Structures of Norbornane and Dodecahedrane by Molecular Mechanics Calculations (MM3), X-ray Crystallography, and Electron Diffraction

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Abstract: Many molecules including the title compounds contain carbon–carbon bonds, which are eclipsed or nearly so, and these bond lengths were calculated to be too short by the MM2 molecular mechanics program. This has been corrected in MM3 with the aid of a torsion–stretch interaction. This correction has been examined computationally and experimentally by electron diffraction and crystallographic methods with reference to several important molecules, including cyclopentane, norbornane, and several compounds related to dodecahedrane. The structures for these compounds calculated with MM3 are in good agreement with experiment, whereas those from MM2 were noticeably deficient.

The MM2 force field, a general molecular mechanics force field, has proven to be of reasonable accuracy and of wide applicability and has found many uses.[1-3] Since it was first published in 1977, a great deal of new gas-phase experimental work on relatively simple structures has become available, low-temperature crystallographic studies have become more plentiful, and additional neutron diffraction information, which accurately locates hydrogen atoms, has been reported. It is now clear that while MM2 represents a useful first approximation for the calculations of the structures of many kinds of organic molecules, the original version does not produce certain kinds of structures that are reliably competitive in accuracy with the good quality experiments being carried out today. As far as we know, the *general method* is capable of yielding results that are competitive with current high-quality experiments, although apparently with some modest modifications in addition to simple parameter changes. We have for some years, therefore, been developing a new force field, which we will call MM3, in which we try to take into account the large amount of recent accurate structural data now available. Because the amount of data is so large and because we have studied so many different classes of compounds, and a number of different physical phenomena are involved in interpreting the results, it will not be possible to describe MM3 in a single paper. Rather, we will discuss in general the several items that require changes in the force field equations, in addition to simple parameter changes, which we have judged to be necessary to reach the next calculational level of accuracy. In detail, this paper will be concerned with only one topic, namely the amount of stretching in a bond as a function of torsional angle, and we will focus on the carbon–carbon single bond. We want to see what happens quantitatively as a structure goes from a staggered to an eclipsed conformation. Since eclipsed and partly eclipsed bonds are very widespread in organic molecules, it is important that this effect, which does not seem to have been fully appreciated, be properly taken into account in molecular mechanics calculations.

In MM2 and in other force fields, if we consider ethane as a simple starting point, as the molecule goes from the ground-state staggered conformation to an eclipsed saddle point, which separates two of the three indistinguishable ground-state conformations, the carbon–carbon bond stretches and the carbon–carbon–hydrogen bond angles open out.[1-3] This is interpreted in terms of our physical model as a repulsion between the hydrogens, and quantum mechanical calculations[4] show that indeed this is what happens. In the molecular mechanics model, this qualitative result is obtained because of the van der Waals repulsions between the hydrogens on opposite ends of the molecule. The force each hydrogen exerts on the two closest hydrogens at the other end of the molecule increases with decreasing distance quite sharply and is sufficiently greater in the eclipsed conformation to cause bond stretching and angle bending as described. The only problem in MM2 is that the stretching and bending that occur are considerably less than we believe actually occur. There are various ways in which additional stretching and bending could be introduced into the force field; the most obvious would be by increasing the van der Waals repulsions. However, these van der Waals terms also determine things like the spacing between molecules in crystals and the heats of sublimation of crystals. We have not found it possible to change the van der Waals terms in such a way as to increase this stretching and bending and yet fit all of the other kinds of data mentioned. So we have concluded that it is expedient, if not absolutely necessary, to introduce additional terms into the force field equations to bring about any extra desired stretching and bending. Additional equations in the force field are undesirable for two main reasons. One is practical. More equations mean more computations, which means more computing time and more programming time. But for the present changes, these problems are minor. The major difficulty is that more equations means more parameters, and it is already quite tedious to evaluate all of the parameters that are needed for force field calculations (in fact, this is now the principle limiting factor that prevents force field calculations from being broadly extended to all possible kinds of structures). Because the force field parameters tend to be cor-

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(1) The MM2 force field for hydrocarbons was first described: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Extensions to functionalized molecules and all other sorts of special problems have been described in subsequent papers, which are summarized in ref 2. The original version of the program (MM2(77)) is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, Program 395. The latest version of the MM2 program, which is referred to as MM2(85), is available from the Quantum Chemistry Program Exchange and is also available from Molecular Design Ltd., 2132 Farallon Dr., San Leandro, CA 94577. The MM3 program is still under development, but it is intended to make it available shortly.

(2) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(3) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Altona, C. L.; Faber, D. H. *Top. Curr. Chem.* **1974**, *45*, 1. (c) Dunitz, J. D.; Burgi, H. B. In *MTP International Reviews of Science, Series 2: Chemical Crystallography*; Robertson, J. M. R., Ed.; Butterworths: London, 1975; p 81. (d) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (e) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161. (f) Bartell, L. S. *J. Am. Chem. Soc.* **1977**, *99*, 3279. (g) Niketic, S. R.; Rasmussen, K. *The Consistent Force Field*; Springer: Berlin, 1977. (h) Warshel, A. In *Modern Theoretical Chemistry*; Segal, G., Ed.; Plenum: New York, 1978; Vol. 7, p 133. (i) White, D. N. J. In *Molecular Structure by Diffraction Methods*; Chemical Society: London, 1978; Vol. 6, p 38. (j) Osawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117.

(4) Veillard, A. *Theor. Chim. Acta* **1970**, *18*, 21.

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Table I. Calculated Cyclopentane Geometries

	Boggs			MM2			MM3		
	D_{5h}	C_2	C_s	D_{5h}	C_2	C_s	D_{5h}	C_2	C_s
r12	1.556	1.562	1.544	1.534	1.540	1.534	1.547	1.553	1.537
23		1.548	1.555		1.535	1.537		1.541	1.547
34		1.543	1.565		1.534	1.541		1.537	1.556
θ512	108.0	106.2	103.0	108.0	106.3	102.3	108.0	106.1	102.9
123		105.3	104.2		105.2	103.9		105.3	104.3
234		103.4	105.9		102.7	106.0		103.3	106.0
ω12	0	12.6	39.4	0	13.2	40.5	0	12.8	39.2
23		33.1	24.2		34.5	25.1		33.5	24.2
34		41.1	0		42.6	0		41.4	0

related with one another to some extent, it is time-consuming to obtain enough data to actually evaluate all of the parameters accurately and uniquely. More parameters simply complicate this already difficult problem.

We have decided to introduce only one additional term in the force field to account for the extra stretching that a bond undergoes when eclipsing, a torsion–stretch interaction term. Torsion–stretch interactions have previously been used by Ermer as part of a complicated force field designed to fit structural, thermochemical, and (primarily) vibrational data.[5] While we could introduce torsion–bend interactions (and in fact we did this in the MM1 force field[6]), the effect of this interaction is relatively small, while problems resulting from the introduction of the new parameters would be relatively large; and so we have decided to forego adding this quantity, at least at this time. But the torsion–stretch interaction assumes a major role in determining bond lengths, and hence overall molecular geometries, in a number of molecules in which there exist bonds that are more or less eclipsed. We initially examined the ethane molecule, where ab initio calculations long ago[4] predicted the amount of stretching that ethane undergoes upon eclipsing to be 0.019 Å. The MM2 value calculated was 0.003 Å, and clearly this was too small. Because the ab initio value is an approximation to the r_e distance and the molecular mechanics value is r_g, these two quantities do not have to be quite the same, but it seems that they should be quite similar. Since we are comparing here a change in bond length (rather than the bond length itself), most of the difference in the two bond length types (due to the vibrational motion) should cancel. The MM3 value for this bond length change is 0.012 Å, which is clearly much better. Cyclopentane, norbornane, and dodecahedrane are other prime examples where MM2 fails to calculate bond lengths that are of experimental accuracy (the calculated bond lengths are on the average too short by about 0.010–0.015 Å) and where improvement is clearly needed. We chose these three molecules as tests of the torsion–stretch interaction.

Cyclopentane. Shown in Table I are the MM2 and MM3 geometries calculated for cyclopentane in the D_{5h}, C_2, and C_s conformations, compared with ab initio values reported by Saebo, Cordell, and Boggs,[7] using the 4-31G basis set and geometry relaxation. It may be noted that the valence and torsion angles show only very minor differences among the three sets of calculated results but that the bond lengths are quite different.

