

# Molecular Mechanics (MM3) Calculations on Conjugated Hydrocarbons<sup>1</sup>

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The MM3 molecular mechanics program has been extended to conjugated systems. A VESCF method is applied to the pi-system to calculate bond orders, from which various stretching and torsional parameters are obtained. The procedure gives somewhat better results than the analogous MM2 calculations. It has been applied to a study of 81 compounds of aromatic and other conjugated hydrocarbons, as well as 45 alkenes and unconjugated polyenes. The structures calculated are generally in good agreement with experiment, and the heats of formation of these compounds can be calculated with a rms value of 0.62 kcal/mol, which may be compared with the average experimental error of 0.61 kcal/mol. In addition, vibrational frequencies for five representative conjugated model structures are calculated, with an rms value of 46 cm<sup>-1</sup>, and from these, other properties such as entropy can be calculated.

## INTRODUCTION

Over the past 20 years or so, molecular mechanics has become a powerful tool for the study of molecular structure and related properties.<sup>4</sup> The MM2 force field was first applied to saturated hydrocarbons, and subsequently extended to many functional groups,<sup>4,5</sup> and to conjugated hydrocarbons,<sup>6</sup> and heterocyclic<sup>7</sup> systems as well. The simplest kind of a valence force field may be described as diagonal (no cross terms), and harmonic (no cubic or higher terms). Early force fields were, apart from the van der Waals' terms, essentially of this most simple variety, although more recent force fields, including MM2, are slightly more complicated. Over the years, many shortcomings of the MM2 force field became apparent.<sup>8</sup> Some of these shortcomings resulted from the force field being too simple, while others resulted from inadequate parameters. These errors have all been much reduced with the MM3 force field.<sup>9</sup>

Additionally, there were two other significant errors in the original version of MM2 as applied to conjugated systems.<sup>6</sup> One of these had to do with how torsion barriers were calculated when aromatic systems were deformed. The original method proved not to be very general, and it sometimes allowed systems to deform much too easily. This problem was corrected later for MM2.<sup>10</sup> The same corrected method has been used here. Further, because the C—H bond was

taken to be nonpolar in MM2, certain aspects of benzene-benzene interactions, such as in dimers, and as in the benzene crystal, were not adequately accounted for.<sup>11</sup> This was discussed with the alkenes,<sup>12</sup> and the bond dipoles assigned here are the same as those used with alkenes. Crystal packing calculations with MM3 were discussed earlier.<sup>9,11</sup> It was also desired to similarly update the calculations on pi-systems. One improvement that was obviously desired consisted of the inclusion of non-neighbor overlaps in the pi-system calculation. A second improvement was the VESCF calculation,<sup>13</sup> in place of the SCF calculation. The MM2 pi-system calculation had both of these things the other way around, so as to utilize still earlier work<sup>14</sup> on heat of formation calculations. In the present work, we began with the MM3 force field for alkanes and alkenes, and rederived the necessary formulation for the heat of formation calculations following Lo and Whitehead, but using nonneighbor overlap and a VESCF calculation as the fundamental pi-system treatment. The basic theory for obtaining the heats of formation from the pi-system calculation using a straight SCF method has been given previously,<sup>4,6</sup> and will not be repeated here. A parallel derivation was made, utilizing the VESCF approximation,<sup>13</sup> with the inclusion of nonneighbor overlap. As far as the geometry, the pi-system calculation is run on the starting geometry, and this gives the bond orders for the bonds which are part of the conjugated system. These bond or-

ders are related to the bond lengths, the stretching force constants, and the  $V_2$  torsion constant by linear relationships,<sup>4,6</sup> which were parameterized to fit known structures (ethylene, benzene, and butadiene). The use of a VESCF method in place of an SCF method makes no difference in the case of alternate hydrocarbons, but in a few hydrocarbons (such as fulvene and azulene) the charge distribution is nonuniform,<sup>15</sup> and the VESCF method leads to a partial equilization of charges. The pi-system dipole moments for non-alternant hydrocarbons are calculated to be much larger than the experimental values with a straight SCF method (by about a factor of 2 or 3). The VESCF method reduces this difference, but the calculated moments are still too large. Physically, this can be seen to result from the fact that there is an induced moment in the sigma-system which tends to counteract the pi-system moment. Having no convenient way<sup>16</sup> to determine the induced sigma-system moments, we have arbitrarily taken them to be opposite to the pi-moment, and 0.35 the magnitude of the latter. This correction gives for the azulene molecule calculated and observed moments of 1.03 and 0.80 D, respectively. More accurate approximations along these lines will be considered in the future.

Theory tells us that the sigma-pi separation is valid as long as the system is planar. Accordingly, our SCF calculations, and force parameter evaluations are determined on the planarized pi-system. Forces are then allowed to act, and if the system becomes nonplanar, the calculation is a molecular mechanics calculation at that point, and the sigma-pi separation no longer matters. It is, however, essential to determine at the beginning of the calculation whether or not the system is planar. If it is, only one pi calculation is required. But if it is nonplanar, then one has to do the pi calculation on the planar system to determine the torsion parameters, but then again on the nonplanar system in order to determine the bond stretching parameters. If the system is planar, there is no point to do the calculation twice. Accordingly, in MMP1 and MM2, the user designated whether or not the system was planar. We found this led to great difficulties, however, because the definition of "planar" was not always understood. For present purposes, the system is planar if all of the pi orbitals are parallel, to within some small amount. If some are planar, and others are not, as in the case of a twisted biphenyl, for example, then the system must be treated as nonplanar. However, we have decided to let the program determine whether the system is planar, as this will save the user from making errors due to misunderstanding. This option can be overridden if desired, but the default allows the program to determine if the system is planar.

This is determined by calculating the moments of inertia for the pi-system, which includes all of the atoms that are contributing a pi orbital in the calculation, plus all of the atoms bound to them. If the inertial defect of this fragment is 0, then the system is planar. If it is a larger value, the system is nonplanar<sup>17</sup> (actually, we chose 0.1 in atomic units as the cutoff number).

For the molecules for which we have good structures, the MM3 calculations give agreement with experiment in almost every case. Many structures must be compared with room temperature X-ray data, and these are much less accurate. The structures of the compounds will be considered individually. There appear to be a few cases where the calculated structures do not agree with experiment. These are of interest and will be discussed in detail. The final set of geometric parameters arrived at is given in Table I, the dipole moments of some selected compounds are given in Table II, and the structures themselves are summarized in Table III.

## RESULTS AND DISCUSSION

### Dipole Moments

The dipole moments of several conjugated compounds are listed in Table II. Azulene and fulvene

**Table I.** MM3 Parameter set for conjugated hydrocarbons (kcal/mol, °).<sup>a</sup>

Torsional parameters (* for four- and five-membered rings).							
Angle				V1	V2	V3	
1	2	2	2	-0.61	7.00	0.00	
2	2	2	2	-0.67	10.00	0.00	
2	2	2	2	0.25	9.00	-0.55	
2	2	2	2	-0.99	7.80	0.00	*5
1	2	2	2	-0.10	7.00	0.00	*5
2	2	2	57	-0.67	7.00	0.00	
2	2	57	57	-0.67	7.00	0.00	
2	57	57	2	-0.67	7.00	0.00	
2	57	57	5	0.25	9.00	-0.55	
2	57	57	57	-0.67	7.00	0.00	
2	57	57	56	-0.61	7.00	0.00	
5	2	2	57	0.25	9.00	-0.55	
5	2	57	57	0.25	9.00	-0.55	
5	57	57	57	0.25	9.00	-0.55	
57	57	57	57	-1.00	7.00	0.00	*4
Bending parameters							
Angle		K <sub>b</sub>	Type 1	Type 2	Type 3		
2	2	2	0.76	122.00	121.70		
2	2	2	0.55	121.20	121.50		*5
2	2	57	0.76	121.00			
2	57	57	0.76	127.20			
57	57	57	0.25	122.00			*4

<sup>a</sup>Atom types: 1,  $sp^3$  carbon; 2,  $sp^2$  carbon; 5, hydrogen; 56,  $sp^3$  carbon in a four-membered ring; 57,  $sp^2$  carbon in a four-membered ring.

**Table II.** Dipole moments of conjugated compounds.

Compound	Exp. (gas)	Ref.	Calc. <sup>c</sup>	$\pi$	$\sigma$
<i>t</i> -1,3-pentadiene	0.585	a	0.284		
<i>c</i> -1,3-pentadiene	0.500	a	0.247		
isoprene	0.26	a	0.255		
cyclopentadiene	0.419	a	0.213		
1,3-cyclohexadiene	0.437	a	0.442		
toluene	0.375	a	0.289		
fulvene	0.44	a	0.225	0.237	0.012
dimethylfulvene	1.52(CCl <sub>4</sub> )	a	0.591	0.253	0.338
azulene	0.796	b	1.026	0.991	0.115

<sup>a</sup>A. L. McClellan, *Tables of Experimental Dipole Moments*, Vol. 2, 1974.

<sup>b</sup>H. J. Tobler, A. Bauder, and H. H. Guenthard, *J. Mol. Spec.*, **18**, 239 (1965).

<sup>c</sup>The induced  $\sigma$  moment is included in the  $\pi$  moment.

derivatives have significant  $\pi$  dipole moments, because the electrons strongly shift toward the five-membered rings.

## Geometries and Energy Differences

We have listed the average CC bond length for many molecules. Typically, in an electron diffraction experiment this number can be determined with rather high accuracy, but if there are non-equivalent bonds present, the individual values are frequently much less accurate. Accordingly, when the calculation indicates values which differ from those of an electron diffraction experiment, one really needs to look and see how good the agreement is with respect to the average values. The molecular mechanics calculations are for the most part now good enough that if the average values agree, the individual errors are more likely to be in the electron diffraction values than in the calculated values. Of course, in crystallography, no such relationship applies. However, a comparison of the average bond lengths is still useful. If the X-ray structure has been de-

**Table III.** Structures of conjugated hydrocarbons<sup>a</sup>

Compound	Bond	Calc.	Exp.	Calc.-Exp.	Method
Ethylene <sup>b</sup> (1965)	<i>a</i>	1.337	1.337 ± 0.001	0.000	ED ( <i>r<sub>g</sub></i> )
Butadiene <sup>c</sup> (1966)	<i>a</i>	1.344	1.344 ± 0.001	0.000	ED ( <i>r<sub>g</sub></i> )
	<i>b</i>	1.468	1.467 ± 0.001	0.001	
	<i>ab</i>	122.4	122.9 ± 0.5	-0.5	
	<i>av</i>	1.385	1.385	0.000	
Benzene <sup>d</sup> (1976)	<i>a</i>	1.397	1.399 ± 0.001	-0.002	ED ( <i>r<sub>g</sub></i> )
Naphthalene <sup>e</sup> (1981)	<i>a</i>	1.421	1.417 ± 0.004	0.004	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.374	1.381 ± 0.002	-0.007	
	<i>c</i>	1.429	1.422 ± 0.003	0.007	
	<i>d</i>	1.412	1.412 ± 0.008	0.000	
	<i>av</i>	1.406	1.405 ± 0.004	0.001	
<i>trans</i> -Stilbene <sup>f</sup> (1975)	<i>a</i>	1.355	1.338	0.017	X-ray (-160°C)
	<i>b</i>	1.477	1.473	0.004	
	<i>c</i>	1.410	1.406	0.004	
	<i>d</i>	1.395	1.393	0.002	
	<i>e</i>	1.397	1.394	0.003	
	<i>f</i>	1.394	1.391	0.003	
	<i>g</i>	1.397	1.390	0.007	
	<i>h</i>	1.407	1.402	0.005	
	<i>av</i>	1.407	1.402	0.005	
	<i>abc</i>	1.7	5.2	-3.5	
<i>cis</i> -Stilbene <sup>g</sup> (1975)	C=C <sub>av</sub> (AB)	1.400	1.397 ± 0.003	0.003	ED ( <i>r<sub>g</sub></i> )
	<i>a</i>	1.479	1.488 ± 0.002	-0.009	
	<i>b</i>	1.350	1.338 ± 0.006	0.012	
	<i>av</i>	1.407	1.405	0.002	
	<i>ab</i>	125.9	129.5 ± 0.3	-3.6	
	<i>ph-b</i>	37.3	43.9 ± 1.3	-6.6	
	1-13-14-7	6.7	—	—	
Biphenyl twisted <sup>h</sup> (1985)	<i>a</i>	1.396	1.396 ± 0.008	0.000	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.396	1.395 ± 0.006	0.001	
	<i>c</i>	1.403	1.403 ± 0.004	0.000	
	<i>d</i>	1.488	1.503 ± 0.004	-0.015	
	<i>av</i>	1.405	1.406	-0.001	
	<i>cdc'</i>	46.2	44.4 ± 1.2	-0.5	
Biphenyl planar <sup>i</sup> (1976)	<i>a</i>	1.393	1.385	0.008	X-ray, (RT)
	<i>b</i>	1.396	1.388	0.008	
	<i>c</i>	1.412	1.397	0.015	
	<i>d</i>	1.497	1.496 ± 0.003	0.001	
	<i>av</i>	1.407	1.398	0.009	

Table III. continued

Compound	Bond	Calc.	Exp.	Calc.-Exp.	Method
Azulene <sup>j</sup> (1966)	<i>a</i>	1.401	1.399 ± 0.009	0.002	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.409	1.418 ± 0.010	-0.009	
	<i>c</i>	1.395	1.383 ± 0.008	0.012	
	<i>d</i>	1.396	1.406 ± 0.016	-0.010	
	<i>e</i>	1.399	1.403 ± 0.014	-0.004	
	<i>f</i>	1.472	1.501 ± 0.005	-0.029	
	<i>av</i>	1.407	1.411	-0.004	
Cyclobutadiene <sup>k</sup> (1989)	<i>a</i>	1.581	1.565	0.016	<i>ab initio</i> MP2/6-31G*
	<i>b</i>	1.342	1.343	-0.001	
1,2-Dimethylenecyclobutane <sup>l</sup> (1985)	<i>a</i>	1.497	1.486 ± 0.008	0.011	ED ( <i>r<sub>g</sub></i> )
	<i>b</i>	1.527	1.529 ± 0.006	-0.002	
	<i>c</i>	1.568	1.577 ± 0.018	-0.009	
	<i>d</i>	1.338	1.342 ± 0.002	-0.004	
	<i>av</i>	1.466	1.468 ± 0.007	-0.002	
	<i>I<sub>x</sub></i>	17.09	17.03	0.4%	
	<i>I<sub>y</sub></i>	20.72	20.52	0.9%	
	<i>I<sub>z</sub></i>	36.67	36.46	0.5%	
3,4-Dimethylenecyclobutene <sup>m</sup> (1983)	<i>a</i>	1.355	1.368 ± 0.002	-0.013	MW ( <i>r<sub>s</sub></i> )
	<i>b</i>	1.504	1.479 ± 0.003	0.025	
	<i>c</i>	1.503	1.497 ± 0.001	0.006	
	<i>d</i>	1.338	1.338 ± 0.004	0.000	
	<i>av</i>	1.423	1.417 ± 0.003	0.006	
	<i>I<sub>x</sub></i>	15.19	15.07	0.9%	
	<i>I<sub>y</sub></i>	19.93	19.69	1.2%	
	<i>I<sub>z</sub></i>	35.12	34.77	1.0%	
Biphenylene <sup>n</sup> (1966)	<i>a</i>	1.427	1.423 ± 0.002	0.004	X-ray (Low Temp.)
	<i>b</i>	1.398	1.385 ± 0.004	0.013	
	<i>c</i>	1.368	1.372 ± 0.002	-0.004	
	<i>d</i>	1.411	1.426 ± 0.003	-0.015	
	<i>e</i>	1.510	1.514 ± 0.003	-0.004	
	<i>av</i>	1.415	1.416 ± 0.003	-0.001	
Diphenylbicyclodecapentaene <sup>o</sup> (1980)	<i>a</i>	1.496	1.535	-0.039	X-ray (RT)
	<i>b</i>	1.340	1.336	0.004	
	<i>c</i>	1.464	1.432	0.032	
	<i>d</i>	1.348	1.374	-0.026	
	<i>e</i>	1.473	1.415	0.058	
	<i>f</i>	1.498	1.446	0.052	
	<i>g</i>	1.371	1.403	-0.032	
	<i>av</i>	1.422	1.412	0.010	
Cyclopentadiene <sup>p</sup> (1965)	<i>a</i>	1.521	1.509 ± 0.002	0.012	MW ( <i>r<sub>s</sub></i> )
	<i>b</i>	1.347	1.342 ± 0.003	0.005	
	<i>c</i>	1.472	1.469 ± 0.002	0.003	
	<i>av</i>	1.442	1.434	0.008	
	<i>I<sub>x</sub></i>	10.07	9.96	1.1%	
	<i>I<sub>y</sub></i>	10.29	10.20	0.9%	
	<i>I<sub>z</sub></i>	19.80	19.65	0.8%	
Dimethylfulvene <sup>q</sup> (1970)	<i>a</i>	1.474	1.476 ± 0.008	-0.002	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.356	1.340 ± 0.006	0.016	
	<i>c</i>	1.464	1.462 ± 0.009	0.002	
	<i>d</i>	1.356	1.347 ± 0.010	0.009	
	<i>e</i>	1.509	1.510 ± 0.010	-0.001	
	<i>av</i>	1.437	1.430 ± 0.008	0.007	
1,3-Cyclohexadiene <sup>r</sup> (1969)	<i>a</i>	1.345	1.350 ± 0.004	-0.005	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.466	1.468 ± 0.014	-0.002	
	<i>c</i>	1.510	1.523 ± 0.016	-0.013	
	<i>d</i>	1.540	1.534 ± 0.020	0.006	
	<i>av</i>	1.453	1.458 ± 0.012	-0.005	
	<i>ab</i>	120.5	120.1	0.4	
	<i>ac</i>	120.9	120.1	0.8	
	<i>cd</i>	111.8	110.7	1.1	
	<i>aba'</i>	13.3	18.3	-5.0	
	<i>I<sub>x</sub></i>	100.08	99.63	0.5%	
	<i>I<sub>y</sub></i>	100.66	99.86	0.7%	
	<i>I<sub>z</sub></i>	189.40	187.12	1.2%	

