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A Molecular Mechanics Study of Cyclopropanes within the MM2 and MM3 Force Fields

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Abstract: The MM2 and the new MM3 force fields have been extended to include hydrocarbons containing cyclopropane rings. In addition to simple cyclopropyl systems, many highly strained structures have been examined. The calculated structures are in a reasonable agreement with experiment, giving a 0.004-Å (MM2, standard deviation) and 0.003-Å (MM3) difference from the average C-C bond length obtained from gas electron diffraction analysis, for a set of 17 compounds. The MM3-calculated moments of inertia are within 0.7% (SD) of the microwave results. Enthalpies of formation have also been fit by using all available experimental data (19 compounds), ranging from -8 to +136 kcal/mol. The standard deviations between the calculated and the experimental values are 0.44 and 0.28 kcal/mol, for MM2 and MM3, respectively.

Introduction

Cyclopropanes present an interesting and quite challenging class of compounds for molecular mechanics treatment. Even the simplest structures among them are highly strained and manifest unusual bond lengths and angles, far beyond the small deviations often found when dealing with saturated hydrocarbons. Hence, it became obvious long ago¹ that a cyclopropane carbon should be treated separately by assigning a special atom type (22 in MM2).

Though quite a few works have been published²⁻⁹ that make

use of the MM2 force field for calculations on cyclopropane derivatives, the parametrization scheme for this type of compound has never been completed. The existing force fields suffer from several shortcomings, especially with regard to energy, which lead to large errors in the calculated heats of formation (e.g., **15**,⁷ Figure 1), and in some cases incorrect location of global minima (e.g., **16**,¹⁰ **19**). It was also found that the large variation in bond lengths between cyclopropane carbon atoms observed both experimentally and in ab initio calculated structures (vide infra) is not reproduced by the previous force fields. A comparatively large amount of additional experimental data,¹¹⁻⁵⁰ as well as theoretical (mainly

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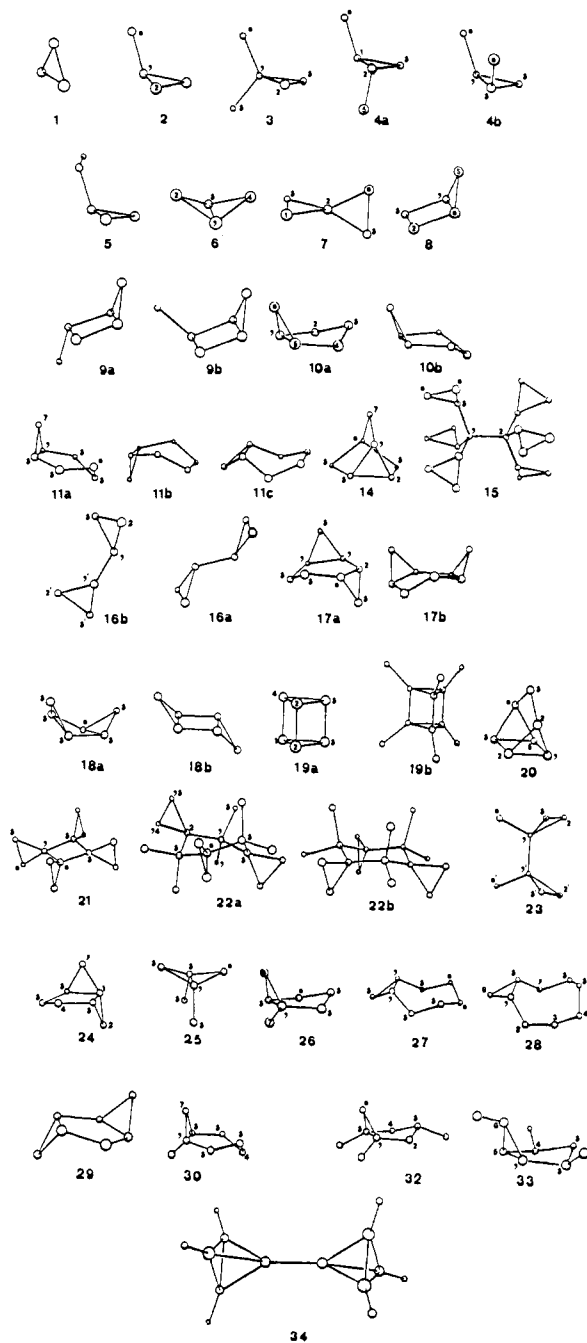


Figure 1.

ab initio) calculations,^{5,9,51-62} both of higher quality and accuracy, have been accumulated since the first cyclopropane parameters

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were introduced into MM2. This made it possible to deal with a wider range of compounds containing three-membered homo-

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cyclic rings in order to develop a reliable scheme and parameter set.

The recent presentation of the new MM3 force field⁶³ served as an excellent opportunity to reexamine the basic scheme for describing the small ring systems. Thus, it was possible to go beyond the somewhat limited corrections made for MM2, imposed by all the other parameters that have already been fixed.

The Osawa-Ivanov MM2'

The most serious attempt to include cyclopropanes in an MM2-like force field was that of E. Osawa et al.^{2a} and P. M. Ivanov,^{2b} using the Osawa MM2' version. Their main modification was intended to solve the problem of a bond connecting two cyclopropyl moieties, which is not included in such a ring (e.g., 1-1' in **16**). This bond is considerably shorter than a "regular" endocyclic 22-22 bond, and the difference could not be reproduced by using the same natural bond length l_0 for all cases. The method they used was to assign a different atom type, 29, for such a carbon (member of a cyclopropyl ring that is also connected to another three-membered ring). This approach, though successful in getting structural and energetical features with satisfactory accuracy for quite a number of compounds, has some obvious deficiencies: (i) Being a part of a three-membered ring, there is no real justification in assigning this atom a different type. (ii) This assignment brings about a large number of unnecessary parameters (all the bonds, angles, torsional angles, and van der Waals parameters involving the new 29 atom type), while most of them should have the same value as their type 22 counterpart. (iii) Technically, the introduction of the new atom type 29 is not enough to account for the different bonds between cyclopropane carbons. There are actually three kinds of bonds: a short one—in an acyclic position (e.g., **16**), or as a part of a medium-size ring (**17**), a long one—included in a four-membered (but not in a three-membered) ring (**18-21**), and the regular endocyclic one, altogether ranging from ca. 1.46 to 1.54 Å. For instance, in quadracyclane (**20**) there are, according to the Osawa-Ivanov scheme, four 29-type atoms and two pairs of 29-29 bonds. These bonds differ in length by at least 0.02 Å (MOCED, MO⁵⁹), an effect that cannot be reproduced by using a single value for l_0 . A more extreme case is demonstrated by the [3]-prismane (**19**), in which all the C-C bonds are of the 29-29 type. Ab initio calculations from STO-3G up to 6-31G*^{57a,b,58} indicate that the three bonds included only in the four-membered rings are about 0.04 Å longer than the other six cyclopropane bonds. To solve this problem, a further correction was introduced by the researchers (ref 2a, Table II), making the above described distinction between the three 29-29 bond types. In fact, all this could have been achieved by using a single cyclopropane atom type, 22 (vide infra), thus avoiding the need for an additional atom type. It should be further noted that the Osawa-Ivanov parameter set was optimized within the MM2' framework, and is not directly applicable to MM2.

Modification and Reparametrization of the MM2 Force Field

The goal of this work was to be able to reconstruct the geometrical, as well as the energetical, experimental data, concerning cyclopropanes. This, while introducing as few changes as possible to the already well established, and extensively used, MM2 force field.

The scheme adopted in the present study is an extension of the one already used in MM2 for bending potentials, for which dis-

inction is made between different possible positions of an angle consisting of the same three atom types. Thus, the bending parameters may differ for angles included in a three-membered, a four-membered, and a higher order ring (or acyclic). Following this scheme, the 22-22 bond was assigned three different natural bond lengths, for those three cases (the stretching constant has been left the same; see Table VII). The large differences in bond length reflect probable variation in bonding energy, and as a logical step, different bond increments have been given to the three 22-22 bond types for the heat of formation calculation. Other stretching, bending, and torsional parameters have been revised to get a better fit of geometry and energy with the experimental data. A comparatively large set of compounds has been used in the parametrization process. It included, for geometry comparisons, 20 structures for which electron diffraction (ED) analysis results and/or microwave spectra (MW) could be found and 19 compounds for heats of formation. Those examples represent most of the possible arrangements of small to medium size rings such as fused (3.3, 3.4, 3.5, and 3.6), spiro (3.3, 3.4, 3.6), and connected by a single bond (3.3), and include several examples for each of the three 22-22 bond types.

The MM3 Force Field

Besides some minor changes in the basic potential functions, and the introduction of additional cross terms, such as limited bend-bend and torsion-stretch interactions, the most important additional feature of the new force field is its ability to calculate vibrational spectra.^{63b} This is due to the utilization of the full matrix minimization option that was not available in MM2. In addition to the advantage in getting calculated vibrational frequencies, this may serve to impose further restrictions on the (mainly) stretching and bending force constants used, thus avoiding some of the arbitrariness involved when the number of parameters is relatively large in comparison with the number of experimental data. In the present study, only the second goal has been achieved, and that only to a limited extent: While trying to fit the experimental vibrational spectra, it became clear that additional cross terms, not yet included in the force field, are needed for a better description of the CH₂ vibrational modes (vide infra). A simultaneous fitting of all the CH₂-related frequencies, with the current force field, proved to be impossible.

Starting from cyclopropane itself, and its methyl derivatives, the basic parameters used for the stretching and bending potentials were reestablished, making the natural C-C-C and C-C-H bond angles (θ_0) closer to the actual values. The reduction in the bending strain achieved in the simple, single-ring compounds simplified the handling of the more complex cases, while eliminating some of the unreasonable changes in bond length caused by the large stretch-bend interaction.

Another important difference between MM3 and MM2 is the treatment of four- and five-membered rings: While the carbon atoms composing the former have been assigned a special atom type (56), the concept of treating angles as special cases within a small ring (3 and 4 in MM2) has been expanded to include cyclopentane rings as well. When dealing with the cyclobutane ring, it was suggested that a bond angle correction should be used when one or two of the bonds constituting the angle are included in such rings (two different rings in the second case). This scheme has been adapted and expanded in the present study for cases of three-membered rings, and structures containing three- and four- or three- and five-membered rings attached in a fused or spiro fashion. Three types of corrections were defined: (i) when only one bond is included in a single cyclopropane ring, (ii) only one bond is shared by two small (3 and 3, 3 and 4, or 3 and 5) rings, and (iii) both bonds are included in (different) small rings. (It may be noted here that the more extreme case of the propellane structures, in which the central bond is included in three small rings, was excluded from this study.) All the angle corrections are suppressed when they occur inside an additional small ring. These changes added quite a few degrees of freedom for the parametrization process, and allowed a better description of some of the most strained structures.