The C–C bond lengths calculated by Boggs may be examined first. The planar form shows a C–C length of 1.556 Å, while the average for each of the puckered forms is 1.553 Å. These bond lengths, being approximate r_e values, may be off in absolute value by perhaps 0.010 Å or more from the r_g values. The latter quantities come out of our molecular mechanics calculations and can be obtained from an electron diffraction study. Differences between properly calculated ab initio bond lengths of the same chemical nature, however, should be highly accurate. It is therefore significant to note that the C–C length stretches slightly when the molecule goes from the average puckered to the planar conformation. With MM2, the planar conformation has a slightly *shorter* bond length (1.534 Å) than the average value for the puckered forms (1.537 Å), a result which is clearly incorrect. In contrast, the planar form in MM3 has a bond length (1.547 Å) that is slightly *longer* than the average of the puckered forms (1.545 Å), a result in agreement with the ab initio calculations. Moreover, the latter absolute value is in good agreement with the average C–C bond length (1.546 (1) Å; r_g type) determined by Adams, Geise, and Bartell[8] by electron diffraction. In this context it is important to realize that the experimental average value is accurate, although individual C–C bonds could not be determined.

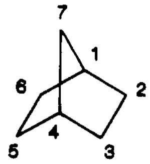

Figure 1. Structural formula of norbornane with atomic numbering scheme.

Norbornane. This ring system is an important one, and many norbornane derivatives have had their structures determined by various methods. Our evaluation of previous structural data will be outlined below. The molecular orbital constrained electron diffraction (MOCED) analysis, in combination with microwave and infrared/Raman data,[9] and the available X-ray information[10] agree with ab initio relaxed geometry calculations at the 4-21G level[9,10] that $C_2C_3 > C_1C_2 \sim C_1C_7$ (see Figure 1 for the atomic numbering scheme). MM3 reproduces this qualitative conclusion whereas MM2 failed.

Before going into more quantitative details it seems appropriate to discuss the considerable difficulties involved in obtaining reliable reference values for the individual C–C bond lengths of norbornane. One has to consider the way in which the raw experimental data were analyzed, the influence of thermal motions, as well as the fact that various methods produce various types of geometry (r_g, r_α, r_a, r_e, etc.). The MM2 and MM3 force fields have been designed to fit r_g bond lengths, so this is the geometry type we will refer to here. A standard electron-diffraction analysis gives r_a values which are commonly converted to r_g values with the relation $r_g = r_a + U^2/r_a$, where U represents the mean amplitude of vibration of the bond at hand. This presents no difficulties with simple molecules, but, in molecules containing two or more slightly different bond lengths, strong correlation between the parameters occurs. Then it is quasi-impossible to determine simultaneously accurate r_a and U values for each of the bonds. In such cases one may introduce constraints for some geometrical parameters (e.g. from ab initio calculations) and furthermore constrain some or all of the U parameters to calculated values (e.g. from IR/Raman fitted force fields). These procedures, although

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(5) Ermer, O. *Aspekte von Kraftfeldrechnungen*; W. Bauer Verlag: München, 1981.

(6) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579.

(7) Saebo, S.; Cordell, F. R.; Boggs, J. E. *J. Mol. Struct.* (*Theochem*) **1983**, *104*, 221.

(8) Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013.

(9) Doms, L.; Van den Enden, L.; Geise, H. J.; Van Alsenoy, C. *J. Am. Chem. Soc.* **1983**, *105*, 158–162.

(10) Doms, L.; Van Hemelrijk, D.; Van de Mieroop, W.; Lenstra, A. T. H.; Geise, H. J. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *B41*, 270–274.

Table II. Comparison of the Geometries (r_g type[a]) of Norbornane by Various Methods

	X-ray[b]	electron diffraction[c]	ab initio[d]	MM2	MM3
		Bond Lengths, Å			
C1–C2	1.544	1.536	1.543	1.542	1.548
C1–C7	1.537	1.546	1.541	1.538	1.540
C2–C3	1.559	1.573	1.564	1.541	1.557
⟨CC⟩	1.546	1.548	1.548	1.541	1.548
		Valence Angles, deg			
C1–C2–C3	103.0	102.7	103.1	102.8	103.3
C2–C1–C6	108.2	109.0	108.0	109.2	107.9
C2–C1–C7	101.8	102.0	101.6	102.2	101.3
C1–C7–C4	94.3	93.4	94.6	92.5	95.0
		Torsion Angles, deg			
C6–C1–C2–C3	71.2	71.6	71.3	71.4	71.0
C2–C1–C7–C4	55.5	56.3	55.7	56.5	55.5
C7–C1–C2–C3	35.1	35.8	35.1	36.2	34.9
C1–C2–C3–C4	4.8	0.0	0.0	0.0	0.0

[a] We take the angles to be the same for r_g and r_α structures. [b] r_α values of ref 10 were converted to r_g using $r_g = r_\alpha + k_0$, where k_0 is the amplitude of vibration perpendicular to the bond. k_0 values, calculated for the free molecule from the force field of ref 9, are +0.002 Å for bonded C–C. [c] From ref 9, Table I. [d] From ref 9, Table V, column A with $r_g = r$(4-21G) − 0.008 Å for C–C. Note that in ref 10, Table V contains a printing error; the ab initio value (converted to r_α) for C2–C3 should read 1.567 Å.

Table III. Summary of Disagreement Factors[a] for MMCED and MOCED Analyses of Norbornane[b]

	R(ED)	R(MW)	R(tot)
MMCED (Ermer and Lifson ff)	1.98	0.06	0.90
MMCED (MM2 ff)	2.12	0.06	0.96
MMCED (MM3 ff)	1.94	0.05	0.88
MOCED (4-21G)	1.80	0.02	0.82

[a] $R = [\Sigma w(I_{obsd} - I_{calcd})^2/\Sigma w I_{obsd}^2]^{1/2}$, where w represents the weight of an observation. [b] R(ED), disagreement factor for the electron diffraction data; R(MW), disagreement factor for the microwave data; R(tot), disagreement factor for the combination of electron diffraction and microwave data.

quite powerful at times, make the geometry resulting from such an analysis dependent on the reliability of the constraints and also to some extent on the refinement strategy. In the case of norbornane,[9] the uncertainties in the individual C–C bond lengths (r_g type) were estimated to be as high as 0.015–0.024 Å.

Doms et al.[10] took a statistical approach to the geometry of norbornane by analyzing the X-ray geometries of 51 selected norbornane derivatives. They had to assume that the median value of the distribution of a particular bond length over the 51 sampling points is a true estimate of the corresponding bond length in free norbornane. The validity of the assumption could only be judged a posteriori, and no error limits could be set. The obtained median values are of the r_α type, which are in general slightly shorter than the r_g values. The difference, however, is usually no more than 0.002 Å for C–C bonds in rigid molecules. Finally, the geometry-relaxed 4-21G ab initio model[9] is of the r_e type. The absolute values must deviate from the experimental ones because of the use of a finite basis set and the neglect of electron correlation, as well as from the intrinsic difference between an equilibrium structure and a real vibrating molecule. The 4-21G calculated bond lengths were converted to r_g values with the help of empirical corrections, necessarily of limited accuracy.[11] The uncertainties in the ab initio values thus obtained for the C–C bond lengths are estimated to be on the order of 0.005–0.020 Å.

However, despite the considerable uncertainties, it is gratifying to see that the three methods converge to a norbornane structure with reasonable narrow ranges for the individual bond lengths and angles. If we consider that the three structures listed in Table II under the headings of X-ray, electron diffraction, and ab initio are the three "experimental structures" with which we compare our force field calculations; we can note the following upon inspection. With MM2, the average C–C bond length is calculated to be too short, 1.541 Å versus experimental numbers ranging from 1.546 to 1.548 Å. The MM3 calculations give 1.548 Å. As stated before, in each of the three experimental structures the C2–C3 bond length is the longest one (1.559–1.573 Å). In the MM2 structure, this bond was slightly shorter than the C1–C2 bond length (1.541 versus 1.542 Å) and was just equal to the average bond length in the molecule. In the MM3 structure, the C2–C3 bond length has stretched out to 1.557 Å, making it longer than the other bonds and longer than the average bond length of 1.548 Å. It is only slightly shorter than the experimental range (1.559–1.573 Å). The extra stretch of C2–C3 in the MM3 structure is due almost entirely to the torsion–stretch interaction.

