Conformational Analysis. 122. Heats of Formation of Conjugated Hydrocarbons by the Force Field Method[1,2]

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Abstract: A scheme for the calculation of the heats of formation of conjugated hydrocarbons (gas phase, 25 °C) has been developed, which begins with geometries obtained by molecular mechanics calculations. The energies of the σ part of the molecule (from molecular mechanics) and from the π part (from an SCF π calculation) are summed to yield the heat of formation. The method is applicable to planar and nonplanar systems of a wide variety of structural types. The average deviation from experiment obtained was 1.34 kcal/mol for a representative group of 65 compounds. This method is far superior in both generality and in accuracy to any previously published competitive calculational scheme.

Although the Pariser–Parr–Pople self-consistent-field molecular-orbital (PPP–SCF–MO) theory of π electron systems[3] has been successfully applied to the prediction of electronic transition energies,[3,4] comparatively few applications of the method have been made to ground state properties. Past calculations of the heats of atomization $\Delta H_a{}^\circ$ or heats of formation $(\Delta H_f{}^\circ)$ of conjugated systems have been especially few. Chung and Dewar[5] were the first to develop an SCF–MO treatment for the ground state properties of conjugated hydrocarbons, and this was later modified to some extent.[6] Lo and Whitehead[7] and Lorquet[8] employed different parameter schemes within their SCF–MO treatments and achieved results for hydrocarbons comparable in accuracy to those obtained by Dewar and co-workers. Two major handicaps of the PPP–SCF–MO method were evident from this work; namely the limitation of the method to planar structures, and its inability to allow for strain and nonbonded interactions. It is surprising that no extensive systematic application of the method including strain and nonbonded interactions has yet been reported.[9] Recent applications of SCF methods to the calculation of heats of formation have been mainly of the all valence electron (MINDO) type.[4,10]

The force field method has been widely examined and has proved to be a good method to calculate geometries, steric energies, and heats of formation $(\Delta H_f{}^\circ)$ for localized molecules.[11] However, there are only two full-scale attempts at grappling with the problem of the use of force field calculations to determine the structures of delocalized molecules that have been reported. Both the Karplus–Warshel[12] and our[11,13] methods for delocalized molecules work pretty well. The approaches are slightly different, and each has certain advantages. The Karplus and Warshel calculations also give $\Delta H_f{}^\circ$ directly, and these seem good, although the number of compounds so far studied has been small. Our method does not give

this information directly, although it seemed likely that procedures for obtaining it could be developed.

Chemists have for years tried to develop correlation schemes which permit one to calculate $\Delta H_f{}^\circ$ from molecular structures.[14] However, most previous schemes are quite limited, especially when they are applied to delocalized systems. Therefore, from the thermochemical and theoretical viewpoint, a *general* and *accurate* method to calculate heats of formation of delocalized systems is now called for.

The present work represents an attempt to develop a general scheme to calculate $\Delta H_f{}^\circ$ of a conjugated molecule by using the force field method in combination with the π SCF method. The ground-state geometry and steric energy are first calculated by the force field program according to a standard recipe.[15] These values are then used as an input into a SCF–MO method[17] to calculate $\Delta H_f{}^\circ$. A computer subroutine for this purpose has been written.[16]

Theoretical Approach

Geometries. The equilibrium geometries for the delocalized hydrocarbons were calculated using the 1973 force field method,[13] which is believed to give results as good as or better than any other method now existing. The procedure is basically as follows. If the unsaturated system is planar, the initial molecular geometry is calculated, and all force field parameters not dependent on the π-system bond orders are assigned from the input data. A variable-electronegativity self-consistent-field (VESCF)[18] calculation is then undertaken on the π system to obtain the bond orders which are used to assign stretching and torsional parameters. If the unsaturated system is nonplanar, an extra hypothetically planar VESCF calculation is necessary to account for the π-bond disruption as rotation occurs about the bond. The natural bond length, l_0, required by the force

field is obtained from the linear relationship[19]

$$l_0 = 1.512 - 0.179p_{ij} \qquad (1)$$

where p_{ij} is the calculated VESCF bond order. The stretching force constants, k_s, for conjugated bonds are calculated by

$$k_s = 5.0 + 4.6p_{ij} \qquad (2)$$

The two-fold torsional constant, V_2, across a double bond is used to measure the π-bond disruption as rotation occurs about the bond. The twofold torsional constants are written as follows:

$$V_{2ij} = 16.25 \times f \times p_{ij}\beta_{ij}{}^0 \text{ kcal/mol} \qquad (3)$$

where V_{2ij} is the twofold torsional constant across bond i–j, and $p_{ij}\beta_{ij}{}^0$ is the product of bond order and resonance integral (β) across bond i–j in the corresponding π-planar conformation. For planar unsaturated systems f is unity.

$$f = \frac{\sum\limits_{i<j} (p_{ij}\beta_{ij}{}^0 - p_{ij}\beta_{ij}(\text{real}))}{\sum\limits_{i<j} p_{ij}\beta_{ij}{}^0(1 - \cos \omega_{ij})} \qquad (4)$$

For nonplanar unsaturated structures where the sum is over all π-bonds, $p_{ij}\beta_{ij}(\text{real})$ is the $p\beta$ product across bond i–j in the real (distorted) π system and ω_{ij} is the dihedral angle across bond i–j. The numerator is the net change in π energy as the molecule goes from the planar to distorted geometry and the denominator is the second-order torsional functions estimation of this same quantity, according to our mechanical model.[13,20] Note also that the resonance integral (β) in eq 3 and 4 is measured by taking the resonance integral of ethylene as unity.

The steric energy is then minimized with respect to geometry using a modified Newton–Raphson scheme. If the geometry has been significantly changed during the minimization step, the VESCF calculations are repeated and the new bond orders are used to assign new stretching and torsional parameters. The minimization–VESCF cycle is repeated until total self-consistency is reached.

Most of the force field and attendant parameters developed in earlier works[20] carry over here. However, certain changes of several parameters adopted previously are necessary to best fit the observed heats of formation. As will be seen later, the present parameterization also gives bond lengths and angles in slightly better agreement with experimental values than those earlier reported.[21]

Heat of Formation. According to our previously described molecular mechanics model,[11] the heat of formation ($\Delta H_f{}^\circ$) is calculated by the equation

$$\Delta H_f{}^\circ = E_s + \Delta H_{\text{bond}} + \Delta H_{\text{str}} + \text{PFC} \qquad (5)$$

where E_s is the steric energy of the molecule calculated by our program, ΔH_{bond} is the sum of the bond enthalpy contributions, ΔH_{str} is the sum of the structural enthalpy contributions, and PFC is the partition function contribution. Following the same logic, we may express the heat of atomization ($\Delta H_a{}^\circ$) by

$$\Delta H_a{}^\circ = E_s + E_{\text{bond}} + E_{\text{str}} + \text{PFC} \qquad (6)$$

where E_{bond} is the sum of the bond energy contributions and E_{str} is the sum of the structural energy contributions.

$\Delta H_f{}^\circ$ can be calculated from $\Delta H_a{}^\circ$ by the definition of $\Delta H_f{}^\circ$,

$$\Delta H_f{}^\circ = 170.90N_C + 52.10N_H - \Delta H_a{}^\circ \qquad (7)$$

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 7 are the conversion factors from $\Delta H_a{}^\circ$ to $\Delta H_f{}^\circ$. 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,

$$E_{\text{bond}} = E_{\text{conj}} + E_{\text{nconj}} \qquad (8)$$

E_{conj} represents the energy contribution from the conjugated bonds of the molecule, which may be written as the sum of two separate terms:

$$E_{\text{conj}} = \sum (E_{\sigma b}{}^{C=C} + E_{\pi b}{}^{C=C})$$
$$= \sum E_b{}^{C=C} \text{ (for hydrocarbons)} \qquad (9)$$

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 ($E_b{}^{C=C}$).

