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A Molecular Orbital Based Molecular Mechanics Approach To Study Conjugated Hydrocarbons[†]

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Abstract: A new technology (MOMM) for calculating molecular structures and energies of conjugated hydrocarbons has been developed, which is a combination of molecular mechanics and molecular orbital theories. This method is proven to be very fast and accurate for a wide variety of structural compounds. This method is shown not only to achieve a better accuracy than any previous method but also to overcome the problems which were found in the previous molecular mechanics methods. The average bond length deviation from experiments was 0.008 Å for a representative group of 30 compounds and the average $\Delta H_f°(g)$ deviation from experiment was 1.10 kcal/mol for a representative of 65 molecules. Conformational analysis has also been performed for 25 compounds, and MOMM results are in good agreement with experimental data.

Thermochemical and structural data often serve as the basis of chemistry. Theoretically, these pieces of information may be obtained from quantum or molecular mechanics calculations.

Recently the ab inito molecular orbital (MO) theory has been proved to be useful in systematic studies of equilibrium geometries, electric dipole moments, charge distributions, relative energies, and conformational analysis of a variety of small compounds.[1-3] However, the computation time required for MO calculations is still, at present, a major practical problem to the application of this method to large molecules. Furthermore, there is a sizable error in the calculated total energy (which is directly related to the heat of formation), although it is occasionally possible to derive correct heats of formation from theoretical heats of reactions in conjunction with experimental enthalpies of formation.[4]

The molecular mechanics (MM) or force field method has been shown to be a very reliable, fast, and efficient way of deriving molecular structures, energies, and other properties for a wide variety of localized molecules.[2,5,6] A handicap of the molecular mechanics method lies in the fact that it is an empirical method and, hence, a great amount of accurate data must be available for a given class of compounds before an appropriate force field can be developed. There are several force fields currently in use worldwide for which extensive usage has been reported. However, it appears that the Allinger's MM2 force field is the most popular one at this time.[7]

Conjugated systems are of special interest to us because they can form aroma-related compounds. However, conjugated systems pose special problems not incurred in localized systems since the former cannot be represented by a single Kêkulê form. There have been two different attempts at grappling with the problem of the use of force field calculations to determine the structures and energies of delocalized molecules. Both methods use the usual MM procedures and the inclusion of a π system MO treatment in the calculations. The Warshel–Karplus[8] approach assumes that the π-σ separation is met and it employs a modified PPP approach (Pariser–Parr–People) for the π system and a Morse function for stretching deformations of the σ systems. The structural optimization is carried out to minimize the total energies of the π and σ systems. Although this approach appears to work fine for many cases examined, it appeared to be less exhaustively tested than the Allinger's approach. The second approach is derived by Allinger et al.[9,10] It utilizes a π-electron MO theory (VESCF in MMPI, VESCF and a modified PPP in MMPI76, a modified PPP in MMP2) to deduce force field parameters related to conjugated systems. Thus, structural optimizations for delocalized systems are not much different from those of localized systems and are very economic. Extensive calculations with MMPI and MMPI76 have been reported for conjugated hydrocarbons.

[†] Presented in part at the 11th Austin Symposium on Molecular Structure, Austin, Texas, 1986.

(1) For reviews see: (a) Pople, J. A.; Radom, L. *MTP Int. Rev. Sci.: Theor. Chem.* **1972**, 71. (b) Pople, J. A. *Tetrahedron* **1974**, *30*, 1605. (c) Pople, J. A. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977. (d) Newton, M. D., in ref. 1c.

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(3) For example: (a) Kao, J.; Seeman, J. *J. Comput. Chem.* **1984**, *5*, 200. (b) Kao, J.; Katz, T. *J. Mol. Struct. Theochem.* **1984**, *108*, 229.

(4) For example, see: Kao, J.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 760 and references cited therein.

(5) For review see: (a) Brukert, U.; Allinger, N. L. *Molecular Mechanics*; American *Chemical Society*: Washington, DC, 1982. (b) Osawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (d) Ermer, O. *Struct. Bonding* (*Berlin*) **1976**, *27*, 161.

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MMP2 results with a π-electron MO theory for conjugated hydrocarbons have not been reported yet although it was claimed that good results had been obtained.[5a] Since the MMP2 program is not in the public domain, there are several reported efforts to extend MM2 to calculate conjugated systems by including a π-system molecular orbital treatment in calculations.[7] However, all of these reported MM2 extensions are limited to conjugated hydrocarbons.

Theoretically, it is a rather straightforward application to extend the same existing formalism (as the one used in MMPI76) to hetero conjugated systems by developing necessary MO and MM parameters. However, this appears to counteract the advance of science since it is well-known that the π-theory has severe limitations and the all-electron (or, at least, all-valence-electron) MO methods have been developed and employed extensively in the past decades. Furthermore, it has also become evident that there are systems that the current MM methods cannot simulate well by simply adding new parameters.[2,5] These unsatisfactory force field results may be due to special orbital interactions, which may not be described well by a simple π-electron theory.

A combination of MM and sophisticated MO methods seems to be a promising solution to these problems discussed above. In our previous preliminary communication,[11] the MNDO method[14] was arbitrarily selected to test this approach simply because of its popularity. We have also demonstrated that a reasonable agreement can be obtained between experimental and calculated structures for planar conjugated systems containing C, H, N, O, and S atoms. Since then, much progress has been made and applications to large systems have been carried out.[12,13] In this paper, we describe our methodology in detail and report extensive calculations for both planar and nonplanar conjugated hydrocarbons.

Design Considerations and Theoretical Approaches

Theoretical calculations have been widely applied to interpret and organize results and to resolve chemical mysteries. The most important role theoretical calculations may play for the future is probably to make correct predictions before any costly experimental work begins. However, no single method is perfect and, thus, these tools should be used complementarily or in a multiple-stage fashion. Furthermore, systematic studies should be encouraged for useful predictions because they increase the effectiveness of "cancellation of errors" and make the systematic corrections possible. These are the reasons tempting us to seek a more practical and systematic appraoch to calculate molecular structures, energies, and other properties.

We are often frustrated by the lack of general, practical, systematic, and accurate approach for calculating molecular properties of interest to us. The molecules of industrial interest are usually large and it is not economically practical to calculate them with use of the sophisticated quantum mechanics procedures. Furthermore, the problem of electron correlation energy always exists in MO calculation and it becomes most critical for less sophisticated methods. For example, in correlating structures with kinetic data or in a quantitative structure activity work, one usually needs to deal with large molecules,[6] which cannot be calculated by conventional MO methods with a desirable accuracy (ca. 0.5 kcal mol^{-1}) and within a reasonable time frame (ca. 1 month).

Rapid advancement of computer technology will certainly make it more feasible to do MO calculations on larger molecules. However, one should not expect to do routine calculations on large molecules using sophisticated MO methods in the near future. The reason behind this is that the CPU time required for MO calculations is not linearly related to the number of atomic orbitals. This becomes clear if one considers the following example. Let us assume that the CPU time required is proportional to N^4 (N is the number of atomic orbitals). Let us also assume that it takes t hours of CPU time to calculate a molecule of 60 orbitals (say $C_{10}H_{10}$ with minimal basis set) using a 10 MIPS (million instructions per second) mainframe. Suppose we have a 800 MIPS supercomputer which is 80 times faster than the mainframe. Within t hours, the size of molecule that can be calculated is the one with ca. 180 orbitals (say $C_{30}H_{30}$ with minimal basis set) which is only 3 times larger than the one that can be calculated with the mainframe. This estimate is probably too optimistic if one considers the increased degrees of freedom for structural optimizations. Thus, the supercomputer will only play a major role in model development in the near future and a practical approach for large molecules or macromolecules is definitely necessary.

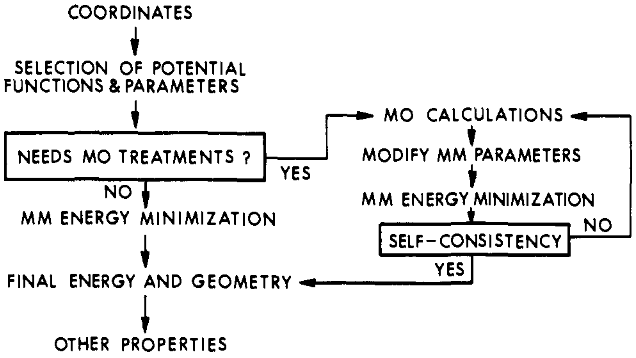

Figure 1. MOMM program flow diagram.

We propose to follow the earlier approach[11] by combining MO and MM calculations to solve many of our problems. In our proposed approach, sophisticated MO calculations are performed to derive or to modify MM parameters in cases where there are doubts about the capabilities of usual MM methods, while MM calculations are used in the structural optimizations. By using this approach, MO calculations are carried out to broaden the usefulness of a normal MM method while the speed and accuracy advantage of MM calculations is fully reserved. The data flow diagram to represent this approach is schematically shown in Figure 1. This approach makes it more feasible to calculate large molecules since one can specify which *portion* of a molecule needs MO treatment. The CPU time required for MO calculations is drastically reduced by this approach which performs *single-point* MO calculations and *partial* MO treatment.

Geometries. Basic assumptions for the linkage between MO and MM are very similar to those in MMPI and MMPI76. Namely, the natural bond langth (l_0) between atoms i and j, the stretching force constant (k_s) between atoms i and j, and the twofold torsional constant (V_2) across a double bond are functions of a descriptor (X) which can be derived from MO calculations; i.e.

$$l_0 = f(X) \tag{1}$$

$$k_s = g(X) \tag{2}$$

$$V_2 = h(X) \tag{3}$$

The following three questions arise after accepting these basic assumptions: (1) which MO and MM methods are to be used, (2) what is X, and (3) what are the exact empirical functions? It appears that there are many possible answers to each question, although some may work better than others.

