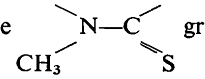
Acta Cryst. (1972). B**28**, 3618

The Crystal Structure of Two *N*-Methylthiolactams Containing Odd-Membered Rings: $C_9H_{17}NS$ and $C_{13}H_{25}NS$

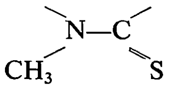
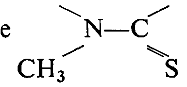
By Judith L. Flippen

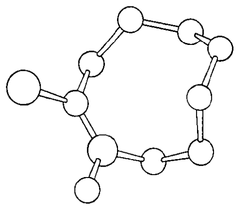
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20390, *U.S.A.*

(*Received* 7 *June* 1972)

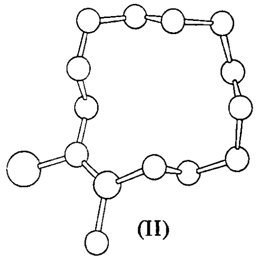
The conformations of two *N*-methylthiolactams containing rings which have an odd number of atoms have been established by X-ray single-crystal analysis They are *syn-N*-methylthiocapryllactam (I), $C_9H_{17}NS$ (9-membered ring) and *syn-N*-methylthiolauryllactam (II), $C_{13}H_{25}NS$ (13-membered ring). The capryllactam crystallizes in the orthorhombic space group *Pna*2_1 with $a=16{\cdot}621$ (3), $b=8{\cdot}729$ (2) and $c=6{\cdot}908$ (2) Å and density $D_x=1{\cdot}32$ g.cm^{-3} ($Z=4$). The lauryllactam crystallizes in space group $P2_12_12_1$ with $a=12{\cdot}266$ (3), $b=17{\cdot}193$ (4) and $c=6{\cdot}435$ (2) Å and density $D_x=1{\cdot}34$ g.cm^{-3} ($Z=4$). The X-ray intensities (872 for I and 1309 for II) were collected on an automatic diffractometer and refined by least squares on *F*-values to final *R*-values of 0·043 for I and 0·053 for II. The structures were solved using the symbolic addition procedure for noncentrosymmetric crystals. The structural results show the ring system in II to be less strained than the ring system in I. The  group is planar and in a *syn* conformation in both molecules.

Introduction

It has been observed, from n.m.r. spectra, that in solutions of large ring systems (12, 13 and 16-membered rings) containing a  moiety, there is a slow-rotation about the N–C bond with the result that both *syn* and *anti* rotational isomers are observable. The activation parameters and thermodynamic equilibrium data for the *syn–anti* interconversion have been measured (Moriarty, Yeh, Curtis & Ramey, 1971). However, in the solid state only one isomer is present. The 9-membered ring analog exists only as the *syn* isomer in solution as well as in the solid state. A note on the chemistry of these molecules and a preliminary description of the structures has been reported (Moriarty, Yeh, Curtis, Yeh, Flippen, Karle & Ramey, 1972). The X-ray study was undertaken to determine the conformation of the 13-membered ring in the solid state as well as to add to the small amount of information currently available concerning the shapes of odd-membered rings. In addition, the molecules are interesting since they are the thio analogs of lactams, which contain peptide linkages as in proteins. Cyclic antibiotics also exhibit this type of peptide linkage. The X-ray results showed the  group to be planar and in a *syn* conformation in both the *N*-methylthiocapryllactam (I) and the *N*-methylthiolauryllactam (II).



(I)



(II)

Experimental

The crystals used in the X-ray analysis were provided by Professor R. M. Moriarty of the University of Illinois. Intensity data were collected at room temperature on a four-circle computer-controlled diffractometer using the θ–2θ technique with a $1{\cdot}9°+2\theta(\alpha_2)-2\theta(\alpha_1)$ scan over 2θ for (I) and a $2{\cdot}0°+2\theta(\alpha_2)-2\theta(\alpha_1)$ scan over 2θ for (II). The scanning rate was 2 deg/min and backgrounds were counted for 10 sec. Physical quantities for both molecules are listed in Table 1. The cell parameters and their standard deviations are based on a least-squares refinement of the diffractometer coordinates of twelve independent reflections. The diffraction pattern for molecule (I) indicated two possible space groups; *Pna*2_1 (acentric) and *Pnam* (centric). *Pnam* was ruled out since it would have required the molecule to possess either a center of symmetry or a mirror plane. The intensities of the capryllactam (I) reflections diminished by approximately 25% during the data collection due to the sublimation of the crystal. This deterioration was monitored by recollecting a set of three standard reflections after every fifty new data points had been measured. These monitors were subsequently used to put all the data on one scale. Lorentz and polarization corrections were applied and normalized structure factor magnitudes $|E|$ as well as structure factor magnitudes $|F|$ were derived.

The structures were solved using the symbolic addition procedure for noncentrosymmetric crystals (Karle & Karle, 1966) using phase determining formulas which are based on inequality (34) (Karle & Hauptman, 1950), and its probability implications. The modified B_3,0 formula (Karle, 1970) was used as an aid in obtaining the basic set of phases for the lauryllactam molecule (II). It was used to help confirm the assumption (made in the symbolic addition procedure) that the cosine invariants employed in the initial part of the phase determination were close to unity. The basic set of phases was expanded by the tangent formula using the computer program *TANGFORM* written by S. A. Brenner of this laboratory.

Some ambiguity was encountered in the solution of the capryllactam (II). The direction of the z axis was not specified during the phase determination and the resulting map contained a pseudo-center of symmetry. This resulted from the fact that the actual phases of the 91 highest $|E|$ values ($|E|>1{\cdot}5$) were approximately centrosymmetric. Of these, 44 had an average deviation of ~18° from 0 and the remaining 47 had an average deviation of ~13° from π. The chemical structure of the molecule was known and was used as an aid in resolving the ambiguity. In both structure determinations the basic set of phases used as input for *TANGFORM* was obtained using a computer program written by R. D. Gilardi of this laboratory for automating parts of the symbolic addition procedure.

