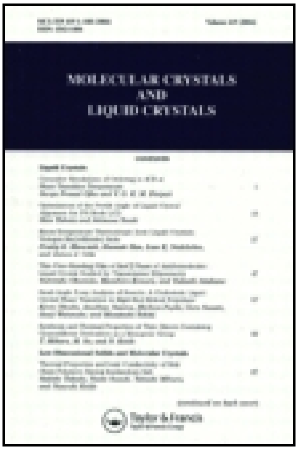


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Crystal Structure of Octyl-D-gluconate: A Mesogenic Structure with Monolayer Head-to-Tail Molecular Packing

Sarama Bhattacharjee [a] , George A. Jeffrey [a] & John W. Goodby [b]

[a] Department of Crystallography, University of Pittsburgh, Pittsburgh, PA, 15260, USA

[b] AT&T Laboratories, Murray Hill, NJ, 07974, USA

To cite this article: Sarama Bhattacharjee , George A. Jeffrey & John W. Goodby (1985): The Crystal Structure of Octyl-D-gluconate: A Mesogenic Structure with Monolayer Head-to-Tail Molecular Packing, Molecular Crystals and Liquid Crystals, 131:3-4, 245-255

To link to this article: http://dx.doi.org/10.1080/00268948508085047

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 245–255
0026-8941/85/1314–0245/$20.00/0

The Crystal Structure of Octyl-D-gluconate: A Mesogenic Structure with Monolayer Head-to-Tail Molecular Packing

SARAMA BHATTACHARJEE and GEORGE A. JEFFREY,
Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, USA

and

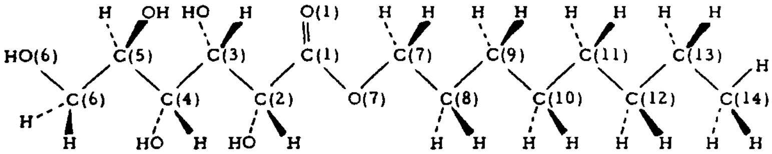
JOHN W. GOODBY
AT&T Laboratories, Murray Hill, NJ 07974, USA

(*Received June 3, 1985*)

Octyl-D-gluconate, $C_{14}H_{28}O_7$, is monoclinic, $P2_1$, $Z = 2$, $a = 4.798(1)$, $b = 32.353(8)$, $c = 5.241(1)$ Å, $\beta = 94.90(1)°$ at room temperature. On heating, the crystal undergoes three crystal-to-crystal transitions, two at 62 to 67°C and a more pronounced one at 90°C. Melting to a liquid crystal smectic phase takes place at 158°C, which melts again within one degree to an isotropic liquid. On cooling, the liquid crystal phase is metastable to 110°, when crystallization takes place through four crystal phases down to room temperature. In the room temperature crystal structure, both the acyclic gluconate moiety and the alkyl chains are in the extended conformation. The gluconate moieties are hydrogen bonded. The molecular packing is monolayer and head-to-tail, in contrast to the bilayer head-to-head packing of the long chain alkyl carbohydrates having cyclic sugar residues. The alkyl chains are aligned parallel with no intercalation.

INTRODUCTION

The crystal structure of the carbohydrate mesogen, n-octyl-D-gluconate, $C_{14}H_{28}O_7$, **I**, differs from those previously reported in this series of investigations,[1-5] in four respects. One, the carbohydrate moiety is acyclic; two, the molecular packing is monolayer and head-to-tail rather than bilayer and head-to-head; three, the parallel alkyl chain packing is not intercalated; and four, there are four crystalline phases prior to the transformation to a liquid crystal phase. In the alkyl glycosides previously studied, only three crystalline phases are observed prior to the liquid crystal transition. It remains to be discovered whether these properties are characteristic of the homologous series with different alkyl chain lengths and with n-octyl gluconamide, the crystal structure of which is isostructural with the gluconate.[6]



(I)

