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The Crystal Structure of Octyl-1-thio-β-*D*-xylopyranoside: A Disordered Smectogenic Structure

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Octyl-1-thio-β-*D*-xylopyranoside, $C_{13}H_{26}O_4S$, forms a mesophase at 373 K and melts at 387 K, with an intermediate solid-to-solid phase transition at 330 K. The structure is disordered at 293 K and remains so at 123 K. The average room temperature [low temperature] crystal structure, at 293 K [123 K], is orthorhombic $P2_12_12_1$, $Z = 4$, with $a = 7.675(2)$ [7.597(3)], $b = 4.830(9)$ [4.762(1)], $c = 40.954(7)$ [40.828(9)] Å, $V = 1518.2$ [1447.0] Å^3, $D_x = 1.216$ g · cm^{-3}, $D_m = 1.218$ g · cm^{-3}. The average structure was solved using MULTAN and refined on 1356 [1573] observations to $R = 0.059$ [0.040], $R_w = 0.066$ [0.059]. The disorder is in the carbohydrate moiety, which has two orientations with equal occupancy. The intercalated alkyl chains are ordered. The diffuse diffraction corresponds to a super lattice a, $2b$, $2c$, with a periodic variation along b.

INTRODUCTION

Octyl-1-thio-β-*D*-xylopyranoside, I, $C_{13}H_{26}O_4S$, is one of a series of alkyl 1-O and 1-S glycopyranosides which have thermotropic liquid crystal phases between room temperature and their melting points.[1-4] As with the *p-n*-alkoxybenzoic acids,[5] all the carbohydrate mesogens hitherto examined have a solid-to-solid phase transition prior to the liquid crystal transition. The heating and cooling thermograms shown in Figure 1 are typical for this type of compound.

In this paper we report the crystal structure of I, which is disordered at room temperature and remains so at liquid nitrogen temperature,

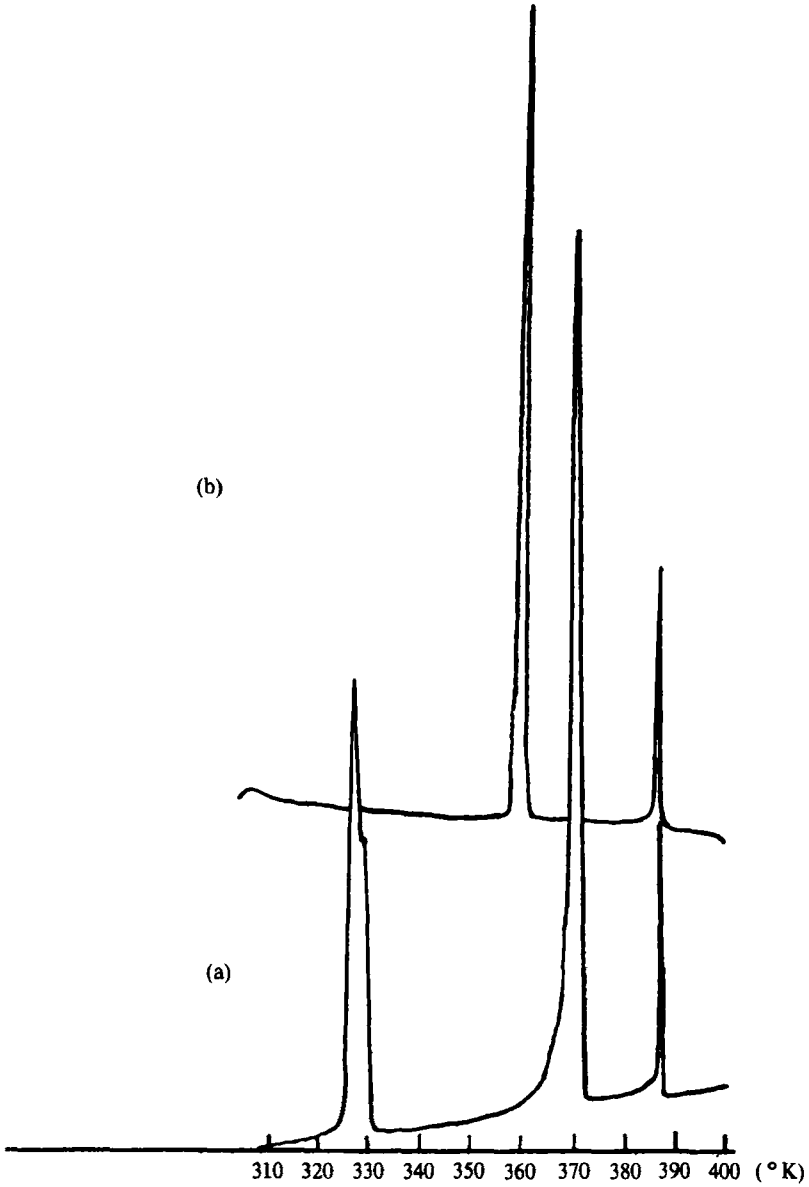
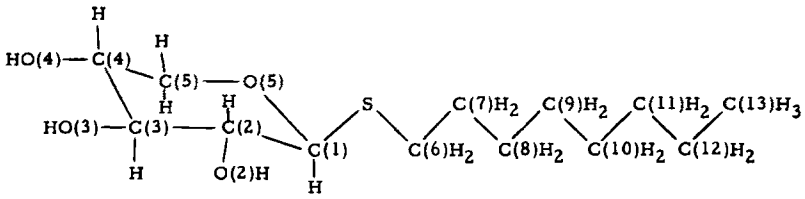