During refinement of the capryllactam molecule (I) the z coordinate of the sulfur atom was held constant to fix the origin for $Pna2_1$. Both molecules were refined on F values using full-matrix least-squares methods (Busing, Martin & Levy, 1962) with the weighting function

$$1/w=1{\cdot}0+\left(\frac{|F_o|-a}{b}\right)^2.$$

where $a=3{\cdot}0$ and $b=20{\cdot}0$ for molecule (I) and $a=0{\cdot}0$ and $b=10{\cdot}0$ for molecule (II). The parameters of the

Table 1. *Physical data*

	N-Methyl-thiocapryllactam	*N*-Methylthiolauryllactam
Molecular formula	$C_9H_{17}NS$	$C_{13}H_{25}NS$
Molecular weight	171·30	227·41
Crystal size		~(0·5 mm × 0·4 mm × 0·5 mm)
Space group	$Pna2_1$	$P2_12_12_1$
a	16·621 (3) Å	12·266 (3) Å
b	8·729 (2)	17·193 (4)
c	6·908 (2)	6·435 (2)
Z	4	4
Density (calc.)	1·32 g.cm^{-3}	1·34 g.cm^{-3}
Radiation	Cu $K\alpha$ (1·54178 Å) Ni filter	Cu $K\alpha$ (1·54178 Å) Ni filter
Number of independent reflections measured	872	1309
Maximum sin θ/λ	0·521	0·521
μ	23·52 cm^{-1}	18·61 cm^{-1}

Table 2. *Fractional coordinates and thermal parameters with standard deviations for N-methylthiolauryllactam*

The thermal parameters are of the form $T=\exp\left[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right]$. The B_{ij}'s are in Å^2 units. Standard deviations are based solely on least squares parameters.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·4411 (1)	−0·0640 (1)	1·2563 (2)	5·54 (5)	4·02 (4)	5·18 (5)	0·44 (3)	0·08 (5)	0·77 (4)
N(1)	0·3603 (2)	0·0695 (2)	1·1222 (5)	3·82 (12)	3·79 (12)	4·46 (13)	0·16 (10)	0·37 (12)	0·51 (12)
C(2)	0·4423 (3)	0·0188 (2)	1·1216 (6)	4·04 (14)	3·85 (14)	3·75 (13)	0·03 (12)	−0·13 (15)	−0·56 (12)
C(3)	0·5430 (3)	0·0388 (2)	0·9930 (6)	3·38 (13)	4·34 (16)	4·56 (16)	−0·07 (12)	−0·26 (14)	−0·43 (14)
C(4)	0·5435 (3)	0·0030 (2)	0·7759 (7)	4·01 (14)	3·43 (14)	4·98 (17)	−0·29 (11)	0·61 (15)	−0·56 (13)
C(5)	0·6511 (3)	0·0171 (2)	0·6628 (7)	4·00 (16)	4·50 (17)	5·31 (18)	0·37 (14)	0·84 (16)	−0·60 (15)
C(6)	0·6825 (3)	0·1033 (2)	0·6377 (8)	3·90 (15)	4·64 (16)	5·19 (20)	−0·62 (13)	0·51 (16)	−0·25 (17)
C(7)	0·6089 (4)	0·1487 (2)	0·4964 (8)	5·79 (20)	4·25 (16)	4·97 (19)	−0·95 (14)	0·08 (18)	−0·01 (16)
C(8)	0·6145 (4)	0·2381 (2)	0·5313 (8)	5·75 (20)	4·28 (16)	5·37 (22)	−0·78 (15)	−0·05 (19)	0·48 (17)
C(9)	0·5558 (3)	0·2644 (2)	0·7279 (8)	4·88 (17)	3·53 (15)	7·21 (24)	−0·73 (13)	−1·12 (21)	−0·27 (17)
C(10)	0·4320 (3)	0·2678 (2)	0·7003 (7)	5·26 (17)	3·32 (14)	6·02 (21)	−0·42 (14)	−0·99 (17)	0·58 (16)
C(11)	0·3694 (4)	0·2794 (2)	0·9071 (9)	5·67 (21)	3·78 (17)	6·89 (25)	0·94 (16)	−0·53 (21)	−0·70 (17)
C(12)	0·3831 (4)	0·2136 (2)	1·0663 (8)	5·19 (19)	3·63 (15)	5·36 (20)	0·17 (14)	0·17 (18)	−0·66 (15)
C(13)	0·3518 (3)	0·1355 (2)	0·9745 (7)	4·02 (15)	3·67 (14)	5·27 (18)	0·07 (12)	−0·35 (16)	−0·10 (14)
C(14)	0·2680 (4)	0·0592 (3)	1·2635 (9)	4·41 (17)	6·52 (22)	6·72 (26)	1·01 (16)	1·92 (20)	0·62 (24)

Table 2 (*cont.*)

	x	*y*	*z*
H(3*A*)	0·053 (4)	0·397 (3)	1·008 (9)
H(3*B*)	0·100 (4)	0·482 (3)	0·947 (9)
H(4*A*)	0·488 (4)	0·029 (3)	0·686 (9)
H(4*B*)	0·473 (4)	0·447 (3)	0·690 (9)
H(5*A*)	0·352 (4)	0·487 (3)	0·995 (10)
H(5*B*)	0·284 (4)	0·492 (3)	0·766 (10)
H(6*A*)	0·195 (4)	0·366 (3)	0·212 (10)
H(6*B*)	0·274 (4)	0·389 (3)	0·419 (10)
H(7*A*)	0·026 (5)	0·359 (3)	0·466 (9)
H(7*B*)	0·133 (5)	0·373 (3)	0·655 (10)
H(8*A*)	0·092 (5)	0·237 (3)	0·592 (10)
H(8*B*)	0·207 (5)	0·250 (3)	0·461 (10)
H(9*A*)	0·069 (5)	0·272 (3)	0·159 (11)
H(9*B*)	0·082 (4)	0·181 (3)	0·242 (10)
H(10*A*)	0·419 (4)	0·310 (3)	0·615 (10)
H(10*B*)	0·406 (5)	0·224 (3)	0·623 (10)
H(11*A*)	0·283 (5)	0·281 (3)	0·875 (11)
H(11*B*)	0·394 (5)	0·330 (3)	0·978 (11)
H(12*A*)	0·348 (5)	0·223 (3)	0·193 (10)
H(12*B*)	0·465 (5)	0·217 (3)	0·101 (10)
H(13*A*)	0·412 (4)	0·122 (3)	0·835 (10)
H(13*B*)	0·278 (5)	0·135 (3)	0·930 (9)
H(14*A*)	0·255 (5)	0·101 (4)	0·349 (12)
H(14*B*)	0·209 (5)	0·060 (4)	0·207 (12)

Table 3. *Fractional coordinates and thermal parameters with standard deviations for N-methylthiocaprylactam*

The thermal parameters are of the form

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

The B_{ij}'s are in Å² units. Standard deviations are based solely on least squares parameters.

