å, although, by applying the aforementioned simple argument, it should be very long due to a considerable δ_{CC} bending of 22°. It seems that the bond lengths of the rings in polycyclic hydrocarbons are the result of the competition of the two opposite interactions: the repulsive forces of the carbon cores and attractive overlap energy. In highly strained rings the C-C overlap is very poor, and it is increased by shortening of the C-C bond distances even at the expense of the increased C-C nonbonded repulsion. In order to take into account these empirical facts we have to extend our correlations 4 and 6, to include the special features of the strained rings. We observe that there are two distinct types of interaction in strained rings, namely the σ and π interaction, and the corresponding overlap integrals should enter into the correlations separately.[25] We performed the IMOA calculations for some 15 characteristic strained cyclic and polycyclic hydrocarbons. The least-squares fit method gave the following resulting correlations between the CC single and double bonds and overlap integrals

$$d(\mathrm{C{-}C}) = -1.166S_{CC}^{\sigma}(b) - k_{CC}^{\pi}S_{CC}^{\pi}(b) + 2.298\ \text{Å} \qquad (7)$$

$$d(\mathrm{C{=}C}) = -0.677(S_{CC}^{\sigma}(b) + S_{CC}^{\pi}) - 1.00S_{CC}^{\pi}(b) + 2.087\ \text{Å} \qquad (8)$$

where (b) refers to the bent bond and k_{CC} is 3.30 for cyclopropyl rings and k_{CC} = 2.278 for all other strained bonds. It should be mentioned that formulas 7 and 8 are reduced to eq 4 and 6 if $S_{CC\pi}$ (b) vanishes. The resulting geometries are summarized and compared with experimental ones in Tables I and II. The obtained linear correlations between the bond lengths and bond overlap integrals are very good indeed, the standard deviations being 0.009, 0.013, and 0.006 for C-H, C-C, and C=C bonds, respectively. The only serious discrepancy is found for tricyclooctane. The bond lengths in cyclopropylacetylene deserve some more comments. Boggs, *et al.*,[26] determined the structure of this molecule by microwave measurements. They argue that the C-C bond length between the cyclopropyl ring and acetylene group is unusually long, 1.466 ± 0.018 Å, being essentially equal to that one in

Table I
Comparison between the Calculated Bond Lengths and Angles and the Corresponding Experimental Data for Some Cyclic and Polycyclic Alkanes

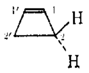
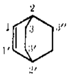
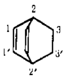
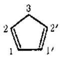
Molecule	Bond	Bond lengths, Å		Angle	Bond angles, deg		Ref
		Calcd	Exptl		Calcd	Exptl	
	C-C C-H	1.552 1.097	1.548 1.092	HCH	111.9	114	*a*
	C_1-C_2 C_1-H C_2-H	1.559 1.087 1.094	1.557 ± 0.002 $(1.109 \pm 0.004)_{av}$	$C_1C_2C_1$	75.1	74.2 ± 0.2	*b*
	C-C C-H	1.552 1.089	1.549 ± 0.003 1.10 ± 0.05				*c*
	C_1-C_2 C_2-$C_{2'}$ C_1-H C_2-H	1.538 1.541 1.099 1.099	1.53 ± 0.01 1.55 ± 0.02 $(1.107 \pm 0.009)_{av}$	$C_1C_2C_2$	109.5	109.7 ± 0.7	*d*
	C_1-$C_{1'}$ C_1-C_2 C_2-$C_{2'}$ C_1-H C_2-H	1.557 1.538 1.546 1.091 1.098	1.558 ± 0.003 1.569 ± 0.005 1.516 ± 0.01 $(1.106 \pm 0.003)_{av}$	α^j	123.7	126.7 ± 0.3	*e*
	C-C C-H	1.516 1.088	1.51 ± 0.002 1.089 ± 0.003	HCH	113.5	115.1 ± 1.0	*f*
	C_1-C_2 C_2-$C_{2'}$ C_2-H	1.495 1.511 1.094	1.469 ± 0.001 1.519 ± 0.003 1.091 ± 0.002				*g*
	C_1-$C_{1'}$ C_1-C_2 C_2-$C_{2'}$ C_1-H C_2-H	1.514 1.512 1.505 1.094 1.094	1.507 ± 0.003 1.507 ± 0.003 1.499 ± 0.016 $(1.103 \pm 0.002)_{av}$	$C_{2'}C_2C_1$ $H_2C_2C_{2'}$ $H_1C_1H_1$	123.7 113.0 113.5	129.9 ± 1.0 110.5 ± 1.0 116.1 ± 0.9	*h*
	C_1-$C_{1'}$ C_1-C_2 C_2-C_3 C_1-H C_2-H	1.514 1.511 1.449 1.094 1.093	$(1.514)_{av}$ 1.466 ± 0.018 $(1.08)_{av}$	β^k	121.3	123.02 ± 0.01	*i*