If we compare the bond angles calculated with those found experimentally, the angle at the C7 peak is most distinctive. It ranges from 93.4° to 94.6° experimentally. The MM2 value is somewhat smaller than this (92.5°), while the MM3 value is just slightly larger (95.2°). The other angles are within about 1° or so, comparing all of the experimental and calculated values. For torsion angles, again the overall agreement is excellent. Any one torsion angle as listed is within about 1° by all calculations and experiments. The only exception is the X-ray value (4.8°) for the C1–C2–C3–C4 torsion angle. Its deviation from 0° has to do with special difficulties encountered in the statistical evaluation of this angle[10] and cannot be considered as significant.

We turn now to the well-known, but unfortunate, situation that for most molecules of interest it is not possible to determine the structure completely, accurately, and unambiguously from the intensities (or their Fourier-transformed analogue, the radial distribution function) obtained from electron diffraction experiments alone. Accordingly, it has become customary to couple together electron diffraction experimental data with other kinds of experimental and calculated data. We will mention only two examples, one of which utilizes ab initio calculated data to give MOCED (molecular orbital constrained electron diffraction) results, in which the *differences* in chosen quantities as determined by ab initio calculations are carried over to the least-squares refinement of the electron diffraction intensities. The second method that has been proven useful is MMCED (molecular mechanics constrained electron diffraction) in which differences as determined by molecular mechanics calculations are carried over to the refinements. In the case of norbornane, the latter seemed to give a noticeably less satisfactory result than the former. In fact, this less satisfactory result was doubtlessly due to the particular force field utilized. Most earlier force fields, including MM2, do not give results for norbornane that are very satisfactory. We will show that MM3 performs a good deal better.

Four series of least-squares refinements were performed on a combination of experimental electron diffraction intensities and microwave rotational constants. In the four series the same refinement strategy was followed: five geometrical and four vibrational parameters were refined; the other parameters were constrained or kept fixed as described by Doms et al.[9] Geometrical constraints were taken from molecular mechanics calculations by using (i) Ermer and Lifson's force field,[12] (ii) MM2, and (iii) MM3. In the fourth series, the constraints were taken from 4-21G ab initio calculations. The disagreement factors, R, between experimentally observed and model based expected data for these series are given in Table III. It follows that the model containing 4-21G constraints (MOCED approach) gives the best agreement with experiment but that, in the corresponding MMCED approach, MM3 performs best of the three molecular mechanics force fields examined. The fit of the MM3-based model can also be judged from the radial distribution function presented in Figure 2. Our conclusion is that a major shortcoming of MM2, namely the eclipsed bond lengths being too short, is corrected in MM3. The difference in performance toward electron diffraction and

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(11) Klimkowski, V. J.; Ewbank, J. D.; Van Alsenoy, C.; Scarsdale, J. N.; Schafer, L. *J. Am. Chem. Soc.* **1982**, *104*, 1476. Van Alsenoy, C.; Klimkowski, V. J.; Schafer, L. *J. Mol. Struct.* (*Theochem*) **1984**, *109*, 321.

(12) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

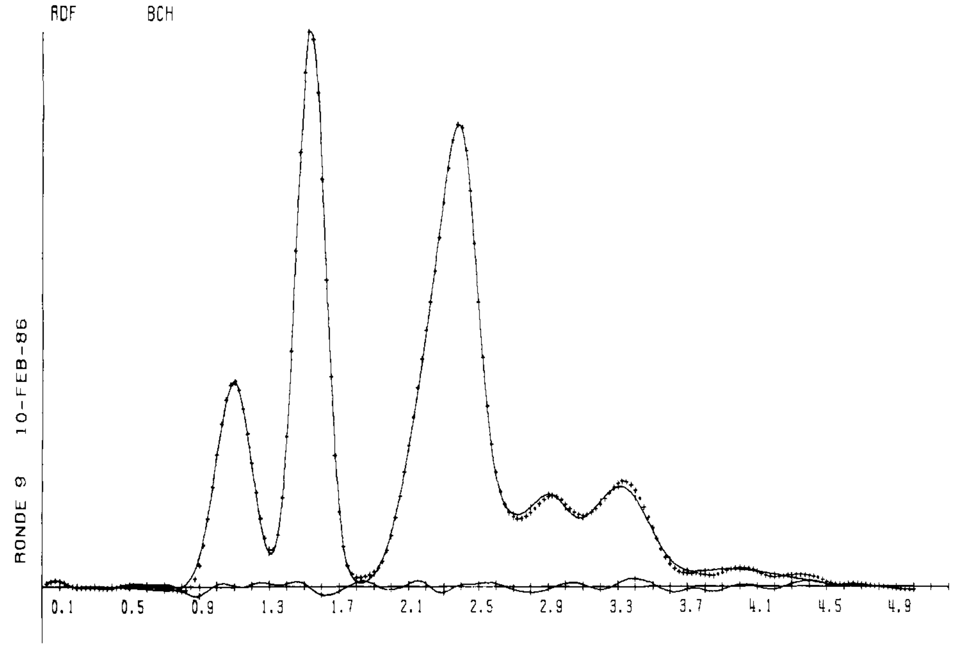

Figure 2. Radial distribution curve for norbornane. The crosses (×) represent the experimental curve and the solid line the MM3 model (r_a type), while the bottom trace gives the difference curve experiment, minus model.

microwave experiments between the MM3 and 4-21G norbornane models seems for a large part situated in the hydrogen parameters. For the heavy-atom skeleton, MM3 is competitive with the 4-21G calculations, and hence MMCED can be more useful than implied in earlier papers.[9]

Dodecahedrane. At the time the MM2 force field was formulated (1976–1977[1]), accurate structural information on five-membered carbocyclic rings was very limited in quantity and accuracy. The gas-phase structure of cyclopentane had been reported earlier.[8] We noted at the time that MM2 did not fit the average C–C bond length of this particular structure very well, but since there was only a single structure and no remedy was apparent, no action was taken. More recently other data on five-membered rings have become available, and they give a consistent picture in that the bonds within five-membered rings tend to be considerably longer than otherwise similar bonds, by about 0.010 Å. Given only this fact, it is not clear that a torsion–stretch effect is being observed. Since the bond angles in the five-membered ring are considerably smaller than tetrahedral, this stretching could also be the result of a torsion–bend interaction, or a stretch–bend interaction, for example. However, studies on other compounds such as norbornane show that the eclipsed bonds are the ones that stretch the most, not the bridge bonds, which show a greater degree of bending.

Dodecahedrane is an interesting molecule in many ways. For present purposes it is of interest because it consists only of five-membered rings that are planar, in contrast with virtually all other five-membered ring compounds. Additionally, the bonds are to tertiary carbons, rather than to secondary carbons as in cyclopentane itself. Compounds of the methyldodecahedrane type show the additional feature of a quaternary carbon, which is contained within the planar five-membered ring structure and is also bonded to an external methyl group. Since quaternary carbons tend to have somewhat longer carbon–carbon bonds than their less substituted analogues (neopentane has a longer bond than ethane, propane, or isobutane), a similar effect is expected here.

The synthesis of 1,16-dimethyldodecahedrane (**1**) was reported in 1981.[13] Shortly thereafter, a crystal structure for this molecule was reported,[14] determined at room temperature but reasonably accurate (R_{wF^2} = 0.088). At the same time a crystal structure was also reported for the seco derivative of that compound, which possesses a number of other interesting features in addition to the planar and almost planar, five-membered rings. This structure, also determined at room temperature, was less accurate than the structure of **1** (R_{wF^2} = 0.154).

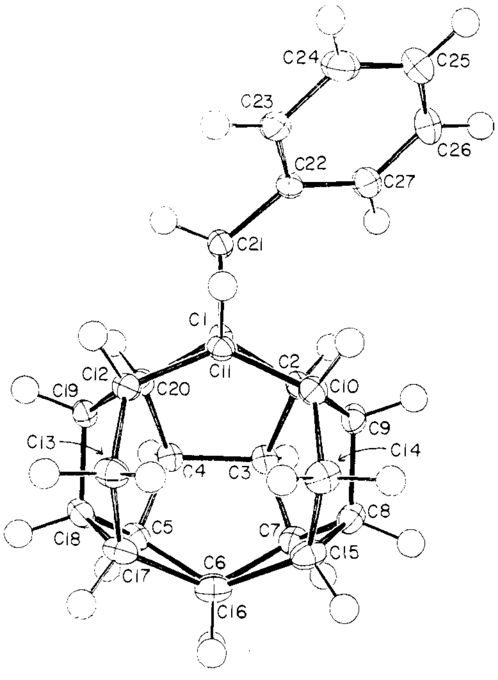

Figure 3. X-ray structure of benzylmonosecododecahedrane.