As expected, selection of X and derivation of empirical functions was found to be the most difficult and time-consuming. Selection of a MM method posed no problem to us since MM2 is the one which is widely tested and well-accepted. However, selection of a MO method was more complicated than we thought. First, we ruled out the π-electron theory because of its crude approximations and we also excluded ab initio theory from consideration because of its extensive CPU time requirement. This left us to all-electron or all-valence-electron semiempirical methods. There were only three semiempirical methods which were of interest to us: MNDO,[14] extended-Hückel (EH),[15] and MCNDO.[16] Although

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[12] Kao, J.; Lilly, A. C. *J. Am. Chem. Soc.*, in press.

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the MCNDO method gives good geometries and energies, it was excluded for further considerations because we could not afford the time needed to derive relevant MO parameters. Thus, the choice of a MO method was narrowed down to MNDO and EH.

In our initial work, the MNDO method was arbitrarily chosen to test our methodology because of its popularity and X was taken to be the product of the MNDO bond order and core Hamiltonian between the atom pair i and j. A linear relationship was used for both $f(X)$ and $g(X)$ in eq 1 and 2,

$$l_0 = l_{\rm I} + l_{\rm II}X \tag{4}$$

$$k_s = k_{\rm I} + k_{\rm II}X \tag{5}$$

where $l_{\rm I}$, $l_{\rm II}$, $k_{\rm I}$, and $k_{\rm II}$ are empirical coefficients specific to atoms i and j. This linear relationship is justified in light of model studies of several appropriate ground-state molecules. We promptly applied these linear relationships to study planar conjugated systems and found a reasonable agreement between experimental and calculated structures.[11] Although these results were impressive, we decided later to discontinue using MNDO in our further studies. Reasons for this decision are (1) MNDO calculations still require a considerable amount of CPU time for a medium-size compound; (2) MNDO calculations (for the version we used) underestimate conjugation effects and give wrong rotational potential functions for molecules such as butadiene, benzaldehyde, etc.; (3) X defined as above is extremely sensitive to the interatomic distance which may slow down structural optimizations for certain cases; and (4) we cannot derive a unique and meaningful empirical function for V_2 to study nonplanar conformations.

For this work, the EH method is used instead of the MNDO method to further reduce the required CPU time. Furthermore, X is assumed to be the bond index as defined by Armstrong et al.[17a] The use of the EH method adds greater possibilities for extensions to organometallic compounds since EH is probably the only method with well-developed parameters for these compounds.[17b]

In this work, the stretching force constant k_s between atoms j and k is also assumed to have a linear equation with X (eq 5), X being the bond index (degree of bonding) between atoms j and k as defined by Armstron et al. However, the natural bond length between atoms j and k is expressed as a quadratic function (eq 6) of bond index X between atoms j and k.

$$l = l_{\rm I} + l_{\rm II}X + l_{\rm III}X^2 \tag{6}$$

The quadratic term is necessary for the C_{sp^2}–C_{sp^2} bond since the bond lengths calculated for several model compounds cannot be simply expressed as a linear function of bond index as shown in eq 4. For bond types other than C_{sp^2}–C_{sp^2}, the use of the quadratic term may not be necessary and the empirical coefficients $l_{\rm II}$ and $l_{\rm III}$ may be set to zero. (In this work, $l_{\rm III}$ is taken to be zero for the C_{sp^3}–C_{sp^3} bond, while both $l_{\rm II}$ and $l_{\rm III}$ are assumed to be zero for the C_{sp^2}–C_{sp^3} bond). It is important to note that although a more complex form (i.e., eq 6 instead of eq 4) has to be used for the natural bond length, the bond index appears to be a better descriptor than the one used in the previous work[11] for the MO–MM link. This is because the bond index is more or less a topological descriptor, which is dependent more on the chemical environment than on the variation of bond distance. The topological nature of the bond index greatly reduces the required MO–MM cycles and hence the CPU time required for structural optimizations.

Derivation of a twofold torsional potential function (V_2) about a conjugated bond is a more difficult task. The proposed V_2 function to account for the disruption of a π bond is defined as the following

$$V_2 = sV_2^\circ \tag{7}$$

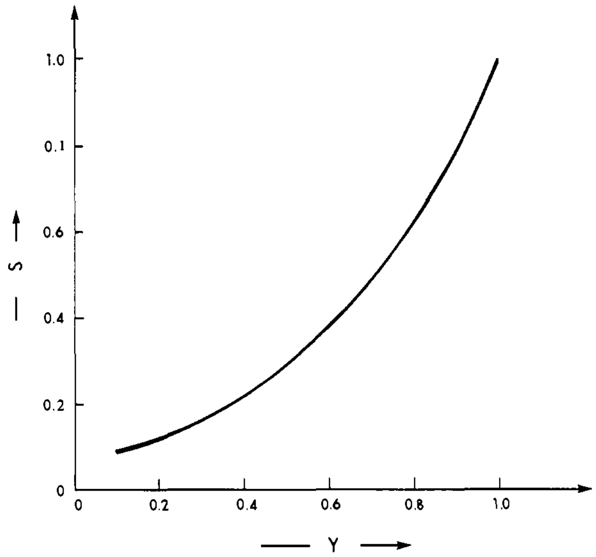

Figure 2. The relationship between s and Y as defined in eq 8 and 9.

where V_2° is an empirical constant which depends on atom types defining a dihedral angle i–j–k–l and s is a scaling factor. The equations to define s are

$$s = s_{\rm I} + s_{\rm II}Ye^{Y-1} \tag{8}$$

and

$$Y = \frac{(X_{\rm jk} - 1)}{(X_{\rm jk} - 1) + \frac{1}{M}\sum_l (X_{\rm ij} - 1) + \frac{1}{N}\sum_l (X_{\rm kl} - 1)} \tag{9}$$

Equation 8 is an empirical equation and $s_{\rm I}$ and $s_{\rm II}$ are empirical constants which are dependent on atom types defining a dihedral angle and are chosen to reproduce experimental values (such as dihedral angles, conformational energies, and heats of formation). M and N in eq 9 are the number of bonds nearest to the j–k bond. The numerator of eq 9, $(X_{\rm jk} - 1)$, is a measure of the extra bond strength beyond a single bond (bond index = 1) for the central bond (j–k). Similarly, $(X_{\rm ij} - 1)$ and $(X_{\rm kl} - 1)$ appearing in the denominator of eq 9 are bond strength measurements for the terminal bonds i–j and k–l. Y as defined in eq 9 has a value of 1.0 for ethylene, which is the upper limit for Y. Y becomes smaller when the central bond j–k has fewer double bond characteristics. Thus, Y is a good descriptor for the conjugation energy along the j–k bond. Figure 2 displays the relation between s and Y. One notes that the equations used to derive V_2 in this work are more meaningful and much simpler than those proposed previously. For this work, $0.09 \le s \le 1.0$.

Examination of calculated results with eq 7–9 reveals that they work satisfactorily for almost every case with the possible exception of the highly strained conjugated 6-membered rings. It is our intuition that the calculated structure for these strained 6-membered rings may be too flexible and reformalization of these equations may be desirable. However, the flexibility or rigidity regarding benzene-type rings is not well-known and further advanced studies (both experimentally and theoretically) should be preceded before we reparametrize our parameters. Thus, in this work, Y values of benzene-type 6-membered rings have been simply scaled up by 20% to slightly improve the overall calculated heats of formation of highly strained molecules.

The parameter values used in this work for eq 8 are 0.045 and 0.955 respectively for $s_{\rm I}$ and $s_{\rm II}$. Listed in Table I are parameter values for natural bond lengths, stretching constants, bending constants, and torsional constants. Force field parameters developed in earlier MM2 works carry over here if these parameters are not specifically mentioned in this paper.

Heats of Formation. According to our previously described model,[10] the heat of atomization (ΔH_a°) can be expressed as

$$\Delta H_a^\circ = E_{\rm bond} + E_{\rm str} - {\rm SE} - {\rm PFC} \tag{10}$$

where $E_{\rm bond}$ is the sum of the bond energy contributions, $E_{\rm str}$ is

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(17) (a) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838. (b) As pointed out by an anonymous referee, the EH density matrix is not duodempotent and, thus, the bond index defined by Armstrong et al. may not be meaningful. In the EH context, it may be more appropriate to employ the Mulliken overlap population as descriptor X.

Table I. Adjusted Values for Force-Field Parameters[a]

Natural Bond Lengths (Å) and Stretching Constants (mdyn $Å^{-1}$)[b]

bond[c]	l_1	l_{11}	l_{111}	k_1	k_{11}
1–1	1.973	−0.446		4.400	
2–2	1.927	−0.560	0.132	2.526	3.521

	bonding constants	
angle	θ_0, deg	k_θ, mdyn Å/rad^2
2–1–2	112.0	0.95
2–2–2	120.0	0.45

	torsional constants[d]		
angle	v_1	v_{i}	v_3
2–2–2–2	0	15.00	2.00
2–1–1–2	3.50	0.27	0.00
2–1–2–2	0	0	0.0
1–2–2–2	0.0	15.00	0
2–1–2–5	0	0	−0.45
2–2–2–5	0.40	15.00	0

[a] If parameters are not specificed in this table, MM2 parameter values are used. [b] See eq 5 and 6. [c] MM2 atom types are used, 1 = C_{sp^3}, 2 = C_{sp^2}, 5 = H. [d] Torsional function used is $(V_1/2)(1 + \cos\theta) + (V_2/2)(1 - \cos 2\theta) + (V_3/2)(1 + \cos 3\theta)$.

