

X-ray Crystallographic Analysis of the Structural Distortions Induced by Substitution and Annulation of the Dodecahedrane Nucleus

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(Received 6 May 1988; accepted 15 November 1988)

Abstract. Methyl dodecahedranecarboxylate, $C_{22}H_{22}O_2$, (4), $M_r = 318.42$, monoclinic, $C2/c$, $a = 12.600$ (2), $b = 7.992$ (4), $c = 28.975$ (7) Å, $\beta = 101.79$ (2)°, $V = 2856$ Å³, $Z = 8$, $D_x = 1.48$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.84$ cm⁻¹, $F(000) = 1360$, $T = 294$ K, $R = 0.044$ for 2109 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. 21-Phenylcyclopropadodecahedrane, $C_{27}H_{24}$, (5), $M_r = 348.49$, tetragonal, $P4_2/n$, $a = 17.528$ (3), $c = 10.752$ (2) Å, $V = 3303$ Å³, $Z = 8$, $D_x = 1.40$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.85$ cm⁻¹, $F(000) = 1488$, $T = 295$ K, $R = 0.053$ for the 1773 unique reflections with $F_o^2 > 1\sigma(F_o^2)$. The molecular geometries of methoxycarbonyldodecahedrane (4) and 21-phenylcyclopropadodecahedrane (5) are compared to those of the parent $C_{20}H_{20}$ hydrocarbon (1) and its 1,16-dimethyl derivative (2). For both (2) and (4), the framework is modestly distorted by the substituents, the intracavity distance being more extended along the axis that contains the pendant group(s). Remarkably for (5), its cyclopropane ring has all C–C bonds and internal angles essentially equal, and those dodecahedrane bonds in the immediate vicinity of the ring fusion are extensively perturbed.

Introduction. The family of spherical compounds known as dodecahedranes is of broad interest for a number of reasons (Paquette, 1981, 1982, 1983, 1984; Santos, Balogh, Doecke, Marshall & Paquette, 1986; Eaton, 1979). The parent hydrocarbon [$C_{20}H_{20}$ (1)] does not deviate significantly from ideal I_h symmetry, its regular polyhedral features surfacing unmistakably in the solid state where the highest possible crystallographic symmetry (T_h) available to it is adopted (Gallucci, Doecke & Paquette, 1986). The central cavity of (1) has provoked considerable speculation, particularly with regard to its actual size and the energetics surrounding inclusion of an atom or ion within the void (Schulman & Disch, 1978; Disch &

Schulman, 1981; Dixon, Deerfield & Graham, 1981). Various theoretical studies (Engler, Andose & Schleyer, 1973; Clark, Knox, Mackle & McKerver, 1975; Schulman, Venanzi & Disch, 1975; Ermer, 1977; Clark, Knox, McKerver, Mackle & Rooney, 1979; Schulman & Disch, 1984; Scamehorn, Hermiller & Pitzer, 1986) have emphasized the unique properties of this class of molecules (Paquette, Weber & Kobayashi, 1988; Olah, Surya Prakash, Kobayashi & Paquette, 1988; Paquette, Kobayashi & Gallucci, 1988).