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·3596 (1)	0·6005 (1)	0·2489	4·89 (6)	4·15 (6)	5·38 (7)	−0·43 (4)	−0·34 (7)	1·91 (6)
N(1)	0·3547 (2)	0·4591 (4)	0·5832 (7)	3·97 (17)	3·43 (18)	3·60 (19)	0·30 (13)	−0·03 (17)	−0·15 (16)
C(2)	0·3306 (3)	0·4630 (5)	0·4016 (8)	3·34 (17)	3·06 (17)	4·15 (22)	0·35 (15)	0·08 (19)	0·51 (18)
C(3)	0·2740 (3)	0·3398 (6)	0·3256 (9)	3·23 (18)	4·94 (23)	4·32 (23)	−0·69 (17)	−0·59 (19)	0·69 (20)
C(4)	0·3158 (3)	0·2022 (6)	0·2273 (10)	5·46 (23)	5·37 (24)	3·82 (22)	−1·44 (20)	−0·37 (25)	−0·30 (26)
C(5)	0·3377 (4)	0·0662 (6)	0·3587 (11)	6·36 (29)	3·51 (20)	5·81 (32)	−1·27 (20)	0·34 (27)	−0·48 (22)
C(6)	0·4253 (4)	0·0556 (7)	0·4239 (12)	5·70 (27)	4·43 (22)	6·50 (36)	0·64 (21)	0·30 (30)	−0·66 (26)
C(7)	0·4604 (3)	0·1916 (6)	0·5320 (9)	3·69 (19)	4·43 (21)	4·91 (25)	0·63 (17)	0·02 (21)	0·32 (22)
C(8)	0·4213 (3)	0·2308 (6)	0·7260 (10)	4·21 (20)	5·15 (22)	3·87 (22)	0·58 (17)	−0·57 (23)	0·80 (25)
C(9)	0·3441 (3)	0·3273 (6)	0·7116 (8)	4·53 (22)	4·49 (22)	3·48 (25)	0·31 (17)	0·76 (20)	0·32 (19
C(10)	0·4074 (5)	0·5774 (8)	0·6620 (12)	5·88 (31)	4·56 (28)	5·69 (29)	−0·97 (24)	−0·20 (26)	−1·11 (25

Table 3 (*cont.*)

	x	*y*	*z*
H(3*A*)	0·238 (3)	0·391 (6)	0·224 (13)
H(3*B*)	0·232 (3)	0·307 (7)	0·430 (10)
H(4*A*)	0·276 (4)	0·163 (7)	0·098 (11)
H(4*B*)	0·362 (4)	0·228 (8)	0·142 (12)
H(5*A*)	0·295 (4)	0·061 (7)	0·489 (14)
H(5*B*)	0·325 (4)	−0·022 (8)	0·294 (12)
H(6*A*)	0·464 (4)	0·046 (6)	0·275 (13)
H(6*B*)	0·435 (4)	−0·051 (7)	0·516 (12)
H(7*A*)	0·522 (4)	0·169 (6)	0·554 (11)
H(7*B*)	0·461 (4)	0·285 (8)	0·454 (12)
H(8*A*)	0·463 (4)	0·285 (7)	0·818 (10)
H(8*B*)	0·405 (4)	0·132 (7)	0·823 (10)
H(9*A*)	0·327 (4)	0·372 (8)	0·856 (10)
H(9*B*)	0·298 (4)	0·267 (7)	0·667 (9)
H(10*A*)	0·460 (5)	0·559 (7)	0·605 (13)
H(10*B*)	0·423 (5)	0·570 (8)	0·837 (13)
H(10*C*)	0·389 (4)	0·673 (9)	0·629 (12)

weighting function were derived from a statistical examination of the least-squares discrepancies and it was used for all the data; no reflections were considered unobserved. The function minimized was $\sum w(|F_o|-|F_c|)^2$ and the atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). Hydrogen atoms were located in difference maps (24 of 25 hydrogens were found for molecule II) and their positional parameters were refined. The hydrogen atoms were assigned temperature factors equal to those of their adjoining atoms and these parameters were not refined. The final *R* values were 0·043 for molecule (I) and 0·053 for molecule (II). No absorption or secondary extinction corrections were applied. Tables 2 and 3 list the coordinates and thermal parameters for the two molecules and the observed and calculated structure factors are compared in Tables 4 and 5.

Discussion

The stereoconfigurations of (I) and (II) are illustrated in Figs. 1 and 2 respectively. Their bond distances and angles are displayed in Figs. 3 and 4 and torsion angles are depicted in Fig. 5.

The average C–C distance in I is 1·531Å (±0·010) and the average C–C–C angle is 116·2° (±0·6). This agrees well with the values that have been found in other rings of comparable size (9 and 10-membered rings; *e.g.* Bryan & Dunitz, 1960; Huber-Buser & Dunitz, 1961; Dunitz & Weber, 1964*a*; Winkler & Dunitz, 1971).

The conformation of (I) is similar to that of one of the two independent molecules of cyclononylamine (III) which has one + synperiplanar torsion angle of 26° (Bryan & Dunitz, 1960). Both molecules exhibit essentially the same conformations, see Fig. 6. In (III) there are 5 transannular H–H distances estimated to be less than 2·20 Å. In (I) there are 2 short intramolec-

Table 4. *Observed and calculated structure factors for the caprylllactam* (I)

The columns are the index h, $10|F_o|$, and $10|F_c|$.

