

On the Crystal Structure of Cyclododecanone

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An X-ray investigation of cyclododecanone, $C_{12}H_{22}O$, has been carried out by growing single crystals at room temperature, cooling them rapidly to $-160\text{ }^{\circ}\text{C}$, and collecting intensity data at this temperature. The dimensions of the monoclinic unit cell are $a=13.089(5)\text{ \AA}$, $b=8.019(4)\text{ \AA}$, $c=5.400(2)\text{ \AA}$, $\beta=100.41(3)^{\circ}$. The space group is $C2/m$ and $Z=2$. The structure was solved by direct methods and refined by full-matrix least-squares technique to an R -value of 6.5% ($R_w=7.2\%$) for 407 reflections recorded on an automatic four circle diffractometer. Four alternative positions of the carbonyl group give the disordered ketone a "square" conformation with C_2 symmetry. Further disorder of the molecule arises from the presence of statistical mirror planes at $y=0$ and $y=\frac{1}{2}$.

Cyclic ketones $(CH_2)_{n-1}CO$ with $n=8,9,\dots,17$ are solids at temperatures above $0\text{ }^{\circ}\text{C}$:

n	M.p. ($^{\circ}\text{C}$)
8	42
9	27
10	25
11	15
12	59
13	28
14	53
15	63
16	61
17	59

However, most of these values do not correspond to "true" melting points inasmuch as the entropy of fusion is abnormally low.¹ In compensation there is at least one transition point with high entropy of transition. Transition points have been determined for $n=8, 9, 13$ and 15 .^{2,3} The modifications stable just below the melting points may be regarded as "half melted", an assumption which is supported by

the fact that the infrared spectra of the liquid phase and the solid phase are almost identical.²

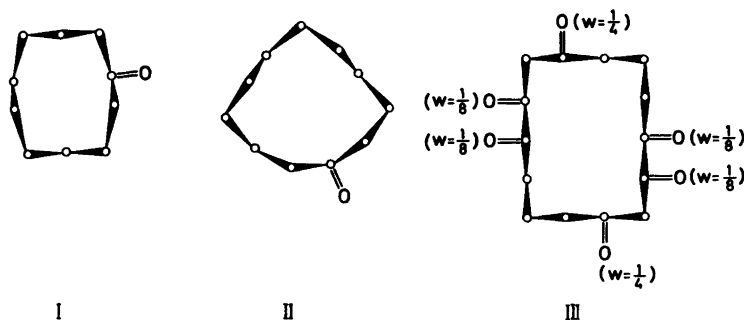
Cyclooctanone and cyclononanone ($n=8$ and 9) have been studied by X-ray diffraction, NMR and DTA.³ The crystalline phases stable at room temperature are highly disordered and no conclusions concerning the ring conformations could be drawn.

Single crystal X-ray investigations of cycloalkanones with $n=10,\dots,17$ in their high temperature phase have been carried out by growing the crystals above $0\text{ }^{\circ}\text{C}$ and then cooling them rapidly to ca. $-160\text{ }^{\circ}\text{C}$. For $n=10$ and 11 ^{4,5} the structures are completely ordered. The ring skeleton of cyclododecanone has the "rectangular" diamond-lattice conformation, I, while the 11-membered ring of cycloundecanone has a "triangular" conformation with the carbonyl group in an asymmetric position, II.

Although the ring skeleton of cyclotetradecanone⁶ ($n=14$) has the expected rectangular conformation without any observable disorder effects, the carbonyl group is disordered, (III).

Space group determinations for cyclopentadecanone and cyclohexadecanone⁴ ($n=15$ and 16) demand disordered structures (still resisting attempts to be solved). Recent preliminary studies of the cases $n=13$ and $n=17$ strongly indicate that also these structures are disordered. Finally cyclododecanone ($n=12$) has been examined, and the results are now reported.

The crystals of $C_{12}H_{22}O$ belong to the monoclinic system with cell dimensions $a=13.089(5)\text{ \AA}$, $b=8.019(4)\text{ \AA}$, $c=5.400(2)\text{ \AA}$, $\beta=100.41(3)^{\circ}$ and $Z=2$. ($D_m=1.06\text{ g cm}^{-3}$, $D_x=1.08\text{ g cm}^{-3}$). These cell dimensions resemble those obtained (at room temperature) for cyclododecane:⁷ $a=13.27\text{ \AA}$, $b=8.28\text{ \AA}$, $c=5.44\text{ \AA}$, $\beta=99.5^{\circ}$. The systematic absences ($h+k=2n+1$) lead to three possible space



groups: $C2$, Cm and $C2/m$ with 4, 4 and 8 equivalent positions, respectively. For cyclododecane (giving the same extinctions) the centrosymmetric space group $C2/m$ turned out to be correct.

With an observed-unobserved cutoff at $2\sigma(I)$, 407 reflections were recorded as observed on an automatic four-circle diffractometer at -160°C (MoK α radiation, $2\theta_{\text{max}}=50^\circ$). The crystal size was $(0.6 \times 0.25 \times 0.15) \text{ mm}^3$ and no corrections for absorption or secondary extinction effects were made.