There are three reasonably successful SCF methods to calculate $\sum E_b{}^{C=C}$ in the literature. Each differs from the other mainly in the means chosen to calculate the resonance integral (β_{ij}). Dewar et al. were the first to employ the thermocycle method successfully to calculate the ground state properties of conjugated molecules.[5,6,22] However, the logic behind the thermocycle method seems quite obscure when it is applied to conjugated systems with atoms triply linked.[7] In 1968, Lo and Whitehead[7] developed a different way to calculate β_{ij}, which is totally based on experimental observables, and they achieved results for hydrocarbons comparable in accuracy to those obtained by the thermocycle method. In 1970, Dewar and Harget[6] adopted the much simpler Mulliken expression to evaluate β_{ij}, because this was found to give similar results to those achieved by the thermocycle method. As far as accuracy is concerned, there is really not much difference between Lo–Whitehead and Dewar–Harget calculations. We decided to calculate $\sum E_b{}^{C=C}$ by the Lo–Whitehead procedure due to its simplicity.

The basic principles of the Lo–Whitehead procedure are summarized as follows. Using PPP–SCF–MO theory, the total π bond energy, $E_{\pi b}{}^t$ ($\sum E_{\pi b}{}^{C=C}$, here), is given by

$$E_{\pi b}{}^t = -\left\{ \sum_i \frac{P_{ii}{}^2}{4} ii + 2 \sum_{i<j} P_{ij}\beta_{ij} \right.$$
$$\left. + \sum_{i<j} ((P_{ii} - 1)(P_{jj} - 1) - \tfrac{1}{2} P_{ij}{}^2))\gamma_{ij} \right\} \qquad (10)$$

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:

$$E_b{}^{C=C} = E_c{}^{C=C} \{2 \exp[-a(R_{ij} - R_c)]$$
$$- \exp[-2a(R_{ij} - R_c)]\} \qquad (11)$$
$$a = \sqrt{k_c/2E_c{}^{C=C}}$$

where $E_c{}^{C=C}$ is the equilibrium bond energy, k_c is the force constant, and R_c is the equilibrium bond length. Lo and Whitehead chose ethylene and benzene as their key molecules to parameterize eq 11, since k_c and R_c for these two molecules are well-known experimental observables. By substituting these experimental quantities into eq 11 and simplifying eq 10 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 9 semiempirically.[23] Although we follow the Lo–Whitehead procedure, parameters in eq 11 have been chosen differently in order to get a better overall fit of $\Delta H_a{}^\circ$. The parameters used are shown in Table

Table I. Parameters Used in Morse Potential Function

	$E_c^{C=C}$, kcal/mol	R_c,[a] Å	k_c,[b] dyn/cm	$a = k_c/ (2E_c^{C=C})^{1/2}$, Å^{-1}
Ethylene	129.37	1.338	9.6×10^5	2.309
Benzene	117.58	1.397	7.6×10^5	2.142

[a] Calculated value. [b] G. Herzberg, "Molecular Spectra and Molecular Structure", Van Nostrand, Princeton, N.J., 1945, p 193; R. C. Lord and D. H. Andrews, *J. Phys. Chem.*, **41**, 149 (1937).

Table II. Values of Bond and Structure Energies

Term[a]	Value, kcal/mol
$C_{sp^2}-H$	103.00
$C_{sp^3}-H$	99.30
$C_{sp^2}-C_{sp^3}$	88.88
$C_{sp^3}-C_{sp^3}$	83.07
	−4.06
	2.80
	6.64
	−0.20
C−methyl	−1.35

[a]Where carbon hybridization is not specified, the parameters apply to both C_{sp^3} and C_{sp^2}.

I. 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,[24] namely,

$$E_{nconj} = E_{C_{sp^2}-H} + E_{C_{sp^3}-H} + E_{C_{sp^2}-C_{sp^3}} + E_{C_{sp^3}-C_{sp^3}} \quad (12)$$

where terms on the right-hand side of eq 12 are constant bond energies for the specified bond type. Values of these parameters along with E_{str} parameters are shown in Table II. All of these parameters were adjusted in the current work.

As mentioned before, E_s is the steric energy of the molecule calculated by our program. Precautions are needed since some steric energies of the molecule are implicitly absorbed in the MO calculation. Thus, the stretching energies of the $C_{sp^2}-C_{sp^2}$ type should not be included in E_s again since these are accounted for in individual $E_{\pi b}^{C=C}$ calculations. As is shown later, the inclusion of E_s in the calculation of ΔH_f° conquers the two main limitations of the standard π approximation, namely its limitations to planar and strainless structures.
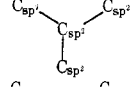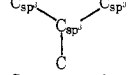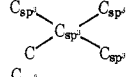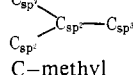
Results and Discussion

Geometries. The calculated and experimental values for bond lengths, dihedral angles, and key bond angles of 30 various hydrocarbons are listed in Table III. Also listed are the average errors in the experimental data as given by the respective investigators, together with the average differences between the experimental values and the values calculated herein. The set of molecules in Table III consists of a good cross-section of conjugated hydrocarbons: aromatic and nonaromatic, and both highly strained and strainless molecules, planar and nonplanar.

Looking first at bond lengths, the average mean difference between the experimental and calculated value is ±0.007 Å, the same as the average experimental error. Only two bonds of 3,4-benzophenanthrene, three of tetracene, one of azulene, one of perylene, one of biphenylene, and two of 4,8-dihydrodibenzo[cd,gh]pentalene, a total of ten bonds, show a deviation significantly larger than the probable experimental error (0.02 Å).

As can be seen in Table III, five out of ten bonds with |Exptl − Calcd| larger than 0.02 Å appear to be over estimated. An examination of the available neutron and x-ray diffraction data[25] suggests the possibility that bond lengths in bonds of high order are experimentally underestimated. Herndon[26] proposed that a shortening effect exists in such an X-ray experiment which should be an approximately linear function of bond order.

Anomalous long bonds are found in bond f of azulene, bond g of tetracene, bond e of 4,8-dihydrodibenzo[cd,gh]pentalene, and bond d of biphenylene. It is possible that these bridged bonds have not been treated well within the force field model, or that the linear bond order–bond length assumption of eq 1 is inaccurate for these cases. However, we think it probable that experimental redeterminations of these structures might re-

solve many of the discrepancies. One notes that many of the supposed anomalies in theoretical predictions have vanished when more accurate experimental data have become available.[13,26] For example, bonds a and h in phenanthrene formally were given as 1.457 and 1.390 Å, respectively,[27] and these values were always troublesome to theoreticians. Bond f in pyrene was always calculated to be 0.02 to 0.03 Å larger than the old experimental value.[28] The currently accepted values agree well with the earlier theoretical predictions. In *trans*-stilbene, the room-temperature x-ray study[29,30] gave a rather short bond length for the central bond (1.318 Å), apparently due to crystal disorder. More recently, both an electron diffraction study[31] and a low-temperature (−160 °C) x-ray determination[30] give longer bond lengths, which are respectively 1.329 ± 0.014 and 1.338 Å. Both recent experimental results are in better agreement with our calculations.

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.

