

Molecular Mechanics. The MM3 Force Field for Alkenes

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The MM3 force field has been extended to include alkenes. Forty-five compounds were examined, and structures, conformational equilibria, heats of formation, and rotational barriers, were calculated. For a smaller representative group, the vibrational spectra and entropies were also calculated. In general, these quantities, except for the vibrational spectra, agree with available data to approximately within experimental error. The vibrational frequencies for a set of eight well-assigned structures were calculated to a root-mean-square error of 47 cm^{-1} .

INTRODUCTION

Molecular mechanics has developed from a rather rudimentary tool 20 years ago into a powerful and practical predictive method today.^{1,2} Earlier there were fairly good force fields available for carrying out calculations on alkenes, and these included MM2,^{2,3} and the Ermer force field.⁴ More recently, the MM3 force field for alkanes has been developed, and it is of greater accuracy and generality than previously existing force fields for saturated hydrocarbons.^{5,6} This work is concerned with extending this MM3 force field to cover alkenes, and in the following article, we have further extended MM3 to cover conjugated hydrocarbons.

As with MM2, we felt the most important things to fit were structure and energy. Under the term "energy," we mean both conformational energies, and also heats of formation. As previously described,⁵ MM3 is of higher accuracy than MM2 for compounds which are highly strained, and we anticipate that that will also be true here.

The changes made in the MM3 alkane force field, relative to MM2 were carried over here. Namely, the torsion-stretch interaction, and the bend-bend interaction were included in the present work. Also, the stretching and bending functions for bonds and angles were carried as far as the fourth and sixth powers, respectively. Van der Waals' potentials were modified somewhat from the MM2 values, so as to permit better crystal packing in hydrocarbons. Finally, vibrational spectra, which we could not fit at all well with MM2, were examined with MM3. With the relatively few cross terms employed, we found that the spectra could be fit fairly well, although not as well as can be done if a larger set of cross

terms were to be employed. Our average overall rms error over eight compounds was 47 cm^{-1} .

An additional difference in MM3 relative to MM2 is the polarity of the C—H bond. Our initial assumption with MM2 was to take all C—H bonds to be nonpolar, unless we subsequently found reason to do otherwise. We have subsequently found no reason to make the C—H bond of an alkane polar, but the C—H bond of an alkene does have to contain a bond dipole in order to fit some of the data which we are now aware of. In part, this has been discussed earlier.⁷ The value for the bond dipole adopted for olefinic C—H was 0.6 D, which is an almost minimal value that leads to the correct packing of the benzene crystal in our model, and, is in agreement with experimental estimates.⁷

We assumed that the van der Waals' parameters for hydrogen are the same when the hydrogen is attached to an olefinic carbon as when it is attached to an alkane carbon. As far as we know, this approximation is adequate. However, we chose a different set of van der Waals' parameters for the olefinic carbon from those which we used for the alkane carbon. They are not very different, but they are certainly not identical. The alkene carbon parameters were chosen by fitting the structure and compressibility of graphite,⁷ and once the van der Waals' function is chosen, the graphite data give unique values for these parameters. These parameters were then modified slightly, so as to improve the fit for crystal packing data for aromatic hydrocarbons.

The problem at this point becomes one of optimizing a great many parameters so as to try to obtain the best force field possible, for fitting all of the available data. Of course, real experimental data contain various errors, for a wide vari-

ety of reasons, and some of the data seem more important than others. It is consequently quite a subjective matter to decide exactly how to optimize this fit. Our guiding principle was to fit both structure and energy as well as possible, and let vibrational frequencies, entropy, and other properties play a secondary role. The general accuracy of the alkane force field is believed to be approximately .005 Å in bond length, 1° in bond angle between non-hydrogen atoms, and 4° in torsion angles in almost all cases. The energies as heats of formation are almost always good to about 0.7 kcal/mol, and conformational energies are generally somewhat better than this. With saturated hydrocarbons, the calculated vibrational frequencies were accurate to an rms value of about 35 cm⁻¹. Since these are limiting values imposed by the alkane part of the force field, we would hope that the alkene fits could be approximately as good, but we cannot expect them to be any better. As previously, our standards to fit were r_g values for bond length and r_{α_0} values for bond angles and torsion angles. When experimental data were available for these quantities which were otherwise determined, for example from microwave or X-ray data, the corrections to transform them to the above basis were in general too difficult to make to be worthwhile. Accordingly, most data from those sources are uncorrected, and we therefore, anticipate that our bond lengths will be longer than the experimental ones, by small or large amounts depending on the nature of the experimental data. The other numbers may be compared directly. In a few cases, we have made corrections to the experimental data where we had sufficient information, and it seemed important to do so. Additionally, we have in a few cases examined the effects of crystal packing forces in distorting the structure when we had to compare with molecules in the solid phase. This latter problem will be discussed separately elsewhere.

We began first with the simple alkenes, for which there are in general good structural data and accurate heats of formation. We tried to examine incidental properties such as rotational barriers, conformational equilibria, dipole moments, and a few other things as we went along. Our general procedure for parameterization of MM3 was to use the MM2 force field parameters (other than ones already evaluated, such as van der Waals' parameters), as an initial approximation, and then adjust the various parameters in systematic ways to fit the available data insofar as possible. In some cases least squares methods were used, but for much of the work, these were not of any help. The problem is that least squares methods are designed to work

on homogenous data sets, not on data sets which contain a large number of different kinds of physical quantities, whose interrelationships are complicated, and whose levels of accuracy and relative importance are also complex.

In general, after an initial reasonable fit was obtained to a wide variety of compounds, the force constants were adjusted, and the vibrational spectra were fit. When these were approximately satisfactory, further adjustments were made in the structure and energy parameters, and this process was continued until it was felt that further significant improvements were not possible. The force field arrived at is presented in Table I.

This article is concerned only with alkenes, or unsaturated hydrocarbons which contain non-conjugated double bonds. Conjugated hydrocarbons are discussed in the following paper.⁸

RESULTS

Since the nature and the amount of data, and the accuracy and importance of the data are quite variable from one compound to the next, the results will be presented on a compound by compound basis. When the numbering system used for a molecule is not specified, it is the system used for nomenclature. The MM3 calculations may be compared directly to electron diffraction structures, as long as these have been corrected for shrinkage.⁹ For microwave structures, the bond lengths determined (r_s , r_z , or r_o) are usually shorter by .002–.010 Å than the MM3 values (r_g). More important is the fit to the moments of inertia. These should usually be 0–1% larger on an r_g basis than from the microwave spectra. For *ab initio* structures determined with a 6-31G* basis, C=C bonds are much too short (because of the neglect of correlation), C—H bonds are quite a bit too short (because of anharmonicity, as they are r_e values) and other parameters appear to be directly comparable. For X-ray structures, C—H bond lengths are too inaccurate to be of use. Other bond lengths, if the structure was determined at liquid nitrogen temperatures, may be corrected approximately by $r_x + .003$ Å = r_g . If the determination was at room temperature, an additional correction for thermal motion is required. This correction must be determined on a bond by bond basis, and usually has a value of about .005–.015 Å, in the direction that the X-ray value is too small.

Ethylene

The structures, calculated by MM3 and determined experimentally are given in Table IIa.