Table III. continued

Compound	Bond	Calc.	Exp.	Calc.-Exp.	Method
1,3-Cycloheptadiene <sup>s</sup> (1972)	<i>a</i>	1.344	1.347	-0.003	ED ( <i>r<sub>g</sub></i> )
	<i>b</i>	1.466	1.450	0.016	
	<i>c</i>	1.506	1.509	-0.003	
	<i>d</i>	1.529	1.522	0.007	
	<i>av</i>	1.460	1.458 ± 0.015	0.002	
	<i>ab</i>	128.7	129.1	-0.4	
	<i>ac</i>	129.9	129.1	0.8	
	<i>aba'</i>	0.0	0.0	0.0	
1,3,5-Cycloheptatriene <sup>t</sup> (1964)	<i>a</i>	1.345	1.356	-0.011	ED
	<i>b</i>	1.461	1.446	0.015	
	<i>c</i>	1.355	—	—	
	<i>d</i>	1.509	1.505	0.004	
	<i>ab</i>	125.4	127.2	-1.8	
	<i>bc</i>	126.9	119.8	7.9	
	<i>ad</i>	124.9	121.8	3.1	
	<i>I<sub>x</sub></i>	23.10	22.71	1.7%	
	<i>I<sub>y</sub></i>	23.29	22.85	1.9%	
	<i>I<sub>z</sub></i>	43.31	41.29	4.8%	
1,3,5,7-Cyclooctatetraene <sup>u</sup> (1966)	<i>a</i>	1.343	1.340	0.003	ED ( <i>r<sub>g</sub></i> )
	<i>b</i>	1.479	1.475 ± 0.007	+0.004	
	<i>ab</i>	124.8	126.1 ± 0.5	-1.3	
Bicyclo[4.4.1]undecapentaene <sup>v</sup> (1965)	<i>a</i>	1.405	1.409	-0.004	X-ray (RT)
	<i>b</i>	1.403	1.383	0.020	
	<i>c</i>	1.426	1.414	0.012	
	<i>d</i>	1.489	1.477	0.012	
	<i>ab</i>	122.0	122.3	-0.3	
	<i>bc</i>	127.6	127.7	-0.1	
	<i>ad</i>	117.0	161.1	0.9	
	<i>dd'</i>	99.1	99.6	-0.5	
<i>trans</i> -Isoprene <sup>w</sup> (1984)	<i>a</i>	1.350	1.340 ± 0.001	0.010	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.475	1.463 ± 0.001	0.012	
	<i>c</i>	1.345	1.340 ± 0.002	0.005	
	<i>d</i>	1.511	1.512 ± 0.002	-0.001	
	<i>av</i>	1.421	1.414	0.007	
	<i>ab</i>	119.7	121.4 ± 0.3	1.7	
	<i>bc</i>	124.0	127.3 ± 0.3	-3.3	
	<i>ad</i>	119.5	121.0 ± 0.2	-1.5	
	<i>I<sub>x</sub></i>	9.910	9.845	0.7%	
	<i>I<sub>y</sub></i>	20.33	20.11	1.1%	
	<i>I<sub>z</sub></i>	29.70	29.43	0.9%	
<i>trans</i> -2,3-Dimethyl-1,3-butadiene <sup>x</sup> (1968)	<i>a</i>	1.349	1.349	0.000	ED ( <i>r<sub>a</sub></i> )
	<i>b</i>	1.487	1.491	-0.004	
	<i>c</i>	1.512	1.511	0.001	
	<i>av</i>	1.441	1.442	-0.001	
	<i>ab</i>	121.1	121.98	-0.9	
	<i>bc</i>	120.2	117.87	2.3	
	<i>aba'</i>	160	180.0	-20.0	
<i>trans</i> -1,3,5-Hexatriene <sup>y</sup> (1968)	<i>a</i>	1.345	1.337 ± 0.002	0.008	ED ( <i>r<sub>g</sub></i> )
	<i>b</i>	1.466	1.458 ± 0.002	0.008	
	<i>c</i>	1.353	1.368 ± 0.004	-0.015	
	<i>av</i>	1.395	1.392	0.003	
1,2-Diphenylcyclopentene <sup>z</sup> (1975)	C=C <sub>av</sub> (A, B)	1.399	1.379	0.020	X-ray RT <i>R</i> = 0.078
	<i>a</i>	1.481	1.478	0.003	
	<i>b</i>	1.523	1.510	0.013	
	<i>c</i>	1.357	1.339	0.018	
	<i>d</i>	1.544	1.525	0.019	
	<i>ac</i>	125.9	128.6	-2.6	
	<i>bc</i>	110.6	111.3	-0.6	
	<i>bd</i>	102.4	104.4	-2.1	
	<i>ph-c</i>	42.4	45.7	-3.3	
	<i>aca'</i>	7.3	7.5	-0.2	

Table III. continued

Compound	Bond	Calc.	Exp.	Calc.-Exp.	Method
Tetraphenylethylene <sup>aa</sup> (1975)	C=C <sub>av</sub> (A, B, C, D)	1.398	1.394	0.004	X-ray L-Temp.
	<i>a</i>	1.491	1.496	-0.005	
	<i>b</i>	1.364	1.356	0.008	
	<i>av</i>	1.410	1.407 ± 0.003	0.003	
		121.4	122.2	-0.8	
		117.3	115.5	1.8	
	<i>abc</i>	9.2	8.4	0.8	
	<i>ph-b</i>	47.5	47.8	-0.3	
cis,cis-1,2,3,4-Tetraphenylbutadiene <sup>bb</sup> (1965)	(C—C) <sub>ph</sub>	1.399	1.405	-0.006	X-ray (RT) <i>R</i> = 0.121
	<i>a</i>	1.360	1.357	0.003	
	<i>b</i>	1.482	1.477	0.005	
	<i>c</i>	1.505	1.518	-0.013	
	<i>d</i>	1.488	1.493	-0.005	
	<i>av</i>	1.411	1.417	-0.006	
	<i>A-a</i>	68.4	75	-6.6	
	<i>B-a</i>	38.0	34	4.0	
	<i>bad</i>	1.1	0	1.1	
	<i>ada'</i>	0.1	0	0.1	
Anthracene <sup>cc</sup> (1964)	<i>a</i>	1.433	1.421	0.012	X-ray L-Temp.
	<i>b</i>	1.367	1.370	-0.003	
	<i>c</i>	1.441	1.440	0.001	
	<i>d</i>	1.424	1.428	-0.004	
	<i>e</i>	1.404	1.405	-0.001	
	<i>av</i>	1.410	1.410	0.000	
Phenanthrene <sup>dd</sup> (1971)	<i>a</i>	1.410	1.394	0.016	Average of X-ray Neutron diffraction
	<i>b</i>	1.382	1.401	-0.019	
	<i>c</i>	1.425	1.409	0.016	
	<i>d</i>	1.412	1.420	-0.008	
	<i>e</i>	1.464	1.465	-0.001	
	<i>f</i>	1.359	1.350	0.009	
	<i>g</i>	1.443	1.453	-0.010	
	<i>h</i>	1.421	1.423	-0.002	
	<i>i</i>	1.378	1.386	-0.008	
	<i>av</i>	1.409	1.412 ± 0.008	-0.003	
4,5-Dimethylphenanthrene <sup>ee</sup> (1987)	<i>af</i>	3.008	2.976 ± 0.006	0.032	X-ray (RT)
	<i>bcd</i>	124.0	125.1 ± 1.4	-1.1	
	<i>abc</i>	123.6	124.0 ± 0.3	-0.4	
	<i>bcde</i>	31.9	31.5 ± 0.3	0.4	
	<i>ab...ef</i>	72.4	67.4 ± 0.4	5.0	
Benzophenanthrene <sup>ff</sup> (1963)	<i>a</i>	1.413	1.409	0.004	
	<i>b</i>	1.379	1.378	0.001	
	<i>c</i>	1.427	1.433	-0.006	
	<i>d</i>	1.412	1.431	-0.019	
	<i>e</i>	1.459	1.446	0.013	
	<i>f</i>	1.362	1.342	0.020	
	<i>g</i>	1.436	1.443	-0.007	
	<i>h</i>	1.423	1.391	0.032	
	<i>i</i>	1.377	1.374	0.003	
	<i>j</i>	1.438	1.430	0.008	
	<i>k</i>	1.401	1.412	-0.011	
	<i>cee'</i>	21.1	—	—	
4,8-Dihydrodibenzo[cd,gh]-pentalene <sup>gg</sup> (1971)	<i>a</i>	1.415	1.405	0.010	X-ray (RT)
	<i>b</i>	1.393	1.382	0.011	
	<i>c</i>	1.542	1.578	-0.036	
	<i>d</i>	1.385	1.378	0.007	
	<i>e</i>	1.419	1.392	0.027	
	<i>av</i>	1.432	1.433 ± 0.009	-0.001	
	<i>aa'</i>	122.0	125.4	-3.4	
	<i>ab</i>	119.0	118.3	0.7	
	<i>bc</i>	135.0	142.3	-7.3	
	<i>cd</i>	106.4	105.7	0.7	
	<i>cc'</i>	103.5	102.9	0.6	
	<i>dd'</i>	126.9	134.2	-7.3	
	<i>de'</i>	111.2	113.2	-2.0	

Table III. continued

Compound	Bond	Calc.	Exp.	Calc.-Exp.	Method
Corannulene <sup>hh</sup> (1976)	<i>a</i>	1.391	1.402 ± 0.005	-0.011	X-ray average of 20°C and -70°C
	<i>b</i>	1.449	1.440 ± 0.002	0.009	
	<i>c</i>	1.375	1.391 ± 0.004	-0.016	
	<i>d</i>	1.419	1.413 ± 0.002	0.006	
	<i>av</i>	1.417	1.417 ± 0.004	0.000	
	<i>dd'</i>	108.0	108.0 ± 0.2	0.0	
	<i>cd</i>	122.0	123.0 ± 0.2	-1.0	
Hexamethylbenzene <sup>ii</sup> (1975)	<i>bc</i>	116.0	114.3 ± 0.1	1.7	ED ( <i>r<sub>g</sub></i> )
	<i>a</i>	1.409	1.417 ± 0.002	-0.008	
	<i>b</i>	1.514	1.530 ± 0.003	-0.016	
	<i>bab'</i>	7.8	9.9 ± 1.8	-2.1	
	<i>aa'a''</i>	3.8	—	—	

<sup>a</sup>Bond lengths in Å, angles in degrees.

<sup>b</sup>K. Kuchitsu, L. S. Bartell, and C. D. Hollowell, *J. Chem. Phys.*, **42**, 2683 (1965).

<sup>c</sup>W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966).

<sup>d</sup>K. Tamagawa, T. Iijima, and M. Kimura, *J. Mol. Struct.*, **30**, 243 (1976).

<sup>e</sup>S. N. Ketkar and M. Fink, *J. Mol. Struct.*, **77**, 139 (1981).

<sup>f</sup>A. Hoekstra, P. Meertens, and A. Vos, *Acta Cryst.*, **B31**, 2813 (1975).

<sup>g</sup>M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.*, **26**, 69 (1975).

<sup>h</sup>A. Almenningen, *J. Mol. Struct.*, **128**, 59 (1985).

<sup>i</sup>G. P. Charbonneau and Y. Delugeard, *Acta Cryst.*, **B32**, 1420 (1976).

<sup>j</sup>O. Bastiansen and J. L. Derissen, *Acta Chem. Scand.*, **20**, 1319 (1966).

<sup>k</sup>S. W. Staley and T. D. Norden, *J. Am. Chem. Soc.*, **111**, 445 (1989).

<sup>l</sup>L. K. Montgomery, C. A. Wilson, and J. D. Wieser, *J. Mol. Struct.*, **129**, 69 (1985).

<sup>m</sup>R. D. Brown, P. D. Godfrey, B. T. Hart, A. L. Ottrey, M. Onda, and M. Woodruff, *Aust. J. Chem.*, **36**, 639 (1983).

<sup>n</sup>J. K. Fawcett and J. Trotter, *Acta Cryst.*, **20**, 87 (1966).

<sup>o</sup>C. Kabuto and M. Oda, *Tetrahedron Letters*, **21**, 103 (1980).

<sup>p</sup>L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).

<sup>q</sup>J. F. Chiang and H. Bauer, *J. Am. Chem. Soc.*, **92**, 261 (1970).

<sup>r</sup>H. Oberhammer and S. Bauer, *J. Am. Chem. Soc.*, **91**, 10 (1969).

<sup>s</sup>K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26**, 3643 (1972).

<sup>t</sup>M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

<sup>u</sup>M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966).

<sup>v</sup>D. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

<sup>w</sup>Reference 27.

<sup>x</sup>C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968).

<sup>y</sup>M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).

<sup>z</sup>J. Bernstein, *Acta Cryst.*, **B31**, 418 (1975).

<sup>aa</sup>A. Hoekstra and A. Vos, *Acta Cryst.*, **B31**, 1722 (1975).

<sup>bb</sup>I. L. Karle and K. S. Dregonette, *Acta Cryst.*, **19**, 500 (1965).

<sup>cc</sup>R. Mason, *Acta Cryst.*, **17**, 547 (1964).

<sup>dd</sup>M. I. Kay, Y. Okaya, and D. E. Cox, *Acta Cryst.*, **B27**, 26 (1971).

<sup>ee</sup>R. N. Armstrong, H. L. Ammon, and J. N. Darnow, *J. Am. Chem. Soc.*, **109**, 2077 (1987).

<sup>ff</sup>F. L. Hirshfeld, S. Sandler, and C. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963).

<sup>gg</sup>B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *J. Am. Chem. Soc.*, **93**, 7275 (1971).