The synthesis of dibenzo[cd,gh]pentalene is of current interest because it is assumed to be an unusually good model for the planar [12]annulene with minimum bond alteration to test the concept of antiaromaticity.[32] The synthetic challenge of this molecule lies in its high strain energy. Our calculated structure for dibenzo[cd,gh]pentalene is included in Table III. From the calculated resonance energy, we suggest the molecule is antiaromatic.[33]

Heats of Formation. Most of the conjugated hydrocarbons for which the $\Delta H_f^\circ(g)$ values are experimentally known were examined in the present work. Table IV lists the experimental and calculated $\Delta H_f^\circ(g)$, differences between experimental and calculated $\Delta H_f^\circ(g)$, as well as the quoted probable experimental errors. It might be noted that while experimental errors in ΔH_f° are typically reported of 0.3–1.0 kcal/mol, results on the same compounds from different laboratories often differ from one another by much more than this. As an extreme example, two attempts to obtain experimentally $\Delta H_f^\circ(g)$ for [18]annulene have been published so far. One determination is based on measurements of the heat of combustion.[34] The reported value is 67 ± 6 kcal/mol. These data seem questionable, since [18]annulene is so sensitive to oxygen that it could

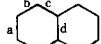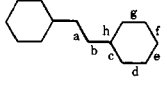Table III. Experimental and Calculated Geometries (in Å or deg)
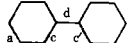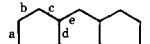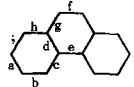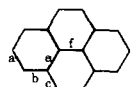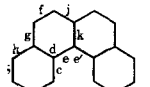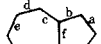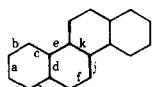
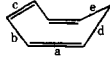| Compd	Bond or angle	Exptl	Calcd	Exptl − Calcd
Ethylene (1965)[a]	a	1.337 ± 0.001	1.338	−0.001 ± 0.001
trans-Butadiene (1966)[b]	a	1.344	1.346	−0.002
	b	1.467 ± 0.002	1.471	−0.004 ± 0.003
	ab	122.9 ± 0.5	122.5	0.4 ± 0.5
Benzene (1976)[c]	a	1.399 ± 0.001	1.397	+0.002
				+0.002
Naphthalene (1961)[d]	a	1.412	1.420	−0.008
	b	1.371	1.377	−0.006
	c	1.422	1.427	−0.005
	d	1.420 ± 0.008	1.412	−0.008 ± 0.007
trans-Stilbene (1975)[e]	a	1.338	1.351	−0.013
	b	1.473	1.477	−0.004
	c	1.406	1.407	−0.001
	d	1.393	1.395	−0.002
	e	1.393	1.397	−0.004
	f	1.391	1.397	−0.006
	g	1.390	1.397	−0.007
	h	1.402	1.405	−0.003 ± 0.004
	abc	5.2	25.0	−19.8
Biphenyl (1958)[f]	a	1.400	1.397	0.003
	b	1.400	1.397	0.003
	c	1.400	1.403	−0.003
	d	1.490	1.491	−0.002 ± 0.003
	cdc'		40.2	
Anthracene (1964)[g]	a	1.418	1.430	−0.012
	b	1.375	1.369	0.006
	c	1.444	1.439	0.005
	d	1.433	1.424	0.009
	e	1.405 ± 0.008	1.405	−0.000 ± 0.005
Phenanthrene (1971)[h]	a	1.394	1.408	−0.014
	b	1.401	1.386	0.015
	c	1.409	1.419	−0.010
	d	1.420	1.412	0.008
	e	1.465	1.460	0.005
	f	1.350	1.361	−0.009
	g	1.453	1.444	0.009
	h	1.423	1.418	0.005
	i	1.386 ± 0.008	1.383	0.003 ± 0.005
Pyrene (1972)[i]	a	1.395	1.396	−0.001
	b	1.406	1.405	0.001
	c	1.438	1.448	−0.010
	d	1.367	1.361	0.006
	e	1.425	1.416	0.009
	f	1.430 ± 0.004	1.433	−0.003 ± 0.005
3,4-Benzophenanthrene (1963)[j]	a	1.409	1.412	−0.003
	b	1.378	1.382	−0.004
	c	1.433	1.421	0.012
	d	1.431	1.412	0.019
	e	1.446	1.450	0.004
	f	1.342	1.366	−0.024
	g	1.443	1.437	0.006
	h	1.391	1.420	−0.029
	i	1.374	1.381	−0.007
	j	1.430	1.437	−0.007
	k	1.412 ± 0.010	1.399	0.013 ± 0.011
	cee'		24.9	
Azulene (1966)[k]	a	1.399	1.401	−0.002
	b	1.418	1.408	0.010
	c	1.383	1.400	−0.017
	d	1.406	1.398	0.008
	e	1.403	1.401	+0.002
	f	1.501 ± 0.011	1.471	0.030 ± 0.010
Chrysene (1960)[l]	a	1.394	1.412	−0.018
	b	1.381	1.383	−0.002
	c	1.409	1.425	−0.016
	d	1.407	1.411	−0.004
	e	1.468	1.455	0.013
	f	1.369	1.366	0.003
	g	1.421	1.434	−0.013
	h	1.428	1.422	0.006
	i	1.363	1.379	−0.016
	j	1.428	1.439	−0.011
	k	1.401 ± 0.010	1.406	−0.005 ± 0.010

Table III (Continued)
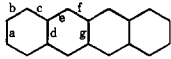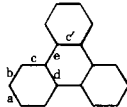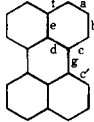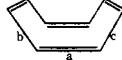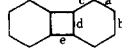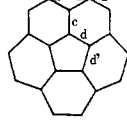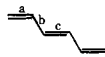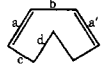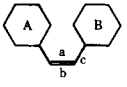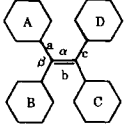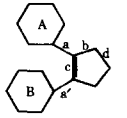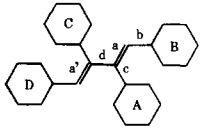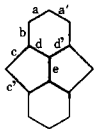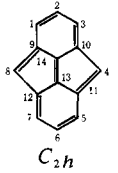
Compd	Bond or angle	Exptl	Calcd	Exptl − Calcd
Tetracene (1961)[m]	a	1.459	1.435	0.024
	b	1.381	1.366	0.015
	c	1.420	1.443	−0.023
	d	1.420	1.431	−0.011
	e	1.390	1.395	−0.005
	f	1.404	1.417	−0.013
	g	1.460 ± 0.010	1.427	0.033 ± 0.015
Triphenylene (1974)[n]	a	1.397	1.402	−0.005
	b	1.381	1.389	−0.008
	c	1.410	1.415	−0.005
	d	1.413	1.412	0.001
	e	1.458 ± 0.006	1.466	−0.008 ± 0.005
	cec'		32.1	
Perylene (1964)[o]	a	1.370	1.375	−0.005
	b	1.418	1.416	0.002
	c	1.397	1.390	0.007
	d	1.425	1.432	−0.007
	e	1.424	1.415	0.009
	f	1.400	1.425	−0.025
	g	1.471 ± 0.004	1.476	−0.005 ± 0.009
	cgc'		14.7	
1,3,5-Cycloheptatriene (1964)[p]	a	1.356	1.348	0.008
	b	1.446	1.462	−0.016
	c		1.355	
	d	1.505 ± 0.006	1.502	0.003 ± 0.008
	ab	127.2	124.1	3.1
	bc	119.8	125.7	−5.9
	ad	121.8	121.6	0.2
	de		111.5	
Cyclooctatetraene (1972)[q]	a	1.340	1.341	−0.001
	b	1.475 ± 0.007	1.482	−0.009 ± 0.005
	ab	126.1 ± 0.5	125.4	0.7 ± 0.7
Cyclopentadiene (1965)[r]	a	1.509	1.511	−0.003
	b	1.342	1.344	−0.003
	c	1.469 ± 0.002	1.475	−0.010 ± 0.004
	ab	109.3	110.0	0.7
	bc	109.4	108.8	0.6
	aa'	102.8	102.4	0.4
Dimethylfulvene (1970)[s]	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 ± 0.008	1.515	−0.005 ± 0.012
Biphenylene (1966)[t]	a	1.423	1.419	0.004
	b	1.385	1.392	−0.007
	c	1.372	1.371	0.001
	d	1.426	1.423	0.003
	e	1.514	1.482	0.032 ± 0.007
Corannulene (1976)[u]	a	1.402	1.392	0.010
	b	1.440	1.440	0.000
	c	1.391	1.397	−0.006
	d	1.413 ± 0.004	1.418	−0.005 ± 0.004
Hexatriene (1968)[v]	a	1.337	1.347	−0.010
	b	1.458	1.468	−0.010
	c	1.368 ± 0.003	1.355	0.013 ± 0.011
1,3-Cycloheptadiene (1972)[w]	a	1.347	1.346	0.001
	b	1.450	1.468	0.002
	c	1.509	1.504	0.005
	d	1.522 ± 0.015	1.527	−0.005 ± 0.004
	ab	129.1	130.4	−1.3
	ac	129.1	127.0	2.1
	aba'	0	0	0
1,3-Cyclohexadiene (1969)[x]	a	1.350	1.346	0.004
	b	1.468	1.469	−0.001
	c	1.523	1.507	0.016
	d	1.534 ± 0.012	1.534	0.000 ± 0.005
	ab	120.1	120.1	0.0
	ac	120.1	120.2	0.1
	cd	110.7	111.6	−0.9
	aba'	18.3	19.2	−0.9