It was decided that it would be advantageous to determine additional structures of this kind at low temperatures, so as to decrease the importance of the rigid-body motions and thus obtain more accurate bond lengths.[19] Two compounds were examined at low temperatures in the present work, the 1,16-dimethyldodecahedrane (**1**) previously studied at room temperature, and also benzylmonosecododecahedrane (**2**). Here we have an even better measure of all of the distortions introduced into this unusual system by the seco unit.

The numbering scheme used for both molecules agrees with that previously used for 1,16-dimethyldodecahedrane and 1,6-dimethylmonosecododecahedrane[14] and is shown in Figure 3 for

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(13) Paquette, L. A.; Balogh, D. W.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 228.

(14) Christoph, G. G.; Engel, P.; Usha, R.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 784.

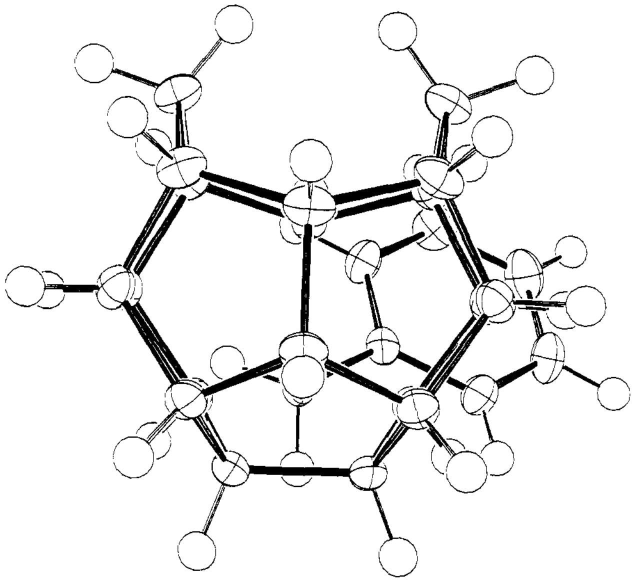

Figure 4. Another view of benzylmonosecododecahedrane.

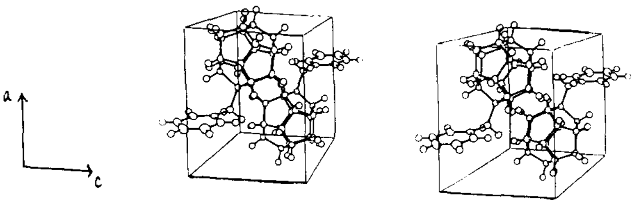

Figure 5. Stereoview of the crystal packing of benzylmonosecododecahedrane.

structure **2**. Another view of structure **2** is shown in Figure 4, and the crystal packing is shown in Figure 5. Final bond distances and angles for structures **1** and **2** appear in Tables IV–VII. The fractional unit cell coordinates and thermal parameters are given in Tables VIII and IX. A comparison of the room-temperature and low-temperature structures for **1** indicates that the metrical parameters for these two structures are not significantly different. The transannular distances and the least-squares planes for the low-temperature structure of **1** show the same trends about the quaternary carbon atom, C1, as seen in the room-temperature structure. In fact, the only differences between these two structures appear to be in the size of the thermal ellipsoids and the cell constants. A comparison of the equivalent isotropic thermal parameters shows that the thermal motion has been reduced, on the average, by 45% at −104 °C. The linear cell constants have decreased from 0.5 to 0.8% on passing from room temperature to −104 °C. This results in one intermolecular H···H contact less than the sum of the van der Waals radii:[15] H11···H19 is 2.34 Å. All the other H···H intermolecular distances remain longer than 2.40 Å.

Table IV. Bond Lengths (Å) for 1,16-Dimethyldodecahedrane (**1**)

C1–C2	1.552 (2)	1.552 (3)[a]
C1–C11	1.551 (2)	
C1–C20	1.552 (3)	
C2–C3	1.542 (2)	1.544 (5)
C2–C9	1.541 (3)	
C11–C10′	1.543 (3)	
C11–C12′	1.545 (3)	
C20–C4	1.544 (2)	
C20–C19	1.549 (2)	
C1–C21	1.529 (2)	
C3–C7	1.546 (2)	1.545 (3)
C4–C5	1.544 (2)	
C9–C8′	1.544 (3)	
C10′–C14′	1.544 (2)	
C12′–C13′	1.546 (2)	
C19–C18′	1.544 (3)	
C3–C4	1.546 (3)	1.543 (3)
C9–C10′	1.540 (3)	
C12′–C19	1.542 (3)	

[a] Average values are weighted.

Table V. Bond Angles (deg) for 1,16-Dimethyldodecahedrane (**1**)

C2–C1–C11	107.0 (2)	107.1 (2)[a]
C2–C1–C20	107.0 (1)	
C11–C1–C20	107.2 (1)	
C1–C2–C3	108.6 (1)	108.5 (2)
C1–C2–C9	108.4 (1)	
C1–C11–C10′	108.5 (2)	
C1–C11–C12′	108.5 (2)	
C1–C20–C4	108.5 (2)	
C1–C20–C19	108.3 (2)	
C2–C3–C4	107.9 (1)	107.9 (3)
C3–C4–C20	107.9 (2)	
C2–C9–C10′	108.2 (2)	
C9–C10′–C11	107.9 (2)	
C11–C12′–C19	107.9 (2)	
C12′–C19–C20	108.0 (2)	
C21–C1–C2	111.7 (1)	111.7 (2)
C21–C1–C11	111.6 (1)	
C21–C1–C20	112.0 (2)	
C2–C3–C7	108.0 (1)	108.1 (2)
C2–C9–C8′	107.9 (2)	
C20–C4–C5	108.2 (1)	
C20–C19–C18′	107.9 (2)	
C11–C10′–C14′	108.2 (2)	
C11–C12′–C13′	108.1 (2)	
C3–C4–C5	108.0 (2)	108.0 (2)
C4–C3–C7	107.9 (1)	
C9–C10′–C14′	108.0 (2)	
C10′–C9–C8′	108.2 (2)	
C12′–C19–C18′	108.2 (2)	
C19–C12′–C13′	107.8 (2)	

[a] Average values are weighted.

The structure of the benzylmonosecododecahedrane (**2**) compares favorably with the room-temperature structure for 1,6-dimethylmonosecododecahedrane.[14] The same distortions of the dodecahedrane framework are observed in **2** as a result of the close proximity of the two methylene carbons, C13···C14 = 3.04 Å, and the attached methylene hydrogen atoms, H131···H141 = 1.84 Å.

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(15) The expression "van der Waals radii" has a different meaning in crystallography from that used in molecular mechanics. The crystallographic meaning (which in molecular mechanics is called the "closest packing distance") is intended in this sentence.

(16) The programs used for data reduction are from the CRYM crystallographic computing package: Duchamp, D. J.; Trus, B. L.; Westphal, B. J., California Institute of Technology, Pasadena, CA, 1964. Modified by: Christoph, G. G., The Ohio State University, Columbus, OH.

(17) Sheldrick, G. M. *SHELX-76. Program for Crystal Structure Determination*; University Chemical Laboratory: Cambridge, England, 1976.

(18) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; Universities of York and Louvain: England and Belgium, 1980.

(19) It is possible to correct the observed bond lengths for rigid-body motion[20] and thus obtain better bond lengths from room-temperature data. This was done[21] in the present cases, and it was found that all of the C–C bonds in the dodecahedrane ring lengthened 0.001–0.002 Å. (One would expect that the corrections would be small here, because of the high melting points of the crystals.) Such corrections can be used to improve the results from room-temperature data, but more reliable results are ordinarily available from low-temperature data.

(20) The version of the program employed here uses the quadratic approximation of Schomaker and Trueblood [*Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 63–76], for the rigid-body motion and the approximation of Dunitz and White [*Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1973**, *A29*, 93–94], for the libration of attached rigid groups on the molecule, including correlations of the internal and overall motion (Schomaker and Trueblood, 1984, 1986). We are grateful to Professor K. N. Trueblood for a copy of the program.

(21) Chen, K.; Allinger, N. L., unpublished results.