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Results and Discussion

I. Vibrational Spectra. Detailed experimental vibrational spectra, with full assignment of the vibrational modes, could be found for the two smallest cyclopropane compounds: the parent compound **1**,^{64a} and the bicyclo[1.1.0]butane (**6**).^{64b,c} A reasonable fit has been achieved for the C–H stretching frequencies in both molecules, by correcting the C–H stretching force constant. The calculated vs experimental frequencies are listed in Table II, first section, and show a standard deviation of 34 wavenumbers. The average difference is only 3 wavenumbers, leaving almost no systematic error. Fitting the rest of the spectra proved to be a much more difficult task: In fact, some of the modes involving CH₂ movements were found to change simultaneously, and in the same direction, when the C–C–H and H–C–H force constants were varied. Thus, modes 5, 7, 9, and 13 (experimentally assigned CH₂ twisting, rocking, bending, and rocking and calculated as mode numbers 21, 12, 10/11, and 8/9, respectively) changed together by ± 75 –125 wavenumbers, when the C–C–H (5–22–22) bending constant was changed by $\pm 20\%$. For every value of the force constant, large differences between the experimental and calculated frequencies, up to a few hundred wavenumbers, still remain, and it was only possible to average the difference among all modes. This was actually done for both compounds simultaneously, giving a standard deviation of 147 wavenumbers and an average difference of 24 (Table II, second and third sections). This result stresses the need for the inclusion of more bend–bend interaction terms, i.e., between angles centered on adjacent atoms, already noticed in simple hydrocarbons.^{63b} In the present case, the mutual dependence of the various CH₂ modes, in the MM3-calculated model, seems even more severe, perhaps due to

the high degree of symmetry of the molecules studied.⁸⁰

II. Geometry and Conformational Energy. As was previously mentioned, the main source of experimental data has been ED results. Though being in accordance with the general MM2/MM3 scheme, this source has certain limitations: The only directly measurable quantities are the average interatomic distances, while the individual bond lengths and 1...3 and 1...4 distances (needed to calculate bond and torsional angles) are set to get the best possible fit between calculated and experimental radial distribution curves. In most cases, more than one model can fit the measured curve, and while the differences in the *R* value are small, the individual bond lengths may vary considerably.⁶⁷ Even combined ED–MW analysis^{25b} is usually not enough when a structure contains several, different but close, bonds.⁵⁴ Perhaps the best way to determine a reliable structure in the gas phase is to analyze the ED data by using geometrical parameters partially constrained by ab initio^{59b} or X-ray results. The second important source for experimental geometries comes from microwave spectroscopy. The number of cases studied, as well as the amount of information that may be obtained from the measurements, is quite limited: only the three moments of inertia, unless extensive isotope substitution is performed. Nevertheless, the method is very accurate, and the measured moments of inertia can be used as a reference for comparison with the calculated values. The bond angles treatment scheme developed for MM3 for small rings is superior to the more limited one used in MM2 in dealing with the bi- and tricyclic structures. In fact, the MM3-calculated interplanar angles, in compounds **6**, **8**, **9a**, **9b**, **10a**, and **18b**, are very close to the experimental (ED and MW) and MO-calculated values, making the MM3–MW differences in moments of inertia as low as 0.7% (standard deviation). Some experimental and calculated structural features of cyclopropanes are listed in Table I, while the deviation of the MM2 and MM3 results from ED (weighted average C–C bond lengths) and MW (moments of inertia) are summarized in Tables IV and V, respectively.

Cyclopropane and Its Methyl Derivatives. The ED (*r_g*) bond length of cyclopropane itself (**1**) has been redetermined recently as 1.514 Å^{11b} (previous value 1.512^{11a}). The MM2-calculated value is 1.510 Å, resulting from a natural bond length (*l₀*) of 1.503, which was found to give the best overall fit for the tested set of compounds. Earlier study of the methyl (**2**) and *trans*-1,2-dimethyl (**4a**) derivatives¹² yielded somewhat shorter bonds of 1.511 and 1.510 Å, respectively, assuming all endocyclic bonds are equal. The MM2-calculated structures fit very well the average bond length (to 0.001–0.002 Å) as well as the individual bonds. Good agreement is also found with MW data for **2**,²⁶ when the differences in calculated vs experimental moments of inertia and dipole moment are 0.5–1.6% and 0.01 D. The experimental rotational barrier of **2**^{34b} is reproduced by MM2 to within 0.2 kcal/mol (Table I). The MM3-calculated bond length for cyclopropane (**1**) is a little closer to the ED one—1.512 Å. This value is reached by using the same *l₀*, despite the larger stretching force constant (0.50, from the fit of the vibrational spectra), and the reduction in the bond-lengthening, stretch–bend interaction (see above). This is probably due to the torsion–stretch interactions around each C–C bond (two couples of eclipsing hydrogen atoms). The overall geometry fit for compounds **1**, **2**, and **4a** is of the same quality as for MM2, but the calculated moments of inertia and barrier for methyl group rotation compare more favorably with MM3 than with MM2.

Bicyclic Compounds. The simplest of the bicyclic cyclopropanes is the bicyclo[1.1.0]butane (**6**). The ED reported structure¹³ (see Table I), though not very detailed, is very close to the calculated one (difference in average C–C bond length of 0.002 Å) except for the angle between the two rings, which comes out a little larger

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in the latter (by 2.8°). A larger difference is observed in the moments of inertia²⁷ (2.5–2.8%), but the bond lengths deduced from that work (C–C av of 1.498 Å) seem too short even when taking into account the difference in bond length definition between the two methods (r_g or r_a vs r_z). The MM3 geometry agrees almost exactly with the ED one, the interplanar angle matching the MW value.

The next compound in this series is bicyclo[2.1.0]pentane (**8**) and its two methyl derivatives **9a,b**. The parent compound has been studied both by ED¹⁵ and MW^{28b} techniques, while structures of the methyl derivatives have been determined by the latter method alone.²⁹ The individual bond lengths derived from the analysis of the ED data of **8** reveal unrealistically short (1.439) and long (1.622) values, which have been criticized⁵⁶ in view of the MW as well as the ab initio (4-21G scaled to r_s values) results. Interestingly, the weighted average (wav) C–C bond length in all methods (ED, MW, MO, MM) lies within a range of 0.003 Å (Table I). Most of the MM2-calculated bond angles are close to the experimental and ab initio values, but the angle between the ring planes is calculated much too flat (by 8.8° , compared to MW), which may explain the large discrepancy in the moments of inertia (av of 4.3% in **8**, but only 1.5% in **9a,b**). When the MW structures of **9a** and **9b** were analyzed, the unavoidable assumption was made that the ring components are identical with that of the parent compound. This leads to C–Me bond lengths that differ slightly from the MM2 values (by less than the reported experimental error). Again, the average C–C bond length is almost exactly the same. The last two, relatively simple, examples demonstrate the difficulty and uncertainty involved in trying to determine a detailed structure on the basis of ED or MW data alone. Again, the MM3 force field, while giving very similar bond lengths, is doing much better regarding the angles, thus matching the reported moments of inertia within 0.8%.

The bicyclo[3.1.0]hexane (**10**) was solved by a combined ED–MW analysis.^{25b} This compound is found to exist in the “boat” form **10a**, both experimentally and by ab initio (4-31G) calculations.⁵⁴ MM2 and MM3 confirm this finding, and give good agreement with both models (all four wav bond lengths are within 0.003 Å, and the rms differences in calculated vs MW moments of inertia are 1.4 and 0.4%, for MM2 and MM3, respectively). An unusually short cyclopropane bond at the bridgehead, suggested by the ED–MW model, is not supported by the ab initio results, nor by the force field calculations. The possible existence of an additional conformer, namely—the “chair” form, has been discussed in the literature. While neither the MW results nor the far infrared data were sufficient to rule out this possibility, the combined study supports a single stable conformer.^{35,65b} A recent ab initio study using the 3-21G, 3-21G*, and 6-31G* basis sets, exploring the potential surface of **10** and some of its oxa and thia derivatives, reached a similar conclusion.^{65c} The barrier for chair–boat conversion was found to be almost zero, making the chair actually nonexistent as a stable conformer. Mapping the ring-puckering potential surface with MM2 using the two dihedral angle driver (Figure 2a) yielded two minima: the chair conformer lying 2.6 kcal above the boat one, but with a barrier of only 0.7 kcal. The MM3 potential (Figure 2b) shows a single minimum with a “shoulder” in the chair location. A closer scrutinizing of the shoulder area, using a 1° driver increment, revealed another, very flat, potential well, separated by only a 0.14-kcal barrier from the lower boat form. Since the lower vibrational mode of the pseudochair form, which is assigned to ring puckering, is calculated to be 114 cm^{-1} , this barrier is below the first vibrational level, consistent with the conclusion drawn from the ab initio study.

The only experimental information available for bicyclo[4.1.0]heptane (**11**) is a rather crude ED study,¹⁶ resulting in an average C–C bond only, and leaving quite a large *R* factor (>8%). While it is not possible to compare the detailed structure in this case, the half-chair conformer, which the researchers concluded was the stable one, is also found to predominate in the MM2/MM3 calculations (by at least 2.3 kcal/mol).

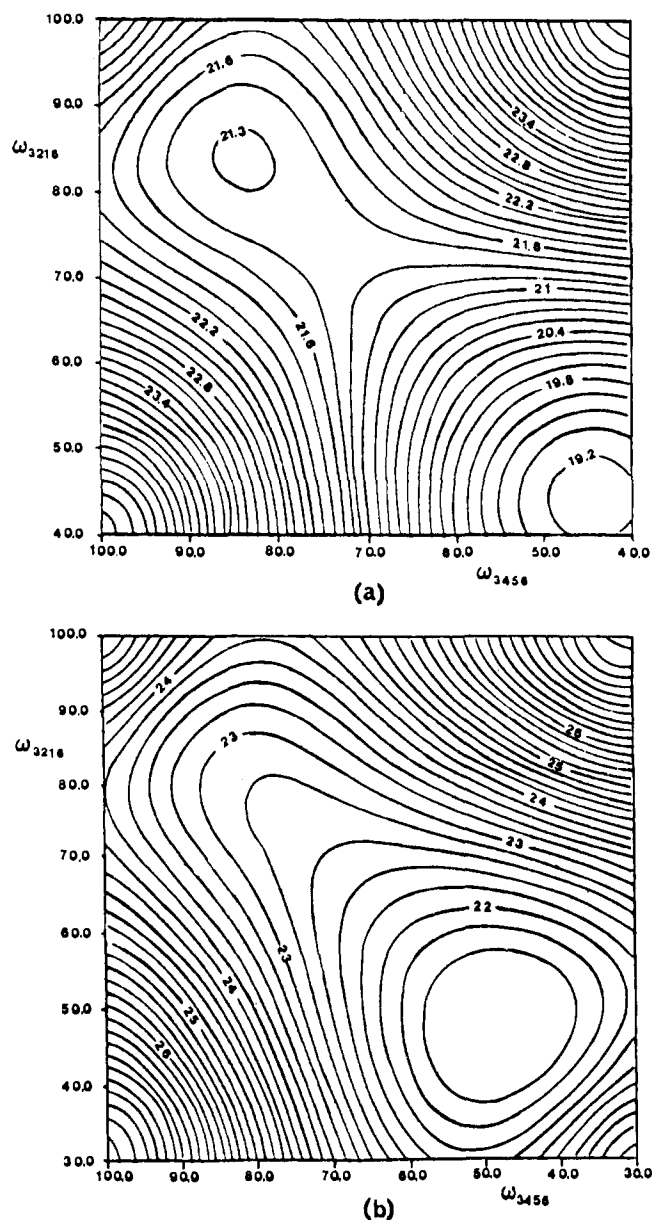


Figure 2. Force field calculated ring-puckering potential surface for bicyclo[3.1.0]hexane (**10**): (a) MM2, (b) MM3.

The following four groups include examples of the two special 22–22 bond types: the shorter (**17a,b**, **16**, **23**) and the longer one (**18**, **19**, **20**, **21**).

Bicyclopropyls. Two representatives of this group are discussed here, namely, the bicyclopropyl (**16**) and its 1,1'-dimethyl derivative (**23**). Compounds **17a** and **17b**, which may be regarded as bicyclopropyl structures constrained within a cyclohexane ring, will be described later.