EXPERIMENTAL

Liquid crystal properties of n-Octyl-D-gluconate

n-Octyl-D-gluconate was shown to exhibit enantiotropic liquid crystalline behavior by both thermal optical microscopy and differential scanning calorimetry. Three studies were carried out using polarizing light microscopy. Firstly, a simple melting study was performed with a crystal sandwiched between a clean microscope slide and coverslip. The material underwent crystal-crystal changes at 65°C and 90°C, the latter change being more pronounced; the integrity of the crystal was maintained to the clearing point. At the clearing point, the crystal broke down to give a liquid crystal which exhibited a homeotropic and oily-streak texture. Within one degree the liquid-crystalline phase melted via spherulites to the isotropic liquid. Cooling of the isotropic phase resulted in the formation of batonnets which coalesced and on adhering to the surface they produced a homeotropic texture. Considerable supercooling of the crystal phase was observed, and the liquid-crystalline phase was obtained over temperature ranges of 20–30°. A second study of the melting process was carried out with a sample sandwiched between two glass plates which had previously been coated with a nylon 6-10 surfactant. On cooling from the isotropic liquid this time, the liquid crystal phase was formed via batonnets; the batonnets coalesced and on adhering to the surface they formed a focal-conic texture, shown in Figure 1. This texture was

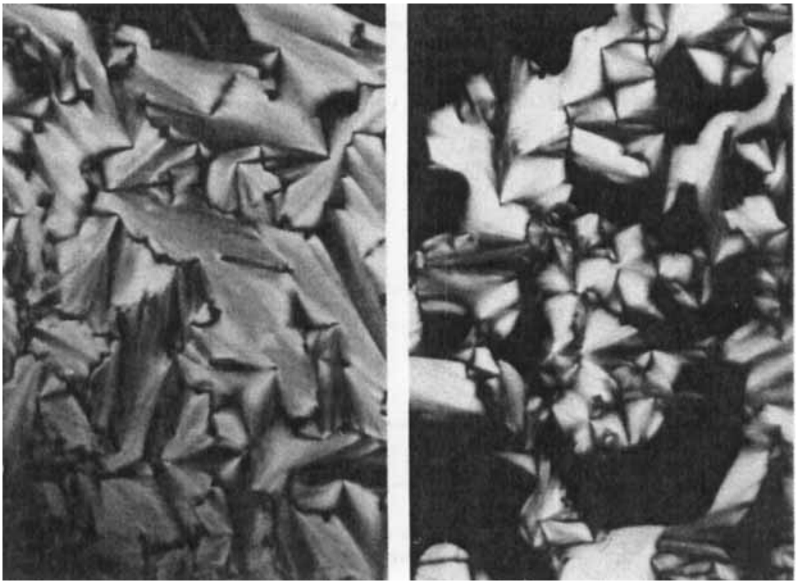


FIGURE 1 (a) The focal-conic defect texture of the smectic phase of octyl D-gluconate. (b) The contact region between the phases of octyl D-gluconate and n-dodecyl-1-O-β-D-glucopyranoside. The continuous texture indicates that the two phases are miscible, and have the same classification.

characterized by crosses of optical discontinuities (ellipse and hyperbola), indicating that the phase is composed of liquid-like layers which are capable of bending in three dimensions. Coupled with the observation that the phase exhibits a homeotropic texture strongly suggests that the phase is of the A type. In a third study, a sharp contact was made between the gluconate and n-dodecyl-1-O-β-D-glucopyranoside in a cell where the glass surfaces had been treated with nylon. This contact preparation was heated to the isotropic and cooled slowly with the contact region under observation. When both materials were in their liquid crystal forms, the texture of the two phases was continuous through the contact region. This demonstrates that the smectic phase of n-octyl-D-gluconate is the same as that of n-dodecylglucopyranoside,[5] which is thought to have an interdigitated smectic A structure. This implies a similar type of association of the molecules in the liquid crystal phase, although the room temperature crystal structure of the gluconate ester is very different from that hitherto found for the alkyl pyranosides.

