

Comparative X-ray Crystal Structure Analysis of C_{2v} -Dimethylmonosecododecahedrane and D_{3d} -Dimethyldodecahedrane. The Remarkable Consequences of a Missing Framework Bond on Molecular Topology

Gary G. Christoph,*^{1a,2} Peter Engel,*^{1b} R. Usha,^{1a} Douglas W. Balogh,^{1a} and Leo A. Paquette^{1a}

Contribution from the Chemistry Department, The Ohio State University, Columbus, Ohio 43210, and the Laboratorium für Chemie und Mineralogisches Kristallographie, Universität Bern, CH-3012 Bern, Switzerland. Received May 11, 1981

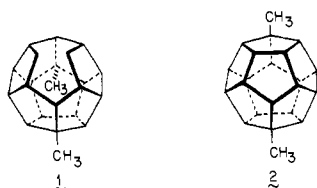
Abstract: Complete single-crystal X-ray diffraction analyses of the title compounds are reported. The monosecododecahedrane (**1**) crystallizes as colorless prisms with the monoclinic space group $P2_1/m$ (C_{2h}^2 , No. 11) and cell constants: $a = 7.858$ (5) Å, $b = 10.618$ (6) Å, $c = 8.898$ (5) Å, $\beta = 91.5$ (1)°. The phase problem was solved by using a combination of direct methods and the M function. Refinement of the structure led to final discrepancy indices $R_F = 0.102$ and $R_{wF^2} = 0.154$ for 1532 unique diffractometer measured intensities. The dodecahedrane (**2**) crystallizes as colorless bisphenoidal orthorhombic prisms having space group $Pbca$ (D_{2h}^8 , No. 61) and cell constants $a = 7.361$ (6) Å, $b = 13.792$ (2) Å, and $c = 13.367$ (1) Å. Automated diffractometer intensities for 1918 unique reflections were used in the direct methods solution and least-squares refinement of the structure, yielding final disagreement factors of $R_F = 0.114$, $R_{wF^2} = 0.088$ and GOF = 1.35. The structure of **1** possesses approximate noncrystallographic C_{2v} point symmetry with the 2-fold axis bisecting the missing framework bond. This latter nonbonded C...C distance is 3.03 Å. Attesting to the pronounced internal stresses resulting from this intramolecular contact are the substantial bond angle distortions of the framework in the vicinity of the missing bond and the flexure of the cyclopentane ring at the gap. These stresses are almost wholly relieved in **2** which possesses noncrystallographic D_{3d} point symmetry within experimental error (beyond its crystallographically imposed center of inversion). The deviations from pure dodecahedral (I_h) symmetry induced by the axial methyl substituents are very slight, amounting to only a 0.062 (4)-Å elongation in the 3-fold direction.

As a direct consequence of its high symmetry and size, the pentagonal dodecahedrane commands the position as the most complex of the structurally intriguing C_nH_n hydrocarbons whose carbon frameworks define regular polyhedra. Particularly striking for its spherical shape and central void, this $C_{20}H_{20}$ molecule has been the focal point of considerable synthetic effort in the last two decades.³ Concurrently, much speculation has arisen concerning the properties of this class of compounds,⁴ the energetics surrounding inclusion of an atom or ion within the cavity,⁵ and, quite naturally, the actual size of the cavity itself. Recently, Paquette and co-workers achieved an expedient synthesis of the C_{2v} -dimethylmonosecododecahedrane **1**,⁶ a development followed

effect of the two methyl groups upon distortions from perfect icosahedral (I_h) symmetry, and approximating the true magnitude of the interior "empty space". Monoseco derivative **1** obviously suffers from serious nonbonded steric interactions in the gap. Coerced by the prevailing proximity factors into a situation which demands relief, the opposed methylene groups are expected to be forced apart and to exert major geometric alterations in the superstructure as a whole. At issue, then, are not only the precise dimensions of **2**, but also the extent to which the framework of **1** must distort to arrive at the potential energy minimum. This investigation provides detailed answers to these timely matters of interest.

Structure Determination of 1. The colorless prismatic crystals of **1** were elongated along what was later determined to be the unique (b) axis with prominent pinacoids $\{101\}$ and $\{1\bar{0}1\}$. Preliminary Weissenberg photographs indicated monoclinic symmetry with systematic absences $0k0$, $k = 2n + 1$, consistent with either space group $P2_1$ or $P2_1/m$. The determination of the lattice parameters and the intensity measurements were performed by using a Nonius CAD-4 automated diffractometer. A small crystal fragment ($0.13 \times 0.18 \times 0.2$ mm) was mounted on a Lindemann glass fiber using clear nail polish (Cutex); 25 reflections with $11^\circ < 2\theta < 23^\circ$ (Mo $K\alpha$) were automatically located and their angle settings carefully optimized by the Nonius automation. Accurate cell parameters were calculated by a least-square procedure, $a = 7.858$ (5) Å, $b = 10.618$ (6) Å, $c = 8.898$ (5) Å, and $\beta = 91.5$ (1)°, leading to a calculated density, assuming two molecules of $C_{22}H_{26}$ per unit cell, of 1.30 g cm^{-3} .

Intensity data were measured at $T = 19$ (1) °C by using the ω - 2θ scan technique with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). All independent reflections in the range $3^\circ \leq 2\theta \leq 52^\circ$ were measured. The orientation of the crystal was checked after every 100 reflection measurements, and the intensity of the 222 reflection was remeasured after every 2.5 h. No deviation from the average intensity greater than 3σ was observed. A total of 1645 reflections were measured. The averaging of multiply measured intensities left 1532 independent



closely by the successful attainment of **2**.⁷ With the availability of **2**, an X-ray crystallographic study was undertaken with a view to measuring precise bond lengths and angles, determining the

- (1) (a) The Ohio State University. (b) Universität Bern.
- (2) Dreyfus Teacher-Scholar.
- (3) Comprehensive review: Eaton, P. *Tetrahedron* **1979**, *35*, 2189.
- (4) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Schulman, J. M.; Venanzi, T.; Disch, R. L. *Ibid.* **1975**, *97*, 5335. (c) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 411.
- (d) Clark, T.; Knox, T. McO.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404.
- (5) (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677. (b) Dixon, D. A.; Deerfield, D.; Graham, G. D. *Chem. Phys. Lett.* **1981**, *78*, 161. (c) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 3297.
- (6) Paquette, L. A.; Balogh, D. W.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 228.
- (7) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. *Science (Washington, D. C.)* **1981**, *211*, 575.

Table I. Final Values of Least Squares Refined Parameters for 1^a

atom	sym equiv	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	equiv B _{iso} , Å ²
C(1)	C(6)'	2115 (4)	4370 (3)	2208 (3)	54 (2)	28 (1)	39 (2)	1 (1)	4 (1)	3 (1)	3.17
C(2)	C(7)'	452 (4)	3681 (3)	2566 (3)	39 (2)	37 (2)	37 (1)	11 (1)	-2 (1)	1 (1)	2.97
C(3)		304 (5)	2500	1553 (5)	34 (2)	41 (2)	35 (2)	0	-5 (2)	0	2.92
C(4)		1814 (7)	2500	0507 (5)	64 (3)	32 (2)	27 (2)	0	5 (2)	0	3.24
C(9)	C(8)'	0591 (4)	3228 (3)	4209 (3)	37 (1)	39 (2)	32 (1)	4 (1)	7 (1)	1 (1)	2.85
C(10)	C(15)'	2313 (4)	3650 (3)	4890 (3)	52 (2)	39 (2)	32 (1)	-0 (1)	-1 (1)	-9 (1)	3.22
C(11)	C(16)'	3365 (4)	4228 (3)	3591 (4)	51 (2)	37 (2)	46 (2)	-13 (1)	3 (1)	-5 (1)	3.53
C(12)	C(17)'	5054 (4)	3649 (4)	2997 (5)	36 (2)	62 (2)	72 (2)	-21 (2)	7 (2)	-6 (2)	4.44
C(13)		5901 (6)	2500	3734 (8)	23 (2)	90 (4)	90 (4)	0	-2 (2)	0	5.35
C(14)		2898 (7)	2500	5800 (5)	60 (3)	54 (3)	34 (2)	0	-10 (2)	0	3.90
C(19)	C(18)'	4690 (5)	3230 (4)	1361 (4)	44 (2)	52 (1)	66 (2)	-7 (1)	28 (2)	2 (2)	4.23
C(20)	C(5)'	2910 (5)	3677 (3)	0867 (4)	61 (2)	37 (2)	37 (2)	-2 (1)	17 (1)	2 (1)	3.52
C(21)	C(22)'	1793 (7)	5767 (4)	1852 (5)	111 (4)	30 (2)	66 (2)	4 (2)	21 (2)	6 (2)	5.41