Propene

This molecule has been investigated by microwave spectroscopy with particular attention paid to internal rotation, and a complete r_g structure has been determined.¹¹ Propene has six C—H dis-

tances (belonging to the methyl and vinyl groups), among which only two are equivalent. They cannot be differentiated by electron diffraction alone, and require the use of the rotational constants to help with the hydrogen positions.¹² The torsional barrier is 1.74 kcal/mol (MM3), 1.95 kcal/mol

Table I. MM3 parameter set for alkenes (kcal/mol, Å, °)^a

Torsional parameters (*for four- and five-membered ring)				V ₁	V ₂	V ₃		
Angle								
1	1	1	2	0.20	-0.20	1.30		
1	1	2	1	0.10	0.20	0.80		
1	1	2	2	-0.70	-0.20	-0.55		
2	1	1	2	1.10	0.00	1.50		
2	1	2	2	0.25	-0.65	0.60		
1	2	2	1	-0.30	9.50	0.00		
1	2	2	5	0.00	10.00	0.00		
1	1	2	1	-0.10	0.03	1.35	*5	
1	1	2	2	-0.90	-0.90	0.30	*5	
1	2	2	1	0.55	10.00	0.00	*5	
2	1	2	2	0.25	-0.40	-0.50	*5	
1	57	56	5	0.80	0.00	0.54		
1	57	56	56	0.06	0.03	1.25		
1	57	57	5	0.00	10.00	0.00		
1	57	57	56	-0.30	10.00	0.00		
2	57	56	5	0.00	0.00	-0.09		
2	57	56	56	-0.80	-0.10	-0.55		
5	1	57	56	0.00	0.00	0.54		
5	1	57	57	0.00	0.00	-0.09		
5	2	57	56	0.00	10.00	0.00		
5	56	56	57	0.00	0.00	0.42		
5	56	57	56	0.00	0.00	0.45		
5	56	57	57	0.00	0.00	-0.09		
5	57	56	56	0.00	0.00	0.01		
5	57	56	57	0.00	0.00	0.80		
5	57	57	5	0.00	11.50	0.00		
5	57	57	56	0.00	10.00	0.00		
57	56	56	57	0.00	0.00	2.37		
57	57	56	57	0.00	-0.40	0.50		
57	56	56	57	0.00	0.00	0.20	*4	
56	57	57	56	-0.48	8.00	0.00	*4	
57	56	56	56	0.00	0.00	1.90	*4	
56	57	56	56	0.00	0.00	1.90	*4	
56	56	57	57	0.00	0.00	-0.70	*4	
Stretching parameters				Lo	Sslope	Tslope	Tlquad4	
Bond type								
2	2	7.50	1.332	2.820	0.170			
1	2	6.30	1.512					*5
1	57	6.30	1.499					
2	57	7.50	1.333	2.820	0.174			
5	57	5.15	1.101					
56	57	6.30	1.519					*4
57	57	7.50	1.338	2.840	0.390	0.152		*4
Torsion-stretch parameter				KTS				
Atom type								
1	2		0.27					
Dipole parameters				Moment				
Bond type								
1	2		0.90					
1	2		0.75	*5				
1	57		0.90					
5	57		0.60					
56	57		0.60	*4				

Table I. Continued

Bending parameters Angle			K_b	Type 1	Type 2	Type 3	
1	1	2	0.54		109.80	110.60	
1	2	1	0.54	117.0			
1	2	2	0.47	122.30			
2	1	2	0.45		115.50	113.00	
2	1	5	0.55			110.40	
1	1	2	0.54		110.20		*5
2	1	2	0.54			114.50	*5
1	57	56	0.54	115.20			
1	57	57	0.47	122.30			
2	57	56	0.76	127.80			
5	1	57	0.49	109.50	109.31	110.40	
5	2	57	0.49	120.00	120.50		
5	56	57	0.49	110.00	109.81	110.90	
5	57	56	0.49	117.50			
5	57	57	0.49	120.00	120.50		
57	56	57	0.54	113.20	108.00	113.00	
56	56	57	0.23	114.00			*4
56	57	56	0.14	115.20			*4
56	57	57	0.14	124.00	123.00		*4
0	2	2	0.20				
0	2	57	0.20				
0	57	1	0.11				
0	57	2	0.20				
0	57	5	0.11				
0	57	57	0.20				
Van der Waals' parameters ^b							
Atom Type			ϵ	R			
2			0.056	1.960			

^aAtom 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. For parameters that are not listed in this table, see reference 5a.

^bIn the van der Waals' calculations, the hydrogen atoms are relocated so that the attached hydrogen distance is reduced by 0.923. The energy parameter of van der Waals' interaction is calculated by equation: $\epsilon = \sqrt{\epsilon_1 \epsilon_2}$, in which ϵ_1, ϵ_2 are the VDW's parameters of the two atoms involved. Exceptions (for hydrocarbons) are for the interactions involving hydrogen or deuterium with sp^3 carbon, which have special parameters (reference 5a).

Table IIa. Ethylene ($\text{\AA}/^\circ$)

	MM3	Exp. ^a
C=C	1.337	1.337
C—H	1.102	1.103
C=C—H	120.9	121.4 (6)

^aReference 10, ED, r_g bond lengths.

(exp.¹³), with the C_2-C_3 bond being calculated longer in the eclipsed form by 0.0113 \AA . The experimental and calculated structures are given in Table IIb. The moments of inertia of propene (and the following compounds) are listed in Table III.

1-Butene

This molecule consists of *cis* and *gauche* conformations, of which the latter predominates. A number of experimental studies have shown that C—C bond lengths adjacent to double bonds are

Table IIb. Propene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.339	1.342 (2)
C—C	2-3	1.504	1.506 (3)
C—H vinyl	1-4	1.102	1.104 (10)
C—H methyl	3-9	1.113	1.117 (8)
C=C—C	1-2-3	124.3	124.3 (8)
C=C—H	2-1-5	120.8	121.3 (14)
C=C—C—H	1-2-3-9	0.2	—
C—C av. ^b		1.421	1.424

^aReferences 11–13, ED, r_g bond lengths.

^bAverage bond length (C—C, C=C).

shorter than normal single bonds.¹⁴ In fact, this is true for propene and *gauche*-1-butene. However, the calculated $C_{sp^2}-C_{sp^3}$ bond length is shorter by 0.002 \AA in propene, and longer by 0.004 \AA in *gauche*-1-butene than the values determined experimentally. The parameters for $C_{sp^2}-C_{sp^3}$ have been adjusted to average out the errors (Tables IV and V).

Table III. Moments of inertia (AU).

Compound	MM3			EXP.		
	I_a	I_b	I_c	I_a	I_b	I_c
Propene	11.168	54.589	62.503	10.970	54.327	62.149 ³⁵
gauche-1-Butene	23.648	121.122	123.221	22.411	121.630	124.631 ²
cis-1-Butene	33.165	92.302	118.992	33.036	90.679	117.479 ²
cis-2-Butene	31.611	99.734	124.855	31.412	98.222	123.605 ⁵⁰
Isobutene ^a	58.644	62.816	114.953	58.151	62.298	114.304 ³⁶
Cyclobutene	39.226	41.599	73.897	39.210	41.348	74.166 ⁴²
Cyclopentene	69.674	70.645	128.384	69.272	69.917	127.932 ⁷
Cyclohexene	107.446	111.532	197.933	106.639	111.209	197.227 ⁶⁴
Norbornene	128.838	147.452	169.654	128.789	147.239	167.626 ⁴⁶

^aThe moments of inertia of isobutene were calculated and determined for (CH₃)₂C=CHD.

Table IV. *gauche*-1-Butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.339	1.340 (4)
C—C	2-3	1.506	1.502 (2)
	3-4	1.534	1.535
C—H	2-7	1.104	—
	4-10	1.113	1.114 (3)
C=C—C	1-2-3	124.4	125.6 (3)
C—C—C	2-3-4	111.9	111.7 (3)
C=C—H	1-2-7	119.1	122.6 (9)
C—C—H	3-4-10	111.4	111.5 (3)
C=C—C—C	1-2-3-4	114.5	119.9
Bond av. ^b		1.460	1.458

^aReferences 15, 16, ED, r_g bond lengths.

^bAveraged over *cis/gauche* using MM3 structures.

Energy Diff. (kcal/m)	MM3	Exp.
$\Delta E(\text{cis-gauche})$	0.69	0.53 (± 0.42)
$\Delta E(\text{trans-gauche})$	2.11	1.73

Table V. *cis*-1-Butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.340	1.340 (4)
C—C	2-3	1.507	1.502
	3-4	1.534	1.526
C—H	1-5	1.103	1.104
	4-10	1.113	1.104
C=C—C	1-2-3	126.6	127.2 (3)
C—C—C	2-3-4	116.0	114.9 (3)
$R(C_1, C_4)$	1...4	2.993	2.962
C—C _{av}		1.460	1.456

^aReferences 15, ED, r_g bond lengths.

cis- and *trans*-2-Butene

cis-2-Butene has been determined to be 1.0 kcal/mol higher in energy than *trans*-2-butene by heats of combustion.⁸ The *cis* isomer is structurally more interesting. In 1972, an MM1 calculation on *cis*-2-butene indicated that the methyl groups are twisted (about 8.0°) away from planarity,

and that the symmetry of the *cis* isomer was C_2 , instead of C_{2v} . The twist angle was calculated to be 0.2° by MM2. However, from a microwave analysis,¹⁷ C_{2v} symmetry was definitely deduced, which conflicted with C_2 symmetry concluded by MM1 and the electron diffraction analysis mentioned above. The angle of C=C—C is 125.4° by ED, 126.7° by MW, and 127.4° by MM3. The repulsion between the inner methyl hydrogens will open the bond angles to allow a minimum energy conformation of strict C_{2v} symmetry, but could also twist the methyls to give a C_2 conformation. From the structure of the *cis* conformer calculated by MM3 (Table VI), it is seen that the inner H...H repulsion causes an opening of the C=C—C angle (127.4°). But twisting of the double bond or the methyl groups in *cis*-2-butene is not an effective mechanism for increasing the short inner H...H distance, since the hydrogens are moved perpendicular to the line connecting them. Angle opening moves the two hydrogens essentially along the connecting line and is much more effective. In other words, a relatively small adjustment of angles has the same effect as comparatively large changes of torsion angles, so that angle bending is preferred to torsional deformations despite the higher force constants involved.

