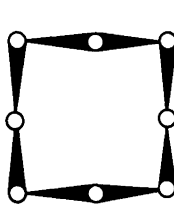


On the Crystal Conformation of Two Eight-membered Rings: Cyclooctaneoxime and Cyclooctanephenylsemicarbazone (at -150°C)

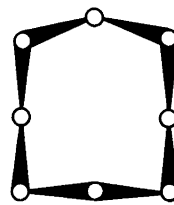
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Crystals were grown at room temperature and cooled rapidly to about -150°C , the temperature at which data were collected on an automatic four-circle diffractometer. Both eight-membered rings have the biangular [26]* conformation, usually called "boat-chair". The sp^2 carbon atom is situated in a position corresponding to maximum relief in transannular hydrogen interactions and eclipsing strain.



[2222]



[26]

According to strain-energy calculations,¹ the conformation of lowest energy for cyclooctane is not the square diamond-lattice type [2222], but a biangular [26], usually called "boat-chair". This conformation seems to be preferred also in most "simple" cyclooctane compounds, including ketones and heterocyclic analogues.² An X-ray diffraction study of crystalline cyclooctane at 0°C ³ gave

* 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 smallest possible.

limited information due to disorder. In contrast to the parent compound, several cyclooctane derivatives and related compounds have had their structures determined by X-ray diffraction (Table 1, Ref. 2). However, the "ketone-case" (one sp^2 carbon in the ring) has not been studied.

Attempts to grow single crystals of cyclooctanone were unsuccessful. The crystals obtained for the oxime were of rather poor quality, while those of the phenylsemicarbazone were satisfactory. In order to supplement the conformational evidence for the saturated eight-membered ring, single crystal X-ray analyses of the oxime, $\text{C}_8\text{H}_{15}\text{NO}$, and the

Table 1. Crystal data for (I) cyclooctaneoxime, and (II) cyclooctanephenylsemicarbazone.

Space group	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	Z	D_m g cm^{-3}	D_x g cm^{-3}	Number of observed reflections
(I) $C2/c$	23.802(10)	6.925(4)	10.469(4)	90.0	108.29(3)	90.0	8	1.13	1.15	1003
(II) $C2/c$	22.934(8)	5.077(2)	24.926(5)	90.0	104.09(2)	90.0	8	1.18	1.22	1611

Table 2. Final fractional coordinates with estimated standard deviations for cyclooctaneoxime. Hn,1 and Hn,2 are bonded to Cn. HO is bonded to O.

ATOM	X	Y	Z
O	.6962(1)	.3998(5)	.4492(3)
N	.7118(1)	.2757(6)	.3547(4)
C1	.6833(2)	.3217(7)	.2336(4)
C2	.6399(2)	.4822(8)	.1956(5)
C3	.5783(2)	.4332(9)	.2041(6)
C4	.5439(2)	.2776(9)	.1101(6)
C5	.5720(3)	.0772(9)	.1311(5)
C6	.6020(3)	.0094(10)	.0280(6)
C7	.6475(3)	.1513(9)	.0051(5)
C8	.6992(2)	.2013(9)	.1270(5)
H21	.632(2)	.535(8)	.101(5)
H22	.659(2)	.591(9)	.255(6)
H31	.559(2)	.567(10)	.198(5)
H32	.583(2)	.396(8)	.298(5)
H41	.538(2)	.310(8)	.023(5)
H42	.500(2)	.267(7)	.103(4)
H51	.540(1)	-.017(7)	.125(4)
H52	.602(2)	.063(6)	.220(4)
H61	.570(3)	-.005(10)	-.050(7)
H62	.622(2)	-.112(10)	.049(5)
H71	.628(2)	.256(7)	-.031(4)
H72	.662(2)	.090(7)	-.059(4)
H81	.727(2)	.281(9)	.098(6)
H82	.715(2)	.086(8)	.171(5)
HO	.730	.336	.521