FIGURE 1 Heating and cooling differential scanning calorimeter thermograms for octyl-1-thio-β-*D*-xylopyranoside (rate 5°C/min). The ordinates are in arbitrary units. (a) During heating; (b) during cooling.

123 K. The disorder gives rise to diffuse diffraction spectra which can be interpreted in terms of a superlattice with two-dimensional periodicity.

EXPERIMENTAL

The sample of I was provided by Dr. M. Claeyssens,[6] Rijksuniversiteit, Ghent, Belgium. Single crystals were obtained by recrystallization from acetone at room temperature. The existence of a mesophase was established by the birefringence behavior of the crystals, by the thermograms shown in Figure 1, and by a powder diffraction pattern at 380 K showing a single intense ring of spacing 25.2 Å. This compares with 20.48 Å for the strong long-spacing (002) of the room temperature powder diffraction pattern and 24.9 Å for the longest spacing of the powder pattern of the intermediate crystal phase. Single crystal Weissenberg photographs at room temperature showed, in addition to the sharp Bragg spectra, pendants of diffuse streaks at half-integral values of k. These streaks along the $\vec{c}^*$ direction indicate the lack of correlation along the $\vec{c}$ direction. There was a small variation in intensity along the diffuse streaks corresponding to the superposition of weak non-discrete spectra. On the basis of the sharp Bragg spectra only, the space group is $P2_12_12_1$, $Z = 4$, with unit cell dimensions $a = 7.675(2)$ [7.597(3)], $b = 4.830(9)$ [4.762(1)], $c = 40.954(7)$ [40.828(9)] Å at 293 K and [123 K], respectively. All the diffraction spectra, including the diffuse maxima can be indexed using a superlattice of cell dimensions $a_s = a$, $b_s = 2b$, $c_s = 2c$, with non-space-group systematic extinctions for the superlattice reflections of h_s00 absent for $h_s = 2n + 1$, $0k_s0$ absent for $k_s = 4n + 2$, $00l_s$ absent for $l_s = 4n + 2$, and $(hkl)_s$ absent for $k_s = 2n$ and $l_s = 2n + 1$. (When referred to the smaller cell, these extinctions are the extinctions for space group $P2_12_12_1$ since $h_s = h$, $k_s = 2k$, $l_s = 2l$.)



(I)

Single crystal Bragg diffraction data were collected at room temperature and at liquid nitrogen temperature using *CuKα* radiation (λ = 1.5418 Å) on a CAD-4 diffractometer in the ω-2θ scan mode with a graphite monochromator. At room temperature, a crystal 0.18 × 0.12 × 0.3 mm^3 gave 1356 intensities with $I > 3\sigma(I)$. At liquid nitrogen temperature, a crystal 0.92 × 0.30 × 0.08 mm^3 gave 1573 intensities with $I > 3\sigma(I)$. The unit cell dimensions were obtained by least-squares analysis from 38 reflections with $20° < 2\theta < 29°$. No corrections were made for absorption ($\mu_{CuK\alpha}$ = 18.8 cm^{-1}) or for extinction. No attempt was made to measure the diffraction intensity distribution along the diffuse streaks.