Table VI. Bond Lengths (Å) for Benzylmonosecododecahedrane (**2**)

C11–C12	1.561 (2)	C11–C10	1.561 (2)	C16–C17	1.561 (2)	C15–C16	1.560 (2)
C1–C20	1.553 (2)	C1–C2	1.548 (2)	C6–C5	1.542 (2)	C7–C6	1.547 (2)
C19–C20	1.536 (2)	C9–C2	1.535 (2)	C18–C5	1.536 (2)	C7–C8	1.535 (2)
C12–C19	1.543 (2)	C10–C9	1.544 (2)	C18–C17	1.546 (2)	C15–C8	1.544 (2)
C20–C4	1.542 (2)	C2–C3	1.549 (2)	C4–C5	1.546 (2)	C3–C7	1.546 (2)
C19–C18	1.551 (2)	C9–C8	1.551 (2)				
C1–C11	1.559 (2)	C16–C6	1.554 (2)				
C12–C13	1.531 (2)	C10–C14	1.530 (2)	C17–C13	1.531 (2)	C15–C14	1.534 (2)
C4–C3	1.539 (2)						
C1–C21	1.544 (2)						
C21–C22	1.505 (2)						
C22–C23	1.392 (2)	C22–C27	1.396 (2)				
C23–C24	1.384 (2)	C27–C26	1.378 (2)				
C24–C25	1.376 (2)	C26–C25	1.380 (3)				
C13..C14	3.037 (2)						

Table VII. Bond Angles (deg) for Benzylmonosecododecahedrane (**2**)

C1–C11–C12	107.0 (1)	C1–C11–C10	106.9 (1)	C6–C16–C17	106.5 (1)	C6–C16–C15	106.6 (1)
C11–C1–C20	107.8 (1)	C11–C1–C2	107.8 (1)	C16–C6–C5	108.7 (1)	C16–C6–C7	108.5 (1)
C11–C12–C13	122.6 (1)	C11–C10–C14	122.4 (1)	C16–C17–C13	122.1 (1)	C16–C15–C14	122.5 (1)
C1–C20–C19	107.8 (1)	C1–C2–C9	108.0 (1)	C6–C5–C18	107.6 (1)	C6–C7–C8	107.6 (1)
C12–C19–C20	108.8 (1)	C10–C9–C2	108.6 (1)	C17–C18–C5	108.6 (1)	C15–C8–C7	108.6 (1)
C1–C20–C4	108.7 (1)	C1–C2–C3	108.5 (1)	C6–C5–C4	107.8 (1)	C6–C7–C3	107.5 (1)
C19–C20–C4	107.9 (1)	C9–C2–C3	107.7 (1)	C18–C5–C4	107.8 (1)	C8–C7–C3	107.8 (1)
C20–C19–C18	108.1 (1)	C2–C9–C8	108.2 (1)	C5–C18–C19	108.0 (1)	C7–C8–C9	108.1 (1)
C12–C19–C18	107.2 (1)	C10–C9–C8	107.1 (1)	C17–C18–C19	106.7 (1)	C15–C8–C9	106.8 (1)
C11–C12–C19	107.5 (1)	C11–C10–C9	107.6 (1)	C16–C17–C18	107.6 (1)	C16–C15–C8	107.8 (1)
C19–C12–C13	103.1 (1)	C9–C10–C14	103.1 (1)	C18–C17–C13	103.3 (1)	C8–C15–C14	103.1 (1)
C20–C4–C3	107.9 (1)	C2–C3–C4	107.9 (1)	C5–C4–C3	108.0 (1)	C7–C3–C4	108.2 (1)
C20–C4–C5	108.2 (1)	C2–C3–C7	108.1 (1)				
C10–C11–C12	124.9 (1)	C15–C16–C17	125.2 (1)				
C2–C1–C20	106.8 (1)	C7–C6–C5	108.1 (1)				
C20–C1–C21	109.2 (1)	C2–C1–C21	113.0 (1)				
C11–C1–C21	112.0 (1)						
C12–C13–C17	106.3 (1)	C10–C14–C15	106.2 (1)				
C1–C21–C22	117.2 (1)						
C21–C22–C23	120.5 (1)						
C21–C22–C27	122.2 (1)						
C23–C22–C27	117.2 (1)						
C22–C23–C24	121.6 (1)						
C23–C24–C25	119.9 (2)						
C24–C25–C26	119.5 (2)						
C25–C26–C27	120.5 (2)						
C26–C27–C22	121.1 (2)						

Table VIII. Final Positional and Thermal Parameters for 1,16-Dimethyldodecahedrane

atom	x^a	y	z	$U_{11}{}^b$ or B, Å^2	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.55989 (27)	1.11928 (12)	0.89565 (12)	0.0181 (10)	0.0155 (8)	0.0169 (8)	0.0011 (6)	0.0001 (8)	0.0001 (8)
C2	0.44835 (27)	1.03678 (12)	0.84449 (12)	0.0210 (10)	0.0175 (8)	0.0138 (7)	0.0009 (6)	−0.0008 (8)	−0.0013 (8)
C3	0.55801 (28)	0.94108 (12)	0.85232 (12)	0.0223 (11)	0.0172 (8)	0.0142 (7)	−0.0022 (7)	0.0013 (8)	0.0012 (8)
C4	0.73704 (29)	0.96294 (12)	0.91017 (12)	0.0188 (11)	0.0174 (8)	0.0175 (8)	0.0005 (7)	0.0040 (8)	0.0029 (8)
C5	0.73388 (25)	0.90380 (12)	1.00900 (12)	0.0163 (9)	0.0172 (7)	0.0204 (8)	0.0027 (7)	0.0011 (8)	0.0034 (7)
C7	0.44475 (28)	0.86828 (12)	0.91562 (12)	0.0237 (10)	0.0138 (8)	0.0157 (8)	−0.0028 (6)	−0.0009 (8)	−0.0022 (8)
C9	0.26745 (27)	1.02359 (12)	0.90261 (12)	0.0165 (10)	0.0198 (9)	0.0173 (8)	0.0017 (7)	−0.0033 (7)	−0.0003 (8)
C11	0.44657 (24)	1.15459 (12)	0.98742 (12)	0.0204 (9)	0.0137 (7)	0.0178 (8)	0.0007 (6)	0.0006 (8)	0.0016 (7)
C19	0.73482 (27)	1.08063 (12)	1.05359 (12)	0.0188 (11)	0.0178 (8)	0.0177 (8)	0.0006 (7)	−0.0033 (8)	−0.0042 (8)
C20	0.73772 (27)	1.07232 (12)	0.93736 (12)	0.0155 (10)	0.0179 (8)	0.0183 (8)	0.0025 (7)	0.0020 (8)	−0.0016 (8)
C21	0.60055 (29)	1.20263 (14)	0.82265 (14)	0.0265 (11)	0.0198 (9)	0.0206 (9)	0.0041 (7)	0.0016 (8)	−0.0008 (9)
H2	0.421 (3)	1.052 (1)	0.771 (1)	1.2 (3)					
H3	0.585 (3)	0.914 (1)	0.784 (1)	1.4 (4)					
H4	0.846 (2)	0.946 (1)	0.869 (1)	0.9 (4)					
H5	0.843 (2)	0.861 (1)	1.016 (1)	1.7 (4)					
H7	0.420 (3)	0.808 (1)	0.876 (1)	1.8 (4)					
H9	0.158 (3)	1.034 (1)	0.857 (1)	2.2 (4)					
H11	0.419 (3)	1.226 (1)	0.982 (1)	1.3 (4)					
H19	0.845 (3)	1.118 (1)	1.078 (1)	1.7 (4)					
H20	0.848 (3)	1.106 (1)	0.909 (1)	1.1 (4)					
H21A	0.680 (3)	1.255 (1)	0.856 (1)	2.4 (4)					
H21B	0.478 (3)	1.236 (1)	0.797 (2)	3.1 (5)					
H21C	0.670 (3)	1.178 (1)	0.761 (1)	2.1 (4)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table IX. Final Positional and Thermal Parameters for Benzylmonosecododecahedrane