H	0	0
2	289	291
4	751	894
6	344	345
8	61	61
10	372	370
12	90	95
14	144	147
16	96	100
18	53	58
H	0	1
2	730	921
4	618	680
6	113	113
8	287	284
10	148	149
12	154	146
14	86	86
16	19	22
18	50	50
H	0	2
0	645	730
2	413	413
4	490	492
6	145	142
8	171	159
10	66	65
12	76	78
14	133	134
18	79	78
H	0	3
2	285	288
4	257	248
6	213	199
8	200	203
10	242	237
12	115	105
14	144	143
16	76	67
16	0	67
H	0	4
0	199	195
2	51	49
4	165	160
6	76	75
8	109	113
10	91	99
12	127	127
14	66	65
16	30	32
H	0	5
2	118	115
4	73	76
6	118	118
10	32	30
12	17	21
14	47	46
H	0	6
0	210	215
2	29	24
4	166	168
6	123	122
10	83	88
12	32	32
H	0	7
2	90	98
4	37	29
6	33	38
8	73	73
H	0	8
0	55	53
H	1	0
1	342	345
2	474	503
3	653	742
4	103	104
5	137	139
6	479	484
8	21	22
9	20	23
10	145	140
11	201	190
12	19	14
13	116	115
14	65	69
15	28	25
16	71	68
17	60	56
18	0	4
19	0	7
H	1	1
0	446	485
1	209	201
2	290	284
3	190	187
4	421	421
5	285	280
6	139	130
8	123	124
9	222	220
10	210	209
11	28	22
12	25	22
13	112	113
14	119	116
15	30	28
16	34	37
17	36	34
18	64	64
19	11	4
H	1	2
1	415	417
2	17	17
3	193	196
4	144	133
5	268	270
6	171	163
7	113	112
8	197	195
9	44	42
10	153	153
11	148	146
12	59	56
13	71	75
14	68	67
15	66	66
16	36	33
17	69	71
18	36	36
H	1	3
0	278	274
1	273	272
3	249	243
4	260	258
5	205	201
6	22	19
7	126	122
8	73	77
9	174	168
10	99	95
12	72	70
13	143	135
14	104	114
15	92	90
16	21	20
17	66	63
H	1	4
1	39	35
2	68	59
3	102	108
4	119	116
5	69	62
6	142	134
7	149	148
8	73	73
9	30	28
10	124	130
12	78	78
13	46	50
14	0	3
15	66	68
16	26	31
H	1	5
0	200	202
1	97	93
2	32	29
3	88	86
4	94	98
5	121	118
6	36	38
7	36	38
8	68	64
9	80	77
10	77	80
12	18	11
13	8	18
14	46	50
H	1	6
1	62	63
2	93	96
3	133	134
4	38	37
5	0	8
6	26	23
7	149	152
8	57	57
9	54	54
10	77	79
12	44	41
H	1	7
0	48	46
1	47	51
2	31	31
3	31	33
4	52	50
5	80	85
6	26	27
7	38	41
8	40	42
9	23	30
H	2	0
0	205	210
1	335	325
2	70	67
3	618	660
4	470	470
5	161	155
6	191	177
7	17	16
8	108	104
9	38	43
10	110	109
11	13	8
12	74	67
13	74	71
14	59	64
15	12	16
16	0	2
17	67	69
18	6	4
H	2	1
1	379	364
2	456	466
3	576	628
4	187	186
5	96	87
6	144	139
7	476	479
8	142	137
9	199	190
10	138	134
11	168	156
12	78	78
13	74	78
14	56	57
15	97	99
16	27	33
17	62	62
18	0	11
H	2	2
0	301	293
1	262	255
2	140	132
3	243	235
4	88	82
5	419	413
6	105	95
7	90	70
8	213	211
9	133	121
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16	27	23
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3	169	172
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13	57	60
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6	25	24
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8	15	18
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13	59	61
14	68	61
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17	0	9
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9	67	69
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17	31	32
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10	108	113
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16	38	39
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16	20	14
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6	118	119
8	124	125
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H	5	5
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3	56	59
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8	66	65
9	91	94
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6	119	114
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6	42	44
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H	7	0
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4	143	144
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6	109	107
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9	44	46
10	38	41
11	0	15
12	99	103
13	21	21
H	7	1
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3	35	36
4	114	119
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7	27	30
8	27	30
9	48	49
10	75	72
11	16	19
12	9	13
13	31	33
H	7	2
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3	72	74
4	113	111
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7	47	47
8	59	59
9	24	21
10	68	68
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1	51	52
2	10	6
3	32	33
4	74	75
5	22	26
6	16	19
H	8	0
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1	218	223
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3	70	70
4	16	14
5	145	154
6	28	25
7	24	20
8	54	55
9	78	79
10	12	16
11	47	45
H	8	1
1	58	57
2	69	73
3	122	122
4	22	19
5	42	44
6	55	55
7	70	69
8	38	39
9	18	19
10	42	41
11	54	56
H	8	2
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1	110	110
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3	82	83
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5	67	70
6	0	12
7	30	34
8	30	33
9	33	38
10	41	39
H	8	3
1	63	63
2	30	34
3	73	73
4	26	30
5	28	30
6	30	32
7	76	76
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H	8	4
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2	13	11
3	40	42
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6	7	11
H	9	0
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4	15	13
5	31	33
6	71	78
7	52	54
8	2	4
H	9	1
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1	77	79
2	25	27
3	90	90
4	33	33
5	83	87
6	22	28
7	0	3
8	43	42
H	9	2
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2	42	43
3	58	59
4	39	41
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6	39	40
7	88	90
H	9	3
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1	38	41
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4	57	56
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H	10	1
1	30	29

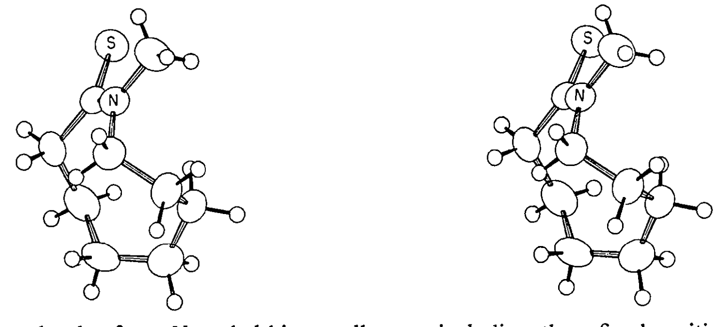


Fig. 1. A stereodrawing of a molecule of *syn-N*-methylthiocapryllactam including the refined positions of the hydrogen atoms. All stereodrawings were made using the *ORTEP* program of Johnson (1965).