The C1–C1' bonds in **16b** and **23** have lengths of 1.499 and 1.510 Å, respectively, from ED analysis.^{6,18} This difference has been attributed⁶ to the repulsion of the gauche methyl groups, but by using the corrected (shortened) l_0 for the C1–C1' bond in those molecules, only a much smaller difference of about 0.002 Å was found. We preferred to fit closely the **23** structure, which has been determined recently, and was found to exist in the gas phase as a homogeneous gauche conformer, both experimentally⁶ and by MM2 (the trans conformer was calculated to be ca. 4.5 kcal/mol less stable). Hence, the calculated wav bond length for **23** is only 0.003 Å shorter than the ED one, and the respective 1...3 and 1...4 distances are also in very good agreement, while the difference in **16b** is 0.006 Å. It may be noted that the X-ray diffraction data for the crystallized form of **16** have been interpreted³⁷ as the trans conformer **16a**. Early versions of MM2

Table I. Geometries and Conformational Energies of Structures 1–24^w

compound	parameter	experimental		calculated			
		ED ^a	other ^b	MM2 ^c	MM3 ^c	MO ^d	
cyclopropane (1)	C–C	1.514 (4) ^{11b}	1.512 (3) ^{R,30b}	1.510	1.512	1.497 ^{IV,55}	
	C–H	1.099 (5)	1.083 (3)	1.088	1.087	1.076	
	H–C–H	114.5 (9)	114.0 (7)	115.2	115.8	114.0	
	C–C–H	117.9	118.1	117.7	117.4	118.1	
methylcyclopropane (2)	C1–C2	1.511 (1) ¹²	1.514 ^{M,26,e}	1.514	1.515	1.515 ^{1,52}	
	C2–C3			1.510	1.512	1.518	
	C1–Me	1.519 (1)	1.522	1.518	1.520	1.516	
	C–C wav ^f	1.513	1.516	1.514	1.515	1.516	
	C–C–Me	118.4 (1)	119.0	117.2	118.8		
	Me–C–H	116.7 (4)		114.6	113.9	114.8	
	H–C2–H	116.4 (6)		115.0	115.6	114.5	
	C–Me–H av	112.1 (4)		110.7	110.9	110.9	
	<i>I</i> _x		5.414	5.498	5.450		
	<i>I</i> _y		13.192	13.120	13.283		
	<i>I</i> _z		15.026	14.838	15.046		
	μ	0.139 (4)		0.15	0.15	0.10	
	rotational barrier		2.86 ^{34b}	2.63	2.85		
	<i>trans</i> -1,2-dimethylcyclopropane (4a)	C1–C2	1.510 (3) ¹²		1.518	1.518	
C1–C3				1.514	1.515		
C1–Me		1.521 (4)		1.518	1.520		
C–C wav		1.514		1.516	1.517		
C2–C1–Me		118.4 (2)		117.0	118.7		
Me–C–H		116.7 (2.4)		114.4	113.9		
H–C3–H		116.9 (1.3)		114.8	115.4		
C–Me–H av		112.1 (4)		110.7	110.9		
C1–C2		1.509 ^g	1.498 (4) ^{M,27}	1.507	1.506	1.503 ^{III,54}	
C1–C3		1.504	1.497 (3)	1.502	1.509	1.485	
bicyclo[1.1.0]butane (6)	C–C wav	1.508	1.498	1.506	1.507	1.499	
	C2–C1–H		128.4 (2)	123.3	129.6		
	θ^h	122.8	121.7 (5)	125.6	122.0	120.2	
	<i>I</i> _x		4.849	4.708	4.865		
	<i>I</i> _y		9.013	9.261	9.057		
	<i>I</i> _z		10.001	10.250	10.064		
	μ		0.67	0.00	0.00	0.74 ^{IV,53}	
	spiropentane (7)	C1–C2	1.521 (3) ¹⁴		1.530	1.515	
		C1–C3	1.471 (1)		1.479	1.483	
		C–C wav	1.488		1.496	1.493	
C1–C3–C2		62.2 (1)		62.3	61.5		
C2–C1–C3		58.9		58.9	59.3		
C1–C3–C4		137.2		137.1	137.6		
C2–C1–H		117.1 (9)		117.6	117.4		
C3–C1–H		115.8 (1.3)		117.5	117.3		
H–C–H		118.4 (9)		115.9	116.3		
bicyclo[2.1.0]pentane (8)		C1–C2	1.543 (11) ¹⁵	1.528 (6) ^{M,28b}	1.534	1.532	1.528 ^{IV,55}
	C1–C4	1.439 (15)	1.536 (3)	1.526	1.518	1.513	1.535
	C1–C5	1.521 (11)	1.507 (4)	1.511	1.509	1.494	1.509
	C2–C3	1.622 (16)	1.565 (3)	1.555	1.560	1.558	1.564
	C–C wav	1.532	1.529	1.529	1.527	1.519	1.529
	C1–C4–C5		59.4	59.7	59.8		
	C1–C5–C4		61.2	60.7	60.4		
	C2–C1–C4		90.6	90.5	90.8		
	C2–C1–C5		109.7	117.1	109.8		
	C1–C2–C3		89.5 (8)	89.5	89.2		
	C2–C1–H	119.0	126.3 (4)	121.1	124.5		
	C4–C1–H	122.0	128.6 (3)	126.3	127.1	129.0	
	C5–C1–H	124.0	121.2 (3)	121.0	123.7	121.7	
	C1–C5–H ex		114.7 (4)	117.4	117.1	115.6	
	C1–C5–H en	120.0	119.0 (2)	117.7	118.3	120.5	
	H–C5–H		116.7 (4)	115.2	114.8		
	C1–C2–H ex	111.0	113.3 (7)	112.4	115.0	113.2	
	C1–C2–H en		115.2 (4)	112.5	116.3	115.9	
	C3–C2–H ex	118.0	111.9 (5)	112.8	111.4	112.1	
	C3–C2–H en		116.6 (7)	114.5	112.9	117.0	
	H–C2–H		109.4 (3)	113.1	110.5		
	θ^h	109.4 (4)	112.7 (4)	121.5	112.6	111.7	
	C1–C2–C3–C4		0.0	0.0	0.0	0.0	
	C3–C2–C1–C4		0.0	0.0	0.0	0.0	
	C3–C2–C1–C5		–57.5	–55.8	–58.0	–57.8	
	C3–C4–C1–C5	109.4 (4)	112.7	121.5	112.5	111.7	
	C2–C1–C5–C4		78.4	73.3	78.9	79.3	
	<i>I</i> _x		9.221	8.858	9.131		
<i>I</i> _y		13.726	14.356	13.859			
<i>I</i> _z		17.550	18.291	17.423			
μ		0.26	0.30	0.30			

Table I (Continued)

compound	parameter	experimental		calculated			
		ED ^a	other ^b	MM2 ^c	MM3 ^c	MO ^d	
<i>exo</i> -2-methylbicyclo[2.1.0]-pentane (9a)	C1-C2		1.536 ^{M,29,i}	1.536	1.535		
	C1-C4		1.528	1.526	1.518		
	C1-C5		1.507	1.510	1.509		
	C2-C3		1.565	1.557	1.561		
	C2-Me		1.519 (15)	1.529	1.532		
	H-C5-H		115.0	115.2	114.8		
	C1-C2-Me		114.8 (1.2)	115.5	113.6		
	C3-C2-Me		115.0 (1.2)	114.1	116.0		
	H-C3-H		108.0	112.9	110.3		
	θ^h		112.7 (4)	121.6	112.8		
	I_x		11.312	11.195	11.365		
	I_y		27.056	27.873	27.293		
	I_z		31.637	32.801	31.860		
	μ		0.176	0.30	0.30		
	<i>endo</i> -2-methylbicyclo[2.1.0]-pentane (9b)	C1-C2		1.536 ^{M,29,i}	1.537	1.536	
C1-C4			1.528	1.527	1.520		
C1-C5			1.507	1.512	1.509		
C2-C3			1.565	1.556	1.559		
C2-Me			1.535 (15)	1.527	1.531		
H-C5-H			115.0	114.9	114.5		
C1-C2-Me			120.1 (1.2)	116.8	115.7		
C3-C2-Me			119.9 (1.2)	115.2	117.7		
H-C3-H			108.0	112.9	110.4		
θ^h			112.7 (4)	121.5	114.3		
I_x			13.411	13.524	13.482		
I_y			24.594	24.802	24.425		
I_z			29.514	29.947	29.262		
μ			0.176	0.30	0.30		
bicyclo[3.1.0]hexane, "boat" (10a)		C1-C2	1.543 (4) ^{C,25b}		1.521	1.521	1.520 ^{11,54}
	C1-C5	1.454 (9)		1.513	1.513	1.509	
	C1-C6	1.515 (8)		1.513	1.513	1.506	
	C2-C3	1.543 (4)		1.541	1.549	1.548	
	C-C wav	1.522		1.523	1.525	1.522	
	C2-C1-C5	109.8 (4)		107.4	108.1	108.3	
	C5-C1-H	125.8 (6.4)		123.3	119.1	121.3	
	C4-C5-C1-H	147.1 (10.1)		141.5	140.4		
	θ^i	109.4 (1.1)		112.8	109.9	111.4	
	ϕ	154.8 (2.8)		150.5	154.1	152.5	
	I_x	15.140		14.943	15.170		
	I_y	19.807		20.160	19.886		
	I_z	26.837		27.089	26.980		
	μ		0.19 ^{46b}	0.29	0.29	0.19 ^{11,53}	
	bicyclo[4.1.0]heptane, half-chair (11a)	chair-boat difference	exclusive boat		2.58	only boat	3.03 ^{11,53}
C1-C2				1.523	1.525		
C1-C6				1.519	1.521		
C1-C7				1.518	1.517		
C5-C6				1.520	1.523		
C6-C7				1.509	1.511		
C-C wav		1.537 (8) ¹⁶		1.524	1.525		
C2-C1-C6 (av)		120 (1)		118.8	119.1		
C2-C3-C4 (av)		112 (1.5)		110.0	110.6		
C3-C2-H (av)		109		109.0	108.8		
C3-C4-H (av)		108		110.0	109.8		
H-C7-H		117		114.4	115.1		
θ^k		109 (2)		106.2	107.8		
nortricyclane (14)		C1-C2	1.515 (15, ass.) ^{17b}		1.514	1.515	
		C1-C7	1.527 (13)		1.522	1.524	
	C3-C4	1.554 (13)		1.550	1.556		
	C-C wav	1.532		1.529	1.531		
	C2-C1-C7	107.0		107.3	107.2		
	C2-C3-C4	96.9 (4)		95.6	96.5		
	C3-C4-C5	101.5		102.6	101.8		
	C2-C1-H	122.6		122.8	120.5		
	H-C3-H	110 (ass.)		110.4	110.8		
	1,1,1,2,2,2,-hexacyclopropyl-ethane (15)	C1-C2		1.625 (6) ^{X,7}	1.627	1.626	
		C1-C3		1.536 (3) ⁱ	1.556	1.554	
		C3-C4		1.504 (5)	1.519	1.520	
		C3-C5		1.507 (5)	1.517	1.519	
		C4-C5		1.489 (5)	1.506	1.507	
		C2-C1-C3		109.3 (2)	109.1	109.2	
C3-C1-C6			109.7 (2)	109.8	109.7		
C1-C3-C4			124.6 (2)	122.3	122.4		
C1-C3-C5			124.6 (2)	121.0	121.4		
C4-C3-C5			59.3 (2)	59.5	59.5		
C3-C4-C5			60.5 (2)	60.2	60.2		