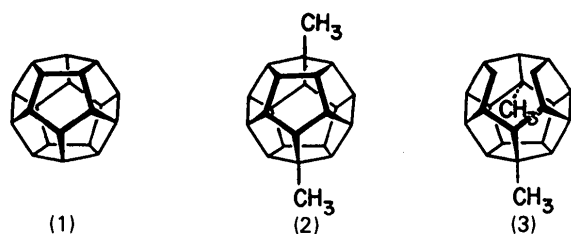
Structural data are available not only for (1) (Gallucci, Doecke & Paquette, 1986) but also for its 1,16-dimethyl derivative (2) (Paquette, Balogh, Usha, Kountz & Christoph, 1981; Christoph, Engel, Usha, Balogh & Paquette, 1982; Allinger, Geise, Pyckhout, Paquette & Gallucci, 1989) and the related secododecahedrane (3) (Christoph, Engel, Usha, Balogh & Paquette, 1982; Ermer, 1983). The considerable steric strain in (3) brought on by the severe H–H nonbonded intramolecular contact in the open seam engenders numerous structural irregularities. Illustrative of this phenomenon is the significant departure from ideality exhibited by the framework bond angles, the least-squares planes for the five-membered rings and the torsion angles about the C–C bonds. In striking contrast, the molecular point symmetry adopted by (2) is essentially D_{3d} within experimental error, with only a center of inversion enforced by the crystal symmetry. A slight distortion of the molecule, either because of induced rehybridization at the methyl-substituted carbon atoms or steric crowding between the methyls and the immediately adjacent hydrogen atoms is apparent along the C1, C16 axis. The elongation in question is most readily seen in the intracavity distances between symmetry-related pairs of atoms: 4.389 (4) Å for C1 to C16 and 4.327 (1) Å for the remaining nine pairs of dodecahedral carbon atoms. For comparison, the structure of (1) exhibits two types of intracavity distances, of 4.310 (3) and 4.317 (5) Å. It should be noted that a regular dodecahedron with center-to-apex distance of 2.157 Å (or an intracavity distance of 4.314 Å) would contain an edge length of 1.539 Å (*International Tables for X-ray Crystallography*,

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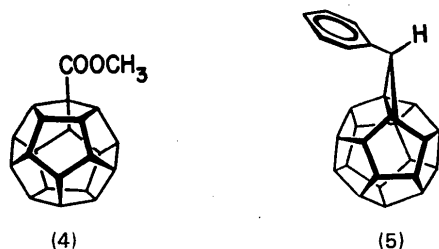
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1959). The bond lengths in dodecahedrane range from 1.535 to 1.541 Å.



On theoretical grounds, any deformation of perfect I_h symmetry for the unsubstituted dodecahedrane is accompanied by steep increases in ground-state energy (Ermer, 1977). Thus, the influence of substituents on dodecahedrane structure holds considerable importance. Since recent synthetic advances in this laboratory have made available the methoxycarbonyl derivative (4) (Paquette, Weber & Kobayashi, 1988) and the annulated cyclopropadodecahedrane (5) (Paquette, Kobayashi & Gallucci, 1988), X-ray analyses of this pair of nicely crystalline molecules have been undertaken. The expectation was that the derived structural data may serve as a reliable foundation for future computational assessments of these unique molecular constructs.



Experimental. *Structure determination of (4).* Examination of the colorless crystals of (4) on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation revealed a monoclinic crystal system. The systematic absences, hkl , $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$, restrict the space-group possibilities to Cc and $C2/c$. At room temperature, the cell constants were determined by a least-squares fit of the setting angles for 25 reflections in the 2θ range 23–29°.

Intensities were measured by the θ - 2θ scan method. Data reduction and all subsequent calculations were performed with the *SDP* system (B. A. Frenz & Associates Inc., 1982). The four standard reflections measured during the course of data collection indicated that the crystal was stable. Further crystallographic details appear in Table 1.

The structure was solved *via* *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) in the $C2/c$ space group. All the carbon and

Table 1. *Additional crystallographic details for (4) and (5)*

	(4)	(5)
Crystal size (mm)	0.09 × 0.18 × 0.23	0.15 × 0.19 × 0.42
2θ limits (°)	$4 \leq 2\theta \leq 55$	$3 \leq 2\theta \leq 55$
Data collected	$+h, +k, \pm l$	$+h, +k, +l$
Unique data	3433	4018
Unique data used in refinement*	2109 with $I > 3\sigma(I)$	1773 with $I > 1\sigma(I)$
Final number of variables	305	244
$R(F)^\dagger$	0.044	0.053
$wR(F)^\ddagger$	0.060	0.052
S , error in observation of unit weight e	2.53	1.33
$(\Delta/\sigma)_{\max}$ in final cycle	0.37	0.01

* $\sigma(I)$ is based on counting statistics only, for (4); for (5) $\sigma(I) = [\sigma_{cs}^2(I) + (0.03I)^2]^{1/2}$ where σ_{cs} is based on counting statistics.

$^\dagger R(F) = \sum |F_o| - |F_c| / \sum |F_o|$.

