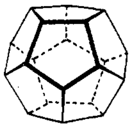
Reports

Crystal and Molecular Structure of a Pentagonal Dodecahedrane

Abstract. *The successful synthesis of a pentagonal dodecahedrane molecule has been achieved. Obtained by a sequence of 20 stereochemically controlled steps beginning with the readily available cyclopentadienide anion, the 1,16-dimethyl derivative has* D_{3d} *symmetry and unusual physical properties. The x-ray crystal structure shows that the alkyl groups cause only small distortions from pure dodecahedral symmetry.*

The very special esteem in which the ancient Greek mathematicians held their "cosmic figures" or regular polyhedra has persisted through the centuries. In the past two decades, the heritage of the Platonic solids has passed inevitably into the realm of organic chemistry. Indeed, practitioners of organic synthesis have already succeeded in constructing from carbon and hydrogen a tetra-*tert*-butyl derivative of tetrahedrane (*1*) and the unsubstituted cubane molecule (*2*). Since octahedrane and icosahedrane do not adapt to the normal tetracovalence of carbon, they do not represent viable synthetic targets. In contrast, compounds of boron exhibit a propensity for existing as icosahedral cages. To our knowledge, no molecule or ion of any type has previously been uncovered that exists in the shape of a regular (pentagonal) dodecahedrane, **1** (*3*). The especially high aesthetic appeal, exquisite shape (point group I_h), and complex nature of **1** have combined to draw substantial theoretical (*4*) and experimental (*5*) interest. Furthermore, a tactical elaboration of **1** would serve to confirm or dismiss the many predictions of novel physical and chemical characteristics already advanced for this fascinating topologically spherical structure.



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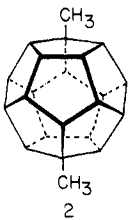

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We have now succeeded in gaining access to a pentagonal dodecahedrane, namely, the D_{3d} symmetric 1,16-dimethyl derivative, **2**. The important stereochemical issue of maintaining all nonframework atoms on the oustide of the sphere has been solved by a suitable experimental strategy, which delivers **2** in only 20 steps from the cyclopentadienide anion, **3**, shown in Fig. 1. The necessarily serial (nonconvergent) synthesis leads, by the so-called domino Diels-Alder pathway, to **4** (*6*, *7*), which is then fashioned into the dichloro diester, **5** (*8*). The four-stage transformation of **5** to **6** serves to craft a molecule requiring merely the installation of three carbon-carbon sigma bonds (*9*). With the introduction of two of these to give **7** (*9*), extreme congestion develops in the area of the gap as a consequence of prevailing nonbonded steric interactions. Since the dodecahedrane nucleus is essentially strain-free, this progenitor molecule, which is not so blessed, was expected to proceed to **2** with substantial thermochemical reward. Under the best conditions uncovered to date, **7** has been converted to **2** upon treatment with trifluoromethanesulfonic acid in dichloromethane solution at room temperature for 10 minutes. Especially noteworthy is the fact that a 1,2-methyl migration occurs during the dehydration-cyclization process, with resultant formation of the D_{3d} isomer. It is at present not known whether this shift occurs before or after closure to the dodecahedrane ring system.

The dimethyldodecahedrane was obtained as elongated colorless orthorhombic bisphenoidal prisms by recrystallization from benzene. When heated in a sealed tube to 350°C, some discoloration of the crystals was noted. A dark brown coloration developed above 410°C, but melting was not observed.

A small brilliant crystal, cleaved to dimensions 0.32 by 0.14 by 0.14 mm, was mounted with its long axis coincident with the ϕ axis of a four-circle automated diffractometer for the data collection. Orthorhombic unit cell parameters at 20°C were obtained by least-squares fit of the setting angles for 20 carefully centered reflections: $a = 7.361(6)$, $b = 13.792(2)$, $c = 13.367(1)$ Å. The systematic absences ($h0\ell$, $\ell = 2n + 1$; $hk0$, $h = 2n + 1$; $0k\ell$, $k = 2n + 1$) unambiguously fixed the space group as $Pbca$ (D_{2h}^{15}, No. 61). The calculated density, ρ_c, was reasonable in comparison to values for other highly polycylic saturated hydrocarbons [for example, 1.279 g/cm^3 for cubane (*10*)] only for four molecules per unit cell ($\rho_c = 1.412$ g/cm^3), requiring **2** to possess a crystallographic center of symmetry. Intensity data were collected with monochromatic Mo$K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å); all reflections having $2\theta \leq 60.0°$ were measured at least once. Of the 1918 unique reflections, only 844 had intensities greater than 3 standard deviations above background due to the small size of the crystal. The structure was solved by direct methods (*11*) and refined by standard full-matrix least-

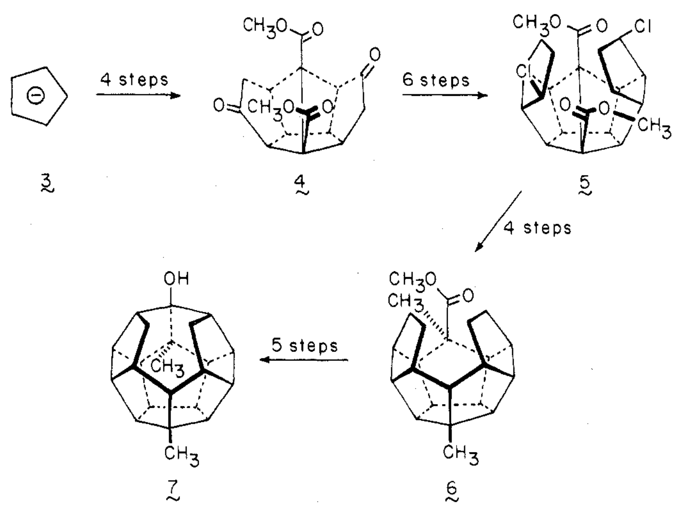

Fig. 1. Stages in the synthesis of 1,16-dimethyldodecahedrane.