Table I (Continued)

compound	parameter	experimental		calculated			
		ED ^a	other ^b	MM2 ^c	MM3 ^c	MO ^d	
<i>trans</i> -bicyclopropyl (16a)	C3-C5-C4		60.2 (2)	60.3	60.3		
	C2-C1-C3-C4		90.7	84.6	84.2		
	C3-C1-C2-C15		-59.8	-60.0	-60.0		
	C3-C1-C2-C18		60.2	60.0	60.0		
	C1-C1'		1.487 ^{X,37}	1.506	1.500		
	C1-C2		1.501	1.515	1.514		
	C2-C3		1.510	1.509	1.512		
	C2-C1-C1'		120.0	116.8	115.9		
	C1-C1'-H		113.0	115.8	116.1		
	H-C2-H		113.0	115.0	115.5		
<i>gauche</i> -bicyclopropyl (16b)	C1-C1'	1.499 (16) ^{18c,m}		1.505	1.500		
	C1-C2	1.507 (3)		1.517 (av)	1.515 (av)		
	C2-C3	1.507 (3)		1.507	1.511		
	C-C wav	1.506		1.512	1.512		
	C2-C1-C1'	120.9		117.3 (av)	118.6 (av)		
	C1-C1'-H	110.5		115.0	113.7		
	H-C2-H	116.1		115.0 (av)	115.2 (av)		
	H-C1-C1'-H	48.7 (7.3)		48.3	46.3		
	trans-gauche difference		0.17 ¹⁰	0.22	0.14		
			0.6 ^{46b}	0.01	0.29		
<i>gauche</i> -1,1'-dimethylbicyclopropyl (23)	syn barrier		1.8-2.6 ^{46b}	2.93	2.79		
	C1-C1'	1.510 ^{6,n}		1.506	1.508		
	C-Me	1.532 (11)		1.520	1.523		
	C-C (CP) ^o	1.512		1.512	1.513		
	C-C wav	1.516		1.513	1.515		
	C2-C1-C1'	119.6 (6)		118.8 (av)	122.2 (av)		
	C1-C1'-Me	115.1 (9)		114.9	112.8		
	H-C2-H (av)	109.8 (3.3)		114.1	115.0		
	Me-C-C-Me	58.1 (1.5)		53.7	57.6		
	trans-gauche difference		only gauche	4.4	4.7		
<i>trans</i> -tricyclo[5.1.0.0 ^{2,4}]octane (17a)	C1-C2	1.447 (10) ¹⁹		1.500	1.498		
	C-C (CP) ^o	1.510 (3)		1.514 (av)	1.515 (av)		
	C5-C6	1.562 (5)		1.534	1.536		
	C-C wav	1.519		1.515	1.516		
	C1-C2-C4	122.1 (6)		120.4	119.8		
	C2-C4-C5	115.1 (6)		117.4	118.7		
	C4-C5-C6	114.7 (7)		116.2	115.5		
	C1-C2-H	110.7 (4.0)		113.8	114.5		
	C4-C2-H	109.2 (4.0)		117.3	118.1		
	H-C5-H	102.4 (7.0)		106.1	106.1		
	H-C3-H	119.4 (4.0)		114.5	115.2		
	C7-C1-C2-C4	16.7 (1.0)		8.1	6.0		
	C4-C5-C6-C7	48.7 (2.0)		42.2	41.7		
	C1-C2-C4-C5	3.5		4.6	6.3		
	H-C1-C2-H	55.6 (1.1)		57.7	56.1		
	θ^p	108.9 (2.0)		107.1	106.7		
	<i>cis</i> -tricyclo[5.1.0.0 ^{2,4}]octane (17b)	C1-C2	1.455 (15) ^{19,q}		1.505	1.504	
C-C (CP) ^o		1.513 (5)		1.515 (av)	1.515 (av)		
C5-C6		1.559 (7)		1.534	1.534		
C-C wav		1.521		1.517	1.517		
C1-C2-C4		122.4 (8)		118.7 (av)	118.2 (av)		
C2-C4-C5		113.8 (1.5)		117.2 (av)	118.6 (av)		
C4-C5-C6		114.3 (1.5)		113.5 (av)	113.3 (av)		
C1-C2-H		110.2 (6.0)		112.5 (av)	113.0 (av)		
C4-C2-H		105.8 (6.0)		117.4 (av)	117.4 (av)		
H-C5-H		103.2 (8.0)		105.9 (av)	106.2 (av)		
H-C3-H		113.1 (6.0)		113.9 (av)	114.5 (av)		
C7-C1-C2-C4		17.9 (3.0)		21.9	21.9		
C4-C5-C6-C7		51.5 (4.0)		52.4	50.3		
C1-C2-C4-C5		3.5		4.7 (av)	3.4 (av)		
H-C1-C2-H		17.9 (3.0)		21.0	18.2		
θ^p		109.7 (3.0)		111.7 (av)	110.6 (av)		
[3]-prismane (19)		C1-C2 (CP)			1.508	1.508	1.536 ^{1,58}
	C1-C4 (CB) ^o			1.539	1.556	1.570	1.549
	C2-C1-H			129.6	130.2	130.2	129.7
	C4-C1-H			132.6	131.9	131.7	132.5
quadracyclane (20)	C1-C2	1.525 ^{D,59b,r}	1.521 (24)	1.517	1.512	1.519 ^{III,59c}	
	C1-C5	1.543	1.546 (24)	1.545	1.555	1.549	
	C1-C7	1.525	1.522 (12)	1.507	1.508	1.519	
	C2-C3	1.514	1.522 (42)	1.527	1.526	1.514	
	C-C wav	1.526	1.526	1.523	1.523	1.524	
	C1-C2-C3	110.6	110.6	110.3	110.3		
	C2-C3-C4	98.7	98.5 (1.8)	98.8	98.9	99.0	
	C1-C5-C4	104.3	104.5	104.8	104.7		
	C3-C2-H	117.2	117.3 (1.0)	119.4	122.0		

Table I (Continued)

compound	parameter	experimental		calculated			
		ED ^a	other ^b	MM2 ^c	MM3 ^c	MO ^d	
[4]-rotane (21)	C2-C1-H	122.8	122.9 (1.0)	126.3	124.8		
	C5-C1-H	128.1	128.2 (1.0)	126.8	127.5		
	C2-C3-H	109.8	109.9 (1.0)	111.6	111.8		
	C1-C2 (CB) ^o	1.536 (2) 23	1.521 (1) ^{X,23}	1.539	1.536		
	C1-C5 (CP)	1.493 (1)	1.496 (1)	1.496	1.493		
	C1-C6 (CP)		1.499 (1)	1.499	1.504		
	C5-C6 (CP)	1.530 (2)	1.518 (1)	1.511	1.506		
	C-C wav	1.513	1.507	1.511	1.510		
	C2-C1-C4	89.7	90.0	90.0	90.0		
	C2-C1-C5 (av)	128.8	127.6	127.6	126.5		
	C5-C1-C6	61.5	60.9	60.6	60.4		
	C-C-H (av)	124.0 (6)		117.7	117.4		
	H-C-H (av)	113.2 (1.2)		115.2	115.8		
	4,4,8,8,12,12-hexamethyl-trispiro[2.1.2.1.2.1]-dodecane, twist-boat (22a)	ϕ^f	180.0	168.2	176.2	176.3	
C-C (CX) ^o		1.532 (10) ⁸		1.561	1.558 ^l		
C-C (CP)		1.514 (8)		1.517	1.518		
C-Me		1.592 (8)		1.559	1.558		
C-C wav		1.541		1.542	1.541		
C2-C1-C6 (CX)		119.4 (1.3)		108.9	107.1		
C1-C2-C3 (CX)		109.5 (7)		116.6	118.9		
C2-C3-C4 (CX)		116.8 (1.1)		110.2	107.7		
C3-C4-C5 (CX)		110.3 (1.7)		117.4	119.6		
Me-C-Me (av)		98.2 (1.8)		101.7	103.3		
C1-C2-C3-C4		54.4 (2.9)		55.1	57.4		
C2-C3-C4-C5		-28.1 (1.3)		-20.5	-24.9		
C3-C2-C1-C6		-25.2 (1.5)		-28.6	-30.1		
chair-twist-boat difference		only TB		10.9	6.2		
tricyclo[3.1.0.0 ^{2,4}]hexane, chair (18b)		C1-C2			1.545	1.549	1.504 ^{1,59a}
		C1-C5			1.512	1.513	1.547
		C1-C6			1.510	1.504	1.512
	C-C wav	1.508 (1) ^{20,u}		1.519	1.517	1.519	
	C2-C1-C6	109.9		118.0	110.4	109.6	
	C2-C1-H	128.8		120.5	123.4	125.6	
	C5-C1-H	127.8		124.6	126.0	128.3	
	C6-C1-H	119.2		121.1	125.0	122.6	
	C1-C6-H en	120.0		117.7	117.9	119.6	
	H-C6-H	110.0		115.3	115.3	114.7	
	θ^j	113.0		122.9	113.8	113.0	
tricyclo[4.1.0.0 ^{1,3}]heptane (24)	C1-C2	1.467 (7) ²⁴		1.515	1.499		
	C1-C3	1.521 (25)		1.549	1.522		
	C2-C3	1.528 (10)		1.486	1.494		
	C3-C4	1.523 (30)		1.526	1.526		
	C4-C5	1.574 (14)		1.542	1.561		
	C-C wav	1.517		1.521	1.516		
	C2-C1-C3	61.5 (5)		58.0	59.3		
	C2-C1-C7	162.4 (1.8)		154.0	160.7		
	C3-C1-C6	105.7 (2.6)		101.5	107.1		
	C1-C3-C2	57.5 (7)		59.9	59.6		
	C1-C3-C4	107.5 (1.3)		112.3	109.0		
	C3-C4-C5	102.3 (3.0)		105.5	106.2		
	H-C2-H	106.3 (8)		113.1	114.2		
	H-C4-H	108.4 (1.3)		107.9	107.8		
	C1-C3-C4-C5	-31.4 (1.2)		-14.6	-13.0		
	C3-C4-C5-C6	37.9 (1.4)		17.2	15.8		
	C4-C3-C1-C6	12.5 (5)		5.6	5.1		
θ^v	50.9 (5)		80.3	78.7			

^aC-C bond lengths were scaled from r_a to r_g values by adding 0.002 Å. ^bM = microwave analysis; X = X-ray diffraction; R = Raman spectroscopy; C = combined ED-MW study; D = MOCED (MO constrained ED). ^cPresent study. ^dBasis sets used: I = 4-21G; II = 4-31G; III = 6-31G; IV = 6-31G*. The 4-21G C-C bond lengths for compounds **8** and **18b** have been scaled from r_a to r_g and r_g values, according to the scheme suggested by L. Schaefer (refs 56 and 59a). ^eAll C-C bond lengths, except C-Me, are assumed values. ^fWeighted average. ^gO. Bastiansen, private communication, cited in ref 13. ^h θ = angle between planes. ⁱThe ring parameters were assumed to have the same values as the parent compound (ref 28a). ^j θ , ϕ = angles between C2-C1-C5-C4 and C1-C5-C6 or C2-C3-C4 planes, respectively. ^k θ = angle between C2-C1-C6-C5 and C1-C6-C7 planes. ^lAverage values, according to the S_6 symmetry. ^m53:47 gauche/trans mixture. ⁿThe C1-C1' bond length was determined indirectly; see ref 6. ^oCP = cyclopropane ring; CB = cyclobutane ring; CX = cyclohexane ring. ^p θ = angle between C1-C2-C4-C5 and C2-C3-C4 planes. ^q C_2 symmetry assumed. ^rED data of ref 22 were reanalyzed by using the MOCED (MO (4-21G) constrained ED) method. The right column is the "best fitting model". ^s ϕ = deviation from planarity. ^tMM bond lengths are average values. ^uThe reported experimental error for the individual bonds is 0.023 Å. ^v θ = angle between C1-C2-C3 and C1-C3-C6 planes. ^wUnits: distances, Å; angles, deg; moments of inertia, gm cm² exp(-39); dipole moments, D; energy, kcal/mol.

calculated the latter to be more stable (by 0.93 kcal^{2b}). This was corrected later by Ivanov, who calculated the gauche form as slightly favored (0.11 kcal^{2b}). In the present study, the gauche is found to be 0.22 kcal lower than the anti conformer (0.17 experimental¹⁰). The low anti-gauche barrier (0.6^{46b}), though

almost nonexistent in the force field calculation (0.01), is apparently enough to keep both (calculated) conformers as separate species.