Table II. Parameters Used in Morse Potential Function

	$E_e^{C=C}$, kcal/mol	R_e, Å	$a = (k_e/2E_e^{C=C})^{1/2}$, $Å^{-1}$
ethylene	128.77	1.337	2.309
benzene	119.76	1.399	2.142

Table III. Values of Bond and Structure Energies

term[a]	value, kcal/mol	term[a]	value, kcal/mol
1–1	82.32	C-1(H)-C	3.35
1–2	89.93	C-1(C)-C	7.34
1–5	99.30	2–2(2)–2	−3.86
2–5	103.00	2–2(2)–1	0.63
1-CH_3	−1.25	1–2(2)–1	4.43
2-CH_3	−1.07	1–2–2–2	−0.70
		2–2–2–2	2.00

[a] When necessary, MM2 atom types are used (1 = C_{sp^3}, 2 = C_{sp^2}, 5 = H).

the sum of the structural energy contributions, SE is the steric energy of the molecule calculated by our program, and PFC is the partition function contribution, which is assumed to be 2.4 kcal/mol throughout this paper.

$\Delta H_f°$ can be calculated from $\Delta H_a°$

$$\Delta H_f° = 170.90 N_C + 52.10 N_H - \Delta H_a° \qquad (11)$$

where N_C and N_H are respectively the number of carbon and hydrogen atoms in the molecule. The first two terms on the right-hand side of eq 11 are the conversion factors from $\Delta H_a°$ to $\Delta H_f°$. The coefficients 170.90 and 52.10 are respectively the heats of formation of gaseous carbon atoms and gaseous hydrogen atoms in their ground states at 298.15 K from the elements in their standard states.

E_{bond} of a conjugated molecule may be expressed as the sum of two individual parts

$$E_{bond} = E_{conj} + E_{nconj} \qquad (12)$$

where E_{conj} represents the energy contribution from the conjugated bonds of the molecule. It may be written as the sum of two separate terms for hydrocarbons

$$E_{conj} = \sum E_b^{C=C} = \sum (E_{\sigma b}^{C=C} + E_{\pi b}^{C=C}) \qquad (13)$$

where the summation is over all conjugated bonds. $E_{\sigma b}^{C=C}$ and $E_{\pi b}^{C=C}$ are respectively the σ and π bond energies of a C_{sp^2}–C_{sp^2} bond in the conjugated part of the molecule. The sum of $E_{\sigma b}^{C=C}$ and $E_{\pi b}^{C=C}$ gives the bond energy of a C_{sp^2}–C_{sp^2} double bond ($E_b^{C=C}$).

For simplicity,[18] the Lo–Whitehead procedure[19] is used to calculate E_{conj}. The basic principles of the Lo–Whitehead procedure are summarized as follows. With use of PPP–SCF–MO theory, the total π bond energy, $E_{\pi b}^{C=C}$, is given by

$$\sum E_{\pi b}^{C=C} = -\left\{ \sum_i \frac{P_{ii}^2}{4}\gamma_{ii} + 2\sum_{i<j} P_{ij}\beta_{ij} + \sum_{i<j} [(P_{ii} - 1)(P_{jj} - 1) - 1/2P_{ij}^2]\gamma_{ij} \right\} \qquad (14)$$

where P_{ij} is the density matrix, γ_{ij} is the repulsion integral, and β_{ij} is the resonance integral which is a quantity to be determined in their treatment. The dependence of $E_b^{C=C}$ on atomic distance R_{ij} is expressed by a Morse potential function

$$E_b^{C=C} = E_e^{C=C}\{2 \exp[-a(R_{ij} - R_e)] - \exp[-2a(R_{ij} - R_e)]\}$$

$$\text{and} \qquad a = (k_e/2E_e^{C=C})^{1/2} \qquad (15)$$

where $E_e^{C=C}$ is the equilibrium bond energy, k_e is the force constant at the equilibrium geometry, and R_e is the equilibrium bond length. Lo and Whitehead chose ethylene and benzene as their key molecules to parametrize eq 15, since k_e and R_e for these two molecules are well-known experimental observables. By substituting these experimental quantitites into eq 15 and simplifying eq 14 for these compounds using the symmetry of the density matrix, Lo and Whitehead are able to define their own β_{ij} and therefore calculate $E_{\sigma b}^{C=C}$ and $E_{\pi b}^{C=C}$ of eq 13 semiempirically.[23] Although we follow the Lo–Whitehead procedure, parameters in eq 15 have been chosen differently in order to get a better overall fit of $\Delta H_a°$. The parameters used are shown in Table II. Note that they are quite similar to those used by Lo and Whitehead.

E_{nconj} represents the energy contribution from the nonconjugated part of the molecule or the energy contribution from σ bonds of the molecule. E_{nconj} may be expressed as a sum of different bonds, namely

$$E_{nconj} = E_{C_{sp^2}-H} + E_{C_{sp^3}-H} + E_{C_{sp^2}-C_{sp^3}} + E_{C_{sp^3}-C_{sp^3}} \qquad (16)$$

where terms on the right-hand side of eq 16 are constant bond energies for the specified bond type. Values of these parameters along with E_{str} parameters (eq 10) are shown in Table III. All of these parameters were adjusted in the current work. As is shown later, the inclusion of E_{str} in the calculation of $\Delta H_f°$ conquers the two main limitations of the standard π approximation, namely its limitations to planar and strainless structures.

Results and Discussion

(A) **Geometries.** The set of 30 molecules employed in the MMPI76 work[10] was used to test the practical applicability of our approach and to derive necessary force field parameters. That set of molecules consists of a good cross-section of conjugated hydrocarbons: aromatic and nonaromatic, highly strained and strainless molecules, and planar and nonplanar.

Listed in Table IV are the calculated and experimental values for bond lengths, key bond angles, and dihedral angles of these various hydrocarbons. Also listed are the differences between the experimental values and the values calculated herein. Looking first at bond lengths, the average mean difference between the

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(18) One may ask why we did not directly employ EH results to calculate $\Delta H_a°$. The reason is that steric effects have been partially accounted for within the EH (or any semiempirical method) and there are practical limitations that prevent such calculations from being accurate. Thus, it is impossible to know which steric effect and by how much it should be reduced before adding the steric energy obtained from MM calculations to accurately calculate $\Delta H_a°$.

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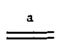
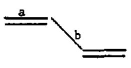
Chart I



(I)



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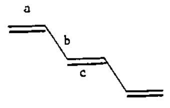

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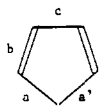
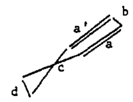


(IV)



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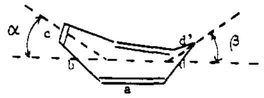

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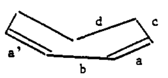
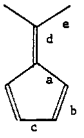


(VII)

(VIII)

Chart II



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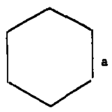

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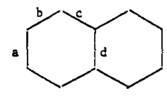

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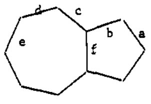

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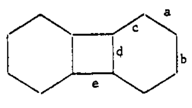

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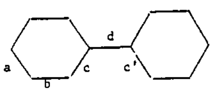

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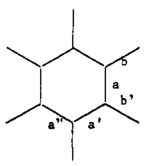

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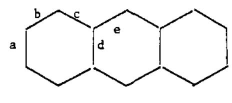
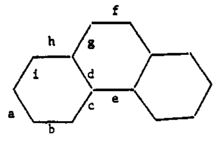


(XVI)

experimental and calculated values is 0.008 Å, about the same as both the average experimental error and our previous result for the same set of compounds. Reasonable agreement between experimental and calculated results is also obtained for bond angles.

Specific note should be taken of the torsional angles since they describe whether or not a molecule is planar. Those conformational features will be discussed later. However, it is worth pointing out now that the agreement in dihedral angles is good if it is realized that we are usually comparing the calculated structure of an isolated molecule with that found experimentally in a crystal. Since the force constants for torsional motion are usually quite small, the crystal packing forces may play an important role in determining dihedral angles.

Chart III



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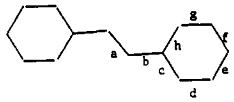

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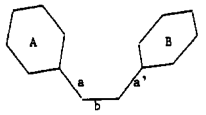

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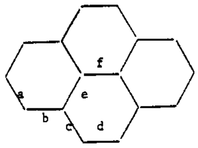

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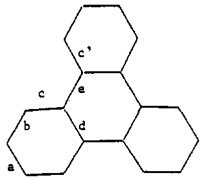

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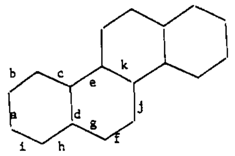

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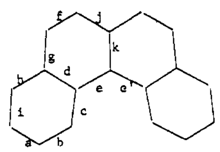

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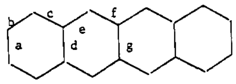

(XXIV)

By comparing structures presented in Table IV, one observes several important and interesting structural changes in going from small to large acenes. Whether MOMM can reproduce these changes is important for its applications in polymers.[12] As can be seen from Table IV, there are substantial elongations of the central bonds in large acenes, both experimentally and theoretically. The experimental and theoretical (in parentheses) data for these central bonds are respectively 1.399 (1.399) for benzene,[26] 1.422 (1.435) for naphthalene,[27] 1.433 (1.477) for anthracene,[28] as well as 1.420 (1.452) and 1.460 (1.455) for tetracene.[29] One notes that changes in the experimental bond length in going from small to large molecules are well reproduced by the theory.

Theoretically, these bond elongations can be rationalized by considering oligomers as composed of two small parts. These compounds may be treated as an attachment of a four π electron system to a two π electron system (i.e., omitting the rest of oligomers as a first approximation). The donor–acceptor interaction (XXXI) involves two electrons and will stabilize the system. The structural consequence due to interaction XXXI is a bond elongation of the donor bond.

In short, as far as geometries of the above 30 molecules are concerned, the obtained results are in good agreement with experimental data. The accuracy of this method is clearly demonstrated in Table IV.

The objective of this work is to explore a new general method which can perform well for both ordinary cases (where any other MM methods can do) and special cases (where other MM methods

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(26) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(27) Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 26.

