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Structure of *N*-Decyl-D-ribonamide

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Abstract. $C_{15}H_{31}NO_5$, $M_r = 305.42$, triclinic, $P1$, $a = 4.825$ (1), $b = 5.452$ (2), $c = 16.100$ (5) Å, $\alpha = 87.08$ (3), $\beta = 93.10$ (2), $\gamma = 96.10$ (2)°, $V = 420.1$ (2) Å³, $Z = 1$, $D_x = 1.21$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.96$ cm⁻¹, $F(000) = 168$, $T = 291$ K, $R = 0.034$ for 1038 observed reflections. Because of strong cohesion by hydrogen bonds the molecules are arranged in monolayers. The D-ribose moiety adopts a conformation very similar to that found in other compounds. The decyl chain is in an extended all-*trans* conformation.

Introduction. Neat *N*-decylribonamide has been shown recently (Baeyens-Volant, Cuvelier, Fornasier, Szalai & David, 1985) to form a lamellar mesomorphic phase between 372 and 424 K. This phase has been identified with the polarizing microscope by examination of the textures formed in the liquid-crystalline phase. X-ray investigation of the mesogenic crystal can afford valuable information about the spatial arrangement of the molecules in the mesomorphic state. Indeed, it seems (Doucet, 1979) that smectogenic crystals have a structure characterized by layers and that in nematogenic crystals all the molecular long axes are

approximately parallel. The transition to the mesophase thus probably mainly involves loss of the lateral order of the molecules. In the present case, extensive reorganization of the positional order of the molecules is not probable on passing from the crystal to the viscous lamellar phase. Furthermore, X-ray investigation of the ordered mesomorphic phase gives only information at the molecular level whereas the atomic parameters are obtained by studying the monocystal.

Experimental. Crystals obtained by evaporation from tetrahydrofuran. Parallelepiped crystal with dimensions 0.25 × 0.18 × 0.07 mm. Lattice parameters refined using 15 reflections in the range $5 \leq 2\theta \leq 20^\circ$. Syntex $P2_1$, graphite-monochromatized $Mo K\alpha$ radiation. 1247 $h, \pm k, \pm l$ independent reflections with $\sin\theta/\lambda < 0.561$ Å⁻¹, $0 \leq h \leq 5$, $-6 \leq k \leq 6$, $-17 \leq l \leq 18$, 1038 with $I \geq 2.5(I)$. Standard reflection (01 $\bar{3}$) checked every 50 reflections: no significant deviation. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *DIRDIF81* (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). H

atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX76*; Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor ($B = 3.7 \text{ \AA}^2$). $w = 1/(\sigma^2 + 0.00371F^2)$, $R = 0.034$, $wR = 0.039$, $S = 0.75$ for 1038 observed reflections.* Final $(\Delta/\sigma)_{\max} = 0.5$. Max. and min. heights in final difference Fourier synthesis = 0.13 and -0.15 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are given in Table 1. Fig. 1 is a view of the molecule, showing the numbering of the atoms; Fig. 2 shows the packing in the unit cell and the monolayers in the crystal (program *PLUTO*; Motherwell & Clegg, 1978). Bond distances and angles are given in Table 2.

As shown in Table 3, the D-ribose moiety adopts a conformation very similar to those of D-ribose *S,S'*-diphenyl and *S,S'*-diethyl dithioacetals (Ducruix, Horton, Pascard, Wander & Prangé, 1978). The decyl chain is in an extended all-*trans* conformation. All the C—C—C—C torsion angles are very close to 180° in the chain. Strong cohesion between molecules occurs in planes parallel to (001) through multiple hydrogen bonds. Fig. 3 illustrates the pattern of these bonds and Table 4 gives the hydrogen-bond lengths.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42667 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

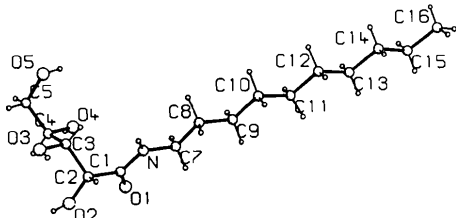


Fig. 1. View of the molecule and atom numbering.

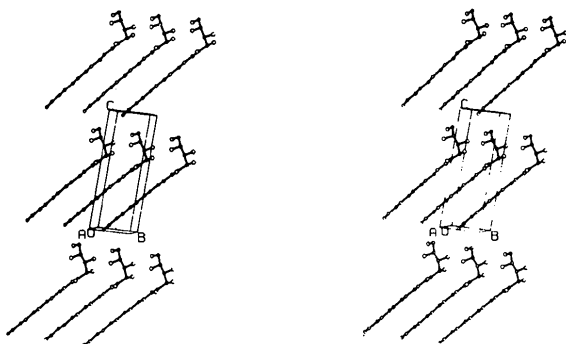


Fig. 2. Packing in the unit cell.