Table VI. *cis*-2-Butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.342	1.346 (3)
C—C	1-2	1.505	1.506
C—C=C	1-2-3	127.4	125.4 (4)
C—C—H	2-1-10	113.3	—
	2-1-11	110.7	110.5 (54)
C_1/C_4		3.170	3.091
H_7/H_{10}		2.088	2.0866
C=C—C—H	2-3-4-7	1.0	4.9 (20)
	3-2-1-10	0.6	—
C—C=C—C	1-2-3-4	0.0	—
Bond Av.		1.451	1.453

^aReferences 13, 18, ED, r_a bond lengths.

Table VII. *trans*-2-Butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.341	1.347 (3)
C—C	1-2	1.504	1.508 (2)
C—H	2-H	1.104	—
	1-H	1.112	—
C—C=C	1-2-3	124.3	123.8 (4)
C—C—H ₁₀		112.2	—
C—C=C—C	1-2-3-4	179.9	—
C=C—C—H	3-2-10	0.5	—
Bond Av.		1.450	1.454

^aReferences 13, 18, ED, r_a bond lengths.

The increased energy of *cis*-2-butene as compared with the *trans* isomer is mainly due to the higher angle strain of the former. The non-bonded energy (van der Waals) of the *cis* isomer is 0.45 kcal/mol above that of *trans*-2-butene.

Isobutene

Two methyl hydrogen atoms in isobutene are in the plane of the four carbon atoms, and the in-plane C—H bonds point away from the symmetry axis.

2-Pentenenes

Since the electron diffraction values for the C—C bond lengths in *cis*-2-pentene are different from the MM3 values by more than expected, and the various C—C bonds are not resolved experimentally, we feel that the experimental values contain systematic errors. The average C—C bond length has been calculated for both the experimental and MM3 structures. If the difference between r_g (MM3) and r_a (exp.) is allowed for by adding .002 Å to the latter, the agreement is very good. Thus we conclude that the experimental value for the 4-5 bond is too long and the others are too short. The MM3 values will certainly be more correct in this case. The data are given in Tables IX and X for the *cis* and *trans* isomers, respectively. Similar bond length considerations apply to the *trans* isomer.

Table VIII. Isobutene(Å/°).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.342	1.342 (2)
C—C	1-2	1.507	1.508 (2)
C—H	3-11	1.102	1.095 (2)
	1-8	1.112	1.119 (7)
C=C—C	1-2-3	122.2	122.2 (2)
C=C—H	2-3-11	121.1	121.3 (15)
C=C—C—H	3-2-4-5	0.4	—
	3-2-4-7	120.5	—
	3-2-4-6	-119.8	—
Bond Av.		1.452	1.453

^aReferences 13, 19, 20, ED, r_g bond lengths.**Table IX.** *cis*-2-Pentene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.342	1.338 (2)
C—C	1-2	1.505	1.490 (1)
	3-4	1.508	1.490 (1)
	4-5	1.534	1.561 (2)
C—C=C	1-2-3	127.3	127.4 (2)
	2-3-4	127.2	127.4 (2)
C—C—C	3-4-5	111.7	112.4 (4)
C—C=C—C	1-2-3-4	0.3	—
C=C—C—C	2-3-4-5	106.2	—
H—C=C—H		1.2	—
Bond av.		1.472(r_g)	1.470(r_a)

^aReferences 21, ED, r_a bond lengths.**Table X.** *trans*-2-Pentene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.341	1.334 (2)
C—C	1-2	1.504	1.484 (1)
	3-4	1.507	1.484 (1)
	4-5	1.534	1.576 (5)
C—C=C	2-3-4	124.4	125.4
	1-2-3	124.2	—
C—C=C—C	1-2-3-4	179.6	—
C=C—C—C	2-3-4-5	114.7	—
H—C=C—H		179.8	—
Bond Av.		1.473	1.470

^aReference 22, ED, r_a bond lengths.

2,3-Dimethyl-2-butene

Steric effects lead to conspicuous bond stretching here relative to propene, both in the C=C bond (from 1.339 to 1.353), and in the C—C bonds (1.504 to 1.512), and the experimental values are in agreement with this. The molecule is slightly non-planar (D_2 symmetry), with C—C=C—C 4.6°, and C=C—C—H 17.1°.

Cyclopentene

The conformation of cyclopentene is C_s with the symmetry plane perpendicular to the double bond and containing the I_a axis. Hence, the C—C=C—C torsion angle is zero. From far infrared,²⁴ microwave,²⁵ and electron diffraction²⁶ experi-

Table XI. 2,3-Dimethyl-2-butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C		1.353	1.355 (4)
C—C		1.513	1.511 (2)
C—H		1.113	1.118 (4)
C—C=C		123.8	123.9 (5)
H—C—H	(11-1-12)	107.5	107.0 (10)
	(10-1-12)	106.2	—
	(10-1-11)	107.7	—
C—C _{av}		1.480	1.479

^aReferences 13, 23, ED, r_g bond lengths.

Table XII. Cyclopentene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.340	1.343 (10)
C—C	2-3	1.519	1.519
	3-4	1.551	1.546
C—C=C	1-2-3	111.9	111.0
C—C—C	2-3-4	102.2	103.0
	3-4-5	105.7	104.0
C—C=C—C	3-2-1-5	0.0	—
C—C _{av}		1.496	1.495

^aReferences 24–27, ED, r_a bond lengths.

ments, ring puckering angles of $23.3^\circ \pm 1$, $22.3^\circ \pm 2$, and $29.0^\circ \pm 2.5$ were derived, respectively. The value of 25.4° calculated by MM3 is in agreement with these. The angle calculated by MM2 was 19° . The energy difference between the envelope and planar conformations was deduced by Lord²⁴ to be $232 \pm 5 \text{ cm}^{-1}$ (or 0.66 kcal/mol). The value 0.41 kcal/mol was obtained by MM2, and the calculated value by MM3 for this barrier is 0.68 kcal/mol.

Cyclohexene

It is known that the boat isomer is the transition state in the pseudo-rotation from one chair form to another.²⁸ The study of Bucourt²⁹ concluded that the boat is $7.52 (\pm 0.67)$ kcal/mol less stable than the chair, and that they are not separated by an energy barrier. The low temperature NMR study of Anet³⁰ found a value of 5.3 kcal/mol (ΔG^\ddagger) for the energy difference between the boat and chair. The barrier of 6.6 kcal/mol is calculated by MM3 (one negative eigenvalue from the force constant matrix for the boat).

The energy difference between the *cis*-chair and *trans*-cyclohexene is calculated to be 35.23 kcal/mol (33.03 kcal/mol from MM2), and has not yet been determined experimentally. However, the energy difference between the *cis*- and *trans*-1-phenylcyclohexene has been determined to be 44.7 kcal/mol.³¹ As one twists the double bond, one destroys the bonding character, and the system becomes more like two isolated free radicals. If we put a phenyl on one of those carbons, the phenyl will conjugate with and stabilize one of the radicals, while nothing happens to the other one. Therefore, if we compare *trans*-cyclohexene with the alpha phenyl derivative, the phenyl should make the diradical more stable than it was otherwise. This would cause the difference in energy between *cis* and *trans* to decrease. However, the phenyl group might have some special effects on the energy difference which are not yet known.

Norbornene

The angle determined by electron diffraction between planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$ is

Table XIII. Cyclohexene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.342	1.341 (9)
C—C	2-3	1.508	1.503 (9)
	3-4	1.537	1.535 (9)
	4-5	1.533	1.535 (9)
C—C=C	1-2-3	123.3	124.0 (20)
C—C=C—C	3-2-1-6	0.8	—
C—C—C—C	3-4-5-6	62.8	—
Bond av.		1.494	1.492

^aReferences 28–32, ED, r_a bond lengths.

