

On the Crystal Conformations of Cyclic Oximes, (CH₂)_{n-1}CNOH with $n = 10, \dots, 14$

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Crystals were grown at room temperature and cooled rapidly to about -160°C , the temperature at which data were collected on an automatic four-circle diffractometer. Cyclodecaneoxime has the [1333] conformation (different from the "rectangular" [2323] conformation of the corresponding ketone). Cycloundecaneoxime has the quinquangular [12323] conformation, while the triangular, [355], is preferred in the crystals of cycloundecanone. The OH group is disordered. For cyclododecaneoxime the expected "square" conformation, [3333] is found. Some disorder, the degree of which seems to vary from one crystal to another, is apparently present. In the crystals of cyclotridecaneoxime the disorder arises from the presence of statistical pseudo mirror planes, and the ring conformation may be described as [337]. Cyclotetradecaneoxime has the expected "rectangular" [3434] conformation with the oxime group in one fixed position (as opposed to the corresponding ketone). All compounds are dimers with $\text{O}-\text{H}\cdots\text{N}'$ hydrogen bonds in the range 2.62–2.81 Å. Preliminary investigations of the cases $n=15, \dots, 18$ indicate highly disordered structures.

The "half-melted" modifications stable just below the melting points of cyclic ketones (CH₂)_nCO with

$n=10, \dots, 17$ have been studied by X-ray diffraction.¹⁻⁴ Except for the cases $n=10$ and 11,^{1,2} all the structures are disordered. Among these, structure determinations have been successfully carried out for $n=12$ and 14, only.^{3,4} By introducing the possibility of stabilising *inter-molecular* hydrogen bonds, less disorder might be hoped for. The corresponding oximes, (CH₂)_{n-1}CNOH, have therefore been synthesized and investigated by X-ray methods. Some results are now reported.

Crystal data for the compounds with $n=10, \dots, 14$ are given in Table 1 (cell dimensions for Dirichlet's reduced cell). The crystals were grown at room temperature and cooled rapidly to about -160°C , the temperature at which data were collected on a four-circle automatic diffractometer (MoK α -radiation, $2\theta_{\text{max}} = 50^\circ$). No corrections for absorption or secondary extinction were made (maximum crystal size $0.5 \times 0.5 \times 0.3$ mm). The structures were solved by direct methods⁵ and refined by full-matrix least squares technique.⁶ * Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

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

Table 1. Crystal data for the cyclic oximes (CH₂)_{n-1}CNOH with $n=10, \dots, 14$.

n	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	D_m gcm ⁻³	D_x gcm ⁻³	Number of observed reflections
10	$P\bar{1}$	5.447(1)	7.688(1)	12.802(2)	77.83(1)	70.11(1)	74.19(1)	2	1.12	1.16	1326
11	$P\bar{1}$	5.565(1)	7.873(1)	12.642(3)	88.32(2)	78.69(2)	80.92(1)	2	1.12	1.13	1279
12	$P\bar{1}$	5.395(1)	8.263(2)	13.894(3)	98.79(2)	98.37(2)	103.30(2)	2	1.08	1.12	887
13	$P\bar{1}$	5.317(1)	8.476(1)	14.563(2)	92.88(1)	100.49(1)	96.63(1)	2	1.08	1.10	1031
14	$P\bar{1}$	5.176(1)	8.728(1)	15.189(2)	99.89(1)	90.81(1)	91.65(1)	2	1.10	1.11	1520

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

where C_T is the total number of counts, and C_N the net count. The form factors used were those of Hanson *et al.*⁷ except for hydrogen.⁸ Standard deviations in bond distances and angles are calculated from the correlation matrix of the final least squares refinement.

$$n = 10$$

Hydrogen atom positions were calculated except for HO which was found in a difference Fourier map. Anisotropic temperature factors were used for oxygen, nitrogen, and carbon atoms. Refinement converged at $R = 3.2\%$ ($R_w = 3.1\%$). Final fractional coordinates with estimated standard deviations are

Table 2. Final fractional coordinates with estimated standard deviations for $(\text{CH}_2)_9\text{CNOH}$. Hn,1 and Hn,2 are bonded to Cn. HO is bonded to O.

Atom	x	y	z
O	.80183(21)	.13224(13)	.09379(8)
N	.74229(23)	-.03247(15)	.08522(9)
C1	.51683(27)	-.05490(18)	.15246(11)
C2	.32613(30)	.07891(20)	.22999(12)
C3	.37915(32)	.06597(20)	.34240(13)
C4	.44015(29)	-.12825(20)	.40336(12)
C5	.73725(29)	-.21790(20)	.36501(12)
C6	.80734(30)	-.42610(20)	.38131(12)
C7	.71921(30)	-.51409(20)	.30712(12)
C8	.84356(30)	-.46339(21)	.18011(12)
C9	.64700(31)	-.39080(20)	.11202(12)
C10	.43104(28)	-.22489(19)	.15157(12)
H21	.1489(29)	.0625(18)	.2433(11)
H22	.3328(30)	.2047(22)	.1917(13)
H31	.2173(32)	.1409(21)	.3917(13)
H32	.5288(29)	.1220(19)	.3304(12)
H41	.3294(26)	-.2038(18)	.3931(10)
H42	.3845(27)	-.1243(18)	.4851(13)
H51	.8283(27)	-.1732(18)	.4060(11)
H52	.8142(27)	-.1721(18)	.2835(12)
H61	.7264(28)	-.4734(19)	.4626(12)
H62	1.0012(30)	-.4671(18)	.3651(11)
H71	.5255(29)	-.4828(18)	.3261(11)
H72	.7642(29)	-.6483(22)	.3241(12)
H81	.9656(32)	-.5707(22)	.1488(12)
H82	.9521(26)	-.3741(19)	.1683(11)
H91	.5567(28)	-.4884(19)	.1135(11)
H92	.7497(29)	-.3611(19)	.0327(13)
H101	.3198(28)	-.2572(18)	.2282(12)
H102	.3145(27)	-.1914(18)	.1050(11)
HO	.9564(37)	-.1307(24)	.0399(16)