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

DISTANCE	(Å)	DISTANCE	(Å)
O - N	1.44(1)	N - C1	1.28(1)
C1 - C2	1.48(1)	C1 - C8	1.53(1)
C2 - C3	1.53(1)	C3 - C4	1.51(1)
C4 - C5	1.53(1)	C5 - C6	1.54(1)
C6 - C7	1.54(1)	C7 - C8	1.51(1)

ANGLE	(°)	ANGLE	(°)
C - N - C1	111.(1)	N - C1 - C2	124.(1)
N - C1 - C8	114.(1)	C1 - C2 - C3	115.(1)
C2 - C1 - C8	122.(1)	C1 - C8 - C7	115.(1)
C2 - C3 - C4	117.(1)	C3 - C4 - C5	115.(1)
C4 - C5 - C6	117.(1)	C5 - C6 - C7	115.(1)
C6 - C7 - C8	116.(1)		

DIHEDRAL ANGLE	(°)
C8 - C1 - C2 - C3	102.(1)
C1 - C2 - C3 - C4	-64.(1)
C2 - C3 - C4 - C5	63.(1)
C3 - C4 - C5 - C6	-104.(1)
C4 - C5 - C6 - C7	52.(1)
C5 - C6 - C7 - C8	59.(1)
C6 - C7 - C8 - C1	-69.(1)
C7 - C8 - C1 - C2	-41.(1)

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

DISTANCE (Å)		DISTANCE (Å)	
0 - C9	1.233 (2)	N1 - N2	1.385 (2)
N1 - C1	1.283 (3)	N2 - C9	1.358 (3)
N3 - C9	1.365 (2)	N3 - C10	1.406 (3)
C1 - C2	1.510 (3)	C1 - C8	1.510 (3)
C2 - C3	1.538 (3)	C3 - C4	1.518 (3)
C4 - C5	1.532 (3)	C5 - C6	1.530 (3)
C6 - C7	1.525 (4)	C7 - C8	1.514 (3)
C10 - C11	1.389 (3)	C10 - C15	1.396 (3)
C11 - C12	1.384 (3)	C12 - C15	1.384 (3)
C13 - C14	1.373 (3)	C14 - C15	1.383 (3)

ANGLE (°)		ANGLE (°)	
0 - C9 - N2	120.4 (2)	0 - C9 - N3	124.2 (2)
N2 - N1 - C1	118.1 (2)	N1 - N2 - C9	120.1 (2)
N1 - C1 - C2	114.4 (2)	N1 - C1 - C8	123.8 (2)
N2 - C9 - N3	115.4 (2)	C9 - N3 - C10	127.6 (2)
N3 - C10 - C11	123.6 (2)	N3 - C10 - C15	117.1 (2)
C1 - C2 - C3	115.2 (2)	C2 - C1 - C8	121.6 (2)
C1 - C8 - C7	117.5 (2)	C2 - C3 - C4	117.2 (2)
C3 - C4 - C5	114.6 (2)	C4 - C5 - C6	114.8 (2)
C5 - C6 - C7	115.2 (2)	C6 - C7 - C8	113.6 (2)
C10 - C11 - C12	119.6 (2)	C11 - C10 - C15	119.3 (2)
C10 - C15 - C14	120.1 (2)	C11 - C12 - C13	121.0 (2)
C12 - C13 - C14	119.4 (2)	C13 - C14 - C15	120.6 (2)

DIPEDRAL ANGLE (°)	
C8 - C1 - C2 - C3	-93.0 (3)
C1 - C2 - C3 - C4	69.8 (3)
C2 - C3 - C4 - C5	-65.4 (3)
C3 - C4 - C5 - C6	104.6 (3)
C4 - C5 - C6 - C7	-57.1 (3)
C5 - C6 - C7 - C8	-55.7 (3)
C6 - C7 - C8 - C1	80.2 (3)
C7 - C8 - C1 - C2	21.0 (3)

