

The MMP2 Calculational Method

Joseph T. Sprague*, Julia C. Tai†, Young Yuh, and Norman L. Allinger

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received 4 April, 1986, accepted 1 August, 1986

The molecular mechanics (MMP2) program and procedures for the treatment of conjugated hydrocarbons, and some of the results which they can achieve are described. The program is an updated version of the similar MMP1 program, but contains some differences. It is based on an SCF π system calculation, rather than on the VESCF method used earlier. All parameters are compatible with those in the MM2 program. Hence it is possible to calculate heats of formation, resonance energies, and structures for conjugated hydrocarbons in a way that is consistent with the calculations on non-conjugated molecules. The overall results as far as structure and energy are somewhat better than they were with the MMP1 program.

In an earlier article¹ we described a force field for calculations designed to give good structures and energies for saturated hydrocarbons (MM1), and various functional groups were subsequently added so that molecules which did not contain conjugated systems could be dealt with in a reasonably general and satisfactory way.² For conjugated systems, it was necessary to include some type of π system quantum mechanical calculation in order to determine some of the bond lengths and force constants for the conjugated part of the molecule.³ Once these were found, the ordinary force-field calculation proceeded as usual. Thus conjugated hydrocarbons (and conjugated ketones) could be treated with the MMP1 program.⁴ In principle, heterocyclic conjugated systems could be treated, but the parameterization was never completed.

Subsequently, problems with the calculations on alkanes at the MM1 level were overcome with the aid of low-order torsion terms replacing large van der Waals interactions between hydrogens, and the MM2 program was developed.^{5,6} This article is concerned with the updating of the MMP1 program to the MMP2 level. Important changes

occur in the calculations that involve the saturated portion of the molecule, and those have already been described for the MM2 program, and will not be discussed further here.^{5,6} We will now discuss only the way in which the MM2 version was converted to MMP2, especially insofar as it differs from the way in which MM1 was converted to MMP1.

There were several problems with the MMP1 type of calculation which were pointed out in the original article.³ Some of these problems still remain. Only a few fundamental changes occur in MMP2 relative to MMP1. The results are different and better, largely in saturated portions of the molecule and because of matters that are not directly concerned with the π system.

One serious disadvantage with the MMP1 program was that it was originally designed to calculate structures, but not heats of formation.³ Some years later, the calculation for heats of formation was appended to the original work.⁷ It was found at that time that the heat of formation parameters used for saturated compounds could not be carried over to the conjugated systems, but rather a new parameter set had to be developed. This worked well as long as the saturated parts of the molecule were minor, and one was dealing essentially with a π system. But it was clear that if one went to a system that was largely saturated, the parameters could not be carried over that far, and the scheme would not

*Permanent address: Dr. Joseph T. Sprague, State University of New York, Agricultural and Technical College, Cobleskill, NY 12043.

†Permanent address: Dr. Julia C. Tai, Department of Natural Sciences, University of Michigan-Dearborn, 4901 Evergreen Road, Dearborn, MI 48128.

work well. The only solution was to go back to the beginning, and simultaneously develop the parameters for the conjugated system along with those for the saturated part of the molecule. Since this would have been a very major effort, it was decided to leave it until the MM2 level of development could be incorporated into the treatment. This has now been done, and the MMP2 program (now a subroutine of MM2⁴) uses a parameter set which is totally consistent with MM2 parameters. Not only are all of the structural parameters identical, but all heat of formation parameters are also identical. Hence we have a completely internally consistent method for treating molecules which are conjugated, nonconjugated or a mixture of the two types. This article is concerned only with hydrocarbons. A later article will discuss the extension of these calculations to aromatic heterocycles and related compounds.⁸

We began with simple alkenes in this work, and developed all of the necessary parameters at the MM2 level for these compounds, and these same parameters were then carried over into the conjugated system treatment. The parameter set is given in full in the original version of the MM2.⁴ No changes have been made, and none are advocated in the alkene part of that original set. Briefly, the development followed that given in our earlier article.⁵ The small molecules ethylene, propene, 1-butene, *cis*- and *trans*-2-butene, and isobutylene were all fit as accurately as possible in terms of structure. Only two points seem worthy of comment here. The geometries of the 2-butenes were not fit very well with MM1, nor was the equilibrium between the conformers of 1-butene. The former item is still not fit as well as one would like at the MM2 level, although it is better than it was with the MM1 calculation. The offending item is the C—C—C bond angle. Experimentally, this angle has the value 120–125°, while the MM1 value was 128°. The MM2 value is 127°. The other problem item concerned the conformational equilibrium in 1-butene. The experimental values have been subject to revision since the MM1 work was carried out. At that time the available data indicated that the two conformations were equal in energy. This was determined by NMR, but subsequent determinations by the same method have now revised the equi-

librium to favor the skew conformation over the *cis* by 0.4 kcal/mol. Good quality *ab initio* calculations (431-G basis, fully optimized geometries) give this energy difference as 0.4 kcal, and MM2 now calculates 0.4 kcal/mol.

A parameter set was arrived at which was consistent with the MM2 alkane force field, and which gave good structures and heats of formation for alkenes in general. For the most part, these quantities were already fit well with earlier force fields, and the MM2 version in general was at least as good as earlier attempts. This parameterization was included in the earliest public version of the MM2 program, and in all subsequent versions. The necessary parameters are all included in the program itself, and can be gotten from that source, so they will not be repeated here in detail.

METHOD

Geometries

The optimized geometries are calculated by a method similar to that used in the 1973 force field.⁵ The procedure is basically as follows. If the unsaturated system is *completely* 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 self-consistent-field (SCF) calculation is then undertaken on the π system to obtain the bond orders, which are used to assign stretching and torsional parameters using eqs. 1–3 below. If the unsaturated system is non-planar, an extra SCF calculation is necessary on the (hypothetical) planar molecule, since torsional constants must be derived from a planar π system. (The "planarization" is carried out by deleting the direction cosine terms that describe the deviation from planarity of the *p* orbitals.) The natural bond length, l_0 , required by the force field for each bond (*ij*) is obtained from the linear relationship:

$$l_0 = 1.503 - 0.166p_{ij} \quad (1)$$

where p_{ij} is the calculated SCF bond order. The stretching force constant, k_s , for each conjugated bond is calculated by

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

The twofold 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:

$$V_{2ij} = 15.0 \times \bar{f} \times p_{ij}^\circ \beta_{ij}^\circ \text{ kcal/mol} \quad (3)$$

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

When double bonds are distorted from planarity, the distortion may either be by a simple torsion, or it may be by out-of-plane-bending, or by a combination of the two. The MM2 series program (and the MM1 series as well) all are written to handle the general case with specific approximations. A recent article discussed this question, and prompts us to comment here on our treatment of the problem.⁹ If the system is planar, the p orbital in question is perpendicular to the plane defined by the three attached substituents. If the system is nonplanar, then the sigma-pi separation assumption is no longer valid. But if the deviation from planarity is small, it may still be an acceptable approximation. In that event we need to consider the disruption of the pi system by the nonplanarity. The overlap between the sigma and pi systems can be neglected to a first approximation, since the sigma orbitals lie at much lower energies than do the π orbitals. Hence the three substituents define a plane, and we wish to put the p orbital on the central carbon in an orientation that would at first glance seem to need to be perpendicular to this plane. However, this is correct only in the case where the three bond lengths are equal. What our program does is to determine unit vectors which point from the carbon atom in question towards the attached substituents. The plane is then defined, not by the substituents, but by the ends of the unit vectors. The p orbital is then placed on the carbon atom and perpendicular to that plane. The orientation will then be correct in all directions. It is essential that this orientation be properly determined so that the overlap integrals, resonance integrals, and any other dependent properties be correctly determined. This approach is valid only insofar as there is no "rehybridization". That is, the p orbital on

the nonplanar atom which is part of the conjugated system must not have s character added to it or the description given is inadequate. In that case, one should use hybrid orbitals, as has been described by Haddon.⁹

For planar unsaturated systems \bar{f} is unity. For nonplanar unsaturated structures the value of \bar{f} is given by eq. 4, 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 the distorted geometry, and the denominator is the second-order torsional functions estimation of this same quantity, according to our mechanical model.^{3,10} Note also that the resonance integral (β) in eqs. (3) and (4) is measured by taking the resonance integral of ethylene as unity.

$$\bar{f} = \frac{\sum_{i<j} [p_{ij}^\circ \beta_{ij}^\circ - p_{ij}\beta_{ij}(\text{real})]}{\sum_{i<j} p_{ij}^\circ \beta_{ij}^\circ (1 - \cos^2 \omega_{ij})} \quad (4)$$

The factor \bar{f} used in eq. (3) can be understood if one looks at a molecule like butadiene. As a rotation about the central bond occurs, the bond order will fall off, and if that were all that happened, then eq. (3) (without the factor, \bar{f}) would correctly describe the change in energy. However, the energy of the system is not raised by that great an amount, because the bond orders of the 1,2 and 3,4 bonds increase with the decreasing bond order of the 2,3 bond. This means that the energy increase upon rotation is less than would be expected from simply an examination of the 2,3 bond, and what one must in fact do is look at the energy increase which results from rotation about the 2,3 bond, and subtract from this the energy decrease which is gained by the increase in bond order of the other bonds. The factor, \bar{f} , accounts for this energy decrease by a reduction in the torsional constants across π bonds appropriate to the overall π -energy difference of planar and nonplanar forms.¹¹

The steric energy is then minimized with respect to geometry using our standard modified (block diagonal) Newton-Raphson scheme.⁶ If the geometry has been significantly changed during the minimization step, the SCF calculations are repeated and the new bond orders are used to assign new stretching and torsional parameters. The

minimization SCF cycle is repeated until self-consistency is reached.