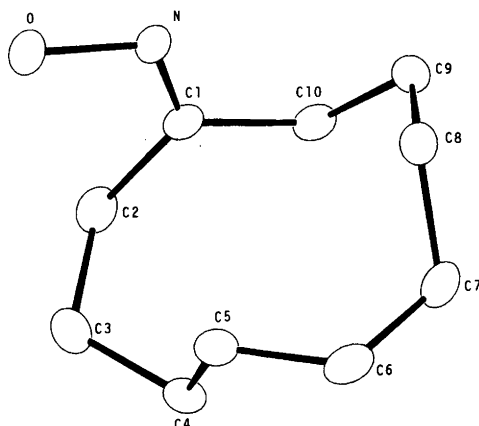
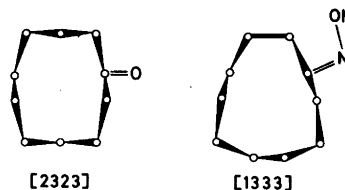


Fig. 1. Schematic drawing of the cyclodecaneoxime molecule.

given in Table 2. Maximum root-mean-squares anisotropic thermal amplitudes range from 0.15 to 0.19 Å. Fig. 1 is a schematic drawing of the molecule showing the numbering of atoms. The bond distances and angles, listed in Table 3, have normal values, and dimers are formed by hydrogen bonds of length $\text{O} \cdots \text{N}' = 2.807(1)$ Å. The torsional angles of Table 3 show that, in contrast to cyclodecanone, which has the lowest-enthalpy "rectangular" diamond-lattice conformation, [2323],^{1,9} cyclodecaneoxime has the [1333] conformation,* corresponding to one of the two found as a mixture in the crystal of 4,4,8,8-tetramethylcyclodecanecarboxylic acid.¹⁰



$$n = 11$$

The nitrogen atom appeared as the largest peak in the *E*-map. Peaks Nos. 3, ..., 13 could be interpreted as the ring carbon atoms. Two peaks, the second highest and No. 14, were situated symmetrically with respect to the $\text{C1}=\text{N}$ bond at distances of

* 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.

Table 3. Bond distances and angles and dihedral angles with estimated standard deviations for $(\text{CH}_2)_{10}\text{CNOH}$.

Distance (Å)	Distance (Å)
O–N 1.425(1)	N–C1 1.275(2)
C1–C2 1.508(2)	C1–C10 1.508(2)
C2–C3 1.541(2)	C3–C4 1.538(2)
C4–C5 1.534(2)	C5–C6 1.527(2)
C6–C7 1.534(2)	C7–C8 1.544(2)
C8–C9 1.529(2)	C9–C10 1.525(2)
Angle (°)	Angle (°)
O–N–C1 112.4(1)	N–C1–C2 124.8(1)
N–C1–C10 117.5(1)	C1–C2–C3 115.8(1)
C2–C1–C10 117.6(1)	C1–C10–C9 118.0(1)
C2–C3–C4 115.3(1)	C3–C4–C5 112.0(1)
C4–C5–C6 116.1(1)	C5–C6–C7 114.5(1)
C6–C7–C8 114.3(1)	C7–C8–C9 115.7(1)
C8–C9–C10 114.9(1)	
Dihedral angle (°)	
C10–C1–C2–C3 98.4(2)	
C1–C2–C3–C4 –45.2(2)	
C2–C3–C4–C5 87.3(2)	
C3–C4–C5–C6 –156.2(1)	
C4–C5–C6–C7 67.7(2)	
C5–C6–C7–C8 60.6(2)	
C6–C7–C8–C9 –127.8(1)	
C7–C8–C9–C10 56.1(2)	
C8–C9–C10–C1 59.6(2)	
C9–C10–C1–C2 –156.7(1)	

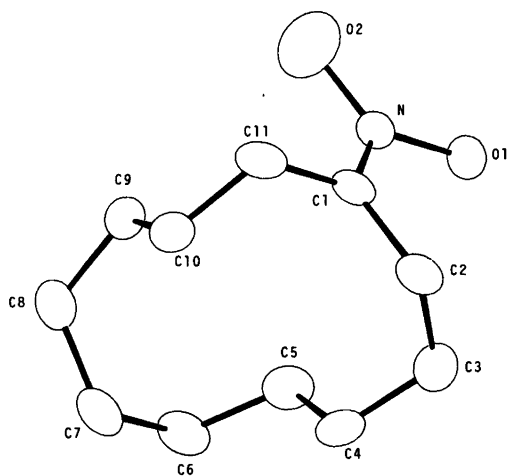


Fig. 2. Schematic drawing of the cycloundecane-oxime molecule.