$^\ddagger wR(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

oxygen atoms were located in the electron-density map. Successful full-matrix least-squares refinement of the model in $C2/c$ indicated that the correct choice of the space group had been made. The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the assigned weights are defined as $w = 1/\sigma^2(F_o) = 4F_o^2 / [\sigma^2(F_o^2) + (pF_o^2)^2]$ with $p = 0.03$. All of the hydrogen atoms were located in difference electron-density maps and they were added to the model and allowed to refine isotropically. The final refinement cycle with anisotropic thermal parameters for the non-hydrogen atoms and isotropic hydrogen atoms gave $R = 0.044$ and $wR = 0.060$ for the 2109 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 305 variable parameters. The final difference electron-density map with a maximum peak height of 0.26 e Å⁻³ showed no significant features. Final positional parameters are reported in Table 2.* The analytical forms of the scattering factors for neutral atoms were used throughout the analysis (Cromer & Waber, 1974).

Structure determination of (5). This hydrocarbon crystallized as clear, colorless, rectangular rods having a tetragonal crystal system with $4/m$ Laue symmetry. The systematic absences, $00l$, $l = 2n + 1$ and hkl , $h + k = 2n + 1$, uniquely determine the space group as $P4_2/n$. At room temperature, the cell constants are based on a least-squares refinement of the setting angles for 25 reflections, measured with graphite-monochromated Mo $K\alpha$ radiation, in the 2θ range 26 to 30°.

Intensities were measured by the θ - 2θ scan method on a Rigaku AFC5 diffractometer. Six standard reflections measured after every 150 reflections indicated the crystal to be stable during the course of data

* Tables of calculated hydrogen-atom positions for (5) and of final anisotropic thermal parameters, bond angles, observed and calculated structure-factor amplitudes and least-squares planes, and stereodrawings of the unit cells, all for (4) and (5), have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51619 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final positional parameters for (4)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O1	0.8652 (2)	0.2006 (2)	0.75030 (5)	4.44 (4)
O2	0.8771 (1)	0.4133 (2)	0.70319 (5)	4.02 (4)
C1	0.8794 (2)	0.1440 (3)	0.67000 (6)	2.17 (4)
C2	0.9733 (2)	0.1940 (3)	0.64516 (7)	2.31 (4)
C3	0.9235 (2)	0.2429 (3)	0.59386 (7)	2.48 (4)
C4	0.7993 (2)	0.2236 (3)	0.58616 (7)	2.48 (4)
C5	0.7637 (2)	0.0865 (3)	0.54871 (7)	2.74 (4)
C6	0.8664 (2)	0.0212 (3)	0.53320 (7)	2.84 (4)
C7	0.9646 (2)	0.1173 (3)	0.56122 (7)	2.79 (4)
C8	1.0391 (2)	-0.0091 (3)	0.59222 (7)	2.89 (4)
C9	1.0438 (2)	0.0379 (3)	0.64401 (7)	2.69 (4)
C10	0.9950 (2)	-0.1081 (3)	0.66761 (7)	2.58 (4)
C11	0.8932 (2)	-0.0425 (3)	0.68338 (7)	2.33 (4)
C12	0.7941 (2)	-0.1383 (3)	0.65532 (7)	2.53 (4)
C13	0.8354 (2)	-0.2641 (3)	0.62257 (7)	2.79 (4)
C14	0.9599 (2)	-0.2452 (3)	0.63033 (7)	2.77 (4)
C15	0.9875 (2)	-0.1843 (3)	0.58364 (7)	2.80 (4)
C16	0.8804 (2)	-0.1653 (3)	0.54721 (7)	2.86 (4)
C17	0.7866 (2)	-0.2149 (3)	-0.57141 (7)	2.85 (4)
C18	0.7147 (2)	-0.0590 (3)	0.57240 (7)	2.79 (4)
C19	0.7194 (2)	-0.0122 (3)	0.62426 (7)	2.57 (4)
C20	0.7711 (2)	0.1630 (3)	0.63279 (7)	2.28 (4)
C21	0.8738 (2)	0.2505 (3)	0.71240 (7)	2.49 (4)
C22	0.8608 (2)	0.5245 (3)	0.74056 (9)	4.56 (6)
H2	1.015 (1)	0.286 (2)	0.6620 (6)	1.8 (4)*
H3	0.947 (2)	0.356 (3)	0.5890 (7)	3.0 (5)*
H4	0.764 (2)	0.329 (3)	0.5746 (7)	2.9 (5)*
H5	0.711 (1)	0.129 (3)	0.5209 (7)	2.7 (5)*
H6	0.865 (2)	0.034 (3)	0.4997 (7)	3.5 (5)*
H7	1.000 (2)	0.177 (3)	0.5401 (7)	3.2 (5)*
H8	1.112 (2)	-0.008 (3)	0.5832 (8)	3.6 (5)*
H9	1.118 (2)	0.057 (3)	0.6634 (8)	3.3 (5)*
H10	1.045 (1)	-0.154 (3)	0.6937 (6)	2.7 (5)*
H11	0.902 (2)	-0.055 (3)	0.7167 (7)	3.2 (5)*
H12	0.756 (2)	-0.198 (3)	0.6764 (7)	3.2 (5)*
H13	0.816 (2)	-0.378 (3)	0.6292 (7)	3.6 (5)*
H14	0.996 (2)	-0.351 (3)	0.6423 (7)	2.9 (5)*
H15	1.036 (2)	-0.266 (3)	0.5742 (7)	3.0 (5)*
H16	0.885 (2)	-0.236 (3)	0.5202 (7)	2.7 (4)*
H17	0.743 (2)	-0.307 (3)	0.5536 (7)	2.8 (4)*
H18	0.637 (2)	-0.081 (3)	0.5545 (7)	3.3 (5)*
H19	0.642 (2)	-0.012 (3)	0.6336 (8)	4.7 (6)*
H20	0.723 (1)	0.243 (2)	0.6425 (6)	2.0 (4)*
H22	0.915 (2)	0.489 (3)	0.774 (1)	6.7 (7)*
H23	0.887 (2)	0.639 (4)	0.732 (1)	8.1 (9)*
H24	0.793 (2)	0.509 (3)	0.744 (1)	7.7 (9)*