Differential scanning calorimetry shows that the ester possesses four crystal phases on the first heating cycle. The enthalpy for the

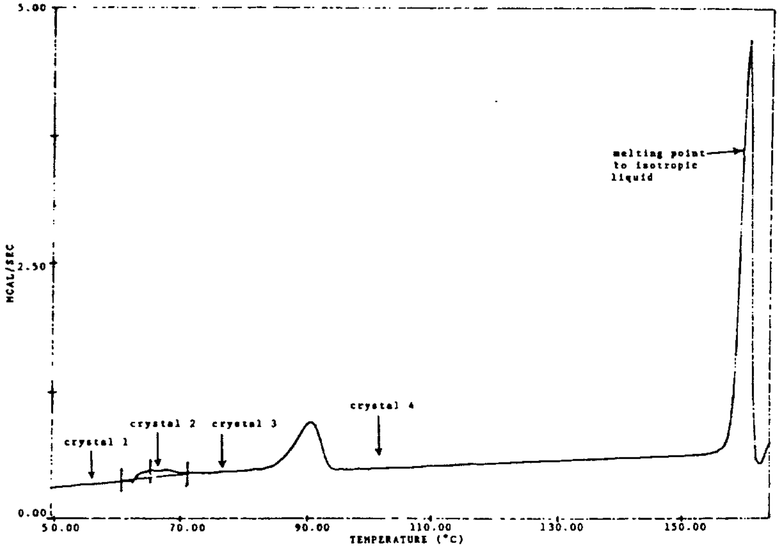


FIGURE 2 (a) The first heating cycle for octyl D-gluconate by differential scanning calorimetry showing a crystal 3 to crystal 4 change at 90.41°C and a clearing point at 160.08°C.

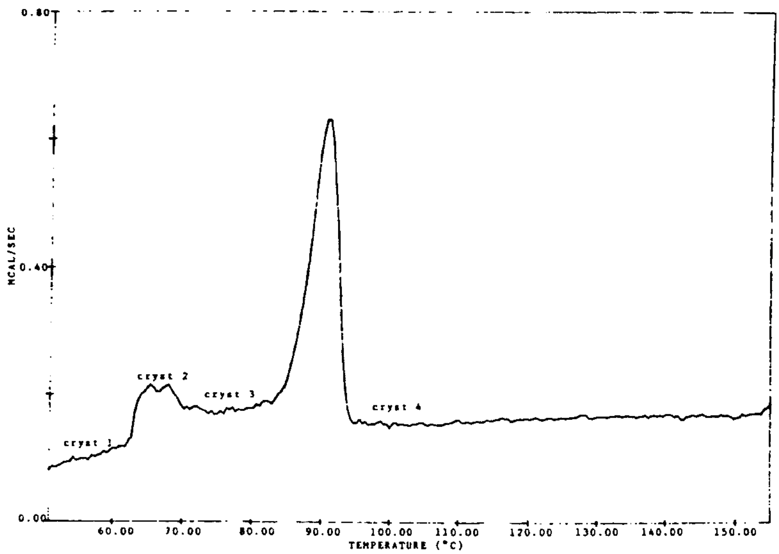


FIGURE 2 (b) The first heating cycle for octyl D-gluconate showing crystal 1 to crystal 2 to crystal 3 changes at 65.16°C.

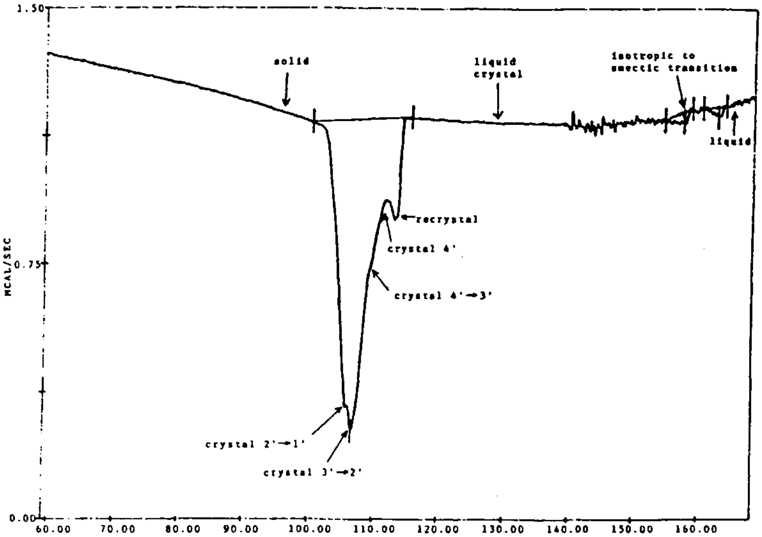


FIGURE 2 (c) First cooling cycle of octyl D-gluconate after 30 minutes at 160°C. The liquid crystal phase is metastable to 110°C, then crystalline through four phases. The phases may not be the same as in the melting process.

