

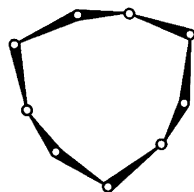
# On the Crystal Conformations of Two Nine-membered Rings: Cyclononaneoxime and Cyclononanephylsemicarbazone (at $-150\text{ }^{\circ}\text{C}$ )

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Crystals were grown at room temperature and cooled rapidly to about  $-150\text{ }^{\circ}\text{C}$ , the temperature at which data were collected on an automatic four-circle diffractometer. Both nine-membered rings have a conformation which may be described as either quinquangular [1 2 2 2 2] or triangular [2 2 5]. There is no resemblance at all to the triangular type [3 3 3] with the lowest calculated enthalpy.

Strain-energy minimization calculations<sup>1–4</sup> show that the lowest-enthalpy conformation of cyclononane is of the triangular type [3 3 3].\*

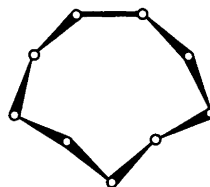


[333]

The same conformation (with  $D_3$  symmetry) has also been established experimentally<sup>5</sup> by low-temperature  $^{13}\text{C}$  NMR. In the crystals, the structures of cyclononane and cyclononanone are highly disordered.<sup>6</sup> Only two crystal structure determinations of saturated nine-membered rings

\* A shorthand notation for conformational type, consisting of a series of numbers within brackets, each giving the number of bonds in one "side", starting with the shortest. The direction around the ring is so chosen that the following number is the smallest possible.

have been reported: cyclononylammonium bromide<sup>7</sup> and the 1:1 addition compound mercuric chloride-cyclononanone.<sup>8</sup> In both, the ring conformation could be defined as quinquangular [1 2 2 2 2] (or alternatively as triangular [2 2 5]):



[12222] (or [225])

This conformation has no similarity at all to the [3 3 3] conformation, and the difference in strain energy amounts to something between 9.2 kJ/mol and 12.1 kJ/mol.<sup>1,3,4</sup> In order to supplement the conformational evidence for the saturated nine-membered ring, single crystal X-ray analyses of the oxime,  $\text{C}_9\text{H}_{17}\text{NO}$ , and the phenylsemicarbazone,  $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}$ , have been carried out.

Crystal data for the two compounds are given in Table 1. Intensities were measured (at *ca.*  $-150\text{ }^{\circ}\text{C}$ ) on a four-circle automatic diffractometer (MoK $\alpha$ -radiation) with  $2\theta_{\text{max}} = 50^{\circ}$ . No corrections for absorption or secondary extinction were made (maximum crystal size  $0.3 \times 0.3 \times 0.2$  mm). The structures were solved by direct methods<sup>9</sup> and refined by full-matrix least squares technique.<sup>10,\*</sup> Weights in least squares were obtained from the

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

Table 1. Crystal data for (I): cyclononaneoxime and (II): cyclononanephenylsemicarbazone.

	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	<i>Z</i>	$D_m$ g cm <sup>-3</sup>	$D_x$ g cm <sup>-3</sup>	Number of observed reflections
I)	$P\bar{1}$	5.633(1)	7.217(2)	12.180(5)	81.14(3)	78.94(2)	72.55(2)	2	1.12	1.09	760
II)	$P2_1/n$	14.514(4)	6.208(2)	16.600(4)	90.0	102.75(2)	90.0	4	1.21	1.20	1572

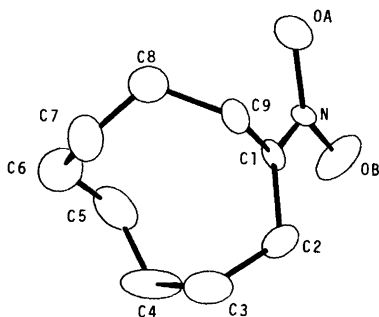


Fig. 1. Schematic drawing of the cyclononaneoxime molecule.

Table 2. Final fractional coordinates with estimated standard deviations for cyclononaneoxime. Hn,1 and Hn,2 are bonded to Cn.