Table III *(Continued)*

Compd	Bond or angle	Exptl	Calcd	Exptl – Calcd
cis-Stilbene (1975)[y]	C=C$_{av}$(A,B)	1.398	1.399	−0.001
	a	1.489	1.476	0.013
	b	1.334 ± 0.002	1.350	−0.016 ± 0.003
	abc		13.3	
	Ph−b	43.2	29.4	
	ab	129.5	126.5	3.0
Tetraphenylethylene (1975)[z]	C=C$_{av}$ (A,B,C,D)	1.394	1.398	−0.004
	a	1.496	1.487	0.009
	b	1.356 ± 0.003	1.360	−0.004 ± 0.005
	abc	8.4	9.0	−0.6
	Ph−b	47.8	42.8	5.0
	α	122.2	122.2	0.0
	β	115.5	115.5	0.0
1,2-Diphenylcyclopentene (1975)[aa]	C=C$_{av}$ (A,B)	1.379	1.398	−0.019
	a	1.478	1.479	−0.001
	b	1.510	1.513	−0.003
	c	1.339	1.351	−0.012
	d	1.525 ± 0.008	1.537	−0.012 ± 0.014
	Ph−c	45.7	30.5	15.2
	aca'	7.5	17.6	−10.1
cis,cis-1,2,3,4-Tetraphenyl-butadiene (1965)[bb]	C=C$_{av}$ (A,B,C,D)	1.405	1.399	0.006
	a	1.357	1.357	0.000
	b	1.477	1.480	−0.003
	c	1.518	1.503	0.015
	d	1.493 ± 0.010	1.482	0.011 ± 0.006
	Ph (A)−a	75	64.1	10.9
	Ph (B)−a	34	33.7	0.3
	bad	0	0	0
	ada'	0	0	0
4,8-Dihydrodibenzo[*cd,gh*]-pentalene (1971)[cc]	a	1.405	1.414	−0.009
	b	1.382	1.394	−0.012
	c	1.578	1.536	−0.042
	d	1.378	1.380	0.002
	e	1.392 ± 0.009	1.425	0.033 ± 0.015
	aa'	125.4	125.4	0.0
	ab	118.3	118.7	−0.4
	bc	142.3	143.0	−0.7
	bd	112.0	109.6	2.4
	cd	105.7	107.4	−1.7
	cc'	102.9	103.4	−0.5
	dd'	134.2	138.2	−4.0
	de	113.2	110.0	3.2
Hexamethylbenzene (1975)[dd]	a	1.417	1.406	0.011
	b	1.530 ± 0.003	1.518	0.012 ± 0.012
	bab'	9.9	9.9	0.0
	aa'a''		5.4	

	Type	Calcd, Å	Type	Calcd, deg
Dibenzo[*cd,gh*]pentalene			1−2−3	126.9
	1−2	1.408	2−3−10	118.7
	2−3	1.425	3−10−14	108.4
	1−9	1.419	3−10−4	146.9
	3−10	1.403	4−10−14	104.7
	10−14	1.407	9−14−10	139.3
	9−14	1.407	10−14−13	110.2
	4−10	1.442	9−14−13	110.5
	8−9	1.424	1−9−14	108.0
	13−14	1.362	8−9−14	105.5
			1−9−8	146.9
			2−1−9	118.7
			10−4−11	109.6

C_{2h}

[a] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, 42, 2683 (1965). [b] W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, 20, 1226 (1966). [c] K. Tamagawa, T. Iijima, and M. Kimura, *J. Mol. Struct.*, 30, 243 (1976). [d] O. Bastiansen and P. N. Skancke, *Adv. Chem. Phys.*, 3, 323 (1961). [e] A. Hoekstra, P. Meertens, and A. Vos, *Acta Crystallogr., Sect. B*, 31, 2813 (1975). [f] A. Almenningen and O. Bastiansen, *Skr., K. Nor. Vidensk. Selsk.*, No. 4, 1, (1958). [g] R. Mason, *Acta Crystallogr.*, 17, 547 (1964). [h] Average of x-ray and neutron diffraction data: M. I. Kay, Y. Okaya, and D. E. Cox, *Acta Crystallogr., Sect. B*, 27, 26 (1971). [i] A. C. Hazell, F. K. Larsen, and M. S. Lehmann, *ibid.*, 28, 2977 (1972). [j] F. L. Hirshfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963). [k] O. Bastiansen and J. L. Derissen, *Acta Chem. Scand.*, 20, 1319 (1966). [l] D. M. Burns and J. Iball, *Proc. R. Soc. London, Ser. A*, 257, 491 (1960). [m] R. B. Campbell, J. M. Robertson, and J. Trotter, *Acta Crystallogr.*, 15, 289 (1962). [n] Average of x-ray and neutron diffraction data: W. C. Herndon, *J. Am. Chem. Soc.*, 96, 7605 (1974). [o] A. Camerman and J. Trotter, *Proc. R. Soc. London, Ser. A*, 279, 129 (1964). [p] M. Traetteberg, *J. Am. Chem. Soc.*, 86, 4265 (1964). [q] J. Bordner, R. G. Parker, and R. H. Standford, Jr., *Acta Crystallogr., Sect. B*, 28, 1069 (1972). [r] G. Liebling and R. E. Marsh, *Acta Crystallogr.*, 19, 202 (1965). [s] J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, 92, 261 (1970). [t] J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, 20, 87 (1966). [u] J. C. Hanson and C. E. Nordman, *Acta Crystallogr., Sect. B*, 32, 1147 (1976). [v] M. Traetteberg, *Acta Chem. Scand.*, 22, 628 (1968). [w] K. Hagen and M. Traetteberg, *ibid.*, 26, 3643 (1972). [x] H. Oberhammer and S. Bauer, *J. Am. Chem. Soc.*, 91, 10 (1969). [y] M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.*, 26, 69 (1975). [z] A. Hoekstra and A. Vos, *Acta Crystallogr., Sect. B*, 31, 1716, 1722 (1975). [aa] J. Bernstein, *ibid.*, 31, 418 (1975). [bb] I. L. Karle and K. S. Dragonette, *Acta Crystallogr.*, 19, 500 (1965). [cc] B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *J. Am. Chem. Soc.*, 93, 7275 (1971). [dd] R. R. Karl, Jr., Y. C. Wang, and S. H. Bauer, *J. Mol. Struct.*, 25, 17 (1975).

well be partly oxidized in the bomb prior to combustion. The other determination is based on the thermal rearrangement study of [18]annulene in solution, which gives $\Delta H_f°(g) = 124 \pm 6$ kcal/mol.[35] The values differ by more than 57 kcal/mol, although the sum of the quoted errors is only 12 kcal/mol. Further examples can be found in Table IV. Experimental values cited in Table IV are mainly from the compilation of Cox and Pilcher.[36] Some new data, which may be more reliable, are also cited in Table IV. The deviation is taken as the difference between calculated and experimental values. If there is more than one experimental value available in Table IV, the one nearest to the calculated value was used in the calculation of the difference. As can be seen in Table IV, the calculated results are in fair to excellent agreement with experimental values. The average difference between experimental and calculated values for 65 compounds is ± 1.34 kcal/mol, which may be compared with the average estimated experimental error of ± 0.80 kcal/mol.