[a] A. Almeningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15,** 711 (1961); J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20,** 1703 (1952). [b] A. Almeningen, B. Andersen, and B. A. Nyhus, *ibid.*, **25,** 1217 (1971). [c] E. B. Fleischer, *J. Amer. Chem. Soc.*, **86,** 3889 (1964). [d] A. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **43,** 2017 (1970). [e] J. F. Chiang and S. H. Bauer, *Trans. Faraday Soc.*, **64,** 2249 (1968). [f] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17,** 538 (1964). [g] G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87,** 901 (1968). [h] K. Hagen, C. Hagen, and M. Traetteberg, *Acta Chem. Scand.*, **26,** 3649 (1972). [i] M. J. Collins, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **56,** 4262 (1972). [j] α is the dihedral angle of the cyclobutane ring. [k] β is the angle between the plane of the cyclopropyl ring and the acetylenic group.

methylacetylene, which is incompatible with the current concepts of hybridization and conjugation. Unfortunately, the experimental error is too large to pass a reliable judgment. If the lower experimental limit is adopted, 1.448 Å, then there is a fine agreement with our calculated bond length of 1.449 Å. Now, let us compare the calculated *d*(C-C) distances and relevant hybridization of methylacetylene and cyclopropylacetylene. The C-C bond of the former molecule is described by the $sp^{3.01}$-$sp^{1.18}$ hybrids[19] while the corresponding hybridization of the latter molecule is $sp^{2.62}$-$sp^{1.21}$. The mean hybridizations are $sp^{2.09}$ and $sp^{1.92}$ for methylacetylene and cyclopropylacetylene, respectively. Since the calculated *d*(C-C) bond length in $CH_3C{\equiv}CH$ is 1.460 Å, the qualitative picture—the more s character the shorter bond—is still valid. Of course the *d*(C-C) bond in cyclopropylacetylene might be longer than 1.448 Å, but, until the more accurate experimental distance is known, the conclusions of Boggs, *et al.*,[26] should be considered as premature.

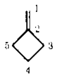
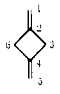
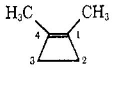
The bond angles calculated by IMOA method are in fine agreement with experimental data (Tables I and II), providing additional justification of the orthogonality requirements (eq 2). By using the linear correlations 6-8 obtained by the present calculations, one can concisely formulate the IMOA method as follows. Maximize the sum of the weighted bond overlap integrals (eq 3) with respect to the hybridization parameters satisfying the constraints: (a) the local hybrid wave function of the same carbon atom are normalized and mutually orthogonal; (b) the directions of the hybrids in the C-H bonds lie along the bond axes; and (c) the bond lengths to be used in the calculation are given by eq 6-8. The IMOA method can be used for the prediction of the bond lengths and angles of the molecules with unknown geometry. Furthermore, the information, so obtained, may help to estimate some properties which depend mainly on the molecular architecture, *e.g.*, second moments of the electronic charge distribution and the related diamagnetic susceptibility.[12,13] It is fair to mention, however, that IMOA method is capable of reproducing only the gross molecular features. It cannot distinguish between cis-trans or endo-exo isomers since the nonbonded repulsions are not explicitly included in this approach. In order to illustrate the IMOA method we calculated bond lengths and angles of molecules for which the experimental data are not available in the literature. The results are cited in the Table III. It is interesting to compare the geometry of 1,1′-dimethylcyclobutene with that of the parent molecule. We note that the

Table II
Comparison between the Calculated Bond Lengths and Angles and the Corresponding Experimental Data for Some Cyclic and Polycyclic Alkenes

