On the Crystal Conformations of Cyclic Phenylsemicarbazones, $(CH_2)_{n-1}CNNHCONHC_6H_5$, with $n = 10,11,12,13$ and 16

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Data were collected at about −150 °C on an automatic four-circle diffractometer. For $n = 10$ the conformation is [1 3 3 3], the same as for the corresponding oxime, but different from the rectangular [2 3 2 3] conformation of cyclodecanone. The triangular conformation [3 5 5] for $n = 11$ was also found in the cycloundecanone crystals, while cycloundecaneoxime has the quinquangular [1 2 3 2 3] conformation. Like all other known saturated twelve-membered rings, the present one ($n = 12$) prefers the square conformation [3 3 3 3]. For $n = 13$ the conformation may be described as [3 3 7] (as in the case of the disordered cyclotridecaneoxime structure). In cyclohexadecanephenylsemicarbazone ($n = 16$) the ring conformation is [3 4 4 5]. All compounds are dimers with N−H−O hydrogen bonds in the range 2.826−2.926 Å.

The "half-melted" modifications stable just below the melting points of cyclic ketones $(CH_2)_{n-1}CO$ with $n = 10, \cdots, 17$ 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 stabilizing intermolecular hydrogen bonds, less disorder might be hoped for. The corresponding oximes, $(CH_2)_{n-1}CNOH$, were therefore investigated.[5] Apart from the facts that the oxime group of cyclotetradecaneoxime is fixed to one position (in the ketone it is disordered[4]), and that the disordered cyclotridecaneoxime structure could be solved (as opposed to the corresponding ketone where no single crystals were obtained), this intermolecular hydrogen bonding possibility did not seem to reduce the degree of disorder. For the larger rings it was even more pronounced. Preliminary investigations of the cases $n = 15, \cdots$, 18 indicated highly disordered structures, and the problem of growing good single crystals was no easier than for the corresponding ketones. Recently it has been found that the problem of disorder is avoided for the 15-membered ring by synthesizing the phenylsemicarbazone of cyclopentadecane.[6]

The phenylsemicarbazones, $(CH_2)_{n-1}$-CNNHCONHC$_6$H$_5$, with $n = 8, \cdots, 18$ (except for $n = 15$) have been studied by X-ray diffraction methods at *ca.* −150 °C. Preliminary investigations indicated a highly disordered structure for $n = 17$. In the cases $n = 14$ and 18 ordered structures seem probable, but no good single crystals have been obtained so far. Both are triclinic with two molecules in the unit cell. The $n = 14$ crystals were extremely thin needles, while those of $n = 18$ were twins. The structure determinations for $n = 8$ and $n = 9$ will be presented elsewhere. The results for $n = 10, 11, 12, 13$ and 16 are now reported.

Crystal data are given in Table 1 (Dirichlet's reduced cell for triclinic crystals). Data were collected at about −150 °C on an automatic four-circle diffractometer (Mo$K\alpha$-radiation, $2\theta_{max} = 50°$. No corrections for absorption or secondary extinction were made (maximum crystal size 0.4 × 0.4 × 0.3 mm). The structures were solved by direct methods[7] and refined by full-matrix least squares technique.[8,*] Weights and 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

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

Table 1. Crystal data for the cyclic phenylsemicarbazones $(CH_2)_{n-1}CNNHCONHC_6H_5$ with $n=10, \cdots, 13, 16$.

n	Space group	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\alpha(°)$	$\beta(°)$	$\gamma(°)$	Z	D_m g cm^{-3}	D_x g cm^{-3}	Number of observed reflections
10	$P\bar{1}$	5.522(1)	10.669(2)	13.966(4)	77.08(2)	83.47(2)	81.31(2)	2	1.18	1.20	2058
11	$P2_1/c$	5.551(2)	14.367(4)	21.172(6)	90	97.08(2)	90	4	1.18	1.19	1364
12	$P2_1/c$	15.161(4)	5.491(2)	23.594(4)	90	115.04(2)	90	4	1.16	1.18	966
13	$P\bar{1}$	8.084(5)	8.580(8)	13.711(12)	82.84(7)	81.43(6)	74.94(7)	2	1.18	1.20	1494
16	$P\bar{1}$	9.314(2)	11.181(3)	11.887(3)	91.29(2)	104.69(2)	111.11(2)	2	1.00	1.11	2065

Fig. 1. Schematic drawing of the cyclodecane-phenylsemicarbazone molecule.

Fig. 2. Schematic drawing of the cycloundecanephenyl semicarbazone molecule.

Table 2. Some results for the cyclic phenylsemicarbazones $(CH_2)_{n-1}CNNHCONHC_6H_5$ with n = 10, $\cdots$, 13, 16. Final R-values, ranges for maximum r.m.s. anisotropic thermal amplitudes, angles, α, between the planes of the phenyl rings and the semicarbazone groups, hydrogen bond lengths, and the ranges for C−H and N−H bond lengths.

n	$R(\%)$	$R_w(\%)$	Max. r.m.s. anisotropic thermal amplitude range (Å)	$\alpha(°)$	O−N2' (Å)	C−H range (Å)	N−H range (Å)
10	3.5	3.3	0.16−0.24	5.4	2.826(2)	0.97−1.01	0.87−0.91
11	7.2	6.4	0.20−0.25	14.2	2.855(6)	0.93−1.11	0.89−1.06
12	6.4	4.7	0.15−0.24	6.3	2.894(7)	0.90−1.09	0.86−0.93
13	8.7	6.5	0.18−0.23	17.6	2.897(10)	0.90−1.08	0.95−0.98
16	6.3	5.2	0.16−0.25	8.6	2.926(4)	0.93−1.08	0.97−0.98