<sup>hh</sup>J. C. Hanson and C. E. Nordman, *Acta Cryst.*, **B32**, 1147 (1976).

<sup>ii</sup>R. R. Karl, Jr., Y. C. Wang, and S. H. Bauer, *J. Mol. Struct.*, **25**, 17 (1975).

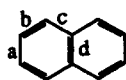
terminated at low temperature, this difference is ordinarily quite small, more or less within experimental error. However, if the molecule is undergoing large thermal librational motions, then the X-ray value will typically be considerably shorter than the molecular mechanics values. If this is found to be the case, then one can judge the magnitude of the thermal motion error by comparing the average values. Finally, if one is comparing microwave data to the molecular mechanics calculations, the former are ordinarily presented in terms of  $r_o$ ,  $r_z$ , or  $r_s$ , and these numbers are typically several thousandths of an Å

shorter than the  $r_g$  values which are commonly reported at the present time in electron diffraction work, and which MM3 aims to calculate. Accordingly, a deviation of this magnitude in the average value may not be a real discrepancy, but simply a result of using a different kind of experimental quantity.

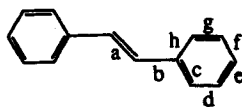
1,3-Butadiene has been the subject of several studies, by electron diffraction,<sup>18</sup> IR,<sup>19</sup> UV,<sup>20</sup> and *ab initio* calculations.<sup>21-25</sup> The trans form predominates, with the cis or gauche conformation being a minor component.<sup>22,23b</sup> It was found by an *ab initio*<sup>22</sup> study at the DZ + P SCF level that



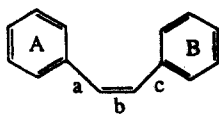
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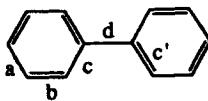
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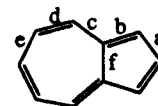
trans-Stilbene



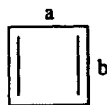
cis-Stilbene



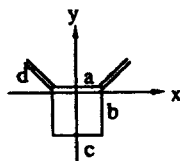
Biphenyl



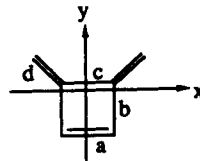
Azulene



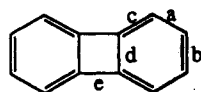
Cyclobutadiene



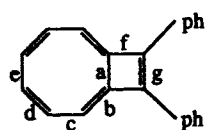
1,2-Dimethylenecyclobutane



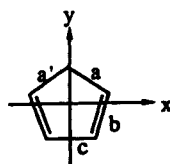
3,4-Dimethylenecyclobutane



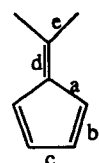
Biphenylene



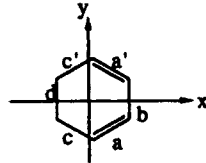
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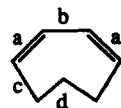
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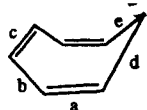
Dimethylfulvene



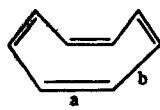
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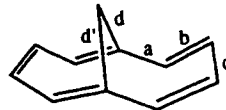
1,3-Cycloheptadiene



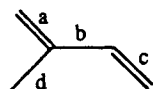
1,3,5-Cycloheptatriene



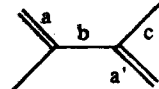
1,3,5,7-Cyclooctatetraene



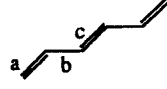
Bicyclo[4.4.1]undecapentaene



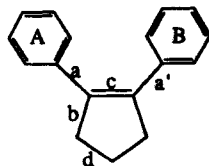
trans-Isoprene



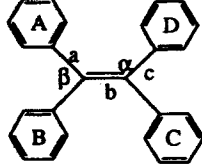
trans-2,3-Dimethyl-1,3-butadiene



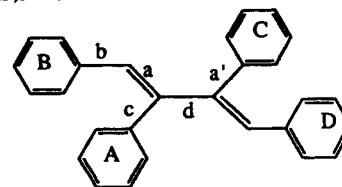
1,3,5-Hexatriene



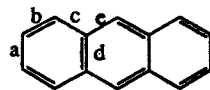
1,2-Diphenylcyclopentene



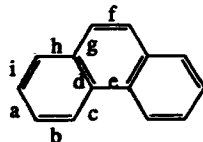
Tetraphenylethylene



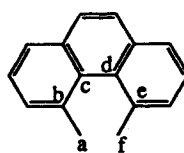
cis,cis-1,2,3,4-Tetraphenylbutadiene



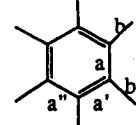
Anthracene



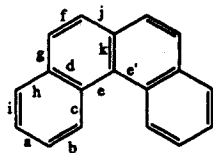
Phenanthrene



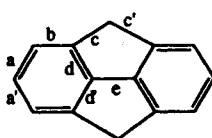
4,5-Dimethylphenanthrene



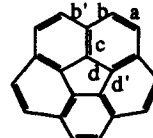
Hexamethylbenzene



3,4-Benzophenanthrene



4,8-Dihydrodibenzo[cd,gh]pentalene



Corannulene



the cis conformer is actually a transition state for the interconversion of the two possible gauche enantiomers, and the gauche forms are more stable than the cis by about 0.4–0.7 kcal/mol. A UV study<sup>20</sup> was interpreted as indicating that the minor conformer was cis, not gauche. An experimental potential curve thought to be quite accurate was determined for rotation about the central bond of 1,3-butadiene by Carreira.<sup>26</sup> The barrier from the trans to cis was determined to be 7.16 kcal/mol, and was calculated to be 7.64 and 7.31 kcal/mol by MM2 and MM3, respectively. The estimated energy difference between the trans and cis was 2.49 and 1.85 kcal/mol from the experiment and MM3, respectively. The MM3 calculations show the cis form (not gauche) to be the energy minimum, from the fact that all of the eigenvalues of the force constant matrix are positive.

*Ab initio* calculations with large basis sets and electron correlation were recently carried out on *cis*- and *gauche*-1,3-butadiene by different groups. They all found that the cis conformation is a transition state for the interconversion of the gauche isomers, which have dihedral angles of about 37°. Bock and coworkers<sup>23c</sup> found that the energy difference between the gauche and cis conformation changes from 0.5 to 0.9 kcal/mol when the basis set is changed from HF/6-31G to MP2/6-31G\*. Calculations carried out by Rice<sup>24</sup> and by Schaefer,<sup>25</sup> with large basis sets (up to triple zeta plus double polarization) and dynamical electron correlation, showed that the gauche is more stable than the cis by 0.4 and 0.5 kcal/mol respectively, after zero point energy correction. These articles appeared after the MM3 parameterization described in the present work had been completed, and hence they could not be taken into account. Whether the cis or the gauche form of butadiene corresponds to the energy minimum is still not clear. The experimental evidence favors, arguably, the cis conformation, while the best *ab initio* calculations to date favor the gauche. The relative energies calculated by MM3 and by *ab initio* calculations are listed in Table IV.

The structure of *trans*-isoprene has been studied by electron diffraction.<sup>27</sup> Like 1,3-butadiene, isoprene has two minima on the potential surface generated by rotation around the central

**Table IV.** The relative energies of 1,3-butadiene conformations.

	MM3	EXP <sup>26</sup>	MM2	<i>ab initio</i> (6-31G) <sup>23</sup>
trans	0	0	0	0
cis	1.85	2.49	2.33	3.54
gauche	—	—	—	3.04(34.8°)
90°	7.42	7.16	7.64	6.16(100.6°)

carbon-carbon bond. The electron diffraction<sup>27</sup> study of isoprene showed that the compound exists predominantly in the *s*-trans form with a *trans*:*gauche* ratio of 19:1, corresponding to an energy difference of 1.8 kcal/mol. The gauche conformer has an experimental (ED) dihedral angle of 73.5°. However, the author also pointed out that "the electron diffraction study does not therefore indicate with absolute certainty that a gauche conformer is present in the gaseous isoprene." Vibrational spectroscopic studies by Compton<sup>28</sup> led to the conclusion that the cis is the second stable conformer, which has a higher energy than the trans form by 1.2 kcal/mol, and that the gauche conformers were not present. The *ab initio* calculations carried by Bock<sup>23c</sup> with electron correlation at single point MP2 and MP3/6-31G\*//HF/6-31G\* levels showed that the cis is the transition state of interconversion of the two gauche enantiomers. The gauche with a dihedral angle of 41.0° is the second stable conformer, and the energy barrier separating the two gauche conformers is 1.23 kcal/mol. The MM3 calculations show that the planar cis form has essentially the same total energy as the gauche form, although the gauche has all positive eigenvalues in the force constant matrix and slightly lower steric energy. Therefore, the second MM3 potential minimum of rotating about the central C—C bond is very shallow and the molecule would in fact oscillate over a wide range of torsion angles. The relative steric energies obtained by calculations and experiment<sup>29</sup> are listed in Table V.

The molecular structure of 2,3-dimethyl-1,3-butadiene has been investigated by electron diffraction<sup>30</sup> in the vapor phase. The most stable conformer is the *s*-trans form, and no evidence of deviation from heavy-atom coplanarity has been observed by experiment. The MM3 calculations

**Table V.** Relative energies of isoprene conformations (kcal/mol).

	MM3	EXP <sup>29</sup>	<i>ab initio</i> (6-31G) <sup>23</sup>
trans	0	0	0
cis	1.67	3.38	3.27
gauche	1.66(8.2°)	2.65(39.2°)	2.30(41.0°)
90°	5.44	5.78	5.38

show that the completely planar form is a transition state (one negative eigenvalue of the force constant matrix) between two enantiomeric gauche forms which have a dihedral angles of  $160^\circ$ , and which were found to be the energy minima (all of the eigenvalues of the force constant matrix are positive). However, the energy difference between the planar form and the twisted gauche forms is only 0.04 kcal/mol, which is much lower than the first vibrational level of the molecule. Therefore, the stable conformer calculated by MM3 still corresponds to the experimentally planar form with a large amplitude torsional motion.

Like its simple analogs 1,3-butadiene and isoprene, the planarity of the minor forms of 2,3-dimethylbutadiene is also a problem. As one would expect, when more hydrogens of butadiene are substituted by methyl groups, the nonbonded strain between the terminal methylene groups and the substituents becomes larger. The central carbon-carbon bond then twists in order to release this strain. This is found to be true by both experiment and MM3 calculations. Squillacote, Semple, and Mui<sup>31</sup> studied the conformation of the minor form of this diene using IR and UV spectroscopy. A gauche conformer with a dihedral angle about  $30\text{--}50^\circ$  was found to be the second energy minimum, and  $\Delta G_{293}^\circ$  corresponds to the gauche and trans energy difference, estimated to be 1.7 kcal/mol. In the MM3 force field, the cis conformer has a dihedral angle of  $33.8^\circ$  and the energy is higher than the trans by 1.20 kcal/mol. A recent *ab initio* calculation<sup>23c</sup> with a 6-31G\* basis set also showed that the gauche is more stable than the cis conformation. The energy difference between the trans and gauche conformations was found to be 1.48 kcal/mol.

### Compounds Containing Four-membered Rings

It was found in previous studies that the atom type of  $C_{sp^3}$  in the four-membered ring required parameters which were somewhat different from those used in open chain compounds.<sup>9a</sup> Since the angle of the C—C—X is unusually large in the four-membered ring compounds, if the same parameters used in the open chain compounds are adopted here, the bond length of C—X will become much too short from the stretch-bend effect. This is also true with unsaturated four-membered rings. Therefore, it was decided to use a different atom type (number 57) for the  $C_{sp^2}$  carbon in the four-membered ring. The parameters arrived at for the four-membered ring are listed in the table at the beginning of this part. The parameters were optimized based on the data

from the structures of six compounds and five heats of formation.

A quadratic term in the bond length-bond order relationship was found to be desirable for four-membered ring compounds, and the relationship is shown in eq. (1).

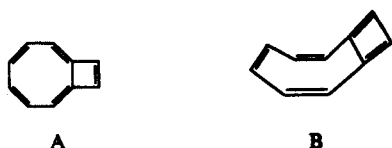
$$l_o(p) = l_o(1) + t(1 - p) - t'(1 - p^2) \quad (1)$$

The natural bond length for a bond order of 1 ( $l_o(1)$ ) was chosen to be 1.338 Å to fit the bond lengths of C=C in cyclobutene and Dewar benzene. The values of  $t$  and  $t'$  were adjusted to fit the bond lengths in 1,2-methylenecyclobutane, 3,4-methylenecyclobutene, and biphenylene. The four bonds in the four-membered ring of biphenylene are not equivalent, according to the X-ray experiment. The two bonds in the benzene rings are shorter than the two bonds connecting the benzene rings by a very large amount (0.088 Å). MM2 was unable to fit this difference by using the same linear bond length-bond order relationship employed for the open chain compounds. The MM2 bond length of the short bond was 1.423 Å (X-ray: 1.426 Å) and the length of the long bond was 1.482 Å (X-ray: 1.514 Å) (errors  $-0.003$  Å and  $-0.032$  Å, respectively). By using a quadratic equation, we are able to calculate the difference between them fairly well. However, the bond lengths of both the short and long bonds were calculated to be too short (errors  $-0.015$  Å and  $-0.004$  Å, respectively), because the bond lengths in 1,2-dimethylenecyclobutane and 3,4-dimethylenecyclobutene had to be fit at the same time. The bond order of the longest bond in biphenylene is 0.17, and the bond order of the longest bonds in 1,2-dimethylenecyclobutane and 3,4-dimethylenecyclobutene are 0.25 and 0.19 Å respectively. Changing the long bond lengths of the bonds in the four-membered ring in biphenylene will change the corresponding bonds of 1,2-dimethylenecyclobutane and 3,4-dimethylenecyclobutene by about the same amount. The values for  $t$  and  $t'$  were chosen to get compromised results. The optimized parameters were substituted into eq. (1) to give eq. (2).

$$l_o(p) = 1.338 + 0.390(1 - p) - 0.152(1 - p^2) \quad (2)$$

The structure of biphenylene was studied by electron diffraction<sup>32</sup> and by X-ray diffraction.<sup>33</sup> The molecule is planar both in the crystal lattice and in the gas phase. The benzene rings are distorted, and bond alternation is clearly present. The bond  $d$  distances are almost as long as a  $sp^2\text{--}sp^2$  single bond, while the bond  $c$  lengths are definitely shorter than the C—C bond in benzene. The bond  $e$  is very long indeed, and the MM3 value is much improved over MM2.

The structure of 9,10-diphenylbicyclo[6.2.0]decapentaene has been studied by X-ray diffraction.<sup>34</sup> Unlike cyclooctatetraene itself, the eight-membered ring of this compound is planar in the crystal structure. The driving force of the planarization comes from the conjugation of the 10-membered ring. Therefore, the stable conformer of the parent bicyclo[6.2.0]decapentaene (without the phenyl groups) should also be planar, and this was found to be true with the MM2 force field. In the current study, two stable conformers A and B have been found. The one with planar configuration A is the most stable. The bond alternation in B is different from the bond alternation in A, and the eight-membered ring in B is puckered. Conformer A is more stable than B by 15.9 kcal/mol with the MM3 force field.

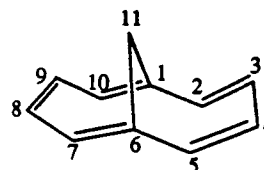


Two stable conformers of 1,3-cycloheptadiene with  $C_s$  and  $C_2$  symmetries were found with the MM3 force field. The  $C_2$  conformer has the higher energy by 3.2 kcal/mol. Only the  $C_s$  conformer was found by electron diffraction.<sup>36</sup>

In 1,3,5-cycloheptatriene, a nonplanar structure with a boat form has been established, but conflicting results concerning the degree of nonplanarity have been published. The microwave structure derived by Butcher<sup>37</sup> was based on many assumptions. The electron diffraction<sup>38</sup> studied by Traetteberg does not agree with Butcher's results very well. The MM3 results are closer to Butcher's estimates. However, the ring is much too flat in the MM3 calculation. Also, the MM3 barrier to inversion is too small (1.3 kcal/mol, 2.6 kcal/mol in MM2, and  $\Delta G^\ddagger = 5.7$  kcal/mol by experiment<sup>39</sup>). The results calculated by MM3 are given in Table VI.