$110.8 \pm 1.5^\circ$, while that between $C_1C_2C_3C_4$ and $C_1C_7C_4$ is 122.3° . The MM3 values are 111.7° and 125.4° , respectively. The I_a and I_c axes lie in the symmetry plane, while I_b is perpendicular to it.

Norbornadiene

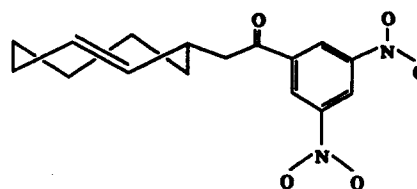
The dihedral angle between planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$ is calculated by MM3 to be 115.7° , and was determined by electron diffraction to be $115.6^\circ (\pm 2.2)$.

The heat of hydrogenation of the first double bond in norbornadiene has a MM3 calculated value of 35.78 kcal/mol and was determined to be 34.98 kcal/mol in acetic acid solution.³⁴ One expects the latter value to have been lowered about 1 kcal/mol in acetic acid solvent.

A few experimental studies have been done on the structure of norbornadiene, but inconsistent results have been obtained. The largest variation is the $C_1—C_7$ bond length which has the extreme values of $1.514 \text{ Å} (\pm 0.004)$ and $1.570 \text{ Å} (\pm 0.010)$ (reference 63). The calculated value of 1.549 Å is within the experimental range.

trans-Cyclooctene

An electron diffraction study was carried out on *trans*-cyclooctene,³⁶ and a neutron diffraction study was carried out at room temperature on the 2,4-dinitrobenzoate derivatives of 2-*trans*-cyclooctenol. The two structures are in fair agreement, and they are compared with the MM3 structure in Table XVI.



Thermal racemization of optically active (+ or -) *trans*-cyclooctene was studied experimentally.³⁷ The energy barrier between (+) and (-) cyclooctene was determined to be $\Delta E_a^\ddagger = 35.6 \text{ kcal/mol} (\pm 0.9)$, $\Delta H^\ddagger = 34.7 \text{ kcal/mol} (\pm 0.9)$, and $\Delta G^\ddagger = 34.9 \text{ kcal/mol} (\pm 0.02)$ at 155.3°C .

Table XIV. Norbornene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.343	1.336 (2)
C—C	3-4	1.534	1.529 (7)
	4-5	1.550	1.550 (20)
	5-6	1.569	1.556 (5)
	1-7	1.544	1.556 (5)
Bond av.		1.521	1.523
C—C—C	1-7-4	95.1	95.3
	1-2-3	107.7	—

^aReferences 33, ED, and MW, r_g bond lengths.**Table XV.** Norbornadiene ($\text{\AA}/^\circ$).

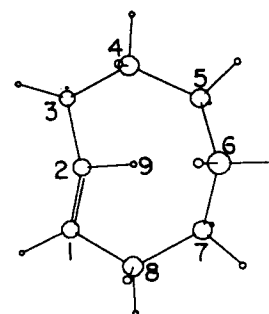
	Numbering	MM3	Exp. ^a
C=C	2-3	1.349	1.343 (3)
C—C	3-4	1.537	1.535 (7)
	1-7	1.549	1.570 (10)
C—H	7-H	1.1138	1.120 (10)
	2-H	1.098	—
C—C—C	1-7-4	94.3	94.0 (30)
C—C=C	1-2-3	107.4	—
H—C—H	14-7-15	108.9	113.0 (80)
C—C _{av}		1.493	1.496

^aReference 63, ED, r_g bond lengths.**Table XVI.** *trans*-Cyclooctene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a	
			(ED ³⁶)	(Neutron ³⁹)
C=C	1-2	1.340	1.332	1.341
	2-3	1.501	1.499	1.483
	3-4	1.545	1.549	1.543
	4-5	1.553	1.549	1.545
	5-6	1.566	1.549	—
C—C=C	1-2-3	118.8	121.9	121.1
C—C—C	2-3-4	107.2	104.6	105.3
	3-4-5	115.2	113.8	115.7
	4-5-6	116.8	118.8	118.5
	C—C=C—C	135.9	138.1(10)	138.1(2)
Torsion	H—C=C—H	173.2	—	177.2(50)
		1.513	1.509	1.498

^aReferences 36–39, ED, r_a (ED) and r_a (ND) (25°C).**Table XVII.** Transition state for racemization of *trans*-cyclooctene.

	Numbering	MM3 ($\text{\AA}/^\circ$)
C=C	1-2	1.318
	2-3	1.525
	3-4	1.583
	4-5	1.592
	5-6	1.596
	6-7	1.584
	7-8	1.570
C—C—C	3-4-5	122.1
	(C ₅ /H ₉)	1.825
	(C ₆ /H ₉)	1.926
Torsion	C—C=C—C	179.7
	H—C=C—H	177.4



The transition state (with one negative eigenvalue) for the racemization was found by MM3 to lie 37.7 kcal/mol above the ground state. Considering the temperature (155.3°C) at which the experiment was done, the calculated value is in reasonable agreement with that determined experimentally.

The energy difference between the *cis*- and *trans*-cyclooctene was determined to be 10.88 kcal/mol from heats of hydrogenation⁴⁰, and was calculated to be 10.82 kcal/mol by MM3.

gauche-2-Methyl-1-butene

Bond length averages (C—C, C=C) have been calculated again for the calculated and determined structures, and they agree fairly well. The agreement for the rest of the structure is from fair to good (Table XVIII).

Cyclobutene

The structure and moments of inertia of cyclobutene were obtained from a microwave study.²²

Table XVIII. gauche-2-Methyl-1-butene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.343	1.334
C—C	2-3	1.511	1.515
	3-4	1.534	1.535
	2-5	1.508	1.515
C—C=C	1-2-3	121.9	124.9
	1-2-5	121.7	—
C—C—C	2-3-4	113.2	113.0
Torsion	1-2-3-4	111.0	—
	4-3-2-5	68.4	72.7 (50)
C—C _{av}		1.474	1.475

^aReference 41, ED, r_a bond lengths.**Table XIX.** Cyclobutene (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-2	1.345	1.342 (4)
C—C	2-3	1.525	1.517 (3)
	3-4	1.563	1.566 (3)
C—C=C	1-2-3	94.1	94.2
C—C—C	1-4-3	85.9	85.8
C—C=C—C	3-2-1-4	0.0	—

^aReference 42, 43, MW, r_s bond lengths.**Methylenecyclobutane**

The angle between the planes defined by $C_2-C_1-C_4$ and $C_2-C_3-C_4$ was calculated to be 22.5, and determined to be 20.9° (25).

The energy barrier between the two nonplanar isomers (the structure above) was determined by

Table XX. Methylenecyclobutane (Å/°).

	Numbering	MM3	Exp. ^a
C=C	1-5	1.333	1.331 (3)
C—C	1-2	1.525	1.517 (5)
	2-3	1.561	1.565 (4)
C—C _{av}	—	1.501	1.499
C—C—C	2-1-4	89.0	89.25 (6)
	1-2-3	90.0	—
	2-3-4	86.4	—

^aReference 43, ED, r_a bond lengths.**Table XXI.** Dewar benzene (Å/°).^a

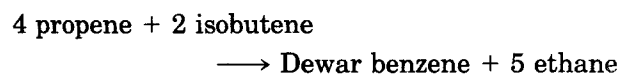
	Numbering	MM3	<i>ab initio</i> ⁴⁴	ED ⁴⁵
C=C	1-2	1.346	1.325	1.345
C—C	1-6	1.522	1.525	1.524
	3-6	1.578	1.553	1.574
Torsion	4-3-6-1	117.2	117.7	117.25(6)
C—C—H	3-6-12	117.0	121.6	108.0(30)
C=C—H	1-2-8	134.0	—	126.7(25)
Bond av.		1.480	1.471	1.480

^aReferences 44, 45, ED, r_g .

Raman spectra to be 0.38 kcal/mol,⁶⁵ and 0.36 kcal/mol by MM3.