ATOM	x	y	z
OA	.2170 (17)	-.1054 (12)	.9097 ( 7)
OB	.0010 (70)	.2186 (58)	.9953 (31)
N	.2031 (16)	.0885 (11)	.9303 ( 6)
C1	.3826 (18)	.1548 (14)	.8782 ( 7)
C2	.3723 (19)	.3593 (16)	.8939 ( 9)
C3	.4224 (24)	.4907 (17)	.7909 (11)
C4	.2050 (21)	.5599 (16)	.7228 (11)
C5	.1293 (22)	.4156 (18)	.6707 (10)
C6	.2916 (23)	.3140 (18)	.5794 (11)
C7	.5553 (21)	.1661 (18)	.5972 ( 9)
C8	.5568 (22)	.0074 (16)	.6844 ( 9)
C9	.6067 (18)	.0296 (14)	.8081 ( 8)
H21	.500	.349	.943
H22	.200	.420	.934
H31	.578	.419	.745
H32	.451	.607	.817
H41	.256	.654	.659
H42	.054	.630	.772
H51	-.033	.484	.642
H52	.102	.309	.732
H61	.324	.418	.519
H62	.193	.239	.553
H71	.663	.243	.614
H72	.632	.109	.524
H81	.689	-.111	.656
H82	.387	-.019	.694
H91	.747	.090	.798
H92	.654	-.103	.850

standard deviations in intensities,  $\sigma(I)$ , taken as  $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$ , where  $C_T$  is the total number of counts, and  $C_N$  the net count. The form factors used were those of Hanson *et al.*<sup>12</sup> except for hydrogen.<sup>13</sup> Standard deviations in bond distances and angles and dihedral angles are calculated from the correlation matrix of the final least square refinement.

## CYCLONONANEOXIME

The crystal quality was very poor and the solution of the phase problem was not quite straightforward. A seven atom fragment was misplaced (being connected to itself by the centre of symmetry). By "moving" the fragment stepwise through the cell, and (for each step) calculating the *R*-value for 100 low-angle reflections, a faint minimum ( $R=49\%$ ) at  $\Delta x=0.32$ ,  $\Delta y=0.08$ ,  $\Delta z=0.42$  was obtained. With the phases corresponding to this position of the fragment, successive weighted Fourier syntheses revealed the rest of the atoms. In fact, one extra peak appeared, symmetrically situated with respect to the C1=N bond at a distance of about 1.4 Å from N (Fig. 1).

Anisotropic temperature factors were used for oxygen, nitrogen and carbon atoms. Methylene hydrogen atoms (calculated positions) were included in the structure factor calculations with a common isotropic temperature factor  $B=2.5 \text{ \AA}^2$ , but not refined. When discarding the 12th peak in the Fourier map, refinement converged at  $R \sim 21\%$ . An oxygen atom with multiplicity factor,  $G=0.15$ , was introduced at the site of peak No. 12 and the *G*-value of the original O-atom was reduced to 0.9. Least squares refinement with these occupancy factors included as parameters led to a final *R*-value of 13.8% ( $R_w=10.7\%$ ). Maximum r.m.s. anisotropic thermal amplitudes range from 0.21 to 0.37 Å. The multiplicity factors arrived at were  $G(OA)=0.81$  and  $G(OB)=0.19$ . It is thought that

Table 4. Final fractional coordinates with estimated standard deviations for cyclononaphenylsemicarbazone. Hm is bonded to Cn (in the phenyl ring), Hn,1 and Hn,2 are bonded to Cn (in the nine-membered ring), HNn is bonded to Nm.