atom	sym equiv	x	y	z	B _{iso} , Å ²	atom	sym equiv	x	y	z	B _{iso} , Å ²
H(2)	H(7)'	-63 (5)	425 (4)	247 (5)	3.0 (9)	H(13)B		707 (9)	250	346 (8)	4.1 (1.6)
H(3)		-80 (6)	250	104 (6)	1.5 (1.0)	H(14)A		211 (7)	250	684 (6)	2.2 (1.2)
H(4)		146 (7)	250	-64 (7)	1.2 (1.0)	H(14)B		401 (10)	250	611 (9)	5.4 (1.0)
H(9)	H(8)'	-39 (5)	347 (4)	483 (5)	1.1 (7)	H(19)	H(18)'	568 (4)	358 (4)	070 (4)	1.6 (7)
H(10)	H(15)'	218 (5)	436 (4)	562 (4)	1.2 (7)	H(20)	H(5)'	288 (5)	421 (4)	-11 (5)	2.6 (8)
H(11)	H(16)'	364 (5)	516 (4)	389 (4)	1.7 (7)	H(21)A	H(22)A'	121 (6)	634 (5)	276 (6)	4.0 (1.0)
H(12)	H(17)'	596 (5)	435 (4)	304 (5)	2.6 (9)	H(21)B	H(22)B'	96 (6)	583 (5)	91 (6)	5.2 (1.3)
H(13)A		604 (10)	250	488 (9)	5.2 (1.8)	H(21)C	H(22)C'	285 (7)	617 (5)	166 (6)	4.9 (1.2)

^a Estimated standard deviations for the least significant digits are given in parentheses. Nonhydrogen coordinates have been multiplied by 10⁴; all other parameters have been multiplied by 10³. The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^*U_{11} + \dots + 2klb^*c^*U_{23})]$.

reflections, of which 508 were "unobserved" as judged by the criterion $I < 2.58\sigma(I)$, where $\sigma(I)$ was calculated by using

$$\sigma^2(I) = P + M^2(B_1 + B_2)$$

(P , B_1 , and B_2 are respectively the peak and background counts and M is the factor necessary to correct the background counting time to equal the scan time). The intensities were corrected for Lorentz and polarization effects,⁸ but because of the small size of the data crystal and of μ (0.736 cm⁻¹), no absorption corrections were applied.

Statistical tests of the intensities indicated the centrosymmetric choice of space group, $P2_1/m$ (C_{2h}^{2h} , No. 11), and the molecule accordingly is required to possess a crystallographic mirror plane. Various attempts with "direct" phasing methods using the multiresolution procedure universally provided E maps possessing but one very large peak and many spurious peaks. A Patterson synthesis suggested that the large peak corresponded to the location of the center of the molecule. Through use of the expected approximate molecular geometry and the position of its center, the M function method⁹ led to a satisfactory solution. Structure factor/Fourier calculations allowed the complete structure to be elaborated, and the parameters for the 22 carbon atoms were then refined by block-matrix (one atom per block) least-squares calculations.

A difference Fourier map calculated at this stage revealed the positions of all of the hydrogen atoms. In the final least squares refinement cycles the carbon atoms were provided with anisotropic thermal parameters, and the hydrogen atom coordinates and isotropic thermal parameters were also refined. The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (4 + F_o + 0.02F_o^2)^{-1}$. Atomic scattering factors were taken from Vol. IV of ref. 10. The final disagreement indices are $R_F = 0.063$ and $R_{wF^2} = 0.082$ for the 1024 observed reflections, and 0.102 and 0.154, respectively, for all 1532 reflections. A final difference Fourier synthesis showed no peak greater than 0.2 e⁻/Å³ in amplitude. All calculations were

performed using the KRIPROG crystallographic program system.¹¹ The final values of the least squares refined parameters are given in Table I. The observed and calculated structure factor amplitudes are included in the supplementary material.

Structure Determination of 2. Brilliant colorless orthorhombic bisphenoidal crystals of **2** were grown by slow evaporation from a hexane/benzene solution. Prominent faces are {001}, {010}, {111}, and {101}. A small crystal, elongated in the a axis direction, of approximate dimensions 0.14 × 0.14 × 0.32 mm was mounted on a glass fiber and coated with a thin layer of epoxy cement. The automated diffractometer setting angles of 21 reflections having 16.5° < 2θ < 32° ($\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$) were carefully optimized and led to the orthorhombic cell constants $a = 7.361(6) \text{ \AA}$, $b = 13.792(2) \text{ \AA}$, $c = 13.367(1) \text{ \AA}$ ($T = 20(1) \text{ }^\circ\text{C}$). A rapid survey of the low angle intensities provided the unambiguous assignment of the space group as P_{BCA} (D_{2h}^{15} , No. 61) (absences: $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$). The paucity of material prevented an experimental density determination; however, a calculated density reasonable in comparison to those of other highly polycyclic hydrocarbons [e.g., **1** and cubane (1.279 g/cm³)¹²] only resulted when a Z of 4 was assumed. This required that the molecules of **2** contain a crystallographically imposed center of symmetry.

Intensity data were measured at $T = 20(1) \text{ }^\circ\text{C}$ by using an automated four-circle diffractometer by the ω -2θ scan technique with graphite-monochromatized Mo Kα radiation. All reflections having 2θ between 4.0° and 60.0° were measured at least once; most were measured at least twice in an effort to improve the signal/noise ratio. Because of the small size of the crystal, most of the intensities, especially at high angles, were quite weak. In all, 5025 intensities were measured, including ten check reflections. The latter were well distributed in reciprocal space and were reexamined after every 100 measurements. The check reflection intensities showed no variations greater than three times their standard deviations over the period of data collection. After averaging of symmetry related forms and multiple measurements, 1918 unique reflections remained, of which 844 were greater than 3σ(I). The disagreement indices for the multiply measured data are $R'_F = 0.057$ and $R'_{wF^2} = 0.054$.¹³ Psi scans for four strong

(8) Hope, H. *Acta Crystallogr. Sect. A* **1971**, *A27*, 392.

(9) (a) Engel, P. "Abstracts of the 6th European Crystallographic Meeting", 1980; Paper 139. (b) Engel, P.; Sobczak, R.; Paquette, L. A. *Z. Kristallogr.* **1980**, *152*, 169.

(10) Ibers, J. A.; Hamilton, W. C. "International Tables for X-Ray Crystallography"; Birmingham: Kynoch Press, 1974; Vol. IV, p 71.

(11) Engel, P. *Acta Crystallogr., Sect. A* **1978**, *A34S*, 348.

(12) Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889.