(28) For example: Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. Mui, P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562. Carreria, L. A. *J. Chem. Phys.* **1975**, *62*, 3851.

(29) DeMare, G. R. *Theochem.* **1984**, *107*, 127.

Table IV. Experimental and Calculated Geometries (in Å or deg)

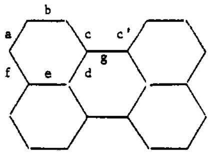
compd	bond or angle	exptl	calcd	exptl − calcd
ethylene (I)	a	1.337	1.337	-0.000
trans-butadiene (II)	a	1.344	1.346	-0.002
	b	1.467	1.469	-0.002
	ab	122.9	120.0	2.9
hexatriene (III)	a	1.337	1.348	-0.011
	b	1.458	1.462	-0.004
	c	1.368	1.361	0.007
cyclopentadiene (IV)	a	1.509	1.503	0.006
	b	1.342	1.356	-0.014
	c	1.469	1.458	0.011
	ab	109.3	110.1	-0.8
	bc	109.4	108.9	0.5
	aa′	102.8	102.0	0.8
1,3-cyclohexadiene (V)	a	1.350	1.349	0.001
	b	1.468	1.470	-0.002
	c	1.523	1.506	0.017
	d	1.534	1.540	-0.006
	ab	120.1	119.7	0.4
	ac	120.1	121.4	-1.4
	cd	110.7	111.1	-0.4
	aba′	18.3	17.3	1.0
1,3,5-cycloheptatriene (VI)	a	1.34	1.350	-0.10
	b	1.47	1.464	0.10
	c	1.34	1.358	-0.20
	d	1.50	1.502	0.00
	ab	124.5	124.3	0.2
	bc	124.5	125.7	-1.2
	ad	124.5	123.8	0.7
	α	29.5	30.1	-0.6
	β	50	45.8	4.2
1,3-cycloheptadiene (VII)	a	1.347	1.351	-0.004
	b	1.450	1.463	-0.013
	c	1.509	1.502	0.007
	d	1.522	1.530	-0.008
	ab	129.1	129.6	-0.5
	ac	129.1	128.4	-0.7
	aba′	0	0	0
cyclooctatetraene (VIII)	a	1.340	1.345	-0.005
	b	1.475	1.482	-0.007
	ab	126.1	125.1	1.0
dimethylfulvene (IX)	a	1.476	1.467	0.009
	b	1.340	1.359	-0.019
	c	1.462	1.451	0.011
	d	1.347	1.365	-0.018
	e	1.510	1.515	-0.005
benzene (X)	a	1.399	1.399	+0.000
naphthalene (XI)	a	1.412	1.422	-0.010
	b	1.371	1.380	-0.009
	c	1.422	1.431	-0.009
	d	1.420	1.434	-0.014
azulene (XII)	a	1.399	1.404	-0.005
	b	1.418	1.418	0.000
	c	1.383	1.403	-0.020
	d	1.406	1.400	0.006
	e	1.403	1.404	-0.001
	f	1.501	1.473	0.028
biphenylene (XIII)	a	1.423	1.431	-0.008
	b	1.385	1.396	-0.011
	c	1.372	1.370	0.002
	d	1.426	1.438	-0.012
	e	1.514	1.496	0.018
biphenyl (XIV)	a	1.400	1.399	0.001
	b	1.400	1.397	0.003
	c	1.400	1.412	-0.012
	d	1.490	1.491	-0.001
	cdc′		38.4	
hexamethylbenzene (XV)	a	1.417	1.416	0.001
	b	1.530	1.516	0.014
	bab′	9.9	7.9	2.0
	aa′a″		4.5	
anthracene (XVI)	a	1.418	1.431	-0.013
	b	1.375	1.374	0.001
	c	1.444	1.440	0.004
	d	1.433	1.447	-0.014
	e	1.405	1.411	-0.006
phenathrene (XVII)	a	1.394	1.412	-0.018
	b	1.401	1.387	0.014
	c	1.409	1.423	-0.014
	d	1.420	1.432	-0.012
	e	1.465	1.465	0.000
	f	1.350	1.365	-0.015
	g	1.453	1.447	0.006
	h	1.423	1.424	-0.001
	i	1.386	1.384	0.002
trans-stilbene (XVIII)	a	1.338	1.357	-0.019
	b	1.473	1.477	-0.004
	c	1.406	1.417	-0.011
	d	1.393	1.395	-0.002
	e	1.393	1.400	-0.007
	f	1.391	1.400	-0.009
	g	1.390	1.396	-0.006
	h	1.402	1.415	-0.013
	Ph–a	5.2	15.4	-10.2
cis-stilbene (XIX)	$C = C_{av}(A,B)$	1.398	1.404	-0.006
	a	1.489	1.481	0.008
	b	1.334	1.353	-0.019
	aba′		6.9	
	Ph–b	43.2	35.5	7.7
	ab	129.5	126.3	3.1
pyrene (XX)	a	1.395	1.399	-0.004
	b	1.406	1.414	-0.008
	c	1.438	1.449	-0.011
	d	1.367	1.368	-0.001
	e	1.425	1.433	-0.008
	f	1.430	1.432	-0.002
triphenylene (XXI)	a	1.397	1.405	-0.008
	b	1.381	1.388	-0.007
	c	1.410	1.423	-0.013
	d	1.413	1.431	-0.018
	e	1.458	1.475	-0.017
	cec′		10.6	
chrysene (XXII)	a	1.394	1.415	-0.021
	b	1.381	1.385	-0.004
	c	1.409	1.428	-0.019
	d	1.407	1.432	-0.025
	e	1.468	1.462	0.006
	f	1.369	1.370	-0.001
	g	1.421	1.438	-0.017
	h	1.428	1.427	0.001
	i	1.363	1.381	-0.018
	j	1.428	1.442	-0.014
	k	1.401	1.427	-0.026
3,4-benzophenanthrene (XXIII)	a	1.409	1.415	-0.006
	b	1.378	1.385	-0.007
	c	1.433	1.429	-0.004
	d	1.431	1.435	-0.004
	e	1.446	1.457	0.010
	f	1.342	1.369	-0.027
	g	1.443	1.441	0.002
	h	1.391	1.426	-0.035
	i	1.374	1.383	-0.009
	j	1.430	1.442	-0.012
	k	1.412	1.422	-0.010
	cec′		22.8	
tetracene (XXIV)	a	1.459	1.434	0.025
	b	1.381	1.372	0.009
	c	1.420	1.443	-0.023
	d	1.420	1.452	-0.032
	e	1.390	1.404	-0.014
	f	1.404	1.421	-0.017
	g	1.460	1.455	0.005
perylene (XXV)	a	1.370	1.380	-0.010
	b	1.418	1.414	0.004
	c	1.397	1.402	-0.005
	d	1.425	1.442	-0.017
	e	1.424	1.437	-0.013
	f	1.400	1.429	-0.029
	g	1.471	1.481	-0.010
corannulene (XXVI)	a	1.402	1.393	0.009
	b	1.440	1.456	-0.016

Table IV (Continued)

compd	bond or angle	exptl	calcd	exptl − calcd
	c	1.391	1.393	−0.002
	d	1.413	1.431	−0.018
	ab	122.0	121.7	0.3
	bc	114.3	112.3	2.0
	bb′	130.1	134.6	−4.5
	cd	123.0	122.4	0.6
	dd′	108.0	108.0	0.0
1,2-diphenylcyclopentene (XXVII)	C = C_{av}(A,B)	1.379	1.403	−0.024
	a	1.478	1.481	−0.003
	b	1.510	1.510	−0.000
	c	1.339	1.362	−0.023
	d	1.525	1.542	−0.017
	Ph–c	45.7	37.4	8.3
	aca′	7.5	8.4	−0.9
4,8-dihydrodibenzo-[*cd,gh*]-pentalene (XXVIII)	a	1.405	1.426	−0.021
	b	1.382	1.400	−0.018
	c	1.578	1.540	−0.038
	d	1.378	1.385	−0.007
	e	1.392	1.413	−0.021
	aa′	125.4	126.1	−0.7
	ab	118.3	117.7	0.6
	bc	142.3	142.6	−0.3
	bd	112.0	110.6	1.4
	cd	105.7	106.8	−1.1
	cc′	102.9	103.7	−0.8
	dd′	134.2	137.2	−3.0
	de	113.2	111.4	1.8
tetraphenylethylene (XXIX)	C = C_{av}(A,B,C,D)	1.394	1.403	−0.009
	a	1.496	1.496	0.000
	b	1.356	1.370	0.014
	aba′	8.4	6.9	1.5
	Ph-b	47.8	48.0	−0.2
	ab	122.2	121.9	0.3
	aa′	115.5	116.1	−0.6
cis,cis-1,2,3,4-tetraphenylbutadiene (XXX)	C = C_{av}(A,B,C,D)	1.405	1.403	0.002
	a	1.357	1.368	−0.011
	b	1.477	1.481	−0.004
	c	1.518	1.499	0.019
	d	1.493	1.491	0.002
	Ph(A)–a	75	68	7
	Ph(B)–a	34	36	2
	bad	0	0	0
	ada′	0	0	0

[a] See ref 10 for the source of experimental data.