The lengthening effect of the C1-C1' bond in the dimethyl derivative is indeed reproduced by MM3: The somewhat different

Table II. Cyclopropanes Vibrational Spectra

C-H Stretching Modes						
mode ^e	symm	experimental ^a		MM3 ^b		
		freq	assignment	no. ^c	freq ^d	difference
Cyclopropane (1)						
6	A2''	3102	CH stretching	1	3082	-20
12	E''	3083	CH stretching	2, 3	3079	-4
1	A1'	3038	CH stretching	4	3015	-23
8	E'	3024	CH stretching	5, 6	2990	-34
Bicyclo[1.1.0]butane (6)						
1	A1	3129	CH stretching	1	3114	-15
14	B1	3042	CH stretching, anti	2	3081	39
2	A1	3038	CH stretching, anti	3	3083	45
20	B2	3117	CH stretching	4	3099	-18
15	B1	2967	CH stretching, sym	5	3004	37
3	A1	2933	CH stretching, sym	6	3002	69
Other Cyclopropane Vibrational Modes						
mode ^e	symm	experimental ^a		MM3 ^b		
		freq	assignment	no. ^c	freq ^d	difference
2	A1'	1482	CH ₂ bending	7	1519	37
13	E''	1187	CH ₂ rocking	8, 9	1426	239
9	E'	1438	CH ₂ bending	10, 11	1370	-68
7	A2''	854	CH ₂ rocking	12	1224	370
3	A1'	1188	ring breathing	13	1209	21
10	E'	1028	CH ₂ wagging	14, 15	1097	69
4	A2'	1070	CH ₂ wagging	16	930	-140
14	E''	738	CH ₂ twisting	17, 18	833	95
11	E'	869	ring deformation	19, 20	803	-66
5	A1''	1126	CH ₂ twisting	21	761	-365
Other Bicyclobutane Vibrational Modes						
mode ^e	symm	experimental ^a		MM3 ^b		
		freq	assignment	no. ^c	freq ^d	difference
17	B1	1367	CH bending	8	1509	142
13	A2		CH bending	11	1324	
4	A1	1493	CH ₂ scissor	7	1518	25
5	A1	1261	CH bending	9	1394	133
19	B1	930	CH ₂ pendulum	10	1377	447
16	B1	1448	CH ₂ scissor	13	1264	-184
21	B2	1108	CH ₂ torsional	14	1237	129
6	A1	1240	skeletal	12	1297	57
18	B1	1143	skeletal	15	1105	-38
11	A2	1078	skeletal	16	1061	-17
23	B2	838	CH ₂ fan	17	968	130
8	A1	648	CH ₂ pendulum	18	954	206
7	A1	1088	skeletal	20	867	-221
12	A2	908	CH ₂ fan	19	869	-39
24	B2	735	CH bending	21	794	59
10	A2	1159? ^e	CH ₂ torsional	22	755	-404
22	B2	980	skeletal	23	745	-235
9	A1	422	ring deformation	24	345	-77

^a Experimental frequencies and assignment taken from refs 64a (cyclopropane) and 64b (bicyclobutane). ^b Present work. ^c Uncertain; in an earlier work (64c), the frequencies assigned to A2 are (in parenthesis the later numbers) 1497 (?), 1091 (1078), 914 (908), [657] (1159?). ^d Standard deviation, 147; average error, 24. Statistics for both compounds. The uncertain assignments, modes 10 and 13 in bicyclobutane, are not included. ^e The numerical value given under "mode" is the value from the experimental paper, and "no." under MM3 is the value in the MM3 output. The data on a single line refer to the same vibration, but these numbers differ because the MM3 numbers are sequential according to decreasing frequency, but the experimental values were divided according to symmetry, and then sequenced. ^f Standard deviation, 34; average error, 3.

(better), van der Waals (vdW) potential used in this force field^{63a} causes the nonbonding interactions involving the methyl groups to be ca. 1.4 kcal more positive in MM3 than in MM2 (the overall MM3-calculated vdW energy of the dimethyl derivative **23** is 1.37 kcal higher than that of the parent compound, while the respective MM2 difference is only 0.48). Partial relief of the nonbonding strain is obviously reached, during the geometry optimization process, through elongation of the bond connecting the two cy-

Table III. MM2/MM3 vs ED Bond Lengths Comparison^a

compound	average C-C bond length				
	ED	MM2 ^c	[difference ^b]	MM3 ^c	[difference ^b]
1	1.514	1.510	[-0.004]	1.512	[-0.002]
2	1.513	1.514	[+0.001]	1.515	[+0.002]
4a	1.514	1.516	[+0.002]	1.517	[+0.003]
6	1.508	1.506	[-0.002]	1.507	[-0.001]
7	1.488	1.496	[+0.008]	1.493	[+0.005]
8	1.532	1.529	[-0.003]	1.527	[-0.005]
10a	1.522	1.523	[+0.001]	1.525	[+0.003]
11a	1.537	1.524	[-0.013]	1.525	[-0.012]
14	1.532	1.529	[-0.003]	1.531	[-0.001]
16b	1.506	1.512	[+0.006]	1.512	[+0.006]
23	1.516	1.513	[-0.003]	1.515	[+0.001]
17a	1.519	1.515	[-0.004]	1.516	[-0.003]
17b	1.521	1.517	[-0.004]	1.517	[-0.004]
20	1.526	1.523	[-0.003]	1.523	[-0.003]
21	1.513	1.511	[-0.002]	1.510	[-0.003]
22a	1.541	1.542	[+0.001]	1.541	[0.000]
18b	1.508	1.519	[+0.011]	1.517	[+0.009]
24	1.517	1.521	[+0.004]	1.516	[-0.001]

^a Bond lengths in angstroms. For compound names and references, see Table I. ^b Difference = [MM] - [ED]. ^c Average error: MM2, -0.0004 (-0.0004); MM3, -0.0003 (-0.0002). Standard deviation: MM2, 0.0053 (0.0037); MM3, 0.0046 (0.0032). The values in parenthesis are error and deviation excluding compounds **11a** and **18b** (see text).

Table IV. MM2/MM3 vs MW Moments of Inertia Comparison^a

compound		moments of inertia		
		MW	MM2 ^b	MM3 ^c
2	<i>I_x</i>	5.412	5.498 (1.59)	5.450 (0.70)
	<i>I_y</i>	13.188	13.120 (-0.52)	13.283 (0.72)
	<i>I_z</i>	15.022	14.838 (-1.22)	15.046 (0.16)
6	<i>I_x</i>	4.847	4.708 (-2.87)	4.865 (0.37)
	<i>I_y</i>	9.010	9.261 (2.79)	9.057 (0.52)
	<i>I_z</i>	9.998	10.250 (2.52)	10.064 (0.66)
8	<i>I_x</i>	9.221	8.858 (-3.94)	9.131 (-0.98)
	<i>I_y</i>	13.725	14.356 (4.60)	13.859 (0.98)
	<i>I_z</i>	17.550	18.291 (4.22)	17.423 (-0.72)
9a	<i>I_x</i>	11.312	11.195 (-1.03)	11.365 (0.47)
	<i>I_y</i>	27.056	27.873 (3.02)	27.293 (0.88)
	<i>I_z</i>	31.637	32.801 (3.68)	31.860 (0.70)
9b	<i>I_x</i>	13.411	13.524 (0.84)	13.482 (0.53)
	<i>I_y</i>	24.594	24.802 (0.85)	24.425 (-0.69)
	<i>I_z</i>	29.514	29.947 (1.47)	29.262 (-0.85)
10a	<i>I_x</i>	15.140	14.943 (-1.30)	15.170 (0.20)
	<i>I_y</i>	19.807	20.160 (1.78)	19.886 (0.40)
	<i>I_z</i>	26.836	27.089 (0.94)	26.980 (0.54)

^a Moments of inertia in gm cm² exp(-39). For compound names and references, see Table I. ^b The values in parenthesis: difference = %-[MM2] - [MW]. ^c The values in parenthesis: difference = %-[MM3] - [MW]. ^d Average error: MM2, 0.97 (0.84); MM3, 0.25. Standard deviation: MM2, 2.52 (2.00); MM3, 0.66. The values in parenthesis are error and deviation excluding **8**.

clopropyl moieties. Thus, it was possible in MM3 to fit the C1-C1' bond length in both **16b** and **23** to within 0.002 Å, while matching almost exactly the ED average C-C bond length for **23**.

Tricyclic Compounds. The calculated geometry of tricyclo[2.2.1.0^{2,6}]heptane (nortricyclane) (**14**) agrees very well with the ED structure,^{17b} and MM2-ED differences being well below the reported experimental errors. The same can be said about the MM3 results, which reproduce even the individual C-C bond lengths and angles given by the ED model, to within 0.002 Å and 0.3°.

Tricyclo[5.1.0.0^{2,4}]octanes *trans*-**17a** and *cis*-**17b** were also investigated by the ED method alone.¹⁹ Here, the individual calculated bonds deviate quite a bit from the ED ones, though the trend is retained, and the difference in the way bond length is only 0.004 Å. The major discrepancy (and probably, the main reason for the others) is the very short (ED) bicyclopropyl-like bond lengths C1-C2 of 1.447 and 1.455 Å in the *trans* and *cis* isomers. The MM2 (MM3) values are much closer to that of

Table V. Heat of Formation (H_f° (g)) of Cyclopropanes^a

compound	exptl	method ^b	ref ^c	MM2 ^d	Δ^e	MM3 ^d	Δ^e
cyclopropane (1)	12.74 (0.14)	HG	C, 40c	13.17	0.43	12.95	0.21
methylcyclopropane (2)	6.19	VP	60	6.58	0.39	6.18	-0.01
1,1-dimethylcyclopropane (3)	-1.97 (0.28)	VP	P, 40	-2.07	-0.10	-1.50	0.47
cis-1,2-dimethylcyclopropane (4b)	1.3	CL	42a	1.62	0.32	0.71	-0.59
ethylcyclopropane (5)	1.1	CL	42a	0.01	-1.09	0.81	-0.29
bicyclo[1.1.0]butane (6)	51.9 (0.2)	HG	C, 42b	51.76	-0.14	52.12	0.22
spiropentane (7)	44.25 (0.18)	HG	C, 41	44.34	0.09	44.15	-0.10
bicyclo[2.1.0]pentane (8)	37.3	H2	42a	37.02	-0.28	37.30	0.00
bicyclo[3.1.0]hexane (10)	9.3 (0.8)	VP	C, 47	8.78	-0.52	8.84	-0.46
bicyclo[4.1.0]heptane (11)	0.4 (1.0)	VP	C, 47	1.45	1.05	0.55	0.15
nortricyclane (14)	19.62 (0.52)	VP	P, 45d	20.00	0.38	20.20	0.58
hexacyclopentane (15)	111.5	VP	7	111.70	0.20	111.47	-0.03
bicyclopropyl (16)	30.9 (0.9)	VP	C, 46b	30.90	0.00	30.90	0.00
[3]-prismane (19a)	136.4	AB	57a	136.73	0.33	136.46	0.06
quadracyclane (20)	81.04 (0.55)	VP	P, 45d	80.55	-0.49	80.94	-0.10
1,3-dimethylbicyclo[1.1.0]butane (25)	39.7	H2	42a	39.84	0.14	39.43	-0.27
1-methylbicyclo[3.1.0]hexane (26)	0.37 (0.31)	VP	P, 49	0.56	0.19	0.46	0.09
bicyclo[5.1.0]octane (27)	-3.8 (0.7)	VP	C, 47	-3.94	-0.14	-4.08	-0.28
bicyclo[6.1.0]nonane (28)	-7.6 (1.0)	VP	C, 47	-7.46	0.14	-7.54	0.06
standard deviation					0.44		0.28

^a Kilocalories per mole. ^b Methods of H_f° (g) evaluation: HG, direct calorimetric measurement in the gas phase; VP, calcd from H_f° (l) (H_f° (s) in **15**), and exptl heat of vaporization; H2, calcd from heat of hydrogenation; CL, estimated by using gas-phase group equivalent values of Franklin; AB, calculated at the MP2/6-31G* level with the use of a homodesmic reaction. ^c C = cited in Cox and Pilcher (ref 39a); P = cited in Pedley, Naylor, and Kirby (ref 39b). ^d This work. ^e [MM] - [exptl].