The statistical average structure was determined by applying MULTAN-78,[7] to 200 room temperature structure amplitudes with E values greater than 1.5. The phase set having the best figure-of-merit revealed the sulfur atoms and the alkyl chains and part of the disordered carbohydrate moiety. Subsequent structure factor calculations and Fourier syntheses progressively resolved the atoms affected by the disorder. A full-matrix least-squares refinement was carried out using SHELX-76,[8] starting with the initial assumption of 0.50 occupancy for the disordered atoms. The function minimized was $\Sigma w(|F_0| - k|F_c|)^2$, where $w = K/\sigma_c^2(|F_0|)$; k is a scale factor and K is an empirical parameter. In the final stages of refinement, the occupancy parameter, x, was a variable and the methylene hydrogen atoms were included assuming tetrahedral angles and C–H = 1.00 Å. The refined value of x = 0.51 is not significantly different from 0.50. The methylene hydrogen atom positions were not refined. The hydroxyl hydrogens, with half-occupancy, were not located and were omitted from the structure factor calculations. The non-hydrogen atoms were refined anisotropically and the methylene hydrogen atoms isotropically. The final agreement factors are R = 0.059 [0.040], R_w = 0.066 [0.057], S = 3.15 [4.40] for 293 K and [123 K], respectively. The high values for the goodness of fit, S, are not unexpected, since we are using a model based on the statistical average of a disordered structure. The atomic parameters are given in Table I. Figure 2 shows the thermal ellipsoids at 293 K and 123 K. Observed and calculated structure factors are available.†

†Tables of observed and calculated structure amplitudes, anisotropic temperature parameters for non-hydrogen atoms, and positional and isotropic temperature parameters for hydrogen atoms have been provided to the editor and are available upon request from the authors.

TABLE I

Non-hydrogen atomic parameters ($\times 10^4$) for octyl-1-thio-β-*D*-xylopyranoside

Atom	x/a	y/b	z/c	U_{eq}
C(1)A	7036(9)	−1193(13)	9211(2)	344(15)
	6767(6)	−1285(8)	9220(1)	223(10)
C(2)A	6872(9)	−1162(13)	9598(2)	348(15)
	6599(6)	−1252(8)	9596(1)	176(10)
C(3)A	8409(10)	390(12)	9740(2)	311(15)
	8109(6)	356(8)	9740(1)	184(10)
C(4)A	10137(10)	−672(12)	9612(2)	301(15)
	9888(6)	−707(8)	9613(1)	161(10)
C(5)A	10148(10)	−698(13)	9238(2)	483(15)
	9837(6)	−752(9)	9241(1)	277(10)
C(6)A	5121(10)	−1461(13)	8651(3)	408(15)
	4875(6)	−1513(8)	8646(1)	192(10)
SA	5288(4)	−3081(6)	9036(1)	477(12)
	5004(2)	−3207(4)	9036(0)	223(6)
O(2)A	5311(7)	218(11)	9689(2)	451(15)
	5024(4)	160(7)	9688(1)	239(9)
O(3)A	8407(8)	193(11)	10089(1)	404(15)
	8131(5)	123(7)	10093(1)	201(9)
O(4)A	11572(8)	1090(11)	9702(2)	487(15)
	11284(4)	1116(7)	9706(1)	237(9)
O(5)A	8703(7)	−2543(12)	9124(2)	481(15)
	8433(5)	−2503(8)	9126(1)	270(10)
C(1)A′	7921(10)	−917(13)	9193(2)	368(15)
	7641(6)	−995(8)	9189(1)	182(10)
C(2)A′	7795(10)	−674(12)	9566(2)	298(15)
	7543(6)	−740(8)	9562(1)	125(10)
C(3)A′	9573(10)	164(13)	9711(2)	299(15)
	9321(6)	120(8)	9705(1)	100(10)
C(4)A′	11024(10)	−1572(13)	9577(2)	353(15)
	10798(6)	−1608(8)	9570(1)	155(10)
C(5)A′	10972(10)	−1600(13)	9204(2)	453(15)
	10730(6)	−1607(9)	9195(1)	202(10)
C(6)A′	5629(10)	−741(13)	8640(3)	368(15)
	5330(6)	−983(8)	8639(2)	169(10)
SA′	5903(4)	−2393(7)	9051(1)	467(12)
	5619(2)	−2542(4)	9054(0)	191(6)
O(2)A′	6525(8)	1326(11)	9660(1)	404(15)
	6277(4)	1305(7)	9655(1)	174(9)
O(3)A′	9469(8)	−210(10)	10059(1)	350(15)
	9236(5)	−228(7)	10057(1)	166(9)
O(4)A′	12697(7)	−532(10)	9684(1)	344(14)
	12439(4)	−502(6)	9679(1)	167(9)
O(5)A′	9344(8)	−2464(13)	9092(2)	580(15)
	9075(5)	−2706(8)	9084(1)	282(10)
C(7)	6622(6)	−2157(10)	8394(1)	492(14)
	6418(3)	−2344(5)	8395(1)	230(8)
C(8)	6307(6)	−881(9)	8058(1)	507(14)
	6152(3)	−1055(5)	8056(1)	217(8)
C(9)	7481(6)	−2090(9)	7792(1)	476(14)
	7407(3)	−2275(5)	7801(1)	225(8)