The nonbonded interaction between atoms 1 and 6 in the boat form is important to both the

structure and the energy of the molecule. The  $\Pi$ -orbital overlap is quite large between these atoms. If atoms 1 and 6 are pulled closer together, the bonding effect becomes larger and will lower the electronic energy of the molecule. However, at the same time the steric energy will increase from bending 1-7-6. The total energy was found to change very slightly (less than 0.2 kcal/mol) when the distance between 1 and 6 was changed over a large range (0.06 Å). This indicates a shallow potential energy curve. The discrepancies between the calculations and experiments may be in part caused by this reason. It now seems likely that the cis conformation of butadiene is higher in energy than the gauche by 0.5–0.9 kcal/mol. That kind of change in the MM3 butadiene potential would have the effect of puckering cycloheptatriene, and increasing the energy barrier to planarity, which would lead to much better agreement of the MM3 results with experiment for this molecule.



The bridge-head atoms 1 and 6 (distance 2.267 Å) in bicyclo[4.4.1]undecapentaene have a bonding interaction similar to that described for 1,3,5-cycloheptatriene. The structure calculated by MM3 in this case agrees with experiment very well. This interaction causes the outer ring bond lengths of bicyclo[4.4.1]undecapentaene to alternate in a naphthalene fashion, which is not expected in the [10]annulene. An X-ray examination<sup>40</sup> showed that the spread in the peripheral bond lengths in bicyclo[4.4.1]undecapentaene is 0.032 Å, while a spread of 0.049 Å is found in naphthalene. This suggests considerable aromatic character in this bridged annulene. The dihedral angles in the 10-membered ring are distorted no

Table VI. Structure of 1,3,5-cycloheptatriene.

	Butcher	Traetteberg	Calc.
1-2	1.34	1.356(5)	1.345
2-3	1.47	1.446(7)	1.461
3-4	1.34	—	1.354
1-7	1.50	1.505(7)	1.509
1-2-3	124.5	127.2	125.4
2-3-4	124.5	119.8	126.9
2-1-7	124.5	121.8	124.9
$I_x$	22.71		23.10(1.7%)
$I_y$	22.85		23.29(1.9%)
$I_z$	41.31		43.28(4.8%)
$ I_z - I_x - I_y $	4.25		3.11

more than  $34.1^\circ$  from planarity, with the average distortion being only  $18.7^\circ$ .

The structure of [18]annulene was investigated by X-ray crystallography<sup>41</sup> in 1965, and it was found that the molecule has slightly distorted  $D_{6h}$  symmetry. Two types of bonds were found in the crystal structure: 12 inner (trans) bonds of mean length  $1.382 \pm 0.003$  Å and six outer (cis) bonds of mean length  $1.419 \pm 0.004$  Å. The average deviation of the ring carbon atoms from the mean plane of the ring is 0.085 Å in the crystal, possibly due to crystal lattice forces. This molecule has been studied by both MM1 and MM2, and the results were a nonplanar-alternate form with  $D_3$  symmetry.

The structure of [18]annulene was reevaluated in the current study to see if the softer hydrogens in the MM3 force field would improve the geometry of this molecule. The results obtained by MM1, MM2 and MM3 are listed in Table VII. The molecule was also calculated to be nonplanar with the MM3 force field, but the degree of nonplanarity was reduced. The mean nonplanarity of the carbon atoms is 0.050 Å by MM3, 0.057 Å by MM2, and 0.102 Å by MM1. The planarity calculated by MM2 and MM3 agreed with the experiment very well. The relative steric energies of forms  $D_{6h}$ ,  $D_{3h}$ ,  $D_3$  were calculated to be

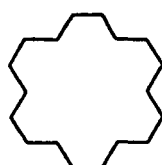
17.0, 2.27, and 0 kcal/mol by MM2, and 25.9, 0.56, and 0 kcal/mol by MM3 respectively. Electron correlation, neglected in all molecular mechanics calculations to date, is believed to be responsible for the equalizing of the bond lengths.<sup>42</sup>

The structure of biphenyl was determined by gas phase electron diffraction<sup>43</sup> and by X-ray crystallography.<sup>44</sup> In the gas phase, the angle between the two rings in biphenyl was found to be  $44.4^\circ$ , while the molecule was planar in the solid state by X-ray.

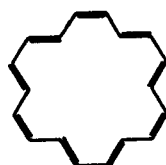
The structural parameters of biphenyl, calculated by MM3 and *ab initio*, and determined by E.D. and X-ray, are listed in Tables VIII and IX. Since the van der Waals radius of deuterium is smaller than that of hydrogen,<sup>46</sup> the central bond  $C_1-C_7$  would be expected to be shorter in deuterated biphenyl in both the twisted and planar forms. This is true by electron diffraction and *ab initio* calculation. However, the MM3 calculation gave the same bond length for biphenyl and perdeuterated biphenyl in the twist forms, and in the planar form the bond length shrinks by an insignificant amount (0.0004 Å) when the hydrogens are substituted by deuterium. The energy calculated by MM3 for the perdeuterated biphenyl is slightly lower than that of biphenyl itself, and the dihedral angle of the twist form of perdeuter-

Table VII. Structure of [18]annulene.

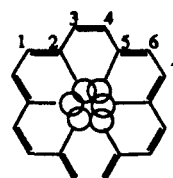
Bond	Number	MM3	MM2	MM1
C—C	1-2	1.357	1.357	1.357
	2-3	1.465	1.465	1.463
	3-4	1.362	1.361	1.361
	4-5	1.465	1.465	1.463
	5-6	1.357	1.357	1.357
	6-7	1.473	1.470	1.467
C—C—C	2-1-18	122.7	122.9	122.7
	1-2-3	125.4	126.0	125.7
	2-3-4	123.0	123.2	123.4
	3-4-5	123.0	123.2	123.4
	4-5-6	125.4	126.0	125.7
	5-6-7	122.7	122.9	122.7
Displacement from mean plane	1	0.029	0.046	0.062
	2	-0.101	-0.116	-0.186
	3	-0.020	-0.012	-0.058
	4	0.020	0.012	0.058
	5	0.101	0.116	0.186
	6	-0.029	-0.046	-0.062
Absolute Av.		0.050	0.057	0.102



$D_{6h}$  Crystal



$D_{3h}$   
planar-alternant



$D_3$   
nonplanar-alternant

**Table VIII.** Structure of biphenyl ( $C_{12}H_{10}$ ).

	twisted			planar	
	MM3( $r_g$ )	E.D.( $r_a$ ) <sup>43</sup>	<i>ab initio</i> ( $r_e$ ) <sup>45</sup>	X-ray(RT) <sup>44</sup>	MM3( $r_g$ )
C1—C7	1.488	1.503(4)	1.5074	1.496(3)	1.497
C1—C2	1.403	1.403(4)	1.3946	1.397	1.411
C2—C3	1.396	1.395(6)	1.3850	1.388	1.396
C3—C4	1.396	1.396(8)	1.3816	1.385	1.393
C—C <sub>av</sub>	1.406	1.406	1.3963	1.398	1.407
C2—C1—C6	118.8	119.4(4)	118.36	117.9(2)	117.0
C1—C2—C3	120.6	119.9(4)	120.84	120.9	121.5
C2—C3—C4	120.1	120.9(5)	120.20	120.7	120.3
C3—C4—C5	119.8	119.0(6)	119.57	118.9(2)	119.4
2—1—7—8	45.3	44.4(1.2)	—	0.0	0.0

ated biphenyl is slightly smaller than that of biphenyl (0.3)°.

4,5-Dimethylphenanthrene is very crowded, because planar models would involve a pair of hydrogen atoms closer than 2.0 Å. The molecular structure and conformational stabilities of 4,5-dimethylphenanthrene have been examined by crystallography<sup>48</sup> and by the temperature dependence of the kinetics of the racemization process.<sup>48</sup> The crystal structure shows the aromatic system to have the expected helical twist

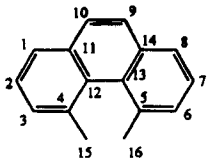
imposed by the methyl groups at the four- and five-positions. The inversion barrier between the two conformational enantiomers was found to be 16.1 kcal/mol by experiment and 17.2 kcal/mol by MM3 (with one negative eigenvalue in the force constant matrix). At the transition state, atoms 4, 5, 12, 13, 15, 16 are co-planar. But the phenanthrene skeleton is not completely planar. The transition structure has  $C_s$  symmetry as shown. The MM3 and experimental structures are listed in Table XI.

**Table IX.** Structure of biphenyl ( $C_{12}D_{10}$ ).

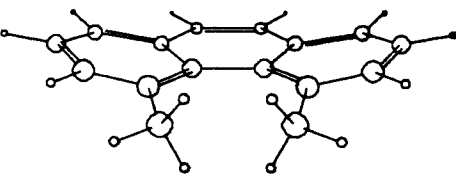
	twisted		planar	
	MM3( $r_g$ )	E.D.( $r_a$ ) <sup>43</sup>	X-ray( $r_a$ ) <sup>47</sup>	MM3( $r_g$ )
C1—C7	1.488	1.489(4)	1.495	1.497
C1—C2	1.403	1.403(5)	1.397	1.411
C2—C3	1.396	1.396(8)	1.390	1.396
C3—C4	1.396	1.398(13)	1.387	1.393
C—C <sub>av</sub>	1.405	1.406	1.399	1.407
C2—C1—C6	118.7	117.9(4)	117.6	117.0
C1—C2—C3	120.6	121.3(4)	121.7	121.5
C2—C3—C4	120.1	119.8(5)	120.0	120.3
C3—C4—C5	119.8	119.8(6)	119.0	119.4
2—1—7—8	45.0	44.5(1.6)	0.0	0.0

**Table XI.** Structure of 4,5-dimethylphenanthrene.

	numbering	X-ray	MM3	MM2
C...C	15...16	2.976(6)	3.008	3.070
C—C—C	4-12-13	125.1(1.4)	124.0	124.6
	12-4-15	124.0(0.3)	123.6	122.9
C—C—C—C	4-12-13-5	31.5(0.3)	31.9	34.6
	15-4...5-16	67.4(0.4)	72.4	74.7



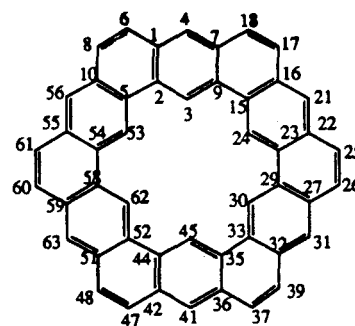
4,5-Dimethylphenanthrene



Transition state

Conformational studies of 4,8-dihydrodibenzo-[cd,gh]pentalene using NMR and X-ray crystallography by the same research group<sup>35</sup> gave different results. The NMR study showed that the molecule has a cup form, and the dihedral angle between the two benzene rings is 114°. However, the X-ray structure is completely planar. Their conclusion was that the NMR method is not suitable for such highly strained molecule. The MM3 calculation shows that both the cup form with  $C_{2v}$  symmetry and the planar form with  $D_{2h}$  symmetry correspond to energy minima. The dihedral angle between the two benzene rings in the cup form is 128.7°. The bond angles in the planar form are very distorted, and the planar form has a large bending energy. This energy can be reduced by puckering the molecule into the cup form and at the same time increase the torsional energy. The cup form is more stable than the planar form by 1.28 kcal/mol in the MM3 force field. It is quite possible that in the crystal lattice the molecule will be flattened by the crystal packing forces, since the energy difference between the planar form and the cup form is small.

The structure of corannulene was determined by the X-ray method.<sup>49</sup> The "best" structure is the average of those structures obtained at +20° and -70°. Thermal corrections were applied, and the *R* indexes at these two temperatures are 6.9% and 7.4% respectively. The molecule is cupped with an average experimental dihedral angle 20.4° between the least-squares planes defined by the five- and six-membered rings in the crystal. The dihedral angles calculated by MM3 are 24.2° and 24.3° for isolated molecule and for the molecule in the crystal lattice, respectively. The energy difference between the planar and cup forms is 14.9 kcal/mol in the MM3 force field.



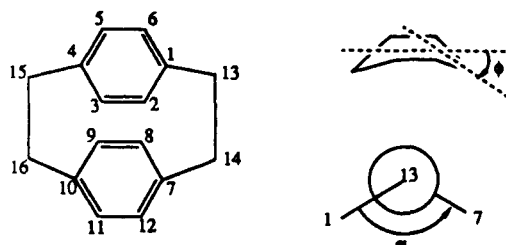
kekulene

The X-ray structure of kekulene was determined by Staab et al.<sup>50</sup> Several interesting features of this molecule were pointed out in their work. The molecule is almost planar in the crystal, despite the overcrowding of the inner hydrogen atoms (similar to [18]annulene). The mean deviation of the carbon atoms from a least-squares plane amounts to only 0.03 Å, and the maximum deviation from this plane is 0.07 Å. In the crystal structure of [18]-annulene, the skeleton of the molecule is planar. It is obvious that the conjugation in the annulene ring is the driving force which makes the molecule planar. However, in kekulene, the  $\pi$ -electrons delocalize in a benzenoid fashion rather than in an annulenoid fashion, i.e., no superaromaticity was found in this molecule. The bond lengths alternate in both the outer and inner rings of the molecule. Molecular mechanics calculations carried out by Lahti<sup>51</sup> using a modified MM2 program gave a structure in agreement with the X-ray data with respect to the above points. However, the bond lengths calculated were systematically shorter than the experimental values. In this work, the structure has been calculated by the MM3 force

Table XII. Kekulene structure.

Atom number	X-ray(RT)	MMPMI	Error	MM3	Error
1—2	1.420	1.420	0.000	1.413	-0.007
1—4	1.410	1.394	-0.006	1.410	0.000
1—6	1.454	1.440	-0.014	1.454	0.000
2—3	1.405	1.385	-0.020	1.400	-0.005
2—5	1.463	1.457	-0.006	1.466	0.003
5—10	1.423	1.416	-0.007	1.413	-0.010
5—53	1.403	1.387	-0.016	1.399	-0.004
6—8	1.366	1.349	-0.017	1.363	-0.003
8—10	1.457	1.446	-0.011	1.454	-0.003
10—56	1.402	1.394	-0.008	1.410	0.008
21—22	1.418	1.396	-0.022	1.410	-0.008
22—23	1.420	1.418	-0.002	1.413	-0.007
22—25	1.448	1.441	-0.007	1.454	0.006
23—24	1.414	1.384	-0.030	1.400	-0.014
23—29	1.463	1.455	-0.008	1.466	0.003
25—26	1.369	1.348	-0.021	1.363	-0.006
C-cav	1.421	1.409	-0.011	1.418	-0.003
		rms.	0.014		0.006

field, and the results agree with the experimental very well. The mean deviation of all carbon atoms from the average plane of the molecule is 0.03 Å, and the maximum deviation is 0.08 Å, which are very similar to the X-ray values. The molecule possesses  $D_{3d}$  symmetry. The results are summarized in Table XII.



The distinguishing features of cyclophanes have been of particular interest to organic chemists. The structures of many compounds in this series have been studied experimentally. Among them, the most extensively studied is [2.2]paracyclophane. The most recent X-ray study, by Trueblood and co-workers<sup>52</sup> 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 about 3°, and proposed that the structure with exact alignment of aromatic rings is an energy maximum. The angle of the out-of-plane ring bending  $\phi$  in the crystal was found to be 12.6°. In conjunction with this bending, the aromatic hydrogens were found to be displaced inward (toward the other ring) from the  $C_2, C_3, C_4, C_5$  plane by about 0.04 Å. The  $\text{CH}_2-\text{CH}_2$  bond was unusually long, 1.569 Å.

