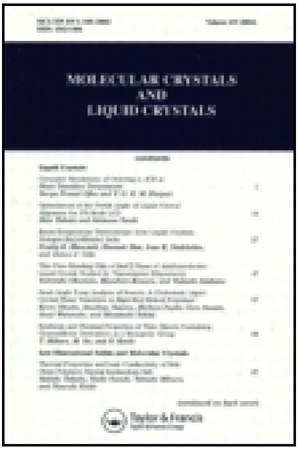

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Crystal Structure of Undecyloxybenzoic Acid

N. K. Lokanath [a] , D. Revannasiddaiah [a] , M. A. Sridhar [a] & J. Shashidhara Prasad [a]

[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, India

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Crystal Structure of Undecyloxybenzoic Acid

N.K. LOKANATH*, D. REVANNASIDDAIAH, M.A. SRIDHAR and
J. SHASHIDHARA PRASAD

Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India

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The crystal and molecular structure studies of the mesogen, undecyloxybenzoic acid are reported. The compound($C_{18}H_{28}O_3$) crystallises in the triclinic space group $P\bar{1}$ with $a = 8.0495(10)$Å, $b = 23.024(4)$Å, $c = 4.7383(14)$Å, $\alpha = 92.97(3)°$, $\beta = 102.910(14)°$, $\gamma = 82.319(19)°$, $V = 848.1(3)$Å^3 $Z = 2$, $D_{(cal)} = 1.145$ Mg/m^3, $\mu = 0.076$ mm^{-1}, $F_{000} = 320$, GoF = 1.072, $R1 = 0.071$. It is shown that the phase transitions and physical properties of the mesogen are strongly dependent on the dimer formation.

Keywords: Crystal structure; mesogen; undecyloxybenzoic acid; dimer

INTRODUCTION

The crystal structure studies of mesogens are important to understand the phase transitions and physical behaviour. In view of this, the crystal structure study of undecyloxybenzoic acid was undertaken. The compound exhibits two mesophases-smectic phase in the range 94–121°C and nematic phase in the range 121–138°C.

EXPERIMENTAL

Clear rectangular shaped crystals of the title compound (procured from M/s Merck Ltd., England) were obtained from a solution in ethyl alcohol. A crystal

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* Corresponding Author: E-mail: mysxrd@giasbg01.vsnl.net.in, Tel: +91–821–516133, Fax: +91–821–516133.

with approximate size of 0.1 × 0.1 × 0.15 mm^3 was mounted on a Rigaku AFC7S diffractometer equipped with a graphite monochromated Mo$K\alpha$ X-ray source (λ = 0.71069Å). The unit cell parameters were obtained by using the method of short vectors followed by least-squares refinement of 16 reflections. All reflections could be indexed with respect to a triclinic cell. Lorentz and polarisation corrections were applied. The data were reduced using teXsan [1] data reduction program. The structure was solved by direct methods using SHELXS-97 [2]. The peak list from SHELXS-97 revealed the partial structure. The difference Fourier map computed after a couple of cycles of full-matrix least-squares refinement showed the positions of the remaining non-hydrogen atoms. The refinement of the structure by full-matrix least-squares using SHELXL-97 [3] with isotropic temperature factors for all non-hydrogen atoms converged to a residual of 0.18. The hydrogen atoms were generated at chemically acceptable positions and were not refined. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was carried out using SHELXL-97 [3] based on 1477 reflections and 195 parameters which converged to $R = 0.072$ for 1340 observed reflections with $I > 2\sigma(I)$. The maximum and minimum peaks on the final difference Fourier map correspond to 0.307 and -0.343 e^-. $Å^{-3}$ respectively and goodness of fit is 1.072.

RESULTS AND DISCUSSION

The positional parameters and equivalent temperature factors for the non-hydrogen atoms are given in Table I. Table II gives the bond lengths, bond angles and torsion angles. Figure 1 represents the ORTEP [4] diagram of the molecule with thermal ellipsoids at 50% probability. Figure 2 shows the packing of molecules in the unit cell down the *c* axis. The packing indicates strong layering of molecules which is a prerequisite for the occurrence of smectic phase. Two molecules are bound into dimers through well defined hydrogen bonds, as is observed in the case of crystalline aggregates of fatty acids [5].