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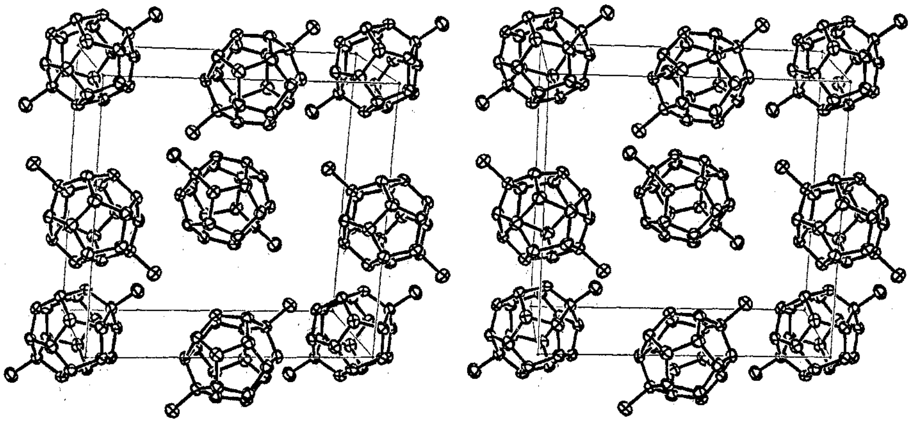

Fig. 2. Stereopair drawing of the crystal packing of **2**, viewed down the *x* axis.

squares and Fourier techniques (*12*). Atomic coordinates for all carbon and hydrogen atoms, anisotropic thermal parameters for the carbon atoms, isotropic temperature factors for the hydrogen atoms, a scale factor, and a secondary extinction parameter (*13*) were all refined in the last least-squares cycles. The current reliability index *R* for all 1918 reflections used in the refinement is 11.4 percent, while that for the observed data (> 3 standard deviations above background) is 5.6 percent, consistent with the large proportion of weak intensities. A difference Fourier synthesis shows no peaks greater than 0.2 $e^-/Å^3$, and the most significant of these are localized in the bonding regions between carbon atoms.

The structure of the molecule is illustrated in the ORTEP diagram on the cover and the molecular packing arrangement is shown in Fig. 2. The carbon-carbon and carbon-hydrogen bond distances of the dodecahedral cage that are related by the noncrystallographic $\bar{3}$ symmetry axis average to 1.546(2) (*14*) and 0.98(1) Å, respectively. The molecule possesses essentially perfect D_{3d} symmetry, although of the point symmetry operations, only a center of inversion is enforced by the crystal symmetry. Either because of induced rehybridization of C-1 and C-16 by the methyl substituents or because of steric crowding between the methyl and neighboring hydrogen atoms, there is a slight elongation of the molecule in the direction of the $\bar{3}$ axis. Although not particularly evident in the bond distances, this distortion from pure dodecahedral symmetry is apparent in the < 108.0° bond angles surrounding the methyl-substituted carbon and by the slight nonplanarity of the flanking five-membered rings. The elongation is most clearly evident in the transcavity distance between symmetry-related pairs of atoms: 4.389(4) Å for C-1 to C-16, but 4.327(1) Å for the remaining nine pairs of dodecahedral carbons. Taking account of the van der Waals radius of carbon (*15*), the transcavity diameter is only 0.9 Å, too small for encapsulation of any but the smallest ions.

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Petroleum Drilling and Production in the United States: Yield per Effort and Net Energy Analysis

Abstract. *For the past three decades the quantity of petroleum (both oil and oil plus gas) found per foot of drilling effort in the United States for any given year can be expressed as a secular decrease of about 2 percent per year combined with an inverse function of drilling effort for that year. Extrapolation of energy costs and gains from petroleum drilling and extraction indicates that drilling for domestic petroleum could cease to be a net source of energy by about 2004 at low drilling rates and by 2000 or sooner at high drilling rates, and that the net yield will be less at higher drilling rates.*

Production and reserves of U.S. liquid and gaseous petroleum peaked in the early 1970's and generally have declined since then despite considerable increases in drilling effort. Continued increases in effort are likely in the near future because imports carry a heavy economic and political price and because recent increases in oil prices have given petroleum corporations considerable quantities of new working capital. But the Carter Administration and Congress have imposed a large "windfall profits tax" on petroleum corporations, which will decrease the capital available for additional exploratory effort. On the other hand, oil industry advertisements and some politicians have promised large new exploratory efforts and oil supplies if government decreases regulation and