net count. Hydrogen atom positions were calculated and anisotropic temperature factors were used for oxygen, nitrogen, and carbon atoms. The form factors were those of Hanson *et al.*[9] except for hydrogen.[10] Standard deviations in bond distances and angles and dihedral angles are calculated from the correlation matrix of the final least squares refinement.
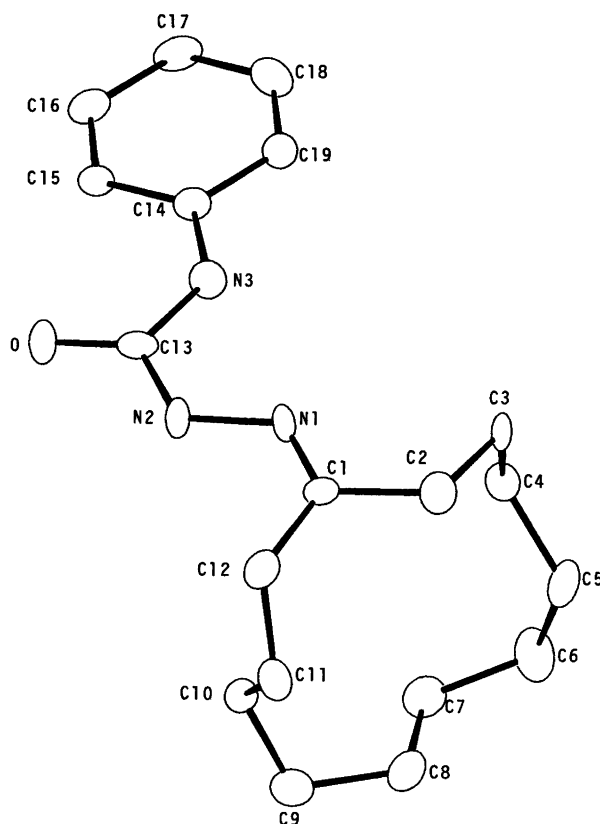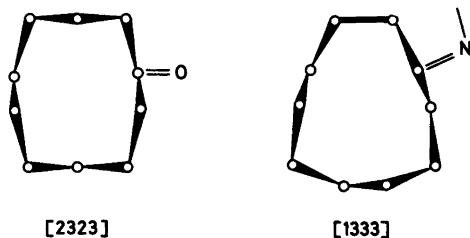

Fig. 3. Schematic drawing of the cyclododecanephenylsemicarbazone molecule.

Table 3. Final fractional coordinates with estimated standard deviations for $(CH_2)_9CNNHCONCH_6H_5$. $H_{n,1}$ and $H_{n,2}$ are bonded to C_n, HN2 and HN3 are bonded to N2 and N3. H_m is bonded to C_m (in the phenyl ring).

ATOM	X	Y	Z
O	.1785(2)	.6018(1)	.9239(0)
N1	-.1844(2)	.4695(1)	.7912(0)
N2	-.0047(2)	.4925(1)	.8715(1)
N3	-.1347(2)	.6341(1)	.7586(0)
C1	.3402(3)	.3877(1)	.8069(1)
C2	.4323(3)	.3119(1)	.9056(1)
C3	.2675(3)	.1853(1)	.9475(1)
C4	-.1773(3)	.0968(1)	.8740(1)
C5	.0629(3)	.1316(1)	.8136(1)
C6	.1122(3)	.0927(1)	.7135(1)
C7	-.0583(3)	.3167(1)	.6354(1)
C8	-.0489(3)	.4000(1)	.6105(1)
C9	.2990(3)	.4481(1)	.6180(1)
C10	.4481(3)	.5790(1)	.7172(1)
C11	.0827(3)	.7161(1)	.8558(1)
C12	.3133(3)	.7613(1)	.7172(1)
C13	.4640(3)	.8391(1)	.7720(1)
C14	.6391(3)	.8728(1)	.7236(1)
C15	.6675(3)	.8288(1)	.6222(1)
C16	.5161(3)	.7511(1)	.5676(1)
C17	.3402(3)	.290(1)	.6148(1)
H21	.596(2)	.366(1)	.898(1)
H22	-.459(3)	.139(1)	.954(1)
H31	.368(3)	.206(1)	1.006(1)
H32	-.117(3)	.098(1)	.973(1)
H41	-.316(2)	.007(1)	.827(1)
H42	-.204(2)	.091(1)	.916(1)
H51	.067(3)	.227(1)	.855(1)
H61	.186(3)	-.003(1)	.804(1)
H62	-.003(3)	.184(1)	.723(1)
H71	-.285(3)	.152(1)	.686(1)
H72	.231(2)	.132(1)	.657(1)
H81	.016(3)	.343(1)	.542(1)
H82	-.054(2)	.339(1)	.655(1)
H91	.400(3)	.390(1)	.566(1)
H92	-.274(2)	.493(1)	.604(1)
H101	.406(3)	.276(1)	.731(1)
H102	.613(3)	.423(1)	.714(1)
HN2	-.132(3)	.458(1)	.936(1)
HN3	.045(3)	.614(1)	.718(1)
H14	.449(2)	.739(1)	.842(1)
H15	.742(3)	.670(1)	.765(1)
H16	.789(2)	.929(1)	.587(1)
H17	.535(3)	.853(1)	.494(1)
H18	.232(3)	.721(1)	.877(1)

Table 4. Bond distances and angles and dihedral angles with estimated standard deviation for $(CH_2)_9CNNHCONHC_6H_5$.

DISTANCE (Å)

O	–	C11	1.235(2)	N1	–	N2	1.388(2)
N1	–	C1	1.284(2)	N2	–	C11	1.369(2)
N3	–	C11	1.369(2)	N3	–	C12	1.406(2)
C1	–	C2	1.510(2)	C2	–	C5	1.547(2)
C3	–	C4	1.536(2)	C4	–	C5	1.537(2)
C5	–	C6	1.533(2)	C6	–	C7	1.531(2)
C7	–	C8	1.543(2)	C8	–	C9	1.532(3)
C9	–	C10	1.526(2)	C12	–	C13	1.395(2)
C12	–	C17	1.391(2)	C13	–	C14	1.387(2)
C14	–	C15	1.380(2)	C15	–	C16	1.388(3)
C16	–	C17	1.385(2)				

ANGLE (°)

