

Crystal Structure of Cyclodecanone at -160°C . Some Crystal Data for Cyclopenta- and Cyclohexadecanone

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The crystals of $\text{C}_{10}\text{H}_{18}\text{O}$ are monoclinic with space group $P2_1/c$, cell dimensions $a = 7.023(2)$ Å, $b = 5.418(2)$ Å, $c = 23.456(4)$ Å, $\beta = 95.16(2)^{\circ}$, and four molecules in the unit cell. The structure was solved by direct methods and refined by full-matrix least-squares technique to an R -value of 3.4 % ($R_w = 4.1$ %) for 1392 reflections recorded on an automatic four circle diffractometer. The ten-membered ring has the "rectangular" diamond-lattice conformation. Crystal data for cyclopentadecanone and cyclohexadecanone are reported.

Strain-minimization calculations of medium and large cycloalkanes have been performed for more than ten years.¹⁻⁴ Detailed structure information of some cyclic ketones have been obtained by single crystal X-ray analyses.⁵⁻⁸

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in the unit cell ($\rho_c = 1.15$ g cm^{-3} , $\rho_o = 1.17$ g cm^{-3}). The intensities were measured (at -160°C) on a Syntex $P\bar{1}$ diffractometer with Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). With an observed-unobserved cutoff at $2.0\sigma(I)$, 1392 reflections were recorded as observed. The radiation was $\text{MoK}\alpha$ and $\theta_{\text{max}} = 50^{\circ}$. The crystal size was $(0.6 \times 0.04 \times 0.3)$ mm³ and no corrections for absorption or secondary extinction have been carried out.

The structure was solved by direct methods⁹ and refined by full-matrix least-squares technique.^{10*} Anisotropic temperature factors were introduced for oxygen and carbon atoms.

* All programs used (except those for phase determination) are included in this reference.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. Expression for anisotropic vibration is: $\exp[-2\pi^2(h^2a^{*2}U11 + \dots + 2klb^*c^*U23)]$. Hmn is bonded to Cm.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O	.45857(11)	.93633(16)	.30856(3)	.0173(4)	.0250(5)	.0253(4)	.0059(3)	.0012(3)	.0005(3)
C1	.69183(15)	.80687(22)	.31022(4)	.0156(5)	.0177(6)	.0122(5)	-.0006(5)	-.0022(4)	-.0030(4)
C2	.76800(18)	.87994(24)	.27698(5)	.0193(6)	.0171(6)	.0154(6)	.0009(5)	.0019(4)	.0006(5)
C3	.97179(16)	.85888(23)	.30645(4)	.0168(6)	.0174(6)	.0176(6)	.0009(5)	.0003(4)	.0001(5)
C4	1.02247(16)	1.04643(23)	.35424(5)	.0139(6)	.0168(6)	.0197(6)	-.0016(4)	.0025(4)	.0002(5)
C5	.89574(16)	1.03596(22)	.40396(5)	.0162(6)	.0143(6)	.0168(5)	-.0005(4)	.0006(4)	-.0006(5)
C6	.91313(16)	.79545(23)	.43855(5)	.0179(6)	.0166(6)	.0157(5)	-.0003(5)	-.0014(4)	-.0001(5)
C7	.74235(17)	.73095(24)	.47291(5)	.0259(6)	.0193(7)	.0163(6)	-.0008(5)	.0040(5)	.0006(5)
C8	.54219(17)	.74718(23)	.44077(5)	.0200(6)	.0176(6)	.0210(6)	-.0006(5)	.0007(5)	.0007(5)
C9	.49301(17)	.55331(23)	.39408(5)	.0179(6)	.0161(6)	.0241(6)	-.0022(5)	.0033(5)	.0007(5)
C10	.60743(17)	.56201(22)	.34133(5)	.0152(6)	.0149(6)	.0195(6)	-.0011(4)	-.0008(4)	-.0002(5)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H21	.7459(19)	1.0479(29)	.2625(5)	1.1(2)	H22	.7573(19)	.7684(20)	.2428(6)	1.3(2)
H41	1.0633(18)	.0815(23)	.2767(5)	1.0(2)	H32	.9937(17)	.6066(27)	.3211(5)	1.2(2)
H41	1.0134(17)	1.2174(26)	.3571(5)	1.2(2)	H42	1.1572(19)	1.0243(23)	.3683(5)	.9(2)
H51	.7613(16)	1.0627(20)	.3089(4)	.3(2)	H52	.9220(17)	1.1709(25)	.4200(5)	1.0(2)
H51	1.0279(18)	.8040(25)	.4660(5)	1.0(2)	H62	.9344(17)	.6526(25)	.4131(5)	1.1(2)
H71	.7420(19)	.8630(27)	.5057(6)	1.4(2)	H72	.7619(22)	.5759(31)	.4905(6)	1.6(2)
H41	.6210(17)	.9157(25)	.4239(5)	1.0(2)	H82	.4481(20)	.7258(27)	.4702(6)	1.6(2)
H91	.3563(20)	.5727(24)	.3814(5)	1.1(2)	H92	.5678(18)	.3668(27)	.4110(5)	1.3(2)
H101	.5532(20)	.4452(26)	.3131(5)	1.3(2)	H102	.7406(20)	.5135(24)	.3505(5)	.7(2)

Table 2. Interatomic distances, bond angles and dihedral angles with estimated standard deviations.