atom	x^a	y	z	$U_{11}{}^b$ or B, Å^2	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.44699 (15)	0.29364 (10)	0.69711 (20)	0.0188 (6)	0.0151 (6)	0.0173 (7)	0.0046 (5)	0.0032 (5)	0.0041 (5)
C2	0.37991 (16)	0.19878 (10)	0.53115 (20)	0.0234 (7)	0.0162 (6)	0.0176 (7)	0.0041 (5)	0.0039 (6)	0.0055 (5)
C3	0.31896 (16)	0.23551 (11)	0.35718 (21)	0.0249 (7)	0.0197 (7)	0.0153 (7)	0.0047 (6)	0.0052 (6)	0.0043 (5)
C4	0.35634 (16)	0.35286 (10)	0.41071 (21)	0.0236 (7)	0.0194 (7)	0.0179 (7)	0.0072 (6)	0.0056 (6)	0.0038 (5)
C5	0.20572 (16)	0.39445 (11)	0.40680 (21)	0.0258 (7)	0.0229 (7)	0.0172 (7)	0.0086 (6)	0.0033 (6)	0.0075 (6)
C6	0.07594 (16)	0.30264 (11)	0.36508 (21)	0.0221 (7)	0.0287 (8)	0.0157 (7)	0.0077 (6)	0.0009 (6)	0.0052 (6)
C7	0.14512 (16)	0.20383 (11)	0.32006 (21)	0.0258 (7)	0.0231 (7)	0.0152 (7)	0.0050 (6)	0.0010 (6)	0.0021 (6)
C8	0.09982 (17)	0.14277 (11)	0.46284 (22)	0.0258 (7)	0.0217 (7)	0.0187 (7)	0.0055 (6)	0.0003 (6)	−0.0024 (6)
C9	0.24514 (16)	0.13955 (11)	0.59331 (21)	0.0263 (7)	0.0166 (7)	0.0193 (7)	0.0058 (6)	0.0018 (6)	0.0010 (5)
C10	0.22842 (16)	0.19562 (10)	0.79865 (21)	0.0229 (7)	0.0210 (7)	0.0172 (7)	0.0090 (6)	0.0016 (6)	0.0017 (5)
C11	0.34138 (15)	0.29868 (10)	0.85418 (20)	0.0182 (6)	0.0186 (6)	0.0149 (7)	0.0046 (5)	0.0016 (5)	0.0041 (5)
C12	0.29492 (16)	0.40661 (10)	0.89447 (21)	0.0214 (7)	0.0203 (7)	0.0151 (7)	0.0020 (6)	0.0015 (6)	0.0074 (5)
C13	0.13045 (17)	0.42229 (12)	0.89611 (22)	0.0225 (7)	0.0296 (8)	0.0198 (7)	0.0046 (6)	0.0039 (6)	0.0105 (6)
C14	0.05752 (17)	0.19077 (13)	0.79115 (23)	0.0235 (7)	0.0313 (8)	0.0222 (8)	0.0109 (7)	0.0044 (6)	−0.0003 (6)
C15	−0.00095 (17)	0.20120 (12)	0.59270 (22)	0.0185 (7)	0.0332 (8)	0.0220 (8)	0.0106 (7)	0.0013 (6)	−0.0023 (6)
C16	−0.00118 (16)	0.30689 (12)	0.54709 (21)	0.0182 (7)	0.0331 (8)	0.0186 (7)	0.0086 (6)	0.0014 (6)	0.0051 (6)
C17	0.06562 (17)	0.41245 (12)	0.68877 (22)	0.0217 (7)	0.0312 (8)	0.0192 (7)	0.0061 (6)	0.0022 (6)	0.0114 (6)
C18	0.20073 (16)	0.46087 (11)	0.60750 (21)	0.0261 (7)	0.0202 (7)	0.0211 (8)	0.0062 (6)	0.0023 (6)	0.0089 (6)
C19	0.34561 (16)	0.45686 (10)	0.73780 (21)	0.0220 (7)	0.0163 (6)	0.0202 (7)	0.0040 (6)	0.0018 (6)	0.0054 (5)
C20	0.43974 (16)	0.38856 (10)	0.61686 (21)	0.0189 (7)	0.0165 (6)	0.0204 (7)	0.0067 (6)	0.0039 (6)	0.0031 (5)
C21	0.61236 (16)	0.29374 (11)	0.77662 (23)	0.0197 (7)	0.0183 (7)	0.0259 (8)	0.0059 (6)	0.0033 (6)	0.0041 (5)
C22	0.64069 (15)	0.21285 (10)	0.87786 (22)	0.0142 (6)	0.0194 (7)	0.0270 (8)	0.0056 (6)	0.0011 (6)	0.0041 (5)
C23	0.65895 (17)	0.23504 (12)	1.07616 (23)	0.0255 (8)	0.0236 (7)	0.0272 (8)	0.0020 (6)	−0.0026 (6)	0.0081 (6)
C24	0.68649 (18)	0.16228 (13)	1.17268 (25)	0.0325 (9)	0.0379 (9)	0.0271 (9)	0.0110 (7)	−0.0026 (7)	0.0081 (7)
C25	0.69918 (20)	0.06573 (13)	1.07234 (27)	0.0404 (10)	0.0294 (9)	0.0422 (11)	0.0174 (8)	−0.0032 (8)	0.0066 (7)
C26	0.68338 (19)	0.04228 (12)	0.87562 (27)	0.0407 (10)	0.0198 (7)	0.0425 (11)	0.0056 (7)	0.0007 (8)	0.0094 (7)
C27	0.65378 (17)	0.11436 (11)	0.77954 (24)	0.0264 (8)	0.0242 (7)	0.0279 (8)	0.0045 (6)	0.0034 (6)	0.0078 (6)
H2	0.4602 (16)	0.1552 (11)	0.4962 (21)	1.2 (3)					
H3	0.3630 (16)	0.2047 (11)	0.2432 (23)	1.6 (3)					
H4	0.4206 (17)	0.3767 (11)	0.3201 (23)	1.7 (3)					
H5	0.1987 (16)	0.4322 (11)	0.3072 (22)	1.4 (3)					
H6	−0.0005 (17)	0.3037 (11)	0.2566 (23)	1.7 (3)					
H7	0.1099 (18)	0.1639 (12)	0.1796 (26)	2.4 (4)					
H8	0.0429 (17)	0.0710 (11)	0.3960 (23)	1.6 (3)					
H9	0.2558 (17)	0.0673 (11)	0.5846 (23)	2.0 (3)					
H10	0.2618 (16)	0.1572 (11)	0.8857 (22)	1.3 (3)					
H11	0.4038 (16)	0.2982 (11)	0.9766 (23)	1.5 (3)					
H12	0.3525 (17)	0.4445 (11)	1.0233 (24)	1.8 (3)					
H131	0.0688 (18)	0.3795 (12)	0.9647 (25)	2.2 (3)					
H132	0.1349 (17)	0.4960 (12)	0.9633 (23)	1.8 (3)					
H141	0.0254 (19)	0.2395 (13)	0.8997 (26)	2.7 (4)					
H142	0.0127 (18)	0.1184 (12)	0.7948 (24)	2.1 (3)					
H15	−0.1067 (18)	0.1640 (12)	0.5554 (24)	2.1 (3)					
H16	−0.1106 (16)	0.3097 (10)	0.5156 (22)	1.4 (3)					
H17	−0.0177 (17)	0.4572 (11)	0.6954 (23)	1.8 (3)					
H18	0.1929 (16)	0.5344 (12)	0.6076 (23)	1.9 (3)					
H19	0.4018 (16)	0.5279 (11)	0.7973 (21)	1.1 (3)					
H20	0.5424 (17)	0.4249 (11)	0.6238 (22)	1.4 (3)					
H211	0.6505 (17)	0.3632 (12)	0.8663 (23)	1.8 (3)					
H212	0.6752 (19)	0.2890 (12)	0.6669 (26)	2.8 (4)					
H23	0.652	0.305	1.151	3.0					
H24	0.697	0.180	1.315	3.6					
H25	0.720	0.013	1.141	3.9					
H26	0.693	−0.028	0.802	3.7					
H27	0.641	0.096	0.637	3.1					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}kha^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

In Table X (supplementary material) are given the least-squares planes of the molecule, which indicate that the two five-membered rings containing the methylene carbons are the least regular of the cyclopentane rings; each ring is folded into an envelope conformation with dihedral angles of 36.8 and 36.5°. And again the four pentagonal rings opposite the missing framework bond are the most nearly planar. The bonds to the two methylene carbon atoms are again rather short, ranging from 1.530 to 1.534 Å, and the interior angles of the five-membered rings containing the methylene carbons are smaller than the ideal 108° of a regular pentagon. The C3–C4 bond length at 1.539 (2) Å is not as short as the analogous bond in the dimethylmonoseco derivative, 1.527 (6) Å.