The atoms of the phenyl ring along with the carbonyl group O1 to C11 are planar. The extended chain of alkyl atoms (C14 to C21) are in a plane. The torsion angles are given in Table II. The alkyl chain is bent at C13 atom. The plane of the alkyl atoms makes an angle of 75.1(2)° with the plane containing atoms O1 to C11. The alkyl chain is fully extended and nearly parallel to the *b* axis. The angle between the aliphatic atoms and the *b* axis is 3.5(2)°. This angle increases with the chain length: the angle in the case of octyioxy benzoic acid is 56.93° [6]. The intermolecular hydrogen bond between atoms O3-H3···O1 has length 2.625(4)Å and angle 168(4)° with symmetry code $1 - x$, $1 - y$, $- z$ (O3-H3 – 1.02Å, H3···O1 – 1.62Å).

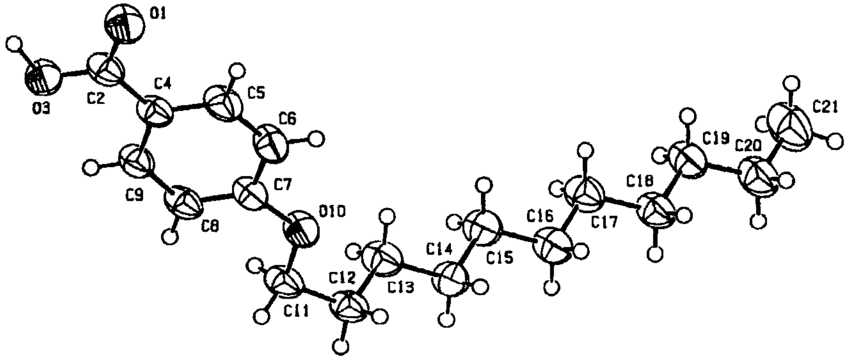

FIGURE 1 ORTEP of the molecule at 50% probability

TABLE I Atomic coordinates and equivalent thermal parameters (Å^2) of the non-hydrogen atoms

Atom	*x*	*y*	*z*	U_{eq}
O1	0.5373(3)	0.44265(11)	0.2292(6)	0.0658(11)
C2	0.3778(6)	0.45718(17)	0.2118(8)	0.0499(12)
O3	0.2950(3)	0.50052(13)	0.0595(6)	0.0607(11)
C4	0.2833(4)	0.42444(16)	0.3618(8)	0.0453(12)
C5	0.3673(5)	0.37666(17)	0.5282(9)	0.0574(13)
C6	0.2804(5)	0.34544(16)	0.6728(8)	0.0558(13)
C7	0.1048(5)	0.36029(16)	0.6501(8)	0.0456(12)
C8	0.0211(5)	0.40793(17)	0.4918(8)	0.0504(12)
C9	0.1094(5)	0.43934(15)	0.3460(8)	0.0486(12)
O10	0.0311(3)	0.32545(10)	0.7956(6)	0.0570(10)
C11	–0.1486(4)	0.33929(17)	0.7907(9)	0.0549(12)
C12	–0.1995(5)	0.29023(15)	0.9376(8)	0.0540(12)
C13	–0.1987(5)	0.23293(16)	0.7663(8)	0.0599(13)
C14	–0.2327(5)	0.18118(15)	0.9176(8)	0.0555(12)
C15	–0.2263(5)	0.12451(16)	0.7383(8)	0.0592(13)
C16	–0.2496(5)	0.07119(15)	0.8913(8)	0.0602(13)
C17	–0.2428(5)	0.01463(16)	0.7142(8)	0.0601(13)
C18	–0.2624(5)	–0.03915(16)	0.8690(8)	0.0591(13)
C19	–0.2589(5)	–0.09533(16)	0.6916(8)	0.0601(13)
C20	–0.2774(5)	–0.14861(17)	0.8483(10)	0.0706(14)
C21	–0.2780(6)	–0.20474(18)	0.6688(10)	0.0893(17)

TABLE II Road Lengths (Å), bond angles(°) and torsion augles(°)

Atoms	*Length*	*Atoms*	*Length*
O1-C2	1.268(4)	C11-C12	1.504(5)
C2-O3	1.282(4)	C12-C13	1.513(5)
C2-C4	1.450(6)	C13-C14	1.508(5)
C4-C9	1.383(5)	C14-C15	1.521(5)
C4-C5	1.393(5)	C15-C16	1.511(5)
C5-C6	1.369(5)	C16-C17	1.513(5)
C6-C7	1.390(5)	C17-C18	1.514(5)
C7-O10	1.356(4)	C18-C19	1.506(5)
C7-C8	1.372(5)	C19-C20	1.507(5)
C8-C9	1.383(5)	C20-C21	1.510(5)
O10-C11	1.434(4)		