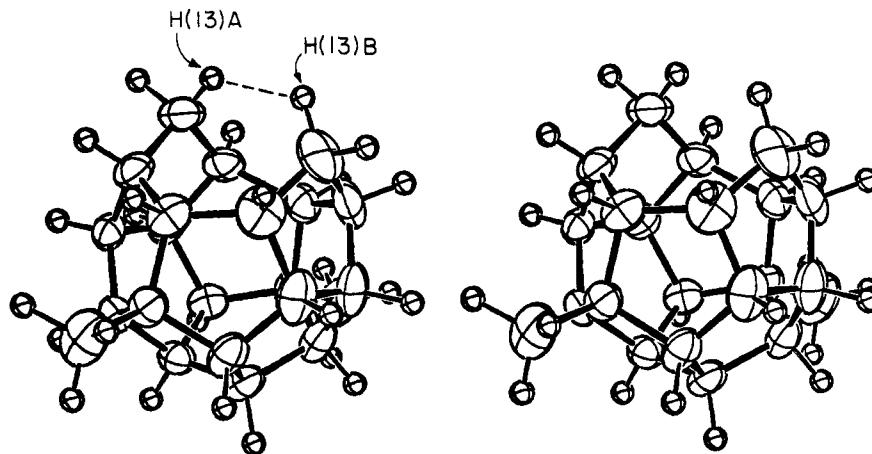


Figure 1. ORTEP stereoview of the monosecododecahedrane, **1**. Thermal ellipsoids are shown at the 50% probability level and the hydrogen spheres are shown reduced in size for clarity. The very short hydrogen-hydrogen contact is indicated by a dashed line.

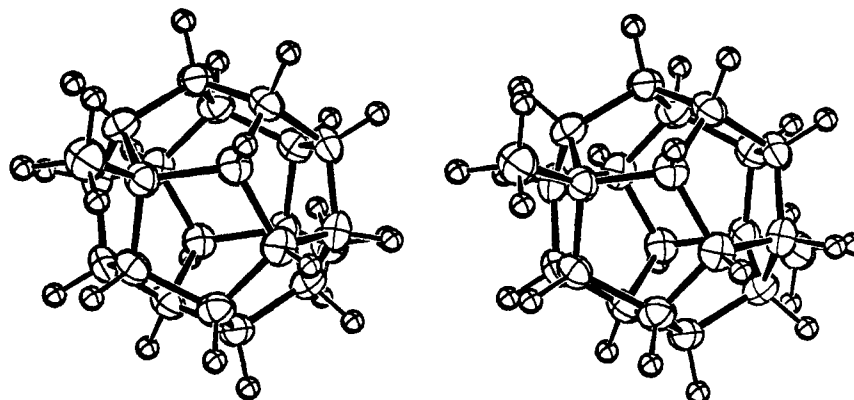


Figure 2. ORTEP stereoview of 1,16-dimethyldodecahedrane, **2**. Thermal ellipsoids as in Figure 1. The molecule is shown in the identical orientation as in Figure 1; the 1,2 shift of the one methyl group is apparent.

reflections having $|\chi - 270^\circ| \leq 30^\circ$ showed no significant dependence upon the psi angle. This observation, plus the small size and symmetric cross section of the data crystal, and the consequently low μr factors ($\mu(\text{Mo K}\alpha) = 0.736 \text{ cm}^{-1}$) allowed us to safely ignore absorption effects. The intensities were corrected for Lorentz and polarization effects (including consideration of the plane of monochromatization of the incident beam) and were reduced to F^2 in the usual way.¹⁴ The standard deviations in the observations were estimated from

$$\sigma^2(F^2) = \frac{1}{LP} [S + G^2(B_1 + B_2) + (0.02I)^2]$$

where S , B_1 , and B_2 are the scan and stationary background counts

(13) The disagreement indices are defined as

$$R'_F = \frac{\sum_{hkl} \sum_{j=1}^{n_j} |F_{av}| - |F_j|}{\sum_{hkl} (n_j F_{av})}$$

$$R'_{wF^2} = \left[\frac{\sum_{hkl} \sum_{j=1}^{n_j} w_j (F_{av}^2 - F_j^2)^2}{\sum_{hkl} \sum_{j=1}^{n_j} w_j F_{av}^4} \right]^{1/2}$$

where

$$F_{av} = \frac{1}{n_j} \sum_{j=1}^{n_j} F_j$$

$$F_{av}^2 = \frac{\sum_{j=1}^{n_j} w_j F_j^2}{\sum_{j=1}^{n_j} w_j}$$

$$w_j' = \frac{1}{\sigma^2(F_j^2)}$$

and

$$w_j = \frac{1}{\sigma^2(F_{av}^2 - F_j^2)}$$

(14) Christoph, G. G.; Beno, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 3156.

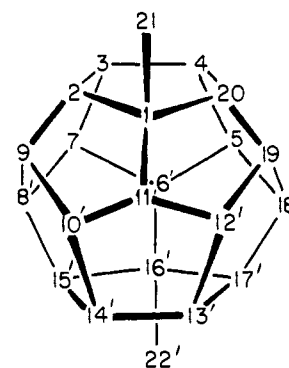


Figure 3. The numbering scheme for the 1,16-dimethyldodecahedrane molecule **2**. The primed atoms are related to the unprimed atoms by the crystallographic inversion center at the molecular centroid.

measured at each end of the scan and G is the factor (in this case $G = 2$) to correct for the proportion of time spent scanning compared to that counting backgrounds. The last term is included to represent components of the error not accounted for by counting statistics.

The structure was solved by using the direct methods program MULTAN,¹⁵ fully elucidated by several structure factor/Fourier calculations, and refined by standard full-matrix least-squares techniques. Hydrogen atoms were located by using difference Fourier maps and their coordinates and isotropic temperature factors refined (the carbon atoms were assigned anisotropic thermal parameters). A secondary extinction correction¹⁶ was also refined in the final cycles. Convergence was assumed when

(15) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B26*, 274.

(16) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

Table II. Final Values of Least Squares Refined Parameters for 2, 1,6-Dimethyldodecahedrane^a

atom	sym equiv	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	equiv B _{iso} , Å ²
C(1)	C(16)'	5590 (3)	11 189 (1)	8959 (1)	32 (1)	25 (1)	26 (1)	-1 (2)	2 (1)	2 (1)	2.42
C(2)	C(17)'	4492 (3)	10 366 (1)	8452 (1)	35 (1)	30 (1)	22 (1)	-2 (1)	-2 (1)	2 (1)	2.47
C(3)	C(13)'	5576 (3)	9 413 (1)	8533 (1)	41 (1)	28 (1)	23 (1)	3 (1)	4 (1)	-5 (1)	2.56
C(4)	C(14)'	7353 (4)	9 631 (1)	9106 (1)	29 (1)	31 (1)	33 (1)	4 (1)	7 (1)	0 (1)	2.66
C(5)	C(10)'	7325 (3)	9 043 (1)	10092 (2)	29 (1)	31 (1)	36 (1)	7 (1)	3 (1)	3 (1)	2.68
C(7)	C(12)'	4425 (3)	8 689 (1)	9164 (1)	43 (1)	23 (1)	26 (1)	-4 (1)	-2 (1)	-6 (1)	2.56
C(9)	C(18)'	2693 (3)	10 232 (1)	9028 (1)	30 (1)	34 (1)	30 (1)	0 (1)	-8 (1)	3 (1)	2.64
C(11)	C(6)'	4468 (3)	11 537 (1)	9873 (1)	36 (1)	22 (1)	31 (1)	3 (1)	1 (1)	2 (1)	2.47
C(19)	C(8)'	7330 (3)	10 806 (1)	10530 (1)	32 (2)	30 (1)	33 (1)	-9 (1)	-6 (1)	-1 (1)	2.69
C(20)	C(15)'	7356 (3)	10 721 (1)	9377 (1)	24 (1)	31 (1)	32 (1)	-3 (1)	4 (1)	4 (1)	2.52
C(21)	C(22)'	6002 (3)	12 021 (2)	8233 (2)	47 (1)	31 (1)	34 (1)	-2 (1)	2 (1)	5 (1)	3.26

atom	sym equiv	x	y	z	B _{iso} , Å	atom	sym equiv	x	y	z	B _{iso} , Å
H(2)	H(16)'	423 (3)	1055 (1)	775 (1)	2.3 (4)	H(11)	H(6)'	419 (2)	1224 (1)	980 (1)	2.2 (4)
H(3)	H(13)'	588 (3)	914 (1)	788 (1)	2.6 (4)	H(19)	H(8)'	834 (3)	1117 (1)	1076 (1)	2.8 (5)
H(4)	H(14)'	847 (3)	946 (1)	872 (1)	2.4 (4)	H(20)	H(15)'	846 (2)	1105 (1)	910 (1)	1.4 (4)
H(5)	H(10)'	838 (2)	860 (1)	1013 (1)	2.4 (4)	H(21)A	H(22)A'	671 (3)	1252 (2)	858 (2)	3.5 (5)
H(7)	H(12)'	425 (3)	814 (1)	878 (1)	2.2 (4)	H(21)B	H(22)B'	483 (3)	1234 (2)	798 (1)	3.7 (5)
H(9)	H(18)'	165 (3)	1035 (1)	859 (1)	2.2 (4)	H(21)C	H(22)C'	666 (3)	1180 (1)	763 (2)	3.0 (4)