O	–	C11	–	N2	121.1(1)	O	–	C11	–	N3	124.0(1)
N2	–	N1	–	C1	116.5(1)	N1	–	N2	–	C11	118.6(1)
N1	–	C1	–	C2	126.8(1)	C11	–	N3	–	C10	116.5(1)
N2	–	C11	–	N3	114.9(1)	N3	–	C12	–	C17	120.6(1)
N3	–	C12	–	C13	124.1(1)	C12	–	C13	–	C14	116.7(1)
C1	–	C2	–	C3	115.0(1)	C2	–	C3	–	C4	116.7(1)
C3	–	C4	–	C5	117.5(1)	C4	–	C5	–	C6	115.1(1)
C6	–	C7	–	C8	112.4(1)	C7	–	C8	–	C9	116.2(1)
C8	–	C9	–	C10	114.9(1)	C9	–	C10	–	N3	114.5(1)
C12	–	C13	–	C14	119.0(1)	C12	–	C17	–	C16	119.0(1)
C13	–	C14	–	C15	120.6(2)	C14	–	C15	–	C16	121.3(2)
C16	–	C17	–		119.2(2)	C15	–	C16	–	C17	120.2(2)

DIHEDRAL ANGLE (°)

C10	–	C1	–	C2	–	C3	98.1(2)
C1	–	C2	–	C3	–	C4	-47.1(2)
C2	–	C3	–	C4	–	C5	87.5(2)
C3	–	C4	–	C5	–	C6	-155.4(2)
C4	–	C5	–	C6	–	C7	69.3(2)
C5	–	C6	–	C7	–	C8	59.7(2)
C6	–	C7	–	C8	–	C9	-127.1(2)
C7	–	C8	–	C9	–	C10	54.9(2)
C8	–	C9	–	C10	–	C1	62.6(2)
C9	–	C10	–	C1	–	C2	-157.5(1)

Table 6. Bond distances and angles and dihedral angles with estimated standard deviations for $(CH_2)_{10}CNNHCONHC_6H_5$.

DISTANCE (Å)

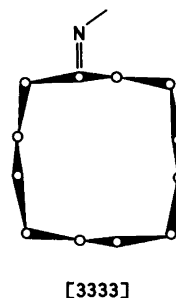|					
O - C12	1.233(7)		N1 - N2	1.397(6)
N1 - C1	1.284(7)		N2 - C12	1.390(7)
N3 - C12	1.347(7)		N3 - C13	1.420(7)
C1 - C2	1.520(8)		C1 - C11	1.517(8)
C2 - C3	1.516(8)		C3 - C4	1.532(8)
C4 - C5	1.538(8)		C5 - C6	1.534(8)
C6 - C7	1.521(8)		C7 - C8	1.517(8)
C8 - C9	1.529(8)		C9 - C10	1.401(8)
C10 - C11	1.578(9)		C13 - C14	1.395(8)
C13 - C18	1.370(8)		C14 - C15	1.375(8)
C15 - C16	1.372(8)		C16 - C17	1.395(8)
C17 - C18	1.403(8)			

ANGLE (°)

O - C12 - N2	120.2(6)		O - C12 - N3	125.0(6)
N2 - N1 - C1	117.8(5)		N1 - N2 - C12	116.9(5)
N1 - C1 - C2	115.9(6)		N1 - C1 - C11	125.8(6)
N2 - C12 - N3	114.7(6)		C12 - N3 - C13	128.7(6)
N3 - C13 - C14	122.5(6)		N3 - C13 - C18	117.5(6)
C1 - C2 - C3	117.2(6)		C2 - C3 - C4	118.2(6)
C1 - C11 - C10	114.2(6)		C2 - C1 - C11	114.7(6)
C3 - C4 - C5	116.0(5)		C4 - C5 - C6	114.6(5)
C5 - C6 - C7	114.6(5)		C6 - C7 - C8	113.3(5)
C7 - C8 - C9	114.7(5)		C8 - C9 - C10	118.6(5)
C9 - C10 - C11	117.2(5)		C13 - C14 - C15	118.1(6)
C14 - C13 - C18	120.0(6)		C13 - C18 - C17	121.0(6)
C14 - C15 - C16	121.7(6)		C15 - C16 - C17	120.1(6)
C16 - C17 - C18	119.0(6)			

DIHEDRAL ANGLE (°)

C11 - C1 - C2 - C3	166.4(6)
C1 - C2 - C3 - C4	-66.1(7)
C2 - C3 - C4 - C5	-60.1(7)
C3 - C4 - C5 - C6	128.6(6)
C4 - C5 - C6 - C7	-63.9(7)
C5 - C6 - C7 - C8	-68.1(7)
C6 - C7 - C8 - C9	174.7(5)
C7 - C8 - C9 - C10	-47.9(8)
C8 - C9 - C10 - C11	-63.9(8)
C9 - C10 - C11 - C1	87.1(6)
C10 - C11 - C1 - C2	-110.2(5)

Table 5. Final fractional coordinates with estimated standard deviations for $(CH_2)_{10}CNNHCONHC_6H_5$. $H_{n,1}$ and $H_{n,2}$ are bonded to C_n. HN2 and HN3 are bonded to N2 and N3. H_m is bonded to C_m (in the phenyl ring).