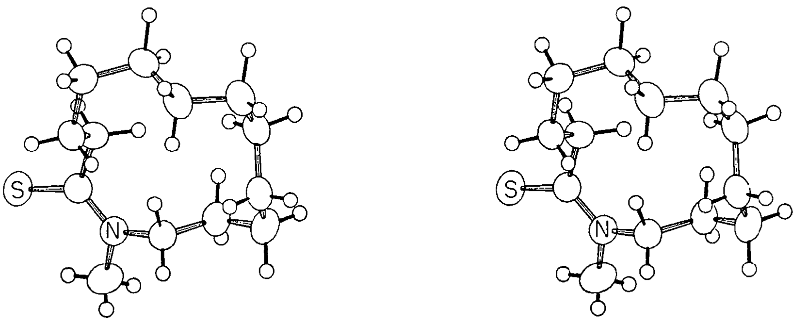
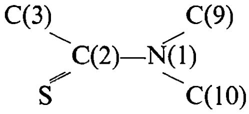


Fig. 2. A stereodrawing of a molecule of *syn-N*-methylthiolauryllactam including the refined positions of the hydrogen atoms. One of the methyl hydrogen atoms is drawn at an assumed position.

ular H–H distances; H(3*B*)···H(9*B*) at 2·00 Å and H(5*A*)···H(9*B*) at 2·18 Å. The



group is planar (±0·11 Å) and the C(3)–C(2)–N(1)–C(9) torsion angle is 12·8° indicating that it is a *syn* junction. There are no other planar segments in the molecule and of the remaining torsion angles (see Fig. 5) there are 4 ±*syn*-clinal (±30–90°) torsion angles and 4 unfavorable ±*anti*-clinal (±90–150°) torsion angles (see Klyne & Prelog, 1960 for a discussion on the labeling of torsion angles). These findings are consistent with the fact that 9–, 10– and 11–membered hydrocarbon rings are known, from thermodynamic

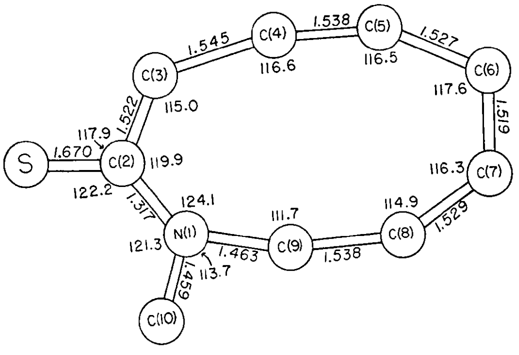


Fig. 3. Bond distances and angles for *syn*-*N*-methylthiocapryllactam. Standard deviations estimated from the least-squares refinement are 0·010 Å for bond lengths and 0·6° for the angles.

Table 5. *Observed and calculated structure factors for the laurylllactam* (II)

The columns are the index *h*, 10|F_o|, and 10|F_c|.