liquid crystal to isotropic liquid phase change is unfortunately incorporated into the enthalpy for the crystal to mesophase transition. However, on cooling this transition is seen quite clearly. The cooling cycle shows considerable supercooling of the solid, and with the onset of recrystallization, a mesophase-crystal and three crystal-crystal phase changes are observed. The four crystals formed, however, are not the same as those formed in the melting process because cycling of the sample does not duplicate the original melting. The differential scanning thermograms shown in Figure 2 were obtained on a Perkin-Elmer DSC-4-TADS system (scan rate 2°/min). For the optical studies, a Zeiss universal transmitted light polarizing microscope fitted with a Mettler FP52 hot-stage in conjunction with a FP5 control unit was used.

The crystal structure analysis

The best crystals available were adequate for the determination of the molecular packing, but were not good enough to permit an accurate analysis of the molecular structure. The crystal data for the room temperature phase are given in Table I. The unit cell dimensions

TABLE I

Crystal and structure analysis data for octyl-D-gluconate

$C_{14}H_{28}O_7$
Space group $P2_1$, $Z = 2$
Cell dimensions: $a = 4.798(1)$, $b = 32.353(8)$, $c = 5.241(1)$ Å,
$\beta = 94.90(1)^\circ$
Density: 1.266 g cm^{-3} (calc); 1.254 g cm^{-3} (obs, by flotation)
Size of crystal: 0.25 × 0.37 × 0.28 mm^3
Diffractometer: CAD-4 in ω-2θ mode
Radiation: CuKα Ni-filter
Number of intensities: 1556, with $\theta \leq 50^\circ$
Final agreement factors: $R = 0.098$, $R_w = 0.105$

were obtained from a least squares analysis of the θ values for 25 reflections with $32^\circ < \theta < 43^\circ$. No corrections were made for absorption (μCuKα = 7.5 cm^{-1}).

The crystal structure was determined by the direct method, MULTAN-78,[7] from 184 structure amplitudes with E-values > 1.5. The E-map based on the phase set with the best combined figure of merit gave the positions of 20 of the 21 non-hydrogen atoms. A subsequent Fourier synthesis revealed the last atom, which was C(14) of the alkyl chain. Parameter refinement was by full-matrix least squares using SHELX-76.[8] The quantity minimized was $\Sigma w(|F_o|-k|F_c|)^2$, where $w = K/\sigma^2(|F_o|)$; k is a scale factor and K is an empirical factor which was adjusted after each refinement cycle. The methylene hydrogen atoms were included at calculated positions, and were assigned isotropic temperature factors equivalent to the anisotropic factors of the carbon atoms to which they are bonded. At this stage, peaks corresponding to hydroxyl hydrogens were sought on a difference map at positions consistent with reasonable geometry. Since these positions gave atomic coordinates for the hydroxyl hydrogens which could not be refined, they remained undetermined. The final coordinates of non-hydrogen atoms are given in Table II. Observed and calculated structure factors are available.†

The molecular and crystal structure

The conformation of the molecule, shown in Figure 3, is fully extended except for the terminal primary alcohol group of the gluconate residue. The hydroxyl O(6)H is oriented –synclinal about C(5)-C(6)