In order to more easily take advantage of previous work in the heat of formation calculations, we used the SCF method, rather than the VESCF method. These two methods yield somewhat different charge densities, but that seems to have a negligible effect on the geometries obtained. However, the VESCF method utilized the resonance integrals between all pi atoms, while the standard SCF method used here includes resonance integrals only between atoms bonded together. This exclusion of nonbonded resonance integrals causes differences which for the most part were overcome by the parameterization. But in a few cases there were special problems which seemed correctable only with the inclusion of nonneighbor resonance integrals. These integrals have large values for atoms bound together, smaller but still significant values for atoms bound 1,3 or 1,4, and usually negligible values for atoms 1,5 or further removed. The effects of the 1,3 and 1,4 integrals can mostly be absorbed in the parameterization. Hence a problem arises mainly when a 1,3 or 1,4 distance is quite abnormal, or if a 1,5 or greater distance is unusually short because of folding of the molecule. In such cases an option is included to request the program to calculate the resonance integrals and include them between pairs of atoms which are specifically indicated. It is necessary for the user to recognize when such cases occur, and include the necessary input statements. Examples are given later as a guide.

Resonance integrals between bonded carbons are calculated in a way to be consistent with the heat of formation calculations. The equation used is as follows¹²:

$$\beta_{ij}(R_{ij}) = 1.5[E_b^{C=C}(R_{ij})_{\text{benzene}} - E_b^{C=C}(R_{ij})_{\text{ethylene}} - \gamma_{11}/4 + 5\gamma_{12}/18 - \gamma_{14}/36] \quad (5)$$

where $E_b^{C=C}(R_{ij})_{\text{benzene}}$ and $E_b^{C=C}(R_{ij})_{\text{ethylene}}$ are bond energies of bonds of length R_{ij} in benzene and in ethylene, respectively. γ_{11} is the one center repulsion integral, γ_{12} the repulsion integral evaluated at a bond length of R_{ij} , and γ_{14} the integral evaluated at a bond length of $2R_{ij}$. The derivation of eq. (5) will be discussed in the next section. The repulsion integrals are evaluated using Ohno's empirical formula¹³ $\gamma_{ij} = 1/(R_{ij} + 1/\gamma_{ii}^2)^{1/2}$.

In cases where resonance between nonbonded carbons must be included, eq. (5) was found to be inadequate because $-\beta_{ij}$ calculated there shows a minimum at $R = 1.77\text{\AA}$. In other words, the value of $-\beta$ increases with bond length when R is greater than 1.77\AA . Hence β is taken to be proportional to the overlap integral^{14,15} at longer distances. The effective nuclear charge and the proportionality constant were chosen so that the β vs. distance curve meshes smoothly with the one calculated by eq. (5) at around 1.5\AA . Since for nonbonded atoms the p orbitals may be quite far from being parallel, β_{ij} is calculated as $a_i a_j \beta_\sigma + (b_i b_j + c_i c_j) \beta_\pi$ where a , b , and c are the direction cosines of the orbitals with the internuclear axis as the x axis. The values of β_σ and β_π are calculated by eqs. (6) and (7):

$$\beta_\sigma = 4.86(1 + P + P^2/5 - 2P^3/15 - P^4/15) \exp(-P) \quad (6)$$

$$\beta_\pi = 4.86(-1 - P - 2P^2/5 - P^3/15) \exp(-P) \quad (7)$$

where $P = 2.51R$.

It should be mentioned here that two other research groups, being impatient to be able to extend MM2 calculations to conjugated systems, have reported grafting together the VESCF calculations from MM1, and the force field from MM2.¹⁶ The formalism for these programs is similar to that described here. Those programs will run, and will give structures which should be at least reasonable for the most part, and may in fact be excellent. Since exhaustive comparisons have not been made, it is hard to say. They would not be expected to give good heats of formation.

Heats of Formation

For nonconjugated molecules, MM2 calculates the heat of formation by

$$\Delta H_f^\circ = E_s + \Delta H_{\text{bond}} + \Delta H_{\text{str}} + \text{PFC} \quad (8)$$

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 plus other statistical thermodynamic terms. Our previous method^{7,17} for conjugated ΔH_f° 's used the similar equation

$$\Delta H_f^\circ = 170.9N_C + 52.1N_H + E_S - E_{\text{conj}} - E_{\text{str}} + \text{PFC} - E_{\text{conj}} \quad (9)$$

where N_C and N_H are the numbers of carbon and hydrogen atoms in the molecule, E_S is the steric energy minus the conjugated $C_{sp^2} - C_{sp^2}$ stretching (this stretching is implicitly absorbed in E_{conj} and cannot be easily removed), and E_{nonconj} and E_{conj} represent the energy contribution from the nonconjugated and the conjugated bonds of the planar molecule, respectively. E_{conj} may be written as the separate terms:

$$E_{\text{conj}} = \sum (E_{\sigma b}^{C=C} + E_{\pi b}^{C=C}) = \sum E_b^{C=C} \quad (\text{for hydrocarbons}) \quad (10)$$

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

Using Pople's SCF pi theory¹⁷ the total π -bond energy, $E_{\pi b}(\sum E_{\pi b}^{C=C}$, here), is given by

$$E_{\pi b} = -\left\{ \sum_i \frac{p_{ii}^2}{4} \gamma_{ii} + 2 \sum_{i<j} p_{ij} \beta_{ij} \right\} + \sum_{i<j} \left[(p_{ii} - 1)(p_{jj} - 1) - \frac{1}{2} p_{ij}^2 \right] \gamma_{ij} \quad (11)$$

where p is the density matrix. The dependence of $E_b^{C=C}$ on atomic distance R_{ij} is expressed by a Morse potential function:

$$E_b^{C=C} = E_e^{C=C} \{ 2 \exp[-\alpha(R_{ij} - R_e)] - \exp[-2\alpha(R_{ij} - R_e)] \} \\ \alpha = [k_e / 2E_e^{C=C}]^{1/2} \quad (12)$$

where $E_e^{C=C}$ is the equilibrium bond energy, k_e is the force constant, and R_e is the equilibrium bond length. For ethylene and benzene, all the parameters in eq. (12) are known. Lo and Whitehead¹² worked out the $E_{\pi b}$ for ethylene and benzene using eq. (11). By sub-

stituting the results from eq. (11) and eq. (12) into eq. (10) both for ethylene and for benzene, they were able to obtain expressions for $\beta_{ij}(R_{ij})$ and $E_b^{C=C}(R_{ij})$ as functions of $E_b^{C=C}(R_{ij})_{\text{benzene}}$ and $E_b^{C=C}(R_{ij})_{\text{ethylene}}$. The expression for β_{ij} is given in eq. (5), and is used in eq. (11). $E_{\sigma b}^{C=C}$ is given by the following expression

$$E_{\sigma b}^{C=C}(R_{ij}) = 0.5[(E_b^{C=C}(R_{ij})_{\text{ethylene}} + E_b^{C=C}(R_{ij})_{\text{benzene}} + 3\gamma_{11}/4 + 10\beta_{ij}(R_{ij})/3 - 13\gamma_{12}/18 - \gamma_{14}/36)] \quad (13)$$

Using eq. (11) to calculate $E_{\pi b}$, and eq. (13) to calculate $E_{\sigma b}^{C=C}$, one can now obtain E_{conj} from eq. (10). Although we follow the Lo and Whitehead procedure, the parameters in eq. (12) have been chosen differently in order to get a better overall fit of ΔH_f° . The parameters used are shown in Table I.

A problem with this overall method with respect to the present work is that because eq. (9) is derived from a different basis than eq. (8), the quantities ΔH_{bond} and ΔH_{str} in eq. (8), which have been determined for the MM2 alkane force field, cannot be carried over to eq. (9). Thus to calculate ΔH_f° with eq. (9), one would have to develop new parameters, E_{nonconj} and E_{str} for the saturated part of the molecule also. Since the MM2 ΔH_f° calculations are quite good, we felt it important to calculate the alkane portions of conjugated molecules with the MM2 force field, and add the conjugated π contribution to this. All structural parameters should be consistent with the MM2 force field as well.

Equation (9) was therefore rewritten as

$$\Delta H_f^\circ = E_S + \Delta H_{\text{bond}} + \Delta H_{\text{str}} + \text{PFC} - E_{\text{conj}} \quad (14)$$

where all terms are as described above except that ΔH_{bond} and ΔH_{str} values are now the same as used in the MM2 program. Additional values, as required by the conjugated systems, are listed in Table II.

Table I. Parameters used in morse potential function.

	$E_e^{C=C}$	R_e^a	K_e^b	$\alpha = [k_e / (2E_e^{C=C})]^{1/2}$
	kcal/mol	Å	dyn/cm	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, 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	Value (kcal/mole)	
	Strain	Strainless
$C_{sp^2}-C_{sp^2}$	152.75	152.85
$\begin{array}{c} \text{H} \\ \\ \text{C}_{sp^2} \\ / \quad \backslash \\ \text{C}_{sp^2} \quad \text{C}_{sp^2} \end{array}$	-28.54	-29.167
$\begin{array}{c} \text{C}_{sp^3} \\ \\ \text{C}_{sp^2} \\ / \quad \backslash \\ \text{C}_{sp^2} \quad \text{C}_{sp^2} \end{array}$	-0.22	-0.248
$\begin{array}{c} \text{C}_{sp^2} \\ \\ \text{C}_{sp^2} \\ / \quad \backslash \\ \text{C}_{sp^2} \quad \text{C}_{sp^2} \end{array}$	-55.78	-58.158

Comparing eq. (14) with eq. (9), one sees that the N_c , N_H , and the E_{ncoj} terms of eq. (9) are absorbed into the energy terms of Table II.

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.¹⁸ The set of molecules in Table III consists of a good cross section of conjugated hydrocarbons: aromatic and nonaromatic, and both strained and strainless, planar and nonplanar.

These results are in general agreement with our previous calculations.^{3,7} Softer hydrogens, however, have relieved the phenanthrene-type H...H crowding allowing biphenyl, perylene, and triphenylene to become significantly more planar than was found with MMP1. The problem with certain anomalous long bond lengths remains. We still think it probable that a careful experimental redetermination of these structures at low temperatures will resolve most of the discrepancies.

Certain calculated structures deserve further comment. In cycloheptatriene, a nonplanar structure has been established, but conflicting results concerning the degree of nonplanarity have been published. The quantitative estimate made by Butcher¹⁹ from the rotational constants of the normal isotopic species (no detailed structural information could be obtained directly from the spectroscopic data) was determined using many assumptions. Traetteberg²⁰ later determined

Table III. Experimental and calculated geometries (in Å or deg).