0	K	0
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6	639	707
8	164	145
10	329	338
12	29	27
14	332	337
16	109	114
18	106	112
0	K	1
1	116	114
2	168	167
3	285	295
4	622	622
5	273	283
6	343	327
7	354	362
8	227	232
9	72	73
10	241	251
11	175	167
12	65	54
13	199	208
14	161	157
15	72	69
16	73	76
17	0	2
18	21	23
19	43	44
0	K	2
0	384	393
1	530	563
2	666	711
3	160	167
4	390	365
5	222	208
6	396	398
7	248	218
8	317	329
9	211	197
10	18	3
11	69	66
12	193	201
13	44	38
14	133	126
15	16	18
16	224	223
17	62	64
18	128	128
19	11	7
0	K	3
1	63	67
2	220	218
3	92	86
4	296	287
5	50	56
6	371	362
7	32	38
8	35	26
9	77	72
10	178	171
11	152	157
12	102	116
13	57	49
14	70	74
15	17	17
16	136	133
17	26	31
18	42	46
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3	75	47
4	18	26
5	159	152
6	87	92
7	199	209
8	93	92
9	91	89
10	280	282
11	110	115
12	20	15
13	83	84
14	96	93
15	28	27
16	105	105
0	K	5
1	136	142
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3	122	123
4	179	185
5	74	79
6	49	54
7	36	41
8	38	46
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10	114	113
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12	111	110
13	15	17
14	58	55
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4	51	46
5	0	1
6	110	111
7	0	3
8	122	126
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10	14	9
11	19	18
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2	20	5
3	0	2
4	30	32
5	29	29
6	7	0
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3	118	90
4	40	38
5	376	400
6	289	280
7	432	452
8	433	426
9	438	444
10	377	368
11	103	97
12	359	338
13	27	22
14	111	103
15	231	227
16	150	144
17	41	34
18	97	110
19	21	17
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3	475	491
4	496	511
5	223	217
6	305	315
7	111	104
8	687	700
9	11	20
10	221	206
11	96	89
12	87	89
13	134	128
14	144	148
15	33	43
16	122	129
17	21	24
18	17	27
19	29	28
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3	126	122
4	292	295
5	376	400
6	386	386
7	298	302
8	197	191
9	241	248
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12	381	384
13	99	90
14	83	79
15	36	35
16	62	59
17	76	68
18	75	74
19	40	40
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3	171	173
4	389	385
5	195	184
6	274	273
7	13	14
8	291	292
9	123	119
10	177	180
11	46	45
12	136	133
13	164	174
14	57	53
15	13	11
16	87	80
17	48	48
18	28	29
1	K	4
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3	43	37
4	292	295
5	116	113
6	200	187
7	79	82
8	118	118
9	59	62
10	135	142
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12	79	74
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16	28	27
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5	24	22
6	107	104
7	12	11
8	174	172
9	81	86
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11	27	15
12	50	54
13	5	6
14	47	46
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2	128	127
3	96	105
4	104	105
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7	57	56
8	33	26
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11	34	35
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4	692	801
5	153	164
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7	12	18
8	60	44
9	188	175
10	189	179
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12	60	71
13	156	152
14	82	88
15	120	127
16	74	81
17	40	37
18	48	54
19	31	26
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6	283	267
7	453	446
8	268	250
9	18	28
10	329	339
11	142	139
12	201	200
13	200	190
14	259	258
15	117	121
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18	39	34
19	25	30
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3	303	301
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5	158	158
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7	141	134
8	113	120
9	161	160
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11	20	18
12	176	171
13	150	152
14	147	144
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16	134	142
17	87	86
18	64	63
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8	127	121
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10	201	204
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16	70	63
17	71	64
18	37	37
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3	121	114
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5	273	284
6	183	187
7	98	96
8	111	106
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10	78	80
11	161	164
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13	88	84
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15	32	29
16	47	47
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7	157	161
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9	56	58
10	67	62
11	47	52
12	45	42
13	51	51
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7	26	21
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5	44	40
6	28	27
3	K	0
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3	62	73
4	326	315
5	348	330
6	33	43
7	425	403
8	155	162
9	174	173
10	74	66
11	33	44
12	256	243
13	18	13
14	45	36
15	167	173
16	33	35
17	32	39
18	92	91
19	5	11
3	K	1
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2	334	342
3	610	632
4	205	197
5	436	414
6	29	19
7	40	36
8	52	32
9	225	239
10	63	54
11	256	252
12	115	120
13	238	232
14	41	53
15	175	166
16	63	64
17	9	8
18	43	41
19	67	65
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2	141	143
3	239	238
4	351	360
5	197	190
6	305	306
7	196	192
8	34	29
9	292	286
10	112	107
11	114	116
12	60	45
13	79	87
14	39	32
15	21	22
16	61	63
17	47	48
18	31	32
3	K	3
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1	214	208
2	165	154
3	348	359
4	283	273
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6	202	204
7	196	197
8	292	287
9	205	208
10	82	77
11	160	165
12	66	60
13	140	140
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16	48	52
17	53	51
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3	58	62
4	95	96
5	153	148
6	39	29
7	169	169
8	82	84
9	100	95
10	31	25
11	56	53
12	153	149
13	33	38
14	12	16
15	81	81
16	17	15
3	K	5
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3	227	231
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5	118	110
6	93	98
7	103	99
8	88	88
9	57	55
10	102	101
11	88	85
12	83	84
13	77	77
14	39	38
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7	70	71
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9	57	61
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4	23	18
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3	441	461
4	43	40
5	417	420
6	71	65
7	146	151
8	162	172
9	55	62
10	11	8
11	421	420
12	19	12
13	282	280
14	151	150
15	90	89
16	40	60
17	76	69
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19	31	39
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2	176	189
3	314	313
4	108	115
5	95	95
6	119	117
7	167	171
8	117	119
9	252	260
10	53	42
11	69	64
12	87	89
13	203	198
14	28	31
15	173	179
16	19	18
17	96	97
18	22	17
4	K	2
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1	282	275
2	205	197
3	160	179
4	144	147
5	356	358
6	50	53
7	258	241
8	102	100
9	237	244
10	151	148
11	221	219
12	118	118
13	156	145
14	119	120
15	43	42
16	32	31
17	66	69
18	30	26
4	K	3
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2	152	138
3	138	132
4	27	30
5	186	180
6	166	169
7	216	214
8	109	106
9	139	139
10	46	45
11	110	114
12	100	98
13	95	92
14	25	24
15	115	117
16	22	19
17	92	91
4	K	4
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2	192	182
3	296	297
4	136	134
5	228	238
6	94	89
7	148	155
8	120	126
9	61	71
10	35	41
11	74	69
12	17	16
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14	12	22
15	33	33
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1	208	209
2	110	105
3	46	41
4	119	122
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12	59	51
13	37	37
4	K	6
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1	45	47
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8	36	36
9	59	51
10	43	45
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2	27	22
3	53	53
5	K	0
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2	96	90
3	219	195
4	248	223
5	52	26
6	45	46
7	243	263
8	78	83
9	102	97
10	46	66
11	59	48
12	21	27
13	82	70
14	37	27
15	8	3
16	49	48
17	86	83
18	22	28
5	K	1
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1	132	131
2	449	447
3	415	418
4	202	191
5	292	276
6	22	18
7	131	124
8	65	69
9	189	188
10	73	70
11	209	196
12	56	57
13	136	133
14	51	58
15	38	32
16	26	30
17	50	49
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2	238	236
3	113	110
4	258	240
5	243	255
6	203	197
7	281	278
8	250	248
9	293	298
10	99	94
11	165	160
12	130	129
13	39	37
14	52	55
15	103	102
16	48	48
17	44	51
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2	70	71
3	169	165
4	53	56
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7	83	81
8	75	81
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10	106	110
11	63	63
12	66	71
13	102	90
14	37	35
15	44	47
16	45	42
5	K	4
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2	56	47
3	27	31
4	128	132
5	186	182
6	108	115
7	301	306
8	59	68
9	227	225
10	93	100
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12	53	52
13	90	91
14	35	35
15	90	87
5	K	5
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1	50	42
2	30	23
3	40	39
4	28	26
5	62	63
6	33	30
7	44	45
8	63	67
9	70	68
10	92	88
11	54	52
12	36	37
13	49	49
5	K	6
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2	35	31
3	30	29
4	21	21
5	60	61
6	13	11
7	101	108
8	16	17
9	79	77
6	K	0
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2	139	128
3	298	292
4	254	245
5	315	334
6	172	188
7	30	20
8	141	141
9	203	202
10	172	176
11	86	91
12	66	61
13	216	221
14	53	51
15	27	19
16	52	48
17	29	29
18	34	37
6	K	1
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3	249	247
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5	100	97
6	84	79
7	79	71
8	29	27
9	133	133
10	243	248
11	132	137
12	138	143
13	49	72
14	137	136
15	166	169
16	42	42
17	78	81
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1	175	173
2	153	149
3	75	72
4	13	14
5	103	115
6	204	204
7	88	98
8	220	232
9	47	48
10	133	131
11	192	187
12	95	89
13	20	29
14	82	79
15	29	32
16	91	88
17	62	66
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2	116	117
3	144	139
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5	68	69
6	36	36
7	251	246
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11	73	68
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13	105	106
14	59	57
15	113	116
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6	164	164
7	110	111
8	109	107
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9	129	124
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5	69	69
6	30	31
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2	329	322
3	145	150
4	166	162
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6	139	131
7	56	51
8	79	84
9	110	111
10	67	64
11	115	115
12	229	234
13	114	107
14	28	31
15	16	23
16	34	28
17	32	30
7	K	1
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2	372	361
3	178	178
4	53	51
5	232	226
6	94	80
7	110	102
8	187	182
9	146	145
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11	151	154
12	89	87
13	133	129
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16	56	51
17	17	16
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6	220	227
7	204	211
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10	66	62
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12	84	86
13	63	59
14	34	34
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16	34	39
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3	214	210
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5	145	141
6	170	166
7	149	147
8	270	273
9	130	129
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12	10	10
13	53	53
14	86	82
15	32	32
7	K	4
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4	23	13
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7	78	75
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9	25	27
10	43	44
11	40	45
12	69	70
13	47	44
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2	46	53
3	65	62
4	84	81
5	63	64
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7	33	25
8	107	101
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3	44	42
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6	24	34
8	K	0
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1	19	22
2	260	262
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5	172	164
6	120	111
7	106	103
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9	16	7
10	28	24
11	89	96
12	75	80
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14	50	48
15	18	17
16	70	74
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4	301	302
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7	123	117
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6	159	164
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11	106	102
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13	81	82
14	117	119
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4	234	220
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7	108	104
8	119	123
9	14	18
10	104	102
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6	107	109
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8	126	128
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8	K	5
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4	75	78
5	17	11
6	93	97
7	18	19
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8	K	6
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9	K	0
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3	147	153
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6	136	134
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3	72	67
4	239	236
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6	158	160
7	84	85
8	73	70
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12	111	113
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7	45	47
8	153	149
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13	41	37
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2	110	116
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5	93	90
6	85	78
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6	78	73
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13	22	17
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1	77	69
2	83	74
3	162	153
4	105	107
5	88	88
6	61	70
7	45	36
8	98	92
9	32	22
10	40	35
11	80	81
12	80	79
13	30	20
10	K	3
0	46	43
1	40	60
2	60	58
3	34	38
4	125	124
5	24	25
6	61	60
7	115	111
8	46	47
9	97	94
10	70	66
11	45	43
10	K	4
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1	38	35
2	49	44
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6	64	62
7	44	42
8	37	41
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10	K	5
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2	26	15
3	0	9
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6	32	40
7	32	32
8	90	103
9	79	89
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11	K	1
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1	128	125
2	94	95
3	46	45
4	105	108
5	56	55
6	108	111
7	27	27
8	137	142
9	71	67
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11	72	73
12	37	36
11	K	2
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2	74	66
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6	64	44
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11	K	4
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2	39	32
3	0	12
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12	K	0
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2	28	33
3	13	17
4	82	94
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6	0	11
7	43	51
8	13	12
9	37	51
10	16	13
12	K	1
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2	60	62
3	104	108
4	17	23
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6	31	30
7	76	84
8	28	28
9	71	74
10	21	22
12	K	2
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7	45	41
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3	25	14
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12	K	4
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3	0	9
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6	16	16
7	43	52
8	28	33
13	K	1
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1	24	25
2	45	44
3	89	85
4	29	26
5	62	56
6	31	27
7	19	15
13	K	2
0	45	44
1	47	47
2	51	47
3	27	27
4	10	24
5	21	31
6	59	59
13	K	3
0	28	30
14	K	0
0	26	25
1	33	35
2	8	9
3	66	66
14	K	1
0	14	15
1	58	61
2	30	27