TABLE I *Continued*

Atom	x/a	y/b	z/c	U_{eq}
C(10)	7174(6)	−848(9)	7455(1)	487(14)
	7153(3)	−1027(5)	7460(1)	214(8)
C(11)	8317(6)	−2075(10)	7190(1)	492(14)
	8393(3)	−2274(5)	7201(1)	218(8)
C(12)	8014(7)	−827(10)	6853(1)	555(14)
	8147(4)	−1007(6)	6862(1)	253(9)
C(13)	9154(7)	−2060(10)	6588(1)	721(15)
	9391(4)	−2240(6)	6605(1)	333(9)

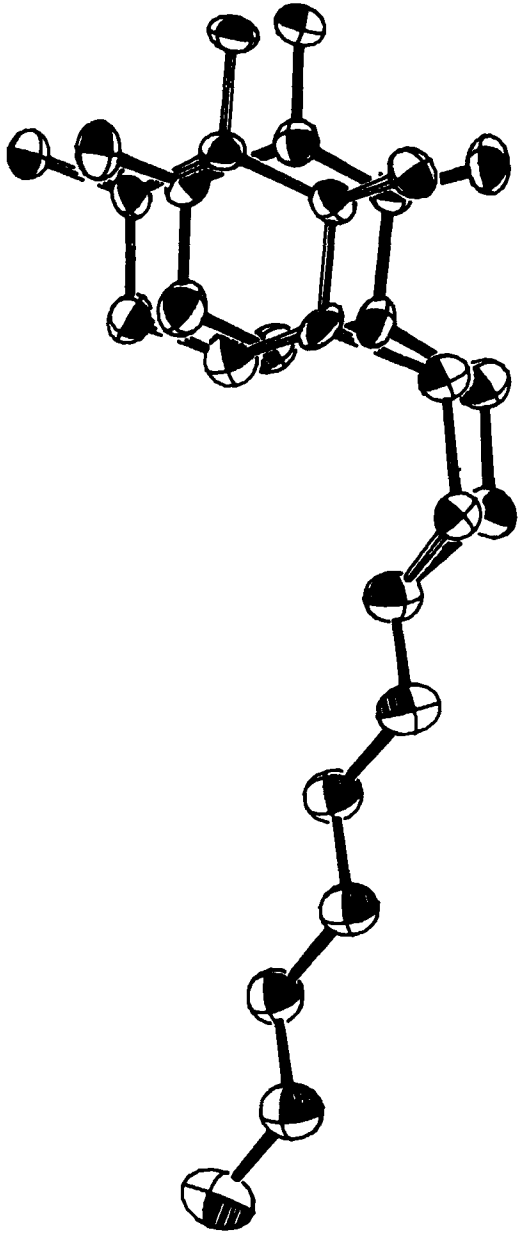
For each atom, the first value is at 293 K, the second at 123 K. Atoms A have occupancy factors $x = 0.5075$ for 293 K, 0.5182 for 123 K. Atoms A' have occupancy factors $1 - x$. E.s.d.'s given in parentheses refer to the least significant digit. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_i U_j a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$.

The average structure

The molecular structure is shown in Figure 2 and the molecular packing is illustrated in Figures 3(a) and 3(b). The alkyl chains are intercalated as in the crystal structure of the analogous mesogen, heptyl-1-thio-α-*D*-mannopyranoside.[2] From C(7) to the terminal methyl C(13), the alkyl chains are ordered. The carbohydrate molecules are hydrogen-bonded in layers parallel to the (001) plane. The occurrence of many O ··· O separations in the range 2.6 to 3.0 Å indicates extensive hydrogen-bonding, but in the absence of information relating to the positions of the hydroxyl hydrogens, the intermolecular bonding could not be described precisely as in the heptyl-1-thio-α-*D*-mannopyranoside crystal structure.