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

ATOM	X	Y	Z
0	.71370(6)	-.38853(31)	.04364(5)
N1	.81294(7)	.09581(36)	.11263(6)
N2	.75163(7)	.06548(37)	.07056(6)
N3	.73705(8)	-.25512(40)	.13438(6)
C1	.84872(9)	.26831(43)	.10075(7)
C2	.86055(10)	.43632(49)	.14901(8)
C3	.94137(10)	.32859(51)	.18212(8)
C4	.95310(11)	.33143(53)	.15396(9)
C5	.98450(12)	.15865(54)	.10343(9)
C6	.96840(12)	.29264(63)	.04764(9)
C7	.91198(11)	.46298(51)	.03745(9)
C8	.85656(11)	.31440(50)	.04307(8)
C9	.74206(9)	-.24573(45)	.08097(7)
C10	.69922(8)	-.41822(42)	.15656(7)
C11	.66793(9)	-.63144(44)	.12856(8)
C12	.63154(10)	-.78063(48)	.15365(8)
C13	.62593(10)	-.72104(48)	.20634(8)
C14	.65746(10)	-.51239(47)	.23425(8)
C15	.69405(9)	-.36854(46)	.20996(8)
H21	.8538(8)	.4517(39)	.1745(7)
H22	.8850(8)	.6235(43)	.1368(7)
H31	.9359(8)	.1330(43)	.1938(7)
H32	.9526(8)	.4371(43)	.2171(8)
H41	1.0228(9)	.2723(44)	.1817(8)
H42	.9992(8)	.5276(47)	.1436(8)
H51	.9527(9)	.0079(44)	.1042(7)
H52	1.0211(10)	.0423(51)	.1062(8)
H61	.9621(9)	.1566(47)	.0160(9)
H62	1.0042(11)	.4135(52)	.0450(9)
H71	.9050(8)	.5489(43)	-.0012(8)
H72	.9174(9)	.6332(46)	.0632(8)
H81	.8578(8)	.1391(44)	.0246(7)
H82	.8205(9)	.4885(48)	.0218(8)
H92	.7848(9)	-.0872(48)	.0362(9)
H93	.7567(10)	.1318(50)	.1538(9)
H11	.6711(8)	.76710(38)	.0915(7)
H12	.6896(8)	-.9280(41)	.1331(7)
H13	.6006(8)	-.8522(40)	.2225(7)
H14	.6539(8)	-.4732(41)	.2715(8)
H15	.7160(8)	-.2122(42)	.2292(7)

phenylsemicarbazone, $C_{15}H_{21}N_3O$, have been carried out.

Crystal data for the two compounds are given in Table 1. Intensities were measured (at *ca.* -150°C) on a four-circle automatic diffractometer (MoK α -radiation) with $2\theta_{\text{max}}=50^\circ$. No corrections for absorption or secondary extinction were made (maximum crystal size $0.35 \times 0.28 \times 0.4$ mm). The structures were solved by direct methods⁴ and refined by full-matrix least squares technique.^{5*} Weights in least squares were obtained from the 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 form factors used were those of Hanson *et al.*⁶ except for hydrogen.⁷ Standard

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

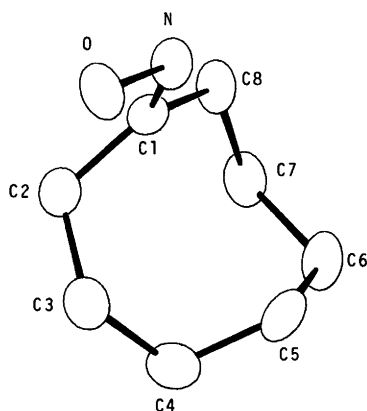


Fig. 1. Schematic drawing of the cyclooctaneoxime molecule.