Compd	Bond or angle ^a	Exptl	Calcd	Exptl-Calcd
Ethylene (1965) ^a	a	1.337 ± 0.001	1.339	-0.002 ± 0.001
<i>trans</i> -Butadiene (1966) ^b	a	1.344	1.346	-0.002
	b	1.467 ± 0.002	1.467	0 ± 0.003
	ab	122.9 ± 0.5	122.0	0.9 ± 0.5
Benzene (1976) ^c	a	1.399 ± 0.001	1.397	+0.002
Naphthalene (1961) ^d	a	1.412	1.421	-0.009
	b	1.371	1.375	-0.004
	c	1.422	1.428	-0.006
	d	1.420 ± 0.008	1.408	-0.012 ± 0.007
<i>trans</i> -Stilbene (1975) ^e	a	1.338	1.355	-0.017
	b	1.473	1.473	0
	c	1.406	1.407	-0.001
	d	1.393	1.395	-0.002
	e	1.393	1.396	-0.003
	f	1.391	1.395	-0.004
	g	1.390	1.397	-0.007
	h	1.402	1.405	-0.003 ± 0.004
	*abc	5.2	0.2	5.0
Biphenyl (1958) ^f	a	1.400	1.396	0.004
	b	1.400	1.396	0.004
	c	1.400	1.403	-0.003
	d	1.490	1.484	0.006 ± 0.003
	cdc'	41.6	36.7	

Table III. (continued)

Anthracene (1964) ^g	a	1.418	1.431	-0.013
	b	1.375	1.368	0.007
	c	1.444	1.440	0.004
	d	1.433	1.419	0.014
	e	1.405 ± 0.008	1.404	0 ± 0.005
Phenanthrene (1971) ^h	a	1.394	1.408	-0.014
	b	1.401	1.384	0.017
	c	1.409	1.420	-0.011
	d	1.420	1.408	0.012
	e	1.465	1.458	0.007
	f	1.350	1.360	-0.010
	g	1.453	1.443	0.010
	h	1.423	1.418	0.005
	i	1.386 ± 0.008	1.381	0.005 ± 0.005
Pyrene (1972) ⁱ	a	1.395	1.396	-0.001
	b	1.406	1.404	0.002
	c	1.438	1.448	-0.010
	d	1.367	1.361	0.006
	e	1.425	1.413	0.012
	f	1.430 ± 0.004	1.437	-0.007 ± 0.005
	g	1.409	1.412	-0.003
3,4-Benzophenanthrene (1963) ^j	b	1.378	1.380	-0.002
	c	1.433	1.423	0.010
	**d	1.431	1.408	0.023
	e	1.446	1.4511	0.005
	**f	1.342	1.365	-0.025
	g	1.443	1.437	0.006
	**h	1.391	1.421	-0.030
	i	1.374	1.379	-0.005
	j	1.430	1.437	-0.007
	k	1.412 ± 0.010	1.396	0.016 ± 0.011
	cee'		22.8°	
	a	1.399	1.397	0.002
	b	1.418	1.408	0.010
Azulene (1966) ^k	c	1.383	1.400	-0.017
	d	1.406	1.396	0.010
	e	1.403	1.400	0.003
	* **f	1.501 ± 0.011	1.462	0.039 ± 0.010
	a	1.394	1.412	-0.018
Chrysene (1960) ^l	b	1.381	1.381	0
	c	1.409	1.426	-0.017
	d	1.407	1.407	0
	e	1.468	1.453	0.015
	f	1.369	1.365	0.004
	g	1.421	1.433	-0.012
	h	1.428	1.422	0.006
	i	1.363	1.378	-0.015
	j	1.428	1.439	-0.011
	k	1.401 ± 0.010	1.403	-0.002 ± 0.010
	**a	1.459	1.437	0.022
	b	1.381	1.364	0.017
	**c	1.420	1.446	-0.026
Tetracene (1961) ^m	d	1.420	1.428	-0.008
	e	1.390	1.392	-0.002
	**f	1.404	1.419	-0.015
	g	1.460 ± 0.010	1.421	0.039 ± 0.015
	a	1.397	1.398	-0.001
	b	1.381	1.386	-0.005
	c	1.410	1.416	-0.006
Triphenylene (1974) ⁿ	d	1.413	1.411	0.002
	e	1.458 ± 0.006	1.467	-0.009 ± 0.005
	cec'		0.4°	
	a	1.370	1.373	-0.003
	b	1.418	1.416	0.002
Perylene (1964) ^o	c	1.397	1.388	0.009
	d	1.425	1.434	-0.009
	e	1.424	1.412	0.012
	f	1.400	1.425	-0.025

Table III. (continued)

	g	1.471 ± 0.004	1.473	-0.002 ± 0.009
	cgc'		0.4°	
1,3,5-Cycloheptatriene (1964) ^p	a	1.356	1.349	0.007
	b	1.446	1.459	-0.013
	c		1.352	
	d	1.505 ± 0.006	1.501	0.003 ± 0.008
	**ab	127.2	124.9	2.3
	**bc	119.8	126.2	-6.4
	* **ad	121.8	124.5	2.7
	de		112.0	
Cyclooctatetraene (1972) ^q	a	1.340	1.344	-0.004
	b	1.475 ± 0.007	1.480	-0.005 ± 0.005
	ab	126.1 ± 0.5	124.6	1.5 ± 0.7
Cyclopentadiene (1965) ^r	a	1.509	1.509	0
	b	1.342	1.349	-0.007
	*c	1.469 ± 0.002	1.456	0.013 ± 0.004
	*ab	109.3	113.0	3.7
	*bc	109.4	107.8	1.6
	*aa'	102.8	98.3	4.5
Dimethylfulvene (1970) ^s	a	1.476	1.468	0.008
	b	1.340	1.356	-0.016
	c	1.462	1.451	0.011
	d	1.347	1.356	-0.009
	e	1.510 ± 0.008	1.512	-0.002 ± 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	1.374	0.028
	b	1.440	1.436	0.004
	c	1.391	1.395	-0.004
	*d	1.413 ± 0.004	1.435	-0.022 ± 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	1.347	0
	b	1.450	1.463	0.002
	c	1.509	1.502	0.007
	d	1.522 ± 0.015	1.530	-0.008 ± 0.004
	ab	129.1	129.4	-0.3
	ac	129.1	128.3	0.8
	aba'	0	0	
1,3-Cyclohexadiene (1969) ^x	a	1.350	1.347	0.003
	b	1.468	1.462	0.006
	c	1.523	1.506	0.017
	d	1.534 ± 0.012	1.536	-0.002 ± 0.005
	ab	120.1	119.9	0.2
	ac	120.1	121.5	-1.5
	cd	110.7	111.2	-0.5
	aba'	18.3	15.2	3.1
cis-Stilbene (1975) ^y	C=C _{av} (A,B)	1.398	1.398	0
	a	1.489	1.476	0.013
	b	1.334 ± 0.002	1.351	-0.017 ± 0.003
	abc		9.3	
	Ph-b	43.2	33.8	
	ab	129.5	126.6	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

Table III. (continued)

<i>cis,cis</i> -1,2,3,4-Tetraphenylbutadiene (1965) ^{bb}	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
	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
	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
	a	1.417	1.403	0.010
	b	1.530 ± 0.003	1.515	0.015
Hexamethylbenzene (1975) ^{dd}	bab'	9.9	10.7	0.8
	aa'a''		2.7	
	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

* Difference worth noting.

** Agrees with previous calculated value but still quite different from experiment.

^a L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kichitsu, 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. Almenningsen 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 C. 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. Stanford, Jr., *Acta. Crystallogr., Sect. B*, **28**, 1069 (1972).
^r G. Liebling and R. F. 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, Ca. 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).
^{ee} For definitions of bond lengths and angles, see ref. 7.

the total molecular structure by electron diffraction and her results do not agree very well with Butcher's. Our results, listed in Table IV agree fairly well with Butcher's estimates. Our ring is overall a bit too flat (our I_c moment is too large by 1.8%) which also accounts for the somewhat low barrier.

The barrier to inversion in this molecule has been measured,²¹ $\Delta G^\ddagger = 5.7$ kcal/mol. Without the inclusion of nonbonded overlap, the barrier calculated by MMP2 is much too small, 1.70 kcal/mol. (MMP1, which automatically included 1,6-overlap, gave a reasonable barrier height. A study of this molecule was subsequently also reported by Lindner²², with results similar to ours.) When 1,6 overlap is included in the MM2 formulation, the planar form is stabilized slightly (by 2.06 kcal), because of what then becomes "aromatic" resonance. This resonance is not

very effective, however, because the 1,6 distance is rather long. In the nonplanar conformation the resonance becomes somewhat more effective, because instead of pure π - π overlap, there is now σ - σ overlap in addition, which is appreciably greater at these distances. This extra bonding between atoms 1 and 6 should pull these atoms closer together, lowering the energy still further. In MM2 this doesn't happen automatically because 1 and 6 are not formally bonded together. While the program could be modified to take care of this, at present one must manually move the atoms together until the minimum of energy is found. At this point (the angle 1-7-6 is 108.8°) we have our calculated structure, and the inversion barrier is now 2.32 kcal/mol. The stabilization of the boat form, relative to the corresponding form without 1,6 overlap, is 2.68 kcal/mol. The cal-

Table IV. Geometry of 1,3,5-Cycloheptatriene

	Butcher ^a	Traetteberg ^b	Calcd
Bond, Å			
1-2	1.34 ^c	1.356 ± 0.005	1.349
2-3	1.47 ^c	1.446 ± 0.007	1.459
3-4	1.34 ^c		1.355
1-7	1.50 ^c	1.505 ± 0.007	1.501
Angle, deg			
1-2-3	124.5	127.2	124.5
2-3-4	124.5	119.8	125.5
2-1-7	124.5	121.8	124.5
1-7-6	105		108.8
α	29.5 ± 4	40.5 ± 2	26.5°
β	50 ± 5	36.5 ± 2	46°
I_A	22.71		22.81
I_B	22.85		23.11
I_C	41.29		42.02

^a Reference 19.

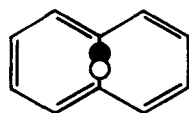
^b Reference 20.