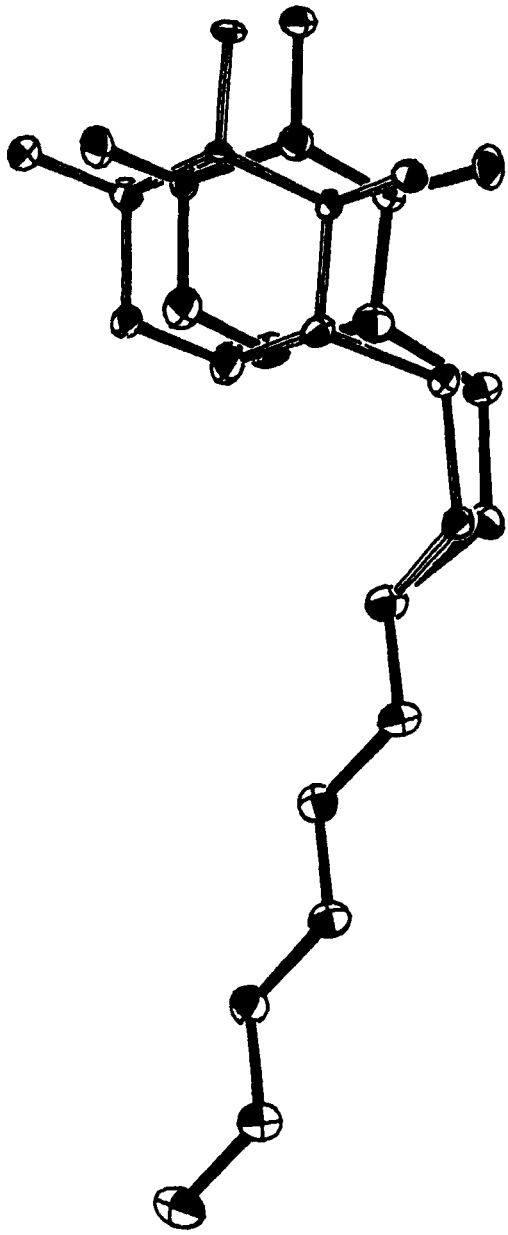
Since the separation of many of the pairs of disordered atoms lies in the range of 0.5 to 1.0 Å, the atomic positions derived for C(1) to C(6) are less accurate than those of the terminal alkyl carbon atoms C(7) to C(13). The carbohydrate moiety has the normal $^4C_1$ chair conformation with C—C and C—O bond lengths and valence angles not significantly different from the standard values. The observed C—C and C—O bond lengths range respectively from 1.51 to 1.59 Å [1.50 to 1.54 Å] and 1.39 to 1.48 Å [1.42 to 1.45 Å]. C—S bond lengths are 1.77 to 1.87 Å [1.79 to 1.86 Å]. The glycosidic torsion angle O(5)—C(1)—S—C(6) has a normal *exo-anomeric* value of −86 to −88°.

More precise dimensions are obtained for the C(7) to C(13) part of the alkyl chain. These values are shown in Figure 4. It is interesting to note that despite the contraction in the unit cell dimensions at the lower temperature and the variations in the individual bond lengths



(a)

FIGURE 2 Molecular structure of octyl-1-thio-β-*D*-xylopyranoside. Thermal ellipsoids at 50% probability. (a) At 293 K; (b) at 123 K.



(b)