Table VI. Strain in Cyclopropanes

compound	C ^a	MM2		MM3	
		SI ^b	SI/C ^c	SI ^b	SI/C ^c
bicyclopropyl (16)	6	55.86	9.31	54.39	9.07
cyclopropane (1)	3	28.03	9.34	27.58	9.19
bicyclo[2.1.0]pentane (8)	5	56.67	11.33	53.34	10.67
spiropentane (7)	5	63.97	12.79	64.08	12.82
bicyclo[1.1.0]butane (6)	4	51.74	12.94	64.74	16.19
quadracyclane (20)	7	98.23	14.03	95.27	13.61
[3]-prismane (19a)	6	148.63	24.77	145.12	24.19

^a Number of carbon atoms. ^b SI (inherent σ strain) = steric energy + bond enthalpy - strainless bond enthalpy. ^c SI per carbon atom.

the open chain structures of **16** and **23**: 1.500 (1.498) and 1.505 (1.504) Å, respectively. While the angle between the cyclopropane rings and the plane defined by the two 1,2 substituents (θ in Table I) is calculated within the reported experimental error for both isomers, a larger difference is found for the "gauche bicyclopropyl" angle (dihedral angle C7-C1-C2-C4) in the trans form **17a**.

Only a single value is given (ED²⁰) for the bond lengths in the chair isomer of tricyclo[3.1.0.0^{2,4}]hexane (**18b**). This value, 1.508 Å, seems much too short even in comparison with cyclopropane itself, without considering the, usually longer, cyclobutane bonds. Ab initio (4-21G) calculations, when scaled to r_g values, give a wav bond identical with the MM2 one—1.519, and an experimental scaling problem has been raised as an explanation for the difference.^{59a} The 4-21G structure suggests the C1-C2 bond to be short (1.504) and the C1-C5 to be long (1.547) in the cyclobutane ring. The opposite sequence is obviously given by MM2 in analogy with the other cases of a 22-22 bond included in a cyclobutane (but not a cyclopropane) ring. Interestingly, the boat isomer is calculated (4-21G^{59a}) to have the regular sequence in bond lengths, in close agreement with the MM2 values. While these phenomena are mentioned here, no attempt has been made to explain them. As in the similar 3:4 structure in the bicyclo compounds **8** and **9**, the interplanar angle is calculated too flat by MM2. While providing the correct ED/MO interplanar angles, the MM3 wav bond length still resembles the MO/MM2 values (1.517) and bond length sequence given by MM2.

Tetracyclic Compounds. Two tetracyclic structures have been investigated in this study. The highly symmetrical (D_{3h}) tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane ([3]-prismane) was the last of the valence isomers of benzene to be synthesized.⁶⁸ The structure of the parent compound **19a** is not known experimentally, but has been studied extensively by ab initio^{57,58} and semiempirical⁶⁶ methods. An ED study on the hexamethyl derivative **19b**²¹ resulted

in several models in which the C1-C2 bond (in the cyclopropane rings) ranges from 1.500 to 1.546 Å, while the cyclobutane bond C1-C4 varies between 1.544 and 1.588 Å. The researcher's selection of one of the higher R factor models, with only minor differences between the two bonds (1.540 and 1.551) as his preferred one,⁶⁹ has been questioned in view of the ab initio (4-21G) results.⁵⁸ Indeed, all of the basis sets used, from STO-3G to 6-31G*,^{57b} clearly indicate that the cyclobutane bond is 0.03-0.04 Å longer than the cyclopropane one. As the latter results are in agreement with the scheme presented for such bonds in MM2 and MM3 (see above), we decided not to include **19b** in the data set. The force field structures thus obtained closely resemble the 6-31G* results, both in C-C bond lengths and in C-C-H bond angles. Another problem existed in older versions of MM2 in that the D_{3h} form of **19** was actually a high-energy saddle point, and a crude starting geometry always lead to the lower symmetry D_3 conformation. This error has been corrected by changing the appropriate torsional potential (type 22-22-22-22 in a four-membered ring; see Tables VII and VIII), while still maintaining sufficient strain as is needed to calculate a reasonable heat of formation (vide infra).

A previous ED study of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadracyclane) (**20**)²² has been revised using constraints from ab initio (4-21G) calculations.^{59b} Two similar models have been proposed for the compound, with almost the same R factor, both quite different in individual bond lengths from the original models. All those models, as well as ab initio calculations with several basis sets (STO-3G,^{59c} 4-21G,^{59a,b} 6-31G^{59c}), show the C1-C5 bond to be much longer than the C1-C7 one. The MM2 structure agrees well with the "best fitting" model of ref 59b (see Table I). MM3, while giving a slightly larger C1-C5 to C1-C7 difference, still comes out with the same average bond length, and very similar C-C-C bond angles.

Compounds Containing a Spiro Configuration. The smallest possible spiro configuration [3.3] presents a highly strained structure, in which the central carbon has two small C-C-C angles of about 62°, and two widely open ones of ca. 137°. For the parent compound spiropentane (**7**), the ED analysis¹⁴ (D_{2d} symmetry assumed) shows a very short wav bond length of 1.488 Å. Short bonds are also calculated by MM2 with a similar sequence (the bond connected to the central carbon being 0.05 Å shorter than the peripheral one), but the average bond length is 0.008 Å longer than the ED value. The deviations in bond angles are fully reproduced. A slightly smaller difference between the longer and shorter bonds is calculated by MM3 (0.04 vs 0.05 Å in ED and MM2), but the wav bond length is closer to the ED value (only

Table VII. MM2 Parameters for Cyclopropanes^a

stretching parameters			bending parameters				
bond	K_s	l_0	angle	K_b	θ_0		
					type 1 ^c	type 2	type 3
1-22 ^b	4.40	1.502	22-22-22	0.35	119.14	120.70	
(3) 22-22	4.40	1.503	(4) 22-22-22	0.45	112.50	98.00	
(4) 22-22	4.40	1.528	(3) 22-22-22	0.45	55.80	60.00	60.00
22-22	4.40	1.474	22-1-22	0.45	112.00		105.00
5-22	4.60	1.086	1-22-22	0.60	118.20	118.20	
			(4) 1-22-22	0.34		119.30	
			1-1-22	0.45	112.40	112.40	112.40
			(4) 1-1-22	0.34		112.30	112.30
			1-22-1	0.45	120.00		
			5-1-22	0.36	109.41	109.41	109.41
			1-22-5	0.36	123.50		
			5-22-22	0.36	124.50	119.70	
			5-22-5	0.32	120.60		

Torsional Parameters							
angle	V1	V2	V3	angle	V1	V2	V3
22-22-22-22	-0.520	0.000	0.160	22-1-22-1	0.200	0.270	0.093
(4) 22-22-22-22	6.070	0.000	-0.880	1-1-1-22	0.200	-0.200	0.600
22-1-22-22	0.000	0.000	0.300	5-22-22-22	0.000	0.000	0.167
1-22-22-22	0.200	0.270	0.093	5-22-22-5	0.000	0.000	0.137
(4) 1-22-22-22	0.200	0.270	1.533	1-22-22-5	0.000	0.000	0.120
1-22-22-1	0.200	0.270	0.240	5-1-22-22	0.000	0.000	0.120
(4) 1-22-22-1	0.200	0.270	2.500	22-1-22-5	0.000	0.000	0.120
22-1-1-22	0.200	0.270	0.093	5-1-22-1	0.000	0.000	0.690
(4) 22-1-1-22	0.200	0.270	1.533	5-1-1-22	0.000	0.000	0.167
1-1-22-22	0.300	0.000	0.450	1-1-22-5	0.000	0.000	0.267
(4) 1-1-22-22	0.200	0.270	1.533	5-1-22-5	0.000	0.000	0.690

Heat Parameters					
bond/structural feature	normal	strainless	bond/structural feature	normal	strainless
1-22	-2.239	0.493	four-membered ring correction	1.827	0.000
5-22	-3.205	-3.125	acyclic correction	-9.446	0.000
22-22	7.553	0.493	cyclopropane ring	2.485	0.000

^a Atom types: 1 = C (sp³); 5 = H (-C); 22 = C (in a cyclopropane ring). ^b (4) = within a four-membered ring; (3) = within a three-membered ring. ^c Type 1 = -CR₂-; type 2 = -CRH-; type 3 = -CH₂-.

0.005 Å longer), and the angles still deviate by only 0.5° (av) from the ED model.⁸¹

In tricyclo[4.1.0.0^{1,3}]heptane (**24**), the [3.3] spiro structure is further distorted by the ethylene bridge. The average bond length calculated by MM2 is only 0.004 Å longer than the ED²⁴ value, but the shortest bond is found to be the peripheral C2-C3 bond in the spiro system, rather than one of the bonds containing the quaternary carbon—C1-C2, according to the interpretation of the ED data. The researchers suggest a strong tendency of the C2-C1-C7 bonds toward an sp hybridization, since the respective bond angle reaches 162° (154° in MM2). The effect is probably much too large for the mechanism included in the force field to account for small variations in bond lengths due to distorted adjacent bond angles (and vice versa), namely, the stretch-bend coupling term. In fact, the distortion around the spiro center is so severe that its four substituents point in the same direction, resembling the arrangement in [1.1.1]propellane. The relatively poor description of this extreme case by MM2 is further manifested in the dihedral angles and the angle between the cyclopropane ring and the C1-C3-C6 plane (θ in Table I), resulting in a (MM2 calculated) much too flat cyclopentane ring. The situation is slightly improved in MM3: The ED-MM bond angle differences are only about half of those found with MM2 (with a C2-C1-C7 angle of 160.0°), and closer bond lengths. The

shortest bond is still found to be C2-C3, but C1-C2 is only 0.005 Å longer, and the wavy C-C bond length is actually identical with the ED value. The MM3-calculated dihedral and interplanar angles are calculated closer to the MM2 values, rather than to the experimental ones.

A series of compounds constructed of only cyclopropane carbons, the polycyclopropylspiranic derivatives, or [n]-rotanes, has been synthesized and investigated.^{23,38,70} The only one of them to have had its structure determined in the gas phase is the tetraspiro[2.0.2.0.2.0.2.0]dodecane ([4]-rotane) (**21**), which was studied recently by the Oslo group,²³ in a combined ED/X-ray analysis. The results, listed in Table I, show a good agreement between the calculated and experimental geometries, the main points being a relatively long bond (1.536 Å, ED; 1.539 and 1.536 in MM2 and MM3, respectively) in the cyclobutane ring, and much shorter ones (1.490–1.500 Å) in the three-membered rings. The central ring was found to be planar in the crystal but slightly bent (168.2°, ED) in the gas phase. The MM2/MM3 models describe an intermediate structure with a deviation from planarity of ca. 176°. Earlier X-ray diffraction analysis³⁸ resulted in a significantly different geometry, despite the common origin of the sample used.²³ The reported bond lengths were 1.463 (5) and 1.477 (4) Å for the cyclobutane and 1.515 and 1.496 Å for the peripheral cyclopropane rings, giving an average C-C bond of 1.499 Å, considerably shorter than the later results.⁷¹ Since the earlier work was clearly of lower quality (done at room temperature by using only 478 reflections, as opposed to 2184 reflections collected at 115 K by the Oslo group), we preferred the later work as a reference. Accordingly, the X-ray structures of the other rotanes ([3], [5], [6]) determined by the same researchers,^{38b} were not considered for parametrization purposes. (The quoted bond lengths are nevertheless quite close to the MM2-calculated ones.⁷² For example, in [3]-rotane, the observed

(81) According to MM3, the stable structure for spiroheptane has C_2 symmetry, and so it is a double minimum. The D_{2d} structure lies between the two C_2 structures and has two negative eigenvalues in its force constant matrix, but lies only 0.16 kcal/mol above the C_2 structure. This means that the MM3 potential surface is actually quite complicated in the vicinity of the minimum. It seems likely that these complications are artifacts of the computational method, rather than being physically real. In any event, these complications lie well below the first vibrational level, and have little influence on the actual structure of the molecule.