^a Estimated standard deviations for the least significant digits are given in parentheses. Nonhydrogen coordinates have been multiplied by 10⁴; all other parameters have been multiplied by 10³. The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2k^2h^*c^*U_{23})]$.

Table III. Interatomic Distances in 1

atoms	dist, ^a Å	atoms	dist, ^a Å	atoms	dist, ^a Å
C(1)-C(2)	1.539 (4)	C(3)-C(4)	1.527 (6)	C(9)-C(10)	1.535 (4)
C(1)-C(20)	1.548 (4)	C(2)-C(9)	1.539 (4)	C(12)-C(19)	1.541 (6)
C(1)-C(11)	1.561 (5)	C(19)-C(20)	1.531 (5)	C(12)-C(13)	1.530 (5)
C(1)-C(21)	1.535 (5)	C(8)'-C(9)	1.546 (4)	C(10)-C(14)	1.529 (5)
C(2)-C(3)	1.547 (4)	C(18)'-C(19)	1.551 (4)	C(10)-C(11)	1.565 (5)
C(4)-C(20)	1.547 (4)	C(13)···C(14)	3.030 (8)	C(11)-C(12)	1.567 (5)
C(2)-H(2)	1.05 (4)	C(12)-H(12)	1.03 (4)	C(20)-H(20)	1.04 (4)
C(3)-H(3)	0.97 (5)	C(13)-H(13)A	1.02 (8)	C(21)-H(21)A	1.12 (5)
C(4)-H(4)	1.04 (5)	C(13)-H(13)B	0.95 (7)	C(21)-H(21)B	1.06 (5)
C(9)-H(9)	0.99 (3)	C(14)-H(14)A	1.13 (6)	C(21)-H(21)C	0.95 (5)
C(10)-H(10)	1.00 (3)	C(14)-H(14)B	0.92 (8)	H(13)A···H(14)B	1.95 (11)
C(11)-H(11)	1.05 (4)	C(19)-H(19)	1.05 (4)		

average framework C-C bond distance (excluding bonds to C(11), methylene carbon atoms, and C(3)-C(4)) = 1.542 (1) Å
average C-H bond distance = 1.025 (12) Å

^a In this and following tables the estimated standard deviations are given in parentheses for the least significant digits.

Table IV. Interatomic Angles for 1

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
C(2)-C(1)-C(20)	107.2 (3)	C(1)-C(2)-C(9)	107.8 (3)	C(9)-C(10)-C(14)	103.0 (3)
C(1)-C(2)-C(3)	108.4 (2)	C(1)-C(20)-C(19)	108.1 (2)	C(19)-C(12)-C(13)	104.0 (4)
C(1)-C(20)-C(4)	108.0 (3)	C(2)-C(9)-C(10)	108.8 (2)	C(10)-C(13)-C(15)'	106.0 (3)
C(2)-C(3)-C(4)	107.9 (2)	C(20)-C(19)-C(12)	109.1 (3)	C(12)-C(13)-C(17)'	105.8 (4)
C(20)-C(4)-C(3)	108.1 (2)	C(9)-C(10)-C(11)	107.5 (2)	C(8)'-C(9)-C(2)	108.2 (2)
C(2)-C(3)-C(7)'	108.3 (2)	C(19)-C(12)-C(11)	107.1 (3)	C(18)'-C(19)-C(20)	108.1 (3)
C(20)-C(4)-C(5)'	107.9 (3)	C(10)-C(11)-C(1)	106.6 (3)	C(8)'-C(9)-C(10)	107.0 (2)
C(11)-C(1)-C(2)	108.1 (2)	C(12)-C(11)-C(1)	107.0 (2)	C(18)'-C(19)-C(12)	106.8 (3)
C(11)-C(1)-C(20)	107.7 (3)	C(10)-C(11)-C(12)	124.3 (3)	C(21)-C(1)-C(2)	111.5 (3)
C(3)-C(2)-C(9)	107.6 (2)	C(11)-C(10)-C(14)	123.2 (4)	C(21)-C(1)-C(20)	111.6 (2)
C(4)-C(20)-C(19)	108.0 (3)	C(11)-C(12)-C(13)	122.1 (2)	C(21)-C(1)-C(11)	110.6 (3)

no parameter shift exceeded 5% of its esd (derived from the diagonal elements of the final least-squares matrix). All 1918 unique reflections were utilized in the refinement. The final disagreement indices were (values for observed data ($>3\sigma(I)$ in parentheses): $R_F = 0.114$ (0.056), $R_wF^2 = 0.088$ (0.072), $GOF = 1.35$ (1.79).¹⁷ The atomic form factors were taken from usual

(17) The definitions of the R factors are $R_F = \sum |F_o| - |F_c| / \sum |F_o|$, $R_wF^2 = \{S / \sum w_F^2\}^{1/2}$, and $GOF = \{S / (n_{\text{obs}} - n_{\text{param}})\}^{1/2}$, where $S = \sum w(F_o^2 - F_c^2)^2$, the function minimized in the least-squares refinement using $w = \sigma^{-2}(F_o^2)$. The programs used in this study were CRYM crystallographic computing system (DuChamp, D. J. "Program and Abstracts", American Crystallographers Association Meeting Bozeman, MT, 1965, ORTEP (Johnson, C. K. Oak Ridge National Laboratory Report ORNL-3794, 1965), and several locally coded routines.

sources.¹⁸ The final difference Fourier map showed no features greater than ± 0.20 e⁻/Å³, many located in bonding regions between the carbon atoms. The final values of the least squares refined parameters are given in Table II; the tabulated structure factor amplitudes are provided in the supplementary material.¹⁹

Results and Discussion

The interatomic distances and angles for **1** and **2** are presented in Tables III-VI. The comparison stereoviews of the two mol-

(18) Carbon: "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1962; Vol. 3. Hydrogen: Steward, R. F.; Davidson, E.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(19) Supplementary material consists of observed and calculated structure factor amplitudes for **1** (7 pages) and **2** (6 pages). See any masthead page for ordering information.