Chart IV



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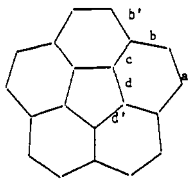

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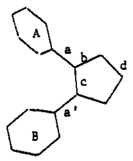

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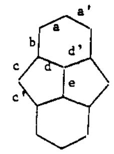

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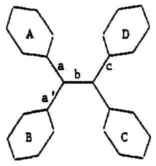

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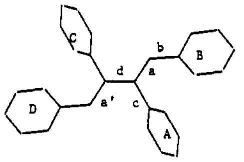
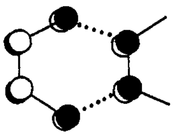
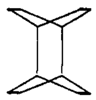


(XXX)

Chart V



(XXXI)



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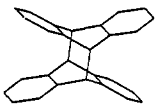

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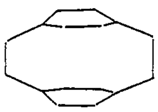

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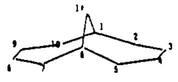

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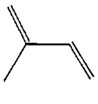

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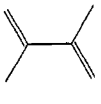

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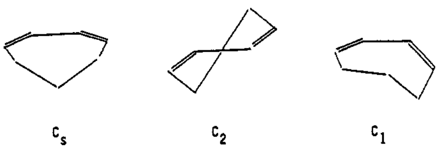


(XXXVIII)

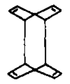
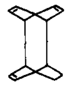
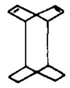
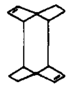
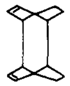
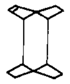
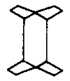
may fail). The *p,p′*-dibenzene (XXXII), 9,9′,10,10′-dianthracene (XXXIII), 2,2-paracyclophane (XXXIV), and bicyclo[4.4.1]undecapentaene (XXXV) molecules illustrate interesting limitations in the previous MM calculations. These molecules are of special interest and they will be explicitly discussed here.

Gleiter has shown theoretically that the parallel alignment of the p-orbitals of the π-systems and the C_{s^3}–C_{sp^3} σ bonds in 2,2-paracyclophane leads to a large overlap and large π–σ interactions.[20] These large π–σ interactions are predicted to cause the lengthening of the C_{sp^3}–C_{sp^3} σ bond. Indeed, our calculated bond length for the C_{sp^3}–C_{sp^3} bond of 2,2-paracyclophane is 1.58 Å which is considerably longer than a normal C_{sp^3}–C_{sp^3} single bond (1.54 Å).

Similarly, Mislow and his co-workers have recently employed MINDO/3 to study electronic structures of *p,p′*-dibenzene and its hydrogenated derivatives.[21] After a detailed analysis of calculated results, they concluded that through-bond coupling of the four π systems would lead to an elongation of the bridged σ bond. This effect is expected to occur whenever similar geometrical conditions prevail. In fact, compilation of experimental structures for similar compounds does support their view. Our calculated results using MM2 and MOMM methods for *p,p′*-dibenzene and its hydrogenated derivatives are shown in Table V, together with the MINDO/3 values obtained by Mislow et al. The MM2 method gives short bond lengths for the bridged bonds and, thus, it fails to show this type of through-bond interactions. On the other hand, MOMM correctly predicts bond-elongations in this series of molecules. A similar trend of bond lengthening has been shown by MINDO/3 calculations. Although the experimental structure of *p,p′*-dibenzene is unknown, the experimental geometry for 9,9′,10,10′-dianthracene is available.[22] A long bond length is indeed observed for the bridged σ bond of the latter. It is important to note that our calculated value (1.61 Å) is in excellent agreement with the experimental one (1.61 Å).[22]

An X-ray examination of a crystalline carboxybicyclo[4.4.1]-undecapentaene indicates that the bond lengths of the peripheral bonds are much more constant (<0.05 Å) than in naphthalene.[23]

Table V. Geometries of *p,p′*-Dibenzene and Hydrogenated Derivatives (Å)

compd	MM2	MOMM	MINDO/3[a]
	1.551	1.608	1.595
	1.551	1.595	1.591
	1.551	1.588	1.591
	1.551	1.578	1.589
	1.552	1.585	1.590
	1.553	1.574	1.588
	1.558	1.571	1.586

[a] See ref 21.

Table VI. The Geometry of Bicyclo[4.4.1]undecapentaene (XXXV) (Å, or deg)

parameter	X-ray	MMPI	MOMM
1-2	1.409	1.406	1.420
2-3	1.383	1.400	1.400
3-4	1.414	1.423	1.437
1-11	1.477	1.470	1.479
1-2-3	122.3	120.4	121.0
2-3-4	127.7	128.6	127.9
2-1-11	116.1	115.8	116.9
1-11-6	99.6	99.1	102.3
1-2-3-4	20	17	25
2-3-4-5	1	0	0
3-2-1-10	146	150	148

This suggests considerable aromatic character in bicyclo[4.4.1]undecapentaene (1,6-methano-10-annulene) (XXXV). The MMPI method has been applied to XXXV and the calculated geometry is generally in good agreement with the X-ray structure as shown in Table VI. However, the calculated bond length by MMPI for the conjugated part of the molecule shows a much smaller alternation in the naphthalene sense (where 2–3 < 1–2 < 3–4, see Table VI).[5a,24] Recently, Lindner[24] has employed a special bond order–bond length relationship for this 1,6-interaction, applied as a perturbation to his own force field, to this problem and the results are good. Our calculated results are also shown in Table VI, and they are in excellent agreement with experimental values. Specifically, bond alternation in the naphthalene sense is well reproduced by MOMM. Thus, the problem with MMPI for this type of molecule may be due to incorrect α–π separation approximation instead of the omission of bond order–bond length approach for the 1,6-interaction as proposed previously.

(B) Heats of Formation. Most of the conjugated hydrocarbons for which the ΔH_f°(g) values are experimentally known were examined in the present work. Table VII lists the experimental and calculated ΔH_f°(g), differences between experimental and calculated ΔH_f°(g), as well as the quoted probable experimental errors. It might be noted that while experimental errors in ΔH_f° are typically reported of less than 1.0 kcal/mol, results on the same compounds from different laboratories often differ from one another by much more than this amount. The common problems imposed on ΔH_f° measurements of these compounds are usually their instability toward air. Partial oxidation in the bomb prior to combustion will certainly underestimate heat of combustion and make the measurement unreliable. Experimental values cited in Table VII are mainly from the compilation of Cox and Pilcher.[25] Some new data, which may be more reliable, are also cited in Table VII.[10] The deviation is taken as the difference between calculated and experimental values. If there are more than one experimental values cited in Table VII, the one nearest to the calculated value was used in the calculation of the difference. As can be seen in Table VII, the calculated results are in fair to excellent agreement with experimental values. The average difference between experimental and calculated values for 65 compounds is 1.10 kcal/mol, which may be compared with the average estimated experimental error of 0.80 kcal/mol. The average difference is reduced to 0.93 kcal/mol for 63 compounds if compounds with experimental error greater than 4 kcal/mol are excluded from calculations.

There are ten molecules listed in Table VII for which the calculated values differ from the experimental ones by more than 2.0 kcal/mol. These are generally polybenzoid molecules for which the experimental measurements were done a long time ago (about 30 years), or where the reported experimental error is large, or where the experimental results are open to question. It is difficult to obtain samples of the higher acenes in such a state of purity as is necessary for the precise determination of their thermochemical properties, since they all undergo photooxidation and must be handled with care under nitrogen. It is important to note that only 5 out of these 10 molecules, tetracene, 1′,9-dimethyl-1,2-benzanthracene, acenaphthane, pyrene, and fluoranthene, have deviations more than 4 times the reported experimental error. The chemical behavior of tetracene suggests that it is the least stable of the isomeric tetracyclic hydrocarbons: triphenylene, chrysene, 3,4-benzophenanthrene, 1,2-benzanthrene, and tetracene. Therefore, the reported ΔH_f° of tetracene seems too small when compared with those of isomeric compounds. The unusual large deviation in the case of 1′,9-dimethyl-1,2-benzanthracene is likely due to experimental error, since we can get a reasonable fit for 4,5-dimethylphenathrene, and both 4,5-dimethylphenanthrene and 1′,9-dimethyl-1,2-benzanthracene are structurally similar. Similarly, large deviations for pyrene, acenaphthane, and fluoranthene cannot be rationalized but the rather good fit in similar compounds leads one to question the experimental results. One notes that the heats of formation of these compounds always have been troublesome to theoreticians.

In short, we would suspect that some of the larger differences found in Table VII are due to experimental inaccuracy, and we would suggest that new measurements of ΔH_f° would be desirable. It is also possible, of course, that there are errors inherent in our approach which only manifest themselves in certain instances.

Comparisons of six different methods with this work are made in Table VIII. To show how much improvement is obtained with the MOMM procedure, we have depicted, for the same set of molecules, the mean deviations obtained from these different methods and the current approach. The first three schemes shown in Table VIII (Dewar–de Llano, Dewar–Harget, and Lo–Whitehead) did not explicitly account for steric strains and were limited to planar structures. There were several highly strained molecules used in the Dewar–de Llano and Dewar–Harget calculations, and this gives larger mean deviations than those obtained by the Lo–Whitehead approach. When the same set of compounds is used, these methods do not differ much in the overall accuracy. For all three sets, the same accuracy is obtained from the current MOMM method. It is obvious that the present method is not only more general but also more accurate. Comparisons with the two most popular semiempirical MO schemes, MINDO/3 and MNDO, reveal that our calculated results are much superior than those MO methods. A substantial improvement (20%) over MMPI76 is also achieved by this approach.

