

Short Communications

On the Crystal Structure of
Cyclotetradecanone at -157°C

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By semiempirical calculations Dale¹ has found the rectangular diamond-lattice conformation of cyclotetradecanone to be of lowest enthalpy. This is also the observed conformation in liquid and solution.²

The crystals of $\text{C}_{14}\text{H}_{26}\text{O}$ belong to the triclinic system with cell dimensions (for Dirichlet's reduced cell) $a = 5.391(2) \text{ \AA}$, $b = 7.974(3) \text{ \AA}$, $c = 8.404(4) \text{ \AA}$, $\alpha = 64.23(3)^{\circ}$, $\beta = 89.77(3)^{\circ}$, $\gamma = 81.81(3)^{\circ}$. There is one molecule in the unit cell, and the space group $P\bar{1}$ (determined on basis of statistical tests) demands the structure to be disordered.

771 observed reflections were measured on an automatic four circle diffractometer at -157°C ($\text{MoK}\alpha$ -radiation). No corrections for absorption or secondary extinction were carried out (crystal size = $(0.05 \times 0.25 \times 0.32) \text{ mm}^3$).

The structure was solved by direct methods³ and refined by full-matrix least squares technique.^{4*} No disorder effects could be observed

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

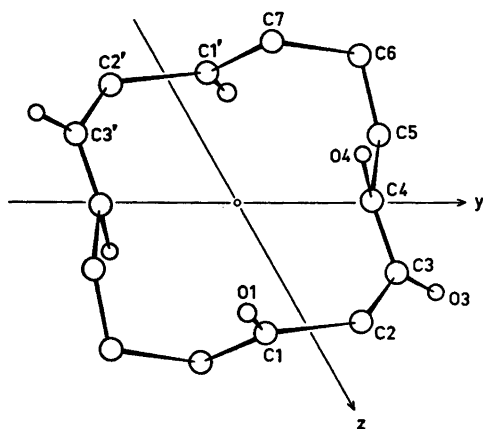


Fig. 1. The molecule viewed along $[100]$.

for the ring skeleton, and anisotropic temperature factors were introduced for carbon atoms. With a half-oxygen bonded to C1 (Fig. 1), the R -factor converged at about 15%. A Fourier map based on the corresponding phases contained relatively large peaks in the vicinity of C3 and C4. Three oxygens were therefore introduced (at C1, C3, and C4) with multiplicity factors 0.250, 0.125, and 0.125, respectively. These were refined simultaneously together with isotropic temperature factors. The multiplicity factors of hydrogens, the positions of which had been calculated, were adjusted for those at C1, C3, C4. No hydrogen parameters were refined. The R -value dropped to 6.4% ($R_w = 6.0\%$) for 771 observed reflections. The oxygen multiplicity factors arrived at were $G(\text{O1}) = 0.250$, $G(\text{O3}) = 0.100$, $G(\text{O4}) = 0.132$. 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.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of thermal vibration ellipsoids for carbon atoms were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes range from 0.182 to 0.197 \AA (corresponding B -values 2.61 and 3.06 \AA^2).

Interatomic distances, bond angles and dihedral angles for the ring skeleton are listed in Table 2. The rectangular diamond-lattice conformation of the ring is shown in Fig. 1, where the molecule is viewed along $[100]$.

Mean value of C—C—C bond angles is 114.4° which corresponds closely to that of cycloundecanone⁵ (114.6°). The average C—C bond distance is 1.526 \AA , while the corresponding value for cycloundecanone is 1.528 \AA .