Table V. Interatomic Distances for 2

atoms	dist, Å	atoms	dist, Å
C(1)-C(2)	1.550 (3)	C(3)-C(7)	1.547 (3)
C(1)-C(11)	1.549 (3)	C(4)-C(5)	1.548 (3)
C(1)-C(20)	1.554 (3)	C(9)-C(8)'	1.548 (3)
av (A-B) ^a	1.551 (2)	C(10)' ⁻ -C(14)'	1.548 (3)
C(2)-C(3)	1.541 (3)	C(12)' ⁻ -C(13)'	1.547 (3)
C(2)-C(9)	1.543 (3)	C(19)-C(18)'	1.548 (3)
C(11)-C(10)'	1.545 (3)	av (C-C')	1.548 (2)
C(11)-C(12)'	1.543 (3)	C(3)-C(4)	1.546 (3)
C(20)-C(4)	1.548 (3)	C(9)-C(10)'	1.545 (3)
C(20)-C(19)	1.546 (3)	C(12)' ⁻ -C(19)	1.541 (3)
av (B-C)	1.544 (1)	av (C-C)	1.544 (2)
C(1)-C(21)	1.533 (3)	C(11)-H(11)	0.99 (2)
C(2)-H(2)	0.98 (2)	C(19)-H(19)	0.95 (2)
C(3)-H(3)	0.98 (2)	C(20)-H(20)	0.99 (2)
C(4)-H(4)	1.00 (2)	C(21)-H(21)A	0.98 (2)
C(5)-H(5)	0.99 (2)	C(21)-H(21)B	1.03 (2)
C(7)-C(7)	0.92 (2)	C(21)-H(21)C	0.98 (2)
C(9)-H(9)	0.97 (2)	av (C-H)	0.98

^a Bonds related by D_{3d} symmetry have been averaged. See structure for Table VIII for A, B, C, and C' designations.

Table VI. Interatomic Angles for 2

atoms	angle, deg	atoms	angle, deg
C(2)-C(1)-C(11)	107.1 (2)	C(21)-C(1)-C(2)	112.0 (2)
C(2)-C(1)-C(20)	106.7 (2)	C(21)-C(1)-C(11)	111.9 (2)
C(11)-C(1)-C(20)	106.8 (1)	C(21)-C(1)-C(20)	112.0 (2)
av (B-A-B) ^a	106.9 (2)	av (Me-A-B)	112.0 (2)
C(1)-C(2)-C(3)	109.0 (2)	C(2)-C(3)-C(7)	108.2 (2)
C(1)-C(2)-C(9)	108.5 (2)	C(2)-C(9)-C(8)'	108.1 (2)
C(1)-C(11)-C(10)'	108.7 (1)	C(20)-C(4)-C(5)	108.0 (1)
C(1)-C(11)-C(12)'	108.8 (1)	C(20)-C(19)-C(18)'	108.1 (1)
C(1)-C(20)-C(4)	108.6 (2)	C(11)-C(5)-C(14)'	107.9 (2)
C(1)-C(20)-C(19)	108.6 (2)	C(11)-C(12)' ⁻ -C(13)'	108.0 (2)
av (A-B-C)	108.7 (1)	av (B-C-C')	108.0 (1)
C(2)-C(3)-C(4)	107.9 (2)	C(3)-C(4)-C(5)	108.0 (2)
C(3)-C(4)-C(20)	107.8 (2)	C(4)-C(3)-C(7)	107.9 (2)
C(2)-C(9)-C(10)'	108.1 (1)	C(9)-C(10)' ⁻ -C(14)'	108.0 (1)
C(9)-C(10)' ⁻ -C(11)	107.6 (2)	C(10)' ⁻ -C(9)-C(8)'	108.0 (1)
C(11)-C(12)' ⁻ -C(19)	107.9 (2)	C(12)' ⁻ -C(19)-C(18)'	107.9 (2)
C(12)' ⁻ -C(19)-C(20)	107.9 (2)	C(19)-C(12)' ⁻ -C(13)'	107.9 (1)
av (B-C-C)	107.9 (1)	av (C-C-C')	108.0 (1)

^a Angles related by D_{3d} symmetry have been averaged. See structure for Table VIII for explanation of A, B, C, and C' designations.

ecules, given in Figures 1 and 2, respectively, confirm a chemically significant result. Thus, while the methyl groups in **1**, a molecule of essentially C_{2v} point symmetry, are disposed at what would ultimately be the 1- and 6-positions of the completed dodecahedrane,²⁰ those in **2** are located in the 1- and 16-positions. Since the dimethyldodecahedrane in hand possesses idealized D_{3d} point symmetry, one of the methyl groups in the monosecododecahedrane precursor to **2** (an unsaturated analogue of **1**) has had to migrate under the strongly acidic conditions via a 1,2 shift, either during or subsequent to the final ring closure.^{7,21} The timing and precise mechanism of the methyl migration remains to be elucidated.

The second main point of comparison between **1** and **2** is the considerable steric strain evident in **1**, a consequence of the severe H(13)A...H(14)B nonbonded intramolecular contact, and the contrasting almost perfect absence of distortions from pure dodecahedral symmetry in **2**. The conformation of **1** is best discussed

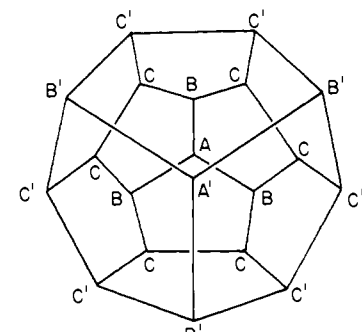
(20) To facilitate comparison, the atoms in the two molecules have both been numbered by the scheme for the dodecahedrane nucleus. Hydrocarbons **1** and **2** possess different crystallographically imposed symmetries. In each, the asymmetric unit consists of half a molecule. Accordingly, symmetry-related atoms, despite their unique atom number, are always indicated by primes. Both labels are given in Tables I and II for the reader's convenience.

(21) Paquette, L. A.; Balogh, D. W., preceding paper in this issue.

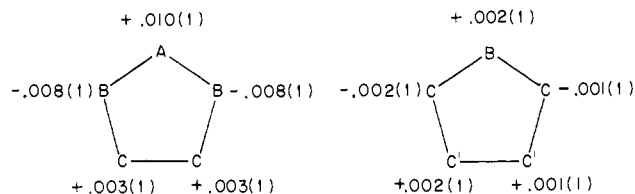
Table VII. Transannular Distance for 1 and 2

1		2	
atoms	dist, Å	atoms	dist, Å
C(1)-C(16)'	4.125 (5)	C(1)-C(16)'	4.389 (4)
C(2)-C(17)'	4.389 (5)	C(2)-C(17)'	4.324 (4)
C(3)-C(13)	4.761 (6)	C(3)-C(13)'	4.327 (4)
C(4)-C(14)	4.764 (7)	C(4)-C(14)'	4.332 (4)
C(5)-C(10)'	4.385 (6)	C(5)-C(10)'	4.331 (4)
C(6)-C(11)'	4.125 (5)	C(6)-C(11)'	4.321 (4)
C(7)-C(12)'	≡C(2)-C(17)'	C(7)-C(12)'	4.327 (4)
C(8)-C(19)	4.429 (5)	C(8)-C(19)'	4.327 (5)
C(9)-C(18)'	≡C(8)-C(19)'	C(9)-C(18)'	4.323 (4)
C(15)-C(20)	≡C(5)-C(7)'	C(15)-C(20)'	4.328 (4)
		av (excluding C(1)-C(16)')	4.327 (1)

Table VIII. Deviations from Least-Squares Planes for 2



atom type	atom	dev, Å	atom	dev, Å	atom	dev, Å	av dev, Å
Apical Rings							
C _A	C(1)	+0.012	C(1)	+0.008	C(1)	+0.009	+0.010 (1)
C _B	C(2)	-0.009	C(2)	-0.006	C(11)	-0.008	-0.008 (1)
C _B	C(11)	-0.010	C(20)	-0.007	C(20)	-0.007	-0.008 (1)
C _C	C(9)	+0.003	C(3)	+0.002	C(12)	+0.004	+0.003 (1)
C _C	C(10)	+0.004	C(4)	+0.004	C(19)	+0.002	+0.003 (1)
Equatorial Rings							
C _B	C(2)	+0.002	C(11)	+0.002	C(20)	+0.002	+0.002 (1)
C _C	C(3)	-0.002	C(10)	-0.001	C(4)	+0.000	-0.001 (1)
C _C	C(9)	-0.002	C(12)	-0.002	C(19)	-0.002	-0.002 (1)
C _C	C(7)	+0.000	C(13)	+0.001	C(5)	-0.002	+0.000 (1)
C _C	C(8)	+0.000	C(14)	+0.001	C(18)	+0.002	+0.001 (1)



in terms of its departures from ideality. Accordingly, we will first examine the structural features of **2**.