While the molecular mechanics scheme previously described for conjugated polyenes is applicable to a great variety of compounds, there are a few special cases where problems develop. This can be seen by looking at 1,3,5-cycloheptatriene as an example. If the molecule were planar, there would be a certain (relatively small) interaction between the p orbitals on C-1 and on C-6. As the molecule becomes nonplanar, these p orbitals tilt in toward one another, and the overlap increases, and the bonding character between them increases. In the molecular mechanics calculations, the stretching force constant and natural bond length are functions of bond order, but only between bonded atoms. Since these atoms are not formally bonded, the calculation does not take into account this increase in bonding character with bending. The result is that the nonplanar form has an extra stability from this bonding which is not accounted for in the calculations. The calculated heat of formation for 1,3,5-cycloheptatriene should also be in error, because of the additional stability from this bonding, which has not been taken into account.

If we look at the entries in Table IV, we see that the calculated heat of formation of cycloheptatriene is too positive by 1.29 kcal/mol. Similarly, the heat of formation of cyclooctatetraene is too positive by 1.80 kcal/mol. The barrier to inversion for cycloheptatriene is also too small by 2.5 kcal/mol. These numbers are all consistent with additional bonding amounting to 1 or 2 kcal/mol in these molecules, although the number is too small to confidently assign it to such a cause. Although it is possible to invent an ad hoc scheme for dealing with this kind of problem in a limited number of cases, we will not do so here. We wish at this time only to point out that a difficulty exists in cases of the sort described, and while the problem is significant, it does not seem to be extremely serious (Table IV), and so will be ignored for the time being.

There are molecules listed in Table IV for which the calculated values differ from the experimental ones by more than 2.0 kcal/mol. These are generally molecules for which the experimental measurements were done a long time ago, or where the reported experimental error is large, or where the experimental results are open to question. The heats of combustion of chrysene, 3,4-benzophenanthrene, and tetracene were measured more than 25 years ago when many modern techniques were not available. It is doubtful, even now, that we can 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. 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 $\Delta H_f°$ of tetracene seems too small when compared with those of isomeric compounds. The

unusual large deviation in the case of 4,5-dimethylphenanthrene is likely due to experimental error, since we can get a rather good fit for 1',9-dimethyl-1,2-benzanthracene, and both 4,5-dimethylphenanthrene and 1',9-dimethyl-1,2-benzanthracene are structurally similar. Rather large deviations for pyrene, acenaphthane, [2.2]-paracyclophane, 1,2,4,5-tetrahydronaphthalene, and fluoranthene cannot be rationalized but the rather good fit in similar compounds in Table IV leads one to suspect that the experimental results may be inaccurate. One notes that the experimental $\Delta H_f°$ of pyrene has been always troublesome to theoreticians since the predicted values are reasonably (5–10 kcal/mol) larger than the reported experimental value.

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

Our predicted values for the heats of formation of dibenzo[cd,gh]pentalene, 4,8-dihydrodibenzo[cd,gh]pentalene, 1,2-diphenylcyclopentene, paracene, dibenzo[b,f]cycloheptatriene, dimethyldibenzo[b,f]cycloheptatriene, corannulene, hexahelicene, cis,cis-1,2,3,4-tetraphenylbutadiene, and tetraphenylethylene are also shown in Table IV for future reference. All of these compounds are highly strained.

Comparison with Other Methods

Geometries. Throughout the last 20 years or so numerous schemes for predicting the molecular structures of conjugated hydrocarbons have been developed in an attempt to bypass the difficult and time consuming experimental methods of structure determination. The majority of these investigations based on MO methods have been concerned with correlating the experimental bond lengths of certain molecules with the calculated π bond orders, using quantum mechanical calculations of varying sophistication. They give no geometrical parameters for the molecule except for bond lengths among the various π atoms, and they do not account for steric deformations of these bonds. On the other hand, the present method gives all of the geometric features and is thus of much wider applicability. The accuracy of the method is also clearly superior to other methods, as can be realized by examining the data in Table III.

Heats of Formation. Comparisons are made in Table V. The first three schemes shown in Table V (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. Using the same set of compounds, the methods do not differ much in their overall accuracy.) To show how much improvement is obtained with our procedure, we have depicted in Table V the mean deviations for three sets of molecules identical to those used by the other authors. Obviously, the present method is not only more general, it is also more accurate. Also note that MINDO/3,[10] currently the best available all valence electron semiempirical MO method specifically designed to give good heats of formation, gives almost 20 times the mean deviations of our method for the set of compounds that appeared both in ref 10 and in Table V.

Energy Differences. Calculated energy differences between two conformations are depicted in Table VI. Also listed are several experimental results. The lack of direct experimental data makes it impossible to compare quantitatively with calculated values, but it is still possible to draw some qualitative conclusion about our predictions through other observations.

Table IV. Comparison of Experimental and Calculated $\Delta H_f^\circ(g)$ [a]