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\frac{1}{3} \{a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab(\cos\beta)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}\}.$$

collection. Data reduction and all further calculations were performed with the *TEXSAN* package of crystallographic programs (Molecular Structure Corporation, 1987).

The structure was solved by the direct-methods program *MITHRIL* (Gilmore, 1983) and all the carbon atoms were easily located on the electron-density map. Full-matrix least-squares isotropic refinement of the model converged at an *R* value of 0.12. After a cycle of anisotropic refinement all the hydrogen atoms were located on a difference electron-density map. The hydrogen atoms were included in the model as fixed contributions at their calculated positions with the assumptions C—H = 0.98 Å and *B*₁₁ = 1.2 × *B*_{eq} (attached carbon atom). All full-matrix least-squares refinements were based on *F* so that the function minimized in least squares was: $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final refinement cycle for the 1773 intensities with $F_o^2 > 1\sigma(F_o^2)$ and the 244 variables (anisotropic carbon atoms, fixed hydrogen atoms)

Table 3. Final positional parameters for (5)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} *
C1	0.80507 (18)	0.05800 (17)	0.29953 (29)	2.4 (1)
C2	0.87883 (18)	0.02572 (19)	0.25143 (32)	2.8 (2)
C3	0.90076 (18)	0.07864 (20)	0.14209 (33)	3.1 (2)
C4	0.84186 (19)	0.14392 (18)	0.13319 (33)	3.0 (2)
C5	0.79996 (19)	0.13711 (19)	0.00755 (32)	2.9 (2)
C6	0.83282 (18)	0.06783 (19)	-0.06192 (30)	3.0 (2)
C7	0.89539 (18)	0.03170 (21)	0.02084 (33)	3.2 (2)
C8	0.86963 (19)	-0.05008 (20)	0.05403 (33)	3.3 (2)
C9	0.85953 (18)	-0.05444 (19)	0.19716 (32)	2.8 (2)
C10	0.77373 (18)	-0.07097 (17)	0.22309 (29)	2.4 (1)
C11	0.74204 (17)	0.00032 (17)	0.28258 (28)	2.2 (1)
C12	0.67697 (17)	0.03575 (18)	0.21078 (29)	2.4 (1)
C13	0.67247 (17)	-0.01138 (19)	0.08956 (30)	2.7 (2)
C14	0.73220 (19)	-0.07662 (18)	0.09668 (30)	2.8 (2)
C15	0.79110 (19)	-0.06367 (20)	-0.00704 (31)	3.0 (2)
C16	0.76887 (19)	0.00864 (20)	-0.07922 (29)	2.9 (2)
C17	0.69592 (18)	0.04149 (20)	-0.01920 (29)	2.9 (2)
C18	0.71491 (18)	0.12076 (19)	0.03437 (29)	2.7 (1)
C19	0.70338 (18)	0.11816 (18)	0.17708 (30)	2.6 (1)
C20	0.78255 (19)	0.13244 (18)	0.23799 (30)	2.7 (1)
C21	0.76349 (19)	0.02708 (18)	0.41117 (29)	2.6 (1)
C22	0.80131 (19)	-0.02302 (18)	0.50537 (30)	2.6 (1)
C23	0.86694 (20)	0.00073 (19)	0.56611 (32)	3.1 (2)
C24	0.90063 (21)	-0.04378 (22)	0.65685 (33)	3.7 (2)
C25	0.86974 (22)	-0.11323 (22)	0.68795 (32)	3.7 (2)