Molecule	Bond	Bond lengths, Å Calcd	Bond lengths, Å Exptl	Angle	Bond angles, deg Calcd	Bond angles, deg Exptl	Ref
	$C_1{-}C_{1'}$	1.343	1.342 ± 0.004	$H_1C_1C_{1'}$	136.6	133.5	
	$C_1{-}C_2$	1.521	1.517 ± 0.003				
	$C_2{-}C_{2'}$	1.559	1.566 ± 0.003	HC_2H	112.0	109.2	*a*
	$C_1{-}H$	1.077	1.083 ± 0.003	$H_2C_2C_{2'}$	113.5	114.5	
	$C_2{-}H$	1.096	1.094 ± 0.005				
	$C_1{-}C_{1'}$	1.334	1.341 ± 0.008	$C_{1'}C_1C_2$	113.9	114.2 ± 0.6	
	$C_1{-}C_2$	1.506	1.509 ± 0.015	$C_3C_2C_{3''}$	108.4	107.6	*b*
	$C_2{-}C_3$	1.539					
	$C_3{-}C_{3'}$	1.539	$(1.549 \pm 0.008)_{av}$	$C_2C_3C_{3'}$	109.3	109.3	
	$C_2{-}H$	1.102					
	$C_3{-}H$	1.103	$(1.112 \pm 0.008)_{av}$	α	120.8	121.2 ± 2.1	
	$C_1{-}H$	1.086					
	$C_1{-}C_{1'}$	1.334	1.339 ± 0.005	$C_{1'}C_1C_2$	113.5	113.5 ± 7	
	$C_2{-}C_3$	1.540	$(1.553 \pm 0.017)_{av}$				*b*
	$C_3{-}C_{3'}$	1.536					
	$C_1{-}C_2$	1.508	1.521 ± 0.008				
	$C_2{-}H$	1.099	$(1.105 \pm 0.012)_{av}$	α^d	121.7	123.4 ± 2.2	
	$C_3{-}H$						
	$C_1{-}C_{1'}$	1.472	1.469 ± 0.002	$C_2C_3C_{2'}$	102.8	101.1	
	$C_1{-}C_2$	1.338	1.342 ± 0.003	$C_1C_{1'}C_{2'}$	109.4	108.6	*c*
	$C_2{-}C_3$	1.508	1.509 ± 0.002				
	$C_1{-}H$	1.081					
	$C_2{-}H$	1.081					
	$C_3{-}H$	1.100					

[a] B. Bak, J. J. Led, L. Nyggaard, J. Rastrup-Andersen, and C. O. Sørensen, *J. Mol. Struct.*, **3,** 369 (1969). [b] A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **44,** 1783 (1971). [c] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43,** 2765 (1965). [d] α is the dihedral angle between the 233′2′ and 211′2′ planes.

Table III
The Estimated Bond Lengths and Angles for Some Interesting Molecules as Obtained by IMOA Method

Molecule	Bond	Lengths, Å	Bond angle	Angles, deg
	$C_1{-}C_2$	1.335	$C_5C_2C_3$	107.8
	$C_2{-}C_3$	1.529	$C_2C_3C_4$	74.2
	$C_3{-}C_4$	1.570	$C_3C_4C_5$	103.8
	$C_1{-}H$	1.081		
	$C_3{-}H$	1.089		
	$C_4{-}H$	1.100		
	$C_1{-}C_2$	1.336	$C_6C_2C_3$	104.6
	$C_2{-}C_3$	1.528	$C_2C_3C_4$	75.4
	$C_1{-}H$	1.080		
	$C_3{-}H$	1.091		
	$C_1{-}C_{methyl}$	1.501	$C_4C_1C_2$	94.1
	$C_1{-}C_4$	1.344	$C_1C_2C_3$	85.90
	$C_1{-}C_2$	1.521		
	$C_2{-}C_3$	1.561		
	$C_{methyl}{-}H$	1.100		
	$C_2{-}H$	1.094		
Tetrahedrane	C–C	1.491		
	C–H	1.065		

skeleton of the cyclobutene is practically unaffected by substitution of the two methyl groups. This is compatible with chemical evidence that methylation does not appreciably change the electronic structure of the molecule. The C–C bonds adjacent to a double bond in methylenecyclobutane and dimethylenecyclobutane exhibit the characteristic shortening due to the increased s character of the involved hybrids. The geometry of the former molecule might be useful in order to extract the "experimental" diamagnetic and paramagnetic contributions to the molecular susceptibility from the available microwave data.[27] A very interesting molecule is tetrahedrane which has not been synthetized as yet. Our estimated C–C bond length, 1.491 Å, is by 0.02 Å shorter than the corresponding bond length in cyclopropane. This can be compared with 1.48 Å prediction of Weltner who used the VB approach.[27] The C–H bond length is practically that found in acetylene providing a justification to name tetrahedrane as "acetylenic" hydrocarbon.[28]