The observed C—O bond lengths C1—O1 = 1.09 \AA , C3—O3 = 1.05 \AA , C4—O4 = 1.15 \AA are greatly influenced by the methylene hydrogens and have no physical significance. Corresponding bond angles are:

$$\begin{array}{ll} \text{C2—C1—O1} = 122^{\circ} & \text{C7—C1—O1} = 123^{\circ} \\ \text{C2—C3—O3} = 125^{\circ} & \text{C4—C3—O3} = 117^{\circ} \\ \text{C3—C4—O4} = 119^{\circ} & \text{C5—C4—O4} = 118^{\circ} \end{array}$$

Table 1. Final fractional coordinates and thermal parameters (multiplied by 10^5 for C and by 10^4 for O and H atoms). Expression for anisotropic vibration is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. Hn1 and Hn2 are bonded to Cn.

ATOM	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
C2	25479(59)	8938(44)	38124(39)	2477(138)	1276(76)	725(69)	-1865(163)	338(142)	-875(113)
C1	35591(63)	-8724(43)	28812(48)	1794(129)	1184(74)	874(62)	-382(154)	-386(140)	-755(112)
C3	881(63)	19343(43)	19920(43)	2287(133)	929(68)	817(69)	-315(153)	338(141)	-671(105)
C4	377(63)	25647(44)	-93(41)	2377(135)	1158(72)	875(68)	-1267(162)	358(147)	-774(108)
C5	-25687(58)	34409(42)	-9386(39)	2489(136)	950(68)	933(63)	-214(152)	110(147)	-997(110)
C6	-26979(61)	40141(43)	-29310(40)	2591(141)	1117(73)	832(61)	-413(160)	-199(146)	-713(112)
C7	-18739(57)	23944(42)	-34318(39)	2237(131)	1094(71)	815(59)	-935(154)	170(138)	-716(106)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
O1	5438(18)	-1077(13)	2355(12)	3,3(,3)	H32	-1259	1080	2580	2,0
O3	-1423(40)	2588(30)	2461(28)	2,5(,7)	H41	579	1460	-179	2,0
O4	1754(29)	3138(21)	-751(20)	2,3(,5)	H42	1940	3560	-489	2,0
H11	3736	-449	1530	2,0	H51	-3255	4550	-737	2,0
H12	5110	-1309	3510	2,0	H52	-3746	2448	-392	2,0
H21	3839	1794	2463	2,0	H61	-1462	4940	-3443	2,0
H22	2913	586	4273	2,0	H62	-4388	4624	-3443	2,0
H31	-459	3080	2280	2,0	H71	-111	1784	-3015	2,0
					H72	-1933	2960	-4825	2,0

Table 2. Interatomic distances, bond angles and dihedral angles with estimated standard deviations for the ring skeleton.

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
C1 - C2	1,520(4)	C2 - C3	1,520(4)	C3 - C4	1,532(4)
C4 - C5	1,522(4)	C5 - C6	1,532(4)	C6 - C7	1,533(4)
C7 - C1'	1,526(4)				

ANGLE	(°)	ANGLE	(°)
C1 - C2 - C3	114,4(3)	C2 - C3 - C4	115,1(3)
C3 - C4 - C5	112,7(3)	C4 - C5 - C6	114,0(3)
C5 - C6 - C7	114,6(3)	C6 - C7 - C1'	114,2(3)
C7 - C1' - C2'	115,0(3)		

DIHEDRAL ANGLE	(°)	DIHEDRAL ANGLE	(°)
C1 - C2 - C3 - C4	-57,8(4)	C2 - C3 - C4 - C5	174,9(3)
C3 - C4 - C5 - C6	-177,4(3)	C4 - C5 - C6 - C7	59,0(4)
C5 - C6 - C7 - C1'	64,8(4)	C6 - C7 - C1' - C2'	-170,4(3)
C7 - C1' - C2' - C3'	60,7(4)		

Cyclotetradecanone has been studied by ^{13}C and ^1H nuclear magnetic resonance⁶ with the following result: "The cmr spectra of cyclotetradecanone reveal the presence of at least two different kinds of conformations. At -160° , there are two carbonyl bands (intensity ratio 3:2) separated by 1.3 ppm, and the α -carbon resonance is complex".

No short inter-molecular contacts are observed.

A list of observed structure factors is available by request to the author.

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