^c Assumed value.

culated planar resonance energy (see later) is 4.42 kcal/mol, and the nonplanar resonance energy is -0.40 kcal/mol.

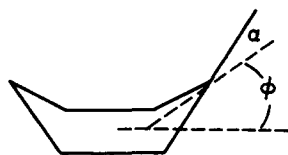
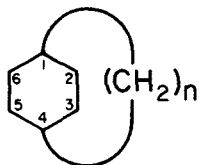
The bridged [10] annulenes and related compounds are additional examples of cases where the structure and energy are dependent on the inclusion of the 1,5-resonance integral between the spatially near pair of atoms. This integral causes the bond alternation characteristic of naphthalene, although less pronounced. If it is omitted, the molecule has approximately equal bond lengths, as might be expected from a [10] annulene. The geometry calculated by MM2 has been previously reported,²³ it has been discussed by Lindner,²² and the geometry was well calculated already by MMP1.³

With [10] annulene itself, the 1-5 overlap is of the Mobius type, and in this case a naphthalene type of bond length distribution is not observed. Rather a structure is found with 2 trans and 3 cis short bonds as shown. (There is a C_2 horizontal axis.) Another structure that corresponds to a stationary point is 6.3 kcal/mole higher in energy, and has essentially all benzenoid bond lengths.



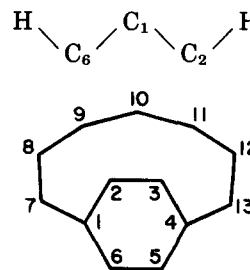
[10]-Annulene

The [n]paracyclophanes are a group of compounds which have as their distinguishing feature a benzene ring, the para positions of which are joined together by means of a cyclic side chain. This series of compounds has been of particular interest, because as n gets sufficiently small, the benzene ring is bent from planarity. As the ring distorts, the protons on



C_2 , C_3 , C_5 , and C_6 end up above the common plane of these four carbon atoms. Calculations on molecules of this class were reported earlier.²⁴ In agreement with our calculations, the crystal structures of [8]- and [2.2]paracyclophane show similar type displacements.^{25,26} The MM2 calculated structural features are listed in Table V. The preferred conformations have either C_2 or C_s

symmetries (shown in ref. 24). The experimental and calculated structures of [6]-, [7]-, and [8]paracyclophane are compared with Table VI.



The [n,m]-cyclophanes introduce no new features as far as our mechanical model is concerned, however, the factors causing ring deformations are sufficiently different from those in the [n]-cyclophanes that a brief study of some known homologs seemed appropriate. Of this class of compounds, the most extensively studied is [2,2]paracyclophane. Qualitative structural data is available from the electronic spectrum³¹ which has been interpreted in terms of ring bending and interring overlap. The more direct x-ray diffraction studies all find the benzene rings deformed by $11-14^\circ$, but they are at variance with regard to many other structural features.^{26,32}

The most recent x-ray study, by Trueblood and co-workers²⁶ (1972), was undertaken in order to get a precise molecular structure and analysis of the thermal motion. They found the crystal to be disordered by the twist of the aromatic rings ($\alpha \sim 3^\circ$) and proposed that the structure with exact alignment of the aromatic rings is an energy maximum. This was supported by an anomaly in the heat capacity near 50° K which is interpreted as the molecule acquiring sufficient energy to permit the twisting to become an active vibrational mode at this temperature, while at lower temperatures the molecule will remain in one or the other of the twist forms.²⁷ The angle of ring bending in the crystal was found to be 12.6° . In conjunction with this bending, the aromatic hydrogens are found to be displaced inward (toward the other ring) from the C_2, C_3, C_5, C_6 plane by about 0.04 \AA . The CH_2-CH_2 bond was unusually long, 1.569 \AA .

Boyd³³ determined the conformation of minimum potential energy for this and several other cyclophanes by an empirical valence force-field method, and he found close agreement with some features of the diffrac-

Table V. Relative strain energies and structural features of the $[n]$ paracyclophanes.

Compound	Strain ^a Energy (kcal/mole)	Ring Angle (ϕ)	Side-Chain Angle (α)
$[5]C_s$	40.12	26.5°	28.6°
$[5]C_2(u)$	49.51	29.9°	31.8°
$[5]C_2(d)$	81.01	26.6°	24.6°
$[6]C_2$	28.74	22.4°	18.1°
$[7]C_s$	20.97	18.2°	10.2°
$[7]C_2(u)$	23.12	20.8°	15.1°
$[7]C_2(d)$	30.43	23.8°	11.6°
$[8]C_2$	16.43	12.5°	5.1°
$[9]C_s$	15.16	4.4°	2.0°
$[9]C_2(u)$	12.25	8.5°	4.0°
$[9]C_2(d)$	13.41	10.4°	4.8°
$[10]C_2$	13.41	8.4°	-4.4°

^a Calculated according to the method outlined in ref. 28.

Table VI. Structures of the [6]-, [7]-, and [8]-paracyclophanes.

	[6]		[7]		[8]	
	Exp. ^a	Calc'd.	Exp. ^b	Calc'd.	Exp. ^c	Calc'd.
Symmetry	C_2	C_2	C_s	C_s	C_2	C_2
ϕ	19.5	22.4	17°	18.2°	9.1°	12.5°
α	19.9	18.1	6.5°	10.2°	5.6°	5.1°
Aliphatic						
C—C—C	106–117°	110–116°	111–117°	112–116°	110–116°	113–115°
$C_2 \cdots C_{10}$		3.49	3.15	3.38	3.36	3.38
$C_6 \cdots C_{10}$		3.79	3.65	3.62	3.61	3.69
$\omega_{8-9-10-11}$	144.6	142.3		150.1	156.1°	165.3°

^a Reference 29.

^b Reference 30.

^c Reference 25.

tion structures. His model is very limited, however, in that it requires a new set of empirical parameters for each different class of compound, since group potentials are used.

Our calculated structure for [2,2]paracyclophane assuming D_{2h} symmetry (exact alignment of the benzene rings), has rings bent (ϕ) 12.4° and ring-ring separation ($C_2 \cdots C_8$) of 3.06 Å. Allowing the benzene rings to twist relative to one another by removing some of the symmetry constraints, it was found that the D_{2h} form is indeed a transition state between twist (D_2) forms. Since the calculated relative conformational energy of the D_{2h} is 2.69 kcal/mole above the D_2 form, the molecule should rapidly oscillate between twist forms at room temperature. The minimum energy twist form, characterized by a 13.1° ring bending (ϕ) and 4.8° twist (α) is compared with experiment in Table VII. We find the aromatic hydrogens displaced 0.105 Å inward toward the other aromatic ring.

Perturbations in the electronic spectrum³⁴ of [2,2]-metaparacyclophane indicate appre-

ciable ring bending here also, and indeed, a crystallographic determination³⁵ finds the para ring bent 14°, about the same value as found for [2,2]-paracyclophane. In view of our results with the ring spacing in this latter molecule, we were most interested in the interring nonbonded distances reported for the metapara-isomer. These distances along with other structural features are compared with our calculated values in Table VIII. As can be seen the agreement is pretty good and

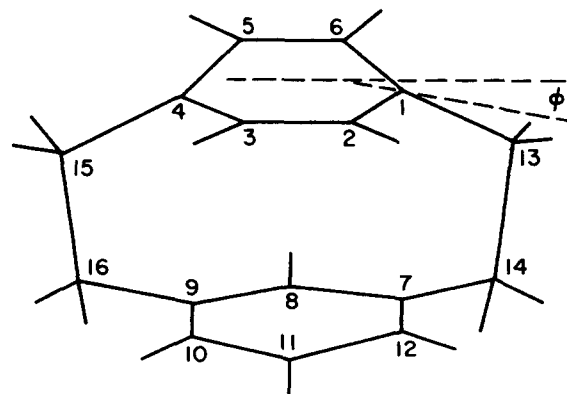


Table VII. Geometries of [2,2]-paracyclophane.

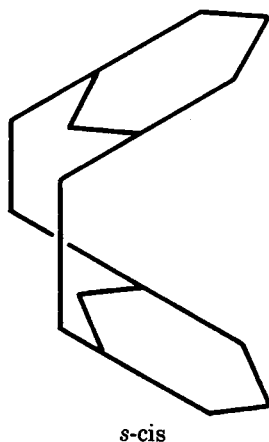
	Brown ^a	Lonsdale ^a		Trueblood ^b	Boyd ^c	Present Calculations	
		291° K	93° K			D_2	D_{2h}
Symmetry	D_{2h}	D_{2h}	D_{2h}	D_2	D_{2h}	D_2	D_{2h}
1-2	1.39	1.380	1.388	1.394	1.390	1.401	1.400
2-3	1.40	1.420	1.415	1.394	1.390	1.397	1.397
1-13	1.54	1.547	1.534	1.514	1.548	1.517	1.514
13-14	1.55	1.630	1.558	1.569	1.570	1.549	1.551
6-1-2	118.6°	119.7°	118.4°	117.0°	---	118.3°	118.5
1-13-14	114.6°	111.2°	112.9°	113.7°	112.7°	111.5°	112.8
ϕ	11°	14.0°	14.0°	12.6°	11.8°	13.1°	
α	--	(4°)	(3°)	3.2°	--	4.8°	--
$C_1 \cdots C_7$	2.83	2.751	2.749	2.78	2.777	2.79	2.72
$C_2 \cdots C_8$	3.09	3.087	3.093	3.09	3.054	3.13	3.06

^a Reference 32.^b Reference 26.^c Reference 33.