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2)

$$B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}
C(1)	4663	8129	5623	2.28
O(1)	7175 (10)	8172 (10)	5516 (3)	2.95
C(2)	3530 (11)	9883 (11)	6192 (4)	2.34
O(2)	5742 (10)	11638 (10)	6446 (3)	2.63
C(3)	1974 (12)	8619 (11)	6947 (4)	1.97
O(3)	489 (12)	10398 (11)	7306 (3)	2.85
C(4)	3859 (12)	7627 (11)	7641 (4)	2.23
O(4)	5297 (11)	5795 (9)	7292 (3)	2.60
C(5)	2276 (13)	6550 (13)	8375 (4)	2.59
O(5)	87 (11)	4692 (11)	8161 (3)	2.86
N	2750 (11)	6582 (10)	5236 (3)	2.69
C(7)	3559 (12)	4938 (11)	4623 (4)	2.61
C(8)	1054 (12)	3461 (11)	4220 (4)	2.64
C(9)	1985 (13)	1794 (12)	3576 (4)	3.14
C(10)	-368 (12)	203 (12)	3147 (4)	3.07
C(11)	653 (14)	-1333 (12)	2488 (4)	3.44
C(12)	-1624 (13)	-2975 (12)	2028 (4)	3.41
C(13)	-505 (14)	-4436 (13)	1366 (4)	3.75
C(14)	-2705 (14)	-6126 (12)	894 (4)	3.85
C(15)	-1489 (16)	-7561 (15)	249 (5)	4.81
C(16)	-3642 (20)	-9210 (16)	-244 (6)	5.85

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

O(1)—C(1)	1.231 (5)	C(2)—C(1)—O(1)	122.0 (4)
C(2)—C(1)	1.520 (6)	N—C(1)—O(1)	122.5 (4)
N—C(1)	1.333 (5)	N—C(1)—C(2)	115.5 (3)
O(2)—C(2)	1.413 (5)	O(2)—C(2)—C(1)	108.4 (3)
C(3)—C(2)	1.555 (6)	C(3)—C(2)—C(1)	115.1 (3)
O(3)—C(3)	1.428 (5)	C(3)—C(2)—O(2)	111.9 (3)
C(4)—C(3)	1.517 (5)	O(3)—C(3)—C(2)	108.6 (3)
O(4)—C(4)	1.428 (5)	C(4)—C(3)—C(2)	114.6 (3)
C(5)—C(4)	1.502 (6)	C(4)—C(3)—O(3)	106.4 (3)
O(5)—C(5)	1.424 (6)	O(4)—C(4)—C(3)	106.8 (3)
C(7)—N	1.461 (5)	C(5)—C(4)—C(3)	112.6 (3)
C(8)—C(7)	1.514 (6)	C(5)—C(4)—O(4)	110.7 (4)
C(9)—C(8)	1.529 (6)	O(5)—C(5)—C(4)	113.4 (4)
C(10)—C(9)	1.512 (6)	C(7)—N—C(1)	120.6 (4)
C(11)—C(10)	1.517 (6)	C(8)—C(7)—N	112.0 (3)
C(12)—C(11)	1.526 (7)	C(9)—C(8)—C(7)	110.3 (3)
C(13)—C(12)	1.517 (7)	C(10)—C(9)—C(8)	114.5 (4)
C(14)—C(13)	1.526 (7)	C(11)—C(10)—C(9)	112.4 (4)
C(15)—C(14)	1.510 (8)	C(12)—C(11)—C(10)	115.0 (4)
C(16)—C(15)	1.518 (9)	C(13)—C(12)—C(11)	113.0 (4)
		C(14)—C(13)—C(12)	114.9 (5)
		C(15)—C(14)—C(13)	113.0 (5)
		C(16)—C(15)—C(14)	114.1 (6)

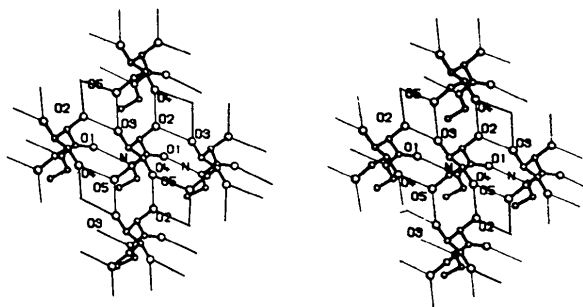


Fig. 3. Pattern of hydrogen bonds.