Several numerical measures of irregularities in the structure immediately suggest themselves: framework bond angles, torsion angles about the C-C bonds, least-squares planes for the five-membered rings, and transannular C...C distances across the center of the molecule. The last of these considerations is the simplest, and a listing of these values is presented in Table VII. Except for the internal gap separating C(1) atom C(16)', which atoms carry the methyl substituents, the transannular distances are seen to be remarkably consistent. In point of fact, the C(1)-C(16)' distance is only 0.062 Å longer (but some 15σ) than the mean transannular distance between the remaining pairs (which are centrosymmetrically disposed in this molecule). This lengthening presumably reflects both the substituent-induced rehybridization at C(1) and intramolecular steric contacts between methyl and framework hydrogen atoms (vide infra). The bonding geometry

Table IX. Torsion Angles for 2

apical rings		equatorial rings	
atoms	angle, deg	atoms	angle, deg
C(11)-C(10)-C(9)-C(2)	0.00	C(5)-C(4)-C(3)-C(7)	-0.02
C(1)-C(11)-C(10)-C(9)	1.09	C(4)-C(3)-C(7)-C(6)	0.28
C(2)-C(1)-C(11)-C(10)	-1.74	C(3)-C(7)-C(6)-C(5)	-0.39
C(9)-C(2)-C(1)-C(11)	1.73	C(7)-C(6)-C(5)-C(4)	0.35
C(10)-C(9)-C(2)-C(1)	-1.07	C(6)-C(5)-C(4)-C(3)	-0.17
C(11)-C(12)-C(19)-C(20)	0.08	C(9)-C(8)-C(7)-C(3)	0.00
C(12)-C(19)-C(20)-C(1)	0.80	C(8)-C(7)-C(3)-C(2)	0.15
C(19)-C(20)-C(1)-C(11)	-1.38	C(7)-C(3)-C(2)-C(9)	-0.27
C(20)-C(1)-C(11)-C(12)	1.44	C(3)-C(2)-C(9)-C(8)	0.28
C(1)-C(11)-C(12)-C(19)	-0.97	C(2)-C(9)-C(8)-C(7)	-0.18
C(2)-C(3)-C(4)-C(20)	0.02	C(19)-C(20)-C(4)-C(5)	0.00
C(3)-C(4)-C(20)-C(1)	0.78	C(20)-C(4)-C(5)-C(18)	0.19
C(4)-C(20)-C(1)-C(2)	-1.30	C(4)-C(5)-C(18)-C(19)	-0.30
C(20)-C(1)-C(2)-C(3)	1.34	C(5)-C(18)-C(19)-C(20)	0.30
C(1)-C(2)-C(3)-C(4)	-0.88	C(18)-C(19)-C(20)-C(4)	-0.16
Averages (See Structure for Table VIII)			
C _B -C _C -C _C -C _B	0.03	C _{C'} -C _C -C _C -C _{C'}	-0.01
C _C -C _C -C _B -C _A	0.89	C _C -C _C -C _{C'} -C _{B'}	0.21
C _C -C _B -C _A -C _B	-1.47	C _C -C _{C'} -C _{B'} -C _{C'}	-0.32
C _B -C _A -C _B -C _C	1.50	C _{C'} -C _{B'} -C _{C'} -C _C	0.31
C _A -C _B -C _C -C _C	-0.97	C _{B'} -C _{C'} -C _C -C _C	-0.17

at C(1) is only slightly, albeit significantly, different from that at all the other carbon centers. The framework C-C-C angles at C(1) average 106.9 (2)°, smaller than the 108.0° expected for a regular pentagon. The bond distances to C(1), excluding the C(1)-C(21) bond (to the methyl), are marginally longer than the other framework C-C distances.

The apical elongation due the methyl substituents appears to affect only C(1). This is evident both in the calculated deviations of atoms from least-squares planes (Table VIII) and in the torsion angles about the five-membered rings (Table IX). Of the six crystallographically independent pentagons, the three equatorial rings are planar within experimental error, while the three rings containing C(1) are in the envelope conformation with dihedral angles at the C_B-C_B line (see legend for Table VIII) of ca. 1.0°.

The molecular point symmetry of 2 is *D*_{3d} within experimental error, although only an inversion center is crystallographically imposed. Averaged values for equivalent bond distances and angles assuming this high point symmetry are reported in the various tables. The actual values in all cases are well within 3σ of the appropriate mean value. None of the distances and angles are remarkable; the average framework C-C distance is quite close to the value for cyclopentane (1.546 (1) Å).²²

Intermolecular contacts are all longer than the minimal van der Waals H...H distances (2.40 Å).²³ The only intramolecular contacts in 2 worthy of discussion are those between the methyl hydrogen atoms and the neighboring framework hydrogens. The orientation of the methyl linkage is seen to be gauche, with resultant minimization of the H...H intramolecular contacts. These six contacts average 2.51 Å, with none smaller than 2.48 (3) Å. Thus, there is approximately 0.1-Å excess distance between the methyl and framework hydrogen atoms, suggesting that the slight pyramidalization of C(1) may arise primarily from an electronic rather than a steric origin. H...H contact distances between neighboring framework hydrogen atoms range from 2.19 (3) to 2.30 (3) Å. These C-H bonds are all perfectly eclipsed and are undoubtedly the major contributor to the inherent strain energy of the molecule. The molecular packing in the crystal is illustrated in Figure 4.

In contrast to the very slight deviations from idealized dodecahedral symmetry present in 2, the topology of 1 is severely

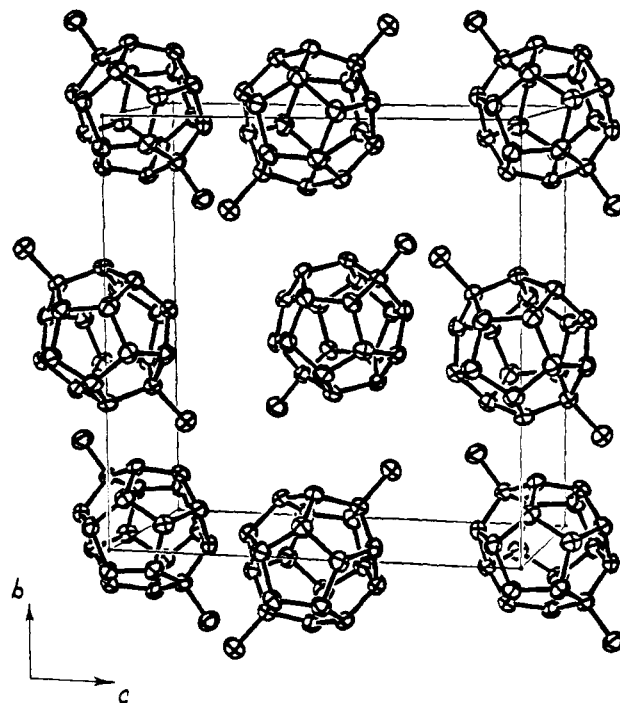
Figure 4. Packing diagram for 2, projected down the crystallographic *a* axis.