In the MM3 calculation, the twist forms with  $D_2$  symmetry were found to be the ground state. The conformation with  $D_{2h}$  symmetry is indeed a transition state between the twist forms with an energy higher than them by 2.2 kcal/mol. The minimum energy twist form, characterized by a 12.5° ring bending and 33.7° twist, is compared

with experiment in Table XIII. The aromatic hydrogens were found to be displaced 0.08 Å inward toward the other aromatic ring. The twist angle of the ground state calculated by MM3 is much larger than the one obtained experimentally. The reason may be that the activation energy for oscillation between the two twist forms is small enough that the twist angle can be compressed by the crystal packing forces.

In the MM2 calculation, the bond 13—14 was calculated 0.02 Å shorter than the experimental value. Also, as mentioned before, the MM2 heat of formation of this compound is 2.5 kcal/mol lower by calculation than by experiment. These facts indicated that the repulsion calculated between the benzene rings was not big enough. In the MM2 method, the bond moment of the  $C_{sp^2}-\text{H}$  bond is 0, and that of the  $C_{sp^2}-C_{sp^3}$  bond is 0.30 D. Therefore, there are only weak dipole-dipole interactions between the two benzene rings in [2.2]paracyclophane. In MM3 a bond moment of 0.60 D was assigned to the  $C_{sp^2}-\text{H}$  bond, and 0.9 D to the  $C_{sp^2}-C_{sp^3}$  bond. Because of these changes, the heat of formation was calculated more accurately and the structure was fit better by MM3 than by MM2.

The benzene rings in [2.2]metaparacyclophane are also bent. A crystallographic determination<sup>53</sup> found the para ring to be bent 14 deg, 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 XIV. As can be seen, the agreement is pretty good.

A transition state for rotation of the meta bridged ring (with one negative eigenvalue for the force constant matrix) of  $C_2$  symmetry was found with the plane of the meta ring perpendicular to the average plane of the para ring. The meta ring is slightly twisted around the  $C_2$  axis away from the mirror plane. The  $\Delta H^\ddagger$  for meta

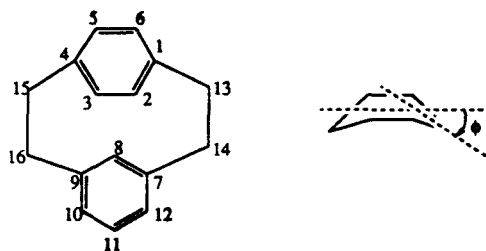
Table XIII. Structure of [2.2]paracyclophane.

	Trueblood	MM3		MM2	
	$D_2$	$D_2$	$D_{2h}$	$D_2$	$D_{2h}$
1—2	1.394	1.404	1.402	1.401	1.400
2—3	1.394	1.397	1.397	1.397	1.397
1—13	1.514	1.517	1.515	1.517	1.514
13—14	1.569	1.563	1.574	1.549	1.551
6—1—2	117.0	118.4	118.5	118.3	118.5
1—13—14	113.7	111.7	112.7	111.5	112.8
$\phi$	12.6	12.5	12.3	13.1	12.4
$\alpha$	3.2	33.7	0	4.8	0
C1...C7	2.78	2.81	2.74	2.78	2.72
C2...C8	3.09	3.12	3.05	3.13	3.06

**Table XIV.** Structure of *s-trans*-[2.2]metaparcyclophane.

	X-ray	MM3	MM2
1—13—14	107	110.3	110.5
7—14—13	112	112.4	111.5
$\phi$	14	13.8	14.2
C1...C7	2.7	2.84	2.82
C2...C8	3.0	3.10	3.11

ring rotation was calculated to be 19.7 kcal/mol. Cram<sup>54</sup> has reported  $\Delta H^\ddagger$  values of about 18 kcal/mol, based on low temperature NMR measurements, for several para-ring substituted [2.2]metaparcyclophanes.



The [2.2]metacyclophane may exist as two possible conformations, *s-cis* and *s-trans*, with our calculations favoring the *s-trans* by 12.4 kcal/mol. X-ray data<sup>55</sup> are available for the *s-trans* and, as shown in Table XV, are in favorable agreement with our calculated structure.

Room temperature NMR<sup>57</sup> indicated that [3.3]paracyclophane exists as a mixture of boat and chair conformers with a boat:chair ratio of 2:1 in solution. The MM3 calculation showed that the boat form is more stable than the chair form by only 0.10 kcal/mol. The structure of the chair conformer was determined by crystallography.<sup>56</sup> In the crystal, the benzene rings are shifted relative to one other by crystal packing forces. This shift can be reproduced by MM3 calculations of the molecule in the crystal environment. However, the structure of the isolated molecule calculated by MM3 possesses  $C_{2h}$  symmetry (with all positive eigenvalues in the force constant matrix) which has an exact alignment of the two benzene rings. The distances calculated by MM3 between the two benzene rings and the angle of 13—14—15 are too small for either the isolated molecule or molecules in the crystal lattice. Also, the heat of formation of [3.3]paracyclophane was calculated to be lower than the experimental value by 8.5 kcal/mol. While there is a small but real problem with the structure here, it is doubtful that the MM3 heat of formation can be significantly in error. The structures calculated by MM3 for the isolated molecule and the molecule in the crystal environment are listed in Table XVI, together with the X-ray structure.

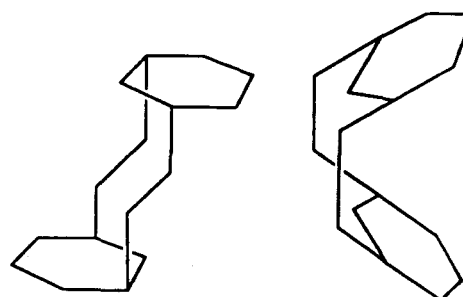
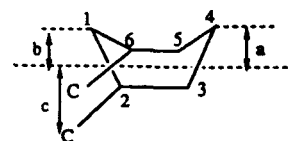
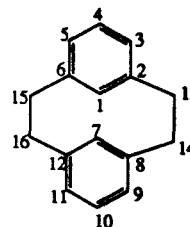
## Hexaphenylethane and Related Compounds

For more than half a century following Gomberg's discovery of the triphenylmethyl radical,<sup>59</sup> its dimer was believed to be hexaphenylethane (HPE). It was not until 1968 that the correct structure of the dimer, first proposed by Jacobson in 1905, was established by Lankamp, Nauta, and MacLean.<sup>60</sup> According to their work, the structure is the methylenecyclohexadiene derivative 2. Since the dimerization is reversible, this indicates that the energy of the methylenecyclohexadiene derivative is lower than that of HPE. MM3 calculations were carried out on both HPE and the methylenecyclohexadiene derivative, and they gave the expected answers. The relative energies of the  $D_3$  and  $S_6$  conformers of HPE and compound 2 are listed in Table XVII. They show that compound 2 is 9.5 kcal/mol more stable than the most stable conformer of HPE.

Conformational studies of HPE were carried out by Osawa<sup>60</sup> and co-workers using different force fields. Two conformations with  $D_3$  and  $S_6$

**Table XV.** Structure of *s-trans*-[2.2]metacyclophane.

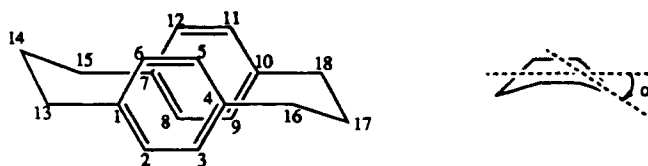
	X-ray	MM3	MM2
1—22	1.389(10)	1.403	1.400
2—3	1.383(9)	1.400	1.398
2—13	1.525(20)	1.515	1.515
13—14	1.56	1.554	
2—13—14	110.3(0.5)	111.9	111.2
a	0.048	0.050	0.07
b	0.162	0.176	0.19
c	0.402	0.395	0.43

*s-trans**s-cis*



**Table XVI.** Structure of [3.3]paracyclophane (chair form).

Bond	Number	X-ray	MM3	MM3(crystal)
C=C	1-2	1.390	1.401	1.402
	2-3	1.382	1.396	1.397
$C_{sp2}-C_{sp3}$	1-13	1.517	1.511	1.511
	7-15	1.507	1.512	1.508
$(C_{sp2}-C_{sp3})_{av}$		1.512	1.512	1.510
$C_{sp3}-C_{sp3}$	13-14	1.525	1.544	1.543
	14-15	1.537	1.544	1.542
$(C_{sp3}-C_{sp3})_{av}$		1.531	1.544	1.543
$C_{sp2}-C-C$	1-13-14	115.9	114.6	115.8
	7-15-14	113.6	114.5	113.9
$C_{sp2}-C-C)_{av}$		114.8	114.6	114.9
C-C-C	13-14-15	116.8	116.0	115.9
C...C	1...7	3.14	3.05	3.05
	2...8	3.30	3.19	3.17
	1...8	3.39	3.42	3.54
	2...7	3.32	3.42	3.27
$\alpha$		6.4	5.5	4.7

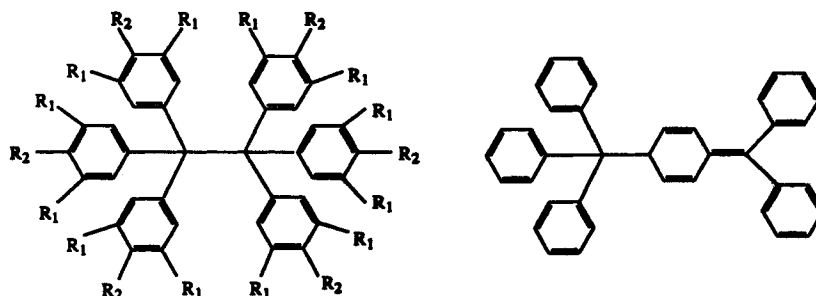


symmetries were found to be the stable conformers of this compound. There are discrepancies between the MM3 results and the other calculations concerning the stability of these two conformers. The full matrix optimization method

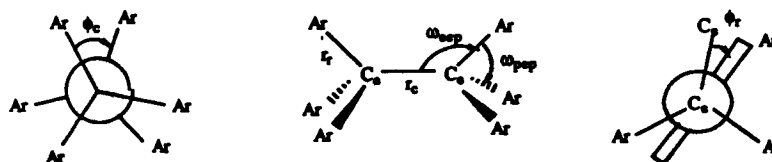
was used in the MM3 calculations to minimize the energies of the  $D_3$  and  $S_6$  conformers. The conformer with  $S_6$  symmetry was found more stable, while the one with  $D_3$  symmetry has been found the more stable conformer by

**Table XVII.** Relative energies of hexaphenylethane and compound 2 (Kcal/mol).

	Current work		Osawa				
	MM3	MM2(87)	AM	MMI	MMPI	MM2(77)	MNDO
Compound 2	0						
HPE S6	9.9	3.0	2.55	4.42	2.01	3.66	2.57
HPE D3	23.2	0	0	0	0	0	0



- 1  $R_1 = R_2 = H$   
 3  $R_1 = t\text{-Bu}, R_2 = Ph$   
 4  $R_1 = t\text{-Bu}, R_2 = H$



other calculation methods. However, two hexaphenylethane derivatives, hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane<sup>61</sup> and hexakis(3,5-di-*tert*-butylphenyl)ethane,<sup>62</sup> were found to possess  $S_6$  symmetry in crystals. This discrepancy between the MM3 and other calculations is easy to explain. The dipole-dipole interactions favor the  $S_6$  conformer over the  $D_3$  conformer, because the phenyl rings of the  $S_6$  conformer of HPE are roughly perpendicular to each other as in the benzene crystal, while the phenyl rings are approximately parallel to each other in the  $D_3$  conformer. This phenomenon can be calculated correctly by MM3, but not by MM2, in part because the MM3 force field includes the C—H dipole moment.<sup>11</sup> The force fields which do not have C—H dipole moment will tend to calculate the parallel phenyl ring conformation to be too stable. The structures calculated by MM3 and other methods are listed in Table XVIII.

Although the parent compound hexaphenylethane has not been synthesized to date, some substituted hexaphenylethanes are more stable than their methylenecyclohexadiene derivatives. The first unbridged hexaphenylethane derivative prepared was hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (3). Its crystal structure, determined by Stein,<sup>61</sup> possesses  $S_6$  symmetry, which is consistent to the results obtained by MM3 calculations on hexaphenylethane.

Another known hexaphenylethane derivative is hexakis(3,5-di-*tert*-butylphenyl)ethane (4). The crystal structure was determined by Kahr et. al.<sup>62</sup> This molecule also possesses  $S_6$  symmetry in the crystal form. MM3 calculations were carried out on the  $S_6$  and  $D_3$  conformers of this compound, and on its isomeric compound, the methylenecyclohexadiene derivative. The relative energies of the three structures are in order 0.0, 15.4, and 26.5 kcal/mol, which shows that

**Table XIX.** Structure of hexakis(3,5-di-*tert*-butylphenyl)ethane ( $S_6$ )

	X-ray (RT)	MM3
$r_c$	1.670(7)	1.678
$r_r$	—	1.550
$w_{\text{pep}}$	—	106.8
$w_{\text{eep}}$	—	112.0
$\phi_c$	—	60.0
$\phi_r$	—	54.4

the HPE derivative is indeed more stable than the cyclohexadiene derivative in this case. Also, the  $S_6$  conformer is more stable than the  $D_3$  by MM3. The structure of the  $S_6$  conformer is summarized in Table XIX.

In Table XX is summarized some conformational information as calculated in the present work, and experimental comparisons are given.

## HEATS OF FORMATION

We have examined the heats of formation of 66 conjugated and 45 unconjugated hydrocarbons in this work. Many of these were considered when the MM2 parameterization was worked out. The MM2 results can now be seen to be better than they appeared at the time, because several of the molecules which MM2 fit poorly have had their heats of combustion redetermined subsequent to that work. In each case, the agreement between MM2 and experiment was much improved after the experimental redetermination. The molecules involved were pyrene, tetracene, triphenylene, and chrysene.

In the current work, the set of compounds used in the parameterization is much larger than anything previously studied. The compounds studied, together with their calculated and experimental heats of formation, are given in

**Table XVIII.** Structure of hexaphenylethane ( $S_6$  and  $D_3$ ).

	Current work			Osawa			
	MM3	MM2	AM	MMI	MMPI	MM2	MNDO
$S_6$ Conformer							
$r_c$	1.685	1.640	1.636	1.623	1.602	1.606	1.682
$r_r$	1.547	1.553	1.576	1.555	1.547	1.551	1.569
$w_{\text{pep}}$	106.9	106.1	104.1	105.1	106.3	105.4	106.2
$w_{\text{eep}}$	111.9	112.7	114.8	113.5	112.4	113.3	112.5
$\phi_c$	60.0	60.0	60.1	60.0	60.0	60.0	60.0
$\phi_r$	53.9	55.0	52.3	53.4	55.1	52.9	53.7
$D_3$ Conformer							
$r_c$	1.676	1.631	1.639	1.607	1.631	1.602	1.681
$r_r$	1.554	1.554	1.576	1.552	1.552	1.548	1.570
$w_{\text{pep}}$	107.9	106.0	103.6	105.4	106.7	105.5	106.2
$w_{\text{eep}}$	111.0	112.8	114.4	113.4	112.2	113.2	112.6
$\phi_c$	29.3	5.1	3.0	2.5	3.1	4.5	9.7
$\phi_r$	31.9	50.6	50.2	49.8	50.8	50.4	51.1

Table XX. Relative energies of conformations (kcal/mol).

