# Molecular Structure of Germylcyclopentadiene † in the Crystalline Phase at 160 K and in the Gas Phase

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The molecular structure of the title compound $GeH_3(C_5H_5)$ has been determined by *X*-ray and electron diffraction in the solid and gas phases respectively. Principal bond lengths ($r_a$) in the gas-phase structure are: Ge–C(1) 1.969(5), C(1)–C(2) 1.478(13), C(2)–C(3) 1.350(5), and C(3)–C(4) 1.468(22) Å. Crystals of the compound (at 160 K) are monoclinic with $a$ = 4.90, $b$ = 9.54, $c$ = 13.11 Å, $\beta$ = 98.4° [estimated standard deviations (e.s.d.s) 0.3% assumed], space group $P2_1/c$, and $Z$ = 4. The structure has been determined and refined to $R$ = 0.049 using 713 unique intensities obtained from microdensitometer measurements of the Weissenberg levels $h$0—6$l$ and $hk$0—7 taken with Cu-$K_\alpha$ radiation. The Ge–C(1) distance is 1.965(9) Å; The C–C ring distances taken cyclically from C(1) are 1.49, 1.35, 1.44, 1.34, and 1.46 (e.s.d.s ≈ 0.013) Å. In both phases the ring is essentially planar, with ring angles close to 109° at all carbon atoms except C(1), where the angle is 104.0(7) (solid phase) or 100(3)° (gas phase).

IN the liquid phase at room temperature the germyl group of germylcyclopentadiene exchanges among the five carbon-atom sites of the cyclopentadienyl ring at a rate which is fast with respect to the n.m.r. time scale,[1] but at lower temperature the exchange rate decreases and n.m.r. spectra of a species with the germyl group bound to a single carbon atom [C(1)] are obtained. The implication of this is that the instantaneous molecular geometry involves a monohapto-cyclopentadienyl ring with a σ Ge–C bond, rather than a π-bonded pentahapto-ring as in cyclopentadienyl(methyl)beryllium.[2] However, structural data for the cyclopentadienyls of silicon and germanium are sparse. An electron-diffraction study [3] of $SiH_3(C_5H_5)$ indicated a monohapto-structure with a planar cyclopentadienyl ring, very similar to those of σ-$C_5H_5$ transition-metal systems.[4-6] In contrast, the electron-diffraction data for $SiMe_3(C_5H_5)$ [7] and $GeMe_3(C_5H_5)$ [8] have been interpreted in terms of non-planar configurations for the cyclopentadienyl rings with angles between the C(2)C(1)C(5) and C(2)C(3)C(4)C(5) planes of 22 and 24° respectively. The crystal structure of ferrocenyldiphenylsilane [9] suggests that the σ-bonded diphenylsilyl group has little effect on the cyclopentadienyl ring to which it is attached.

TABLE 1

Weighting functions, scale factors, correlation parameters, and electron wavelengths

| Camera height mm | $\Delta_s$ | $s_{min.}$ | $sw_1$ nm$^{-1}$ | $sw_2$ | $s_{max.}$ | Correlation parameter | Scale factor | Electron wavelength pm |
|---|---|---|---|---|---|---|---|---|
| 250 | 4 | 76 | 90 | 260 | 300 | 0.267 | 0.791(20) | 5.673(5) |
| 500 | 2 | 30 | 43 | 140 | 150 | 0.496 | 0.927(26) | 5.666(5) |
| 1 000 | 1 | 13 | 23 | 60 | 70 | 0.473 | 0.684(25) | 5.659(5) |

We report here the results of our studies of the molecular structure of the simplest germylcyclopentadiene species, in both gaseous and crystalline phases.

## EXPERIMENTAL

A sample of germylcyclopentadiene was prepared from sodium cyclopentadienide and germyl bromide.[1] Its purity was checked spectroscopically.

*Electron Diffraction.*—Scattering intensities were recorded on Ilford N60 photographic plates using a Balzers' KD.G2 diffraction apparatus at the University of Manchester Institute of Science and Technology. Data were obtained in digital form using a Joyce–Loebl microdensitometer. The sample was maintained at 298 K and the nozzle at 328 K during experiments. Data were collected with three camera heights, 250, 500, and 1 000 mm, covering the range 13—260 nm$^{-1}$ in the scattering variable, $s$.