Distance	(Å)	Distance	(Å)
O - C1	1.220(1)	C1 - C2	1.518(2)
C2 - C3	1.537(2)	C3 - C4	1.531(2)
C4 - C5	1.530(2)	C5 - C6	1.534(2)
C6 - C7	1.535(2)	C7 - C8	1.535(2)
C8 - C9	1.534(2)	C9 - C10	1.535(2)
C10 - C1	1.515(2)		

Angle	(°)	Angle	(°)
O - C1 - C2	120.2(1)	O - C1 - C10	120.6(1)
C10 - C1 - C2	119.1(1)	C1 - C2 - C3	118.7(1)
C2 - C3 - C4	115.2(1)	C3 - C4 - C5	114.9(1)
C4 - C5 - C6	114.2(1)	C5 - C6 - C7	114.7(1)
C6 - C7 - C8	117.4(1)	C7 - C8 - C9	117.9(1)
C8 - C9 - C10	117.0(1)	C9 - C10 - C1	114.9(1)

Dihedral Angle	(°)
C1 - C2 - C3 - C4	-70.2(1)
C2 - C3 - C4 - C5	59.6(1)
C3 - C4 - C5 - C6	65.2(1)
C4 - C5 - C6 - C7	-158.6(1)
C5 - C6 - C7 - C8	51.4(2)
C6 - C7 - C8 - C9	66.1(2)
C7 - C8 - C9 - C10	-64.6(1)
C8 - C9 - C10 - C1	-56.0(1)
C9 - C10 - C1 - C2	152.3(1)
C10 - C1 - C2 - C3	-49.1(2)

Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts, and C_N the net count. The atomic form factors were those of Hanson *et al.*¹¹ except for hydrogen.¹² The R -value arrived at was 3.4% (weighted value $R_w = 4.1\%$) for 1392 observed reflections.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. Maximum root mean squares anisotropic thermal amplitudes for oxygen and carbon range from 0.14 to 0.17 Å. No rigid-body analyses have been performed.

Interatomic distances, bond angles, and dihedral angles are given in Table 2 together with standard deviations, computed from the final correlation matrix. Fig. 1, a schematic drawing of the molecule, illustrates the "rectangular" diamond-lattice conformation of the ten-membered ring. Bond distances are normal.

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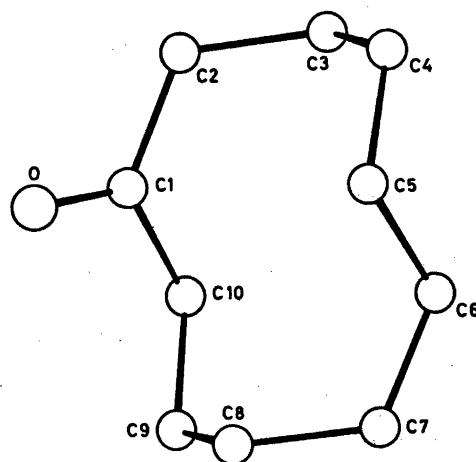


Fig. 1. Schematic drawing of the molecule.

The average C-C-C angle (excluding C10-C1-C2) of 116.1° is somewhat larger than in cycloundecanone (114.6°).⁷

A list of observed and calculated structure factors is available from the author.

Intensity data from single crystals of cyclopentadecanone and cyclohexadecanone have also been collected at -160°C .

The crystals of $(\text{CH}_2)_{14}\text{C}=\text{O}$ are orthorhombic $a = 5.589(3)$ Å, $b = 7.814(4)$ Å, and $c = 15.990(8)$ Å. The number of molecules in the unit cell is two ($\rho_c = 1.06$ g cm⁻³). The systematic absences, $0kl: k+l=2n$, correspond (by changing axes) to space groups No. 31, $Fmn2_1$, and No. 59, $Fm\bar{m}n$, with four and eight equivalent positions, respectively. With $Z=2$ both space groups demand a disordered structure. 512 reflections were recorded as observed.

The crystals of $(\text{CH}_2)_{15}\text{C}=\text{O}$ are also orthorhombic. The cell dimensions are $a = 5.395(2)$ Å, $b = 8.315(6)$ Å, and $c = 16.926(11)$ Å and $Z = 2$ ($\rho_c = 1.04$ g cm⁻³). The extinctions lead to the space group No. 17, $P222_1$, (with four equivalent positions), again demanding a disordered structure. 734 observed reflections were recorded.

Attempts to solve these structures by direct methods were not successful.

Lists of observed structure factors are available from the author.

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