Dewar Benzene

The torsion angle $C_4-C_3-C_6-C_1$ is the angle between the two four-membered rings in Dewar benzene, for which the same value has been derived by electron diffraction and by *ab initio* calculation. The angle calculated by MM3 is in fair agreement with that value. The bond lengths calculated by MM3 are in good agreement with those from ED. Usually *ab initio* calculations do not give values for bond lengths which are very close to r_g values, and this was found here. However, the *ab initio* calculation was carried out at the 6-31G* (SCF) level, and gives a value of 94.0 kcal/mol for the heat of formation. This value has been taken as the "experimental" heat of formation of Dewar benzene. The *ab initio* calculation of heats of formation from homodesmotic reactions⁴⁴ as used above requires heats of formation, zero-point energies, and enthalpy corrections for ethane, ethylene, propene, and isobutene. The homodesmotic reaction for Dewar benzene is

**Barrelene**

There are problems with the barrelene series of compounds in molecular mechanics, both with the heats of formation, and also with the structures. It may be seen from the data in Table XXII that the calculated double bonds are longer than the experimental values by 0.008 Å. In 1982, Kuchitsu and Ermer reported an investigation on molecules of this series by electron diffraction and force field calculations.⁴⁶ The same problems (the heats of hydrogenation of the double bonds, and their calculated double bonds were too long by 0.008 Å), occurred in their work as well. The average bond length (C—C, C=C) is 1.468 Å by MM3, and 1.473 Å by electron diffraction. The calculated structures of the other two members of barrelene series are in better agreement with those of electron diffraction.

Table XXII. Barrelene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.346	1.338 (2)
C—C	1-2	1.529	1.541 (1)
C—C—C	2-1-6	106.3	105.9 (2)
	1-2-3	112.5	112.9 (2)
C—H	2-10	1.100	1.105 (4)
C—C—H	1-2-10	122.6	125 (1)
C—C _{av}		1.468	1.473

^aReference 46, ED, r_g bond lengths.**Bicyclo[2.2.2]octadiene**

The calculated double bonds are longer than those determined experimentally by only 0.003 \AA , which is within experimental error. The C—C single bonds can be considered to be in good agreement with those determined by electron diffraction unless the huge uncertainty in the experiment (0.017 \AA) can be reduced. The torsion angle between the $C_1-C_2-C_3-C_4$ and $C_1-C_6-C_5-C_4$ planes was determined to be 123.4° (22), and calculated to be 125.0.

Bicyclo[2.2.2]octene

In contrast with the cases of barrelene and bicyclo[2.2.2]octadiene, the MM3 double bond of bicyclo[2.2.2]octene is shorter than that determined by only 0.002 \AA , which is much smaller than the experimental error (0.008 \AA). Again, the experimental standard deviations in the

bond lengths are large, so that it is difficult to judge how well the calculation agrees with the experiment.

Data for the barrelene series are summarized in Table XXV. The double bonds are all shorter from the *ab initio* calculation than the experimental values (from the omission of electron correlation), however, they show the same trends as the experimental values, which are opposite to the MM3 results. The differences are small, however. The double bonds in the triene are shorter than those in diene, which are shorter than those in monoene, according to experiment.

It may be noted that the average carbon-carbon bond length is correctly calculated for the monoene and for the diene. The triene, however, has an average bond length longer than calculated. This is consistent with a special orbital interaction in the triene, which raises the energy and causes the bonds to stretch in an effort to avoid one another in a way not allowed for by MM3.

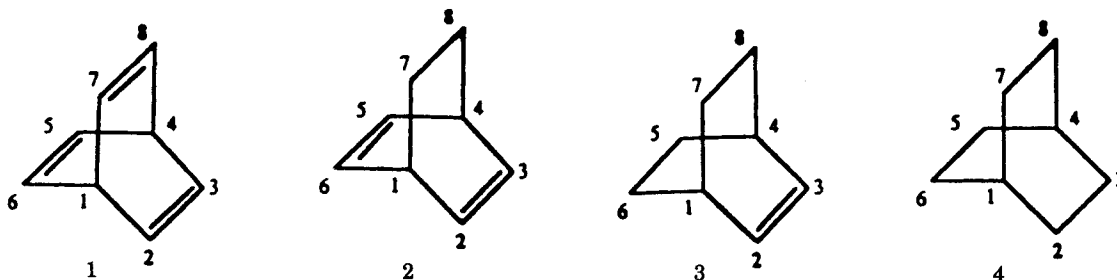
Table XXIII. Bicyclo[2.2.2]octadiene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.343	1.339 (5)
C—C	1-2	1.524	1.521 (8)
	1-7	1.548	1.553 (17)
	7-8	1.564	1.553 (17)
C—C=C	1-2-3	113.7	113.5 (5)
C—C—C	3-4-5	108.6	107.7
Bond av.		1.494	1.491

^aReferences 46, 47, ED, r_g bond lengths.**Table XXIV.** Bicyclo[2.2.2]octene ($\text{\AA}/^\circ$).

	Numbering	MM3	Exp. ^a
C=C	2-3	1.340	1.341 (8)
C—C	1-2	1.522	1.509 (15)
	5-6	1.556	1.549 (8)
	1-6	1.543	1.549 (8)
C—C=C	1-2-3	114.5	114.2 (6)
C—C—C	2-1-6	106.9	107.6
Bond av.		1.519	1.517

^aReferences 18, 47, ED, r_g bond lengths.

**Table XXV.** Selected geometric parameters for compounds 1–4.^a

Internal coordinate data source	Compound			
	4	3	2	1
C1—C2 (Å)				
ED	1.538 ^b	1.509 ^c	1.521 ^c	1.541 ^d
3-21G//3-21G ^e	1.541	1.514	1.523	1.543
C2—C3 (Å)				
ED	1.552 ^b	1.341 ^c	1.339 ^c	1.338 ^d
3-21G//3-21G ^e	1.561	1.319	1.317	1.313
C3—C2—C1 (degrees)				
ED	109.7 ^b	114.2 ^c	113.5 ^c	112.9 ^d
3-21G//3-21G ^e	109.7	114.6	114.0	113.2
C2—C1—C6 (degrees)				
ED		108.0 ^c	106.8 ^c	105.9 ^d
3-21G//3-21G ^e	109.2	108.0	108.6	105.4

^aHeats of formation were determined from single point calculations at the 6-31G* level.^bReference 59.^cReference 47.^dReference 46.^eReference 69.

1,4-Pentadiene

Several conformational studies of 1,4-pentadiene^{48–50} have shown it to have three stable isomers, which are formed by rotating about the two single C—C bonds. However, the energy differences between the isomers are not experimentally known. From the MM3 parameterization, the most stable isomer has C_2 symmetry.

1,4-Cyclohexadiene

The MM3 calculation, as well as MM2, agree that 1,4-cyclohexadiene has a planar D_{2h} structure as was proved by the experimental evidence. Dallinga and Toneman⁵¹ analyzed their electron diffraction results as strongly favoring the planar D_{2h} model. The nonplanar (C_{2v}) structure found by Oberhammer and Bauer⁵² seems to result from an

Table XXVI. 1,4-Pentadiene (C_2) (Å/°).

	Numbering	MM3	CNDO/2	Exp. ^a
C=C	1–2	1.339	1.342	1.336 (1)
C—C	2–3	1.505	1.493	1.501 (1)
C—H	3–6	1.114	—	1.074 (2)
C—C=C	1–2–3	124.4	125.4	125.0 (10)
C—C—C	2–3–4	112.8	112.1	113.0 (10)
C—C _{av}		1.422	1.418	1.419

^aReferences 48–50, ED, r_x bond lengths.**Table XXVII.** MM3 Conformations of 1,4-Pentadiene.

	$C_1—C_2—C_3—C_4$	$C_2—C_3—C_4—C_5$	E (kcal/mol)
C_2	114.7°	114.7°	0.00
C_s	113.6°	–113.1°	0.21
C_1	–19.5°	112.8°	1.40
C_{2v}	0.0	0.0	8.00 (transition state)

inadequate treatment of shrinkage. As support for the nonplanarity of their structure, they cite 9,10-dihydroanthracene derived from an X-ray crystal structure analysis. However, dihydroanthracene has more bending and van der Waals' interactions, which control the conformation. The difference between these two cases has been discussed by Burkert and Allinger.² The energy difference between the planar structure and the boat structure with dihedral angles C=C—C—C fixed at 25° is 2.64 kcal/mol by MM3. The MM2 result was 1.25 kcal/mol. Lord estimated⁵³ that this energy difference is about 2.5 kcal/mol.

Cycloheptene

It was reported in 1981⁵⁷ from experiment that the isomerization of *trans*- going to *cis*-cycloheptene has an activation enthalpy (ΔH_{270}^\ddagger) of 18.2 ± 1.2 kcal/mol.