Table X. Deviations from Least-Squares Planes for 1

atom	dev, Å	atom	dev, Å	atom	dev, Å
C(8)'	+0.067	C(1)	+0.050	C(9)	-0.006
C(9)	+0.067	C(2)	-0.015	C(8)'	-0.006
C(10)	-0.186	C(9)	-0.026	C(7)'	+0.016
C(14)	+0.237	C(10)	+0.056	C(3)	-0.020
C(15)'	-0.186	C(11)	-0.065	C(2)	+0.016
C(19)	+0.064	C(1)	+0.049	C(19)	-0.006
C(18)'	+0.064	C(11)	-0.064	C(18)'	-0.006
C(17)'	-0.176	C(12)	+0.055	C(5)'	+0.015
C(13)	+0.224	C(19)	-0.025	C(3)	-0.019
C(12)	-0.176	C(20)	-0.015	C(20)	+0.015
C(1)	-0.032	C(11)	+0.023		
C(2)	+0.027	C(10)	-0.016		
C(3)	-0.011	C(14)	+0.004		
C(4)	-0.009	C(13)	+0.007		
C(20)	+0.026	C(12)	-0.018		

distorted. The high connectivity of the molecule constrains the two methylene groups to be closely juxtaposed. The enforced approach of the hydrogen atoms carried by these methylene carbons results in considerable flexing of the violated dodecahedral framework as it attempts to alleviate the close contact. The *H*(13)*A*...*H*(14)*B* distance is 1.95 Å, ca. 0.47 Å smaller than twice the van der Waals radius for hydrogen. Furthermore, the C(13)...C(14) distance is 3.03 Å, nearly 1.5 Å greater than the normal C-C single bond distance. This expansion in the C(13)...C(14) direction draws the two other sides of the framework toward each other, forming a somewhat flattened pouch, as is apparent from the pertinent transannular distances listed in Table VII. The deviations from the least-squares planes through the five-membered rings (Table X) and the torsion angles (Table XI) show that although all of the pentagonal rings are affected, the four located on the opposite side of the cavity from the missing bond are the most regular. Nearly 1 Å of the 1.5-Å increase in the C(13)...C(14) distance is accommodated by folding the two methylene-containing cyclopentane rings into highly folded envelope conformations with dihedral angles of 37.2 and 35.1°. The remaining 0.5 Å is made possible by combined small flexures within the remaining rings. Although the torsion angles for these two highly folded cyclopentane rings, Table XI, are somewhat smaller in magnitude than for free cyclopentane, the inherent strain

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

(23) Pauling, L. "The Nature of the Chemical Bond", 3rd ed; Cornell University Press: Ithaca, NY, 1960; p 260.

Table XI. Torsion Angles for 1^a

atoms	angle, deg	atoms	angle, deg
C(15)'-C(8)'-C(9)-C(10)	0.00	C(12)-C(19)-C(18)-C(17)'	0.00
C(8)-C(9)-C(10)-C(14)	-21.95	C(19)-C(18)'-C(17)'-C(13)	-20.92
C(9)-C(10)-C(14)-C(15)'	36.42	C(18)'-C(17)'-C(13)-C(12)	34.54
C(10)-C(14)-C(15)'-C(8)'	-36.42	C(17)'-C(13)-C(12)-C(19)	-34.54
C(14)-C(15)'-C(8)'-C(9)	+21.95	C(13)-C(12)-C(19)-C(18)'	20.92
C(1)-C(2)-C(9)-C(10)	1.04	C(1)-C(20)-C(19)-C(12)	-0.91
C(2)-C(9)-C(10)-C(11)	-7.17	C(20)-C(19)-C(12)-C(11)	6.89
C(9)-C(10)-C(11)-C(1)	10.40	C(19)-C(12)-C(11)-C(1)	-10.13
C(10)-C(11)-C(1)-C(2)	-9.82	C(12)-C(11)-C(1)-C(20)	9.63
C(11)-C(1)-C(2)-C(9)	5.52	C(11)-C(1)-C(20)-C(19)	-5.47
C(2)-C(9)-C(8)'-C(7)'	0.00	C(20)-C(19)-C(18)'-C(5)'	0.00
C(9)-C(8)'-C(7)''-C(3)	-1.9	C(19)-C(18)'-C(5)''-C(4)	1.84
C(8)''-C(7)''-C(3)-C(2)	3.09	C(18)''-C(5)''-C(4)-C(20)	-2.97
C(7)''-C(3)-C(2)-C(9)	-3.09	C(5)''-C(4)-C(20)-C(19)	+2.97
C(3)-C(2)-C(9)-C(8)'	1.90	C(4)-C(20)-C(19)-C(18)'	-1.84
C(2)-C(3)-C(4)-C(20)	0.10	C(10)-C(14)-C(13)-C(12)	-0.02
C(3)-C(4)-C(20)-C(1)	3.05	C(14)-C(13)-C(12)-C(11)	2.34
C(4)-C(20)-C(1)-C(2)	-5.03	C(13)-C(12)-C(11)-C(10)	-4.81
C(20)-C(1)-C(2)-C(3)	5.12	C(12)-C(11)-C(10)-C(14)	4.64
C(1)-C(2)-C(3)-C(4)	-3.27	C(11)-C(10)-C(14)-C(13)	-2.08

^a Right and left columns are chemically equivalent under C_{2v} symmetry.

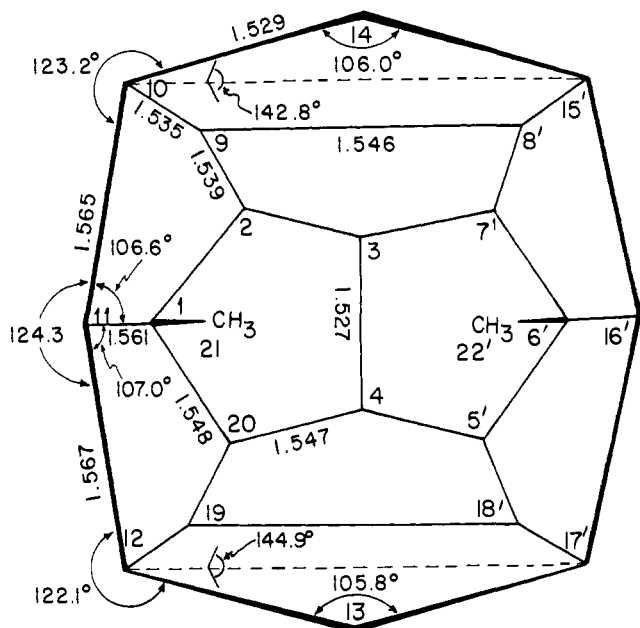


Figure 5. Atomic numbering scheme and selected distances and angles for the monosecododecahedrane, 1. The primed atoms are related to the unprimed atoms by a crystallographic mirror plane which bisects the figure vertically.

is actually greater because the framework strongly restricts the rotations of the four nonmethylene carbons.

Curiously, the framework bonds to the two methylene carbon atoms are, at 1.530 (3) Å, somewhat shorter than both the 1.546 Å of cyclopentane²² and the 1.542 (1) Å average of the framework bonds of the "normal" central four rings. This is perhaps a compensatory result of the angle strain at the C(10) and C(14) centers, which each also share a very long bond to C(11) (average 1.566 (3) Å). The exterior C-C-C angles at these three carbon atoms are all much larger than pentagonal and tetrahedral values, averaging about 123°. The geometry at peripheral carbon C(11) is the most severely distorted of all, as can be seen in Figure 5. All of its bonds are longer than normal. Furthermore, C(11) suffers most severe angle strain as it accommodates the wider opening of the "mouth" of the pouch.