| Compd | | $\Delta H_f^\circ(g)$ | | Dev[b] (Calcd − Exptl) | Reported probable errors |
Formula	Name	Calcd	Exptl		
C_2H_4	Ethylene	12.40	12.45	−0.05	0.10
C_4H_6	*trans*-Butadiene	26.19	26.11	0.08	0.15
C_5H_6	Cyclopentadiene	31.49	31.94	−0.45	0.28
C_5H_8	*cis*-1,3-Pentadiene	19.77	19.13, 19.78	−0.01	0.24
	trans-1,3-Pentadiene	18.35	18.12	0.23	0.16
	2-Methyl-1,3-butadiene	18.51	18.06	0.45	0.20
C_6H_6	Benzene	20.01	19.81	0.02	0.13
C_6H_8	1,3-Cyclohexadiene	25.67	25.38	0.29	0.19
C_6H_{10}	2,3-Dimethyl-1,3-butadiene	11.87	10.78	1.09	0.30
C_7H_8	1,3,5-Cycloheptatriene	45.19	43.90	1.29	0.36
C_7H_{10}	Toluene	11.95	11.99	−0.04	0.10
	1,3-Cycloheptadiene	22.27	22.56	−0.29	0.24
C_8H_8	Cyclooctatetraene	72.93	71.13	1.80	0.33
	Styrene	35.57	35.30	0.27	0.25
C_8H_{10}	Ethylbenzene	7.43	7.15	0.28	0.19
	o-Xylene	4.13	4.56, 4.23	−0.43	0.26
	m-Xylene	4.01	4.14, 3.59	−0.13	0.18
	p-Xylene	3.87	4.31, 3.97	−0.44	0.24
	Dimethylfulvene	32.86	32.1	0.76	1.3
C_9H_8	Indene	40.02	39.08	0.94	0.37
C_9H_{10}	Indan	13.87	14.42	−0.55	0.53
C_9H_{12}	*n*-Propylbenzene	2.42	1.89	0.53	0.19
	Isopropylbenzene	0.89	0.96	0.07	0.26
	1-Methyl-2-ethylbenzene	1.00	0.39	0.61	0.27
	1-Methyl-3-ethylbenzene	−0.55	−0.43	−0.12	0.29
	1-Methyl-4-ethylbenzene	−0.65	−0.76	+0.11	0.34
	1,2,3-Trimethylbenzene	−2.78	−2.26	−0.52	0.29
	1,2,4-Trimethylbenzene	−3.82	−3.31	−0.51	0.26
	1,3,5-Trimethylbenzene	−3.96	−3.81	−0.15	0.33
$C_{10}H_8$	Azulene	74.55	69.06,[c] 73.5	1.05	0.9
	Naphthalene	35.66	35.85,[c] 36.05	−0.19	0.25
$C_{10}H_{12}$	1,2,3,4-Tetrahydronaphthalene	3.60	6.57[m]	−2.97	0.6
$C_{10}H_{14}$	*n*-Butylbenzene	−2.57	−3.18[d]	−0.61	0.30
	Isobutylbenzene	−5.15	−5.14	−0.01	0.33
	sec-Butylbenzene	−3.53	−4.15	0.62	0.31
	tert-Butylbenzene	−5.40	−5.40	0.00	0.31
$C_{12}H_8$	Biphenylene	104.49	104.43,[c] 115.2	0.06	1.5
	Acenaphthalene	58.15	62.04,[c] 61.6	−3.55	1.2
$C_{12}H_{10}$	Biphenyl	43.28	43.57,[c] 43.53	−0.25	0.60
	Acenaphthene	41.09	37.4	3.69	0.7
$C_{12}H_{18}$	Hexamethylbenzene	−21.14	−20.7	−0.44	0.62
$C_{14}H_8$	Dibenzo[*cd,gh*]pentalene	131.89			
$C_{14}H_{10}$	Anthracene	55.29	55.44,[e] 55.2	0.09	1.1
	Phenanthrene	49.08	49.52,[c] 49.5	−0.42	1.1
	4,8-Dihydrodibenzo[*cd,gh*]pentalene	84.74			
$C_{14}H_{12}$	*trans*-Stilbene	56.84	56.43,[c,f] 52.48[f]	−0.41	0.5
	cis-Stilbene	59.33	60.31	−0.98	0.42
	1,1-Diphenylethene	61.02	58.7	2.32	1.1
	Paracene	55.23			
	9,10-Dihydroanthracene	39.71	38.2	1.51	1.1
$C_{15}H_{12}$	Dibenzo[*b,f*]cycloheptatriene	57.26			
$C_{16}H_{10}$	Fluoranthene	63.55	69.78,[c] 69.08	−5.53	0.56
	Pyrene	54.76	51.59[g]	3.17	0.64
$C_{16}H_{14}$	2,7-Dimethylphenanthrene	32.91	34.20	−1.29	0.50
	4,5-Dimethylphenanthrene	40.16	46.26	−6.10	1.46
	9,10-Dimethylphenanthrene	38.26	40.0	−1.74	2.1
$C_{16}H_{16}$	[2.2]Paracyclophane	47.61	57.6[n]	−9.99	1
	[2.2]Metacyclophane	40.50	40.08	0.42	1.7
$C_{17}H_{16}$	Dimethyldibenzo[*b,f*]cycloheptatriene	52.61			
	1,2-Diphenylcyclopentene	51.02			
$C_{18}H_{12}$	Triphenylene	62.62	63.4	−0.78	1.2
	Chrysene	64.84	62.8	2.04	1.2
	3,4-Benzophenanthrene	66.83	69.6	−2.77	1.2
	1,2-Benzanthracene	67.13	69.63,[i] 65.97[j]	1.16	3.0
	Tetracene	76.69	69.8	6.89	1.1
$C_{18}H_{14}$	Diphenylfulvene	92.49	96.1	−3.61	4.0
	5,12-Dihydrotetracene	55.48	53.1	2.38	1.1
$C_{18}H_{18}$	[18]Annulene	128.42	124.0,[k] 67[l]	4.42	6.0
$C_{20}H_{10}$	Corannulene	101.27			
$C_{20}H_{12}$	Perylene	73.17	73.7	−0.53	1.1

Table IV (*Continued*)

Compd		$\Delta H_f^\circ(g)$		Dev[b] (Calcd −	Reported[a] probable
Formula	Name	Calcd	Exptl	Exptl)	errors
$C_{20}H_{16}$	1′,9-Dimethyl-1,2-benzanthracene	58.79	60.1	−1.31	1.1
$C_{24}H_{18}$	1,3,5-Triphenylbenzene	89.60	90.02,[g] 88.0	−0.42	1.7
	Tetraphenylethylene	104.69			
$C_{26}H_{16}$	Hexahelicene	96.46			
$C_{28}H_{22}$	*cis,cis*-1,2,3,4-Tetraphenylbutadiene	124.57			
Mean deviations				1.34	0.80

[a] All enthalpy values at 298.15 K. Except as noted, experimental data (Exptl) are the best values selected by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [b] When there is more than one experimental value listed in the table, the one nearest to the calculated value is used to calculate deviation. [c] The vaporization enthalpy is given by E. Morawetz, *J. Chem. Thermodyn.*, **4**, 455 (1972). [d] The heat of formation is given by W. D. Good, *ibid.*, **5**, 707 (1973). [e] The heat of sublimation is given by L. Malaspina, R. Gigli, and G. Bardi, *J. Chem. Phys.*, **59**, 387 (1973). [f] The heat of formation is given by S. Marantz and G. T. Armstrong, *J. Chem. Eng. Data*, **13**, 118, 455 (1968). [g] The heat of sublimation is given by L. Malaspina, G. Bardi, and R. Gigli, *J. Chem. Thermodyn.*, **6**, 1053 (1974). [i] The heat of sublimation is given by N. Wakayama and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **40**, 2267 (1967). [j] J. D. Kelley and F. O. Rice, *J. Phys. Chem.*, **68**, 3794 (1964), give the heat of sublimation as 24.99 kcal/mol. Herndon (ref 14b) gives 24.14 ± 0.21 kcal/mol. The latter was used. [k] J. F. M. Oth, J. Bunzli, and Y. J. Zelicourt, *Helv. Chim. Acta*, **57**, 2276 (1974). [l] A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc.*, 216 (1965). [m] W. D. Good and S. H. Lee, *J. Chem. Thermodyn.*, **8**, 643 (1976). [n] D. L. Rogers, E. F. Westrum, Jr., and J. T. S. Andrews, *ibid.*, **5**, 733 (1973).

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

Method	No. of compds examined	Reported[a] mean dev, kcal/mol	Present work mean dev on same compd set
Dewar-de Llano[6]	20	7.80	1.69
Dewar-Harget[6]	19	6.80	1.40
Lo-Whitehead[7]	17	2.32	1.16
MINDO/3[10,b]	10	8.65	0.54
This work	65	1.34	

[a] 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. [b] Comparisons are made for molecules which appear both in Table IV and in ref 10.

(I) Nonbenzenoid Compounds. The rotational barrier for ethylene was fit in the force-field parameterization and is calculated to be 64.0 kcal/mol (experimental value, 65.0 kcal/mol[37]).

The s-trans form of 1,3-butadiene is found to be favored over the s-cis by 2.6 kcal/mol, and similar values are given by ab initio calculations[38] (2.05 kcal/mol) and by experiment (2.50 kcal/mol).[39] We also calculate the rotational barrier from the s-trans form to be 7.29 kcal/mol, in agreement with the experimental value 7.16 obtained by Carreira[39] and the value 6.73 obtained by ab initio calculations.[38]

Traetteberg[40] found 1,3,5-cycloheptatriene to be nonplanar by the electron diffraction method. The low-temperature NMR spectra of 1,3,5-cycloheptatriene have been interpreted[41] in terms of rapidly interconverting chair forms with an activation energy of about 6 kcal/mol at the planar form. We calculate the nonplanar form to be more stable than the planar form by 3.55 kcal/mol.

Anet[42] examined the ring inversion of cyclooctatetraene by low-temperature NMR and found $\Delta G^{\ddagger}$ to be 13.7 kcal/mol for mechanical inversion. We found the tub favored over the planar form by 12.5 kcal/mol.