The phase problem was solved by direct methods⁸ under the assumption of space group $C2/m$ (implying a disordered structure), and refined by the full-matrix least-squares technique. All programs used, except those for phase determination, are included in Ref. 9. Anisotropic temperature factors were introduced for the six "half carbon atoms". Two carbonyl groups were found in the E -map [at C4 and C6 (Fig. 1)]. The oxygens were given multi-

plicity factors 0.125 and refined isotropically. Hydrogen atom positions were calculated and the occupancy factors of those at C4 and C6 were set to 0.25, while the others were given the same value, 0.5, as for the carbon atoms. Hydrogen atoms were included in structure factor calculations (with common $B=5.0 \text{ \AA}^2$), but not refined. Weights for 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. Atomic form factors were those of Hanson *et al.*¹⁰ except for hydrogen.¹¹ The final R -value was 6.5% (weighted value $R_w=7.2\%$) for 407 observed reflections. A tentative refinement in space group $C2$ converged at $R=20\%$ ($R_w=23\%$).

Final fractional coordinates with estimated stand-

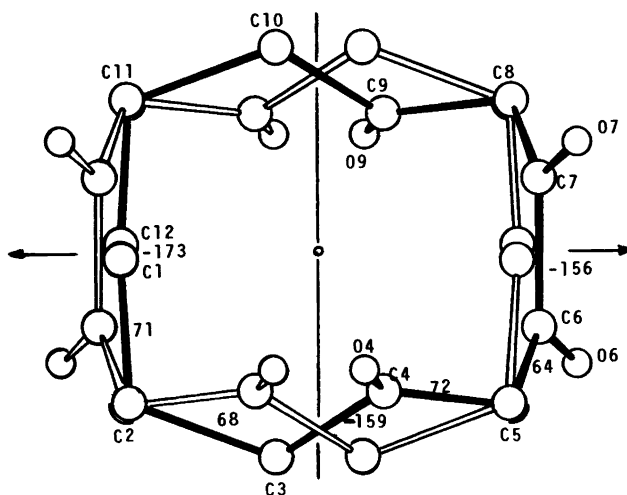


Fig. 1. Schematic drawing of the structure viewed along $[001]$.

Table 1. Final fractional coordinates with estimated standard deviations. Hmn is bonded to Cm.

ATOM	X	Y	Z
C1	.0166(4)	.2489(6)	.1444(8)
C2	.1341(8)	.2590(25)	.2410(34)
C3	.1718(2)	.4447(5)	.1830(7)
C4	.1320(3)	.5817(6)	.3351(8)
C5	.1340(10)	.7436(18)	.2167(35)
C6	.0563(4)	.7787(7)	-.0172(11)
O4	.1297(7)	.5578(11)	.5161(19)
O6	.0720(9)	.8268(17)	-.1824(26)
H11	-.012	.351	.211
H12	-.008	.147	.210
H21	.169	.176	.132
H22	.152	.229	.413
H31	.149	.472	.001
H32	.250	.447	.224
H41	.177	.581	.506
H42	.059	.554	.348
H51	.205	.762	.192
H52	.121	.825	.360
H61	.066	.693	-.137
H62	.073	.892	-.072

Table 2. Bond distances and angles.

Distance	(Å)	Angle	(°)
C12-C1	1.54(1)	C12-C1-C2	115(1)
C1-C2	1.53(1)	C1-C2-C3	108(1)
C2-C3	1.62(2)	C2-C3-C4	114(1)
C3-C4	1.52(1)	C3-C4-C5	112(1)
C4-C5	1.45(2)	C4-C5-C6	119(1)
C5-C6	1.50(2)	C5-C6-C7	115(1)
C6-C7	1.52(1)	C3-C4-O4	118(1)
C4-O4	1.00(1)	C5-C4-O4	127(1)
C6-O6	1.03(1)	C5-C6-O6	126(1)
		C7-C6-O6	117(1)

ard deviations are given in Table 1. Principal axes of the thermal vibration ellipsoids for carbon atoms were calculated from the final thermal parameters (available from the author). Maximum root-mean-square amplitudes range from 0.28 to 0.35 Å. Bond distances and angles are listed in Table 2.

Fig. 1 illustrates the structure viewed along $[001]$. Numbering of atoms, dihedral angles, and symmetry elements are also shown. It may be seen that the ring skeleton possesses two-fold symmetry of rotation and has the expected¹² "square" conformation (not of the diamond-lattice type) which was also found to be the preferred conformation of cyclododecane⁷ and 2,12-dibromo-cyclododecanone.¹³ The ketone maintains the C_2 symmetry by alternating positioning (four sites in all) of the carbonyl group. Furthermore, there is a disorder of the molecule arising from the presence of statistical mirror planes at $y=0$ $y=\frac{1}{2}$, again corresponding to

the results of the cyclododecane structure determination.

Dihedral angles agree roughly with those of cyclododecane. It may be pointed out that the four-membered chain C11-C12-C1-C2 (with no carbonyl groups) is more close to planar than the three others. The abnormal bond distances C2-C3 (1.62 Å) and C4-C5 (1.45 Å) are possibly related to the fact that C2 and C5' (of the mirror image) are separated by 0.13 Å, and thus may have been improperly refined. This is also reflected in the standard deviations in coordinates of these atoms (Table 1). The C-O bond lengths of 1.00 Å and 1.03 Å, respectively, are greatly influenced by the methylene hydrogens and have no physical significance. The same effect was observed in the case of cyclotetradecanone⁶ (with the values 1.09, 1.05 and 1.15 Å).

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

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