FIGURE 2 *Continued*

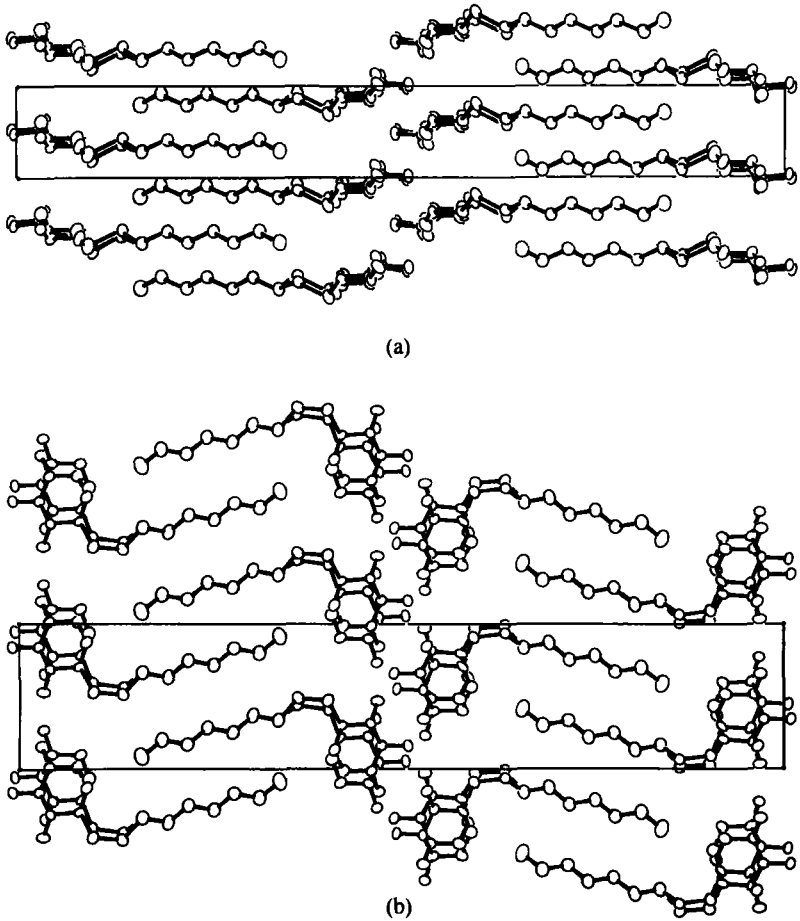


FIGURE 3 Molecular packing in the crystal structure of octyl-1-thio-β-*D*-xylopyranoside. (a) View down *a* axis; *b* axis vertical; (b) view down *b* axis; *a* axis vertical.

and angles at the two temperatures, the overall length from C(7) to C(13) is almost constant (7.647 Å [7.649 Å]).

The superlattice structure

The weak diffuse reflections, which are present at the half-integral values of k, correspond to a superlattice $a, 2b, 2c$ with almost uniform diffraction parallel to the $\vec{c}^*$ direction. This indicates almost no correlation of the modulation along the $\vec{c}$ direction, with complete correlation along the $\vec{a}$ direction. The total diffraction spectra were interpreted as follows.

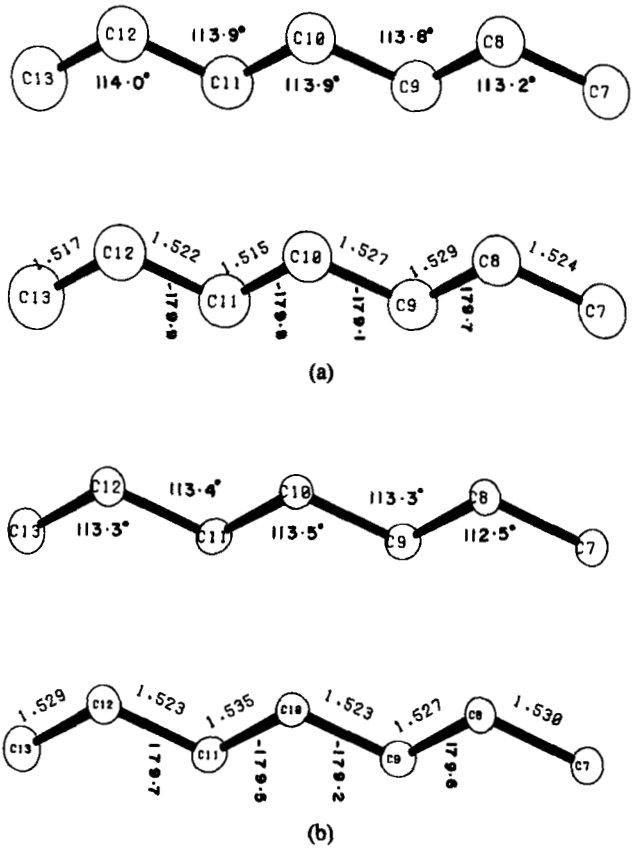


FIGURE 4 Molecular dimensions of the ordered C(7)—C(13) component of the crystal structure of octyl-1-thio-β-*D*-xylopyranoside. (a) At 293 K; (b) at 123 K.

Let $\vec{r}_j$ be the position vector of the jth atom from a suitably chosen origin:

$$\vec{r}_j = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} + \vec{R}_j \qquad (1)$$

a, b, c are the dimensions of the smaller unit cell and $\vec{R}_j$ is the position vector of the jth atom in the unit cell.