All calculations were carried out on ICL 4-75 and 2970 computers using established data-reduction [10] and least-squares refinement [11] programs. The weighting points used in setting up the off-diagonal weight matrix are given in Table 1, together with other pertinent experimental data. In all calculations, the scattering factors of Schäfer *et al.*[12] were used.

In the least-squares refinements, $C_{3v}$ symmetry for the $CGeH_3$ fragment and overall $C_s$ symmetry were assumed. The refinable geometrical parameters were chosen to be the Ge–C, C(1)–C(2), C(2)–C(3), C(3)–C(4), Ge–H, and mean C–H bond lengths, the angle C(2)C(3)C(4), the angle between the C(2)C(1)C(5) and C(2)C(3)C(4)C(5) planes, and the angle between the Ge–C bond and the C(2)C(1)C(5) plane. There were also four angles determining hydrogen-atom positions: none of these could in practice be refined. It was possible to refine all the geometrical parameters involving heavy atoms, but as the three C–C peaks overlapped in the radial distribution curve (Figure 1), as did the three C · · · C peaks, there were strong correlations ‡ between the bond lengths and angles determining the ring geometry. For this reason

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† Systematically, 5-germylcyclopenta-1,3-diene.

‡ The final least-squares correlation matrix, the full listing of interatomic distances and amplitudes of vibration, the molecular scattering intensity data, (*X*-ray) thermal parameters, and a list of observed and calculated (*X*-ray) structure factors have been deposited as Supplementary Publication No. SUP 22704 (10 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

it was necessary to fix some amplitudes of vibration at reasonable values. The most important molecular parameters are listed in Table 2: errors quoted in this table are estimated standard deviations obtained in the least-squares analyses, increased to allow for systematic errors. The combined molecular intensity curve and final difference curve are shown in Figure 2. The lowest $R$ factor ($R_G$) [11] was 0.15.

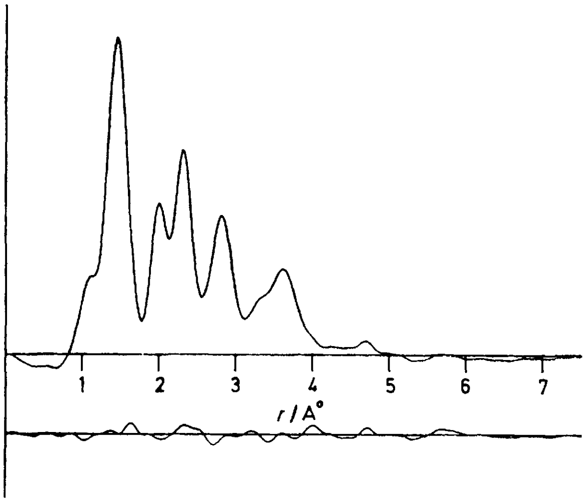

FIGURE 1 Radial distribution curve, $P(r)/r$, for $GeH_3(C_5H_5)$. Before Fourier inversion the data were multiplied by $s.\exp[-0.000\ 02\ s^2/(z_{Ge} - f_{Ge})(z_C - f_C)]$

TABLE 2

Gas-phase molecular parameters for $GeH_3(C_5H_5)$

| Independent distances | Distance (Å) | Amplitude (Å) |
|---|---|---|
| Ge–C(1) | 1.969(5) | 0.047(7) |
| C(1)–C(2) | 1.478(13) | 0.049 * |
| C(2)–C(3) | 1.350(5) | 0.049 * |
| C(3)–C(4) | 1.468(23) | 0.049 * |
| C–H(mean) | 1.059(9) | 0.079 * |
| Ge–H | 1.500 * | 0.075 * |
| Dependent distances | | |
| C(1) · · · C(3) | 2.354(21) | 0.054(18) |
| C(2) · · · C(4) | 2.269(40) | |
| C(2) · · · C(5) | 2.270(12) | |
| Ge · · · C(2) | 2.773(6) | 0.108(6) |
| Ge · · · C(3) | 3.626(13) | 0.143(7) |
| Independent angles | Angle (°) | |
| C(2)–C(3)–C(4) | 107.3(15) | |
| plane C(2)C(1)C(5)–plane C(2)C(3)C(4)C(5) | 1.4(17) | |
| Bond Ge-C(1)–plane C(2)C(1)C(5) | 115.9(7) | |
| H(3)–C(3)–C(4) | 127.0 * | |
| H(2)–C(2)–C(3) | 127.0 * | |
| Ge–C(1)–H(1) | 109.0 * | |
| C(1)–Ge–H | 109.0 * | |
| Dependent angles | | |
| C(2)–C(1)–C(5) | 100.3(27) | |
| C(1)–C(2)–C(3) | 112.6(30) | |
| Ge–C(1)–C(2) | 106.3(4) | |

