Crystal Structure of Cyclotetradecane at −157°C

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A recent study of cyclotetradecanone, $C_{14}H_{26}O$,[1] revealed a disordered structure with respect to the oxygen atoms while the ring skeleton had the "rectangular" diamond-lattice conformation (without observable disorder). For cyclotetradecane, $C_{14}H_{28}$, this conformation has the lowest calculated enthalpy [2] as well as being the observed one in liquid and solution.[3] It has been stated that it is also the experimental crystal conformation.[2] However, to the best of the author's knowledge no results have yet been published on the conformation in the solid state, and will therefore now be presented.

The crystals of $C_{14}H_{28}$ are triclinic with cell dimensions (for Dirichlet's reduced cell) $a=5.340(4)$ Å, $b=8.041(6)$ Å, $c=8.424(7)$ Å, $\alpha=64.4(1)°$, $\beta=89.5(1)°$, $\gamma=82.0(1)°$. There is one molecule in the unit cell and the space group is $P\bar{1}$.

894 observed reflections were measured on an automatic four-circle diffractometer at −157 °C (Mo$K\alpha$-radiation). No corrections for absorption or secondary extinction were carried out (crystal size = (0.1 × 0.2 × 0.4) mm³).

The structure was solved by direct methods [4] and refined by full-matrix least-squares technique.[5]* Anisotropic temperature factors were introduced for the carbon atoms. 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 R-value arrived at was 5.1 % (weighted value $R_w=5.2$ %) for 894 observed reflections.

Final fractional coordinates with estimated standard deviations are given in Table 1. Maximum root-mean-square anisotropic thermal amplitudes for the carbon atoms range from 0.16 to 0.18 Å. No rigid-body analysis has 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" conformation of the 14-membered ring.

From Table 2 it may be seen that the C−C bond lengths are equal within limit of error (mean value 1.534 Å). The bond angle C2−C3−C4 (112.3°) is significantly smaller than the others which are equal with an average of 114.6°. This value corresponds closely to those of cyclotetradecanone [1] (114.4°) and cycloundecanone [6] (114.6°). Fig. 1 shows that C3 is

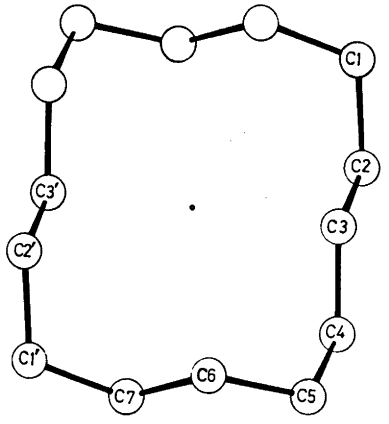

Fig. 1. Schematic drawing of the molecule.

* 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. The expression for anisotropic vibration is exp [$-2\pi^2(h^2a^{*2}U11+..+2klb^*c^*U23)$]. Atom Hmn is bonded to atom Cm.

ATOM	x	y	z	U11	U22	U33	U12	U13	U23
C1	.76758(43)	.13041(29)	.79436(26)	.0295(12)	.0228(11)	.0179(11)	.0003(9)	-.0028(9)	-.0067(9)
C2	.75636(38)	.15557(30)	.59558(26)	.0244(11)	.0209(11)	.0201(11)	-.0010(9)	.0019(8)	-.0105(9)
C3	.49516(37)	.24515(29)	.58176(25)	.0247(11)	.0207(11)	.0172(10)	-.0038(9)	.0015(8)	-.0092(9)
C4	.49943(39)	.30767(30)	.38218(26)	.0280(12)	.0209(11)	.0168(10)	-.0029(9)	.0014(8)	-.0086(9)
C5	.24602(39)	.41099(29)	.19893(26)	.0262(11)	.0273(12)	.0148(11)	-.0063(9)	-.0001(8)	-.0087(9)
C6	.14111(39)	.58705(28)	.22006(27)	.0212(11)	.0259(12)	.0163(11)	-.0001(9)	-.0020(8)	-.0076(9)
C7	.31337(40)	.73767(28)	.15645(26)	.0267(12)	.0247(11)	.0132(10)	-.0032(9)	.0017(8)	-.0067(9)

ATOM	x	y	z	B	ATOM	x	y	z	B
H11	.6438(39)	.0055(29)	.8498(27)	1.8(4)	H12	.9427(44)	.8409(31)	.8469(29)	2.8(4)
H21	.8159(37)	.0432(29)	.5751(26)	1.6(4)	H22	.8809(35)	.2398(26)	.5401(23)	.9(3)
H31	.4382(34)	.3458(28)	.5318(24)	1.3(4)	H32	.3643(37)	.1572(27)	.5490(25)	1.4(3)
H41	.5421(38)	.2002(31)	.2779(27)	2.1(4)	H42	.6407(36)	.3862(26)	.2594(24)	1.0(3)
H51	.1092(36)	.3277(26)	.2287(24)	1.1(3)	H52	.2656(39)	.4441(29)	.0734(31)	2.1(4)
H61	.1077(36)	.5547(27)	.3433(29)	1.5(4)	H62	-.0279(43)	.6365(29)	.1564(28)	2.2(4)
H71	.3169(36)	.7977(27)	.0192(29)	1.8(4)	H72	.4931(38)	.6794(25)	.2042(25)	1.2(3)

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

DISTANCE	(Å)	DISTANCE	(Å)
C1 - C2	1.535(3)	C2 - C3	1.528(3)
C3 - C4	1.533(3)	C4 - C5	1.536(3)
C5 - C6	1.531(3)	C6 - C7	1.538(3)
C7 - C1'	1.536(3)		

ANGLE	(°)	ANGLE	(°)
C1 - C2 - C3	114.7(2)	C2 - C3 - C4	112.3(2)
C3 - C4 - C5	114.7(2)	C4 - C5 - C6	114.6(2)
C5 - C6 - C7	114.2(2)	C6 - C7 - C1'	114.4(2)
C7 - C1' - C2'	114.7(2)		

DIHEDRAL ANGLE	(°)
C1 - C2 - C3 - C4	176.6(2)
C2 - C3 - C4 - C5	-176.8(2)
C3 - C4 - C5 - C6	58.8(3)
C4 - C5 - C6 - C7	61.8(2)
C5 - C6 - C7 - C1'	-178.1(2)
C6 - C7 - C1' - C2'	64.4(3)
C7 - C1' - C2' - C3'	58.6(3)

the middle atom at the long "edge" of the "rectangle". Since this is the least strained position, one would expect an angle more close to 109.5° at C3 than at any other atom. In cyclotetradecanone the corresponding angle is 112.7°. The dihedral angles of Table 2 are also in very good agreement with the values found for cyclotetradecanone: 177.4, −174.9, 57.8, 60.7, −170.4, 64.8, 59.0°. C−H bond distances range from 0.95 to 1.04 Å. No short *inter*-molecular distances are observed.

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

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