Table 3. *Torsion angles in the ribose fragment* ($^{\circ}$)

	A	B	C
C(1)–C(2)–C(3)–O(3)	-167	-166	-155
O(2)–C(2)–C(3)–O(3)	69	72	54
C(1)–C(2)–C(3)–C(4)	75	74	90
C(2)–C(3)–C(4)–C(5)	177	176	179
O(3)–C(3)–C(4)–O(4)	178	179	-178
O(3)–C(3)–C(4)–C(5)	57	56	60
C(2)–C(3)–C(4)–O(4)	-62	-60	-60
O(4)–C(4)–C(5)–O(5)	-65	-64	-67
C(3)–C(4)–C(5)–O(5)	55	59	55

References: A this work ($\sigma = 1^{\circ}$); B D-ribose *S,S'*-diethyl dithioacetal (Ducruix, Horton, Pascard, Wander & Prangé, 1978); C D-ribose *S,S'*-diphenyl dithioacetal (Ducruix, Horton, Pascard, Wander & Prangé, 1978).

Table 4. *Hydrogen-bond lengths* (\AA)

O(1)···N(1)	2.977 (5)
O(2)···O(3)	2.741 (5)
O(2)···O(4 ⁱⁱ)	2.736 (5)
O(3)···O(5 ⁱⁱ)	2.805 (5)
O(4)···O(5)	2.742 (5)

Symmetry code: (i) $x+1, y, z$; (ii) $x, y+1, z$.

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Structure of 2,2-Dibromo-3,4-dihydro-1(2H)-naphthalenone

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Abstract. $C_{10}H_8Br_2O$, $M_r = 304.0$, monoclinic, $P2_1/n$, $a = 8.626$ (1), $b = 8.184$ (2), $c = 14.800$ (3) \AA , $\beta = 106.92$ (2) $^{\circ}$, $V = 999.6$ (6) \AA^3 , $Z = 4$, $D_x = 2.020$ g cm^{-3} , $\lambda(\text{Mo } K\alpha) = 0.71073$ \AA , $\mu = 85.5$ cm^{-1} , $F(000) = 584$, ambient temperature, 1013 observed reflections, $R = 0.038$. The C=O bond is essentially coplanar (3.2°) with the aromatic ring due to resonance of its π -system with that of the ring. The non-aromatic ring has a chair conformation, with C(3), the β carbon, displaced by 0.560 (9) \AA from the plane of the aromatic ring. One of the two C–Br bonds, C–Br(axial), is perpendicular to the aromatic ring. The Br(axial)–C–Br(equatorial) angle [107.1 (2) $^{\circ}$] is close to the sp^3 -hybrid angle. The Br(equatorial)–C–C(C=O) angle [109.6 (4) $^{\circ}$] is slightly larger than the Br(axial)–C–C(C=O) angle [104.0 (4) $^{\circ}$] due to repulsion of the Br(equatorial) by the carbonyl oxygen.

Introduction. α -Halocarbonyls have been used with limited success in the preparation of halohydrins irrespective of whether the reduction of α -halocarbonyls is catalytic (Augustine, 1965), nucleophilic

(Yoon & Brown, 1968), or electrophilic (Brown, 1972). Recently, Jensen, Jewett-Bronson, Hadley & French (1982) reported a high yield of aryldihaloalcohols by reduction of α,α -dihalo ketones by a variety of electrophilic reducing agents. Pertinent to this work, the reduction of the haloketone 2,2-dibromo-3,4-dihydro-1(2H)naphthalenone (2,2-dibromo- α -tetralone) with the electrophilic reducing agent diisobutylaluminium hydride gave an 84% yield of the corresponding alcohol. Extensive studies on the rearrangement of α -aryl-2,2-dihalo- α -alkanones with methylmagnesium iodide have been reported by De Kimpe, Verhe, De Buyck & Schamp (1979). The mechanism for the rearrangement proceeds *via* an initially formed carbonyl adduct, and leads to highly sterically hindered alcohols as proven by the synthesis of authentic reaction intermediates. At this department, attempts at the reduction of α -halo-carbonyls, and specifically 2,2-dihalo- α -carbonyls, seemed also to be stereospecific and in particular dependent on the disposition of the C=O bond relative to the C–X bonds (Dirania, 1979). In order to account for the steric factors involved in the reduction of