about 1.4 Å from N. When discarding peak No. 14, refinement converged at $R \sim 10\%$ with a maximum r.m.s. anisotropic thermal amplitude of 0.41 Å for oxygen (amplitudes for the other atoms ranged from 0.18 to 0.24 Å). An oxygen atom with multiplicity factor, $G=0.1$, was introduced at the position of peak 14 (the G -values of the original O and HO atoms being reduced to 0.9). Least squares refinement with these occupancy factors included as parameters led to a final R -value of 6.3% ($R_w=6.2\%$). The multiplicity factors arrived at were $G(\text{O}1)=G(\text{HO}1)=0.85$ and $G(\text{O}2)=0.15$, and the corresponding r.m.s. amplitudes 0.20 and 0.37 Å

Table 4. Final fractional coordinates with estimated standard deviations for $(\text{CH}_2)_{10}\text{CNOH}$. Hn,1 and Hn,2 are bonded to Cn. HO1 is bonded to O1.

Atom	x	y	z
O1	.1209(12)	–.0940(4)	.0970(4)
O2	.0500(40)	.1779(27)	–.0172(17)
N	.1639(4)	.0755(3)	.0648(2)
C1	.3147(5)	.1341(4)	.1128(2)
C2	.4450(6)	.0318(5)	.1932(2)
C3	.2984(7)	–.0209(5)	.3015(3)
C4	.1527(7)	.1277(4)	.3754(2)
C5	–.1033(7)	.1869(5)	.3532(3)
C6	–.2394(7)	.3538(5)	.4103(3)
C7	–.1302(7)	.5189(4)	.3794(3)
C8	–.1604(7)	.5972(5)	.2705(3)
C9	–.0209(7)	.4959(4)	.1699(3)
C10	.2561(6)	.4495(4)	.1631(3)
C11	.3771(7)	.3089(5)	.0792(2)
H21	.544(6)	–.076(4)	.152(2)
H22	.565(6)	.099(4)	.208(2)
H31	.187(6)	–.092(4)	.286(2)
H32	.423(6)	–.092(4)	.342(2)
H41	.138(6)	.090(4)	.454(3)
H42	.261(6)	.227(4)	.368(2)
H51	–.097(6)	.196(4)	.271(3)
H52	–.212(6)	.086(4)	.376(2)
H61	–.406(7)	.375(4)	.392(2)
H62	–.250(6)	.331(4)	.486(3)
H71	–.218(6)	.613(4)	.433(2)
H72	.053(6)	.504(3)	.382(2)
H81	–.337(7)	.619(4)	.269(2)
H82	–.111(7)	.708(5)	.269(3)
H91	–.100(5)	.399(4)	.162(2)
H92	–.047(6)	.568(4)	.106(3)
H101	.338(6)	.560(4)	.145(2)
H102	.294(6)	.416(4)	.235(2)
H111	.326(6)	.342(4)	.012(3)
H112	.551(7)	.299(4)	.071(2)
HO1	.037(16)	–.105(6)	.125(6)

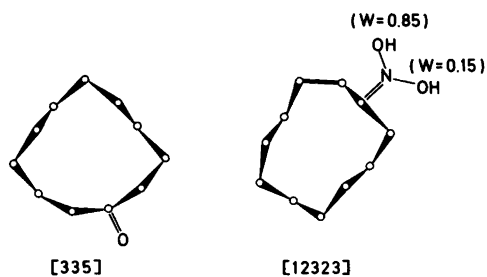
Table 5. Bond distances and angles and dihedral angles with estimated standard deviations for $(\text{CH}_2)_{10}\text{CNOH}$.

Distance	(Å)	Distance	(Å)
O1-N	1.427(6)	O2-N	1.473(21)
N-C1	1.276(4)	C1-C2	1.504(5)
C1-C11	1.502(5)	C2-C3	1.533(5)
C3-C4	1.538(5)	C4-C5	1.505(5)
C5-C6	1.531(5)	C6-C7	1.530(5)
C7-C8	1.520(5)	C8-C9	1.527(5)
C9-C10	1.513(5)	C10-C11	1.534(5)
Angle	(°)	Angle	(°)
O1-N-O2	124.7(10)	O1-N-C1	114.2(3)
N-O1-O2	112.1(7)	O2-N-C1	121.2(10)
N-C1-C2	123.3(3)	N-C1-C11	117.0(3)
C1-C2-C3	120.7(3)	C2-C1-C11	119.6(3)
C1-C11-C10	113.3(3)	C2-C3-C4	115.8(3)
C3-C4-C5	112.8(3)	C4-C5-C6	114.9(3)
C5-C6-C7	117.8(3)	C6-C7-C8	116.9(3)
C7-C8-C9	117.4(3)	C8-C9-C10	114.9(3)
		C9-C10-C11	112.9(3)
Dihedral angle	(°)		
C11-C1-C2-C3	119.1(4)		
C1-C2-C3-C4	-60.9(5)		
C2-C3-C4-C5	87.4(4)		
C3-C4-C5-C6	-169.9(3)		
C4-C5-C6-C7	64.5(5)		
C5-C6-C7-C8	73.7(5)		
C6-C7-C8-C9	-67.1(5)		
C7-C8-C9-C10	-55.4(5)		
C8-C9-C10-C11	164.3(3)		
C9-C10-C11-C1	-71.7(4)		
C10-C11-C1-C2	-77.9(4)		

(amplitudes of other atoms practically unchanged). Attempts to localize HO2 in a difference Fourier map were not made.