ATOM	X	Y	Z
O	.1660(7)	.4072(2)	1.0284(1)
N1	-.3554(8)	.3324(3)	.9309(2)
N2	-.1874(9)	.3946(3)	.9621(2)
N3	-.0105(9)	.2626(4)	1.0028(2)
C1	-.5354(11)	.3665(4)	.8942(2)
C2	-.7174(9)	.2964(4)	.8630(2)
C3	-.6370(11)	.1956(4)	.8621(2)
C4	-.4325(11)	.1765(3)	.8215(2)
C5	-.4478(10)	.2005(4)	.7503(3)
C6	-.2971(10)	.2619(4)	.7244(3)
C7	-.2712(11)	.3586(4)	.7535(3)
C8	-.4938(11)	.4206(4)	.7353(3)
C9	-.4839(11)	.5153(4)	.7685(3)
C10	-.4129(11)	.5187(3)	.8400(2)
C11	-.5877(11)	.4692(4)	.8829(3)
C12	-.0073(12)	.3564(4)	1.0011(3)
C13	.1860(10)	.2027(4)	1.0361(3)
C14	.4153(10)	.2341(4)	1.0625(3)
C15	.5741(11)	.1698(4)	1.0947(2)
C16	.5128(12)	.0778(4)	1.0994(3)
C17	.2896(12)	.0467(4)	1.0722(3)
C18	.1264(11)	.1105(4)	1.0402(3)
H21	-.773(7)	-.321(2)	.816(1)
H22	-.871(8)	-.302(2)	.887(2)
H31	-.775(8)	-.153(3)	.846(2)
H32	-.582(7)	-.174(2)	.908(1)
H41	-.382(8)	-.112(2)	.826(2)
H42	-.289(8)	-.215(3)	.841(2)
H51	-.647(8)	-.235(3)	.741(2)
H52	-.511(8)	-.147(2)	.722(2)
H61	-.326(8)	-.268(3)	.673(2)
H62	-.144(8)	-.224(3)	.733(2)
H71	-.124(7)	.391(2)	.735(2)
H72	-.231(9)	.359(3)	.806(2)
H81	-.651(8)	.386(3)	.751(2)
H82	-.507(10)	.424(4)	.684(2)
H91	-.639(10)	.544(4)	.766(2)
H92	-.356(9)	.548(3)	.747(2)
H101	-.406(10)	.585(4)	.854(2)
H102	-.242(9)	.488(4)	.857(2)
H111	-.742(10)	.481(3)	.857(2)
H112	-.568(7)	.499(3)	.925(2)
HN2	-.212(8)	.467(3)	.963(2)
HN3	.116(9)	.236(3)	.980(2)
H14	.452(5)	.303(2)	1.059(1)
H15	.729(10)	.194(3)	1.111(2)
H16	.639(9)	-.032(3)	1.116(2)
H17	.238(7)	-.021(3)	1.072(2)
H18	-.031(9)	.093(3)	1.025(2)

The most striking aspect of the molecular packing is the H-bonding between molecules related by a centre of symmetry. This interaction certainly contributes to the existence of ordered large-ring structures. In Table 2 one may find the R-values arrived at, the ranges for maximum root-mean-squares anisotropic thermal amplitudes, the angles, α, between the planes of the phenyl rings and the semicarbazone groups, the hydrogen bond lengths, and the ranges for C−H and N−H bond lengths. No short inter-molecular contacts are observed.

n = 10

Final fractional coordinates with estimated standard deviations are given in Table 3, Fig. 1 is a schematic drawing of the molecule, showing the numbering of atoms. The bond distances and angles, listed in Table 4, have normal values within estimated limits of error. The torsional angles of Table 4 show that the ten-membered ring has the [1 3 3 3] conformation,* the same as found in the crystals of the corresponding oxime,[5] but different from the rectangular diamond-lattice conformation, [2 3 2 3], of cyclodecanone[1] which has the lowest calculated enthalpy.[11]

[2323]   [1333]

n = 11

Final fractional coordinates with estimated standard deviations are listed in Table 5. The bond distances and angles of Table 6 are normal within error limits. Fig. 2 is a schematic drawing, showing the numbering of atoms. For the cycloundecane ring, as many as four conformations have about

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* 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.

equally low enthalpies.[11] One of them, the triangular [3 3 5], was preferred in the crystals of cycloundecanone.[2] From the dihedral angles of Table 6 it may be seen that this conformation again is preferred (as opposed to the result for the ten-membered ring). The phenylsemicarbazone group is situated in an asymmetric position corresponding to that of the carbonyl group of the ketone. The eleven-membered ring of cycloundecaneoxime has the rather ill-defined conformation [1 2 3 2 3].[5]

(W = 0.85)

[335]   [12323]

n = 12

Final fractional coordinates with estimated standard deviations are given in Table 7. Fig. 3 is a schematic drawing of the molecule, showing the numbering of atoms. The bond distances and angles of Table 8 are normal. Like all other known saturated twelve-membered rings,[4,5,12] the present one prefers the square conformation (not of the diamond lattice type) with approximate C_2 symmetry [3 3 3 3].

[3333]

Table 7. Final fractional coordinates with estimated standard deviations for (CH₂)₁₁CNNHCONHC₆H₅. $H_{n,1}$ and $H_{n,2}$ are bonded to C_n, HN2 and HN3 are bonded to N2 and N3. H_m is bonded to C_m (in the phenyl ring).

ATOM	X	Y	Z
O	.4941(3)	.1351(10)	.4325(2)
N1	.3271(4)	-.3478(12)	.3993(2)
N2	.4039(4)	-.1932(11)	.4333(2)
N3	.3760(4)	.0067(12)	.3397(2)
C1	.3041(5)	.5159(15)	.4278(3)
C2	.2191(5)	.6778(15)	.3880(3)
C3	.1554(5)	.5939(15)	.3220(3)
C4	.0913(5)	.3756(16)	.3199(3)
C5	.1102(5)	.4375(15)	.3401(3)
C6	.0306(6)	-.2190(16)	.3623(3)
C7	.0438(6)	-.1038(15)	.4224(3)
C8	.0740(7)	.2674(15)	.4801(3)
C9	.1670(7)	-.1845(16)	.5350(3)
C10	.2598(6)	-.2335(16)	.5255(3)
C11	.3522(5)	-.5723(12)	.5304(3)
C12	.4284(6)	.0117(16)	.4027(3)
C13	.3760(5)	-.1689(15)	.2968(3)
C14	.4396(5)	.3687(15)	.3131(3)
C15	.4344(5)	.5334(14)	.2673(3)
C16	.3679(6)	.5000(16)	.2048(3)
C17	.3066(6)	.3042(16)	.1891(3)
C18	.3117(5)	.1360(15)	.2343(3)
H21	.183(3)	-.708(9)	.414(2)
H22	.247(3)	-.837(10)	.301(2)
H31	.111(4)	-.740(10)	.301(2)
H32	.202(3)	-.554(9)	.303(2)
H41	.057(4)	-.303(12)	.272(2)
H42	.135(4)	-.239(10)	.351(2)
H51	.037(3)	-.561(9)	.378(2)
H52	-.058(4)	-.509(10)	.306(2)
H61	-.049(4)	-.264(11)	.366(2)
H62	.050(4)	-.070(10)	.333(2)
H71	.021(4)	.057(11)	.433(2)
H72	.108(3)	.065(10)	.420(2)
H81	.003(3)	.442(9)	.469(2)
H82	.019(3)	.260(8)	.495(2)
H91	.182(4)	.279(10)	.545(2)
H92	.162(3)	.009(11)	.545(2)
H101	.325(4)	.142(12)	.562(2)
H102	.248(3)	.171(8)	.482(1)
H111	.226(3)	.609(10)	.511(2)
H112	.315(3)	.543(11)	.571(2)
H121	.371(4)	.746(17)	.503(2)
H122	.416(7)	.471(19)	.516(4)
HN2	.435(4)	-.208(12)	.473(2)
HN3	.335(3)	-.138(12)	.321(2)
H15	.467(3)	.389(9)	.360(2)
H16	.477(4)	.665(12)	.276(2)
H17	.363(3)	.623(9)	.172(2)
H18	.255(4)	.273(10)	.143(2)
H19	.264(3)	-.022(10)	.223(2)

