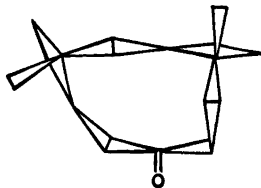# Short Communications

The Crystal Conformation of 4,4,7,7-Tetramethylcyclononanone at −156°C

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On basis of dynamic ^{13}C NMR spectroscopy, Borgen and Dale [1] have discussed the asymmetric nature of the conformation of 4,4,7,7-tetramethylcyclononanone ($C_{13}H_{24}O$). Although their conclusions concerning conformational exchange processes are somewhat uncertain, there are strong evidences in favour of an asymmetric triangular ring-conformation [234]* with the carbonyl group in a non-corner position:

Since the same conformation persists in the solid (shown by IR-spectroscopy [3]), a crystal structure determination has been performed in order to establish the conformation of this nine-membered ring.

The crystals belong to the orthorhombic system with space group *Pbca*, cell dimensions $a = 9.122(2)$ Å, $b = 10.910(2)$ Å, $c = 24.550(7)$ Å, and eight molecules in the unit cell ($D_m = 1.05$ g cm^{-3}, $D_x = 1.06$ g cm^{-3}). 1209 observed reflections were measured on an automatic four circle diffractometer at −156°C (Mo$K\alpha$-radiation). No corrections for absorption and secondary extinction were carried out [crystal size = (0.25 × 0.30 × 0.32) mm^3].

The structure was solved by direct methods [4] and refined by full-matrix least-squares technique.[5]** Methylene hydrogen positions were calculated. Methyl hydrogens were localized as the twelve largest peaks in a difference Fourier map. Anisotropic temperature factors were introduced for O and C atoms, and weights in least-squares were calculated from the

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* This notation indicates the number of bonds in each "side" separating the "corner" atoms.[2]
** All programs used, except those for phase determination, are included in this reference.

standard deviations in intensities, $\sigma(I)$, taken as

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

where C_T is the total number of counts and C_N the net count. The final weighted R-value was 3.5 % (conventional $R = 4.5$ %) for 1209 observed reflections. The form factors used were those of Hanson et al.[6] except for hydrogen.[7]

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of thermal vibration ellipsoids for the oxygen and carbon atoms were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes range from 0.152 to 0.208 Å (corresponding B-values 1.81 and 3.41 Å^2). No rigid-body analysis has been carried out.

Bond distances and angles and dihedral angles are given in Table 2. The standard deviations (in parentheses) are estimated from the correlation matrix of the final least-squares refinement cycle. Fig. 1 is a schematic drawing of the molecule showing that the nine-membered ring has the [234] conformation. The numbering of atoms is also indicated.

The dihedral angles agree well with those obtained by strain energy calculations for the [234] conformation of cyclononane.[8] The values are given in Table 2. These calculations give [9] the distance between hydrogens at C1 and C6, respectively, as the shortest (1.79 Å). This interaction is thus avoided in the ketone. The next shortest calculated value (1.83 Å) between H-atoms at C5 and C8 corresponds to the shortest contact of the present compound, H51···H81 of (2.04 Å).

As may be seen from Table 2, bond distances are normal. The mean value of C−C bonds (excluding C1−C2 and C1−C9) is 1.536 Å, while the corresponding average for cyclo-undecanone [10] is 1.532 Å. C1=O is 1.212(3) Å for the present compound and 1.213(3) Å
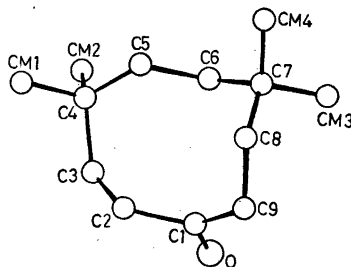

Fig. 1. Schematic drawing of the molecule.