These findings suggest that the crystals are built up of a mixture of two forms of cycloundecane-oxime molecules, differing only in the N-OH group orientation. About 85% of the molecules have oxygen at the site of O1 (Fig. 2) while in 15% it is situated at the O2 position. The dimers are formed by hydrogen bonds of lengths $\text{O1} \cdots \text{N}' = 2.810(6)$ Å and $\text{O2} \cdots \text{N}' = 2.62(2)$ Å, respectively. Final fractional coordinates with estimated standard deviations are listed in Table 4. Bond distances and angles, shown in Table 5, are normal within error limits. For the cycloundecane ring as many as four conformations have about equally low enthalpies.⁹ One of them, the triangular [355], was observed to be preferred in the crystals of cycloundecanone.² The dihedral angles of Table 5 show that the

present 11-membered ring has the quinquangular rather ill-defined conformation [12323].



$n = 12$

The quality of the cycloundecaneoxime crystals was rather poor. Anisotropic temperature factors were introduced for heavy atoms. Methylene hydrogen positions were calculated and HO could be localized in a difference Fourier map. Hydrogen

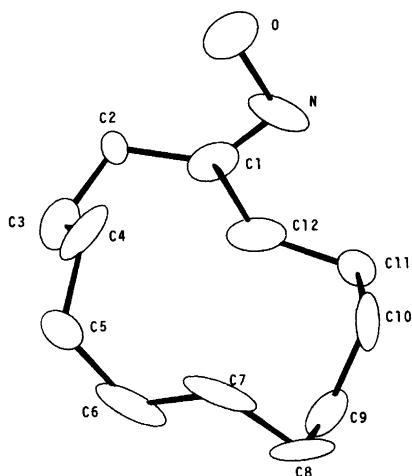


Fig. 3. Schematic drawing of the cyclododecaneoxime molecule.

atoms were not refined. The final R -value was as high as 13.8% ($R_w = 11.2\%$) and maximum r.m.s. anisotropic thermal amplitudes ranged from 0.19 to 0.41 Å. Fig. 3 is a schematic drawing which shows the numbering of atoms and the degree of anisotropy. Only three atoms, C2, C5 and C11, have "normal" amplitudes, the others, being very large, indicate a disordered structure. A Fourier map based upon the phases corresponding to $R = 13.8\%$ indeed showed several small extra peaks. However, no reasonable interpretation could be made. Another crystal, apparently of somewhat better quality than the first one, was selected, and a new set of data obtained. Attempts to solve the structure by direct methods with these reflections were unsuccessful. By comparing structure amplitudes of corresponding reflections, a very bad correlation was observed. Refinement of the parameters of crystal No. 1, using the latter set of data, converged at $R \sim 18\%$.

A reasonable conclusion to be drawn from these findings is that the structure of cyclododecaneoxime is disordered, and that the degree of disorder may vary from one crystal to another. Final fractional coordinates with estimated standard deviations (from the crystal No. 1 refinement) are listed in Table 6. Bond distances and angles and torsional angles are given in Table 7. It may be stated that crystal No. 1 of the present investigation contains mainly the "square" conformation (not of the

diamond lattice type) with approximate C_2 symmetry [3333].

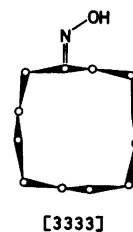


Table 6. Final fractional coordinates with estimated standard deviations for $(\text{CH}_2)_{11}\text{CNOH}$. Hn,1 and Hn,2 are bonded to Cn. HO is bonded to O.

Atom	x	y	z
O	1.0074(15)	.1888(9)	.4839(5)
N	.8513(17)	.1028(12)	.5531(6)
C1	.7157(22)	.2090(15)	.5932(7)
C2	.7238(20)	.3769(12)	.5777(7)
C3	.8609(26)	.5176(15)	.6677(9)
C4	1.1304(24)	.5223(15)	.6984(9)
C5	1.2579(22)	.6108(13)	.8102(8)
C6	1.1645(24)	.4973(18)	.8821(9)
C7	1.2824(22)	.3586(18)	.8806(8)
C8	1.1402(23)	.2091(17)	.9288(7)
C9	.8604(29)	.1097(16)	.8684(10)
C10	.8629(27)	.0119(14)	.7730(10)
C11	.5986(19)	-.0277(13)	.6960(7)
C12	.5613(22)	.1305(15)	.6574(8)
H21	.537	.382	.560
H22	.812	.399	.522
H31	.772	.506	.729
H32	.853	.637	.655
H41	1.235	.578	.652
H42	1.141	.398	.688
H51	1.202	.722	.825
H52	1.450	.641	.820
H61	.970	.452	.864
H62	1.207	.570	.952
H71	1.468	.402	.921
H72	1.291	.310	.812
H81	1.123	.258	.997
H82	1.243	.124	.931
H91	.748	.192	.857
H92	.764	.030	.909
H101	.899	-.101	.782
H102	1.007	.075	.745
H111	.455	-.077	.728
H112	.607	-.115	.637
H121	.576	.224	.718
H122	.371	.102	.621
HO	.097	1.103	.433

Table 7. Bond distances and angles and dihedral angles with estimated standard deviations for $(\text{CH}_2)_{11}\text{CNOH}$.