measurements, to have relatively high strain energies (Dunitz, 1968).

The average value for C–C bonds in (II) is 1·530 Å (±0·007) and the average C–C–C angle is 113·4° (±0·4), several degrees smaller than that observed in the 9-membered ring. These values are in good agreement with values found in other large ring compounds (12 atoms and higher, *e.g.* Dunitz & Weber, 1964*b*; Dunitz & Meyer, 1965; Brown, 1966). Also, more recent strain minimization calculations have been based on a zero-strain angle of 112·7° (Bixon & Lifson, 1967) which would indicate little, if any, Baeyer strain present in molecule (II).

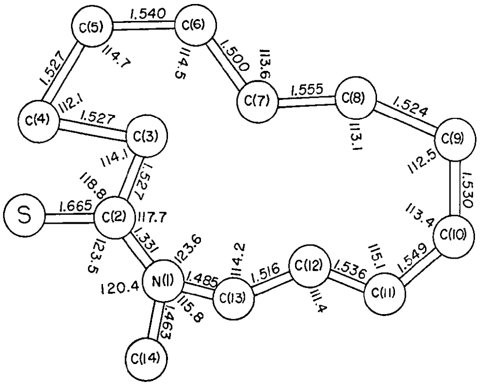


Fig. 4. Bond distances and angles for *syn*-*N*-methylthiolauryllactam. Standard deviations estimated from the least-squares refinement are 0·007 Å for bonds and 0·4° for angles.