ATOM	X	Y	Z
O	.0073(1)	.1002(3)	.4077(0)
N1	.1463(1)	.3663(3)	.4492(1)
N2	.0856(1)	.2012(3)	.4594(1)
N3	.1079(1)	.0563(3)	.3365(1)
C1	.1692(1)	.5073(4)	.5072(1)
C2	.2306(1)	.6910(4)	.4914(1)
C3	.3225(1)	.7315(4)	.5555(1)
C4	.3982(1)	.5581(4)	.5628(1)
C5	.3749(1)	.3309(4)	.5673(1)
C6	.3660(1)	.3001(5)	.6763(1)
C7	.2826(1)	.4050(4)	.7025(1)
C8	.1830(1)	.3418(4)	.6526(1)
C9	.1351(1)	.5048(4)	.5871(1)
C10	.0632(1)	.0436(4)	.4006(1)
C11	.1103(1)	.0967(4)	.2746(1)
C12	.0694(1)	.3000(4)	.2729(1)
C13	.0766(1)	.4442(4)	.2108(1)
C14	.1238(1)	.3896(4)	.1499(1)
C15	.1642(1)	.1876(4)	.1518(1)
C16	.1580(1)	.0415(4)	.2132(1)
H21	.192(1)	.827(4)	.488(1)
H22	.244(1)	.667(3)	.438(1)
H31	.307(1)	.705(3)	.609(1)
H32	.348(1)	.871(4)	.540(1)
H41	.456(1)	.605(4)	.604(1)
H42	.418(1)	.554(4)	.509(1)
H51	.427(1)	.229(4)	.579(1)
H52	.316(1)	.270(3)	.550(1)
H61	.420(1)	.349(4)	.716(1)
H62	.361(1)	.131(4)	.687(1)
H71	.291(1)	.566(4)	.704(1)
H72	.286(1)	.361(4)	.761(1)
H81	.141(1)	.325(3)	.692(1)
H82	.187(1)	.193(3)	.624(1)
H91	.142(1)	.657(3)	.610(1)
H92	.065(1)	.475(3)	.574(1)
HN3	.056(1)	.190(4)	.503(1)
HN2	.142(1)	.165(4)	.338(1)
H14	.037(1)	.344(3)	.315(1)
H15	.046(1)	.508(4)	.211(1)
H16	.128(1)	.490(3)	.106(1)
H17	.195(1)	.146(4)	.108(1)
H18	.187(1)	.100(3)	.214(1)

Table 3. Bond distances and angles and dihedral angles with estimated standard deviations for cyclononaneoxime.

DISTANCE	(Å)	DISTANCE	(Å)
OA - N	1.44(1)	OH - N	1.43(5)
N - C1	1.27(1)	C1 - C2	1.50(1)
C1 - C9	1.51(1)	C2 - C3	1.49(2)
C3 - C4	1.53(2)	C4 - C5	1.50(2)
C5 - C6	1.44(2)	C6 - C7	1.58(2)
C7 - C8	1.44(2)	C8 - C9	1.62(1)

ANGLE	(°)	ANGLE	(°)
OA - N - C1	116.(1)	OR - N - C1	117.(2)
N - C1 - C2	118.(1)	C1 - C9 - C9	122.(1)
C1 - C2 - C3	117.(1)	C2 - C1 - C9	121.(1)
C1 - C9 - C8	114.(1)	C2 - C3 - C4	113.(1)
C3 - C4 - C5	120.(1)	C4 - C5 - C6	121.(1)
C5 - C6 - C7	121.(1)	C6 - C7 - C8	117.(1)
C7 - C8 - C9	119.(1)		

DIPEDRAL ANGLE	(°)
C9 - C1 - C2 - C3	51.(1)
C1 - C2 - C3 - C4	74.(1)
C2 - C3 - C4 - C5	-64.(2)
C3 - C4 - C5 - C6	-68.(2)
C4 - C5 - C6 - C7	65.(2)
C5 - C6 - C7 - C8	56.(2)
C6 - C7 - C8 - C9	-95.(1)
C7 - C8 - C9 - C1	77.(1)
C8 - C9 - C1 - C2	-104.(1)

Table 5. Bond distances and angles with estimated standard deviations for cyclononaphenylsemicarbazone.

DISTANCE		(Å)	DISTANCE		(Å)
O - C10	1.228	(3)	N1 - N2	1.385	(3)
N1 - C1	1.289	(3)	N2 - C10	1.369	(3)
N3 - C10	1.368	(3)	N3 - C11	1.413	(3)
C1 - C2	1.506	(4)	C1 - C9	1.515	(3)
C2 - C3	1.533	(4)	C3 - C4	1.524	(4)
C4 - C5	1.526	(4)	C5 - C6	1.524	(4)
C6 - C7	1.521	(4)	C7 - C8	1.540	(3)
C8 - C9	1.538	(3)	C11 - C12	1.397	(3)
C12 - C13	1.394	(3)	C13 - C14	1.393	(3)
C14 - C15	1.382	(4)	C15 - C16	1.382	(3)