Distance	(Å)	Distance	(Å)
O-N	1.52(1)	N-C1	1.37(1)
C1-C2	1.43(1)	C1-C12	1.44(2)
C2-C3	1.53(2)	C3-C4	1.44(2)
C4-C5	1.59(2)	C5-C6	1.54(2)
C6-C7	1.43(2)	C7-C8	1.59(2)
C8-C9	1.58(2)	C9-C10	1.44(2)
C10-C11	1.59(2)	C11-C12	1.53(1)
Angle	(°)	Angle	(°)
O-N-C1	109(1)	N-C1-C2	127(1)
N-C1-C12	111(1)	C1-C2-C3	114(1)
C2-C1-C12	122(1)	C1-C12-C11	123(1)
C2-C3-C4	113(1)	C3-C4-C5	116(1)
C4-C5-C6	111(1)	C5-C6-C7	112(1)
C6-C7-C8	114(1)	C7-C8-C9	113(1)
C8-C9-C10	113(1)	C9-C10-C11	114(1)
C10-C11-C12	112(1)		
Dihedral angle	(°)		
C12-C1-C2-C3	69(1)		
C1-C2-C3-C4	61(1)		
C2-C3-C4-C5	-158(1)		
C3-C4-C5-C6	75(1)		
C4-C5-C6-C7	75(1)		
C5-C6-C7-C8	-164(1)		
C6-C7-C8-C9	67(1)		
C7-C8-C9-C10	68(1)		
C8-C9-C10-C11	-157(1)		
C9-C10-C11-C12	73(1)		
C10-C11-C12-C1	69(1)		
C11-C12-C1-C2	-164(1)		

The same conformation was also found in the (disordered) structures of cyclododecane¹¹ and cyclododecanone.⁴ Dimers are linked by hydrogen bonds of length $\text{O} \cdots \text{N}' = 2.69(1)$ Å.

$n = 13$

To the best of the authors knowledge no crystal structure evidence on the conformation of a saturated 13-membered ring has been reported. Attempts to obtain X-ray data for cyclotridecanone⁴ have so far been unsuccessful. Preliminary oscillation and Weissenberg diagrams of the corresponding oxime indicated a disordered structure. As may be seen from the schematic drawing (Fig. 4), the disorder of the molecule arises from the presence of statistical pseudo mirror planes. Methylene hydrogen positions were calculated while those of the

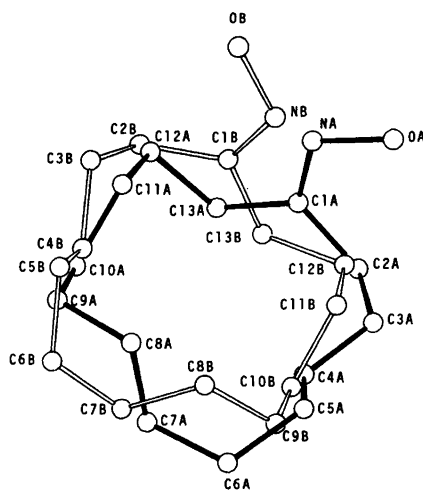


Fig. 4. Schematic drawing of the cyclotridecanone-oxime molecule.

Table 8. Final fractional coordinates with estimated standard deviations for $(\text{CH}_2)_{12}\text{CNOH}$. The hydrogen atoms An,1 and An,2 are bonded to CnA; Bn,1 and Bn,2 to CnB. HOA is bonded to OA, HOB to OB.

Atom	x	y	z
OA	.9238(12)	-.1245(7)	.0726(4)
NA	.8285(15)	.0268(11)	.0692(6)
C1A	.6775(18)	.0465(12)	.1283(7)
C2A	.6148(37)	-.0725(23)	.1969(14)
C3A	.8379(22)	-.0808(15)	.2743(8)
C4A	.9121(36)	.0633(24)	.3404(14)
C5A	1.1781(23)	.0867(16)	.3994(9)
C6A	1.2474(20)	.2452(14)	.4679(8)
C7A	1.1835(21)	.3956(15)	.4184(8)
C8A	1.3249(19)	.4328(12)	.3393(7)
C9A	1.2169(24)	.5664(15)	.2842(10)
C10A	.9414(39)	.5076(26)	.2247(14)
C11A	.9570(21)	.4119(14)	.1322(8)
C12A	.6856(41)	.3345(27)	.0748(15)
C13A	.5643(20)	.1972(13)	.1276(7)
OB	.9363(12)	.1750(7)	-.0275(4)
NB	.8316(15)	.0985(11)	.0436(6)
C1B	.6900(17)	.1821(12)	.0819(6)
C2B	.6569(19)	.3505(13)	.0638(7)
C3B	.8881(33)	.4672(21)	.1006(12)
C4B	.9516(21)	.4920(14)	.2051(8)
C5B	1.2175(40)	.5599(25)	.2471(14)
C6B	1.2768(26)	.5851(19)	.3584(10)
C7B	1.1968(20)	.4458(14)	.4047(8)
C8B	1.3102(30)	.2902(19)	.3847(11)
C9B	1.1867(22)	.1432(15)	.4174(9)
C10B	.9116(24)	.0885(16)	.3546(9)
C11B	.9202(33)	-.0036(22)	.2615(13)
C12B	.6535(22)	-.0419(14)	.1956(8)
C13B	.5507(44)	.1080(28)	.1556(16)
A21	.520	.372	.093
A22	.542	-.180	.164
A31	.467	-.037	.229
A32	1.004	-.096	.245
A41	.820	-.183	.311
A42	.789	.054	.391
A51	.874	.160	.309
A52	1.313	.115	.358
A61	1.230	.004	.438
A62	1.424	.250	.501
A71	1.125	.220	.516
A72	1.229	.491	.466
A81	.992	.390	.391
A82	1.309	.330	.297
A91	1.515	.462	.366
A92	1.330	.609	.240
A101	1.193	.658	.327
A102	.833	.594	.203
A111	.834	.430	.257
A112	1.052	.316	.147