Interconversion pathways between various forms (chair, boat, and twist) of *cis*-cycloheptene were studied many years ago⁵⁸ using MM1, and a few possible transition states between the conformers were proposed. However, since the full matrix method of geometry optimization by

which a transition state can be confirmed was not available in MM1, it was desirable to repeat the calculations on the conformational interconversions of cycloheptene with MM3. The full matrix method of MM3 was used to locate the transition state of the *trans*- going to the *cis*- isomer. It was found that the transition state (one negative eigenvalue for the force constant matrix) is higher in energy than the *trans* isomer by 9.6 kcal/mol. The C—C=C—C torsion angle in the transition state is 43.7°.

The *cis*- (chair form) is calculated to be 22.1 kcal/mol below *trans*-cycloheptene. The C—C=C—C torsion angle is 0.0° in the *cis*, and is 105.3° in the *trans*.

For the *cis* isomer, if the energy of the chair form is taken as zero, the boat and twist conformers have energies of 5.83 and 1.01 kcal/mol, respectively (Fig. 1). The transition states for paths A and B have been found by the full matrix method in MM3 (Fig. 2, Fig. 3), each has a single negative eigenvalue in the force constant matrix. The barriers (from the chair form) are 10.7 kcal/mol and 2.6 kcal/mol, respectively. These values are not experimentally known.

Table XXVIII. 1,4-Cyclohexadiene (Å/°).^a

	Numbering	MM3	Exp. Data	
			Ref. 51	Ref. 52
C=C	2-3	1.339	1.334(2)	1.347(4)
C—C	1-2	1.504	1.496(1)	1.511(4)
C—H	1-7	1.114	1.096(12)	1.114(3)
	2-9	1.104	1.079(10)	1.103(3)
C—C=C	2-3-4	122.7	122.7	123.4
C—C—C	2-1-6	114.6	113.3	111.9
C—C=C—C	2-3-4-5	0.2	0.0	20.7
	2-1-6-5	0.2	0.0	20.7
C—C average		1.449	1.442	1.456
C—C—C average		118.6	117.3	118.4

^aReferences 51–56, ED, r_a bond lengths.

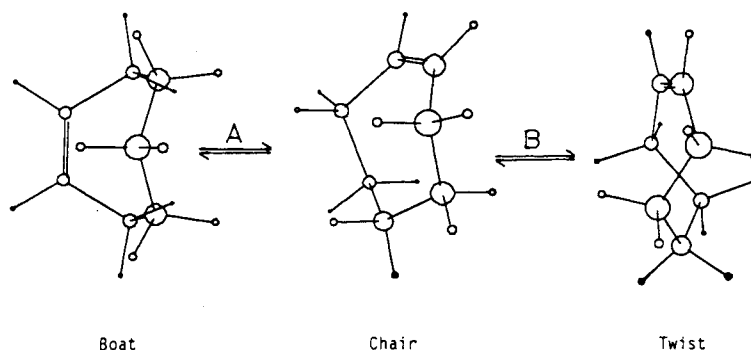


Figure 1. Conformational interconversion of cycloheptene.

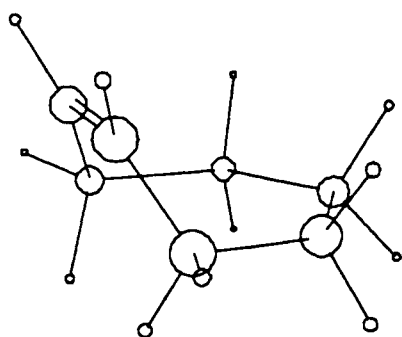


Figure 2. Cycloheptene (transition B).

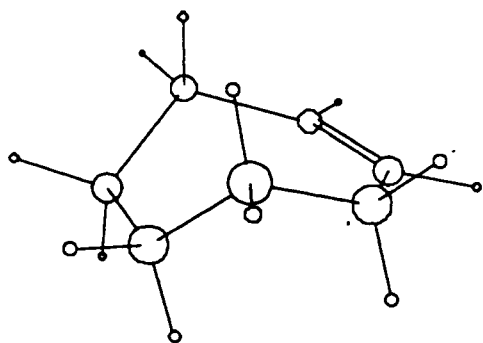


Figure 3. Cycloheptene (transition A).

ROTATIONAL BARRIERS IN ALKENES

The rotational barriers are determined by calculating energies as a function of torsion angle. The maximum energy along the minimum-energy path then corresponds to the transition state geometry, and its energy relative to the ground-state geometry is the rotational energy barrier.

Propene

The barrier to internal rotation of the methyl group in propene was first found to be 1.95 kcal/mol by a thermodynamic method in 1946.² A barrier height of 1.978 was determined by the microwave splitting technique in 1957.² The most recent value for the barrier height is 1.994 kcal/mol.² The calculated MM3 results are in Table XXIX.

It has been found by *ab initio* calculations (a 4-31G* basis with Gaussian 82), that the $C_{sp^2}-C_{sp^3}$ bond length is a function of the torsion angle ($H-C_{sp^2}-C_{sp^3}-H$). The $C_{sp^2}-C_{sp^3}$ bond is

Table XXIX. Internal rotation of propene.

Angle $H-C_{sp^2}-C_{sp^3}-H$	Energy	Bond Length $C_{sp^2}-C_{sp^3}$
0.0°	1.74 kcal/mol	1.515 Å
180.0°	0.00 kcal/mol	1.504 Å

longer by 0.011 Å (calculated by MM3), and 0.010 Å (calculated by *ab initio*), when one of the methyl hydrogens eclipses the $C_{sp^2}-H$ bond (torsion angle 0.0°) than when the methyl hydrogen eclipses the double bond in propene (the torsion angle equals 180.0°).

Isobutene

A barrier height of 1.99 kcal/mol was determined by the microwave splitting method in 1972.² In 1974, Kuchitsu concluded that the barrier should be around 1.5 kcal/mol.¹⁹ The ground state has the double bond eclipsed by methyl hydrogens of both methyl groups. The MM3 barrier is 1.64 kcal/mol, and the single bond stretches from 1.507 Å in the ground state to 1.519 Å in the transition state.

trans-2-Butene

The barrier in *trans*-2-butene has been reported to be 1.95 kcal/mol from a heat capacity study, and determined to be 1.53 kcal/mol by the IR and Raman spectrum of gaseous *trans*-2-butene.² In the present MM3 study, the barrier was found to be 1.72 kcal/mol.

cis-2-Butene

The barrier height of *cis*-2-butene has been determined to be 450 cal/mol from heat capacity data and to be 764 cal/mol from the microwave spectrum.² A value of 0.98 kcal/mol was found by MM3.

The methyl rotation barrier in *cis*-2-butene is lower by 0.73 kcal/mol from MM3, and by 1.5 kcal/mol from experiment,² than that in *trans*-2-butene. This can be explained as follows. The *cis* has a higher ground state energy than the *trans*-isomer because of the repulsion between the inner hydrogens. Even though the transition state energy of the methyl rotation for the *cis* is higher than that for the *trans*-isomer, the barrier for the *cis* is still relatively lower than that for the *trans*-isomer, due to the repulsion mentioned above.

2,3-Dimethyl-2-Butene (Tetramethylethylene)

A barrier of 680 cal/mol for the gas phase was determined.² In contrast with *cis*-2-butene, the MM3 value for 2,3-dimethyl-2-butene (580 cal/mol) is lower than the experimental value. The double bond is almost eclipsed by hydrogens of each methyl in the ground state.

2-Methyl-2-Butene (Trimethylethylene)

There are three different kinds of Me groups in the molecule, therefore, three non-equivalent torsional rotations should exist. The MM3 drive method has been applied to the three rotations separately. The results are as follows. The highest barrier is 1.53 kcal/mol for the geminal methyl in the *trans* position, 0.79 kcal for the *cis* non-geminal methyl, and 0.73 kcal/mol for the *cis* geminal methyl.

There has been no experimental determination of the heights of the rotational barriers for this molecule. Assuming a harmonic model, a barrier (did not mention which one) was calculated to be 2.4 kcal/mol.¹³

1-Butene

The rotational energy of 1-butene as a function of torsion angle is given in Table XXX.

The barrier between the two *gauche* conformers is calculated to be 2.11 kcal/mol. This barrier has been determined⁵⁹ to be 1.73 kcal/mol by a microwave study.