Table 8. Bond distances and angles and dihedral angles with estimated standard deviations for (CH₂)₁₁CNNHCONHC₆H₅.

DISTANCE (Å)

		(Å)				(Å)
O	C13	1.242(9)	N1	N2	1.389(7)
N1	C1	1.275(9)	N2	C13	1.370(9)
N3	C13	1.357(8)	N3	C14	1.407(9)
C1	C2	1.510(10)	C1	C12	1.502(9)
C2	C3	1.515(10)	C3	C4	1.532(10)
C4	C5	1.533(10)	C5	C6	1.535(10)
C6	C7	1.522(10)	C7	C8	1.531(10)
C8	C9	1.533(10)	C9	C10	1.526(12)
C10	C11	1.537(11)	C11	C12	1.534(10)
C14	C15	1.389(10)	C14	C19	1.390(9)
C15	C16	1.385(9)	C16	C17	1.403(10)
C17	C18	1.365(11)	C18	C19	1.389(10)

ANGLE (°)

			(°)				(°)
O	C13	N2	120.4(7)	O	C13	N3	124.3(8)
N2	N1	C1	119.2(6)	N1	N2	C13	119.3(6)
N1	N2	C2	116.6(7)	N1	C1	C12	127.0(7)
N2	C13	N3	115.3(8)	C13	N3	C14	128.5(7)
N3	C13	C15	123.9(7)	N3	C14	C19	116.6(8)
C1	C2	C3	117.5(6)	C1	C2	C4	116.4(7)
C1	C12	C11	112.8(6)	C3	C4	C6	113.0(6)
C3	C4	C5	113.5(7)	C5	C6	C8	114.8(7)
C5	C6	C7	113.7(7)	C7	C8	C6	114.2(7)
C7	C8	C9	113.5(7)	C9	C10	C8	113.7(7)
C9	C10	C11	114.3(7)	C11	C14	C10	115.0(7)
C14	C15	C16	120.4(8)	C14	C15	C19	115.0(8)
C16	C17	C18	119.4(8)	C16	C17	C19	119.5(7)
				C18	C19		120.9(8)
						C19	120.4(7)

DIHEDRAL ANGLE (°)

				(°)
C12	C1	C2	C3	166.9(7)
C1	C2	C3	C4	-71.6(9)
C2	C3	C4	C5	-69.5(8)
C3	C4	C5	C6	158.0(6)
C4	C5	C6	C7	-65.7(9)
C5	C6	C7	C8	-66.7(8)
C6	C7	C8	C9	163.1(8)
C7	C8	C9	C10	-73.4(9)
C8	C9	C10	C11	-72.3(9)
C9	C10	C11	C12	156.5(6)
C10	C11	C12	C1	-58.6(9)
C11	C12	C1	C2	-71.7(8)

Table 11. Final fractional coordinates with estimated standard deviations for $(CH_2)_{12}CNNHCONHC_6H_5$. $H_{n,1}$ and $H_{n,2}$ are bonded to C_n, HN2 and HN3 are bonded to N2 and N3. H_m is bonded to C_m (in the phenyl ring).

ATOM	X	Y	Z
O	.6289(5)	-.1494(5)	.4334(3)
N1	.4909(7)	.1971(6)	.2748(4)
N2	.5261(7)	.1049(6)	.3642(3)
N3	.6671(6)	-.0940(6)	.2649(4)
C1	.3706(8)	.3305(7)	.2760(4)
C2	.3378(8)	.4164(7)	.1752(4)
C3	.3557(8)	.5913(7)	.1607(4)
C4	.2777(9)	.6809(7)	.0708(5)
C5	.2991(9)	.8568(7)	.0464(5)
C6	.2649(9)	.9543(8)	.1382(5)
C7	.0908(9)	.9702(7)	.1981(5)
C8	.0817(9)	1.0290(7)	.3005(5)
C9	.1788(8)	.9025(8)	.3725(5)
C10	.0867(8)	.7707(7)	.4159(5)
C11	.1958(9)	.6314(7)	.4786(5)
C12	.3336(8)	.5090(7)	.4173(5)
C13	.2580(8)	.4003(7)	.3656(5)
C14	.6097(9)	-.0557(8)	.3599(5)
C15	.7318(8)	-.2504(8)	.2286(5)
C16	.7589(8)	-.3914(7)	.2902(4)
C17	.8163(9)	-.5400(7)	.2496(5)
C18	.8486(9)	-.5458(7)	.1489(5)
C19	.8233(8)	-.4032(8)	.0872(4)
C20	.7644(8)	-.2552(7)	.1269(5)
H21	-.210(4)	-.413(4)	-.175(2)
H22	-.422(7)	-.350(7)	-.126(4)
H31	.487(5)	-.589(5)	-.158(3)
H32	-.295(7)	-.645(6)	-.224(3)
H41	-.151(5)	-.687(5)	-.077(3)
H42	-.336(5)	.621(5)	-.012(3)
H51	-.424(6)	-.915(7)	.001(4)
H52	-.285(6)	-.865(6)	-.008(4)
H61	.365(5)	1.054(5)	-.121(4)
H62	-.052(7)	.909(5)	-.182(3)
H71	-.005(6)	-.869(7)	-.208(4)
H72	-.039(6)	1.046(6)	-.157(4)
H81	-.135(5)	1.055(5)	-.335(4)
H82	-.205(6)	1.126(5)	-.288(3)
H91	-.041(8)	-.936(6)	.426(3)
H92	.301(7)	.854(5)	.340(3)
H101	-.041(7)	.734(7)	.359(5)
H102	-.017(7)	.822(6)	.457(4)
H111	-.123(6)	.561(6)	.519(4)
H112	-.257(6)	.678(6)	.523(4)
H121	.412(6)	.439(6)	.457(4)
H122	.404(6)	.566(6)	.366(4)
H131	-.216(7)	.473(7)	.337(4)
H132	-.142(7)	.322(6)	.415(4)
HN2	.468(6)	-.135(6)	.428(4)
HN3	.662(6)	-.011(7)	.208(5)
H16	.729(6)	-.390(6)	.361(4)
H17	.830(5)	-.645(5)	.291(3)
H18	.895(7)	-.638(6)	.118(4)
H19	.847(6)	-.499(5)	.014(3)