There are a few features of these calculations that should be mentioned. Previous calculations[5a,10] cannot reproduce experimental data well for 1,3,5-cycloheptatrience and cyclooctatetraene. These discrepancies have been attributed to significant non-

Table VII. Comparison of Experimental and Calculated $\Delta H_f°(g)$

formula	name	$\Delta H_f°(g)$, kcal mol^{-1} calcd	exptl	dev (calcd-exptl)	reported probable errors
C_2H_4	ethylene	12.45	12.45	0.00	0.10
C_4H_6	*trans*-butadiene	26.35	26.11	0.24	0.15
C_5H_6	cyclopentadiene	32.16	31.94	0.22	0.28
C_5H_8	*cis*-1,3-pentadiene	19.29	19.13, 19.78	0.16	0.24
	trans-1,3-pentadiene	18.22	18.12	0.10	0.16
	2-methyl-1,3-butadiene	18.19	18.06	0.13	0.20
C_6H_6	benzene	19.86	19.81	0.05	0.13
C_6H_8	1,3-cyclohexadiene	25.07	25.38	−0.31	0.19
C_6H_{10}	2,3-dimethyl-1,3-butadiene	10.93	10.78	0.15	0.30
C_7H_8	1,3,5-cycloheptatriene	43.56	43.90	−0.34	0.36
C_7H_{10}	toluene	11.88	11.99	−0.11	0.10
	1,3-cycloheptadiene	22.60	22.56	0.04	0.24
C_8H_8	cyclooctatetraene	70.97	71.13	−0.16	0.33
	styrene	35.41	35.30	0.11	0.25
C_8H_{10}	ethylbenzene	7.17	7.15	0.02	0.19
	o-xylene	4.55	4.56, 4.23	−0.01	0.26
	m-xylene	3.91	4.14, 3.59	−0.23	0.18
	p-xylene	3.86	4.31, 3.97	−0.11	0.24
	dimethylfulvene	32.10	32.1	0.0	1.3
C_9H_8	indene	40.64	39.08	1.56	0.37
C_9H_{10}	indan	15.33	14.42	0.91	0.53
C_9H_{12}	*n*-propylbenzene	1.92	1.89	0.03	0.19
	isopropylbenzene	0.58	0.96	−0.38	0.26
	1-methyl-2-ethylbenzene	1.22	0.39	0.83	0.27
	1-methyl-3-ethylbenzene	−0.81	−0.43	−0.38	0.29
	1-methyl-4-ethylbenzene	−0.85	−0.76	−0.09	0.34
	1,2,3-trimethylbenzene	−2.07	−2.26	0.19	0.29
	1,2,4-trimethylbenzene	−3.47	−3.31	−0.16	0.26
	1,3,5-trimethylbenzene	−4.06	−3.81	−0.25	0.33
$C_{10}H_8$	azulene	74.40	69.06, 73.5	0.9	0.9
	naphthalene	35.85	35.85, 36.05	−0.00	0.25
$C_{10}H_{12}$	1,2,3,4-tetrahydronaphthalene	5.98	6.57	−0.59	0.6
$C_{10}H_{14}$	*n*-butylbenzene	−3.31	−3.18	−0.13	0.30
	isobutylbenzene	−5.24	−5.14	−0.10	0.33
	sec-butylbenzene	−3.71	−4.15	0.44	0.31
	tert-butylbenzene	−5.41	−5.40	−0.01	0.31
$C_{12}H_8$	biphenylene	103.48	104.43, 115.2	−0.6	1.5
	acenaphthylene	61.27	62.04, 61.6	−0.3	1.2
$C_{12}H_{10}$	biphenyl	42.49	43.57, 43.53	−1.04	0.60
	acenaphthane	43.90	37.4	6.5	0.7
$C_{12}H_{18}$	hexamethylbenzene	−19.04	−20.7	1.7	0.62
$C_{14}H_{10}$	anthracene	55.83	55.44, 55.2	0.39	1.1
	phenanthrene	48.84	49.52	−0.68	1.1
$C_{14}H_{12}$	*trans*-stilbene	56.34	56.43, 52.48	−0.09	0.5
	cis-stilbene	59.19	60.31	−1.22	0.42
	1,1-diphenylethene	59.93	58.7	1.2	1.1
	9,10-dihydroanthracene	37.90	38.2	−0.3	1.1
$C_{16}H_{10}$	fluoranthene	66.08	69.78, 60.08	−3.70	0.56
	pyrene	55.31	51.59	3.72	0.64
$C_{16}H_{14}$	2,7-dimethylphenanthrene	32.75	34.30	−1.55	0.50
	4,5-dimethylphenanthrene	43.91	46.26	−2.35	1.46
	9,10-dimethylphenanthrene	40.14	40.0	0.1	2.1
$C_{16}H_{16}$	[2,2]paracyclophne	55.89	57.6	−1.7	1
	[2,2]metacyclophane	45.38	40.08	5.3	1.7
$C_{18}H_{12}$	triphenylene	62.70	63.4	−0.7	1.2
	chrysene	64.18	62.8	1.4	1.2
	3,4-benzophenanthrene	67.48	69.6	−2.1	1.2
	1,2-benzanthracene	67.21	69.63, 65.97	1.24	3.0
	tetracene	77.58	69.8	7.8	1.1
$C_{18}H_{14}$	diphenylfulvene	91.76	96.1	−4.3	4.0
	5,12-dihydrotetracene	54.07	53.1	1.0	1.1
$C_{18}H_{18}$	[18]annulene	130.88	124.0, 67	6.9	6.0
$C_{20}H_{12}$	perylene	72.88	73.7	−0.8	1.1
$C_{20}H_{16}$	1′,9-dimethyl-1,2-benzanthracene	64.86	60.1	4.8	1.1
$C_{24}H_{18}$	1,3,5-triphenylbenzene	87.62	90.02, 88.0	−0.4	1.7

[a] See ref 10 for the data source.

neighbor resonance interactions, which were considered beyond the scope of the molecular mechanics method at that time. However, examination of calculated results indicates that heats of formation and inversion barriers (vide infra) for these compounds are reasonably well reproduced by MOMM. It is thus appropriate to say that MOMM can handle cases of significant non-neighbor interactions and its scope is beyond any previous MM methods.

(C) Conformational Analysis. In this section, we shall discuss the rotational potential functions and conformational energies. It is important to note that the comparison between experimental and theoretical data can only be made in a qualitative sense due to the lack of accurate and direct experimental data.

Ethylene (I). As for any molecular mechanics method, the experimental rotational barrier for ethylene (65 kcal/mol)[26] was fit in parametrization to derive the twofold torsional parameter.

Table VIII. Comparison of Different Methods ($\Delta H_f^\circ(g)$ kcal/mol)

methods[a]	no. of[b] compds examined	reported[c] mean dev, kcal/mol	present work mean dev on the same compd set
Dewar-de Llano	20	7.80	1.30
Dewar–Harget	19	6.80	1.20
Lo–Whitehead	17	2.32	1.20
MINDO/3	11	8.91	0.14
MNDO	12	3.09	0.13
MMPI76	65	1.34	1.10

[a] See ref 10 for references. [b] Comparisons are made for molecules which appear both in Table IV and in the appropriate reference. [c] New experimental values for biphenylene, azulene, and [18]annulene, listed in Table IV, are used to calculate mean deviations whenever it helps improving their reported deviations.

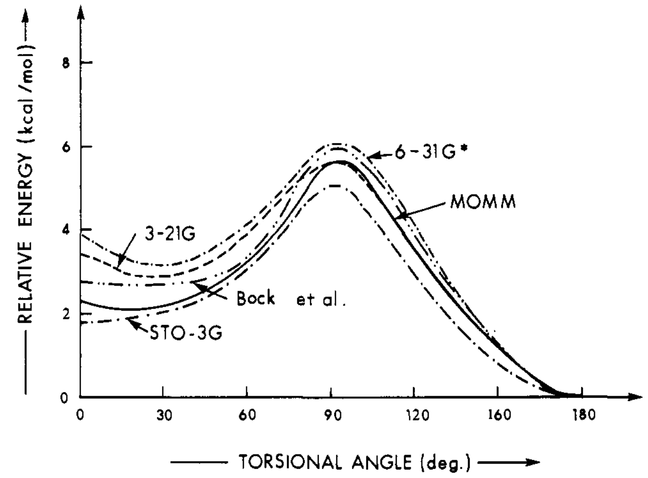


Figure 3. Rotational potential functions around the C–C single bond of butadiene.

The energy difference between planar and perpendicular forms is calculated to be 60 kcal/mol for the steric energy and 65 kcal/mol for the theoretical enthalpy. However, a point of interest is worthy of mentioning here, which distinguishes the MOMM force field from previous ones (such as MM1, MM2, and MMPI). According to MOMM, there is a substantial C–C bond lengthening (0.10 Å) in going from the planar to the perpendicular form of ethylene. No such size of bond elongation is predicted by previous MM methods. Bond elongation is expected in terms of the π bond disruption in going from planar to perpendicular forms and is also predicted by MO calculations (STO-3G, 0.08 Å; 4-31G, 0.07 Å).

1,3-Butadiene (II). 1,3-Butadiene is the simplest model for conjugated systems. The structure and conformational analysis of 1,3-butadiene has been the subject of many experimental and theoretical investigations.[27,28] The planar anti conformation has been shown to be the most stable form by almost all these studies. However, there has been a considerable disagreement as to whether the second stable conformation exists and if it is planar or not, i.e., an syn or a gauche (nonplanar syn). Shown in Figure 3 is the schematic potential curve about the C_{sp^2}–C_{sp^2} single bond of 1,3-butadiene derived from various approaches. After an extensive analysis and evaluation of the existing experimental and theoretical data, Bock et al.[27] proposed a potential curve that had a second minimum (gauche) at ca. 30° and a gauche-trans energy difference of 2.7 kcal/mol. The barrier at syn was estimated to be 0.1 kcal/mol while the barrier between anti and gauche was about 6.0 kcal/mol at 97°. The recent extensive ab initio calculations[29,30] with structural optimizations agree quite well with their potential curve. As can be seen from Figure 3, these potential curves are reasonably reproduced by MOMM calculations. The anti–syn energy difference obtained from MOMM is 2.3 kcal/mol, which is lower than most of the ab initio calculations but is in agreement with the experimental value of 2.5 kcal/mol.