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

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O	.30619(20)	1.04453(18)	.54105(7)	.0386(12)	.0261(11)	.0375(12)	-.0026(11)	.0051(10)	.0030(10)
C1	.30459(30)	.93556(27)	.54792(10)	.0281(16)	.0292(18)	.0132(14)	-.0029(16)	.0078(12)	-.0016(14)
C2	.16805(30)	.86275(26)	.53295(11)	.0304(18)	.0193(18)	.0174(15)	.0060(16)	-.0005(14)	.0027(13)
C3	.02805(32)	.91436(26)	.55865(11)	.0214(16)	.0229(18)	.0225(15)	.0031(14)	-.0044(14)	.0019(13)
C4	-.03215(27)	.84777(25)	.60998(9)	.0180(14)	.0258(16)	.0184(13)	.0003(14)	-.0005(13)	-.0011(12)
C5	.08970(30)	.79510(26)	.64636(11)	.0214(16)	.0207(15)	.0187(14)	-.0018(15)	.0015(13)	.0021(13)
C6	.20742(28)	.86646(25)	.66473(11)	.0231(17)	.0202(15)	.0174(14)	.0037(14)	.0016(13)	-.0009(14)
C7	.36334(29)	.83468(23)	.67007(10)	.0223(15)	.0222(15)	.0221(15)	.0029(14)	-.0023(13)	-.0032(13)
C8	.42055(32)	.78127(28)	.61609(11)	.0189(16)	.0310(18)	.0298(16)	.0047(16)	-.0037(14)	-.0026(15)
C9	.43915(32)	.86901(29)	.56793(11)	.0242(17)	.0336(19)	.0242(16)	.0015(17)	.0062(14)	-.0028(15)
CM1	-.12875(35)	.74085(30)	.59190(13)	.0253(18)	.0347(19)	.0320(18)	-.0042(17)	-.0031(17)	.0028(17)
CM2	-.12595(33)	.93974(31)	.64141(12)	.0204(16)	.0355(20)	.0279(17)	.0015(17)	.0011(15)	-.0007(16)
CM3	.46418(36)	.93696(32)	.69017(13)	.0272(19)	.0371(20)	.0322(19)	.0031(18)	-.0045(17)	-.0048(16)
CM4	.36205(36)	.73088(29)	.71210(12)	.0309(18)	.0323(20)	.0248(17)	.0058(18)	-.0061(16)	-.0010(14)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H21	.1825(23)	.7757(21)	.5402(8)	.8(5)	H22	.1589(23)	.8748(20)	.4943(9)	1.5(5)
H31	-.0508(25)	.9155(21)	.5324(9)	1.5(5)	H32	.0494(25)	1.0043(21)	.5671(8)	1.3(5)
H51	.1409(23)	.7291(21)	.6255(8)	1.0(5)	H52	.0457(25)	.7567(20)	.6791(9)	1.1(5)
H61	.1752(22)	.9271(19)	.6980(8)	.2(4)	H62	.2113(20)	.9580(20)	.6391(7)	.1(4)
H81	.3567(25)	.7130(23)	.6045(9)	1.8(5)	H82	.5191(26)	.7415(21)	.6242(8)	1.0(5)
H91	.4762(27)	.8237(22)	.5375(10)	2.3(6)	H92	.5163(26)	.9372(24)	.5753(9)	2.2(6)
HM11	-.0708(29)	.6860(24)	.5696(10)	2.5(6)	HM12	-.2156(27)	.7739(23)	.5688(10)	2.7(6)
HM13	-.1679(28)	.6950(24)	.6236(10)	2.9(6)	HM21	-.0648(27)	1.0077(22)	.6559(8)	1.8(5)
HM22	-.1802(26)	.8964(23)	.6720(10)	2.5(6)	HM23	-.2079(25)	.9752(21)	.6178(9)	2.3(6)
HM31	.4312(26)	.9687(22)	.7260(9)	2.2(5)	HM32	.4650(28)	1.0081(24)	.6648(10)	2.7(6)
HM33	.5685(29)	.9052(22)	.6951(9)	2.1(6)	HM41	.3021(26)	.6571(23)	.7009(9)	1.8(5)
HM42	.3229(24)	.7580(20)	.7465(10)	1.3(5)	HM43	.4653(30)	.7001(24)	.7194(10)	3.0(6)

Table 2. Bond distances and angles and dihedral angles with estimated standard deviations. Dihedral angles from strain minimization calculations are also included.

DISTANCE	(Å)	DISTANCE	(Å)
O - C1	1.212(3)	C1 - C2	1.522(4)
C2 - C3	1.532(4)	C3 - C4	1.555(3)
C4 - C5	1.533(3)	C5 - C6	1.529(4)
C6 - C7	1.538(4)	C7 - C8	1.538(4)
C8 - C9	1.531(4)	C9 - C1	1.508(4)
C4 - CM1	1.528(4)	C4 - CM2	1.528(4)
C7 - CM3	1.530(4)	C7 - CM4	1.531(4)

ANGLE	(°)	ANGLE	(°)
O - C1 - C2	119.5(3)	O - C1 - C9	120.8(3)
C1 - C2 - C3	113.0(2)	C2 - C3 - C4	117.2(2)
C3 - C4 - C5	112.8(2)	C4 - C5 - C6	116.3(2)
C5 - C6 - C7	115.7(2)	C6 - C7 - C8	112.4(2)
C7 - C8 - C9	117.8(2)	C8 - C9 - C1	117.5(2)
C9 - C1 - C2	119.6(3)	C3 - C4 - CM1	109.0(2)
C3 - C4 - CM2	107.5(2)	C5 - C4 - CM1	107.9(2)
C5 - C4 - CM2	110.7(2)	CM1 - C4 - CM2	109.0(2)
C6 - C7 - CM3	108.2(2)	C6 - C7 - CM4	108.9(2)
C8 - C7 - CM3	110.5(2)	C8 - C7 - CM4	107.7(2)
CM3 - C7 - CM4	109.1(2)		

DIHEDRAL ANGLE	(°)	(°) *
C1 - C2 - C3 - C4	-101.2(3)	-110
C2 - C3 - C4 - C5	34.4(3)	41
C3 - C4 - C5 - C6	54.2(3)	50
C4 - C5 - C6 - C7	-145.3(2)	-137
C5 - C6 - C7 - C8	59.3(3)	52
C6 - C7 - C8 - C9	62.8(3)	70
C7 - C8 - C9 - C1	-59.9(4)	-58
C8 - C9 - C1 - C2	-53.5(4)	-51
C9 - C1 - C2 - C3	131.3(2)	131

* Values from strain minimization calculations

in cycloundecanone. The C−C−C angles at C2, C4, and C7 are significantly smaller than the other ring angles. No such pattern was observed in the case of cycloundecanone. At C4 and C7 the effect is possibly connected with the methyl substitution. It may also be mentioned that the angle C1−C2−C3 of 113.0(2)° agrees with the result of strain energy calculations [8] where the C−C−C angle at C2 comes out as the smallest one with a value of 113.1°.

C−H bonds range from 0.96 Å to 1.04 Å, while C−C−H and H−C−H angles are obtained between 105 and 113°. No short inter-molecular contacts are observed. A list of observed and calculated structure factors is available on request to the author.

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