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

TABLE II

Non-hydrogen atomic parameters ($\times$ 10^4) for octyl-D-gluconate

	x/a	y/b	z/c	U_{eq}
C(1)	7857(23)	−222(4)	8386(18)	364(57)
C(2)	6059(19)	−593(4)	8588(15)	302(48)
C(3)	7671(18)	−970(4)	7865(16)	284(50)
C(4)	5880(18)	−1345(4)	7046(16)	266(46)
C(5)	7633(20)	−1703(4)	6169(16)	308(50)
C(6)	5965(24)	−2088(4)	5382(19)	379(60)
C(7)	10851(24)	322(4)	10346(16)	369(57)
C(8)	12010(25)	476(4)	12996(16)	407(61)
C(9)	13825(25)	855(4)	12721(18)	402(60)
C(10)	14874(25)	1033(4)	15335(17)	390(58)
C(11)	16573(26)	1418(4)	15178(18)	467(64)
C(12)	17657(27)	1611(4)	17717(19)	457(66)
C(13)	19195(36)	1999(5)	17497(20)	630(88)
C(14)	20355(34)	2203(5)	20047(21)	693(92)
O(1)	8631(20)	−111(3)	6251(12)	600(53)
O(2)	5184(14)	−633(3)	11082(11)	380(39)
O(3)	9770(12)	−1067(3)	9874(11)	260(31)
O(4)	4417(13)	−1508(3)	9071(11)	332(36)
O(5)	9194(14)	−1558(3)	4102(11)	342(37)
O(6)	3894(15)	−1996(0)	3262(12)	376(41)
O(7)	8919(18)	−25(3)	10526(13)	559(51)

Estimated standard deviations given in parentheses refer to the least significant digit.
$U_{eq} = \frac{1}{3}\Sigma\Sigma U_i U_j a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$.

with respect to O(5)H. The molecule has two segments with a twist at C(1)-C(2) so that carbon atoms C(2) to C(6) and and atoms C(1), O(1), O(7), C(7)-C(14) lie approximately in two planes inclined to each other with a dihedral angle of 72°.

The molecular dimensions are given in Table III. They are normal within the experimental errors. No significance is attached to the variation in the C-C bond lengths. The packing of the molecules is shown in Figure 4. The gluconate moieties form layers, one residue wide, which extend in the *ac* directions. The alkyl chains pack in parallel alignment without intercalation. The volume per (CH_2) group is 22 Å^3, and the alkyl chain axis makes an angle of 46° with *b*. The structure is isostructural with that of octyl-D-gluconamide[6] (I with O(7) replaced by NH), and may be representative of a whole class of compounds in which the carbohydrate moiety is acyclic.

This packing arrangement is different from that observed in decyl-1-O-α-glucopyranoside,[9] heptyl-1-S-α-D-mannopyranoside,[1] octyl-1-S-D-xylopyranoside,[2] and glycosylphytosphingosine hydrochloride,[10] where the polar sugar moieties form double molecular layers and the alkyl chains intercalate to form a bilayer arrangement. Packing with-