2-Methyl-1,3-butadiene (XXXVI) and 2,3-Dimethyl-1,3-butadiene (XXXVII). Relatively less experimental and theoretical data have been reported for structural and conformational investigations on 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene.[30,31] However, it is suggested that there are two stable conformations, anti and gauche, for each molecule and their conformational characteristics are very similar to those for their parent molecule, 1,3-butadiene. The minor yet significant differences come from the steric repulsions in the planar forms which are larger in the syn C=C—C=C conformation than the anti form. These steric repulsions in the planar form effectively increase the relative stability of a gauche with respect to the syn and increase the syn–anti energy difference. the calculated relative energies for syn, gauche, and anti are respectively 2.5, 1.8, and 0.0 kcal/mol for 2-methyl-1,3-butadiene and 2.7, 0.7, and 0.0 kcal/mol for 2,3-dimethyl-1,3-butadiene. A similar trend and yet larger relative energies were predicted by ab initio calculations.[30] The torsional angle for the stable gauche form is calculated by MOMM to be 46 and 37° respectively for 2-methyl-1,3-budiene and 2,3-dimethyl-1,3-butadiene, which is in good agreement with ab initio results.

1,3-Cyclohexadiene (V). A semiquantitative estimate of the degree of nonplanarity in 1,3-cyclohexadiene was made by Butcher[32] from an analysis of the ground vibrational state rotational constants. A torsional angle of 17.5 ± 2° for C=C—C=C was deduced from his study and confirmed by pertinent electron diffraction structures.[33] Our calculated value is 17° and the energy difference between planar and nonplanar π conformation is 2.2 kcal/mol which is comparable with the experimental value[34] of 3.1 kcal/mol. In our opinion, the experimental value appears too high for such a small (17°) difference in torsional angle.

1,3,5-Cyclcoheptatriene (VI). Traetteberg[35] found 1,3,5-cycloheptatriene to be nonplanar by the electron diffraction method. The low-temperature NMR studies[36] of 1,3,5-cycloheptatriene have been interpreted in terms of rapidly interconverting chair forms with an activation energy of 5.7–6.3 kcal/mol. Recent STO-3G calculations[37] with structural optimizations (within 0.2 kcal/mol) indicate the planar form is indeed a transition state, which is 5.1 kcal/mol higher in energy than the boat. Single point calculations with STO-3G optimized geometry and different levels of theory further increase the inversion barrier.[37] We calculate the nonplanar (boat) form to be more stable than the planar form by 4.0 kcal/mol. The calculated dipole moment is 0.30 D, which is in good agreement with the microwave value, 0.25 D.[38] Our calculated planar and boat structures agree with STO-3G results within 3° for both bond and torsional angles.

1,3-Cycloheptadiene (XXXVIII). Conflicting conclusions have been published concerning the conformation of 1,3-cycloheptadiene. Gas-phase electron-diffraction studies indicated that the C_s form with six carbons coplanar fits the data better than any of a variety of other planar and nonplanar structures. On the other hand, Crews,[40] studying the NMR coupling constants of the C_2 and C_3 protons, concluded that the C_2–C_3 bond was twisted about 20°. Our current force field calculates that the C_s

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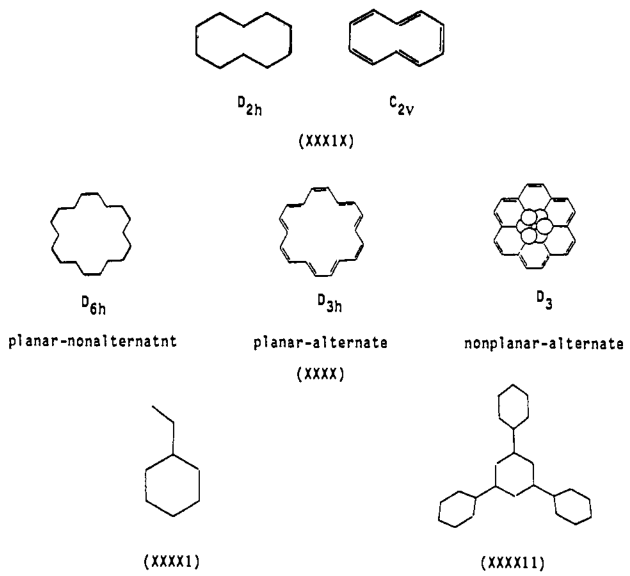
Chart VI



form is more stable than the C_2 form by 1.1 kcal/mol, which is in agreement with the electron diffraction data and MMP2 calculations. Details of our calculated structures for the C_s conformation are shown in Table III. Furthermore, we predict that 1,3-cycloheptadiene can undergo a wide pseudorotational motion *around* the C_s form. This can be demonstrated by calculating the energy of a C_1-symmetry form (through restricting C_2, C_3, C_4, C_5, and C_6 atoms on the same plane). The C_1 form with a 27° dihedral angle along the C_2–C_3 bond is only 0.5 kcal/mol less stable than the C_s form. Thus, experimental data are probably best interpreted as a wide amplitude motion around the C_s form.

Cyclooctatetraene (VIII). The ring inversion of cyclooctatetraene was examined by low-temperature NMR and the ring inversion barrier was found to be 13.7 kcal/mol. We found the tub favored over the planar form by 14.5 kcal/mol.

[10]Annulene (XXXIX) and [18]Annulene (XXXX). Both [10]annulene and [18]annulene have been the focus of annulene chemistry, because of the interest in the aromaticity and the demarcation point between bond alternation and equilization. MO calculations on the basis of single determinant Hartree–Fock theory predict bond alternations for both molecules.[43,44] However, these calculations are not definite and may be wrong since it has been shown[44,45] that electron correlation greatly favors the bond-equalized structure over the bond-alternate configuration for several compounds. Thus, it is interesting to check whether MOMM can correctly account for electron correlation.

For [10]annulene, MOMM calculations show that the planar bond equalized structure is more stable than the planar bond-alternate structure and the results are in agreement with ab initio results which take correlation energy into proper consideration. Three conformations of [18]annulene have been examined in this work. The nonplanar-alternant structure (D_3) is calculated to be favored over the planar-alternate (D_{3h}) and planar-nonalternate (D_{6h}) conformations by ca. 4 kcal/mol each. Although calculations do not show the D_{6h} form to be the most stable, the maximum bond variation in the D_3 form is only 0.06 Å which is comparable to the experimental[46] value of 0.04 Å. Previous MM calculations show a much larger bond alternation (0.11 Å) for the D_3 form. The MOMM calculated $\Delta H_f°$ for [18]annulene, 131 kcal/mol, is in agreement with the experimental value, 124 ± 6 kcal/mol.

Styrene (XXXXI). Styrene and its derivatives have been the subject of considerable attention because of its important role as a polymerizing monomer. We calculate that the potential function around the planar form is extremely shallow and a gauche conformation with a torsional angle of ca. 16° is the most stable which is only 0.03 kcal/mol lower in energy than the planar conformation. The calculated barrier height at the perpendicular form around the bond between phenyl and olefin groups is 3.2 kcal/mol, in good agreement with experimental estimates of 1.8–3.3 kcal/mol.[47]

Biphenyl (XIV). The gas-phase value[48] for the torsional angle about the central bond of biphenyl is 42 ± 5° and the MOMM calculated value is 38°. The experimental value corresponds to the mean value according to Boltzman distribution while the calculated one corresponds to the potential minimum. Various theoretical estimates of the barrier heights have been reported with the values spanning quite a range of 1.2–4.8 kcal/mol at the planar form and 2.0–4.5 kcal/mol at the perpendicular form.[49] Our calculated barrier heights are 1.8 and 1.9 kcal/mol respectively at the planar and perpendicular forms.

1,3,5-Triphenylbenzene (XXXXII). Experimental investigations[50] have shown that 1,3,5-triphenylbenzene is nonplanar both in the crystal and in the gas phase. MOMM calculations show that the peripheral phenyl rings are twisted out of the plane of the central ring by 40° which is in agreement with the gas–phase value of 46 ± 5°.[50] The nonplanar form (C_3) is calculated to be 6.9 kcal/mol more stable than the planar conformation (C_{3h}), which is more than three times the barrier found in biphenyl.

***trans*-Stilbene (XVIII).** The gas-phase structure of *trans*-stilbene has been determined by the electron-diffraction method and found to be nonplanar and to possess C_2 symmetry.[51] The phenyl groups were found to be rotated 30 ± 15° about the C–Ph bonds in the gas phase and 5° in the crystal. Our calculations show that the central C=C bond is planar and phenyl groups are indeed twisted about the C–Ph bonds. However, the potential curve for energy vs. the dihedral angle is very shallow and the energy minimum is somewhere around 15°. The calculated energy barrier at the planar form (C_2) is only 0.2 kcal/mol, which is comparable with the one found in styrene.

***cis*-Stilbene (XIX).** The *cis*-stilbene molecule is shown experimentally[52] by the electron-diffraction method to possess C_2 symmetry and may be described as having a propeller-like conformation with phenyl groups rotated ca. 43° about the C–Ph bonds. Our calculated structure is in good agreement with the experimental one except for the magnitude of the torsional angles. However, a twist along the central double bond and the distortion of phenyl rings were not considered in the diffraction study. We note that the sum of the dihedral angles calculated by us (Ph-b and aba′, see Table III, 35.5 and 6.9°, respectively) gives a value close to that reported for the dihedral angle for Ph—C=C—Ph (43.2°). The steric strain in the molecule is also revealed by large valence angles at the central carbon–carbon bond (C—C=C: 129.5° (exptl); 126.3° (calcd)). As can be seen from a model, a planar *cis*-stilbene is extremely crowded because a pair of hydrogen atoms is closer than 2.0 Å. The calculated energy difference between planar (C_{2v}) and nonplanar conformations is 15.7 kcal/mol.

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1,2-Diphenylcyclopentene (XXVII). The most stable conformations of 1,2-diphenylcyclopentene are calculated to be those with nonplanar π systems, which are consistent with experiment.[53] The agreement in dihedral angle is good for the distortion of the ethylenic double bond.