Table VIII. MM3 Parameters for Cyclopropanes^a

stretching parameters			bending parameters				
bond	K_s	l_0	angle	K_b	θ_0		
					type 1 ^c	type 2	type 3
1-22 ^b	5.00	1.511	22-22-22	0.36	119.50	112.50	
(5) 1-22	5.00	1.510	(3) 22-22-22	0.85	55.00	60.00	60.00
(3) 22-22	5.00	1.503	(4) 22-22-22	0.70	96.50	96.50	
(4) 22-22	5.00	1.552	(5) 22-22-22	0.55	122.00	108.50	
22-22	5.00	1.485	1-22-22	0.60	112.00	116.30	
(4) 22-56	4.40	1.526	(5) 1-22-22	0.60	112.00	117.00	
5-22	5.08	1.086	22-1-22	0.48	112.60	114.00	
			(5) 22-1-22	0.50			112.00
			1-22-1	0.67	120.00		
			1-1-22	0.35	114.40		114.40
			(5) 1-1-22	0.60			112.00
			1-56-22	0.67		111.20	
			(4) 22-22-56	0.20		112.00	
			(5) 22-22-56	0.60		111.60	
			(4) 22-56-56	0.20		114.00	114.00
			5-22-56	0.36	113.00		
			5-56-22	0.36	112.00	112.00	
			5-22-22	0.65	116.80	114.20	
			5-22-5	0.25	116.50		
			1-22-5	0.60	117.10		
Small Rings Angle Corrections ^d							
			type 1	type 2	type 3		
	[3]		3.00	11.00	-10.00		
	[3:4]			6.70	-9.00		
	[3:5]			0.00	-4.30		
Torsional Parameters							
angle	V1	V2	V3	angle	V1	V2	V3
22-22-22-22	-0.940	0.600	0.160	(4) 22-56-56-22	0.200	0.270	1.533
(4) 22-22-22-22	5.220	-0.450	-1.200	(4) 56-22-22-56	0.200	0.270	1.533
(5) 22-22-22-22	-0.500	2.800	2.200	22-22-56-1	0.185	0.170	0.495
1-22-22-22	0.200	0.000	0.093	1-56-56-22	0.185	0.170	0.495
(5) 1-22-22-22	0.000	0.000	0.500	5-56-56-22	0.000	0.000	0.167
22-1-22-22	-0.060	0.000	0.220	5-22-56-56	0.000	0.000	0.267
(5) 22-1-22-22	0.700	0.400	0.700	5-22-22-56	0.000	0.000	0.120
1-1-22-22	0.000	0.000	0.250	22-22-56-5	0.000	0.000	0.120
(5) 1-1-22-22	0.050	-0.200	1.000	5-22-56-5	0.000	0.000	0.690
22-1-1-22	0.500	0.200	0.300	5-1-56-22	0.000	0.000	0.280
(5) 22-1-1-22	0.400	0.000	0.300	5-22-56-1	0.000	0.000	0.280
1-22-22-1	0.200	0.270	0.093	1-1-22-5	0.000	0.000	0.170
(5) 1-22-22-1	0.200	0.270	0.500	5-1-22-22	0.000	0.000	0.350
1-22-1-22	0.185	0.170	0.520	5-1-22-5	0.000	0.000	0.700
1-1-22-1	0.000	0.000	0.300	5-1-1-22	0.000	0.000	0.167
(5) 1-1-1-22	-0.600	-0.400	0.650	5-1-22-1	0.000	0.000	0.690
22-22-22-56	0.200	0.270	0.093	22-1-22-5	0.000	0.000	0.120
(5) 22-22-22-56	0.200	0.270	0.093	1-22-22-5	0.000	0.000	0.120
(4) 22-22-56-56	0.200	0.270	1.533	5-1-22-22	0.000	0.000	0.350
(5) 22-22-56-56	0.300	0.000	0.450	5-22-22-22	0.000	0.000	0.167
				5-22-22-5	0.000	0.000	0.137
Torsion-Stretch Parameters							
	bond			k_{TS}			
	22-22			0.0530			
Heat Parameters							
bond/structure	normal	strainless	bond/structure	normal	strainless		
1-22	2.335	3.506	four-membered ring correction	-7.198	0.000		
5-22	-4.590	-4.590	acyclic correction	-12.342	0.000		
22-56	5.529	3.506	cyclopropane ring	-4.095	0.000		
22-22	12.661	3.506					

^a Atom types: 1 = C (sp³); 5 = H (-C); 22 = C (in a cyclopropane ring); 56 = C (in a cyclobutane ring). ^b (*n*) = within an *n*-membered ring, *n* = 3, 4, 5. If the bond is common to two or more rings of different sizes, the smallest value is always used. ^c Type 1 = -CR₂-; type 2 = -CRH-; type 3 = -CH₂-. ^d [*n*] = *n*-membered ring; [*n*:*m*] = fused *n*- and *m*-membered rings; see text for the definitions of the various cases.

(calculated) bonds are 1.465 (1.468) and 1.499 (av 1.495) for the central and peripheral rings, respectively.)

Turning to the only sample of a [3.6] spiro structure that has been solved in the gas phase, 4,4,8,8,12,12-hexamethyltrispiro-[2.1.2.1.2.1]dodecane (**22**),⁸ we find a preference of a twist boat conformation for the cyclohexane ring over the chair one. The

large calculated difference between the two forms (ca. 11 kcal/mol in MM2, and 6.2 in MM3) is in accordance with the ED interpretation, which shows a much better fit of the TB model **22a** to the experimental radial distribution curve. The central ring in the chair conformer **22b** is calculated to be flattened considerably compared with that of cyclohexane (ring torsional angles

of $\pm 43^\circ$ vs 54° , see also MM2 calculations in ref 8). What seem to be similar force field calculations, using the Osawa-Ivanov MM2',^{2b} indicate no such effect in the chair form, while finding it to be slightly favored by 0.2 kcal. The difference in the results can be attributed to the use of large V_3 terms in the 22-1-22-1 and 22-1-22-22 torsional potentials⁸ by these researchers. The latter V_3 terms were also included in earlier versions of MM2 ($V_3 = 4.8$), but have now been replaced by a more realistic barrier of 0.3 kcal (Table VII). The MM2/MM3 wav C-C bond lengths of **22a** (the TB conformer) are almost exactly the same as the ED ones, and this is also true for the cyclopropane rings, although most of the individual bond lengths and angles are slightly different. The low symmetry (C_2) of this molecule and its relatively large size (18 heavy atoms) result in many different overlapping bonded and nonbonded distances (132 of the latter, excluding C...H and H...H), and make the RD curve quite flat and difficult to resolve.⁸ A noticeable difference between the MM2/MM3 and the ED models is in the cyclohexane ring bond angles: Those were found to alternate between $109.5-111^\circ$ and $117-119.5^\circ$ for the spiro and *gem*-dimethyl positions, respectively. MM2/MM3 find the same alternation ($107.1-110.2^\circ$ and $116.6-119.6^\circ$), but in the reverse order, making the ring angle containing the spiro carbon more widely open. As the angle between the two substituents is obviously much smaller in the latter case, and ED result seems somewhat odd. Being aware of this contradiction, the researchers have remarked that "more accurate data on other overcrowded cyclohexanes are needed to establish whether the observed angle differences are artifacts or represent real physical phenomena".

In this context, it may be worthwhile mentioning another crowded compound, 1,1,1,2,2,2-hexacyclopentane (**15**). The S_6 structure has been solved only in the solid phase (X-ray diffraction analysis⁷), and hence was not used in refining the geometry parameters. Nevertheless, it is interesting to note that the MM2/MM3-calculated structure went through a significant relaxation after relieving the redundant strain originating from the above-mentioned unrealistic 22-1-22-22 torsional potential. This also resulted in a structure closer to the experimental one, in particular concerning the central C-C bond, which is one of the longest known for saturated hydrocarbons (1.625 (6) Å according to the X-ray, 1.627 and 1.626 in MM2 and MM3), and the C2-C1-C3-C4 torsional angle (90.7 and $84.6/84.3^\circ$, respectively; compare earlier MM2 results in ref 7). The exaggerated steric strain caused by the old potential also precluded the possibility of calculating a reasonable heat of formation for **15**, resulting in an overestimation by more than 40 kcal.⁷ Following the adjustment discussed, the experimental value was easily reproduced (see next section).

III. Heat of Formation and Strain Energy. Heat of formation is calculated in MM2 by using the following formula:

$$H_f^\circ = SE + BE + PFC$$

where SE is the "steric energy" calculated by the force field for the global minima (lower conformer), BE is the sum of the bond and structural enthalpy increments, and PFC includes contributions from higher conformational population (POP), torsional contributions (TOR), and a constant translation/rotation term (T/R). Hence, for each case, all the possible low-lying conformers had to be calculated and accounted for.

Most of the strain needed to calculate reasonable heats of formation for cyclopropanes has been introduced by properly adjusting the bending and torsional potentials. The rest were fit by using five heat parameters. Those included, beside the 1-22 and 22-22 bond increments (the 5-22 has been left equal to 1-5), and the three-membered ring structural parameter (no. 47 in MM2, 56 in MM3), two new correction terms: (i) for a 22-22 bond in an open chain or in a ring larger than cyclobutane and (ii) for a 22-22 bond included in a four- (but not three-) membered ring (vide supra). Since in the MM3 force field carbon atoms included in a cyclobutane ring (but not in a cyclopropane one) are assigned a separate type—56, an additional bond increment, namely, 22-56, had to be defined. The heat parameters were

optimized by using an rms procedure, giving a final standard deviation of 0.44 (MM2) and 0.28 kcal (MM3) for 19 compounds. The calculated and experimental gas-phase heats of formation are listed in Table V, together with the references and the experimental errors. Going over the calculated results and their deviation from experimental values, one can see that for MM2 in 17 cases the difference is less than or equal to 0.5 kcal/mol, and almost always well below the experimental error (when given). MM3 yields a calculated - experimental difference of less than 0.6 kcal/mol for all the 19 compounds. Thus, H_f values for saturated hydrocarbons containing three-membered rings may now be calculated with the same degree of accuracy as those for hydrocarbons in general.

It may be pointed out that the MM2 heat parameter scheme for cyclopropanes is not completely consistent with that of saturated (sp^3) hydrocarbons: Originally, the program did not count substituted 22-type carbon centers together with the saturated ones. No special "iso", "neo", and "methyl" parameters have been determined for the appropriate structural units involving a 22-type carbon. Including such parameters in the optimization process did not result in any improvement in the individual calculated heats of formation, nor in the standard deviation. In the new MM3 force field, the substitution degree for the 22-type atoms is included, through counting the cyclopropane atoms together with the other carbons. The regular cyclopentane and cyclobutane structural increments (the latter was 0.0 in MM2) were used in the calculations to account for the rather complicated ring structures. (All three-, four-, and five-membered ring structures are counted, even when they contain smaller rings in a fused fashion).

Some remarks should be made regarding the experimental heats of formation.

(1) The preferred source for gas-phase heat of formation data is a direct calorimetric measurement in the gas phase (indicated by HG in Table V). Only three values in Table V originate from such measurements while eleven others were found by condensed-phase calorimetry and heat of vaporization or sublimation (VP). In addition, there are two values resulting from hydrogenation experiments (HG), a theoretical H_f (MP2/6-31G* using a homodesmotic reaction,^{57a,b} AB) and two others that are only estimated values (marked CL). It may be noted that the two exceptionally large errors in Table V (for MM2, 1.09 and 1.05 kcal for compounds **5** and **11**) consist of one case of estimated H_f (**5**), and another of quite inaccurate measurement (**11**, reported experimental error of 1.0 kcal).








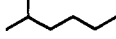

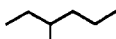



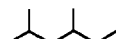

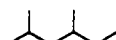



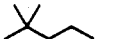

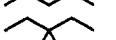

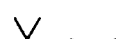

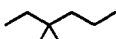










(2) Some compounds for which experimental H_f can be found were not included in Table V.

(i) **Tricyclo[4.1.0.0^{2,4}]heptane (29)** (Figure 1). While this compound may exist as a *cis* or *trans* isomer, no reference can be found in the experimental work⁷³ regarding the isomer tested. Moreover, the reported physical properties (bp, n) do not fit any of the isomers as has been published in an earlier synthetic work.⁷⁴

(ii) **1-Methylbicyclo[4.1.0]heptane (30)**. The reported experimental H_f is -4.96 (0.36) kcal/mol.⁴⁹ This value seems to be much too positive considering the parent compound **11** (0.4 kcal). The difference in H_f for the corresponding bicyclo[3.1.0]hexane couple (**10** and **26**) is 8.9 kcal, and a careful analysis of the change in H_f upon H/Me substitution in hydrocarbons (Table IX) indicates that the difference should be at least 7 kcal. The MM2-calculated H_f is indeed -7.36 kcal/mol (-7.07 in MM3), as expected.