Despite the unusually short C(3)-C(4) bond, which may be under compressional stress, the interior angles of the four "normal" five-membered rings are very close to the ideal 108.0°. The most distorted cyclopentane rings, those carrying the methylene carbons,

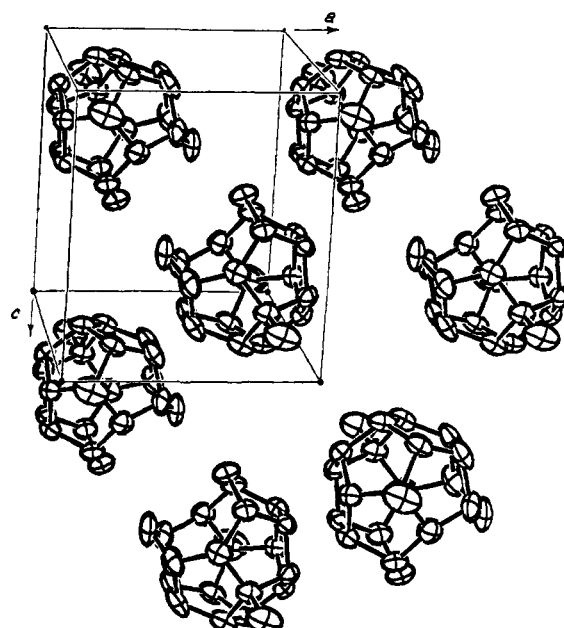


Figure 6. Packing diagram for 1, projected down the *b* axis. The oblateness of the pouch-shaped molecules is apparent in this view.

have *all* of their interior angles smaller, by as much as 5°, than the pentagonal value.

Figure 5 and Tables III and IV well illustrate a final point: the molecular point symmetry is well within experimental error of being C_{2v} . Only the mirror plane, which bisects the cavity of passing through C(3), C(4), C(13), and C(14), is required crystallographically, yet chemically equivalent bond distances and angles are all within 3σ of being equal, many within 1σ .

Figure 6 shows the crystal packing of the molecules. All intermolecular contacts are at normal van der Waals distances.

Theoreticians have speculated that the dodecahedrane cavity may be large enough to encrypt an atom or ion.⁵ Considering the van der Waals radius of carbon, a neutral atom would have to possess a diameter smaller than 0.9 Å to fit within the central cavity of 2. Encapsulation of an atomic ion, several of which possess diameters of this magnitude, seems more feasible, although preparing such a clathrate structure is an imposing challenge. Incorporation of such an ion in a precursor such as 1 appears *not* to be a particularly promising route, simply because the cavity is 0.2 Å narrower than in 2. The encapsulation of a proton in the completed dodecahedrane is perhaps most likely and is one

which constitutes a chemically most exciting prospect.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-7911164), Research Corp., and National Institutes of Health (Grant AI-11490) for their financial support.

Registry No. 1, 80262-54-0; **2,** 77387-50-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

Polymerized Phosphatidylcholine Vesicles. Synthesis and Characterization ¹

Steven L. Regen,* Alok Singh, Günther Oehme,² and Maninder Singh

Contribution from the Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233. Received July 23, 1981

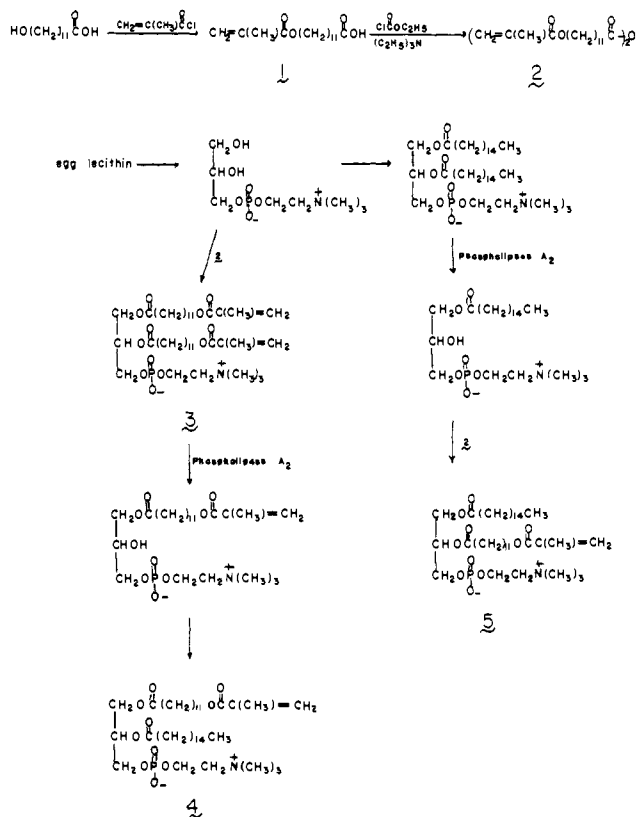
Abstract: The synthesis and characterization of photopolymerized vesicles derived from bis[12-(methacryloyloxy)dodecanoyl]-L- α -phosphatidylcholine (**3**) 1-[12-(methacryloyloxy)dodecanoyl]-2-palmitoyl-L- α -phosphatidylcholine (**4**), and 1-palmitoyl-2-[12-(methacryloyloxy)dodecanoyl]-L- α -phosphatidylcholine (**5**) are described. Ultrasonic irradiation of **3**, **4**, **5**, 20% **3** + 80% **4**, and 20% **3** + 80% **5** in water at 50 °C yields opalescent to optically clear dispersions. Electron microscopy, entrapment of [¹⁴C]sucrose, and permeability measurements provide strong evidence for closed multilamellar vesicles having diameters ranging between 350 and 1400 Å. Fourier transform ¹H NMR spectra of the aqueous dispersions as well as IR spectra of chloroform extracts establish that no significant lipid decomposition occurs during vesicle preparation. Direct UV irradiation (254 nm) produces polymerized analogues of similar size and shape which (1) entrap [¹⁴C]sucrose, (2) show reduced permeability, and (3) exhibit enhanced stability.

Introduction

Phospholipid bilayer vesicles are receiving intense interest as models for biological membranes, devices for solar energy conversion, and carriers of drugs.³⁻¹⁰ Because these aggregates are unstable, having relatively short shelf lives, their use in mechanistic studies and practical applications is seriously limited.³

We have recently introduced the concept of polymerized vesicles and have suggested that phosphatidylcholine derivatives might constitute an important new class of materials.¹¹ Not only would they be expected to exhibit greater stability than liposomes (vesicles formed from naturally occurring phospholipids) but they should also retain many important properties of vesicles, e.g., the ability to (1) promote the separation of charged photoproducts and (2) entrap and slowly release drugs. Moreover, because of the likelihood of increased stability toward biological substances, such vesicles could be used as unique probes in mechanistic studies involving lipid-protein and vesicle-cell interactions. For these

Scheme I



(1) This investigation was supported by PHS Grant No. CA28891-01, awarded by the National Cancer Institute, DHHS, and the National Science Foundation (Grant CHE-77-28366).

(2) On leave from the Central Institute of Organic Chemistry, Academy of Sciences of the GDR.

(3) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7.

(4) Papahadjopoulos, D. *Ann. N.Y. Acad. Sci.* **1978**, *308*, 1.

(5) Juliano, R. L. *Can. J. Physiol. Pharmacol.* **1978**, *56*, 683.

(6) Bangham, A. D. *Prog. Biophys. Mol. Biol.* **1968**, *18*, 29. Bangham, A. D.; Hill, M. W.; Hill, N. G. *Methods Membr. Biol.* **1974**, *11*, 38.

(7) Mangel, M. *Biochim. Biophys. Acta* **1976**, *430* 459. Toyoshima, Y.; Morino, M.; Sukigara, M. *Nature (London)* **1977**, *265*, 187. Stillwell, W.; Tien, H. T. *Biochim. Biophys. Acta* **1978**, *81*, 212.

(8) Weinstein, J. N.; Magin, R. L.; Yatvin, M. B.; Zaharko, D. S. *Science (Washington, D.C.)* **1979**, *204*, 188.

(9) Calvin, M. *Acc. Chem. Res.* **1978**, *11*, 369.

(10) Ford, W. E.; Otvos, J. W. Calvin, M. *Nature (London)* **1978**, *274*, 507. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 3590.

(11) Regen, S. L.; Czech, B.; Singh, A. *J. Am. Chem. Soc.* **1980**, *102*, 6638.

reasons and for the purpose of expanding the concept of the polymerized vesicles, we have set out to synthesize phosphatidylcholine analogues. The following report details our efforts.¹²⁻¹⁴