Compound	Conformation	Calc.	Exp.
1,3-Butadiene <sup>a</sup>	trans	0	0
	cis	1.85	2.49
	90°	7.42	7.16
Isoprene <sup>b</sup>	trans	0	0
	gauche	1.66	2.65
	90°	5.44	5.78
2,3-Dimethyl-1,3-butadiene <sup>c</sup>	trans	0	0
	gauche	1.20	1.7
4,8-Dihydrodibenzo [cd,gh]pentalene	cup form	0	—
	planar	1.28	—
1,3,5-Cycloheptatriene <sup>d</sup>	boat	0	0
	planar	1.3	5.7
1,3,5,7-Cyclooctatetraene <sup>e</sup>	tub form	0	0
	planar	14.1	13.7
[18]Annulene <sup>f</sup>	D3	0.0	0
	D3h	0.56	≤0
	D6h	25.9	≤0
Biphenyl <sup>g</sup>	twist	0	0
	planar	2.52	2.0
	90°	1.10	1.0
1,2-Diphenylethane <sup>h</sup>	trans	0	0
	gauche	0.34	>0
1,2-Diphenylpropane <sup>i</sup>	ph,ph anti;ph, CH <sub>3</sub> gauche	0	0
	ph,ph gauche;ph, CH <sub>3</sub> anti	0.28	0.23
	ph,ph gauche;ph,CH <sub>3</sub> gauche	0.94	0.82
4,5-Dimethylphenanthrene <sup>j</sup>	nonplanar	0	0
	planar	17.2	16.1 ± 1.5
3,4-Benzophenanthrene <sup>k</sup>	nonplanar	0	0
	planar	7.7	5–10
Corannulene	cup form	0	stable
	planar	14.9	—
[2,2]Paracyclophane <sup>l</sup>	D2 twist	0	0
	D2h	2.24	>0
[2,2]Metaparacyclophane <sup>m</sup>	ground state	0	0
	transition state for meta-ring rotation	19.70	18
[2,2]Metacyclophane	s-trans	0	0
	s-cis	12.43	>0
[3,3]Paracyclophane <sup>n</sup>	boat	0	0
	chair	0.10	>0
1,3-Cycloheptadiene	Cs	0	stable
	C2	3.20	—
Styrene <sup>o</sup>	planar	0	0
	90°	3.88	3.90
1,3-Cyclohexadiene <sup>p</sup>	nonplanar	0	0
	planar	2.46	3.1

<sup>a</sup>L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975).<sup>b</sup>Y. N. Panchenko, V. I. Pupyshev, A. V. Abramnikov, M. Traetteberg, and S. J. Cyvin, *J. Mol. Struct.*, **130**, 355 (1985).<sup>c</sup>M. E. Squillacote, T. C. Semple, and P. W. Mui, *J. Am. Chem. Soc.*, **107**, 6842 (1985).<sup>d</sup>J. B. Lambert, L. J. Durham, P. Lepoutere, and J. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).<sup>e</sup>F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).<sup>f</sup>J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Cryst.*, **19**, 227 (1965).<sup>g</sup>A. Almennigen, *J. Mol. Struct.*, **128**, 59 (1985).<sup>h</sup>K. K. Chiu, H. H. Huang, and L. H. L. Chai, *Perkin Trans. Part 2*, 286 (1972).<sup>i</sup>J. Jacobs, *Tetrahedron Letters*, **34**, 2927 (1976).<sup>j</sup>R. N. Armstrong, H. L. Ammon, and J. N. Darnow, *J. Am. Chem. Soc.*, **109**, 2077 (1987).<sup>k</sup>F. L. Hirshfeld, S. Sandler, and C. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963).<sup>l</sup>H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Cryst.*, **B28**, 1733 (1972).<sup>m</sup>D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, **93**, 1073 (1970).<sup>n</sup>P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).<sup>o</sup>J. E. Almlof, P. V. Isacson, P. J. Mjoberg, and M. Ralowski, *Chem. Phys. Lett.*, **26**, 215 (1974).<sup>p</sup>L. A. Carreira, R. O. Carter, and J. R. Durig, *J. Chem. Phys.*, **59**, 812 (1973).

Table XXI. Over the 111 compounds, the rms error when the MM3 values are compared with experiment is 0.62 kcal/mol. The average reported experimental error over the same set is 0.61 kcal/mol. We have excluded a few compounds, because we do not feel that their experimental heats of formation are accurate. We have also excluded a few compounds which MM3 fits very poorly. These were excluded because we feel that there is some special interaction present in them, which is not being properly taken into account. If we do not take the interaction into account, and do not exclude them, then we are biasing the parameterization in an unwanted way. Just what the problems are with these compounds will have to be determined later.

Strain energies have been found of some use, and data for calculating them for compounds studied herein are given in Table XXII.

## RESONANCE ENERGIES

Resonance energies have a long standing tradition in the field of organic chemistry. Unfortunately, they do not have a unique definition, and their numerical values depend on the standards used. In this work, as with MM2, we have adapted the kind of definition advocated by Dewar,<sup>15</sup> which is perhaps as useful as any other definition. According to this definition, ethylene, and linear transoid polyenes, such as 1,3-butadiene, etc., have a zero resonance energy. The difference between our numbers and Dewar's stems from the fact that Dewar worked with idealized structures with standard bond lengths and angles, whereas we use real structures, as calculated by MM3. Hence, our numerical values differ somewhat from his, but the principle is the same. The resonance energy is, as we use it, only defined for planar systems. It does not make sense to take an experimental heat of combustion for a molecule like cyclooctatetraene, and say that this determines the resonance energy. We have here a pi-system, with a resonance energy, and we also have a sigma-system which may or may not be deformed, and the sigma-pi separation is not valid if the system is nonplanar. We, therefore, will discuss only the resonance energy of the planar pi-system, which is a clear and well-defined quantity. In Table XXIII are given some calculated resonance energies for simple compounds. The linear polyenes are made to have resonance energies of zero by choosing bond energy parameters for the single and double bond components of the kekule form of a set of polyenes so as to yield this result. Since one cannot fit a whole series of polyenes exactly, we have chosen to weight a set of simple poly-

nes (ethylene, *t*-butadiene, hexatriene, octatetraene) to approach this result. Hence, we see that with our numbers, *trans*-butadiene has a calculated resonance energy of -0.20 kcal/mol (Table XXIII). Benzene, naphthalene, and azulene then come out to have resonance energies of 18, 27, and 1.3 kcal/mol respectively, similar to those numbers found by Dewar. However, since Dewar and most earlier investigators have compared the experimental energy with that calculated for the kekule structure, the sigma strain and any nonplanarity of the system were not taken into account. Since we know those things, and deal with them separately, we do not mix them in here. Hence, for azulene, our calculated resonance energy is 1.3 kcal/mol, thus a favorable (though small) number. The pi system in azulene is stabilized slightly, although not as much as in naphthalene, by this resonance energy. Of course, the total energy of the molecule is much higher than that number might imply, because there is a good deal of bending strain in the five- and seven-membered rings. On the whole, our resonance energies (Table XXIII) are similar to Dewar's for planar systems.

We have a standard definition for strain energy in saturated systems,<sup>4</sup> and in the conjugated system, the definition is the same, but we call it the *sigma strain energy*. What happens with the pi part of the molecule is summarized in the expression *resonance energy*. With nonplanar systems, again, while earlier workers have compared experimental measurements with calculations on nonplanar systems, it is difficult to understand what these numbers mean. To take cyclooctatetraene as an example, we calculate the resonance energy based on the planar structure, and compare this with the idealized energy for a kekule form with bond energies corresponding to a linear polyene. On this basis we obtain a resonance energy of -3.28 kcal/mol. Thus, resonance in cyclooctatetraene is a small destabilizing effect. Of course, the sigma system would be highly deformed if the molecule were planar, and it forces the molecule into the tub conformation. This raises the pi energy of the molecule, but lowers the total energy of the molecule. One can calculate the pi energy change that is brought about here and obtain a value for the resonance energy (that is, the pi system energy, relative to the usual standard). This is not really valid, because the sigma pi separation is broken down when the system becomes nonplanar. However, one can do the formal calculation, and one obtains a -23 kcal/mol resonance energy for the non-planar cyclooctatetraene. Here the pi energy is quite unfavorable, but is nonetheless overwhelmed by the sigma system.

Table XXI. Heats of formation of unsaturated hydrocarbons.

Best values\*

C=Cd = 155.800	SEC = -33.445
TERT = -65.374	ISOd = -0.804
C—C = -0.180	ISO1 = -2.011
tBUT = -6.391	1122 = 0.884

Fixed values\*

C=Cl = -129.37

Eq	Wt	$H_f^\circ$ Calc.	$H_f^\circ$ Exp.	Difference (calc-exp)	Exp Error	Compound
1	5	13.07	12.56 <sup>(a)</sup>	0.51	0.08	ethylene
2	5	5.50	4.88 <sup>(c)</sup>	0.62	0.16	propene
3	5	0.55	0.02 <sup>(a)</sup>	0.53	0.24	1-butene, gauche
4	5	-0.97	-1.67 <sup>(f)</sup>	0.70	—	cis-2-butene
5	5	-2.03	-2.67 <sup>(f)</sup>	0.64	—	trans-2-butene
6	5	-3.93	-4.04 <sup>(f)</sup>	0.11	—	isobutene
7	5	-6.14	-6.60 <sup>(a)</sup>	0.46	0.24	cis-2-pentene
8	5	-7.01	-7.60 <sup>(a)</sup>	0.59	0.26	trans-2-pentene
9	5	-10.05	-10.12 <sup>(c)</sup>	0.07	0.18	2-methyl-2-butene
10	5	-15.30	-15.96 <sup>(a)</sup>	0.66	0.35	2-methyl-2-pentene
11	5	-16.85	-16.56 <sup>(a)</sup>	-0.29	0.26	2,3-dime-2-butene
12	5	-8.39	-8.44 <sup>(a)</sup>	0.05	0.24	2-methyl-1-butene
13	5	-13.67	-14.51 <sup>(a)</sup>	0.84	0.31	3,3-dime-1-butene
14	5	-14.19	-14.86 <sup>(c)</sup>	0.67	0.27	2,3-dime-1-butene
15	5	-6.44	-6.61 <sup>(c)</sup>	0.17	0.18	3-methyl-1-butene
16	3	-21.22	-21.24 <sup>(a)</sup>	0.02	0.30	t-4,4-dime-2-pentene
17	3	-18.06	-17.37 <sup>(a)</sup>	-0.69	0.36	c-4,4-dime-2-pentene
18	3	-40.53	-39.56 <sup>(b)</sup>	-0.97	0.62	t-di-t-but-ethylene
19	2	-31.11	-30.27 <sup>(b)</sup>	-0.84	0.62	c-di-t-but-ethylene
20	5	9.11	8.56 <sup>(f)</sup>	0.55	—	cyclopentene
21	5	-1.15	-0.91 <sup>(a)</sup>	-0.24	0.17	me-cyclopentene
22	5	2.41	2.78 <sup>(c)</sup>	-0.37	0.50	me-ene-cyclopentane
23	5	1.94	1.76 <sup>(c)</sup>	0.18	0.17	3-me-cyclopentene
24	5	2.19	2.06 <sup>(c)</sup>	0.13	—	4-me-cyclopentene
25	5	-5.05	-4.78 <sup>(k)</sup>	-0.27	0.10	et-ene-cyclopentane
26	5	-10.57	-10.36 <sup>(a)</sup>	-0.21	0.19	methylcyclohexene
27	5	-8.22	-8.22 <sup>(c)</sup>	0.00	0.33	me-ene-cyclohexane
28	5	-1.18	-1.20 <sup>(a)</sup>	0.02	0.17	cyclohexene
29	5	-2.41	-2.20 <sup>(a)</sup>	-0.21	0.26	cycloheptene
30	5	21.20	21.40 <sup>(j)</sup>	-0.20	0.28	norbornene
31	5	57.28	57.37 <sup>(j)</sup>	-0.09	0.36	norbornadiene
32	5	5.26	4.68 <sup>(l)</sup>	0.58	0.71	trans-cyclooctene
33	5	-5.14	-6.20 <sup>(f)</sup>	1.06	—	cis-cyclooctene
34	5	37.72	37.45 <sup>(c)</sup>	0.27	—	cyclobutene
35	5	28.63	28.39 <sup>(i)</sup>	0.24	—	methylcyclobutene
36	5	29.03	29.06 <sup>(a)</sup>	-0.03	0.18	methylenecyclobutane
37	5	94.58	94.00 <sup>(h)</sup>	0.58	—	dewar benzene
38	5	26.35	26.30 <sup>(a)</sup>	0.05	—	1,4-cyclohexadiene
39	5	24.98	25.26 <sup>(a)</sup>	-0.35	0.29	1,4-pentadiene
40	0	73.97	75.38 <sup>(g)</sup>	-1.41	—	barrelene
41	0	38.93	37.54 <sup>(g)</sup>	1.39	—	bi-c[2.2.2]octadiene
42	0	7.22	5.96 <sup>(g)</sup>	1.26	—	bi-c[2.2.2]octene
43	0	-1.96	-2.20 <sup>(a)</sup>	0.24	0.77	me-ene[2.2.2]octane
44	0	-1.16	-4.45 <sup>(a)</sup>	3.29	0.55	me-bi-c[2.2.2]octene
45	5	35.15	34.82 <sup>(a)</sup>	0.33	0.41	ethylene-4norbornene
46	15	13.06	12.56 <sup>(a)</sup>	0.50	0.08	ethylene
47	15	25.47	26.01 <sup>(a)</sup>	-0.54	0.15	trans-butadiene
48	8	18.30	18.06 <sup>(a)</sup>	0.24	0.26	trans-isoprene
49	2	11.78	10.79 <sup>(a)</sup>	0.99	0.26	2,3-dimethyl-butadiene
50	9	17.74	18.12 <sup>(c)</sup>	-0.38	0.16	trans-pentadiene
51	9	18.76	19.13 <sup>(c)</sup>	-0.37	0.24	cis-pentadiene
52	7	32.82	32.12 <sup>(a)</sup>	0.70	0.36	cyclopentadiene
53	9	24.46	25.38 <sup>(a)</sup>	-0.92	0.22	1,3-cyclohexadiene
54	7	21.17	22.56 <sup>(c)</sup>	-1.39	0.20	1,3-cycloheptadiene
55	1	43.78	43.89 <sup>(c)</sup>	-0.11	0.38	1,3,5-cycloheptatriene
56	2	71.01	71.13 <sup>(a)</sup>	-0.12	0.33	1,3,5,7-cyclooctatetraene
57	1	30.55	32.12 <sup>(a)</sup>	-1.57	1.30	dimethylfulvene
58	15	20.29	19.81 <sup>(a)</sup>	0.48	0.13	benzene
59	9	12.16	12.06 <sup>(a)</sup>	0.10	0.14	toluene
60	7	7.04	7.15 <sup>(a)</sup>	-0.11	0.20	ethylbenzene
61	5	4.57	4.56 <sup>(a)</sup>	0.01	0.26	o-xylene