The change in hybridization has considerable influence on various physical and chemical properties of molecules, to mention only C–C and C–H spin-spin coupling constants,[29] thermodynamic acidity of protons,[30] C–H stretching frequencies and bond energies,[31] and molecular heats of formation.[32] By using available linear correlations one can predict these properties and for this purpose we summarize in Table IV the hybridization parameters for the molecules examined in this paper. One also observes from Table IV that the hybridization parameters of the carbon atoms in similar structural units are to a high de-

Table IV
The Calculated Hybridization, Corresponding σ and π Overlap Integrals, C–C–C Interorbital Angles, and Deviation Angles for Molecules Considered in This Paper

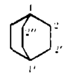
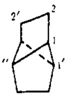
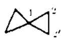
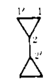
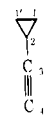
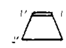
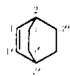
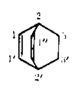
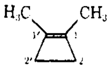
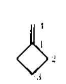
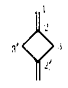
Molecule (registry no.)	Bond	Hybridization sp^{n_i}–sp^{n_j}	σ overlap	π overlap	Angle	C–C–C interhybrid angle, deg	Deviation angle	
							δ	Deg
 (287-23-0)	C–C	3.38–3.38	0.6306	0.0045		107.2	δ	8.6
	C–H	2.68	0.7242					
 (311-75-1)	C_1–C_2	3.43–3.59	0.6055	0.0145	212′	107.2	δ_{12}	15.7
	C_1–H	2.10	0.7354		121′	106.2	δ_{21}	15.5
	C_2–H	2.54	0.7267					
 (277-10-1)	C–C	3.37–3.37	0.6181	0.0112		107.3	δ	13.7
	C–H	2.19	0.7336					
 (280-33-1)	C_1–C_2	3.07–3.15	0.6518	0.00001	212″	109.0	δ_{12}	−0.4
	C_2–C_2	3.16–3.16	0.6495	0.00002	122′	108.5	δ_{21}	−0.5
	C_1–H	2.80	0.7220				$\delta_{22'}$	−0.5
	C_2–H	2.86	0.7211					
 (250-21-5)	C_1–$C_{1'}$	3.46–3.46	0.6163	0.0101	1′11″	106.8	δ_{11}	12.9
	C_1–C_2	2.97–3.24	0.6487	0.0017	211′	108.2	δ_{12}	5.8
	C_2–C_2	3.26–3.26	0.6434	0.0008	122′	107.9	δ_{21}	4.7
							δ_{22}	3.6
 (75-19-4)	C–C	3.69–3.69	0.5789	0.0325		105.7	δ	22.9