If p_x and $p_y = 1 - p_x$ are the occupation probabilities for the ring at the positions x and y, which are different in different unit cells, then the diffraction amplitude as a function of positions $h'k'l'$ (not neces-

sarily integers) in reciprocal space is given by

$$G(h'k'l') = \sum_{\vec{n}} \left[\sum_{j_x} p_x f_{j_x} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_x}\right) + \sum_{j_y} (1 - p_x) f_{j_y} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_y}\right) \right] \tag{2}$$

where $\vec{n} \equiv (n_1 n_2 n_3)$; j_x, j_y are the jth atoms at the x and y positions; f_{j_x}, f_{j_y} are the corresponding atomic scattering factors; and $\vec{S}' = h'\vec{a}^* + k'\vec{b}^* + l'\vec{c}^*$; or,

$$\begin{aligned} G(h'k'l') &= \sum_{\vec{n}} \left[p_x \sum_{j_x} f_{j_x} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_x}\right) + p_x \sum_{j_y} f_{j_y} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_y}\right) \right. \\ &\qquad \left. + (1 - 2p_x) \sum_{j_y} f_{j_y x} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_y}\right) \right] \\ &= \sum_{\vec{n}} \left[p_x \sum_{j} f_j \exp\left(2\pi i \vec{S}' \cdot \vec{r}_j\right) \right. \\ &\qquad \left. + (1 - 2p_x) \sum_{j_y} f_{j_y} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_y}\right) \right] \end{aligned} \tag{3}$$

since

$$\sum_{j_x} f_{j_x} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_x}\right) + \sum_{j_y} f_{j_y} \exp\left(2\pi i \vec{S}' \cdot \vec{r}_{j_y}\right) = \sum_{j} f_j \exp\left(2\pi i \vec{S}' \cdot \vec{r}_j\right) \tag{4}$$

where summation over 'j' runs over all the atoms in the x and y positions.

Now the probability p_x is a function of $\vec{n}$. Since the weak diffuse intensities appear at half integral values of k, we introduce periodic variation of occupation probability along the $\vec{b}$ direction of wave vector $\vec{q}$ of magnitude $1/2b$; p_x is independent of n_1, but it is not independent of n_3. In this approximation, we make the variation completely uncorrelated along the $\vec{c}$ direction by adding an arbitrary phase Φ which depends on n_3. So $p_x = \frac{1}{2} + \delta \exp(2\pi i[\pm \vec{q} \cdot n_2 \vec{b} +$

$\Phi(n_3)]$), where $0 \leq \delta \leq \frac{1}{2}$. Substituting for p_x in Equation (3), we get

$$\begin{aligned} G(h'k'l') = &\sum_{\vec{n}} \left[\tfrac{1}{2} + \delta \exp\left(2\pi i\left[\pm\vec{q}\cdot n_2\vec{b} + \Phi(n_3)\right]\right)\right] \\ &\times \sum_j f_j \exp\left(2\pi i \vec{S}'\cdot\vec{r}_j\right) \\ &- \sum_{\vec{n}} \delta \exp\left(2\pi i\left[\pm\vec{q}\cdot n_2\vec{b} + \Phi(n_3)\right]\right) \\ &\times \sum_{j_y} f_{j_y} \exp\left(2\pi i \vec{S}'\cdot\vec{r}_{j_y}\right) \\ = &\frac{1}{2}\sum_{\vec{n}}\sum_j f_j \exp\left(2\pi i \vec{S}'\cdot\vec{r}_j\right) \\ &+ \sum_{\vec{n}} \delta \exp\left(2\pi i\left[\pm\vec{q}\cdot n_2\vec{b} + \Phi(n_3)\right]\right) \\ &\times \sum_{j_x} f_{j_x} \exp\left(2\pi i \vec{S}'\cdot\vec{r}_{j_x}\right) \end{aligned} \tag{5}$$

using Equation (4).

Now

$$\begin{aligned} \frac{1}{2}\sum_j f_j \exp\left(2\pi i \vec{S}'\cdot\vec{r}_j\right) &= \frac{1}{2}\exp\left(2\pi i\left[n_1\vec{a} + n_2\vec{b} + n_3\vec{c}\right]\right) \\ &\quad\times \sum_j f_j \exp\left(2\pi i \vec{S}'\cdot\vec{r}_j\right) \\ &= \frac{1}{2}F\exp\left(2\pi i \vec{S}'\cdot\left[n_1\vec{a} + n_2\vec{b} + n_3\vec{c}\right]\right) \end{aligned}$$

where F is the structure factor of the molecule with atoms at both x and y positions with full occupancy, and F_x is the structure factor with atoms at position x only. Therefore,

$$\begin{aligned} G(h'k'l') &= \frac{1}{2}F\sum_{\vec{n}} \exp\left(2\pi i \vec{S}'\cdot\left[n_1\vec{a} + n_2\vec{b} + n_3\vec{c}\right]\right) \\ &\quad + F_x\delta\sum_{\vec{n}} \exp 2\pi i\left(\vec{S}'\cdot\left[n_1\vec{a} + n_2\vec{b} + n_3\vec{c}\right] \pm \vec{q}\cdot n_2\vec{b} + \Phi(n_3)\right) \\ &\equiv G_1(\vec{S}') + G_2(\vec{S}') \end{aligned}$$