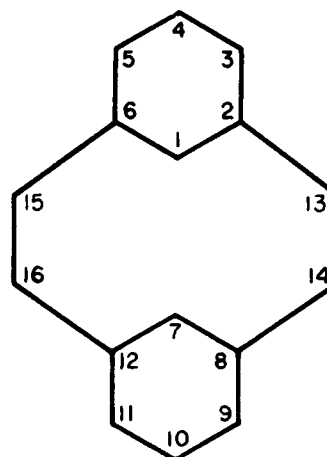
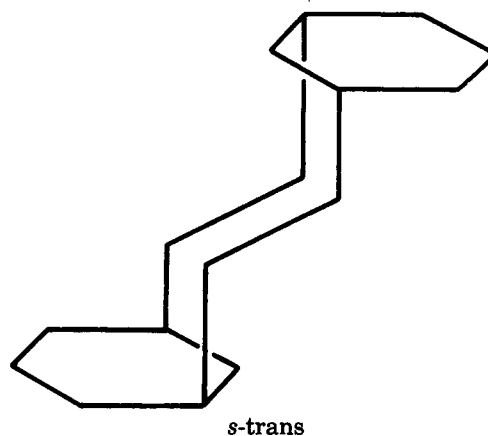
it is tempting to conclude that unusual interactions are responsible for the discrepancy in the para-isomer.

Assuming a transition state of C_{2v} symmetry with the plane of the meta ring perpendicular to the average plane of the para ring, the ΔH^\ddagger for meta ring rotation is calculated to be 30.6 kcal/mole. Since such a structure is not necessarily the transition state or even involved in the rotation, this value is really just an estimate. Cram³⁶ has reported ΔH^\ddagger values of about 18 kcal/mole, based on low temperature NMR measurement, for several para-ring substituted [2,2]-metaparacyclophanes.

The isomer [2,2]-metacyclophane, may exist as two possible conformations, *s*-cis and *s*-trans, with our calculations favoring the



s-trans by 8.45 kcal/mole. X-ray data³⁷ are available for the *s*-trans and, as shown in Table IX, is in favorable agreement with our calculated structure.



The *s*-cis geometry shown has aromatic rings distorted to the same degree (6–13° ring bending) as in the *s*-trans with the relative enthalpy of the *s*-cis due mostly to C/H and H/H eclipsing across the 13-14 and 15-16 bonds.

A number of annulenes were studied to see if the new force field would still produce structures in agreement with experiment. The methylene bridged 10 π -electron system,

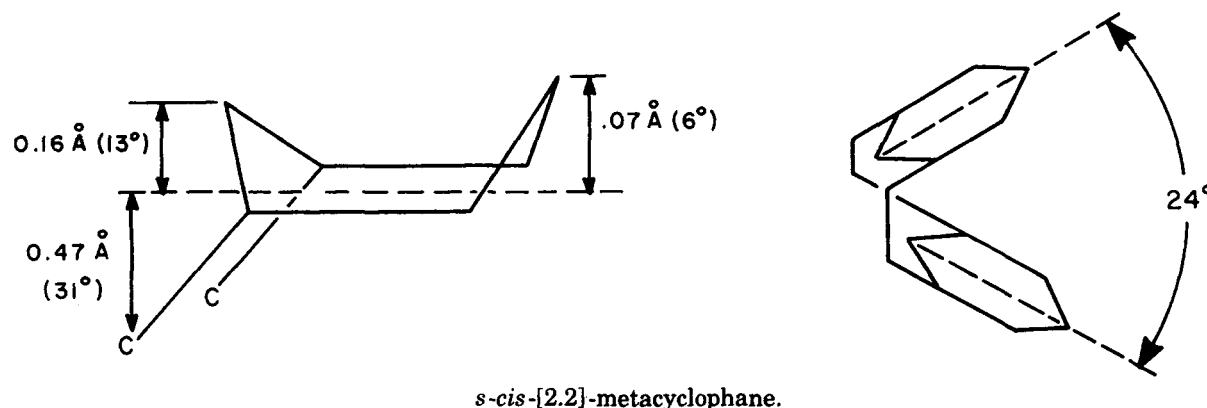
Table VIII. Geometries of [2,2]-metaparacyclophane.

	X-ray	Calcd.
1-13-14	107°	110.5
7-14-13	112°	111.5
ϕ	14°	14.2°
C ₁ ...C ₇	2.7 Å	2.82
C ₁ ...C ₈	3.0 Å	3.11

Table IX. Geometries of *s*-trans-[2,2]-metacyclophane.

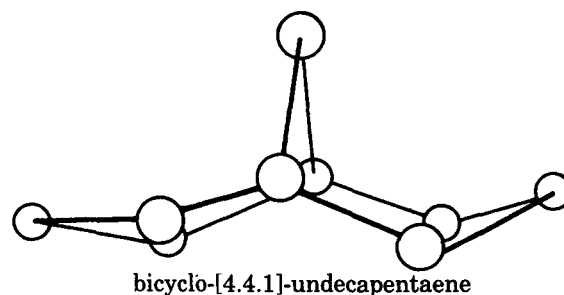
	X-Ray ^a	Calc.
1-2	1.389 ± .010	1.400
2-3	1.383 ± .009	1.398
2-13	1.525 ± .020	1.515
2-13-14	110.3 ± .5	111.2
a	0.042 Å	0.07 (6°)
b	0.143 Å	.19 (17°)
c	0.408 ± .04 Å	.43 (28.5°)

^a Errors are for deviations from *C*_{2h} symmetry and do not include experimental errors.



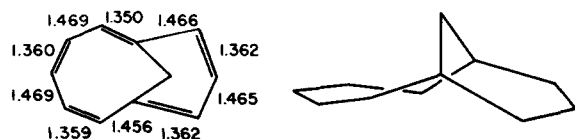
bicyclo [4.4.1] undecapentaene, is experimentally found to be nonaromatic in the chemical sense, although the ultraviolet spectrum suggests extensive conjugation. The NMR spectrum shows eight protons at τ 7.5-6.8 and two protons at τ -0.5, which may be considered as evidence for a ring current.³⁸

An x-ray examination³⁹ of a crystalline carboxybicyclo[4.4.1]undecapentaene indicates a relatively planar structure with the outer ring bond lengths alternating in a naphthalene fashion, but less so (spread 0.031 Å here vs. 0.049 Å) for the difference in the peripheral bonds of naphthalene, and this suggests considerable aromatic character. Our calculated geometry (with no symmetry constraints) is in good agreement with the x-ray structure as shown in Table X when the 1,6 resonance is included. (If 1,6 resonance was not included, the conjugated bonds were essentially benzenoid, all about 1.40 Å in length.) The dihedral angles in the



ten-membered ring are distorted no more than 30° from planarity, with the average distortion being only 19° (the average experimental values (average deviation about 2°) are given in parentheses).

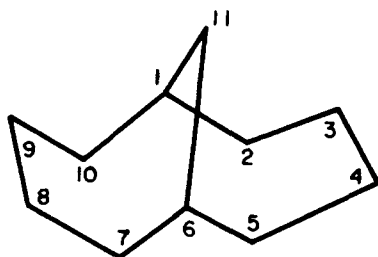
The less symmetrical isomer of this compound, bicyclo[5.3.1]undecapentaene, has a 1,5 methylene bridge and is calculated (including the 1,5 integral) to have almost total bond alternation. The apparent lack of aromaticity is a consequence of σ system constraints which forces several ring dihedral angles to differ up to 55° from planarity, with an average distortion of 26°, effectively gener-



calculated bond lengths in bicyclo[5.3.1]undecapentaene

ating a π system composed of isolated segments, each with an even number of π atomic centers. This compound is thus calculated to be fundamentally quite different from the isomeric [4.4.1] system, even though their average planarities are similar. The [4.4.1] system is a [10]annulene perturbed in the naphthalene sense, while the [5.3.1] system is perturbed in the azulene sense. The latter offers a much smaller resonance stabilization (see ref. 23 for further discussion).

There is reason to think the predictions for the 5.3.1 compound may, however, be in error. Compounds containing this ring system have been prepared. The NMR spectra⁴⁰ shows strong ring currents which would be expected if the bond lengths were more or less equal, but would probably not be expected for the butadiene type structure predicted. A crystallographic study will hopefully resolve the structural question eventually, but it has so far not proved possible to obtain a crystalline derivative of this ring system.⁴¹ It may be that the predicted structure, which is based on a Hartree-Fock calculation for the pi system, is wrong. This could happen if electron correlation stabilizes the benzenoid system by more than it stabilizes the alternating system sufficiently to change the latter structure over to the former, as seems to be the case with [18]-annulene (*vide infra*).



The compound [12]annulene is calculated to have bond alternation with 1 as the most stable conformation (see Table XI). The dihedral angles about the single bonds range from 21 to 67° from planarity, and the molecule is thus more flat than in earlier calculations,³ and the bond alternation is slightly less severe. The activation enthalpy for the interconversion was deduced via NMR to be 3.7 ± 0.2 kcal/mole, and 2 was suggested

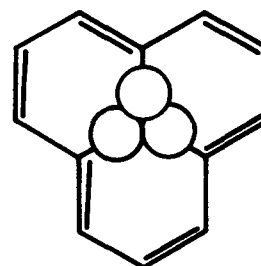
Table X. Geometry of biocyclo-[4.4.1]-undecapentaene.

	X-ray ^{a,b}	Calcd.*
	Bond, Å	
1-2	1.409	1.408
2-3	1.383	1.398
3-4	1.414	1.423
1-11	1.477	1.485
1-11-6	99.6	98.9
2-1-11	116.1	116.9
1-2-3	122.3	121.5
2-3-4	127.7	127.5

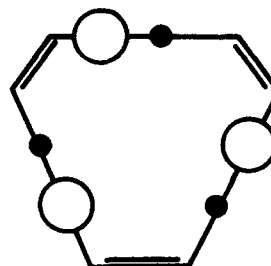
^a Average values. Reported results show bond lengths nonequivalent by 0.01 Å and angles by 2° with standard deviations of 0.01 Å and 0.3°.

^b Reference 39.

as the transition state.^{39,42} We calculate a relative enthalpy of 3.65 kcal/mole for structure 2.



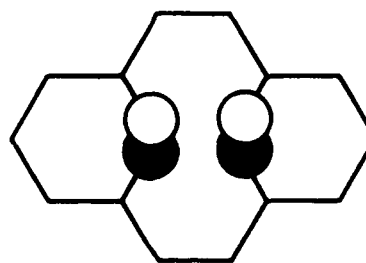
1



2

In [14]annulene, 3 is calculated to be more stable than 4 by 5.93 kcal/mole (2.5 kcal/mole was previous difference³). An x-ray examination indicates the molecule is centrosymmetric.⁴³ Our calculated structures are not very different from those calculated earlier, with the C—C bond lengths all being in the range of 1.402–1.402 Å.