(iii) Different values can be found in the literature for hexamethylprismane (**19b**). Those values (for example, 65.3 kcal/mol by J. F. M. Oth⁵⁰) seem to be much too negative in comparison with the ab initio H_f calculated for prismane itself (**19a**) (136.4^{57a}). The difference, 71 or 11.8 kcal per methyl group, is too high, even if we disregard the *cis*, 1,2 interactions between the methyl groups (six such interactions along the short cyclopropane bonds; for comparison, the difference in H_f between cyclopropane and its methyl derivative is 6.5 kcal, but between cyclopropane and its *cis*-1,2-dimethyl derivative, only 11.4 kcal). We preferred to use the ab initio value for prismane (see above), as this method has

Table IX. Change in the Gas-Phase Heat of Formation upon Methyl Substitution in Hydrocarbons^a

H	R-H → R-Me	$H_f(R-H)$	$H_f(R-Me)$	ΔH_f	av (std dev) ^b
Acyclic Hydrocarbons					
secondary					
		-30.36 (0.16)	-36.85 (0.15)	-6.49 (0.31)	
		-35.10 (0.15)	-41.77 (0.24)	-6.67 (0.39)	
		-35.10 (0.15)	-41.13 (0.24)	-6.03 (0.39)	
		-39.92 (0.18)	-46.52 (0.28)	-6.60 (0.46)	
		-39.92 (0.18)	-45.73 (0.47)	-5.81 (0.65)	
		-41.77 (0.24)	-48.21 (0.29)	-6.44 (0.53)	
		-46.52 (0.28)	-52.40 (0.33)	-5.88 (0.61)	
		-46.52 (0.28)	-53.18 (0.40)	-6.66 (0.68)	
					-6.32 (0.33)
tertiary					
		-36.85 (0.15)	-44.48 (0.24)	-7.63 (0.39)	
		-41.77 (0.24)	-49.20 (0.37)	-7.43 (0.61)	
		-41.13 (0.24)	-48.08 (0.29)	-6.95 (0.63)	
		-46.52 (0.28)	-53.68 (0.32)	-7.16 (0.60)	
		-45.73 (0.47)	-52.58 (0.32)	-6.85 (0.79)	
					-7.20 (0.29)
Cyclic Hydrocarbons					
secondary					
		-18.44 (0.20)	-25.27 (0.18)	-6.83 (0.38)	
		-29.50 (0.15)	-36.98 (0.25)	-7.48 (0.40)	
					-7.16 (0.33)
tertiary					
		-25.27 (0.18)	-33.04 (0.28)	-7.77 (0.46)	
		-36.98 (0.25)	-43.23 (0.47)	-6.25 (0.72)	
					-7.01 (0.76)
Polycyclic Hydrocarbons					
tertiary					
		-32.12 (0.56)	-40.69 (0.99)	-8.57 (1.5)	

^a Experimental $H_f(g)$ taken from Cox and Pilcher (mostly) or from Pedley, Naylor, and Kirby;^{39a,b} cases of 1,2-dimethyl interaction were excluded.

^b All secondary and tertiary substituents av (std dev) = -6.86 (0.72).

been shown to reproduce experimental heats of formation within a very small error.^{57a,b,75}

(iv) The value of -15.5 kcal/mol (-15.2 calcd) cited by P. M. Ivanov,^{2b} among others, as the experimental H_f of 1,3,5-trimethylbicyclo[3.1.0]hexane (**32**), can be traced back to *Reaction Heats and Bond Strengths*, a book by C. T. Mortimer⁷⁶ from the early 1960s. The latter, which is "based on a series of lectures given to postgraduate students at the University of Keele, 1960", does not pretend to give accurate thermodynamic data needed for parametrizing force fields. And indeed, while quoting a reported heat of combustion for the subject compound (the figure shown for this example is of another isomer, **33**, but this may be attributed to merely a drawing error) in the liquid phase (-1369.5 ± 0.5 kcal/mol⁷⁷), it continues: "This leads to a heat of formation of the gaseous compound of about -15.5 kcal/mol". Going over the arithmetic in reverse order, one may calculate the $H_f(l)$ of **32** to be -23.5 kcal/mol, and conclude that a value of 8 kcal for the

heat of vaporization has been used. While the latter may be considered a reasonable estimate for the researcher's purpose (demonstration of strain evaluation in various systems), it is obviously not good enough for our purposes. As was already said, this example has been excluded from the current treatment. Nevertheless, we calculated the MM2 (MM3) H_f for the two isomers of **32**, taking into account all the possible conformers. The results -14.18 (-13.91) and -12.35 (-12.06) were both more positive than the above-mentioned values, but may be considered at least as good: By choosing one of the many methods developed to estimate heat of vaporization in hydrocarbons (Laidler-Lovring⁷⁸) and extending it to three-membered rings (see Table X), a H_v of 9.7 kcal/mol was calculated for **32**. The "corrected" experimental $H_f(g)$ is then -13.8, only 0.4 (0.1) kcal higher than the MM2 (MM3) calculated H_f for the more stable isomer.

According to the usual scheme of MM2, the strainless heat parameters have been assigned as follows: The C-C (1-22, 22-22)

Table X. Cyclopropanes Heat of Vaporization Parameters^a

EQ	WT	H_v (calcd)	H_v (exptl)	difference (calcd - exptl) ^b	compound
1	10	6.52	6.58	-0.06	spiropentane (7)
2	10	6.04	6.00	0.04	1,1-dimethylcyclopropane (3)
3	10	8.13	8.00	0.13	bicyclopropyl (16)
4	10	7.83	7.92	-0.09	bicyclo[3.1.0]hexane (10)
5	10	9.11	8.84	0.27	quadracyclane (20)
6	10	8.74	9.17	-0.43	nortricyclane (14)
7	10	8.95	9.12	-0.17	bicyclo[4.1.0]heptane (11)
8	10	8.23	8.30	-0.07	1-methylbicyclo[3.1.0]- hexane (26)

Best Values

S3 = 0.815 (no. of secondary cyclopropane hydrogens)
T3 = 0.805 (no. of tertiary cyclopropane hydrogens)
Pr3 = 0.463 (no. of methylcyclopropane hydrogens)
C12 = 0.485 (no. of cis-1,2-substitutions on a cyclopropane ring)

^aThe formula and the parameters for cyclopentane and cyclohexane rings were taken from K. J. Laidler^{78a} and E. G. Lovering et al.^{78b} ^bStandard deviation 0.20.

and the C-H (5-22) bond increments have been given the same values as a C(sp³)-C(sp³) (0.493) and C(sp³)-H (-3.125), respectively (the MM3 values are 3.506 and -4.590). The other three parameters (corrections for different 22-22 types, and three-membered ring) were set to zero. With use of these parameters, together with the normal heat parameters and the calculated steric energies, reasonable strain energies (SI) could be calculated for the various polycyclic structures. Some examples are given in Table VI, and with use of a "strain per carbon atom" criteria, the following order (MM2) was found:

bicyclopropyl ≤ cyclopropane < bicyclo[2.1.0]pentane < spiropentane ≤ bicyclo[1.1.0]butane < quadracyclane < prismane

In the MM3 scheme, some extra strain has been attributed to the [1.1.0] structure (compounds 6 and 25), in comparison with the various [2.1.0] ones (e.g., 8, 18, 20). Hence bicyclobutane

(6) precedes quadracyclane (20) in the above sequence.

Conclusions

A new scheme and parameter set for cyclopropanes have been developed and incorporated into the MM2 and MM3 force fields. This improved treatment solves many of the deficiencies existing in earlier versions of MM2, and is superior to other, previously suggested, schemes.² Heats of formation for cyclopropanes are now calculated with the same degree of accuracy as for hydrocarbons in general. Due to a more detailed treatment of the angles (θ_0) in the fused and spiro small ring structures in MM3, the latter performs a little better in reproducing the experimental (especially MW-based) geometries.⁸²

Acknowledgment. We are indebted to the National Institutes of Health (Grant No. R24 RR02165), the National Science Foundation (Grant No. CHE 8614548), and Glaxo Inc. for support of this work.

Registry No. 1, 75-19-4; 2, 594-11-6; 3, 1630-94-0; 4a, 2402-06-4; 4b, 930-18-7; 5, 1191-96-4; 6, 157-33-5; 7, 157-40-4; 8, 185-94-4; 9a, 50338-80-2; 9b, 30163-38-3; 10, 285-58-5; 11, 286-08-8; 14, 279-19-6; 15, 26902-55-6; 16, 5685-46-1; 17a, 50895-58-4; 17b, 50695-42-6; 18b, 21531-33-9; 19a, 650-42-0; 20, 278-06-8; 21, 24375-17-5; 22a, 103495-76-7; 23, 59020-33-6; 24, 174-73-2; 25, 930-25-6; 26, 4625-24-5; 27, 286-43-1; 28, 286-60-2.

(82) After the completion of this study, we were notified of preliminary results of MO ab initio calculations that have been done on bitetrahydyl (34 in Figure 1).⁷⁹ This is a very interesting example for the short, exocyclic, 22-22 bond, since from theoretical considerations, the bond connecting the two tetrahedrane moieties is expected to be the shortest one possible for saturated hydrocarbons. The ab initio calculated bond length was 1.449 (STO-3G) or 1.444 Å (DZ+P). MM3 gives a bond length of 1.449 Å, in good agreement with the MO results. It should be stated that MM2 fails to give the correct geometry of bitetrahydyl, as well as its parent compound tetrahedrane: The large difference between the natural and the actual CCH bond angle causes the whole MM2 structure to converge into a nonsymmetric form. This is avoided in MM3 due to the angle corrections mechanism, which reduces the above gap, while still keeping it large enough to reproduce the extreme shortening of the central (as well as other) bonds. Tetrahedrane and bitetrahydyl were not used in the MM3 parametrization as these ab initio results were obtained after the parametrization was completed.

Theoretical Study of the Reactions of Pentacoordinated Trigonal-Bipyramidal Compounds: PH₅, PF₅, PF₄H, PF₃H₂, PF₄CH₃, PF₃(CH₃)₂, P(O₂C₂H₄)H₃, P(OC₃H₆)H₃, and PO₅H₄⁻

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Abstract: We have studied pseudorotation reactions of some pentacoordinated phosphorus compounds [PH₅, PF₅, PF₄H, PF₃H₂, PF₄CH₃, PF₃(CH₃)₂, P(O₂C₂H₄)H₃, P(OC₃H₆)H₃, and PO₅H₄⁻] to elucidate the reaction mechanisms by using ab initio SCF and MP4 methods. We have calculated the potential surface for the lowest pass of pseudorotation reactions. The geometries of the transition state connecting them have been determined theoretically. The ligands which form the covalent bond with the central phosphorus atom such as hydrogen, methyl, and methylene groups prefer to coordinate in the equatorial position. This nature of the ligands is called as the *equatoriphilicity*. It is possible to predict whether the pseudorotation reaction can occur or not, based on the number of the equatoriphilic ligands in the pentacoordinated molecules. The normal coordinate analyses have been carried out at the stationary points of PH₅ and PF₅. The mechanism of pseudorotation is discussed and explained on a theoretical basis.

1. Introduction

The different behavior in the hydrolysis reaction between DNA and RNA is an interesting fact related to their different roles in the biochemical system. DNA molecules, which work as tapes

for the storage of genetic information show very strong resistance to the decomposition by hydrolysis. Even after a 1-h reaction at 100 °C in 1 N NaOH (aq) DNA molecules do not show any changes.¹ On the other hand, 2-hydroxyethyl methyl phosphate,

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(1) Dugas, H.; Penney, C. *Bioorganic Chemistry. A Chemical Approach to Enzyme Action*; Springer-Verlag: New York, 1981.