Table 10. Bond distances and angles and dihedral angles with estimated standard deviations for $(CH_2)_{12}CNNHCONHC_6H_5$.

DISTANCE	(Å)	DISTANCE	(Å)
O - C14	1.21(1)	N1 - N2	1.40(1)
N1 - C1	1.30(1)	N2 - C14	1.37(1)
N3 - C14	1.37(1)	N3 - C15	1.43(1)
C1 - C2	1.51(1)	C1 - C13	1.50(1)
C2 - C3	1.53(1)	C3 - C4	1.55(1)
C4 - C5	1.55(1)	C5 - C6	1.54(1)
C6 - C7	1.50(1)	C7 - C8	1.52(1)
C8 - C9	1.51(1)	C9 - C10	1.54(1)
C10 - C11	1.54(1)	C11 - C12	1.37(1)
C12 - C13	1.53(1)	C16 - C17	1.39(1)
C15 - C20	1.38(1)	C15 - C16	1.39(1)
C17 - C18	1.37(1)	C18 - C19	1.39(1)
C19 - C20	1.38(1)		

ANGLE	(°)	ANGLE	(°)
O - C14 - N2	122.(1)	O - C14 - N3	125.(1)
C1 - N1 - N2	119.(1)	N1 - N2 - C14	117.(1)
N2 - C14 - N3	112.(1)	N1 - C1 - C2	127.(1)
N2 - C15 - C16	123.(1)	C14 - N3 - C15	129.(1)
C1 - C2 - C3	115.(1)	C2 - C1 - C13	117.(1)
C2 - C13 - C12	115.(1)	C2 - C3 - C4	118.(1)
C3 - C4 - C5	115.(1)	C4 - C5 - C6	111.(1)
C5 - C6 - C7	116.(1)	C6 - C7 - C8	114.(1)
C7 - C8 - C9	114.(1)	C8 - C9 - C10	113.(1)
C9 - C10 - C11	114.(1)	C10 - C11 - C12	114.(1)
C11 - C12 - C13	113.(1)	C15 - C16 - C17	114.(1)
C16 - C15 - C20	120.(1)	C17 - C18 - C19	120.(1)
C16 - C17 - C18	120.(1)	C19 - C20 - C15	120.(1)
C18 - C19 - C20	120.(1)		

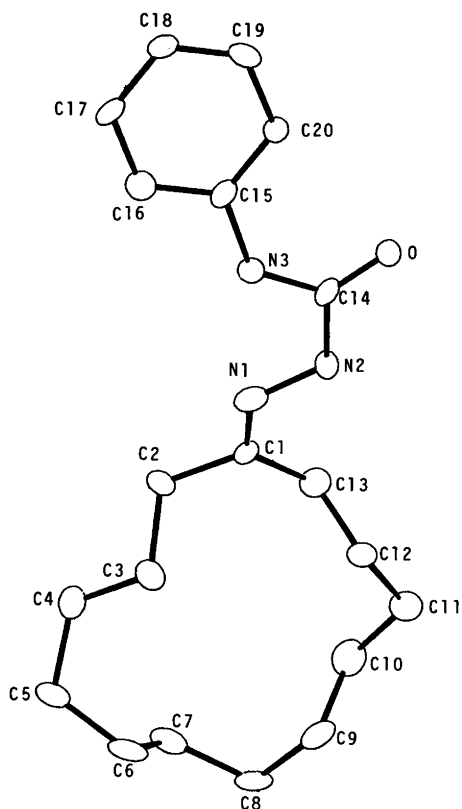| DIHEDRAL ANGLE	(°)
C13 - C1 - C2 - C3	60.(1)
C1 - C2 - C3 - C4	-165.(1)
C2 - C3 - C4 - C5	-177.(1)
C3 - C4 - C5 - C6	-43.(1)
C4 - C5 - C6 - C7	-57.(1)
C5 - C6 - C7 - C8	165.(1)
C6 - C7 - C8 - C9	-72.(1)
C7 - C8 - C9 - C10	-76.(1)
C8 - C9 - C10 - C11	173.(1)
C9 - C10 - C11 - C12	-77.(1)
C10 - C11 - C12 - C13	-72.(1)
C11 - C12 - C13 - C1	156.(1)
C12 - C13 - C1 - C2	-96.(1)