A semiquantitative estimate of the degree of nonplanarity in 1,3-cyclohexadiene was made by Butcher[43] from an analysis of the ground vibrational state rotational constants. Assuming $C_{sp^2}-C_{sp^2}$ bond lengths of 1.34 and 1.46 Å and all other C–C lengths as 1.50 Å, he deduced a torsional angle, ω (the angle

Table VI. Energy Differences between Two Conformations (kcal/mol)

Transformations	$\Delta(\Delta H_f(g))$	
	This work	Exptl[a]
1,3-Butadiene		
Cis → trans	2.62	2.50
1,3-Cyclohexadiene		
π planar → π nonplanar with C_2 symmetry	1.21	1.10
1,3,5-Cycloheptatriene		
π planar → π nonplanar	3.55	6
1,3-Cycloheptadiene		
π planar → π nonplanar	−0.20	
Cyclooctatetraene		
π planar → π nonplanar (tub form)	12.47	13.7
1,2,3-Trimethylbenzene		
π planar → π nonplanar	0.13	
Hexamethylbenzene		
π planar → π nonplanar	3.79	>0
4,5-Dimethylphenanthrene		
π planar → π nonplanar	20.00	18.5
9,10-Dimethylphenanthrene		
π planar → π nonplanar	1.92	
Triphenylene		
π planar → π nonplanar	3.10	>0
3,4-Benzophenanthrene		
π planar → π nonplanar	9.67	5-10
Perylene		
π planar → π nonplanar	0.30	>0
trans-Stilbene		
π planar → π nonplanar	0.50	>0
1,3,5-Triphenylbenzene		
π planar → π nonplanar	12.25	>0
Biphenyl		
π planar → π nonplanar	3.01	>0
cis-Stilbene		
π planar → π nonplanar	17.21	>0
[18]Annulene		
$D_{3h} \rightarrow D_3$	8.32	
Tetraphenylethylene		
π planar (central bond) → π nonplanar (central bond)	1.22	>0
Corannulene		
π planar → π nonplanar (cup form)	1.22	>0

[a] See Results and Discussion for the references and experimental reliability for each molecule.

Table VII. Adjusted Values for Force-Field Parameters

Angle	Bending constants	
	θ_0, deg	k_θ, mdyn Å/rad^2
C_{sp^2}-C_{sp^3}-C_{sp^2}	112.0	0.70
C_{sp^2}-C_{sp^2}-C_{sp^2}	120.0	0.40
C_{sp^3}-C_{sp^2}-C_{sp^2}	121.7,[a] 120.5[b]	0.50

| Angle	Torsional constants[c]		
	V_1	V_2	V_3
C_{sp^2}-C_{sp^2}-C_{sp^2}-C_{sp^2}	0	16.25	2.00
C_{sp^2}-C_{sp^3}-C_{sp^3}-C_{sp^2}	5.0	0	0
C_{sp^2}-C_{sp^3}-C_{sp^2}-C_{sp^2}	0	0	0.30
C_{sp^3}-C_{sp^2}-C_{sp^2}-C_{sp^2}	−0.30	16.25	0
C_{sp^3}-C_{sp^2}-C_{sp^2}-C_{sp^3}	−0.70	16.25	0
H-C_{sp^3}-C_{sp^2}-C_{sp^3}	0	0	1.00
H-C_{sp^2}-C_{sp^3}-C_{sp^3}	0	0	1.00
H-C_{sp^3}-C_{sp^2}-H	0	0	1.00
H-C_{sp^2}-C_{sp^2}-C_{sp^2}	0.40	16.25	0
H-C_{sp^3}-C_{sp^2}-C_{sp^2}	0	0	−1.34
C_{sp^3}-C_{sp^3}-C_{sp^2}-C_{sp^3}	0	0	1.00
C_{sp^3}-C_{sp^3}-C_{sp^2}-C_{sp^2}	0	0	−1.04

[a] Used when no hydrogen atom is attached to the central carbon.
[b] Used when one hydrogen atom is attached to the central carbon.
[c] Torsional function used is $(V_1/2)(1 + \cos \theta) + (V_2/2)(1 - \cos 2\theta) + (V_3/2)(1 + \cos 3\theta)$.

by which an ethylene group is rotated relative to the other about the central C_{sp^2}-C_{sp^2} bond), of 17.5 ± 2°. Pertinent electron diffraction[44] and theoretical[45] structures agree with this. Our calculated ω is 19.2° and the energy difference between planar and nonplanar π conformation is 1.21 kcal/mol comparable with the experimental value,[46] 1.10 ± 0.05 kcal/mol.

Conflicting conclusions have been published concerning the conformation of 1,3-cycloheptadiene. In a gas phase electron diffraction investigation, Chiang and Bauer[47] reported that the C_s form with six carbons coplanar fits the data better than

C_s C_2 C_1
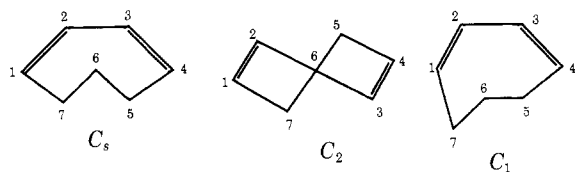
any of a variety of other planar and nonplanar structures. Recently, Hagen and Traetteberg[48] redetermined the electron diffraction spectra and got the same conclusion. In a molecular mechanical study of conjugated cyclic dienes, Favini and co-workers[49] found a C_2 conformation with a 55° dihedral angle across the C_2-C_3 bond to be the most stable conformation, being preferred over the C_s by 4.3 kcal/mol. However, their force field was simplified and not very thoroughly tested. Crews,[50] 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°. This assignment was based on a $J_{2,3}$ of 6.89 Hz for 1,3-cycloheptadiene which is midway between 5.5 Hz for a twisted C_{sp^2}-C_{sp^2} single bond and 8.4 Hz for a planar system.[51] Our 1971 force field program[20] suggested that the molecule has one conformation which undergoes a wide pseudorotational motion between two C_1 forms and a C_s form, and this conformation is in equilibrium with the C_2 form. Our current force field calculates that all three conformations have very similar energies, with the C_1 being slightly favored over the C_s and C_2 forms by 0.2 and 0.7 kcal/mol, respectively. This is in general

agreement with our earlier proposal[20] that experimental results are best interpreted by an equilibrium and a wide pseudorotation among conformations instead of by a single conformation. Details of our calculated structures for the C_s conformation are shown in Table III, along with the diffraction results. The agreement is reasonable. The calculated C_1 conformation has a 28° dihedral angle along the C_2-C_3 bond.

(II) Benzenoid Compounds. The gas phase value[52] for the torsional angle about the central bond of biphenyl is 41.6°, and our calculated value is 40.2°. The energy difference between planar and nonplanar conformations is calculated to be 3.01 kcal/mol. The planar conformation found in crystals[53] is then a result of the intermolecular interactions being larger than the modest intramolecular potential. Since the planar conformation should give more favorable packing, it is reasonable for biphenyl to exist in the crystal in this form.

Magnetic measurements[54] and x-ray structure determination[55] have shown that the 1,3,5-triphenylbenzene molecule is nonplanar in the crystal. A gas phase electron diffraction study by Bastiansen[56] has shown that the molecule is also nonplanar in the vapor and the peripheral benzene rings were estimated to be twisted out of the plane of the central ring by 46 ± 5°. Our calculated value is 41.5°. The nonplanar conformation with the shape of a three-bladed propeller is calculated to be 12.25 kcal/mol more stable than the planar conformation with four benzene rings on the same plane.

The crystal structure proposed by Klug[57a] for triphenylene was shown to be an error by Vand and Pepinsky[57b] and Pinnock et al.[57c] Later, Ahmed and Trotter[57d] confirmed the structure proposed by Pinnock. Statistical tests on the deviations of the carbon atoms from the mean molecular plane show that the molecule is significantly nonplanar. Our calculations show that a nonplanar conformation with all four benzene rings being distorted is preferred over the planar form by 3.10 kcal/mol.