C26	0.80425 (22)	-0.13723 (20)	0.62940 (34)	3.6 (2)
C27	0.77006 (20)	-0.09302 (20)	0.53849 (32)	3.2 (2)

* The form of the equivalent isotropic thermal parameter is: $B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

resulted in agreement indices of *R* = 0.053 and *wR* = 0.052. The final difference electron-density map had maximum and minimum peak heights of 0.23 and -0.27 e Å⁻³ respectively. Scattering factors were obtained from the usual sources [carbon-atom from *International Tables for X-ray Crystallography* (1974) and hydrogen-atom from Stewart, Davidson & Simpson (1965)]. Table 1 contains additional crystallographic details. Final positional parameters are given in Table 3.

Discussion. The metrical parameters for (4) and (5) have been compiled in Tables 4 and 5. An identical numbering scheme has been applied to the dodecahedrane framework for both structures and is shown in Fig. 1 for (4). Final *ORTEP* drawings (Johnson, 1976) for (4) and (5) are displayed in Figs. 2 and 3, respectively. Both molecules are composed of substituents on a dodecahedrane framework and slight distortions in this framework are observed in the immediate vicinity of the substituents. The distortions for (5) are larger than those for (4), and will be discussed first.

Remarkably, the cyclopropane ring in (5) that is fused to the dodecahedrane framework has all C—C bonds and internal angles essentially equal. The phenyl ring is in the 'perpendicular conformation' with respect to the cyclopropane ring (Allen, 1980). This specific conformation is defined by the torsion angle τ , which for (5) is X—C21—C22—C23 = 92° or X—C21—C22—C27 = -91° [for ideal perpendicularity, $\tau = \pm 90^\circ$ (Allen, 1980)] where X is the midpoint of the C1—C11 bond. The orientation of the phenyl ring, the likely result of steric interactions with framework hydrogen

Table 4. Final bond lengths (Å) for (4) with *e.s.d.*'s in the least significant figure given in parentheses

C1—C2	1.557 (2)	C9—C10	1.543 (2)
C1—C11	1.541 (2)	C10—C11	1.538 (2)
C1—C20	1.564 (2)	C10—C14	1.539 (2)
C1—C21	1.508 (2)	C11—C12	1.546 (2)
C2—C3	1.541 (2)	C12—C13	1.544 (2)
C2—C9	1.536 (2)	C12—C19	1.538 (2)
C3—C4	1.543 (2)	C13—C17	1.536 (2)
C3—C7	1.540 (2)	C13—C14	1.547 (2)
C4—C5	1.543 (2)	C14—C15	1.542 (2)
C4—C20	1.544 (2)	C15—C16	1.541 (2)
C5—C6	1.545 (2)	C16—C17	1.545 (2)
C5—C18	1.543 (2)	C17—C18	1.544 (2)
C6—C7	1.540 (2)	C18—C19	1.538 (2)
C6—C16	1.545 (2)	C19—C20	1.543 (2)
C7—C8	1.538 (2)	C21—O1	1.194 (2)
C8—C9	1.536 (2)	C21—O2	1.331 (2)
C8—C15	1.542 (2)	O2—C22	1.447 (2)