* Fixed.

X-*Ray Diffraction.*—*Crystal data.* $C_5H_8Ge$, $M = 140.7$, Monoclinic, $a = 4.90$, $b = 9.54$, $c = 13.11$ Å, $\beta = 98.4°$ (0.3% estimated standard deviations assumed), $U = 606.3$ Å$^3$, $Z = 4$, $D_c = 1.54$, Cu-$K_\alpha$ radiation (Ni filter), $\lambda = 1.541\ 78$ Å, $\mu$(Cu-$K_\alpha$) = 56.8 cm$^{-1}$, space group $P2_1/c$ ($C^5_{2h}$, no. 14) by systematic absences. Melting point 200 K, cell parameters and intensities measured at 160 K.

A pure sample of germylcylopentadiene was sealed into a Lindemann glass capillary (internal diameter 0.5 mm) directly attached to a vacuum line. The capillary was transferred to a Nonius–Weissenberg goniometer fitted with Nonius nitrogen gas stream attachments for low temperatures where crystals were grown *in situ*. Two cylindrical crystals (diameter ≈ 0.5 mm, length ≈ 2 mm) were used for data collection. Intensities for 713 unique reflections were obtained from microdensitometer measurements of equi-inclination Weissenberg film packs for the levels $h0$—$6l$ and $hk0$—7. Microdensitometry and initial data reduction were performed by the S.R.C. Microdensitometer Service at Daresbury Laboratory, Warrington. The intensities were corrected for absorption, Lorentz, and polarisation effects and the data levels were merged and placed on a uniform scale on the basis of common reflections. The structure was solved by Fourier methods and refined by conventional least-squares calculations to minimise the quantity $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic vibration parameters were included for germanium and carbon atoms; hydrogen atoms were positioned from difference-Fourier syntheses and then refined isotropically. The atoms H(3) and H(5) did not refine sensibly and during the later stages of refinement these atoms were held fixed with calculated co-ordinates, $r$(C–H) = 1.0 Å. Atomic scattering factors for Ge, C, and H atoms were from refs. 13, 14, and 15 respectively.

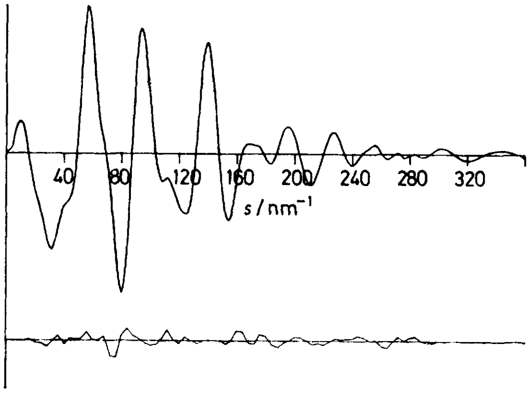

FIGURE 2 Combined experimental and final weighted difference molecular scattering intensities

TABLE 3

Atomic parameters (with estimated standard deviations in parentheses) for the crystal structure