The most stable conformation of perylene has been calculated to be nonplanar with the dihedral angle of cgc' (see Table III) equal to 14.7°, but the nonplanar conformation is only favored over the planar one by 0.30 kcal/mol. The crystal structure[58] reveals that the deviations of the carbon atoms from the best molecular plane, although they are small, are statistically significant. Camerman and Trotter[58] analyzed the structure and proposed that the main reason for the molecular deformation in the crystal is most likely due to crystal packing forces instead of intramolecular steric effects. Our calculations do not conflict with their conclusion since the calculations really show how flexible perylene is, 0.30 kcal/mol being enough to torsionally deform the molecule by 14.7°, and therefore a small packing force is enough to distort the conformation.

There is some controversy about the detailed molecular geometry of hexamethylbenzene. The absorption spectrum of single oriented crystals of hexamethylbenzene in the 2800 Å region was studied at room temperature and 20 K.[59] The low-temperature spectrum shows that near-ultraviolet absorption is polarized perpendicular to the aromatic ring planes. This was shown to arise from the destruction of the reflection symmetry in the plane of the benzene ring and it was concluded that the molecular symmetry is probably S_6. At 116 K, hexamethylbenzene crystals undergo a phase transition and the out-of-plane spectrum found at 20 K disappears. Therefore, C_{6h} symmetry is proposed for hexamethylbenzene crystals above 116 K. Frankosky[60] and Overberger[61] proposed, based on the calorimetric method and the effect of hydrogen repulsive forces, that the average conformation of hexamethylbenzene was nonplanar. Neutron diffraction[62] studies of single crystals of hexamethylbenzene at 298 and at 130 K indicate that the molecule in phase II, refering to the phase stable at room temperature and down to 116 K, has approximate D_{3d} sym-

metry. More recently, Karl et al. reported[63] that gas phase electron diffraction data are consistent with the interpretation of coplanar inner ring with the symmetry D_{6h}, but the outer ring C atoms are not coplanar with the benzene ring, alternately deviating by $9.9 \pm 1.8°$ 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 9.9 and 5.4° as the most stable form. Our calculations suggest that there is a certain deformation inside the benzene ring itself although it is quite small, with the ring carbons being alternately 0.03 Å above and below the mean ring plane.

The crystal structure of 3,4-benzophenanthrene was analyzed crystallographically by Schmidt et al.[64] and theoretically studied by Hirshfeld[65] using the Coulson and Senent method. The molecular structure was determined to be nonplanar with C_2 symmetry. We calculate the nonplanar C_2 conformation, with the dihedral angle cee' (see Table III) about equal to 25°, being preferred over the planar one by 9.3 kcal/mol. An estimate of 5–10 kcal/mol[64] for this energy difference was deduced from the experimental resonance energy.

4,5-Dimethylphenanthrene and cis-stilbene are even more overcrowded because planar models would involve a pair of hydrogen atoms closer than 2.0 Å. The calculated energy differences between planar and nonplanar conformations are 20.00 and 17.21 kcal/mol, respectively. No detailed experimental values are available for 4,5-dimethylphenanthrene as far as we know; however, indirect evidence is available. Theilacker and Baxmann[66] successfully resolved 1,8-diamino-4,5-dimethylphenazine, which has a structure similar to 4,5-dimethylphenanthrene, into optical antipodes, thereby proving that the molecule must be deformed from a planar conformation. The energy barrier to inversion of 9,10-dihydro-4,5-dimethylphenanthrene has been estimated experimentally from polarimetric data to 23.5 kcal/mol.[67] Munday and Sutherland[68] studied in the interconversion of enantiomeric conformations of 4,5-disubstituted phenanthrenes using variable temperature NMR spectroscopy. The energy barrier to racemization for 4,5-di(acetoxymethyl)phenanthrene was determined to be 18.5 ± 1.5 kcal/mol. Since methyl and acetoxymethyl groups are of approximately equal effective bulk,[68,69] the energy barriers to racemization for 4,5-di(acetoxymethyl)phenanthrene and 4,5-dimethylphenanthrene should then be about the same. These values indicate that our predicted value for the inversion barrier of 4,5-dimethylphenanthrene is reasonable.

Stilbene has been the subject of a wide variety of studies, among them photochemical, spectroscopic, and theoretical. One of the central points of interest is that of the difference in the structures and properties of the trans and cis isomers. The crystal structure of trans-stilbene has been reported, but that of cis-stilbene has not been (it is a liquid at room temperature). Recently, the gas phase structure of cis-stilbene has been studied by the electron diffraction method.[70] Both calculated results and electron diffraction data are shown in Table III. As can be seen from Table III, the cis-stilbene molecule is found experimentally 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 was not considered in the diffraction study. We note that the sum of the dihedral angles calculated by us (Ph–b and abc, see Table III, 28.9 and 13.3°, 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); 126.5° (Calcd)).

The molecular structure of trans-stilbene in the solid state has been reported to be approximately planar.[29,30] The gas phase structure has been studied by the electron diffraction method and found to be nonplanar and to possess C_2 symmetry.[31] The phenyl groups were found to be rotated $30 \pm 15°$ about the C–Ph bonds. Our calculations show that the central C=C bond is planar and phenyl groups are 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 25°. The calculated energy barrier corresponding to the C_i conformation is only about 0.50 kcal/mol.

Tetraphenylethylene also has a theoretically important structure, due to its structural similarity with stilbene. A comparison of the low-temperature x-ray crystal structure ($-160 °C$)[71] and our calculated results is shown in Table III. Owing to the strain in the molecule, the C–Ph bond is longer than expected (Calcd, 1.486 Å; Exptl, 1.496 Å). The angles of twist around the ethylenic double bond are small (Exptl, 8.4°; Calcd, 9.0°). The values of the angles around the atoms of the central bond (Exptl, $\alpha = 122.2°$, $\beta = 115.5°$; Calcd, $\alpha = 122.2°$, $\beta = 115.5°$) can be explained qualitatively by considering the repulsion between nonbonded atoms. The energy difference between the most stable nonplanar conformation (D_2) and the most stable planar conformation (D_{2h}) is estimated to be ca. 100 kcal/mol. The energy difference between conformations with the central bond planar and nonplanar is calculated to be 1.2 kcal/mol. The above discussed features all show how rigid tetraphenylethylene is.

The most stable conformations of 1,2-diphenylcyclopentene, analogous to cis-stilbene and cis,cis-1,2,3,4-tetraphenylbutadiene, are calculated to be those with nonplanar π systems, which are consistent with experiment.[72] The agreement in dihedral angle is fair to good.

The conformational analysis of [18]annulene was discussed earlier[13] and will not be repeated here. Our calculated $\Delta H_f°$ for [18]annulene, 128.3 kcal/mol, is quite close to that predicted by MINDO/3,[73] 129.3 kcal/mol, and the experimental value,[74] 124 ± 6 kcal/mol.

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 in the molecule suggest that it is cup shaped.[75] There is evidence from uv spectra[75] 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 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.[76] As can be seen from Table III, its x-ray structure is quite similar to our calculated result. The planar form is calculated to be 1.22 kcal/mol higher in energy.

Our calculations also show that nonplanar conformations of 1,2,3-trimethylbenzene, and 9,10-dimethylphenanthrene are favored over the corresponding planar conformations by energy differences of 0.13 and 1.92 kcal/mol. The former value is much less than RT, so the structure is predicted to be planar, but the latter should definitely be nonplanar.

Conclusions

The method presented here is an extension of the SCF force field method to the calculation of the heats of formation of conjugated hydrocarbon molecules. While previous calculations have treated many individual systems and groups of compounds, the method presented here is quite general and has been applied to a large, diverse group of compounds. The accuracy of the results is competitive with that of high-quality

experimental work. The extension of this approach to conjugated systems containing heteroatoms is in progress.

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