Table 5. Final bond lengths (Å) for (5) with *e.s.d.*'s in the least significant figure given in parentheses

C1—C2	1.503 (4)	C11—C21	1.508 (4)
C1—C21	1.505 (4)	C11—C12	1.511 (4)
C1—C11	1.509 (4)	C12—C13	1.545 (4)
C1—C20	1.515 (4)	C12—C19	1.560 (4)
C2—C3	1.546 (5)	C13—C17	1.548 (4)
C2—C9	1.559 (5)	C13—C14	1.552 (5)
C3—C4	1.544 (5)	C14—C15	1.537 (5)
C3—C7	1.545 (5)	C15—C16	1.536 (5)
C4—C5	1.542 (5)	C16—C17	1.544 (4)
C4—C20	1.546 (4)	C17—C18	1.541 (5)
C5—C6	1.538 (5)	C18—C19	1.548 (4)
C5—C18	1.545 (4)	C19—C20	1.555 (4)
C6—C16	1.539 (5)	C21—C22	1.496 (4)
C6—C7	1.548 (5)	C22—C23	1.387 (5)
C7—C8	1.545 (5)	C22—C27	1.390 (4)
C8—C15	1.544 (5)	C23—C24	1.382 (5)
C8—C9	1.551 (5)	C24—C25	1.374 (5)
C9—C10	1.557 (4)	C25—C26	1.375 (5)
C10—C11	1.510 (4)	C26—C27	1.384 (5)
C10—C14	1.545 (4)		

atoms, gives rise to C_s non-crystallographic point symmetry within the molecule.

Fusion of the cyclopropane ring to the dodecahedrane framework through the C1—C11 bond results in a distortion of the spherical contour of the framework in the immediate vicinity of this bond. As a means of comparison, the parent dodecahedrane (1) has two types of framework bonds C(3)—C(*m*) = 1.541 (2) and C(*m*)—C(*m*) = 1.535 (5) Å and three types of C—C—C bond angles C(*m*)—C(3)—C(*m*) = 108.1 (1), C(3)—C(*m*)—C(3) = 107.7 (2) and C(3)—C(*m*)—C(*m*) = 107.9 (4)°. These values are not significantly different from the C—C bond length of 1.546 Å determined for cyclopentane (Adams, Geise & Bartell, 1970) and from the 108° angle expected for perfect dodecahedral symmetry. For the dodecahedrane framework reported here, atoms C1 and C11 which are part of both the cyclopropane ring and the dodecahedryl core are involved in short C—C bonds ranging from 1.503 to 1.515 Å. The other C—C bonds within the two pentagonal rings which contain the C1—C11 bond (rings C1—C2—C9—C10—C11 and C1—C11—C12—C19—C20) are slightly longer at 1.555–1.560 Å. All of the remaining C—C bonds lie in the range 1.536 to 1.552 Å.

The C—C—C angles also show distortion in the vicinity of the C1—C11 bond. The two pentagonal rings which contain the C1—C11 bond display the following range for the interior angles of these rings: 106.0 to 109.8°. For the two pentagonal rings which contain either C1 or C11 but not both of these carbon atoms (rings C10—C11—C12—C13—C14 and C1—C2—C3—

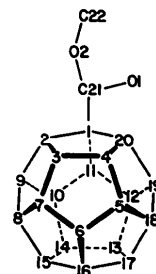


Fig. 1. The numbering scheme for methoxycarbonyldodecahedrane (4). The labeling of the dodecahedrane framework in (5) is identical to that shown here.