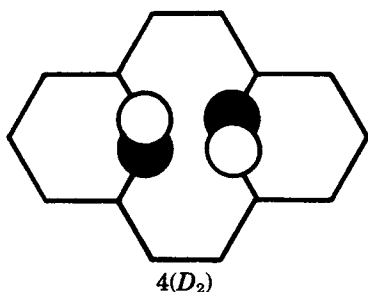
In [18]annulene, the nonplanar-alternant structure (7) is calculated to be favored by



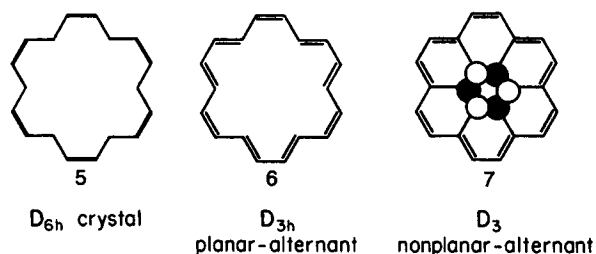
3(C_{2h})

Table XI. Calculated geometry of [12]-annulene.

Bond	Length, Å	Angle	Deg	Angle	Deg
1-2	1.353	12-1-2-3	10.8	1-2-3	120.9
2-3	1.469	1-2-3-4	159.0	2-3-4	126.2
3-4	1.352	2-3-4-5	175.7	3-4-5	120.8
4-5	1.479	3-4-5-6	37.3	4-5-6	123.7
5-6	1.355	4-5-6-7	9.6	5-6-7	121.5
6-7	1.473	5-6-7-8	140.8	6-7-8	123.8
7-8	1.350	6-7-8-9	167.3	7-8-9	125.2
8-9	1.476	7-8-9-10	35.3	8-9-10	126.9
9-10	1.352	8-9-10-11	4.5	9-10-11	124.5
10-11	1.490	9-10-11-12	112.7	10-11-12	124.7
11-12	1.346	10-11-12-1	172.1	11-12-1	119.7
12-1	1.488	11-12-1-2	50.3	12-1-2	121.9



2.27 kcal/mole over the planar-alternant form (6) and (17.0 kcal/mole) over the D_{6h} crystal geometry (5). (Our calculated values³ were 8.89 and 10.15 kcal/mole, respectively). The calculated geometry of 7 is listed in Table XII. (Our current geometry is considerably flatter than our previous one, because the hydrogens are much softer and fit in the interior of the ring more easily. The mean nonplanarity of the carbon atoms is 0.057 Å compared to the previous value of 0.102 Å).



The experimental structure (x-ray) does not show the bond alternation we calculate.

Various interpretations of this discrepancy are possible. The most likely one seems to be that electron correlation favors the more symmetrical structure sufficiently that it becomes more stable than one with D_3 symmetry, and calculations supporting this view have been presented.⁴⁴ If this is indeed correct, then the SCF approximation is just not good enough in this case. While we could carry out configuration interaction calculations on this molecule, we would really have to go back to ethylene and butadiene, and redo the parameterization with this included. But for molecules as large as [18]annulene, the amount of computer time required for the configuration interaction is very large compared with the amount of time needed for the molecular mechanics calculations, which renders this approach unattractive. Another way of including electron correlation in the calculations may be feasible, and this problem will be studied further.

ENERGY DIFFERENCES

Butadiene is a key molecule to fit in determining torsional constants for the force field. The *s-trans* form of 1,3-butadiene is found to be favored over the *s-cis* by 2.34 kcal/mol, and similar values are given by *ab initio*

Table XII. Calculated geometry of [18]-annulene (D_3).

Bond	Calcd. length	Angle	Calcd. angle	Atom	Displacement from mean plane Å
1-2	1.357	18-1-2	122.9	1	0.046
2-3	1.465	1-2-3	126.0	2	-0.116
3-4	1.361	2-3-4	123.2	3	-0.012
4-5	1.465	3-4-5	123.2	4	0.012
5-6	1.357	4-5-6	126.0	5	0.116
6-7	1.470	5-6-7	122.9	6	-0.046

calculations⁴⁵ (2.05 kcal/mol) and by experiment (2.50 kcal/mol).⁴⁶ We also calculate the rotational barrier from the *s-trans* form to be 6.84 kcal/mol, in agreement with the experimental value 7.16 obtained by Carreira⁴⁶ and the value 6.73 obtained by *ab initio* calculations.⁴⁵ There have been several recent studies on the *cis* conformation of butadiene, directed in part at determining whether or not this conformation is planar at the energy minimum, or alternatively if there is a small maximum at that point, and a torsional angle of approximately 30° corresponds to the minimum. Experimental evidence has been quoted as favoring the former⁴⁷ while the best *ab initio* calculations so far reported seem to favor the latter.⁴⁸ It seems pretty certain that the Hartree-Fock level calculation will furnish a small barrier (about 0.7 kcal high) at the *cis* conformation. This barrier will probably be reduced and may disappear when electron correlation is included in the calculation, however. The reason this may be anticipated is similar to why correlation causes a reduction of the calculated barrier over the *cis* conformation of butane.⁴⁹ When atoms are pushed very closely together, well within the sum of the van der Waals radii, there is a strong repulsion between them (an r^{-12} Lennard-Jones term, or equivalent term). There is, however, also a strong attraction from the r^{-6} term in the van der Waals potential, and this is due to electron correlation. The term also becomes quite large when the van der Waals repulsion becomes quite large, namely in the *cis* conformations. The effects of the r^{-12} terms are included in the Hartree-Fock calculation, but to get the effects of the r^{-6} terms, electron correlation must be taken into account. At the time the MM2 parameterization was carried out these latest results were unavailable, and our best belief was that the potential is approximately flat from a torsion angle of 0° out to about 30°, and the values chosen for MM2 give a potential of that kind. Our calculated conformational energy differences here and in what follows are summarized in Table XIII.

In isoprene, the *s-trans* is conformation favored over the *s-cis* by 1.16 kcal/mole (1.2 kcal/mole experimental)⁵⁰ with a 5.37 kcal/mole barrier to rotation.

Styrene is calculated to be planar with a 4.30 kcal/mole barrier to rotation. In the pre-

vious force field,³ the harder hydrogens forced the molecule to be nonplanar.

Biphenyl has two H...H interactions between ortho hydrogens of the type found in styrene, and the minimum energy form has the rings inclined 36.7° to one another (50° was previous value³). This agrees with a gas phase value⁵¹ of 41.6°. The 0° structure is 1.72 kcal/mole higher in energy, and the 90° structure is 1.89 kcal/mole higher. The barrier to rotation (1.89 kcal/mole) is now much lower than in our previous calculations (5.0 kcal/mole) due to the softer hydrogens stabilizing the 0° structure. The 0° structure was the previous energy maximum for rotation.

The energies of the conformations of cycloheptadiene were reevaluated. The previous force field^{3,52} found a C_1 form to be the same energy (0.02 kcal/mole) as the C_s , with a facile pseudorotation between the two C_1 forms through the C_s . The current force field finds the C_s form favored over the C_1 by 1.04 kcal/mole. This is still in agreement with our earlier interpretation⁵² of the NMR data⁵³ as a pseudorotationally averaged C_2C_3 dihedral angle. The C_s form is calculated to be favored over the C_2 by 2.07 kcal/mole (the earlier value was 0.05 kcal/mole^{3,52}), and electron diffraction has found only the C_s form.⁵⁴

Hexamethylbenzene has been subjected to a number of theoretical calculations and experimental measurements. It is generally agreed that the methyl groups lie out of the mean plane of the ring by a significant amount, alternately above and below this plane. The ring carbons themselves also lie out of the plane, but by a smaller amount. Just how big the deviation from planarity is varies with the experiment and/or calculation. The available data is summarized by Melissas and co-workers.⁵⁶ The *ab initio* calculations reported⁵⁶ are in reasonable agreement with neutron and x-ray diffraction, with the ring carbons being out of the plane by about .01 Å, and the methyl groups by about 0.05 Å. Molecular mechanics calculations (MMP1) show somewhat greater pucker (0.03 and .18 Å), and electron diffraction measurements, not corrected for shrinkage, give these numbers as 0 and 0.26 Å. It is known that the hydrogens are too hard in the MM1 force field, and this leads to excessive puckering.

Table XIII. Energy differences between two conformations (kcal/mol).^a

Transformations	This work	$-\Delta[\Delta H_f(g)]$	Exptl ^b
1,3-Butadiene			
Cis \rightarrow trans	2.34		2.50
1,3-Cyclohexadiene			
π planar $\rightarrow \pi$ nonplanar with C_2 symmetry	2.15		1.10
1,3,5-Cycloheptatriene			
π planar $\rightarrow \pi$ nonplanar	2.26		5.7
1,3-Cycloheptadiene			
π planar $\rightarrow \pi$ nonplanar	see discussion		
Cyclooctatetraene			
π planar $\rightarrow \pi$ nonplanar (tub form)	13.64		13.7
1,2,3-Trimethylbenzene			
π planar $\rightarrow \pi$ nonplanar	0.05		
Hexamethylbenzene			
π planar $\rightarrow \pi$ nonplanar	2.44		>0
4,5-Dimethylphenanthrene			
π planar $\rightarrow \pi$ nonplanar	16.75		18.5
9,10-Dimethylphenanthrene			
π planar $\rightarrow \pi$ nonplanar	1.10		
Triphenylene			
π planar $\rightarrow \pi$ nonplanar	0.01		>0
3,4-Benzophenanthrene			
π planar $\rightarrow \pi$ nonplanar	7.27		5-10
Perylene			
π planar $\rightarrow \pi$ nonplanar	0		>0
trans-Stilbene			
π planar $\rightarrow \pi$ nonplanar	0		>0
1,3,5-Triphenylbenzene			
π planar $\rightarrow \pi$ nonplanar			
Biphenyl			
π nonplanar $\rightarrow \pi$ planar (37 \rightarrow 90°)	1.89		>0
[18]-Annulene			
$D_{3h} \rightarrow D_3$	2.27		≤ 0
Corannulene			
π planar $\rightarrow \pi$ nonplanar (cup form)	30.0		>0

^a Reference 55.^b See ref. 7 for literature references.