3-Methyl-1-butene (Isopropylethylene)

Durig and Gerson⁶⁰ have reported the torsional potential energy curve of 3-methyl-1-butene by studying the low frequency vibrational spectrum. The most stable conformer they found is the one with the hydrogen *cis* to the C=C bond. In the second stable conformer, one methyl group is *cis* to the C=C bond. This torsional potential was

Table XXX. Internal rotation of 1-butene (kcal/mol).

Degree (C ₁ —C ₂ —C ₃ —C ₄)	ΔE
180.0°	2.11
114.2°	0.000
50.8°	1.61
0.0°	0.69

Table XXXI. Internal rotation in 3-methyl-1-butene (kcal/mol).^a

C=C—C—H (deg.)	0	60 ^b	120 ^b	180
Exp. ^a	0	2.50	0.42	0.99
MM3	0	2.22	0.91	1.31
MM2	0	0.65	0.67	0.43

^aReference 60.

^bThese are nominal values. The exact MM3 values for the maximum and minimum (which correspond to the energies listed) are 74.0° and 129.5, respectively.

poorly calculated with MM2. The MM3 potential is summarized in Table XXXI.

Heats of Formation

These may be determined by means of a bond energy scheme as previously discussed.^{2,5} However, after studying hydrocarbons containing delocalized systems,⁸ we noted that there were small systematic differences between the simple alkenes and conjugated systems. We chose to have maximum generality in the program, at the expense of a little accuracy, and accordingly, the alkenes were taken together with the conjugated systems, and an overall parameter set for heats of formation was determined. One may, therefore, treat the isolated alkene with MM3 as a conjugated system, or as a nonconjugated system, and the same result will be obtained either way. The details of the heats of formation calculations will not be discussed here, but will be postponed to the paper on conjugated systems.⁸

Vibrational Spectra

As discussed in the alkane work, with the additional parameters, cross terms, and extended potential functions in MM3 relative to MM2, it was possible to calculate vibrational frequencies with an rms of about 35 cm⁻¹ for alkanes. The accuracy of the vibrational calculations could clearly be improved by the addition of more cross term parameters to the force constant matrix. The improvement in the calculated structures and other properties would, however, be negligible, so these refinements have not yet been carried out.

The parameters for alkanes have been used unchanged from the earlier work,⁵ so only parameters which involve carbon type 2 (alkene carbon) were developed in this work, and are included in Table I. With this parameter set, the vibrational frequencies for eight structures (ethylene, propene, 1-butene *gauche* and *anti*, 2-butene, *cis* and *trans*, isobutene, 1,4-cyclohexadiene) were calculated (by the harmonic approximation, according to Wilson, Decius, and Cross⁶¹). The overall rms for eight listed compounds is 47 cm⁻¹. These are compared in Tables XXXII–XXXVIII with the corresponding experimental assignments. Benzene is also included (Table XXXIX), but some of the parameters involved in the conjugated system are obtained in ways described elsewhere. (See reference 8.)

Our spectral assignments agree with the literature in each case, except for isobutene. For the latter Ermer⁴ suggested some revised assignments, but we have retained the original spectroscopic assignments.⁶⁶ As with the alkanes,^{5a} the

Table XXXII. Ethylene: Fundamental vibrational frequencies (cm^{-1}).

Sym. ⁴	Mode	Calc.	Exp. ^{4,66}	(cal.-exp.)
B2u	C—H str.	3107	3106	1
B1g	C—H str.	3103	3103	0
Ag	C—H str.	3023	3026	-3
B3u	C—H str.	2995	2989	6
Ag	C=C str.	1596	1623	-27
B3u	CH2 bend	1449	1444	5
Ag	C=C—H bend	1227	1342	-115
B1g	C=C—H bend	1111	1222	-111
Au	C=C tor.	1089	1023	66
B2g	C=C—H tor.	1067	943	124
B1u	OOP bend	931	949	-18
B2u	C=C—H	923	826	97
rms				68

Table XXXIII. Propene (Cs): Fundamental frequencies (cm^{-1}).

Sym.	Mode	Calc.	Exp. ⁶⁶	(cal.-exp.)
A'	CH2 str.	3107	3090	17
A'	CH str.	3040	3036	4
A'	CH2 str.	3009	2992	17
A'	CH3 str.	2972	2933	39
A''	CH3 str.	2970	2954	16
A'	CH3 str.	2879	2870	9
A'	C=C str.	1667	1652	15
A'	CH3 def.	1478	1474	4
A''	CH3 def.	1444	1443	1
A'	C—H bend	1441	1419	22
A'	CH3 def.	1365	1378	-13
A'	CH2 bend	1226	1298	-72
A'	CH2 wag	1131	1229	-98
A''	C=C tor.	1101	1045	56
A''	C—H bend	982	991	-9
A'	CH3 rock	955	1172	-217
A''	CH2 wag	947	912	35
A'	C—C str.	922	920	2
A''	CH2 twist	588	578	10
A'	C=C—C bend	424	428	-4
A''	CH3 tor.	183	174	9
rms				58

Table XXXIV. Isobutene (C_{2v}): Fundamental frequencies (cm^{-1}).^a

Sym. (MM3)	Sym. ⁴	Mode	Calc.	Exp. ⁶⁶	(cal.-exp.) ⁶⁶
B2	B1*	CH str.	3109	3085	24
A1	A1	CH str.	3013	3019	-6
A1	A1	CH3 str.	2973	2942	31
B1	B1	CH3 str.	2972	2983	-11
B2	B2	CH3 str.	2971	2996	-25
A2	—*	CH3 str.	2971	2950	21
B2	B1*	CH3 str.	2881	2893	-12
A2	A1*	CH3 str.	2880	2884	-4
A1	A1	C=C str.	1628	1655	-27
B2	B2	CH3 def.	1538	1461	77
A1	A1	CH3 def.	1467	1442	25
B1	B1	CH3 def.	1454	1450	4
A2	—*	CH3 def.	1446	1450	-4
B2	B1*	CH3 def.	1441	1383	58
A1	A1	CH2 wag	1428	1416	12

Table XXXIV. *Continued*

Sym. (MM3)	Sym. ⁴	Mode	Calc.	Exp. ⁶⁶	(cal.-exp.) ⁶⁶
A1	A1	CH3 def.	1338	1377	-39
B2	B1*	CH2 wag	1273	1278	-5
B1	B2*	CH3 rock	1025	1058	-33
B2	B1*	CH3 rock	973	1141	-168
A1	A1	CH3 rock	947	1053	-106
B1	B1	CH2 wag	936	887	49
B2	B2	C—C str.	935	970	-35
A2	A2	CH3 rock	929	988	-59
A1	A1	C—C str.	852	802	50
A2	A2	CH2 twist	717	700	17
B1	B1	S.def. ^a	421	391	30
B2	B2	S.def.	414	431	-17
A1	A1	S.def.	380	378	2
B1	B2*	CH3 tor.	172	—	—
A2	A2	—	162	—	—
rms					49

^aThe MM3 symmetries are the same as given by reference 66. The symmetries assigned by reference 4 are also shown, and differences are marked *.

Table XXXV. 1-Butene: Fundamental frequencies (cm⁻¹).

Mode	<i>gauche</i> (C1)			<i>s-cis</i> (Cs)		
	Calc.	Exp. ⁶⁶	(cal.-exp.)	Calc.	Exp. ⁶⁶	(cal.-exp.)
=CH2 str.	3107	3090	17	3113	3090	23
CH str.	3040	3018	22	3032	3018	14
=CH2 str.	3009	2993	16	3012	2993	19
CH3 str.	2965	2980	-15	2966	2980	-14
CH3 str.	2964	2980	-16	2963	2980	-17
CH3 str.	2949	2936	13	2941	2936	5
CH3 str.	2900	2904	-4	2894	2904	-10
CH2 str.	2871	2886	-15	2870	2889	-19
C=C str.	1678	1641	37	1677	1641	36
CH3 def.	1493	1468	25	1513	1468	45
CH3 def.	1461	1459	2	1475	1459	16
CH2 bend	1457	1439	18	1472	1444	28
=CH2 i.p. bend	1443	1414	29	1449	1421	28
CH3 def.	1406	1378	28	1419	1378	41
CH2 wag	1353	1316	37	1383	1323	60
HC=CH i.p. bend	1243	1294	-51	1252	1294	-42
CH2 twist	1190	1262	-72	1235	1258	-23
=CH2 i.p. rock	1129	1175	-46	1101	1180	-79
C—C str.	1080	1076	4	1085	1128	-43
CH3 rock	1021	1028	-7	1021	1018	3
HC=CH o.p. wag	1007	998	9	1014	976	38
=CH2 o.p. wag	988	910	78	987	910	77
CH3 o.p. rock	968	887	81	974	887	87
C—C str.	888	855	33	855	855	0
CH2 rock	812	796	16	820	835	-15
=CH2 twist	608	631	-23	569	554	15
—	418	—	—	483	—	—
—	322	—	—	290	—	—
—	243	—	—	279	—	—
—	100	—	—	117	—	—
rms			35			38

Table XXXVI. *cis*-2-Butene (C_{2v}): Fundamental frequencies (cm^{-1}).