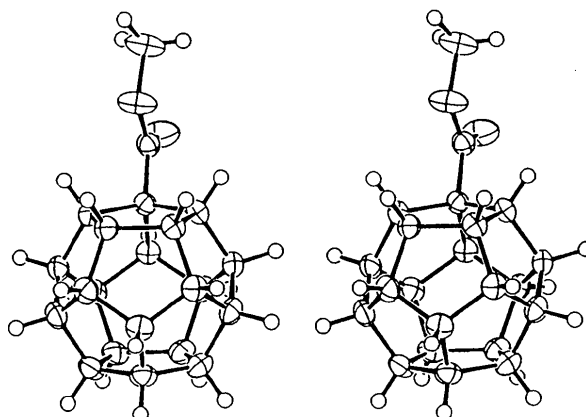


Fig. 2. ORTEP stereoview for (4). The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

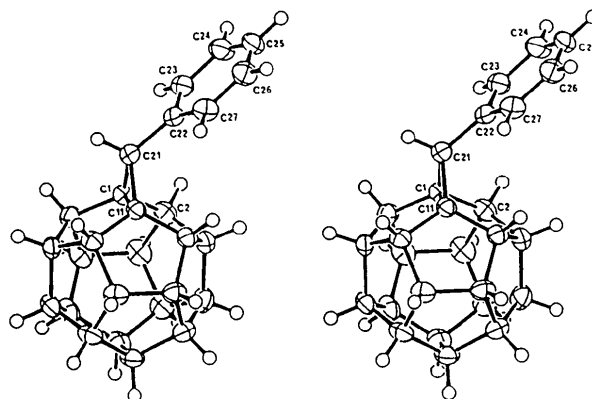


Fig. 3. ORTEP stereoview for (5). The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

C4–C20), the range of internal angles is even greater: 104.5 to 113.7°. All the other pentagonal rings have internal angles much closer to the ideal 108° and these range from 107.2 to 108.6°. Only the four pentagonal rings which surround the C1 and C11 atoms are markedly non-planar, as shown by the deviations from the least-squares planes, listed in Table 6.

Transannular distances across the dodecahedrane cavity in (5) are compiled in Table 7. There are two short distances involving the two carbon atoms in the cyclopropane ring: C1–C16 = 4.211 (5) and C11–C6 = 4.202 (4) Å. The remaining distances span the range 4.334 to 4.352 Å. Overall, the difference between the maximum and minimum intracavity distances is 0.150 Å and this large difference is indicative of the distortion of the framework, where C1 and C11 are pushed slightly inward. The intracavity distances for (1) and (2), cited earlier, afford a striking comparison.

The non-crystallographic point group for structure (4) can also be approximated as C_s . The methyl-ester substituent resides essentially in this mirror plane, as the C11–C1–C21–O1 torsion angle is 10°. The presence of the methyl-ester group causes the C1–C2 and C1–C20 bond lengths to become slightly longer (at 1.557 and 1.564 Å) than the remainder of the dodecahedrane bonds which range from 1.536 to 1.547 Å. The angles within the framework lie within an expected range of values: 107.1 to 108.6°. Least-squares planes through the pentagonal rings do not show any marked deviation from planarity.

A listing in Table 7 of the intracavity distances across the center of the molecule indicates that the framework is only slightly distorted by the presence of the methoxycarbonyl group. The difference between the maximum and minimum distance is 0.023 Å and the longest distance is associated with the carbon atom (C1) bearing the substituent, C1–C16 = 4.334 Å. This case is analogous to that of 1,16-dimethyldodecahedrane where the longest distance (4.389 Å) is likewise between the two functionalized carbon atoms. However, the difference between the maximum and minimum distances in the dimethyl structure is more pronounced at 0.068 Å.

Dodecahedrane substitution by either electron-releasing or electron-withdrawing functional groups leads to modest distortion of the spherical contour. Depending on the particular electronic character of the pendant side chain(s), elongation or compression occurs along that axis that includes the substituent. While this phenomenon was not entirely unexpected, the geometry adopted by (5) has proven to be especially informative about dodecahedrane conformational energetics. While the fused cyclopropane ring is strikingly undistorted, the dodecahedrane bonds in the immediate vicinity of this annulation are rather extensively perturbed. On this basis, alterations in bond angles and torsional angles appear more easily

Table 6. Deviations (Å) from selected least-squares planes for (5)