	C–H	2.49						
 (157-40-4)	C_1–C_2	3.00–3.72	0.5893	0.0351	212′	109.5	δ_{12}	24.4
	C_2–$C_{2'}$	3.60–3.60	0.5921	0.03272	22′1	105.9	δ_{21}	23.2
	C_2–H	2.50	0.7275				$\delta_{22'}$	23.0
 (5685-46-1)	C_1–$C_{1'}$	3.65–3.65	0.5797	0.0328	1′12	106.0	δ_{11}	23.0
	C_1–C_2	3.63–3.60	0.5813	0.0329	121′	106.1	δ_{12}	23.0
	C_2–$C_{2'}$	2.58–2.58	0.6801				δ_{21}	23.0
	C_1–H	2.50	0.7277					
	C_2–H	2.50	0.7276					
 (6746-94-7)	C_1–$C_{1'}$	3.65–3.65	0.5794	0.0330	1′12	106.0	δ_{11}	23.1
	C_1–C_2	3.62–3.58	0.5821	0.0329	121′	106.2	δ_{12}	23.0
	C_2–C_3	2.62–1.21	0.7279				δ_{21}	23.0
	C_3–C_4	0.83–0.84	0.8588					
	C_1–H	1.19	0.7272					
	C_2–H	2.48	0.7279					
	C_4–H	1.19	0.7737					
 (822-35-5)	C_1–$C_{1'}$	1.78–1.78	0.7401	0.0115	1′12	118.7	$\delta_{11'}$	13.3
	C_1–C_2	2.45–3.29	0.6520	0.0073			δ_{12}	11.4
	C_2–$C_{2'}$	3.52–3.52	0.6203	0.0067	2′21	107.1	δ_{21}	10.6
	C_1–H	1.86	0.7469				$\delta_{22'}$	10.6
	C_2–H	2.67	0.7244					
 (931-64-6)	C_1–$C_{1'}$	1.68–1.68	0.7665	0.0008	1′12	120.8	$\delta_{11'}$	3.5
	C_1–C_2	2.27–2.97	0.6781	0.0004			δ_{12}	3.5
	C_2–C_3	3.13–3.12	0.6514		323″	108.7	δ_{21}	2.1
	C_3–$C_{3'}$	3.12–3.12	0.6514		3′32	108.7	δ_{23}	0.30
	C_1–H	2.11	0.7359				δ_{32}	−0.3
	C_2–H	2.80	0.7185				$\delta_{33'}$	−0.3
	C_3–H	2.89	0.7166					
 (500-23-2)	C_1–$C_{1'}$	1.67–1.67	0.7662	0.0007	1′12	120.1	$\delta_{11'}$	3.3
	C_1–C_2	2.38–3.04	0.6762	−0.0005	121″	109.2	δ_{12}	3.3
	C_2–C_3	3.17–3.14	0.6498		321	108.8	δ_{21}	2.5
	C_3–$C_{3'}$	3.05–3.05	0.6534		3′32	108.9	δ_{23}	1.0
	C_1–H	2.03	0.7429				δ_{32}	−0.02
	C_2–H	2.78	0.7213				δ_{33}	−0.02
	C_3–H	2.91	0.7189					
 (542-92-7)	C_1–$C_{1'}$	2.22–2.22	0.7043	0.0022	1′12	120.4	δ_{11}	6.0
	C_1–C_2	1.76–1.71	0.7600	0.0018	123	120.4	δ_{12}	5.8
	C_2–C_3	2.28–3.13	0.6756	0.0011	232′	108.6	δ_{21}	4.8
	C_1–H	2.06	0.7424				δ_{23}	4.8
	C_2–H	2.06	0.7422				δ_{32}	3.8
	C_3–H	2.88	0.7207					
 (1501-58-2)	C_1–$C_{1'}$	1.79–1.79	0.7395	0.0116	1′12	118.7	δ_{11}	13.3
	C_1–C_2	2.42–3.30	0.6522	0.0072	2′21	107.0	δ_{12}	11.3
	$C_{2'}$–C_2	3.54–3.54	0.6189	0.0067			δ_{21}	10.5
	C_2–H	2.65	0.7271				δ_{22}	10.6
	C_3–H	2.92						