Sym.	Mode	Calc.	Exp. ⁶⁶	Exp. ⁴	(cal.-exp. ⁶⁶)
A1	CH str.	3031	3035	3034	-3
B2	CH str.	3017	3052	3030	-13
A1	CH3 str.	2999	2930	2979	20
B2	CH3 str.	2990	2992	2979	11
A2	CH3 str.	2969	2988	2979	-10
B1	CH3 str.	2969	2948	2979	-10
A1	CH3 str.	2889	2902	2931	-13
B2	CH3 str.	2886	2894	—	-8
A1	C=C str.	1714	1668	1669	46
B2	CH3 def.	1552	1458	1462	94
A1	CH3 def.	1458	1444	1462	14
B1	CH3 def.	1450	1454	1462	-4
A2	CH3 def.	1446	1464	1462	-18
B2	CH wag	1441	1422	1462	19
A1	CH3 def.	1403	1384	1389	19
B2	CH3 def.	1368	1408	1397	-40
A1	CH wag	1270	1268	1267	2
A2	CH wag	1101	1050	1044	51
B2	CH3 rock	1089	1134	1134	-45
A1	CH3 rock	1032	1010	1009	22
B1	CH3 rock	968	1037	1016	-48
B2	C—C str.	962	971	978	-9
A2	CH3 rock	952	950	—	2
A1	C—C str.	862	864	881	-2
B1	CH wag	726	685	685	41
B2	S. def. ^a	535	566	581	-31
A2	S. def.	422	396	402	26
A1	S. def.	295	258	304	37
B1	—	133	—	—	—
A2	—	102	—	—	—
rms					31

Table XXXVII. *trans*-2-Butene (C_{2h}): Fundamental frequencies (cm^{-1}).

Sym.	Mode	Calc.	Exp. ⁶⁶	Exp. ⁴	(cal.-exp. ⁶⁶)
Ag	CH str.	3046	3011	3011	35
Bu	CH str.	3039	3036	3021	3
Ag	CH3 str.	2972	2954	2965	7
Bu	CH3 str.	2972	2976	2960	-4
Au	CH3 str.	2970	2948	2960	10
Bg	CH3 str.	2970	2950	2965	5
Ag	CH3 str.	2880	2930	2926	-46
Bu	CH3 str.	2879	2892	—	-13
Ag	C=C str.	1734	1680	1681	54
Bu	CH3 def.	1475	1455	1449	20
Au	CH3 def.	1444	1444	1471	0
Bg	CH3 def.	1444	1457	1455	-13
Ag	CH3 def.	1443	1457	1455	-14
Bu	CH3 def.	1440	1379	1393	61
Ag	CH3 def.	1380	1385	1389	-5
Bu	CH wag	1345	1306	1311	39
Ag	CH wag	1230	1309	1309	-79
Bu	C—C str.	1133	1069	1072	64
Ag	CH3 rock	1072	1138	1145	-66
Bg	CH3 rock	1041	1043	1043	-31
Au	CH3 rock	1012	1024	1057	17
Bu	CH3 rock	963	966	980	-3
Au	CH wag	957	975	964	-7
Ag	C—C str.	887	864	870	23
Bg	CH wag	810	750	746	60
Ag	S. def. ^a	460	501	507	-41
Bu	S. def.	292	290	—	2
Au	S. def.	239	240	—	-1
Bg	CH3 tor.	205	210	210	-5
Au	—	156	—	—	—
rms					34

Table XXXVIII. 1,4-Cyclohexadiene (D_{2h}): Fundamental vibrational frequencies (cm^{-1}).

Sym. ⁴	Calc.	Exp. ⁴	(cal.-exp.)
A _g	3050	3032	18
B _{3u}	3049	3019	30
B _{1u}	3036	3019	17
B _{2g}	3036	3032	4
B _{3g}	2950	2875	75
B _{2u}	2949	2877	72
A _g	2900	2822	78
B _{1u}	2900	2825	75
B _{3u}	1704	1639	65
A _g	1677	1680	-3
B _{2g}	1605	—	—
B _{1u}	1503	1430	73
B _{3u}	1469	1358	111
A _g	1413	1426	-13
B _{1u}	1389	1405	-16
B _{2g}	1365	1377	-12
B _{3u}	1237	1193	44
A _g	1211	1197	14
A _u	1205	—	—
B _{1g}	1195	—	—
B _{3g}	1119	985	134
B _{2g}	1112	1035	77
A _u	1101	—	—
B _{1u}	975	956	19
B _{3u}	962	956	6
A _g	905	854	51
B _{2u}	893	956	-63
B _{3g}	834	—	—
B _{1g}	741	706	35
B _{1u}	731	887	-156
B _{2u}	649	622	27
B _{2g}	512	574	-62
A _g	433	530	-97
A _u	370	—	—
B _{3g}	358	403	-45
B _{2u}	99	108	-9
rms			64

largest errors in the frequencies are for those that involve hydrogen bending motions.

ENTROPIES

From the above information, it is apparent that the calculation of entropies and thermodynamic functions is straightforward.⁶² The information which follows was not used in the parameterization, but is an independent check on the accuracy of the results. Table XL shows MM3 calculated and experimental values for the entropies of a few arbitrarily chosen molecules. Note that there is negligible systematic error, and the rms error is only 0.33 eu.

CONCLUSIONS

The MM3 calculations for alkanes previously described⁵ have been extended to 45 alkenes. The structures where experimentally known are calculated to approximately within experimental error, and others are predicted. For the vibrational frequencies of eight selected molecules, the rms error is 47 cm^{-1} . Entropies (at 25°C) can be calculated to better than 1% error, and heats of formation are well calculated, but will be discussed in a separate paper.⁸

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Table XXXIX. Benzene (D_{6h}): Fundamental frequencies (cm^{-1}).

Sym	Mode	Calc.	Exp. ⁶⁷	(cal.-exp.)
Alg	C—H str. in phase	3058	3062	-4
	Breathing	911	993	-82
A2g	C—H in plane bend	1368	1298	70
B2g	C—H out-of-plane trig.	1119	1016	103
	C—C—C out-of-plane bend	581	685	-104
E2g	C—H stretch	3043	3048	-5
	C—C stretch	1637	1595	42
	C—H in plane bend	1185	1178	7
	C—C—C in plane bend	596	606	-10
Elg	C—H out-of-plane bend	773	850	-77
A2u	C—H out-of-plane in phase	569	671	-102
Blu	C—H trigonal stretch	3038	3060	-22
	C—C—C trigonal bend	947	1010	-63
B2u	C—C stretch	1657	1693	-36
	C—H in-plane trig. bend	1249	1170	79
E2u	C—H out-of-plane bend	1030	985	45
	C—C—C out-of-plane bend	361	400	-39
Elu	C—H stretch	3051	3080	-29
	C—C stretch	1482	1485	-3
	C—H in-plane bend	982	1035	-53
rms				53

Table XL. Heat capacities and entropies of some alkenes ($T = 298$ K).

	Cp° (kcal/mol)		S° (eu)		Error
	Exp ⁶⁸	Calc	Exp ⁶⁸	Calc	
Ethylene	10.41	10.08	52.45	52.34	-0.11
Propene	15.27	15.16	63.80	63.51	-0.29
1-Butene	20.47	20.12	73.04	73.07	0.03
cis-2-Butene	18.86	20.44	71.90	71.32	-0.58
t-2-Butene	20.99	20.64	70.86	70.45	-0.41
Isobutene	21.30	20.87	70.17	69.99	-0.18
2,3-Dimethyl-2-butene	29.54	32.45	87.15	87.60	+0.45
Cyclopentene	17.95	20.09	69.23	69.64	+0.41
Cyclohexene	25.10	24.10	74.27	74.00	-0.27
Cyclobutene	16.03	16.61	62.98	63.23	+0.25
1,4-Pentadiene	25.10	24.03	79.70	79.48	-0.22
Average					= -0.08
rms					= 0.33

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