ANGLE		(°)	ANGLE		(°)
O - C10 - N2	120.7	(2)	O - C10 - N3	124.0	(2)
N2 - N1 - C1	118.6	(2)	N1 - N2 - C10	120.0	(2)
N1 - C1 - C2	116.7	(2)	N1 - C1 - C9	124.5	(2)
N2 - C10 - N3	115.3	(2)	C10 - N3 - C11	127.8	(2)
N3 - C11 - C12	123.6	(2)	N3 - C11 - C16	117.3	(2)
C1 - C2 - C3	117.5	(2)	C2 - C1 - C9	118.4	(2)
C1 - C9 - C8	115.9	(2)	C2 - C3 - C4	116.2	(2)
C3 - C4 - C5	118.4	(2)	C4 - C5 - C6	116.4	(2)
C5 - C6 - C7	117.8	(2)	C6 - C7 - C8	116.2	(2)
C7 - C8 - C9	116.2	(2)	C11 - C12 - C13	119.8	(2)
C12 - C11 - C16	119.0	(2)	C11 - C16 - C15	120.1	(3)
C12 - C13 - C14	121.2	(3)	C13 - C14 - C15	118.8	(2)
C14 - C15 - C16	121.1	(2)			

DIHEDRAL ANGLE		(°)
C9 - C1 - C2 - C3	56.8	(3)
C1 - C2 - C3 - C4	67.3	(3)
C2 - C3 - C4 - C5	-60.7	(3)
C3 - C4 - C5 - C6	-70.7	(3)
C4 - C5 - C6 - C7	68.5	(3)
C5 - C6 - C7 - C8	57.2	(4)
C6 - C7 - C8 - C9	-101.1	(3)
C7 - C8 - C9 - C1	77.9	(3)
C8 - C9 - C1 - C2	-105.7	(3)

the bad crystal quality has the main responsibility for the poor agreement between observed and calculated structure factors, and that these findings suggest that the crystals are built up of a mixture of two forms of cyclononaneoxime molecules, differing only in the N-OH group orientation. About 81 % of the molecules have oxygen at the site of OA (Fig. 1), while in 19 % it is situated at the OB position. A corresponding structure has been found in the crystals of cycloundecaneoxime<sup>11</sup> (with *G*-values 0.85 and 0.15). Dimers are formed by hydrogen bonds OA-N' and OB-N', both 2.75 Å long. Final fractional coordinates with estimated standard deviations are listed in Table 2. The bond distances and angles of Table 3 are normal within error limits, and the dihedral angles show that the ring conformation is [1 2 2 2 2] corresponding to the earlier findings.<sup>7,8</sup>

#### CYCLONONANEPHENYL-SEMICARBAZONE

Hydrogen atom positions were calculated. Anisotropic temperature factors were used for O, N and C atoms. Refinement converged at *R* = 4.0 % (*R<sub>w</sub>* = 3.4 %). Final fractional coordinates with estimated standard deviations are given in Table 4. Maximum root mean squares anisotropic thermal amplitudes range from 0.15 to 0.22 Å. Fig. 2 is a schematic drawing of the molecule, showing the numbering of atoms. The bond distances and angles, listed in Table 5, have normal values, and dimers are formed by hydrogen bonds O-N2' = 2.898(3) Å long. The torsional angles of Table 5 show that the ring conformation [1 2 2 2 2] again is preferred.

The fact that all four cyclononane derivatives so

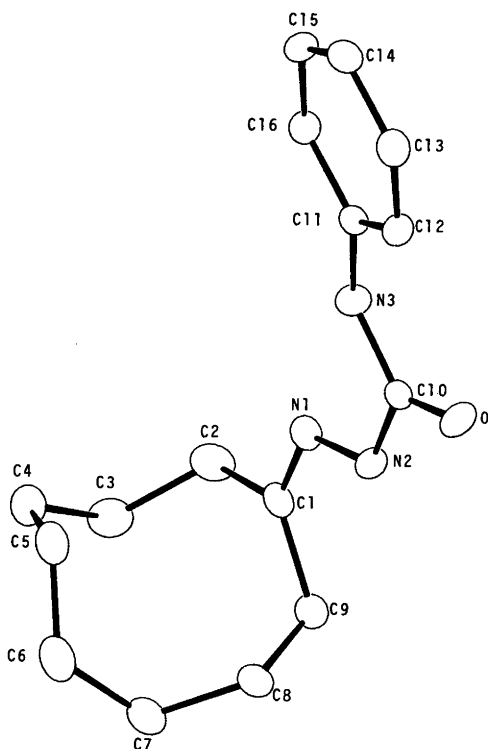


Fig. 2. Schematic drawing of the cyclononanaphenylsemicarbazone molecule.

far examined by X-ray analysis have the [1 2 2 2 2] conformation would seem to indicate that this is the preferred conformation of the saturated nine-membered ring with one  $sp_2$  carbon atom.

Lists of thermal parameters and observed and calculated structure factors are available from the author.

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