Table IV (*Continued*)

Molecule (registry no.)	Bond	Hybridization sp^{n_i}–sp^{n_j}	σ overlap	π overlap	Angle	C–C–C interhybrid angle, deg	Deviation angle δ	Deviation angle Deg
Tetrahedrane (157-39-1)	C–C	4.13–4.13	0.5287	0.0576	CCC	104.0	δ_{CC}	30.2
	C–H	1.41	0.7611					
 (1120-56-5)	C_1–C_2	2.18–3.61	0.6507	0.0046	212′	117.3	δ_{12}	4.8
	C_2–C_3	3.89–3.06	0.6196	0.0024	321	105.6	δ_{21}	15.7
	C_1–C_4	1.72–1.69	0.7667				δ_{23}	15.7
	C_2–H	2.46	0.7330					
	C_3–H	2.94	0.7202					
	C_4–H	2.18	0.7420					
 (2045-78-5)	C_1–C_2	1.76–1.67	0.7674		3′23	119.0	δ_{23}	6.2
	C_2–C_3	2.20–3.62	0.6495	0.0057	2′32	106.0	δ_{32}	15.3
	C_1–H	2.14						
	C_3–H	2.53						

gree similar and therefore transferable, allowing thus a construction of hybrid orbitals in large molecules by using simply that of their molecular fragments. To conclude, we can say that the bond lengths in cyclic and polycyclic alkanes and alkenes correlate nicely with bond overlap integrals obtained by the maximum overlap method. These correlations form a basis for the iterative (IMOA) version of the maximum overlap approximation which can be applied for the calculation of bond lengths and angles in a predictive manner. The question arises now whether the hybridization is responsible for the variation of bond lengths in hydrocarbons. It is very hard to make a reliable answer since correlations 6–8, which form a wishbone of the IMOA method, were obtained by using experimental bond lengths, and one may argue that it is the bond length which determines the hybridization! We would like to avoid here any far reaching or final conclusions and we mention only that *ab initio* study using hybrid basis set and employing a suitable energy partitioning technique would be very helpful in this respect.

Acknowledgment. We would like to thank the referee for many useful comments and suggestions.

References and Notes

(1) M. Krauss, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 635 (1964); R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966), and the references cited therein.

(2) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **49**, 312 (1968).

(3) J. N. Murrell and A. J. Harget, "Semiempirical SCF-MO Theory of Molecules," Wiley-Interscience, London, 1972, p 45.

(4) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970); N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970).

(5) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

(6) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); M. J. S. Dewar and H. N. Schmeising, *ibid.*, **11**, 00 (1960).

(7) M. G. Brown, *Trans. Faraday Soc.*, **55**, 694 (1959).

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

(9) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, **63**, 41 (1941).

(10) M. Randić and Z. B. Maksić, *Chem. Rev.*, **72**, 43 (1972), and the references quoted therein.

(11) R. F. W. Bader and P. M. Beddall, *J. Chem. Phys.*, **56**, 3320 (1972); I. Absar and J. R. Van Wazer, *J. Phys. Chem.*, **75**, 1360 (1971).

(12) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 331 (1972).

(13) Z. B. Maksić and J. E. Bloor, *Chem. Phys. Lett.*, **13**, 571 (1972); Z. B. Maksić and J. E. Bloor, *J. Phys. Chem.*, **77**, 1520 (1973); Z. B. Maksić, *Croat. Chem. Acta*, **45**, 431 (1973).

(14) J. H. Van Vleck, *J. Chem. Phys.*, **1**, 219 (1933).

(15) E. Clementi, *IBM J. Res. Develop Suppl.*, **9**, 2 (1965).

(16) O. Mårtensson and Y. Öhrn, *Theor. Chim. Acta*, **9**, 133 (1967).

(17) Z. B. Maksić and Lj. Vujisić, *ibid.*, **14**, 396 (1969).

(18) A. Hartman and F. L. Hirshfeld, *Acta Crystallogr.*, **20**, 80 (1966).

(19) Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.*, **92**, 424 (1970).

(20) M. Tanimoto, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **42**, 2519 (1969).

(21) M. Randić, Lj. Vujisić, and Z. B. Maksić, to be published.

(22) H. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947).

(23) Z. B. Maksić and M. Eckert-Maksić, *Croat. Chem. Acta*, **42**, 433 (1970).

(24) O. Mårtensson and G. Sperber, *Acta Chem. Scand.*, **24**, 1749 (1970).

(25) The same distinction should be made when the strain energy is discussed: K. Kovačević, M. Eckert-Maksić, and Z. B. Maksić, to be published.

(26) M. J. Collins, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **56**, 4262 (1972).

(27) R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **53**, 4470 (1970).

(28) W. Weltner, Jr., *J. Amer. Chem. Soc.*, **75**, 4224 (1953).

(29) Z. B. Maksić, *Int. J. Quantum Chem. Symp.*, **No. 5**, 301 (1971); Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *Theor. Chim. Acta*, **22**, 70 (1971).

(30) Z. B. Maksić and M. Eckert-Maksić, *Tetrahedron*, **25**, 5113 (1969).

(31) Z. B. Maksić, Z. Meić, and M. Randić, *J. Mol. Struct.*, **12**, 482 (1972); Z. B. Maksić, Z. Meić, and K. Kovačević, *Z. Naturforsch.*, *A* **28**, 797 (1973).

(32) K. Kovačević, M. Eckert-Maksić, and Z. B. Maksić, *Tetrahedron*, submitted for publication.