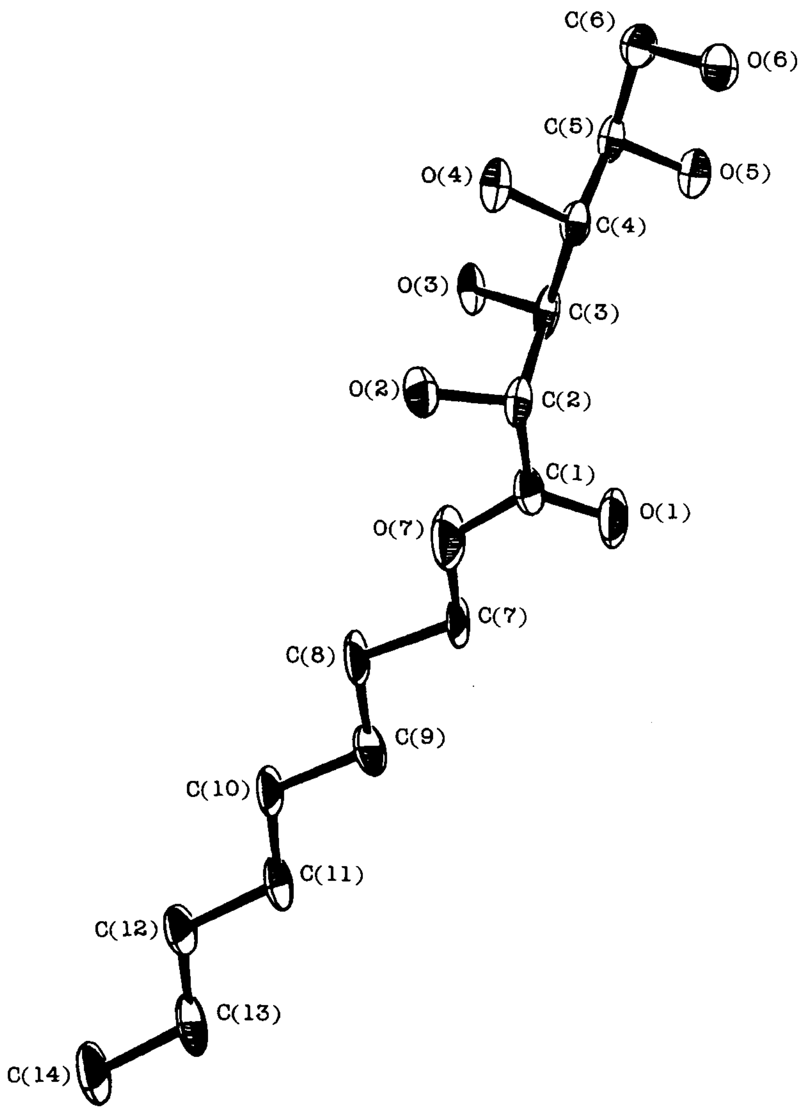

FIGURE 3 Conformation of the molecule. Thermal ellipsoids are shown with 50% probability.

out intercalation of the alkyl chains is observed in the crystal structures of the cerebrosides,[11] but these are bilayer structures with head-to-head arrangements.

In the absence of information about the positions of the hydroxyl hydrogen atoms, the hydrogen bonding scheme could not be determined. All the hydroxyl oxygens except O(2) have two intermolecular

TABLE III

Molecular dimensions of the molecule
The estimated standard deviations are 0.05 Å and 2°. No significance is attached to the variations in C-C bond lengths

(a) *Bond lengths*		(b) *Bond angles*	
C(1)-C(2)	1.49	C(1)-C(2)-C(3)	108.8
C(2)-C(3)	1.51	C(2)-C(3)-C(4)	115.1
C(3)-C(4)	1.53	C(3)-C(4)-C(5)	112.1
C(4)-C(5)	1.53	C(4)-C(5)-C(6)	114.4
C(5)-C(6)	1.52	C(7)-C(8)-C(9)	110.1
C(7)-C(8)	1.53	C(8)-C(9)-C(10)	111.5
C(8)-C(9)	1.52	C(9)-C(10)-C(11)	113.8
C(9)-C(10)	1.53	C(10)-C(11)-C(12)	116.2
C(10)-C(11)	1.49	C(11)-C(12)-C(13)	114.8
C(11)-C(12)	1.52	C(12)-C(13)-C(14)	116.3
C(12)-C(13)	1.47	O(1)-C(1)-C(2)	120.6
C(13)-C(14)	1.55	O(2)-C(2)-C(1)	111.1
C(1)-O(1)	1.26	O(2)-C(2)-C(3)	110.9
C(1)-O(7)	1.35	O(3)-C(3)-C(2)	109.7
C(2)-O(2)	1.41	O(3)-C(3)-C(4)	112.2
C(3)-O(3)	1.43	O(4)-C(4)-C(3)	112.7
C(4)-O(4)	1.42	O(4)-C(4)-C(5)	105.3
C(5)-O(5)	1.45	O(5)-C(5)-C(4)	108.3
C(6)-O(6)	1.46	O(5)-C(5)-C(6)	110.9
C(7)-O(7)	1.46	O(6)-C(6)-C(5)	110.4
		O(7)-C(1)-C(2)	120.1
		O(7)-C(1)-O(1)	118.9
		O(7)-C(7)-C(8)	111.9
		C(1)-O(7)-C(7)	120.3