Table 8. Continued.

A121	1.065	.482	.094
A122	.672	.312	.002
A131	.553	.439	.065
A132	.368	.172	.107
B21	.872	.577	.074
B22	.626	.342	-.004
B31	.907	.394	.239
B32	1.066	.440	.084
B41	1.274	.671	.223
B42	.832	.575	.230
B51	1.168	.675	.373
B52	1.350	.490	.231
B61	.996	.415	.397
B62	1.458	.624	.383
B71	1.502	.306	.417
B72	1.244	.469	.482
B81	1.177	.115	.479
B82	1.310	.287	.315
B91	.842	.197	.333
B92	1.279	.027	.393
B101	.993	-.107	.284
B102	.773	.035	.385
B111	.523	-.110	.229
B112	1.045	.055	.231
B121	.570	.189	.215
B122	.669	-.121	.140
B131	.587	.243	.197
B132	.357	.085	.132
HOA	.125	.135	-.008
HOB	.009	.093	.007

hydrogen bonds were found in a difference Fourier map. With occupancy factors, $G=0.5$, the heavy atoms were refined isotropically (hydrogen atoms were not refined). The R -value arrived at was $R=9.3\%$ ($R_w=6.8\%$). A refinement with G -factors included was not successful.

Final coordinates with estimated standard deviations are listed in Table 8. Bond distances and angles and dihedral angles may be found in Table 9. Within estimated limits of error, bond distances and angles are normal. The torsional angles show that the present conformation formally is the triangular [337], which has a calculated conforma-

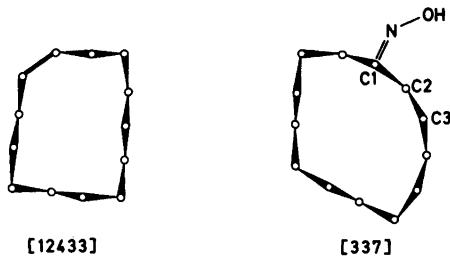


Table 9. Bond distances and angles and dihedral angles with estimated standard deviations for (CH₂)₁₂CNOH.

Distance	(Å)	Distance	(Å)
OA – NA	1.43(1)	NA – C1A	1.30(1)
C1A – C2A	1.51(2)	C1A – C13A	1.47(1)
C2A – C3A	1.49(2)	C3A – C4A	1.49(2)
C4A – C5A	1.50(2)	C5A – C6A	1.60(2)
C6A – C7A	1.54(2)	C7A – C8A	1.51(2)
C8A – C9A	1.53(2)	C9A – C10A	1.57(3)
C10A – C11A	1.56(2)	C11A – C12A	1.58(2)
C12A – C13A	1.57(2)	OB – NB	1.41(1)
NB – C1B	1.27(1)	C1B – C2B	1.49(2)
C1B – C13B	1.53(3)	C2B – C3B	1.48(2)
C3B – C4B	1.50(2)	C4B – C5B	1.47(2)
C5B – C6B	1.59(3)	C6B – C7B	1.45(2)
C7B – C8B	1.55(2)	C8B – C9B	1.48(2)
C9B – C10B	1.58(2)	C10B – C11B	1.54(2)
C11B – C12B	1.55(2)	C12B – C13B	1.54(3)
Angle	(°)	Angle	(°)
OA – NA – C1A	113.(1)	NA – C1A – C2A	124.(1)
NA – C1A – C13A	117.(1)	C1A – C2A – C3A	112.(1)
C2A – C1A – C13A	119.(1)	C1A – C13A – C12A	117.(1)
C2A – C3A – C4A	115.(1)	C3A – C4A – C5A	118.(2)
C4A – C5A – C6A	116.(1)	C5A – C6A – C7A	113.(1)
C6A – C7A – C8A	115.(1)	C7A – C8A – C9A	111.(1)
C8A – C9A – C10A	111.(1)	C9A – C10A – C11A	112.(1)
C10A – C11A – C12A	114.(1)	C11A – C12A – C13A	111.(1)
OB – NB – C1B	113.(1)	NB – C1B – C2B	125.(1)
NB – C1B – C13B	118.(1)	C1B – C2B – C3B	115.(1)
C2B – C1B – C13B	117.(1)	C1B – C13B – C12B	115.(2)
C2B – C3B – C4B	114.(1)	C3B – C4B – C5B	117.(1)
C4B – C5B – C6B	115.(2)	C5B – C6B – C7B	114.(1)
C6B – C7B – C8B	118.(1)	C7B – C8B – C9B	116.(1)
C8B – C9B – C10B	111.(1)	C9B – C10B – C11B	114.(1)
C10B – C11B – C12B	114.(1)	C11B – C12B – C13B	113.(1)
Dihedral angle	(°)	Dihedral angle	(°)
C13A – C1A – C2A – C3A	–108.(2)	C13B – C1B – C2B – C3B	108.(1)
C1A – C2A – C3A – C4A	68.(1)	C1B – C2B – C3B – C4B	–70.(2)
C2A – C3A – C4A – C5A	–160.(2)	C2B – C3B – C4B – C5B	160.(1)
C3A – C4A – C5A – C6A	179.(1)	C3B – C4B – C5B – C6B	180.(2)
C4A – C5A – C6A – C7A	–49.(2)	C4B – C5B – C6B – C7B	50.(2)
C5A – C6A – C7A – C8A	–61.(1)	C5B – C6B – C7B – C8B	58.(2)
C6A – C7A – C8A – C9A	170.(1)	C6B – C7B – C8B – C9B	–168.(1)
C7A – C8A – C9A – C10A	–71.(2)	C7B – C8B – C9B – C10B	72.(2)
C8A – C9A – C10A – C11A	–80.(2)	C8B – C9B – C10B – C11B	81.(2)
C9A – C10A – C11A – C12A	174.(2)	C9B – C10B – C11B – C12B	–174.(1)
C10A – C11A – C12A – C13A	–69.(2)	C10B – C11B – C12B – C13B	69.(2)
C11A – C12A – C13A – C1A	–74.(2)	C11B – C12B – C13B – C1B	72.(2)
C12A – C13A – C1A – C2A	165.(1)	C12B – C13B – C1B – C2B	–161.(1)