With the MM2 force field, the puckering is much reduced, the out-of-plane displacements being now, respectively, 0.005 and 0.081 Å. Thus the MM2 values are in reasonable agreement with the *ab initio* calculations and with the neutron and x-ray diffraction. Only the electron diffraction values now seem out of line.

The crystal structure of 3,4-benzophenanthrene was analyzed crystallographically by Schmidt et al.⁵⁷ and theoretically studied by Hirshfeld⁵⁸ 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 23° being preferred over the planar one by 7.27 kcal/mol. An estimate of 5–10 kcal/mol⁵⁷ for this energy differ-

ence was deduced from the experimental resonance energy.

4,5-Dimethylphenanthrene is even more overcrowded because planar models would involve a pair of hydrogen atoms closer than 2.0 Å. The calculated energy difference between planar and nonplanar conformations is 16.75 kcal/mol. No experimental value is available, however, indirect evidence is available. Theilacker and Baxmann⁵⁹ 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 be 23.5 kcal/mol.⁶⁰ Munday

and Sutherland⁶¹ studied 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,^{61,62} 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.⁶³ 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 propellerlike 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, 33.8 and 9.3, respectively), gives a value close to that reported for the dihedral angle for Ph—C=C—Ph (43.1°). 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.); 126.6° (Calcd.)].

The molecular structure of *trans*-stilbene in the solid state has been reported to be approximately planar.^{64,65} The gas phase structure has been studied by the electron diffraction method and found to be nonplanar and to possess C_2 symmetry.⁶⁶ The phenyl groups were found to be rotated $30 \pm 15^\circ$

about the C—Ph bonds. Our calculations show that the molecule is planar. However, the curve for potential energy vs. the dihedral angle is very shallow, so a wide angle torsional motion is expected.

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.⁶⁷ As can be seen from Table III, its x-ray structure is quite similar to our calculated results. The planar form is calculated to be 30.0 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 0.05 and 1.10 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.

HEATS OF FORMATION⁵⁵

A revision of the heat of formation table from Kao and Allinger (ref. 7) is given in Table XIV. The data were fit with the constraint that all alkane data from MM2 remain unchanged and that unconjugated alkene data be simultaneously fit. Note that the average deviation (calc.-exp.) remains the same. A few comments should be made.

The calculated ΔH_f° of ethylene differs from that of MM2. This problem could easily be solved by adding a structural ΔH term for isolated C=C (when involved in a π calculation) or perhaps, more properly, one should reevaluate the equilibrium bond energies of ethylene and benzene used in the $E_b^{C=C}$ calculation. These terms were changed from those of Lo and Whitehead¹² for our previous study.⁷ Note that MM2 and MMP2 give identical results for any olefin if a π -calculation is not used.

The heats of formation of the larger polycyclic aromatic compounds are all calculated too large by 3–7 kcal/mole (i.e., pyrene, tetracene, triphenylene, etc.). Some correction could be made here but at the expense of naphthalene and other compounds with a $C_{sp^2}(C_{sp^2})_3$ structural feature.

Table XIV. Comparison of Experimental and Calculated $\Delta H_f^\circ(g)$.

Formula	Compd Name	MMP2	$\Delta H_f^\circ(g)$ Exptl	(Calcd.- Exptl) ^h	Probable errors
C ₂ H ₄	Ethylene	13.38	12.45	0.93	0.10
C ₄ H ₆	<i>trans</i> -Butadiene	25.45	26.11	-0.66	0.15
C ₅ H ₆	Cyclopentadiene	32.72	31.94	0.78	0.28
C ₅ H ₈	<i>cis</i> -1,3-Pentadiene	19.74	19.13, 19.78	-0.04	0.24
	<i>trans</i> -1,3-Pentadiene	17.51	18.12	-0.61	0.16
	2-Methyl-1,3-butadiene	18.92	18.06	0.86	0.20
C ₆ H ₆	Benzene	20.24	19.81	0.43	0.13
C ₆ H ₈	1,3-Cyclohexadiene	24.89	25.38	-0.49	0.19
C ₆ H ₁₀	2,3-Dimethyl-1,3-butadiene	12.59	10.78	1.81	0.30
C ₇ H ₈	1,3,5-Cycloheptatriene	45.52	43.90	1.62	0.36
C ₇ H ₁₀	Toluene	12.07	11.99	0.08	0.10
	1,3-Cycloheptadiene	22.76	22.56	0.20	0.24
C ₈ H ₈	Cyclooctatetraene	70.39	71.13	-0.74	0.33
	Styrene	34.15	35.30	-1.15	0.25
C ₈ H ₁₀	Ethylbenzene	6.98	7.15	-0.17	0.19
	<i>o</i> -Xylene	4.49	4.56, 4.23	-0.07	0.26
	<i>m</i> -Xylene	3.91	4.14, 3.59	-0.23	0.18
	<i>p</i> -Xylene	3.90	4.31, 3.97	-0.07	0.24
	Dimethylfulvene	31.59	32.1	-0.51	1.3
C ₉ H ₈	Indene	39.78	39.08	0.70	0.37
C ₉ H ₁₀	Indan	14.23	14.42	-0.19	0.53
C ₉ H ₁₂	<i>n</i> -Propylbenzene	1.53	1.89	-0.36	0.19
	Isopropylbenzene	0.50	0.96	-0.46	0.26
	1-Methyl-2-ethylbenzene	0.71	0.39	0.39	0.27
	1-Methyl-3-ethylbenzene	-1.18	-0.43	-0.75	0.29
	1-Methyl-4-ethylbenzene	-1.19	-0.76	-0.43	0.34
	1,2,3-Trimethylbenzene	-2.42	-2.26	-0.16	0.29
	1,2,4-Trimethylbenzene	-3.65	-3.31	-0.34	0.26
	1,3,5-Trimethylbenzene	-4.21	-3.81	-0.40	0.33
C ₁₀ H ₈	Azulene	74.28	69.06, ^c 73.5	0.22	0.9
	Naphthalene	35.65	35.85, ^c 36.05	-0.20	0.25
C ₁₀ H ₁₂	1,2,3,4-Tetrahydronaphthalene	4.34	6.57 ^m	-2.23	0.6
C ₁₀ H ₁₄	<i>n</i> -Butylbenzene	-3.91	-3.18 ^d	0.73	0.30
	Isobutylbenzene	-5.52	-5.14	-0.38	0.33
	<i>sec</i> -Butylbenzene	-3.99	-4.15	0.16	0.31
	<i>tert</i> -Butylbenzene	-5.58	-5.40	-0.18	0.31
C ₁₂ H ₈	Biphenylene	106.6	104.43, ^c 115.2	2.20	1.5
	Acenaphthalene	61.42	62.04, ^c 61.6	-0.18	1.2
C ₁₂ H ₁₀	Biphenyl	43.28	43.57, ^c 43.53	-0.25	0.60
	Acenaphthene		37.4		0.7
C ₁₂ H ₁₈	Hexamethylbenzene	-20.72	-20.7	0	0.62
C ₁₄ H ₈	Dibenzo-[cd, gh]-pentalene	143.54			
C ₁₄ H ₁₀	Anthracene	55.04	55.44, ^c 55.2	0.16	1.1
	Phenanthrene	50.12	49.52, ^c 49.5	0.60	1.1
C ₁₄ H ₁₂	<i>trans</i> -Stilbene	54.92	56.43, ^{cd} 52.48	-1.51	0.5
	<i>cis</i> -Silbene	58.86	60.31	-1.45	0.42
	1,1-Diphenylethene	58.85	58.7	0.15	1.1
	Paracene	58.37			
	9,10-Dihydroanthracene	40.69	38.2	2.49	1.1
C ₁₅ H ₁₂	Dibenzo-[hf]-cycloheptatriene	60.42			
C ₁₆ H ₁₀	Fluoranthene	70.26	69.78, ^c 69.08	0.48	0.56
	Pyrene	58.37	51.59 ^g	6.78	0.64
C ₁₆ H ₁₄	2,7-Dimethylphenanthrene	33.67	34.20	-0.53	0.50
	4,5-Dimethylphenanthrene	44.64	46.26	-1.56	1.46
	9,10-Dimethylphenanthrene	40.86	40.0	0.86	2.1
C ₁₆ H ₁₆	[2.2]-Paracyclophane	46.41	57.6 ⁿ	-11.2	1.0
	[2.2]-Metacyclophane	39.49	40.08	-0.59	1.7
C ₁₈ H ₁₂	Triphenylene	67.28	63.4	3.88	1.2
	Chrysene	66.61	62.8	3.81	1.2
	3,4-Benzophenanthrene	69.62	69.6	0.02	1.2
	1,2-Benzanthracene	67.96	69.63, ⁱ 65.97 ^j	1.99	3.0
	Tetracene	76.19	69.8	6.39	1.1

C ₁₈ H ₁₄	Diphenylfulvene	94.08	96.1	-2.02	4.0
	5,12-Dihydrotetracene	56.22	53.1	3.12	1.1
C ₁₈ H ₈	[18]-Annulene	125.40	124.0, ^a 67 ^l	1.40	6.0
C ₂₀ H ₁₀	Corannulene	86.42			
C ₂₀ H ₁₂	Perylene	79.00	73.7	5.30	1.1
Av. deviations				0.84°	0.77°

^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, New York, 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, *J. Chem. Thermodyn.*, **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).

^h See ref. 7.

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).

^o We have omitted the results for pyrene, tetracene, perylene, and [2.2]-paracyclophane in calculating the deviation from experiment because we believe the experimental values are seriously in error for the first three and the latter is beyond the scope of the present work (see discussion). If these are included the average deviation and average experimental errors become 1.27 and 0.78 kcal/mol, respectively.