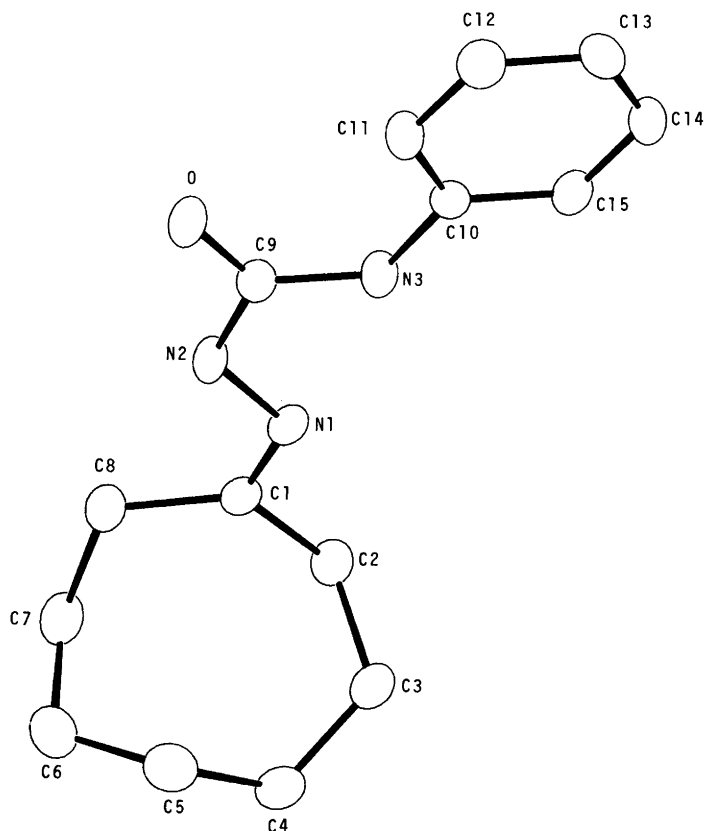


Fig. 2. Schematic drawing of the cyclooctanephylsemicarbazone molecule.

deviations in bond distances and angles and dihedral angles are calculated from the correlation matrix of the final least squares refinement.

Cyclooctaneoxime. Anisotropic temperature factors were used for oxygen, nitrogen and carbon atoms. Hydrogen positions were calculated. The final *R*-value was as high as 10.0% ($R_w = 8.3\%$), probably due to the poor crystal quality. Final fractional coordinates with estimated standard deviations are given in Table 2. Maximum root mean square anisotropic thermal amplitudes range from 0.18 to 0.24 Å. The bond distances and angles of Table 3 are normal within error limits,^{8,9} and the dihedral angles show that the eight-membered ring has the expected boat-chair conformation, [26], with the sp^2 carbon atom in a position corresponding to maximum relief in transannular hydrogen interactions and eclipsing strain.² Except for the hydrogen bond O---N' of length 2.77(1) Å (forming dimers), no short *inter*-molecular contacts are observed.

Cyclooctanephenylicarbazone. With anisotropic temperature factors for O, N, and C atoms, and calculated hydrogen atom positions, the *R*-value arrived at was 3.9% ($R_w = 3.5\%$). Final fractional coordinates with estimated standard deviations are given in Table 4. Principal axes of thermal vibration ellipsoids were calculated from the thermal parameters, and the corresponding maximum r.m.s. amplitudes range from 0.17 to 0.25 Å. The bond distances and angles of Table 5 agree closely with earlier findings,^{9,10} and the torsional angles show that the ring conformation [26] again is preferred, and that the site of the sp^2 carbon atom corresponds to that of cyclooctaneoxime. The similarity of the two rings may also be seen by comparing the schematical drawings, Fig. 1 and Fig. 2. Dimers are formed by hydrogen bonds N2---O' of length 2.884(2) Å. No other short *inter*-molecular contacts are observed.

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

REFERENCES

1. Anet, F. A. L. and Krane, J. *Tetrahedron Lett.* 50 (1973) 5029.
2. Anet, F. A. L. *Fortschr. Chem. Forsch.* 45 (1974) 169.
3. Sands, D. E. and Day, V. W. *Acta Crystallogr.* 19 (1965) 278.

4. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 29 (1971) 368.
5. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
6. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
8. Groth, P. *Acta Chem. Scand. A* 33 (1979) 503.
9. Groth, P. *Acta Chem. Scand. A* 34 (1980) 603.
10. Groth, P. *Acta Chem. Scand. A* 34 (1980) 609.

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