The geometry of the framework of **2**, minus the benzyl group, can be described approximately in terms of C_{2v} symmetry. The set of bond lengths related by this noncrystallographic symmetry which shows the largest discrepancy is the set containing C1–C20, C1–C2, C5–C6, and C7–C6. The C1–C20 bond length of 1.553 (2) Å is slightly longer than the other three bond lengths in this group. The lengthening of this bond might be attributable to the presence of the benzyl group bonded to the C1 carbon atom. A comparison of bond angles about the C1 atom reveals that the C20–C1–C21 angle of 109.2 (1)° is significantly smaller than the C2–C1–C21 angle of 113.0 (1)° and the C11–C1–C21 angle of 112.0 (1)°. Steric interactions between the phenyl ring and the monosecododecahedrane framework may cause these latter two angles to open up slightly at the expense of the third one closing up a bit with a small increase in the C1–C20 bond length associated with this third angle. The orientation of the phenyl ring is described in terms of the torsion angle, C1–C21–C22–C27 of 83°.

The crystal studies on **1** may be compared with the molecular mechanics calculations as follows, considering only the low-temperature (−104 °C) structure. The carbon–carbon bonds within

Table XI. Carbon–Carbon Bond Lengths in 1,16-Dimethyldodecahedrane[a] (**1**)

	exptl	MM3	MM2
quat–tert	1.552 (3)	1.550	1.536
tert–tert	1.544 (3)	1.544	1.530
methyl	1.529 (2)	1.536	1.537

[a] The experimental values are of the r_a type, while the force field values are r_g. The relationship is approximately $r_g = r_a + 0.002$.

Table XII. Structures for Secododecahedrane (Derivatives)[a]

bond	MM2	MM3	high *t*	low *t*
14–15	1.529	1.533	1.529	1.534
15–16	1.540	1.550	1.565	1.560
8–15	1.536	1.549	1.535	1.544
7–8	1.525	1.539	1.539	1.535
8–9	1.533	1.547	1.546	1.551
3–7	1.531	1.545	1.547	1.546
3–4	1.526	1.540	1.527	1.539
13/14	3.028	3.043	3.030	3.037
14–15–16	122.3	121.7	123.2	122.5
15–16–17	125.6	126.6	124.3	125.2
9–10–14–15	36.1	35.8	35/37	36.6
H_{13}/H_{14}	1.89	1.754		

[a] Bond lengths are averaged over chemically equivalent bonds.

the planar five-membered rings are indeed quite long. The bonds to quaternary carbons are 1.552 (3) Å in length, while the MM3 values are 1.550 Å. The bond to the methyl group is somewhat shorter, again consistent with what was expected on the basis of a torsion–stretch interaction, plus small but not insignificant stretch–bend interactions, superimposed upon the van der Waals induced behavior of the quaternary carbon leaning toward longer bond lengths. The experimental and MM3 values are 1.529 (2) and 1.536 Å, respectively. The MM2 values within the ring system were noticeably too short, with the methyl bond being the longest in the molecule. This information is summarized in Table XI.

In Table XII is summarized the information regarding the monosecododecahedrane. Since the low-temperature (−101 °C) structure contains more accurate bond length information, we will concentrate on the structure and comment here only that the room-temperature structure shows thermal bond length shortenings as anticipated, plus some small lengthenings that we attribute to experimental error.

There are several items of interest in this molecule. The distance between carbons numbered 13 and 14, which we calculate to be 3.043 Å in the dimethylmonosecododecahedrane, is found to be 3.037 Å in the monobenzyl derivative. The experimental values for the "flap" torsion angles 9–10–14–15 average 36.6°, and they are equal at 35.8° from MM3. The bond angles 14–15–16 and 15–16–17 are also noteworthy. The calculated values are in fair agreement with experiment, but it is noted that calculationally the latter opens up too far by 1.4°, whereas the former is closed down too far by 0.8° (and since there are two of these, the net effect is to leave the distance between atoms 13 and 14 almost the same by calculation as by experiment). A comparison of the bond lengths is given in Table XII.

The statistics of the bond length comparisons between MM2, MM3, and the crystal structures of dimethylmonosecododecahedrane determined at room temperature and benzylmonosecododecahedrane determined at low temperature are of interest (Table XII). The average discrepancy between MM2 and the high-temperature crystal structure (MM2 − experimental) was −0.008 Å. Thus, on the average, the bond lengths were calculated to be too short by that amount. When the same comparison was made between MM2 and the low-temperature structure, the discrepancy was considerably greater, −0.012 Å. This is because the bond lengths were calculated too short in MM2; in general, the apparent bond length increases with decreasing temperature from suppression of the thermal motions, and hence the discrepancy increased.

If we compare the root-mean-square (rms) values, again between MM2 and the different structures, this quantity was 0.013 Å for the room-temperature structure and 0.012 Å for the low-temperature structure. The reason for this perhaps unexpected behavior is that the biggest error occurs in the C15–C16 bond length, which is calculated to be too short by 0.025 Å for the high-temperature structure. In general the experimental bonds get longer as the temperature is lowered, but this particular bond got shorter, reducing the error to 0.020 Å, hence, the odd rms behavior.

On the other hand, when MM3 is compared with experiment (MM3 − experimental) the average bond length error was +0.000 Å for the room-temperature structure and −0.001 Å for the low-temperature structure. Thus, on the average, the bond lengths are not systematically in error when MM3 is compared with either of the crystal structures. The rms deviations again show something different. The calculated value is 0.009 Å for the room-temperature structure and 0.006 Å for the low-temperature structure. Thus the best agreement is between MM3 and the low-temperature crystal structure, as it should be. When MM3 is compared with the two different crystal structures, since the calculation is the same, the more accurate crystal structure (at low temperature) is found to approach more closely to the MM3 values. It would seem fair to say that the MM3 structure is competitive in accuracy with the low-temperature crystal structures.[22]

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(22) A reviewer inquired as to whether the torsion–stretch interaction was effective only in five-membered rings or whether it was effective in large rings as well. The answer cannot be discussed in detail here, but the effect applies very well indeed to large rings. In cyclooctane, for example, according to 4-21G calculations (Siam, K.; Dorofeeva, O. V.; Mastryukov, V. S.; Ewbank, J. D.; Allinger, N. L.; Schafer, L. *J. Mol. Struct.*, in press), the bond-length variation calculated in cyclooctane (boat–chair conformation) is about 0.012 Å, with the longest bond being the one that is most eclipsed (calculated torsion angle 101.3°). With MM3, the same bond is the longest, with the others being proportionately shorter by up to 0.010 Å, and the dihedral angle of the most eclipsed bond is given by MM3 as 102.2°. The present paper used five-membered rings as specific examples, because they are rather flat, and the effect is large, but the effect is not limited to five-membered rings; it is ubiquitous. A second reviewer has requested that the MM3 parameters for carbon and hydrogen be presented (supplementary material) and some discussion given as to how they were arrived at. The MM3 force field for hydrocarbons was deduced by studying approximately 100 structures and energies of compounds, three of which are discussed in the present manuscript. Crystal packing, unit cell constants, and heats of sublimation were examined for about 10 compounds. Because a very extensive discussion will be required to adequately present all of this material, the outline here will necessarily be brief. Structures were the main things studied in this work. Heats of formation and vibrational frequencies were also examined, but as with MM2, we found that we could not fit everything as well as we wanted to at the same time. We added slightly more parameters than were in MM2, which significantly improved the situation. However, we have given most weight to fitting structures, and the next most weight to fitting heats of formation, and then have fit the vibrational frequencies as well as possible within those constraints. The structures and heats were all fit to essentially within experimental error. For the simple molecules ethane, propane, isobutane, neopentane, and cyclohexane, the rms values in the deviations between the calculated and experimental vibrational frequencies are approximately 40 wavenumbers, better by a factor of 2 or 3 than those from MM2. Of these remaining errors, by far the largest are in the C–H bending frequencies. While these could be further improved by the addition of more cross terms, we have decided not to add these at the present time. The accuracy obtained with MM3 for structure is typified by the three structures discussed herein. The force field has also been extended to cover alcohols, carbonyl compounds, and some other simple functional groups, and the results, including the vibrational frequencies, are similar to those with hydrocarbons. Full details will be published separately, and the program will be publicly available as soon as the parameterization has been completed. It was recognized some years ago with the publication by Ermer of the molecular structures of some highly congested molecules that the hydrogen–hydrogen repulsion potentials in MM2 were too severe at short distances.[23] New potentials for hydrogen (and also for carbon) were therefore derived to fit those facts, while simultaneously fitting to other available information on structures, heats of formation, and also heats of sublimation of aliphatic and aromatic hydrocarbons. Compared with MM2, the potentials are not very much different until one gets to quite short distances. The van der Waals radius of hydrogen is a little larger, and the depth of the potential well is a little more shallow, but the major difference occurs when the hydrogens are closer than 2 Å, where the MM3 potential is somewhat softer. The carbon–carbon and carbon–hydrogen potentials do not differ very much from MM2. The actual van der Waals equation used in MM3 is as follows: $E_v = \epsilon(-2.25(r_v/r)^6 + 1.84(10^5)\exp[-(12.0r/r_v)]$. The value of the constant in the exponent (12.0) is a little smaller than that in MM2, so the repulsion goes up a little less steeply.