(c) *Torsion angles*	
O(7)-C(1)-C(2)-C(3)	-108.7
C(2)-C(1)-O(7)-C(7)	175.6
C(1)-C(2)-C(3)-C(4)	-159.1
C(2)-C(3)-C(4)-C(5)	176.0
C(3)-C(4)-C(5)-C(6)	178.8
C(4)-C(5)-C(6)-O(6)	60.0
O(7)-C(7)-C(8)-C(9)	-175.8
C(8)-C(7)-O(7)-C(1)	-174.9
C(7)-C(8)-C(9)-C(10)	176.5
C(8)-C(9)-C(10)-C(11)	-177.5
C(9)-C(10)-C(11)-C(12)	179.6
C(10)-C(11)-C(12)-C(13)	-177.1
C(11)-C(12)-C(13)-C(14)	-179.5

O...O distances between 2.71 and 2.76 Å, which correspond to hydrogen-bond separations. An unusual feature is that the carbonyl oxygen, which is generally a strong hydrogen-bond acceptor, has no intermolecular O...O distance less than 3.03 Å, which is to the ester oxygen O(7) and therefore cannot be a hydrogen bond. The hydroxyl oxygen O(2) must only be involved in *intra*molecular hydrogen bonding, since it has no intermolecular O...O distances less than 2.97 Å, and two intramolecular separations of 2.73 Å to O(4) and 2.68 Å to the ester oxygen O(7).

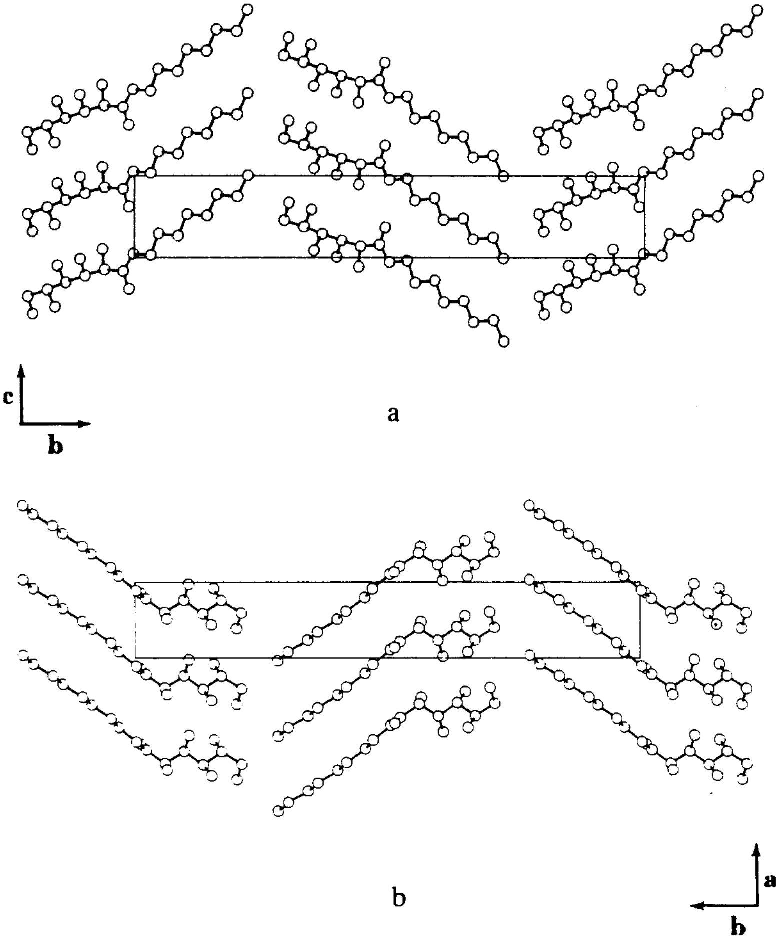

FIGURE 4 Packing of the molecules in the crystal structure. (a) View down the *a* axis, *c* axis is vertical. (b) View down the *c* axis, *a* axis is vertical.

Acknowledgments

This research is supported by the U.S. Public Health Service, National Institutes of Health, Grant No. GM-24526.

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