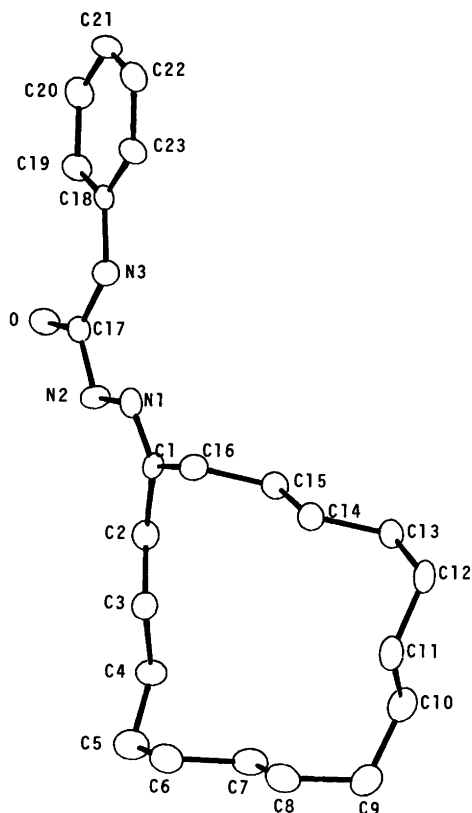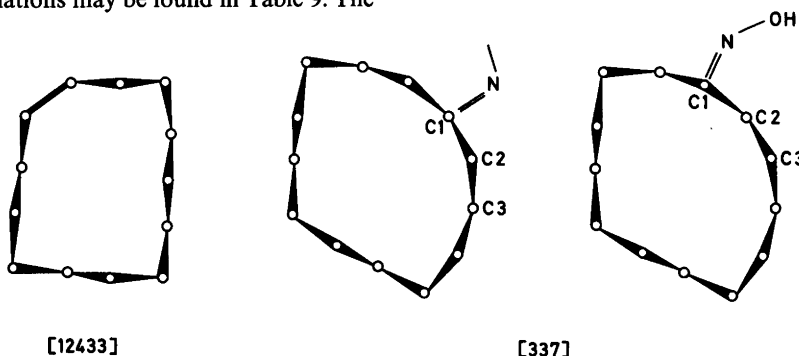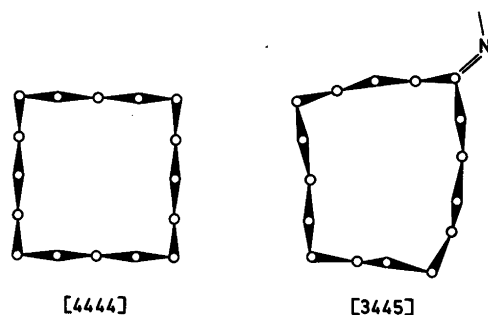*Fig. 4.* Schematic drawing of the cyclotridecane-phenylsemicarbazone molecule.

Fig. 5. Schematic drawing of the cyclohexadecane-phenylsemicarbazone.

It should, however, be pointed out that for the first time no signs of disorder for this ring size can be observed.

n = 13

Final fractional coordinates with estimated standard deviations may be found in Table 9. The

bond distances and angles of Table 10 are normal within error limits. Fig. 4 is a schematic drawing of the molecule. Only one crystal structure determination of a saturated 13-membered ring has been reported.[5] The conformation could formally be described as the triangular [3 3 7] with

[12433]   [337]

Table 11. Final fractional coordinates with estimated standard deviations for $(CH_2)_{15}CNNHCONHC_6H_5$. $H_{n,1}$ and $H_{n,2}$ are bonded to C_n. HN2 and HN3 are bonded to N2 and N3. H_m is bonded to C_m (in the phenyl ring).

ATOM	X	Y	Z
O	-.2048(3)	.9480(2)	-.5128(2)
N1	-.0272(3)	.7556(3)	-.3417(2)
N2	-.0385(3)	.8623(3)	-.3994(2)
N3	-.3142(3)	.7528(3)	-.4415(2)
C1	.1124(4)	.7660(3)	-.2773(3)
C2	.2669(4)	.8843(3)	-.2561(3)
C3	.4240(4)	.8595(3)	-.2240(3)
C4	.5728(4)	.9850(3)	-.1820(3)
C5	.7331(5)	.9721(4)	-.1784(4)
C6	.7626(4)	.8611(4)	-.1180(4)
C7	.7676(4)	.8674(4)	.0136(4)
C8	.8029(5)	.7548(4)	.0719(4)
C9	.8049(5)	.7521(4)	.2027(4)
C10	.6363(5)	.7184(4)	.2232(3)
C11	.5223(5)	.5771(4)	.1815(3)
C12	.3510(5)	.5451(4)	.1967(3)
C13	.2568(4)	.6203(3)	.1247(3)
C14	.2206(4)	.5901(3)	-.0089(3)
C15	.1526(4)	.6804(3)	-.0792(3)
C16	.1146(4)	.6489(3)	-.2142(3)
C17	-.1886(4)	.8598(3)	-.4562(3)
C18	-.4815(4)	.7276(4)	-.4803(3)
C19	-.5850(4)	.6093(4)	-.4576(3)
C20	-.7499(4)	.5769(4)	-.4913(3)
C21	-.8150(4)	.6622(4)	-.5469(3)
C22	-.7118(5)	.7814(4)	-.5676(3)
C23	-.5467(4)	.8151(3)	-.5358(3)
H21	-.935(3)	.639(3)	-.573(2)
H22	-.759(3)	.642(3)	-.610(2)
H31	.438(3)	.814(3)	-.296(3)
H32	.423(3)	.806(3)	-.158(2)
H41	.574(4)	1.015(3)	-.098(3)
H42	.562(4)	1.057(3)	-.227(3)
H51	.815(4)	1.046(3)	-.138(3)
H52	.735(4)	.967(3)	-.260(3)
H61	.877(4)	.865(3)	-.127(3)
H62	.678(4)	.777(3)	-.159(3)
H71	.666(4)	.867(3)	.031(3)
H72	.853(3)	.957(3)	.051(2)
H81	.907(4)	.758(3)	.065(3)
H82	.720(4)	.665(3)	.023(3)
H91	.882(4)	.843(3)	.246(3)
H92	.841(4)	.676(4)	.238(3)
H101	.584(4)	.780(3)	.182(3)
H102	.646(4)	.726(4)	.308(3)
H111	.566(4)	.522(3)	.223(3)
H112	.515(3)	.551(3)	.096(3)
H121	.363(3)	.567(3)	.280(2)
H122	.282(4)	.448(3)	.173(3)
H131	.318(3)	.712(3)	.149(2)
H132	.156(4)	.601(3)	.144(3)
H141	.139(4)	.497(3)	-.031(3)
H142	.324(3)	.549(3)	-.030(2)
H151	.238(3)	.777(3)	-.052(2)
H152	.052(3)	.677(2)	-.063(2)
H161	.009(3)	.569(2)	-.248(2)
H162	.199(3)	.618(2)	-.230(2)
HN2	.054(4)	.931(3)	-.411(3)
HN3	-.280(3)	.692(3)	-.394(2)
H19	-.536(3)	.551(2)	-.420(2)
H20	-.810(4)	.494(3)	-.476(3)
H21	.266(3)	.937(3)	-.193(3)
H22	.263(3)	.932(3)	-.325(2)
H23	-.470(3)	.904(2)	-.544(2)