Table XIII. Crystallographic Details for **1** and **2**

compd	benzylmonoseco-dodecahedrane (**2**)	1,16-dimethyl-dodecahedrane (**1**)
formula	$C_{27}H_{28}$	$C_{22}H_{24}$
formula wt	352.52	288.44
space gp	$P\bar{1}$-C_i^1	$Pbca$-D_{2h}^{15}
a, Å	9.029 (1)	7.302 (2)
b, Å	13.690 (2)	13.724 (4)
c, Å	7.289 (1)	13.286 (3)
α, deg	103.78 (1)	
β, deg	95.93 (1)	
γ, deg	98.02 (1)	
V, Å^3	858	1331
Z	2	4
d_{calcd}, g/cm^3	1.365	1.438
cryst size	0.29 mm × 0.40 mm × 0.65 mm	0.15 mm × 0.17 mm × 0.47 mm
radiatn	Mo Kα with graphite monochromator [$\lambda(K\alpha_1)$ = 0.709 26 Å]	
linear abs coeff, cm^{-1}	0.71	0.75
temp,[a] °C	−101	−104
2θ limits, deg	$4 \leqslant 2\theta \leqslant 58$	$4 \leqslant 2\theta \leqslant 55$
scan speed	2.0–24.0°/min in 2θ	
bckgd time/scan time	0.5	0.5
scan range	(Mo Kα_1 − 1.0)° to (Mo Kα_2 + 1.0)°	(Mo Kα_1 − 1.0)° to (Mo Kα_2 + 1.1)°
data collcd	$+h,\pm k,\pm l$	$+h,\pm k,+l$
unique data	4574	1534
unique data, with $F_o^2 > 0$	4268	1409
final no. of variables	336	148
$R(F)$[b]	0.062	0.064
$R_w(F)$[c]	0.051	0.046
error in observn of unit wt, *e*	1.98	2.11
R(on F) for $F_o^2 > 3\sigma(F_o^2)$)	0.046	0.046

[a] Data collection for both structures was done on a Syntex $P\bar{1}$ diffractometer equipped with an LT-1 low-temperature attachment. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Experimental Section

Structure Determination of 1,16-Dimethyldodecahedrane (1). The structure of 1,16-dimethyldodecahedrane was previously reported at room temperature.[14] The results of a low-temperature data collection at −104 °C are reported here. The morphology of the colorless crystal used for data collection was rectangular bisphenoidal. The unit cell constants at −104 °C were determined to be a = 7.302 (2), b = 13.724 (4), and c = 13.286 (3) Å by the least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range of 19–30°. (λ(Mo K$\bar{\alpha}$) = 0.710 69 Å). As with the room-temperature structure the space group is uniquely determined as *Pbca* with Z = 4, and the molecule contains a crystallographically imposed center of symmetry.

Intensities were again measured by the θ–2θ scan method, and two equivalent sets of reflections were obtained: $+h,+k,+l$ and $+h,-k,+l$. Six standard reflections were measured after every 100 reflections during the course of data collection and showed no indication of a decay problem. The data were corrected for Lorentz and polarization effects and put onto an absolute scale by means of a Wilson plot.[16] Two reflections, which saturated the detector, are omitted from the data set: (002) and (020). No absorption correction was applied to the data as the μ value is small. The disagreement index for the averaging of the symmetry-related reflections is R'_F = 0.034 where $R'_F = \sum_{hkl}(\sum_{j=1}^{n_j}|F_{av}| - |F_j|)/\sum_{hkl}(n_jF_{av})$. Of the 1534 unique reflections, 1036 satisfied the condition $F_o^2 > 3\sigma(F_o^2)$. This is a much larger percentage than for the room-temperature data set and results from the use of both low temperature and a larger crystal.

The positional coordinates of the carbon atoms in the room-temperature structure were used initially as a phasing model. Full-matrix least-squares refinements were done with the SHELX-76 package.[17] As with the room-temperature structure, the hydrogen atoms were located on a difference electron density map and allowed to refine isotropically. The final refinement cycle yielded agreement indices of R = 0.064 and R_w = 0.046 (based on F) for the 1409 intensities with $F_o^2 > 0$ and 148 variables (anisotropic carbon atoms and isotropic hydrogen atoms).

A structure factor calculation for the 1036 reflections with $F_o^2 > 3\sigma(F_o^2)$ gives an R factor of 0.046. The final difference electron density map has maximum and minimum peak heights of +0.37 and −0.28 e/Å^3. Many of these peaks are located in bonding regions between the carbon atoms. Scattering factors used are those supplied with the SHELX-76 package.[17] Additional crystallographic details are listed in Table XIII. Final positional and thermal parameters are displayed in Table VIII.

Structure Determination of Benzylmonosecododecahedrane (2). Crystals of this compound were grown from a solution of acetone and are clear, colorless, multifaceted rods. Initial attempts to work with the crystal at −126 °C proved futile as various crystals appeared to undergo destructive phase transitions; the crystals appeared to be stable at the higher temperature of −101 °C. Preliminary examination of the diffraction pattern indicated no Laue symmetry higher than $\bar{1}$, which limits the space group possibilities to $P1$ and $P\bar{1}$. The unit cell constants at −101 °C were determined to be a = 9.029 (1) Å, b = 13.690 (2) Å, c = 7.289 (1) Å, α = 103.78 (1)°, β = 95.93 (1)°, and γ = 98.02 (1)° by the least-squares fit of the diffractometer setting angles for 24 reflections in the 2θ range 20–30° (λ(Mo K$\bar{\alpha}$) = 0.710 69 Å).

Intensities were measured by the θ–2θ scan method at −101 °C, and the data were corrected for Lorentz and polarization effects and put onto an absolute scale by means of a Wilson plot.[16] Two reflections saturated the detector during data collection and are omitted from the data set: (020) and (11$\bar{1}$). No absorption correction was applied to the data, owing to the small μ value (0.71 cm^{-1}) and the fairly symmetric cross section of the crystal. Six standard reflections were measured after every 100 reflections during data collection. A slight increase in the intensities of all six reflections was observed during the course of data collection, but this was not judged to be significant and no decay correction was applied.

The structure was solved by the direct methods program MULTAN80[18] in the space group $P\bar{1}$. The whole molecule was located on the resultant electron density map. The SHELX-76 package[17] was used for all full-matrix least-squares refinements with the quantity $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$. Isotropic refinement of the carbon atoms converged to an R factor of 0.109. After one cycle of anisotropic refinement, all the hydrogen atoms were easily located on a difference electron density map. The hydrogen atoms on the monosecododecahedrane framework and the methylene hydrogens on C21 of the benzyl group were allowed to refine. The hydrogen atoms on the phenyl ring were included in the model as fixed contributions in calculated positions with C–H = 1.00 Å and $B_H = B_{C(iso)} + 1.0$ Å^2. The final refinement cycle resulted in agreement indices of R = 0.062 and R_w = 0.051 (based on F) for the 4268 intensities with $F_o^2 > 0$ and the 336 variables. A structure factor calculation based on the 3227 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ yields an R factor of 0.046. The final difference electron density map has maximum and minimum peak heights of 0.36 and −0.31 e/Å^3; the maximum peak is located approximately midway along a framework bond. Scattering factors for the carbon and hydrogen atoms are those used by the SHELX-76 package.[17] Further crystallographic details are described in Table XIII. Final positional and thermal parameters are given in Table IX.

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Registry No. 1, 101347-19-7; **2**, 115983-77-2; cyclopentane, 287-92-3; norbornane, 279-23-2; dodecahedrane, 4493-23-6.

Supplementary Material Available: Tables of MM3 parameters, final bond lengths and angles, least-squares planes for **2** (Table X) and 1,6-dimethyldodecahedrane, transannular distances, and torsion angles (11 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(23) Ermer, O.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, *1*, 53.