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ge | 0.220 38(19) | 0.222 76(10) | 0.134 71(7) |
| C(1) | 0.158 0(15) | 0.222 7(11) | 0.279 4(6) |
| C(2) | 0.302 6(17) | 0.347 5(11) | 0.329 0(6) |
| C(3) | 0.519 2(19) | 0.302 2(9) | 0.396 1(7) |
| C(4) | 0.521 9(19) | 0.151 0(13) | 0.397 8(7) |
| C(5) | 0.306 7(18) | 0.104 0(10) | 0.331 9(7) |
| H(1) | −0.050(23) | 0.211(10) | 0.276(8) |
| H(2) | 0.249(17) | 0.461(9) | 0.299(6) |
| H(3) * | 0.658 | 0.365 | 0.438 |
| H(4) | 0.683(18) | 0.096(9) | 0.438(7) |
| H(5) * | 0.259 | 0.001 | 0.320 |
| H(6) | 0.453(19) | 0.213(9) | 0.133(7) |
| H(7) | 0.130(10) | 0.351(6) | 0.086(4) |
| H(8) | 0.062(15) | 0.119(7) | 0.085(6) |

* Held fixed (see text).

An extinction parameter was included in the refinement procedure, while the structure-factor calculations included terms for the real and imaginary parts of the anomalous dispersion effect of Ge with Cu-$K_\alpha$ radiation.[16] The final least-squares weighting scheme was $w^{-1} = 1 + 0.006(F_o - 16)^2$, and the final $R$ factor was 0.049. The final value of the extinction parameter, $g$, was $2.45(11) \times 10^{-4}$ where $|F_c'| = |F_c|[(1 + g|F_c|^2)(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)\sin 2\theta]^{-\frac{1}{4}}$. After completion of refinement a difference-Fourier synthesis showed features around the germanium atom of ±0.8 e $Å^{-3}$, but elsewhere none outside the range ±0.4 e $Å^{-3}$.

TABLE 4

Molecular geometry in the crystal

(*a*) Bond distances (Å) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ge–C(1) | 1.965(9) | Ge-H(7) | 1.42(6) |
| C(1)–C(2) | 1.486(13) | Ge–H(8) | 1.37(7) |
| C(1)–C(5) | 1.462(13) | C(1)–H(1) | 1.02(11) |
| C(2)–C(3) | 1.347(12) | C(2)–H(2) | 1.17(9) |
| C(3)–C(4) | 1.443(15) | C(3)–H(3) | 1.00 |
| C(4)–C(5) | 1.339(12) | C(4)–H(4) | 1.03(8) |
| Ge–H(6) | 1.15(9) | C(5)–H(5) | 1.00 |

(*b*) Bond angles (°)

| | | | |
|---|---|---|---|
| Ge–C(1)–C(2) | 106.9(6) | H(6)–Ge–H(7) | 108(5) |
| Ge–C(1)–C(5) | 108.5(6) | H(6)–Ge–H(8) | 116(5) |
| C(2)–C(1)–C(5) | 104.0(7) | H(7)–Ge–H(8) | 107(4) |
| C(1)–C(2)–C(3) | 108.0(8) | Ge–C(1)–H(1) | 104(6) |
| C(2)–C(3)–C(4) | 109.6(8) | C(2)–C(1)–H(1) | 121(6) |
| C(3)–C(4)–C(5) | 108.7(9) | C(5)–C(1)–H(1) | 112(5) |
| C(4)–C(5)–C(1) | 109.6(9) | C(1)–C(2)–H(2) | 122(4) |
| C(1)–Ge–H(6) | 108(4) | C(3)–C(2)–H(2) | 129(4) |
| C(1)–Ge–H(7) | 111(2) | C(3)–C(4)–H(4) | 121(5) |
| C(1)–Ge–H(8) | 108(3) | C(5)–C(4)–H(4) | 130(5) |

(*c*) Distances (Å) of atoms from least-squares best planes

Plane (1): C(1), C(2), C(5)

[Ge −1.709, H(1) 0.70, H(6) −2.56, H(7) −1.88, H(8) −1.66]

Plane (2): C(2), C(3), C(4), C(5)

[C(2) −0.001, C(3) 0.001, C(4) −0.001, C(5) 0.001, Ge −1.837, C(1) −0.064, H(1) 0.59]