Table XXI. continued

62	5	4.04	4.14 <sup>(a)</sup>	-0.10	0.18	<i>m</i> -xylene
63	5	4.02	3.97 <sup>(c)</sup>	0.05	0.24	<i>p</i> -xylene
64	3	1.74	1.89 <sup>(a)</sup>	-0.15	0.19	<i>n</i> -propylbenzene
65	3	0.99	0.96 <sup>(a)</sup>	0.03	0.25	<i>i</i> -propylbenzene
66	3	-0.28	0.31 <sup>(a)</sup>	-0.59	0.25	1-methyl-2-ethylbenzene
67	3	-1.12	-0.43 <sup>(a)</sup>	-0.69	0.27	1-methyl-3-ethylbenzene
68	3	-1.14	-0.76 <sup>(a)</sup>	-0.38	0.32	1-methyl-4-ethylbenzene
69	3	-2.44	-2.26 <sup>(a)</sup>	-0.18	0.29	1,2,3-trimethylbenzene
70	3	-3.57	-3.31 <sup>(a)</sup>	-0.26	0.25	1,2,4-trimethylbenzene
71	3	-4.09	-3.81 <sup>(a)</sup>	-0.28	0.32	1,3,5-trimethylbenzene
72	3	-3.19	-3.12 <sup>(a)</sup>	-0.07	0.26	<i>n</i> -butylbenzene
73	3	-5.13	-5.14 <sup>(a)</sup>	0.01	0.31	<i>i</i> -butylbenzene
74	3	-4.01	-4.15 <sup>(a)</sup>	0.14	0.29	<i>s</i> -butylbenzene
75	3	-4.37	-5.40 <sup>(a)</sup>	1.03	0.29	<i>t</i> -butylbenzene
76	3	-20.87	-20.75 <sup>(a)</sup>	-0.12	0.62	hexamethylbenzene
77	3	6.01	6.42 <sup>(a)</sup>	-0.41	0.54	tetrahydronaphthalene
78	6	14.71	14.16 <sup>(a)</sup>	0.55	0.43	indane
79	3	37.98	39.03 <sup>(a)</sup>	-1.05	0.61	indene
80	7	34.85	35.31 <sup>(a)</sup>	-0.46	0.29	styrene
81	2	73.26	73.53 <sup>(c)</sup>	-0.27	0.82	azulene
82	8	35.95	35.85 <sup>(a)</sup>	0.10	0.30	naphthalene
83	5	43.42	43.57 <sup>(a)</sup>	-0.15	0.60	biphenyl
84	1	37.86	37.41 <sup>(a)</sup>	0.45	0.64	acenaphthene
85	1	64.44	63.00 <sup>(a)</sup>	1.44	1.11	acenaphthalene
86	1	38.18	38.17 <sup>(a)</sup>	0.01	1.04	9,10-dihydroanthracene
87	1	56.82	56.44 <sup>(a)</sup>	0.38	0.30	<i>trans</i> -stilbene
88	1	59.17	60.31 <sup>(a)</sup>	-1.14	0.47	<i>cis</i> -stilbene
89	2	58.37	58.71 <sup>(a)</sup>	-0.34	1.04	1,1-diphenylethane
90	2	33.23	33.13 <sup>(a)</sup>	0.10	0.43	1,1-diphenylethane
91	2	34.12	34.15 <sup>(a)</sup>	-0.03	0.31	1,2-diphenylethane
92	2	55.23	55.28 <sup>(a)</sup>	-0.05	0.66	anthracene
93	2	50.71	50.67 <sup>(a)</sup>	0.04	0.77	phenanthrene
94	1	45.90	46.26 <sup>(a)</sup>	-0.36	1.44	4,5-dimethylphenanthrene
95	1	39.18	39.93 <sup>(a)</sup>	-0.75	2.02	9,10-dimethylphenanthrene
96	1	34.18	34.20 <sup>(a)</sup>	-0.02	0.47	2,7-dimethylphenanthrene
97	1	59.47	58.48 <sup>(a)</sup>	0.99	0.50	[2.2]paracyclophane
98	1	52.29	52.25 <sup>(a)</sup>	0.04	0.41	[2.2]metaparacyclophane
99	0	43.84	40.76 <sup>(a)</sup>	3.08	1.56	[2.2]metacyclophane
100	0	22.49	31.00 <sup>(a)</sup>	-8.51	0.50	[3.3]paracyclophane
101	1	71.54	70.40 <sup>(a)</sup>	1.14	0.52	fluoranthene
102	1	67.50	65.53 <sup>(a)</sup>	1.97	1.01	triphenylene
103	1	66.96	66.03 <sup>(a)</sup>	0.93	1.09	chrysene
104	1	71.78	69.59 <sup>(a)</sup>	2.19	1.10	benzophenanthrene
105	1	68.62	69.63 <sup>(a)</sup>	-1.01	1.16	1,2-benzanthracene
106	0	58.16	53.94 <sup>(a)</sup>	4.22	0.29	pyrene
107	0	76.24	72.30 <sup>(a)</sup>	3.94	1.25	tetracene
108	1	53.67	53.14 <sup>(a)</sup>	0.53	1.06	5,12-dihydrotetracene
109	0	124.90	124.0 <sup>(d)</sup>	0.90	6.0	[18]-Annulene
			67.0 <sup>(e)</sup>			
110	0	93.04	96.08 <sup>(a)</sup>	-3.04	3.61	diphenylfulvene
111	0	104.78	104.43 <sup>(a)</sup>	0.38	2.20	Biphenylene
		115.2 <sup>(a)</sup>				
rms.				0.62	0.61	
Av.				0.05		

(\*) See Table XXII for explanation.

<sup>(a)</sup> J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, second edition, University of Sussex, 1986.<sup>(b)</sup> See references for corresponding compounds in Ph.D thesis by Fanbing Li.<sup>(c)</sup> J. D. Cox, *Thermochemistry of Organic and Organometallic Compounds*, 1970.<sup>(d)</sup> J. F. M. Oth, J. Buenzli, and Y. J. Zélicourt, *Helv. Chim. Acta*, **57**, 2276 (1974).<sup>(e)</sup> C. T. Mortimer, H. D. Springall, F. Sonheimer, and R. Wolevsky, *J. Chem. Soc.*, 216 (1965).<sup>(f)</sup> S. Benson, F. R. Cruickshank, D. M. Golden, G. R. Hangen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **60**, 279 (1969).<sup>(g)</sup> G. Schröder, *Helv. Chim. Acta*, **54**, 153 (1971); R. B. Turner, *J. Am. Chem. Soc.*, **79**, 4116 (1957); L. R. Schmitz, N. L. Allinger, and K. M. Flurchick, *J. Comp. Chem.*, **9**, 281 (1988).<sup>(h)</sup> J. M. Schulman, R. L. Disch, *J. Am. Chem. Soc.*, **107**, 5059 (1985).<sup>(i)</sup> Calculated from exp. energy difference between 1-methylcyclobutene and methylenecyclobutane.<sup>(j)</sup> D. W. Rogers, L. S. Choi, R. S. Girellini, T. J. Holmes, and N. L. Allinger, *J. Phys. Chem.*, **84**, 1810 (1980).<sup>(k)</sup> N. L. Allinger and D. W. Rogers, *Tetrahedron*, **38**, 1593 (1982).<sup>(l)</sup> D. W. Rogers, H. Voithenberg, N. L. Allinger, *J. Org. Chem.*, **43**, 360 (1978).

**Table XXII.** Heat of formations for conjugated hydrocarbons and simple alkenes (strainless).

Best values <sup>a</sup>					
C=Cd =		153.873	SEC =		-31.819
TERT =		-63.849	ISOd =		-0.545
C—C =		1.760	ISO1 =		-1.893
tBUT =		-4.923	1122 =		0.117
Fixed values <sup>a</sup>					
C=Cl =		-129.370			
Eq	Wt	$H_f^\circ$ Calc	$H_f^\circ$ Exp	Difference (calc-exp)	Compound
1	1	13.06	13.07	-0.01	ethylene
2	1	5.51	5.50	0.01	propene
3	1	-2.04	-2.03	-0.01	<i>trans</i> -2-butene
4	1	-3.93	-3.93	0.00	isobutene
5	1	-13.67	-13.67	0.00	3,3-dime-1-butene
6	1	-7.01	-7.01	0.00	<i>trans</i> -2-pentene
7	1	20.29	20.29	0.00	benzene
8	1	12.16	12.16	0.00	toluene
9	1	4.02	4.02	0.00	<i>p</i> -xylene
10	1	35.95	35.95	0.00	naphthalene

<sup>a</sup>C=Cd: the bond energy of delocalized  $C_{sp^2}$ — $C_{sp^2}$  bond; SEC, TERT: energy increment for each secondary or tertiary  $C_{sp^2}$ , i.e., the  $C_{sp^2}$  carbon attached to two or three other  $C_{sp^2}$  carbons respectively; ISOd: energy increment for each secondary  $C_{sp^2}$  attached to one  $C_{sp^3}$ ; C—C: energy increment for each  $C_{sp^2}$ — $C_{sp^3}$  structure; ISO1: energy increment for each  $C_{sp^2}$  attached to two  $sp^3$  carbons; tBUT: energy increment for each *t*-butyl group attached to  $sp^2$  carbon; 1122:  $V_0$  term of 1-1-2-2 torsional function; C=Cl: C=C bond energy of ethylene in VESCF calculation (This value is added to each C=C bond of the nonconjugated compounds as the electronic energy. Therefore, the heats of formation of nonconjugated compounds can be calculated by either including the VESCF calculation or not and the same results are obtained either way).

## SPECTRA

The vibrational spectra of several simple alkenes were previously calculated with MM3 and reported on.<sup>12</sup> Because of the small number of cross terms used in the MM3 spectroscopic calculation, the results are not as good as one might like, and the rms value was 46  $\text{cm}^{-1}$ . We have examined butadiene, isoprene and benzene in the present work, utilizing the previously described parameterization. The rms difference between the experimental and calculated values for all vibrational frequencies of these five structures is 46  $\text{cm}^{-1}$ . The vibrational frequency analysis allows us to assign values to the force parameters in the MM3 force field more accurately and in a

way that is physically more meaningful than was possible for the MM2 force field. Also, thermodynamic properties can be calculated, based on the calculated vibrational frequencies. The frequencies calculated with MM3, together with the experimental values, are summarized in tables for compounds as follows: benzene, Table XXIV; *trans*- and *cis*-butadiene, Tables XXV and XXVI respectively; and *trans*- and *gauche*-isoprene, Tables XXVII and XXVIII respectively.

The vibrational frequencies of the second stable conformer of butadiene have been assigned to the *gauche*-conformer in Bock's work<sup>65</sup> with the assistance of the *ab initio* calculation. In the current work, the frequencies have been calculated based on the *cis* geometry, and the assignment agrees with Bock's paper. Other experimental work carried out by Mui and Grunwald<sup>67</sup> assigned the frequencies to *s-cis*-butadiene. The assignment of frequencies 21 and 22 are reversed<sup>67</sup> from ours and Bock's assignment.

The previously observed vibrational frequencies of the second stable conformer of isoprene were assigned by Traetteberg and coworkers<sup>27</sup> to the *gauche* conformer. Our calculation agrees with their assignment except for frequency 28. This frequency was assigned to C=C—C bending in the original experimental work,<sup>28</sup> and changed to C—CH<sub>3</sub> wag in the Traetteberg paper. Our calculation agrees with the original assignment, and strongly suggests that the motion

**Table XXIII.** Resonance energies of planar compounds (kcal/mol).

Compounds	MM3
Ethylene	0.0
t-1,3-Butadiene	-0.2
1,3,5-Hexatriene	-0.1
1,3,5,7-Octatetraene	0.1
Cyclobutadiene	-27.2
Benzene	18.2
Cyclooctatetraene	-3.3
Cyclodecapentaene ( <i>cis</i> )	3.1
Naphthalene	27.4
Azulene	1.3
Fulvene	-2.8
[18]-Annulene ( $D_{3h}$ )	-0.7

Table XXIV. Benzene vibrational frequencies ( $D_{6h}$ )

	Sym	Mode	Calc.	Exp. <sup>64</sup>	Calc-Exp
1.	Alg	C—H str. in phase	3058	3062	-4
2.		Breathing	911	993	-82
3.	A2g	C—H in plane bend	1368	1298	70
4.	B2g	C—H out-of-plane trig.	1119	1016	103
5.		C—C—C out-of-plane	581	685	-104
6.	E2g	C—H stretch	3043	3048	-5
7.		C—C stretch	1637	1595	42
8.		C—H in plane bend	1185	1178	7
9.		C—C—C in plane bend	596	606	-10
10.	E1g	C—H out-of-plane bend	773	850	-77
11.	A2u	C—H out-of-plane in phase	569	671	-102
12.	B1u	C—H trigonal stretch	3038	3060	-22
13.		C—C—C trigonal bend	947	1010	-63
14.	B2u	C—C stretch	1657	1693	-36
15.		C—H in-pl. trig. bend.	1249	1170	79
16.	E2u	C—H out-of-plane bend.	1030	985	45
17.		C—C—C out-of-plane bend.	361	400	-39
18.	E1u	C—H stretch	3051	3080	-29
19.		C—C stretch	1482	1485	-3
20.		C—H in-plane bend	982	1035	-53
					rms 53

should be C=C—C bending. The C—C torsion (frequency 32) was not observed for gauche isoprene, and the value listed here is the one for trans-isoprene. The CH<sub>3</sub> torsion was not assigned with great certainty in the experimental work. Therefore, the last two frequencies are not included in the rms calculation.

The MM3 calculated entropies for alkanes were quite good, with rms and average errors of about 0.5% and 0.1%, respectively. For the arbitrary selection of conjugated and aromatic compounds in Table XXIX, there are larger errors.

The errors found for the polyenes are quite small (both 0.0% for the two examples chosen), but the aromatic compounds have substantial systematic errors, with the entropies being calculated too positive, by about 1.5%. There are few or no low frequency (<300 cm<sup>-1</sup>) torsional vibrations in these compounds (These modes are major contributors to the entropy). The lowest out-of-plane bending frequencies are calculated somewhat too low for aromatic compounds. There are compensating (too high) frequency errors, but these occur at higher frequencies and contribute little

Table XXV. 1,3-*trans*-Butadiene vibrational frequencies ( $C_{2h}$ ).

	Sym	Mode	Calc.	Exp. <sup>65</sup>	Exp. <sup>66</sup>	Calc-Exp
1.	Ag	CH2 str.	3108	3101	3105	3
2.		C—H str.	3043	3014	3025	18
3.		CH2 str.	3010	3014	3014	-4
4.		C=C str.	1701	1643	1644	57
5.		CH2 sci.	1474	1442	1441	33
6.		C—H rock	1213	1291	1279	-66
7.		C—C str.	1185	1205	1206	-22
8.		CH2 rock	883	890	887	-4
9.		C=C—C bend	507	513	513	-6
10.	Au	C—H wag.	1101	1013	1022	79
11.		CH2 wag.	955	908	905	50
12.		CH2 twist	508	524	535	-27
13.		C—C tor.	164	163	163	1
14.	Bu	CH2 str.	3108	3102	3103	5
15.		C—H str.	3037	3056	3062	-25
16.		CH2 str.	3009	3010	2986	1
17.		C=C str.	1569	1599	1597	-28
18.		CH2 sci.	1396	1385	1381	15
19.		C—H rock	1253	1296	1297	-44
20.		CH2 rock	1033	991	988	45
21.		C=C—C bend	364	301	301	63
22.	Bg	C—H wag.	1090	967	974	116
23.		CH2 wag.	956	911	908	48
24.		CH2 twist	661	753	754	-93
					rms 47	



Table XXVI. *cis*-1,3-Butadiene Vibrational Frequencies ( $C_{2v}$ )

	Sym	Mode	Calc.	Exp. <sup>65</sup>	Exp. <sup>67</sup>	Calc-Exp
1.	A1	CH2 str.	3120	3103	3088	17
2.	B1	CH2 str.	3116	3103	3095	13
3.	A1	C—H str.	3035	3039	3007	-4
4.	B1	C—H str.	3030	3039	3054	-9
5.	A1	CH2 str.	3017	3014	2992	3
6.	B1	CH2 str.	3012	3014	2984	-2
7.	A1	C=C str.	1670	1633	1612	37
8.	B1	C=C str.	1618	1612	1632	8
9.	A1	CH2 sc.	1495	1425	1425	70
10.	B1	CH2 sc.	1450	1403	1402	47
11.	A1	C—H rock	1287	—	1299	-12
12.	B1	C—H rock	1203	—	1277	-74
13.	A1	CH2 rock	1099	—	1075	24
14.	A2	C—H wag	1094	983	1032	62
15.	B1	CH2 rock	1051	1087	1085	-36
16.	B2	C—H wag	1045	996	995	49
17.	A2	CH2 wag	962	915	915	47
18.	B2	CH2 wag	956	914	913	42
19.	A1	C—C str.	846	—	899	-53
20.	A2	C=C tw.	663	727	742	-64
21.	B1	C=C—C bend	598	596	595	2
22.	B2	C=C tw.	473	468	475	5
23.	A1	C=C—C bend	354	—	—	—
24.	A2	C—C tor.	86	—	136	-50
						rms 40

Table XXVII. *trans*-Isoprene vibrational frequencies ( $C_s$ )