Plane 1		Plane 2		Plane 3		Plane 4	
C1	-0.036 (3)	C1	-0.005 (3)	C1	0.004 (3)	C10	-0.033 (3)
C2	0.031 (3)	C2	0.022 (3)	C11	0.009 (3)	C11	0.039 (3)
C3	0.010 (3)	C9	-0.027 (3)	C12	-0.021 (3)	C12	-0.030 (3)
C4	0.015 (3)	C10	0.020 (3)	C19	0.024 (2)	C13	0.008 (3)
C20	0.031 (3)	C11	-0.008 (3)	C20	-0.018 (3)	C14	0.015 (3)

Table 7. Transannular distances (Å) for (4) and (5)

	(4)	(5)		(4)	(5)
C1–C16	4.334 (3)	4.211 (5)	C6–C11	4.325 (3)	4.202 (4)
C2–C17	4.327 (3)	4.338 (5)	C7–C12	4.315 (3)	4.340 (4)
C3–C13	4.328 (3)	4.338 (4)	C8–C19	4.314 (3)	4.352 (4)
C4–C14	4.326 (3)	4.335 (5)	C9–C18	4.311 (3)	4.350 (4)
C5–C10	4.322 (3)	4.346 (4)	C15–C20	4.331 (3)	4.334 (5)

accomplished within the dodecahedrane structural network than within the cyclopropane ring.

We are grateful to the National Institutes of Health for their generous financial support of this research program (Grant AI-11490).

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Structure of 3,3a,5,6,7,8b-Hexahydro-2H,8H-furo[3,2-b]benzofuran-2,8-dione*

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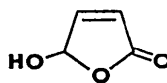
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(Received 16 June 1988; accepted 17 November 1988)

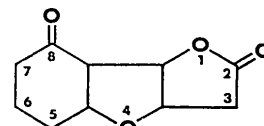
Abstract. C₁₀H₁₀O₄, *M_r* = 194.2, monoclinic, *P*2₁/*c*, *a* = 5.442 (1), *b* = 18.162 (6), *c* = 9.220 (3) Å, β = 105.73 (2)°, *V* = 877 (1) Å³, *Z* = 4, *D_x* = 1.47 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 0.107 mm⁻¹, *F*(000) = 408, *T* = 293 K, *R* = 0.046 for 1167 observed reflections. The X-ray study confirms that the solid state structure is similar to that inferred from chemical and spectroscopic evidence. The six-membered *A* ring adopts a 1,2-diplanar conformation whilst both five-membered rings (*B* and *C*) are intermediate between half-chair and β-envelope. The *A/B* and *B/C* junctions are *cis*. The packing in the crystal is entirely due to intermolecular C–H⋯O contacts and van der Waals forces.

Introduction. The base-catalyzed reaction of 5-hydroxy-2(5*H*)-furanone (1) with several cyclic and acyclic vinylogous amides and 1,3-dicarbonyl compounds was found to provide a smooth method of preparing pyrrole, furan, tetrahydroindole and tetrahydrobenzofuran ring systems (Yuste & Sánchez-Obregón, 1982). The title compound (2) has been synthesized. The empirical formula C₁₀H₁₀O₄ was established by mass spectrometry and the functional

groups present were characterized by NMR, IR and UV spectroscopy (Yuste & Sánchez-Obregón, 1982). We have undertaken the X-ray study of (2).



(1)



(2)

Experimental. Compound (2) was obtained from the reaction of 1.12 g (10 mmol) of 1,3-cyclohexanedione, 1 g (10 mmol) of lactone (1) and 1 ml of 2% sodium hydroxide in 30 ml of ethanol, by refluxing for 2 h. The product crystallized on cooling and subsequent recrystallization from cold ethanol gave colourless crystals, m.p. 430–431 K. Size of crystal 0.14 × 0.14 × 0.42 mm. Nicolet R3 four-circle diffractometer. Unit-cell parameters by least squares from 25 machine-centred reflections with 4.5 < 2θ < 16.5°. 1551 unique reflections measured for two octants, 3 < 2θ < 50°, 1167 with *I* > 2.5σ(*I*) used in analysis, index range *h* ±6, *k* 0→21, *l* 0→10, *R*_{int} = 0.021, 2θ/θ scan mode, variable scan speed, scan width 1.0° (θ). Two standard reflections (131, 130) monitored every 50 measurements, no significant variation. Intensities

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