Angle between planes (1) and (2): 4.1(6)°

TABLE 5

Shortest intermolecular distances (Å) of each type in the crystal

| | | | | |
|---|---|---|---|---|
| (*a*) | H · · · H | | | |
| | H(4) · · · H($7^{I}$) | 2.55 | H(3) · · · H($8^{II}$) | 2.56 |
| | H(1) · · · H($2^{III}$) | 2.71 | H(8) · · · H($2^{III}$) | 2.75 |
| (*b*) | H · · · C | | | |
| | H(1) · · · C($4^{IV}$) | 2.88 | H(1) · · · C($3^{IV}$) | 2.95 |
| (*c*) | H · · · Ge | | | |
| | H(2) · · · $Ge^{V}$ | 3.58 | H(3) · · · $Ge^{II}$ | 3.59 |
| (*d*) | C · · · C | | | |
| | C(1) · · · C($4^{IV}$) | 3.74 | C(1) · · · C($3^{IV}$) | 3.76 |
| (*e*) | C . . . Ge | | | |
| | C(3) · · · $Ge^{VI}$ | 3.65 | C(4) · · · $Ge^{VI}$ | 3.82 |
| (*f*) | Ge · · · Ge, none under 4.5 Å | | | |

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at $x$, $y$, $z$:

| | | | |
|---|---|---|---|
| I | $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ | IV | $x - 1, y, z$ |
| II | $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ | V | $-x, \frac{1}{2} + y, \frac{1}{2} - z$ |
| III | $-x, y - \frac{1}{2}, \frac{1}{2} - z$ | VI | $x, \frac{1}{2} - y, \frac{1}{2} + z$ |

Atomic parameters are listed in Table 3, details of the molecular geometry in Table 4, and shortest intermolecular distances in Table 5. Figure 3 shows the atomic labelling scheme, Figure 4 the arrangement of molecules within the unit cell. Figures were prepared using the computer plotting program PLUTO,[17] and crystallographic calculations were performed using programs written here, and also the program systems ' $X$-RAY '72 '[18] and SHELX.[19]

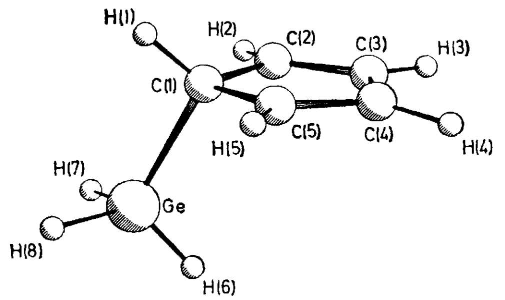

FIGURE 3 General view of the $GeH_3(C_5H_5)$ molecule in the solid showing the labelling scheme

DISCUSSION

There have been few structure determinations of molecular species in both gas and solid phases since compounds volatile enough for electron diffraction tend to require difficult low-temperature crystallisation techniques for $X$-ray analysis. The crystallisation problems are much reduced if the gas-phase species becomes ' ionic ' or otherwise strongly associated in the solid state and hence has an anomalously high freezing point. Our previous crystallographic studies of *low-freezing-point* inorganic compounds containing Si, Ge, or P atoms suggest that even here it is not uncommon