Tetraphenylethylene (XXIX). A comparison of the low-temperature X-ray crystal structure (−160 °C)[54] and our calculated results is shown in Table III, and the agreement is excellent. Owing to the strain in the molecule, the C–Ph bond is longer than expected (calcd 1.496 Å; exptl 1.496 Å). The angles of twist around the ethylenic double bond are small (exptl 8.4°; calcd 6.9°). The values of the angles around the atoms of the central bond (exptl ab = 122.2°, aa′ = 115.5°; calcd ab = 121.9°, aa′ = 116.1°) can be explained qualitatively by considering the repulsion between nonbonded atoms. The energy difference between conformations with the central bond planar and nonplanar is calculated to be only 0.2 kcal/mol.

Alkylbenzenes. Due to the high symmetry (which is sixfold), the barrier to internal rotation of the methyl group in toluene is extremely small (ca. 0.01 kcal/mol) both experimentally[55] and theoretically.

Many experimental and theoretical investigations have been reported on the conformational analysis of ethylbenzene, but their conclusions conflict. The recent low-resolution microwave studies of substituted ethylbenzenes concluded that the ethyl group in ethylbenzene has minimum energy in the perpendicular conformation.[56] This result confirms the conclusions of earlier reports (on electron diffraction, NMR, molecular polarizability, and molecular orbital studies) but contradicts the other reports (on NMR, Raman, and IR studies).[57] The experimental estimate of the rotational barrier around the C_{sp^2}–C_{sp^3} in ethylbenzene ranges from 1.2 to 2.3 kcal/mol. We calculate that the ethylbenzene exists in the orthogonal conformation and the ethyl rotation barrier is 1.0 kcal/mol at the planar form.

The electron-diffraction study[58] of isopropylbenzene indicated the existence of a *single* conformer having the methine hydrogen atom of the isopropyl group eclipsed with the ring. This stable conformation has recently been confirmed by the low-resolution microwave study.[56] The internal rotation barrier around the C_{sp^2}–C_{sp^3} bond is estimated to be 0.25 kcal/mol in the gas phase by low resolution microwave studies and 2.0 kcal/mol in the liquid phase[59] by NMR spin–spin coupling studies. The most stable conformation obtained from our calculations is in agreement with experimental data. The calculated barrier height (2.3 kcal/mol) at the conformation having the methine hydrogen atom of the isopropyl group orthogonal to the ring is in good agreement with the electron-diffraction and NMR data but does not agree well with the low-resolution microwave data.

Neutron-diffraction[60] studies of single crystals of hexamethylbenzene (XV) at 298 and 130 K indicate that the molecule has approximate D_{3d} symmetry. On the other hand, gas-phase electron-diffraction data[61] are interpreted to have the inner ring coplanar with the symmetry D_{6h} and the outer ring C atoms alternately deviating by 9.9 ± 1.8° from the plane of the inner ring. Therefore, the total symmetry point group for the carbon atoms is S_6. We calculate the nonplanar conformation S_6 with dihedral angles bab′ and aa′a″ being respectively 7.9 and 4.5° as the most stable form. Thus, our calculations suggest that there is a certain deformation inside the benzene ring itself although it is small, with the ring carbons being alternately 0.016 Å above and below the mean ring plane. However, this nonplanar inner ring form is only 0.4 kcal/mol more stable than the corresponding planar inner ring conformation (D_{6h}). The S_6 form is more stable than the C_{6h} conformation by 1.6 kcal/mol.

Triphenylene (XXI). The triphenylene structure has been determined by X-ray diffraction and it is shown to be significantly nonplanar by statistical tests on the deviations of the carbon atoms from the mean molecular plane.[62] Our calculations show that a nonplanar conformation with the dihedral angle of cec′ (see Table III) equal to 11° is preferred over the planar form by 0.1 kcal/mol. MOMM calculations show triphenylene is flexible and a small packing force is sufficient to distort the molecule.

3,4-Benzophenanthrene (XXIII). The structure of 3,4-benzophenathrene has been analyzed crystallographically and studied theoretically with the Coulson and Senent method.[63] The molecular structure was determined to be nonplanar with C_2 symmetry. We calculate the nonplanar C_2 conformation, with the dihedral angle cec′ (see Table III) about equal to 23° being preferred over the planar one by 6.0 kcal/mol. An estimate of 5–10 kcal/mol[63] for this energy difference was deduced from the experimental resonance energy.

4,8-Dihydrodibenzo[*cd,gh*]pentalene (XXVIII). X-ray studies have shown that 4,8-dihydrodibenzo[*cd,gh*]pentalene is planar (within 0.02 Å) although molecular models and the application of some empirical correlations between NMR coupling constants and dihedral angles suggest that it is cup shaped.[64] There is evidence from UV spectra[64] that it is planar in solution as well as in the crystalline state. Our calculation suggests that the most stable conformation of 4,8-dihydrodibenzo[*cd,gh*]pentalene is the planar form, even in the gas phase.

Corannulene (XXVI). Corannulene is of interest because of its strain and because of its unique electronic structure. The crystal structure has been shown by X-ray diffraction to be bowl shaped, as a result of strain.[65] As can be seen from Table III, the X-ray structure is quite similar to our calculated result. The planar form is calculated to be only 0.8 kcal/mol higher in energy than the planar form and, hence, corannulene is very flexible in the gas phase.

Conclusions

We have described in detail a new simulation technology, which effectively brings molecular mechanics and molecular orbital calculations together, to calculate molecular structures and energies. A multiple-stage, complimentary approach is used in order to make use of the strength of each individual method. A computer program, MOMM, has been developed for this purpose. The program allows the user to specify which portion of a molecule needs MO treatment. MO calculations are used to modify MM parameters and the geometry is then optimized under the derived force field. An iterative procedure is employed for this approach. In the current version, bond lengths, stretching constants, and torsional constants are expressed as simple functions of EH derived

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MO parameters. Shortcomings of MO problems for conformational analysis and for calculating heats of formation are not carried over here.

This type of simulation scheme is particularly valuable for large molecules since it is a fast and general method assuming that all the force constants are known. The method presented here has been extensively tested by examining a large, diverse group of conjugated hydrocarbons. Many systems which cannot be treated well by previous methods are handled satisfactorily by this method. The accuracy of the results is competitive with that of high-quality experimental work. The extension of this approach to conjugated systems containing heteroatoms will be described elsewhere.

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Methyl Group Dynamics from Relaxation of Double Quantum Filtered NMR Signals: Application to Deoxycholate

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Abstract: An experimental procedure and a theoretical analysis are developed for the extraction of cross-correlation spectral densities from proton NMR resonances of A_3 spin systems. The experiment involves observation of forbidden peak intensities of double quantum filtered one-dimensional spectra as a function of excitation time. When used in combination with T_1 and T_2 data sets, this experiment provides the additional information necessary to characterize multiple internal motions exhibited by groups which contain A_3 spin systems. These methods are applied to isolated methyl groups in micelles of deoxycholate (DOC). Results obtained from simultaneous fits of T_1, T_2, and forbidden peak intensities indicate that the methyls attached to the steroid nulceus are highly ordered, with internal rotations consistent with current micelle models. Prospects for qualitative characterization of internal motions from 2-D spectra are also assessed.

The potential for obtaining information on the structure and dynamics of macromolecular assemblies has advanced substantially over the past few years through the introduction of two-dimensional NMR methods. These methods have made it possible to extract cross-relaxation times from very complex proton NMR spectra. These cross-relaxation times, when converted to interproton distance constraints, form the basis for recent efforts in structure determination.[1,2] These experiments and the interpretation of resulting data are complicated, however, by the fact that protons on many of the more easily observed groups (for example, methyl groups) have interactions modulated by internal as well as overall molecular motion. In assemblies involving many molecules (for example, membrane systems), interactions among spins may also be modulated by both inter- and intramolecular motions. These complicating effects make it difficult to convert observed cross-relaxation times to useful distance information or motional parameters. The idea that some of these complicating factors could be separated on the basis of data available in existing or slightly modified 2-D NMR experiments is an appealing one and is a principal motivation for this study.

Recently, Muller et al. reported on the appearance of forbidden cross-peaks in ^1H multiple quantum filtered correlation spectroscopy and multiple quantum NMR.[3] Typically n quantum filtered spectra consist of peaks associated with spins having resolved scalar couplings to at least $(n - 1)$ equivalent or nonequivalent spins.[4] A simple example where "forbidden" peaks arise in such spectra is in the case of a methyl group connected to a tertiary carbon. In this case, the methyl group forms an A_3 spin system. On the basis of a simple theoretical formalism for multipulse experiments, the single resonance associated with this system should be removed by a multiple quantum filter. Multiple quantum peaks associated with degenerate spin systems of this type do, however, appear in spectra of macromolecules.[3,5,6] While these cross-peaks may complicate interpretation of two-dimensional (2-D) NMR data sets for the purpose of spectral assignment, we believe that their appearance can provide useful information on the motional properties of the participating spins, and ultimately structural properties of the parent molecule. This is due to the fact that the appearance of such forbidden peaks is a direct consequence of cross-correlation effects between pairs of spins.

Previous studies, pioneered by the Volds and co-workers[7,8] and Grant and co-workers[9] have shown cross-correlation spectral density terms to be extremely useful in the extraction of dynamic properties of spin systems. Most spin systems considered to date have been heteronuclear AX_2 or AX_3 systems involving either ^{13}C[7,8] or ^{19}F[10] and ^1H. However, homonuclear cases are quite analogous. Methods of extracting cross-correlation spectral density terms from ^{13}C or ^{19}F spectra have been based largely on fitting T_1 and T_2 relaxation data. Recently, however, Bendall and coworkers have identified cross-correlation effects in methyl groups using polarization transfer sequences such as DEPT and INEPT,[11] while Brondeau and co-workers have developed elegant heteronuclear multipulse schemes to determine cross-correlation spectral density terms for $^{13}CH_2$ groups.[12] A potential drawback of these methods is that they require isotopic enrichment which may prove

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