Table 10. Final fractional coordinates with estimated standard deviations for $(\text{CH}_2)_{13}\text{CNOH}$. Hn,1 and Hn,2 are bonded to Cn. HO is bonded to O.

Atom	x	y	z
O	.04077(32)	-.17792(19)	.01869(10)
N	.19025(36)	-.11005(21)	-.04295(11)
C1	.36353(43)	-.19867(25)	-.08086(13)
C2	.41506(53)	-.36038(28)	-.06420(15)
C3	.37095(46)	-.48516(28)	-.14791(16)
C4	.09205(48)	-.49617(30)	-.18371(16)
C5	.05256(52)	-.60045(30)	-.27519(17)
C6	.20238(51)	-.54751(28)	-.35167(17)
C7	.14361(52)	-.38491(29)	-.36751(17)
C8	.29696(52)	-.33503(30)	-.44323(16)
C9	.25626(56)	-.16921(30)	-.45815(16)
C10	.30308(49)	-.04278(30)	-.37575(16)
C11	.57610(47)	-.03834(29)	-.33549(15)
C12	.60979(49)	.07068(29)	-.24520(16)
C13	.45229(48)	.02300(27)	-.16961(16)
C14	.52883(50)	-.13328(29)	-.14671(17)
H21	.3104(44)	-.3821(24)	-.0154(15)
H22	.5926(50)	-.3652(26)	-.0465(15)
H31	.4202(45)	-.5913(27)	-.1343(15)
H32	.4925(42)	-.4595(23)	-.1964(13)
H41	.0327(40)	-.3905(25)	-.1838(13)
H42	-.0160(48)	-.5362(26)	-.1403(16)
H51	-.1345(50)	-.6070(25)	-.2897(14)
H52	.0967(41)	-.7102(26)	-.2709(13)
H61	.1656(43)	-.6236(26)	-.4071(15)
H62	.3962(44)	-.5496(22)	-.3427(12)
H71	.1765(40)	-.3120(24)	-.3108(14)
H72	-.0395(54)	-.3805(27)	-.3785(16)
H81	.2595(45)	-.4135(27)	-.4997(15)
H82	.4798(44)	-.3499(23)	-.4316(13)
H91	.0795(52)	-.1672(28)	-.4791(15)
H92	.3726(49)	-.1482(27)	-.5069(16)
H101	.1763(43)	-.0625(24)	-.3311(14)
H102	.2718(43)	.0592(26)	-.3924(14)
H111	.7035(45)	-.0011(25)	-.3755(14)
H112	.6235(43)	-.1493(26)	-.3293(14)
H121	.5601(46)	.1794(28)	-.2531(14)
H122	.7952(46)	.0826(24)	-.2281(14)
H131	.2657(44)	.0179(22)	-.1865(13)
H132	.4774(38)	.1054(23)	-.1152(13)
H141	.7121(49)	-.1266(25)	-.1270(14)
H142	.5250(42)	-.2081(25)	-.1997(15)
HO	-.0614(56)	-.0942(32)	.0379(18)

tional strain enthalpy as high as 32.6 J/mol (relative to the lowest one, the completely irregular quin-angular [12433]).⁹ It should, however, be pointed out that the calculations were based upon torsional angles about C1–C2 and C2–C3, quite different from those of the present 13-membered ring. In fact,

the geometry at C2 resembles closely what was found in the crystals of 1,4,7,10-tetraoxacyclododecane¹² where the corresponding dihedral angles were -103° and 75° , respectively.