Therefore the intensity of diffraction is given by

$$|G(h'k'l')|^2 = |G_1(\vec{S}')|^2 + |G_2(\vec{S}')|^2 \tag{6}$$

since the cross-term will vanish because $G_1(\vec{S}')$ and $G_2^*(\vec{S}')$, and *vice versa*, are not non-vanishing at the same points. Now $|G_1(\vec{S}')|^2$ is independent of the "modulation".

The first term in Equation (6) gives the sharp diffraction spectra due to a structure of cell dimensions $\vec{a}, \vec{b}, \vec{c}$ with intensity maxima at points $h = h'$, $k = k'$, $l = l'$, where h, k, l are integers. The structure contains a molecule which has atoms at both the x and y positions, but only of half occupancy.

The second term in Equation (6) describes the diffuse spectra, where

$$|G_2(S')|^2 = F_x^2\delta^2 \frac{\sin^2 N_1\pi(\vec{S}'\cdot\vec{a})}{\sin^2\pi(\vec{S}'\cdot\vec{a})} \cdot \frac{\sin^2 N_2\pi\left(\left[\vec{S}' \pm \vec{q}\right]\cdot\vec{b}\right)}{\sin^2\pi(\vec{S}'\cdot\vec{b})} \cdot N_3 \tag{7}$$

where N_1, N_2, N_3 are the number of lattice points along $\vec{a}, \vec{b}, \vec{c}$ directions, respectively, and $|\Sigma\exp(2\pi i[\vec{S}'\cdot n_3\vec{c} + \Phi(n_3)])|^2 = N_3$ because $\Phi(n_3)$ is arbitrary.

Equation (7) gives intensity maxima at points

$$\left.\begin{array}{c} \vec{S}'\cdot\vec{a} = h \quad \text{or} \quad h' = h \\ (\vec{S}' \pm \vec{q})\cdot\vec{b} = k \quad \text{or} \quad k' = k \pm \frac{1}{2} \end{array}\right\} \tag{8}$$

$\vec{q}$ is in the same direction as $\vec{b}$, therefore $\vec{q}\cdot\vec{b} = \frac{1}{2}$. This describes the reciprocal lattice lines of uniform density parallel to the $\vec{c}^*$ axis at half-integral values of k.

This model describes the observed diffraction data, except for the small variation of intensity along the weak diffuse lines. It is consistent with the crystal structure.

In the $\vec{a}$ direction the carbohydrate rings are in contact, as shown in Figure 3b, and thus their disorder is correlated, whereas in the $\vec{c}$ direction they are separated by the ordered parts of the hydrocarbon chains and their disorder is uncorrelated.

The structure of the liquid crystal phase

In the homologous series from propyl to octyl-1-*S*-β-xylopyranosides, only the heptyl and octyl compounds are thermotropic mesogens. This property is associated with a discontinuity in the melting points; propyl, 107 °C; butyl, 100 °C; pentyl, 115 °C; hexyl, 160 °C; heptyl,

96°C; octyl, 114°C, which suggests that there is a fundamental change in crystal structure between the hexyl and heptyl derivatives, of which only the latter is mesogenic. The heptyl and octyl compounds show a single intensity diffraction ring corresponding to d = 23.5 and 25.2 Å in the liquid crystal phase. The distance from C(13) to C(13′) across the hydrogen-bonded carbohydrate bilayer in the crystal structure is 28 Å. The static bilayer thickness, including a van der Waals radius, is therefore about 32 Å.

If the molecular clusters in the liquid crystal phase correspond to the bilayers formed by the pairs of hydrogen-bonded molecules, the observed mesophase periodicity of 24 Å requires an effective tilt angle, due to thermal motion and misalignment of the alkyl chains of 35–40°.

The intermediate phase might then correspond to the onset of rotational disorder in the alkyl chains, which is necessary prior to the disengagement of the intercalated hydrocarbon chains. It is noteworthy that this intermediate crystal phase is observed in all the carbohydrate liquid crystals so far examined.[4] As shown in Figure 1, the intermediate phase is metastable at room temperature on cooling. (The small inflection on the first peak of the heating curve of the thermogram is reproducible.) The structure analysis of this intermediate crystalline phase should provide a better insight into the nature of the mesophase transition.

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