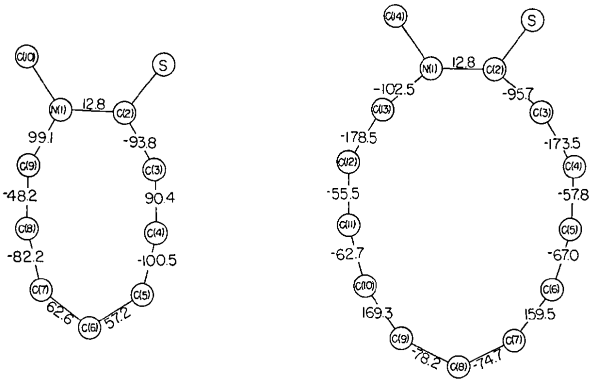
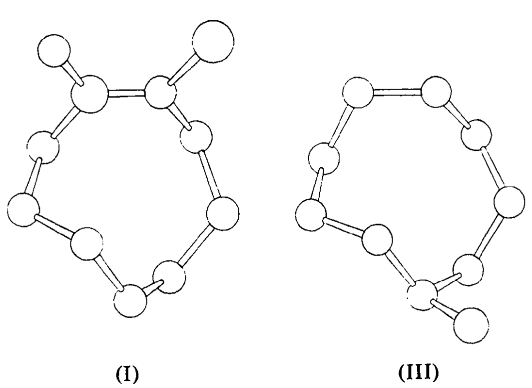


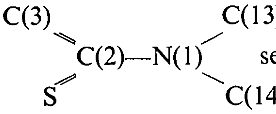
Fig. 5 Torsion angles for molecules (I) and (II), calculated according to conventions defined by Klyne & Prelog, 1960.



(I) (III)

Fig. 6. A comparison of the conformations of *syn*-*N*-methylthiocapryllactam (I) and cyclononylamine (III).

The 13-membered ring in (II) consists of 5 planar segments: plane *a* consisting of atoms N(1)–C(13)–C(12)–C(11) (±0·01 Å), plane *b* composed of atoms C(11)–C(10)–C(9)–C(8) (±0·07 Å), plane *c* made up of atoms C(8)–C(7)–C(6)–C(5) (±0·01 Å), plane *d* consisting of atoms C(5)–C(4)–C(3)–C(2) (±0·04 Å) and plane *e* consisting of 2 atoms from plane *a*, N(1) and C(9), and 2 atoms from plane *d*, C(2) and C(3). Plane *e* is planar to within ±0·06 Å. The entire



segment is planar to within ±0·13 Å. The C(3)–C(2)–N(1)–C(13) torsion angle is 12·8° indicating a *syn* thiolactam junction in this molecule as well as in (I). The central torsion angle of planes *a*–*d* is ±antiperiplanar (±150–180°) indicating 4 *trans* segments of 4 atoms each around the ring. Other torsion angles (not directly involved in the C–N system) are all −*syn*-clinal. This would be an energetically favorable arrangement of partial conformations (Dunitz, 1968). Larger ring systems are able to accommodate more of the favorable antiperiplanar torsions. There are none in the 9-membered rings of (I) and (III) and only 2 in 1-6-*trans*-diaminocyclodecane dihydrochloride (Huber-Buser & Dunitz, 1961) which has a 10-membered ring. There are 4 antiperiplanar torsions in the 12-membered ring in azacyclododecane-hydro chloride (Dunitz & Weber, 1964) as well as in the thiolauryllactam (II) and there are six antiperiplanar torsions in the 14-membered ring in 1-8-diazacyclotetradecane dihydrobromide (Dunitz & Meyer, 1965). There is also an approximate dyad axis with respect to torsion angles (see Fig. 5) in the ring skeleto of (II) passing through the center of the N(1)–C(2) bond and through C(8). There are 5 transannular H–H approaches in II which are <2·2 Å: H(3*A*)···H(11*A*) at 2·04 Å, H(3*A*)···H(13*A*) at 2·08 Å, H(4*B*)···H(6*A*) at 2·11 Å, H(5*B*)···H(8*A*) at 2·13 Å and H(11*B*)···H(13*B*) at 2·17 Å.

Packing arrangements for molecules (I) and (II) are illustrated in Figs. 7 and 8 respectively. In both cases the molecules are held together solely by van der Waals forces. The closest intermolecular approaches in (I) are N(1)···C(4)′ at 3·68 Å and C(9)···C(4)′ at 3·76 Å. For molecule II the closest intermolecular approaches are N(1)···C(1)′ at 3·56 Å and S(1)···C(13)′ at 3·75 Å.

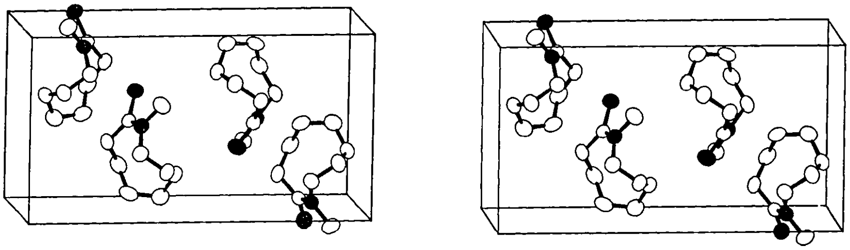


Fig. 7. A stereodrawing of the packing of molecule (I). It is viewed looking down the *c* axis with **a** → and **b** ↑.

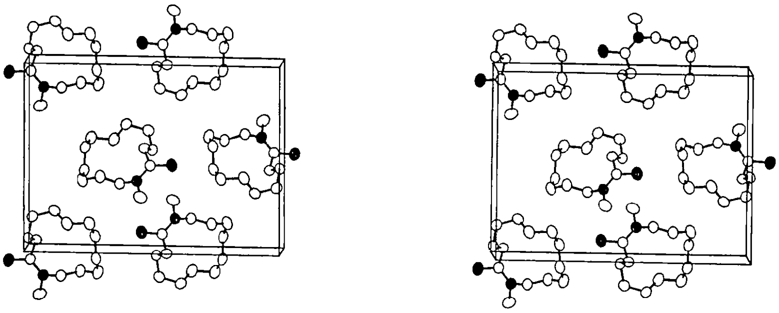


Fig. 8. A stereodrawing of the packing of molecule (II). It is viewed looking down the *c* axis with **b** → and **a** ↑.

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