a calculated conformational strain enthalpy as high as 32.6 kJ/mol (relative to the lowest one, the completely irregular quinquangular [1 2 4 3 3]).[11] From the dihedral angles of Table 10 it is clear that the present conformation is the same, [3 7 7]. However, as pointed out earlier,[5] the strain enthalpy calculations were based upon quite different torsional angles about C1−C2 and C2 −C3, than those of Table 10. The site of the phenylsemicarbazone group is different from that of the oxime group. As opposed to the cyclotridecaneoxime structure, no disorder is observed.

$n = 16$

Final fractional coordinates with estimated standard deviations are listed in Table 11. Fig. 5 is a schematic drawing of the molecule. Bond distances and angles, listed in Table 12, are normal. For cyclohexadecane the square [4 4 4 4] conformation, being of the diamond lattice type, has the lowest enthalpy,[11] This is also the one indicated by infrared spectroscopy of the low-temperature crystal,[13] and the one found in the crystals of 1,1,9,9-tetramethylcyclohexadecane.[14] Attempts to solve the disordered structure of cyclohexadecanone have not been successful.[1] The cyclohexadecaneoxime structure is also disordered.[5] The dihedral angles of Table 12 show that the present 16-membered ring has the conformation [3 4 4 5] with a calculated enthalpy as high as 13.4 kJ/mol relative to [4 4 4 4].[11] It

[4444]   [3445]

should be noted that the site of the phenylsemicarbazone group, somewhat unexpected, is at a "corner" atom.

The phenylsemicarbazone group has clearly a more pronounced ring disorder reducing effect

Table 12. Bond distances and angles and dihedral angles with estimated standard deviations for $(CH_2)_{15}CNNHCONHC_6H_5$.

DISTANCE	(Å)	DISTANCE	(Å)
O - C17	1.239(4)	N1 - N2	1.413(4)
N1 - C1	1.293(5)	N2 - C17	1.379(5)
N3 - C17	1.391(5)	N3 - C18	1.426(5)
C1 - C2	1.521(5)	C1 - C16	1.527(5)
C2 - C3	1.542(6)	C3 - C4	1.535(5)
C4 - C5	1.542(6)	C5 - C6	1.523(6)
C6 - C7	1.552(6)	C7 - C8	1.548(6)
C8 - C9	1.552(6)	C9 - C10	1.561(6)
C10 - C11	1.535(6)	C11 - C12	1.563(6)
C12 - C13	1.546(5)	C13 - C14	1.540(6)
C14 - C15	1.533(5)	C15 - C16	1.557(6)
C18 - C19	1.408(5)	C18 - C23	1.420(5)
C19 - C20	1.390(5)	C20 - C21	1.399(6)
C21 - C22	1.404(6)	C22 - C23	1.390(6)

ANGLE	(°)	ANGLE	(°)
O - C17 - N2	121.1(4)	O - C17 - N3	124.9(4)
N2 - N1 - C1	117.7(3)	N1 - N2 - C17	118.6(3)
N1 - C1 - C2	125.9(4)	N1 - C1 - C16	114.8(3)
N2 - C17 - N3	114.0(3)	C17 - N3 - C18	127.6(3)
N3 - C18 - C19	116.4(3)	N3 - C18 - C23	124.2(4)
C1 - C2 - C3	116.3(3)	C2 - C1 - C16	119.2(3)
C1 - C16 - C15	111.7(3)	C2 - C3 - C4	112.4(3)
C3 - C4 - C5	115.0(4)	C4 - C5 - C6	116.0(4)
C5 - C6 - C7	114.7(4)	C6 - C7 - C8	112.7(4)
C7 - C8 - C9	115.8(4)	C8 - C9 - C10	113.8(4)
C9 - C10 - C11	114.1(4)	C10 - C11 - C12	114.0(4)
C11 - C12 - C13	114.4(3)	C12 - C13 - C14	113.9(4)
C13 - C14 - C15	113.7(4)	C14 - C15 - C16	113.6(4)
C18 - C19 - C20	120.4(4)	C19 - C18 - C23	119.4(4)
C18 - C23 - C22	119.2(4)	C19 - C20 - C21	120.4(4)
C20 - C21 - C22	119.3(4)	C21 - C22 - C23	121.3(4)

DIHEDRAL ANGLE				(°)
C16 - C1 - C2 - C3				28.8(5)
C1 - C2 - C3 - C4				-169.2(3)
C2 - C3 - C4 - C5				-165.2(4)
C3 - C4 - C5 - C6				-48.8(6)
C4 - C5 - C6 - C7				-61.4(5)
C5 - C6 - C7 - C8				-178.3(3)
C6 - C7 - C8 - C9				-176.3(3)
C7 - C8 - C9 - C10				69.5(5)
C8 - C9 - C10 - C11				70.6(5)
C9 - C10 - C11 - C12				-177.3(4)
C10 - C11 - C12 - C13				62.6(5)
C11 - C12 - C13 - C14				63.2(5)
C12 - C13 - C14 - C15				-170.4(3)
C13 - C14 - C15 - C16				-179.4(3)
C14 - C15 - C16 - C1				-157.2(3)
C15 - C16 - C1 - C2				65.4(5)

than the oxime group. Although the 17-membered ring still is a problem, it might be possible to obtain the crystal conformation for $n = 18$.

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

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