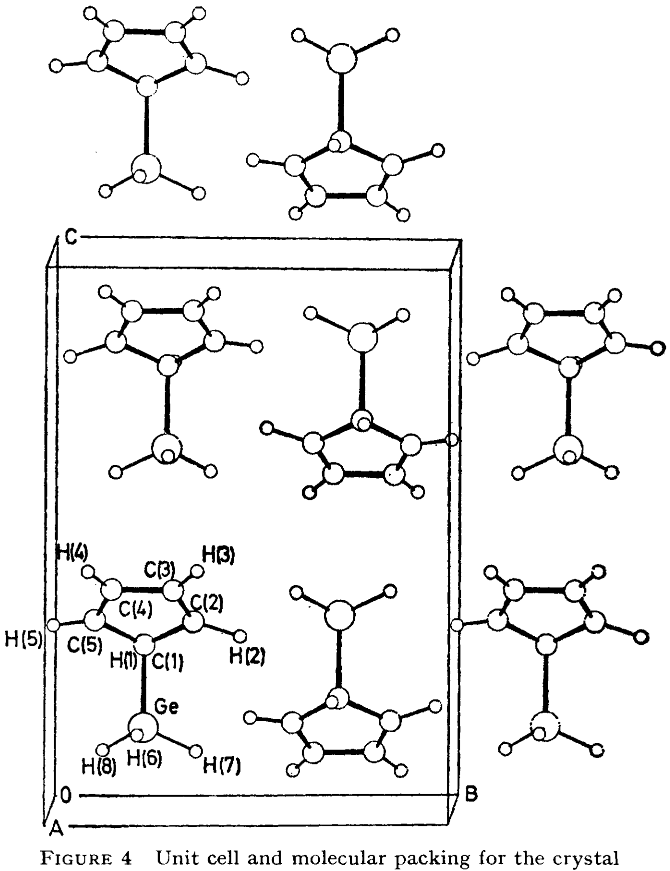

FIGURE 4 Unit cell and molecular packing for the crystal structure of $GeH_3(C_5H_5)$ at 160 K

for molecules to be involved in long-range donor–acceptor interactions in the crystalline state.[20-22] Sometimes these intermolecular interactions are strong enough to perturb the intramolecular geometry relative to the gas-phase structure.[21] However, in solid germylcyclopentadiene there are no close intermolecular contacts; the molecules exist as discrete well separated entities and in this situation we would expect the molecular geometry to be essentially unchanged by the transition from gas to solid phase. The absence of any short, specific, molecular approaches in crystalline germylcyclopentadiene is not unexpected since there are no obvious possibilities for donor–acceptor type interactions. Table 6 shows the close similarity between the electron-diffraction and *X*-ray parameters although it should be noted that these qualities are not *strictly* comparable since the electron-diffraction $r_a$ distances are average internuclear separations whereas *X*-ray diffraction measures the mean positions of the centres of electron distribution (which are assumed to be spherical or ellipsoidal).

TABLE 6

Comparison of gas- and solid-phase molecular geometries for $GeH_3(C_5H_5)$

| Parameter | Gas | Solid |
|---|---|---|
| $r$[Ge–C(1)]/Å | 1.969(5) | 1.965(9) |
| $r$[C(1)–C(2)]/Å | 1.478(13) | 1.474(13) * |
| $r$[C(2)–C(3)]/Å | 1.350(5) | 1.343(12) * |
| $r$[C(3)–C(4)]/Å | 1.468(22) | 1.443(15) |
| C(2)–C(1)–C(5)/° | 100.3(27) | 104.0(7) |
| C(1)–C(2)–C(3)/° | 112.6(30) | 108.8(9) * |
| C(2)–C(3)–C(4)/° | 107.3(15) | 109.2(9) * |
| C(2)C(1)C(5)–C(2)C(3)C(4)C(5)/° | 1.4(17) | 4.1(6) |
| Ge–C(1)–C(2)/° | 106.3(4) | 107.7(9) * |

* Average of values for the two 'halves' of the $GeH_3 \cdot C_5H_5$ molecule assuming approximate $C_s$ symmetry.

In both phases the molecules have approximate $C_s$ symmetry (assumed to be exact for the electron-diffraction analysis) with the germyl group bonded to a single carbon atom at a normal single-bond distance; the Ge $\cdots$ C(2) and Ge $\cdots$ C(5) distances (2.77—2.80 Å) are too long for any appreciable interaction. The geometry of the cylopentadienyl rings shows the three features commonly associated with transition-metal ($\sigma$-$C_5H_5$) systems:[4-6] (*a*) the pattern of C–C distances taken cyclically from C(1) is long, short, medium, short, long; (*b*) all C–C–C angles are *ca.* 109° except at C(1), where the angle is 104 (solid phase) or 100° (gas phase); (*c*) the ring is essentially planar, the dihedral angle between the planes C(2)C(1)C(5) and C(2)C(3)C(4)C(5) being 4° in the crystal and 1° in the gas. The configuration of the $C_5H_5$ ring is thus like that found by electron diffraction in $SiH_3(C_5H_5)$[3] and by *X*-ray diffraction in transition-metal ($\sigma$-$C_5H_5$) complexes,[4-6] but different from those proposed for $SiMe_3(C_5H_5)$ and $GeMe_3(C_5H_5)$[7,8] which were stated to have envelope dihedral angles of 22 and 24° respectively.

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