Dimers are formed by hydrogen bonds of lengths $\text{O}A\cdots\text{N}A' = 2.76(1) \text{ \AA}$ and $\text{O}B\cdots\text{N}B' = 2.77(1) \text{ \AA}$.

$$n = 14$$

Anisotropic temperature factors were used for oxygen, nitrogen and carbon atoms. Methylene hydrogen positions were calculated and HO localized in a difference Fourier map. The final *R*-value was 4.3 % ($R_w = 3.9\%$). R.m.s. amplitudes range from 0.15 to 0.20 Å. The 14-membered ring is conformationally very homogeneous with the "rectangular" diamond-lattice conformation [3434] favoured. In cyclotetradecanone³ the carbonyl group was disordered. No such disorder is observed in the corresponding oxime.

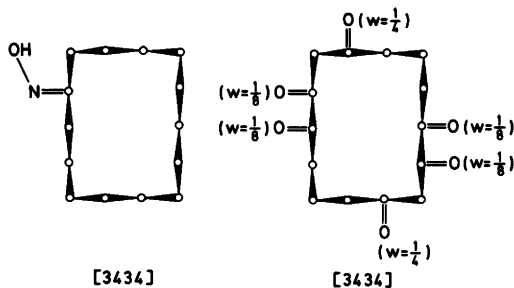


Table 10 gives final coordinates with estimated standard deviations. Bond distances and angles

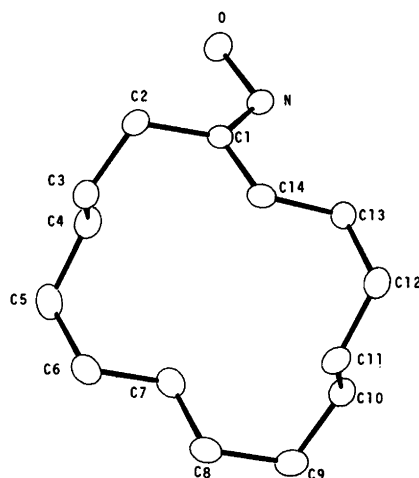


Fig. 5. Schematic drawing of the cyclotetradecane-oxime molecule.

Table 11. Bond distances and angles and dihedral angles with estimated standard deviations of $(\text{CH}_2)_{13}\text{CNOH}$.

Distance	(Å)	Distance	(Å)
O—N	1.419(2)	N—C1	1.280(3)
C1—C2	1.506(3)	C1—C14	1.501(3)
C2—C3	1.535(3)	C3—C4	1.529(3)
C4—C5	1.532(4)	C5—C6	1.535(4)
C6—C7	1.518(3)	C7—C8	1.524(4)
C8—C9	1.523(3)	C9—C10	1.531(3)
C10—C11	1.528(3)	C11—C12	1.533(3)
C12—C13	1.526(3)	C13—C14	1.526(3)
Angle	(°)	Angle	(°)
O—N—C1	113.8(2)	N—C1—C2	125.5(2)
N—C1—C14	116.3(2)	C1—C2—C3	112.9(2)
C2—C1—C14	118.1(2)	C1—C14—C13	116.6(2)
C2—C3—C4	113.2(2)	C3—C4—C5	114.1(2)
C4—C5—C6	115.2(2)	C5—C6—C7	114.6(2)
C6—C7—C8	113.4(2)	C7—C8—C9	115.4(2)
C8—C9—C10	115.3(2)	C9—C10—C11	114.0(2)
C10—C11—C12	113.7(2)	C11—C12—C13	114.9(2)
C12—C13—C14	112.9(2)		
Dihedral angle	(°)		
C14—C1—C2—C3	-62.7(3)		
C1—C2—C3—C4	-61.9(3)		
C2—C3—C4—C5	170.6(2)		
C3—C4—C5—C6	-61.8(3)		
C4—C5—C6—C7	-58.0(3)		
C5—C6—C7—C8	179.5(2)		
C6—C7—C8—C9	-176.6(2)		
C7—C8—C9—C10	54.4(3)		
C8—C9—C10—C11	59.1(3)		
C9—C10—C11—C12	-171.0(2)		
C10—C11—C12—C13	64.8(3)		
C11—C12—C13—C14	63.1(3)		
C12—C13—C14—C1	-172.9(2)		
C13—C14—C1—C2	173.4(2)		

together with torsional angles are listed in Table 11; all values are normal. The schematic drawing of the molecule (Fig. 5) shows the numbering of atoms. Dimers are linked by hydrogen bonds of length $\text{O} \cdots \text{N}' = 2.784(2)$ Å.

Apart from the facts that the oxime group of cyclotetradecaneoxime is fixed to one position, and that the cyclotridecaneoxime structure could be solved, the present *inter*-molecular hydrogen bonding possibility does not seem to reduce the degree of disorder. This is even more pronounced for the larger rings. Preliminary investigations of the cases $n=15, 16, 17$ and 18 indeed indicate disordered structures, and the problem of growing good single

crystals is apparently even worse than for the corresponding ketones.

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

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