	Smy	Mode	Calc.	Exp. <sup>27</sup>	Calc-Exp
1.	A'	=CH2 STR.	3114	3097	17
2.	A'	=CH2 STR.	3109	3092	17
3.	A'	C—H STR.	3035	3020	15
4.	A'	=CH2 STR.	3015	2988	27
5.	A'	=CH2 STR.	3013	2978	35
6.	A'	CH3 STR.	2971	2928	43
7.	A''	CH3 STR.	2970	2956	14
8.	A'	CH3 STR.	2880	2910	-30
9.	A'	C=C STR.	1668	1638	30
10.	A'	C=C STR.	1590	1603	-13
11.	A'	=CH2 DEF.	1506	1466	40
12.	A'	=CH2 SC.	1480	1425	55
13.	A''	CH3 DEF.	1456	1442	14
14.	A'	CH3 DEF.	1434	1414	20
15.	A'	=CH2 SC.	1332	1388	-56
16.	A'	C—C STR.	1314	1303	11
17.	A'	C—H BEND	1238	1291	53
18.	A''	CH3 ROCK	985	1034	-49
19.	A'	CH3 ROCK	940(wag)	1069	-129
20.	A''	C—H WAG	1084	990	94
21.	A'	=CH2 ROCK	970	1012	-42
22.	A''	=CH2 WAG	957	903	54
23.	A'	=CH2 ROCK	1063	953	110
24.	A''	=CH2 TWIST	917	891	26
25.	A'	C—CH3 STR.	780	780	0
26.	A''	=CH2 TWIST	686	755	-69
27.	A''	=CH2 TWIST	615	622	-7
28.	A'	C=C—C BEND	517	523	-6
29.	A'	C=C—CH3 BEND	439	401	38
30.	A''	C—CH3 WAG	366	412	-46
31.	A'	C=C—C BEND	301	288	13
32.	A''	CH3 TOR.	149	199	-50
33.	A''	C—C TOR.	95	153	-58
					rms 49

Table XXVIII. Gauche-isoprene vibrational frequencies ( $C_1$ )

	Mode	Calc.	Exp. <sup>27</sup>	Calc-Exp
1.	=CH2 STR.	3122	3097	25
2.	=CH2 STR.	3118	3092	26
3.	C—H STR.	3034	3020	14
4.	=CH2 STR.	3024	2988	36
5.	=CH2 STR.	3015	2978	37
6.	CH3 STR.	2971	2928	43
7.	CH3 STR.	2968	2956	12
8.	CH3 STR.	2879	2910	-31
9.	C=C STR.	1663	1638	25
10.	C=C STR.	1618	1603	15
11.	=CH2 DEF.	1501	1465	36
12.	=CH2 SC.	1467	1460	7
13.	CH3 DEF.	1448	1460	-12
14.	CH3 DEF.	1431	1430	1
15.	=CH2 SC.	1383	1388	-5
16.	C—C STR.	1269	1303	-34
17.	C—H BEND	1232	1255	-23
18.	=CH2 ROCK	1068	953	115
19.	C—H WAG	1063	1010	53
20.	CH3 ROCK	986	1069	-83
21.	=CH2 ROCK	974	1012	-38
22.	=CH2 WAG	958	920	38
23.	CH3 ROCK	940	—	—
24.	=CH2 TWIST	921	891	30
25.	C—CH3 STR.	778	780	-2
26.	=CH2 TWIST	685	750	-65
27.	=CH2 TWIST	608	635	-27
28.	C=C—C BEND	530	555	-25
29.	C=C—CH3 BEND	408	—	—
30.	C—CH3 WAG	360	—	—
31.	C=C—C BEND	330	311	19
32.	C—C TOR.	47	153	(-106)
33.	CH3 TOR.	29	197	(-168)
				rms 40

to the entropy. The result is that the entropies are calculated somewhat too high in aromatic molecules, in a systematic way. While the entropies could be improved by increasing some of the  $V_2$  terms, other things would get worse, and the present force field is a best compromise, in our judgement.

## CONCLUSIONS

Over 100 alkenes and conjugated hydrocarbons have been examined in this work, with respect to their structures and heats of formation, and in many cases with respect to conformational equilibria, or vibrational spectra. A previously devel-

Table XXIX. Entropies and heat capacities (298°K).

	$S^\circ$ (cal/mol)			$C_p^\circ$ (cal/mol*°K)	
	Exp. <sup>a</sup>	MM3	Error%	Exp. <sup>a</sup>	MM3
1,3-Butadiene	66.6	66.5	0.0	19.01	18.70
Benzene	64.3	65.1	1.2	19.52	20.38
Toluene <sup>b</sup>	76.6	77.7	1.4	24.77	25.65
Styrene	82.5	84.1	1.9	29.18	29.25
Naphthalene	80.2	81.1	1.1	31.68	32.62
Cyclooctatetraene	78.1	77.9	0.0	29.16	29.80
Biphenyl	93.9	94.8	1.0	38.80	40.55

<sup>a</sup>D. R. Stull, E. F. Westrum, Jr., G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons Inc., 1969

<sup>b</sup>The vibrational frequencies which are lower than  $10\text{ cm}^{-1}$  are excluded from the thermodynamic data calculations in the MM3 program. The entropy and heat capacity increments caused by these vibrational motions were found from Pitzer's table (K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942)) and added to the numbers from the program by hand calculation to get the final results.

oped, but substantially modified, theoretical method, in which one first deduced force constants for the conjugated system by a quantum mechanical (VESCF) pi-system calculation was utilized. The structural results, on the whole, are very good, although there is one significant problem which will be mentioned below. The heats of formation are calculated with an accuracy that is competitive with experiment. The vibrational spectra are calculated for five structures with an rms error of  $46\text{ cm}^{-1}$ . While this is not a good result in a spectroscopic sense, it proves to be quite adequate for structural problems.

The most significant discrepancy between the calculation and experiment now appears to come from the fact that we assumed that *cis*-butadiene was planar. The planarity of this structure has been under debate for many years, but the balance of the evidence now favors the *cis* structure as being nonplanar, with a torsion angle of approximately  $35^\circ$ , for the isolated molecule. Unfortunately, to fit this result with MM3 would require going back to the beginning, and redoing the conjugated systems entirely. The overall results would not change much if this were done. While the torsion angle deviation from planarity (about  $35^\circ$ ) in *cis*-butadiene is considerable, the height of the barrier which separates the two enantiomeric *gauche* forms is about 0.7 kcal/mol. Since the lowest vibrational level in this well is about half that value, what this means at the practical level is that there is a very wide amplitude vibrational motion, either across the *cis* structure, or localized into two broad wells on either side of the *cis* structure. We do note, however, that one significant discrepancy between the MM3 results and experiment involves cycloheptatriene, which is a good deal too flat according to MM3. A destabilization of the *cis*-butadiene conformation would noticeably improve the agreement with experiment in this particular case.

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## References

1. Taken mainly from the Ph.D. dissertation of L. Y. submitted to the University of Georgia in partial fulfillment of the Ph.D. degree, 1990.
2. Allinger and Yan are with the University of Georgia.
3. Li is currently at Syntex, 3401 Hillway Ave., Palo Alto, CA 94304.
4. U. Burkert and N. L. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, D.C., 1982.
5. a. The MM2 force field for hydrocarbons was first described in reference 5(b). Extensions to functionalized molecules and other special problems were described in subsequent papers, which are summarized in reference 4. The original version of the program (MM2(77)) is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47405, Program 395. The latest version of the MM2 program, which is referred to as MM2(87), is available to academic users from the Quantum Chemistry Program Exchange, and to commercial users from Molecular Design Limited, 2132 Farallon Drive, San Leandro, California 94577. b. N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).
6. J. T. Sprague, J. C. Tai, Y. H. Yuh, and N. L. Allinger, *J. Comp. Chem.*, **8**, 581 (1987).
7. a. J. C. Tai and N. L. Allinger, *J. Am. Chem. Soc.*, **110**, 2050 (1988). b. J. C. Tai, J.-H. Lii, and N. L. Allinger, *J. Comp. Chem.*, **10**, 635 (1989).
8. K. B. Lipkowitz and N. L. Allinger, *QCPE Bulletin*, **7**, 19 (1987).
9. The MM3 program is available from the Technical Utilization Corporation, Inc., 235 Glen Village Court, Powell, Ohio 43065, and from Molecular Design Limited, 2132 Farallon Drive, San Leandro, California 94577. a. N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8551 (1989). b. J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, **111**, 8566 (1989). c. J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, **111**, 8576 (1989).
10. T. Liljefors, J. C. Tai, S. Li, and N. L. Allinger, *J. Comp. Chem.*, **8**, 1051 (1987).
11. a. N. L. Allinger and J.-H. Lii, *J. Comp. Chem.*, **8**, 1146 (1987). b. I. Pettersson and T. Liljefors, *J. Comp. Chem.*, **8**, 1139 (1987).
12. N. L. Allinger, F. Li, and L. Yan, (accompanying article on alkenes).
13. a. N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theoretica Chim. Acta*, **8**, 101 (1967). b. R. D. Brown and N. L. Heffernan, *Australian J. Chem.*, **12**, 319 (1959).
14. D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027 (1968).
15. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, 1969.
16. There are available standard methods for the calculation of induced dipole moments in molecules which do not contain conjugation, and those methods could be extended to the conjugated case. This extension is somewhat complicated, and has not yet been made. See a. L. Dosen-Micovic, D. Jeremic, and N. L. Allinger, *J. Am. Chem. Soc.*, **105**, 1716 (1983); b. L. Dosen-Micovic, D. Jeremic, and N. L. Allinger, *J. Am. Chem. Soc.*, **105**, 1723 (1983).
17. We are indebted to Dr. Dale Spangler for suggesting this method to us, and to Dr. Ahammadunny Pathiaseril for programming this procedure.
18. a. W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966). b. K. Kveseth, R. Seip, and D. A. Kohl, *Acta. Chem. Scand. A*, **34**, 31 (1980).
19. J. J. Fisher and J. Michl, *J. Am. Chem. Soc.*, **109**, 1056 (1987).
20. P. W. Mui and E. Grunwald, *J. Am. Chem. Soc.*, **104**, 6562 (1982).
21. S. Skaarup, J. E. Boggs, and P. N. Skancke, *Tetrahedron*, **32**, 1179 (1976).
22. J. Breulet, T. J. Lee, and H. F. Schaefer, *J. Am. Chem. Soc.*, **106**, 6250-6253 (1984).
23. a. C. W. Bock, P. George, M. Trachtman, and M. Zanger, *J. Chem. Soc., Perkin Trans.*, **2**, 26 (1979). b. C. W. Bock, Y. N. Panchenko, S. V. Krasnoshchiokov and V. I. Pupyshchev, *J. Mol. Struct.*, **129**, 57 (1985). c. C. W. Bock and Y. N. Panchenko, *J. Mol. Struct.*, **187**, 69 (1989).

24. J. E. Rice, B. Liu, T. J. Lee, and C. M. Rohlifing, *Chem. Phys. Lett.*, **161**, 277 (1989).
25. I. L. Alberts and H. F. Schaefer III, *Chem. Phys. Lett.*, **161**, 375 (1989).
26. L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975).
27. M. Traetteberg, G. Paulen, S. J. Cyvin, Y. N. Panchenko and V. I. Mochalov, *J. Mol. Struct.*, **116**, 141 (1984).
28. D. A. C. Compton, W. O. George, and W. F. Maddams, *J. Chem. Soc., Perkin Trans. 2*, 1666, (1976).
29. Y. N. Panchenko, V. I. Pupyshev, A. V. Abramnikov, M. Traetteberg, and S. J. Cyvin, *J. Mol. Struct.*, **130**, 355 (1985).
30. C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968).
31. M. E. Squillacote, T. C. Semple, and P. W. Mui, *J. Am. Chem. Soc.*, **107**, 6842 (1985).
32. A. Yokozeki, C. F. Wilcox, Jr., and S. H. Bauer, *J. Am. Chem. Soc.*, **96**, 1026 (1974).
33. J. K. Fawcett and J. Trotter, *Acta. Cryst.* **20**, 87 (1966).
34. C. Kabuto and M. Oda, *Tetrahedral Letters*, **21**, 103 (1980).
35. B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *J. Am. Chem. Soc.*, **93**, 7275 (1971).
36. K. Hagen and M. Traetteberg, *Acta. Chem. Scand.*, **26**, 3643 (1972).
37. S. S. Butcher, *J. Chem. Phys.*, **42**, 1833 (1965).
38. M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).
39. J. B. Lambert, L. J. Durham, P. Lepoutere, and J. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).
40. D. Dobler and J. D. Dunitz, *Helv. Chim. Acta.*, **48**, 1429 (1965).
41. J. Bregman, F. L. Hirshreld, D. Rabinovich, and G. M. J. Schmidt, *Acta. Cryst.*, **19**, 227 (1965).
42. H. Baumann, *J. Am. Chem. Soc.*, **100**, 7196 (1978).
43. A. Almenningen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin, and S. Samdal, *J. Mol. Struct.*, **128**, 59 (1985).
44. G. P. Charbonneau and Y. Delugeard, *Acta Crystallogr.*, **B32**, 1420 (1976).
45. G. Häfelinger and C. Regelmann, *J. Comp. Chem.*, **6**, 368 (1985).
46. N. L. Allinger and H. L. Flanagan, *J. Comp. Chem.*, **4**, 399 (1983).
47. A. Bree and M. Edelson, *Chem. Phys. Lett.*, **55**, 319 (1978).
48. R. N. Armstrong, H. L. Ammon and J. N. Darnow, *J. Am. Chem. Soc.*, **109**, 2077 (1987).
49. J. C. Hanson and C. E. Nordman, *Acta. Cryst.*, **B32**, 1147 (1976).
50. H. A. Staab, F. Diederich, C. Krieger, and D. Schweitzer, *Chem. Ber.*, **116**, 3504 (1983).
51. P. M. Lahti, *J. Org. Chem.*, **53**, 4590 (1988).
52. H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Cryst.*, **B28**, 1733 (1972).
53. J. Bernstein and K. N. Trueblood, *Acta Cryst.*, **B27**, 2078 (1971).
54. D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, **92**, 1073 (1970).
55. C. J. Brown, *J. Chem. Soc.*, (B), 3278 (1953).
56. P. K. Gantzel and K. N. Trueblood, *Acta. Crystallogr.*, **18**, 958 (1965).
57. F. A. L. Anet and M. A. Brown, *J. Am. Chem. Soc.*, **91**, 2389 (1969).
58. M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900). *Ber. Dtsch. Chem. Ges.*, **33**, 3150 (1900).
59. P. Jacobson, *Ber. Dtsch. Chem. Ges.*, **38**, 196 (1905); H. Lankamp, W. Th. Nauta and C. Maclean, *Tetrahedron Lett.*, 249 (1968).
60. E. Osawa, Y. Onuki, and K. Mislow, *J. Am. Chem. Soc.*, **103**, 7475 (1981).
61. M. Stein, W. Winter, and A. Rieker, *Angew. Chem. Int. Ed. Engl.*, **17**, 692 (1978).
62. B. Kahr, D. V. Engen, and K. Mislow, *J. Am. Chem. Soc.*, **108**, 8305 (1986).
63. N. Yanoni, B. Kahr, and K. Mislow, *J. Am. Chem. Soc.*, **110**, 6670 (1988).
64. G. Varsanyi and S. Szoke, *Vibrational Spectra of Benzene Derivatives* Academic Press, 1969, pp. 68–71.
65. C. W. Bock, Y. N. Panchenko, S. V. Krasnoshchiokiv, and V. I. Pupyshev, *J. Mol. Struct.*, **129**, 57 (1985).
66. Y. Furukawa, H. Takeuchi, I. Harada, and M. Tasumi, *Bull. Chem. Soc. Jpn.*, **56**, 391 (1983).
67. P. W. Mui and E. Grunwald, *J. Am. Chem. Soc.*, **104**, 6562–6566 (1982).