Resonance Energies

It has long been traditional to discuss the stability of aromatic systems in terms of "resonance energies". These have been defined in various ways, and hence the numerical values, which are definition dependent, tend to vary considerably. We believe the most useful definition is one similar to that given by Dewar.⁶⁸ Our definition is substantially the same as his, but his refers to idealized geometries, where ours refers to numbers actually calculated by molecular mechanics, and based on heats of formation. So our numbers are somewhat different than his, although for six-membered rings the differences are small. Our reference points, like Dewar's, are the two numbers which result from bond energy terms, one for the short bond and one for the long bond, of a conjugated polyene. To determine the resonance energy of a particular molecule (if it is planar), one first writes down the Kekule forms, and from these determines the number of short and long bonds needed to describe the compound as a polyene. Parameters have been chosen so that when this description is read into the program for a simple polyene, the heat of formation is calculated, and from

this a pi energy, and the difference between the latter and idealized polyene pi energy gives the resonance energy. Parameters were chosen to make these resonance energies come out to be zero for ordinary linear all-trans polyenes. The resonance energies calculated for a few simple compounds are: benzene, 20.24 kcal/mol; naphthalene, 33.70 kcal/mol; azulene, 6.74 kcal/mol; cyclobutadiene, -20.06 kcal/mol, etc., values similar to those obtained by Dewar.⁶⁸ For nonplanar polyenes, while one can calculate a resonance energy, it is not clear just what this number means, or how it can be utilized. Making the molecule nonplanar means moving to places on the torsional potential surface away from the minima, and in general that means the resonance energy will be negative (antiaromatic), but this is a steep function of nonplanarity in most cases, and really has nothing to do with the inherent stability of the planar pi system. Accordingly, we defined a quantity "planar resonance energy". This is obtained by taking the actual geometry of the pi part of the molecule and removing the direction cosine terms, so that the molecule is "planarized". The resonance energy then is calculated in the usual way. This corresponds to the resonance energy the molecule would

have if it were planar. This is a well defined quantity, if somewhat remote from reality. It does not involve the sigma system in any way. Resonance energies calculated in this way may be of some use, and they are discussed further elsewhere.²³

CONCLUSIONS

The method presented here is an extension of the MM2-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 overall accuracy of the results is in general competitive with that of good quality experimental work, although there are specific unsolved problems.

We are grateful to the National Science Foundation and to the National Institutes of Health for support of this work (Grant Nos. NSF-CHE8315543 and NIH-R24RR02165, respectively.)

References

1. D. W. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974).
2. For a review, see N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976).
3. N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973).
4. Our earliest publicly available program was MM1, and it dealt only with nonconjugated systems. An extended version dealt with conjugated hydrocarbons and ketones (MMP1). These programs are available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, as program 318 [(QCPE, **11**, 318 (1976)]. Subsequently a better molecular mechanics program was devised by us (MM2). The first application was to saturated hydrocarbons (ref. 5), followed by extension to most common functional groups. This program (MM2/77) is available from QCPE [(QCPE, **12**, 395 (1980)]. Still later the conjugated hydrocarbon part of the program was added (as described in the present work). The resulting program is called MM2/82. (We have decided to drop the MMP2 designation. From MM2/82 on, the same program deals with both conjugated and unconjugated systems). The MM2/82 program is available from Molecular Design, Ltd., 2132 Farallon Drive, San Leandro, California 94577, and from QCPE. A still more recent version (MM2/85) is an extension of earlier programs which also includes conjugated heterocycles. It will be available in due course.
5. N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).
6. For a review see U. Burkert and N. L. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, D.C., 1982.
7. J. Kao and N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 975 (1977).
8. J. C. Tai, R. Li, and N. L. Allinger, to be published.
9. R. C. Haddon, *Pure and Appl. Chem.*, **68**, 137 (1986).
10. N. L. Allinger, J. T. Sprague and T. Liljefors, *J. Am. Chem. Soc.*, **96**, 5100 (1974).
11. The above description is for the *f* factor as it appears in MM2/82 and earlier versions of the program. We have found a few cases where the relatively small values of *f* so calculated permit excessive deformation of pi systems, and thus yield rotational barriers which are too low in a few cases. While this problem will be corrected in MM2/85 and later versions of the program, we wish to alert users of the earlier versions to the potential problem.
12. D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027 (1968).
13. K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).
14. T. Dunning, **53**, 2823 (1970).
15. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
16. (a) D. Rohrer. This program has been called MM2P. It has been incorporated in the Prophet Network, and has been widely used by the Duax group, and others, e.g., T. Darden, J. D. McKinney, K. Gottshalk, A. T. Maynard, L. G. Pedersen, *J. Am. Chem. Soc.*, **108**, 207 (1986); (b) K. B. Lipkowitz, A. M. N^alor, and W. B. Melchior, *Tetrahedron Lett.*, 2297 (1984).
17. J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
18. In electron diffraction work the investigator usually gives three times the standard deviation from the error matrix as the probable error, whereas in crystallography the esd's themselves are usually quoted.
19. S. S. Butcher, *J. Chem. Phys.*, **42**, 1833 (1965).
20. M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4625 (1964).
21. J. B. Lambert, L. J. Durham, P. Lepoutere, and J. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965). F. R. Jensen and L. A. Smith, *J. Am. Chem. Soc.*, **86**, 956 (1964); F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).
22. H. J. Lindner, *Tetrahedron*, **37**, 543 (1981).
23. N. L. Allinger and Young Yuh, *Rev. Pure and Appl. Chem.*, **55**, 191 (1983).
24. N. L. Allinger, J. T. Sprague, and T. Liljefors, *J. Am. Chem. Soc.*, **96**, 5100 (1974).
25. M. G. Newton, T. J. Walter, and N. L. Allinger, *J. Am. Chem. Soc.*, **95**, 5652 (1973).
26. H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Cryst.*, **B28**, 1733 (1972).
27. J. T. S. Andrews and E. F. Westrum, Jr., *J. Phys. Chem.*, **74**, 2170 (1970).
28. N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **93**, 1637 (1971).
29. C. Krieger, J. Ciebe, and W. Tochtermann, *Tetrahedron Lett.*, 707 (1983).
30. N. L. Allinger, T. J. Walter, and M. G. Newton, *J. Am. Chem. Soc.*, **96**, 4588 (1974).
31. D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).
32. (a) C. J. Brown, *J. Chem. Soc. (B)*, (1953), 3265; (b) K. Lonsdale, H. J. Milledge, and K. V. Krishna Rao, *Proc. Roy. Soc.*, **76**, 6132 (1954).
33. R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).
34. D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966).
35. J. Bernstein and K. N. Trueblood, *Acta Cryst.*, **B27**, 2078 (1971).
36. D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, **92**, 1073 (1970).

37. C. J. Brown, *J. Chem. Soc. (B)*, 3278 (1953).
38. E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964).
39. J. F. M. Oth, H. Rottele, and G. Schroder, *Tetrahedron Lett.*, **61**, (1970).
40. L. T. Scott, M. Oda, and I. Erden, *J. Am. Chem. Soc.*, **107**, 7213 (1985).
41. L. T. Scott, personal communication.
42. J. F. M. Oth, J. M. Gilles, and G. Schroder, *J. Am. Chem. Soc.*, **67** (1970).
43. J. Bregman, *Nature (London)*, **194**, 679 (1962).
44. H. Baumann, *J. Am. Chem. Soc.*, **100**, 7196 (1978).
45. L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).
46. L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975).
47. M. E. Squillacote, T. C. Semple, and P. W. Mui, *J. Am. Chem. Soc.*, **107**, 6842 (1985).
48. J. Breulet, T. J. Lee, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **106**, 6250 (1984).
49. F. A. Van-Catledge and N. L. Allinger, *J. Am. Chem. Soc.*, **104**, 6272 (1982).
50. D. A. C. Compton, *Perkin Trans. II*, 1666 (1976).
51. O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).
52. N. L. Allinger and J. T. Sprague, *Tetrahedron*, **29**, 3811 (1973).
53. P. Crews, *Chem. Comm.*, **11**, 583 (1971).
54. K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26**, 3643 (1972).
55. The force-field parameters were chosen for typical molecules, to take butadiene as an example, so as to fit the steric energy differences between the cis and trans isomers, and the transition state separating them. Later, when the heats of formation of molecules were worked out, the calculation was based on the stable form, the trans isomer in the case of butadiene. This leads to an inconsistency, which was not recognized until several years after this work was finished and the program had been widely distributed. The inconsistency is that the pi electronic energy is used to calculate the heat of formation. If one calculates the heat of formation of the cis butadiene, because this number is slightly different from that of the trans isomer, one gets a heat of formation which is not quite consistent with that which one would get from calculation of the heat of formation of the trans isomer. This is a common problem in all of the heat of formation calculations. Fortunately, the errors are small, on the order of tenths of kcal, as far as we are aware. But if one is comparing systems which quite different electronic energies, let's say, for example, a molecule which has in one arrangement bonds of equal bond length, and in a second arrangement, alternating long and short bonds, the bulk of the difference between these two geometries will be reflected in the heat of formation, but not in the steric energies. Hence, in real cases, the heats of formation differences and steric energy differences may give somewhat different results. Which result is better will depend on the nature of a case at hand.
56. V. Melissas, K. Faegri, Jr., and J. Almlof, *J. Am. Chem. Soc.*, **107**, 4640 (1985).
57. Table III, footnote j; also see F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3301 (1954).
58. F. L. Hirschfeld, *J. Am. Chem. Soc.*, 2126 (1963).
59. W. Theilacker and F. Baxmann, *Justus Liebigs Ann. Chem.*, **581**, 117 (1953).
60. K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **86**, 1733 (1964); K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).
61. R. Munday and I. O. Sutherland, *J. Chem. Soc., B*, **1**, 80 (1968).
62. This is true according to rotational barriers in substituted binaphthyl systems. See A. S. Cooke and M. M. Harris, *J. Chem. Soc. C*, 988 (1967).
63. M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.*, **26**, 69 (1975).
64. A. Hoekstra, P. Meertens, and A. Vos, *Acta Crystallogr., Sect. B*, **31**, 2813 (1975).
65. C. J. Finder, M. G. Newton, and N. L. Allinger, *Acta Crystallogr.*, **B30**, 411 (1974).
66. M. Traetteberg, E. B. Frantsen, F. C. Mijlhoff, and A. Hoekstra, *J. Mol. Struct.*, **26**, 57 (1975).
67. J. C. Hanson and C. E. Nordman, *Acta Crystallogr., Sect. B*, **32**, 1147 (1976).
68. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969, p. 173.