Atoms	*Angle*	*Atoms*	*Angle*
O1-C2-O3	121.4(4)	C4-C9-C8	121.1(4)
O1-C2-C4	120.6(4)	C7-O10-C11	118.4(3)
O3-C2-C4	118.0(4)	O10-C11-C12	106.9(3)
C9-C4-C5	118.0(3)	C11-C12-C13	113.8(3)
C9-C4-C2	121.7(4)	C14-C13-C12	115.5(3)
C5-C4-C2	120.2(4)	C13-C14-C15	113.3(3)
C6-C5-C4	121.1(3)	C16-C15-C14	114.4(3)
C5-C6-C7	120.1(4)	C15-C16-C17	114.7(3)
O10-C7-C8	125.4(3)	C16-C17-C18	114.9(3)
O10-C7-C6	115.1(3)	C19-C18-C17	115.0(3)
C8-C7-C6	119.4(4)	C18-C19-C20	114.6(3)
C7-C8-C9	120.2(4)	C19-C20-C21	114.6(4)
C11-C12-C13-C14	174.5(3)	C15-C16-C17-C18	178.8(3)
C12-C13-C14-C15	−178.7(3)	C16-C17-C18-C19	178.9(3)
C13-C14-C15-C16	176.6(3)	C17-C18-C19-C20	179.6(4)
C14-C15-C16-C17	−179.8(3)	C18-C19-C20-C21	178.7(4)

The introduction of an oxygen moiety in the molecule has a drastic effect on the occurrence of liquid crystalline phases. The crystal structures of octyl benzoic acid [7] and nonyl benzoic acid [8] show dimer formation with hydrogen bonds and layering along two directions. The dimer formation endows the mesogens with approximately symmetrical molecular structure with terminal alkyl chains. However, the two mesogens do not show smectic phase. This can be

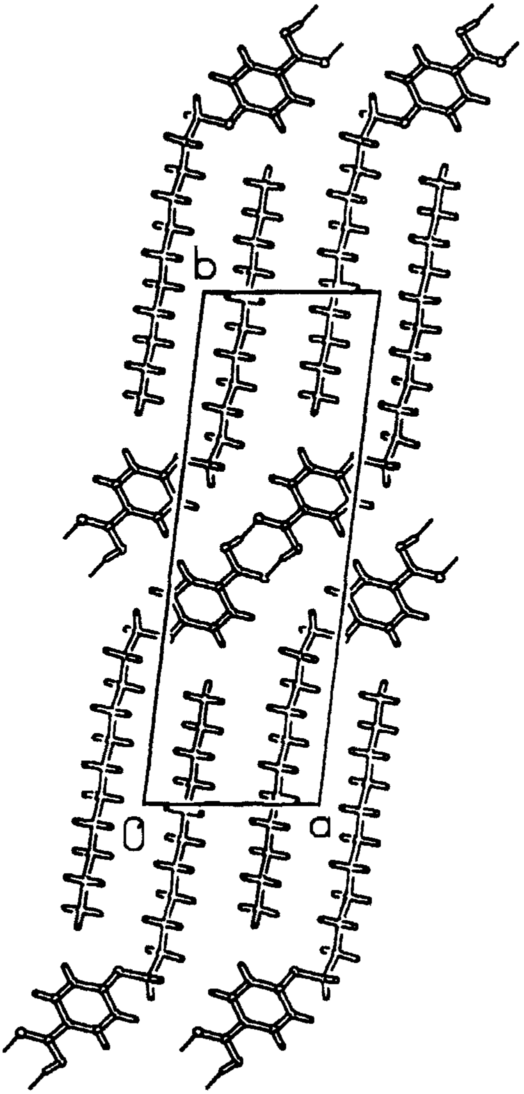

FIGURE 2 Packing of molecules down the *c* axis

explained by the fact that these compounds exhibit cyclic dimers and open dimers simultaneously in the crystalline phase as indicated by the hydrogen bonds which lead to the formation of the dimers. The formation of dimers has been discussed to account for the temperature variation of the dipole moment [9–11].

This is confirmed by the present structural results. Based on the anti parallel arrangement of the molecules in the crystalline state, it can be surmised that the dipole moment is almost zero [12]. However, as the hydrogen bonds binding the two monomers (O3-H3-O1 and its symmetry related bond) break down in steps, open dimer and monomers will be formed consecutively. In the case of octyl benzoic acid there is a low value of dipole moment in the crystalline phase. This can be ascribed to the non-centrosymmetric nature of the crystal. In the case octyloxybenzoic acid and undecyloxybenzoic acid, the dipole moments are zero as the crystalline phases of both are in centrosymmetric space groups. The introduction of an oxygen moiety, as in the case of octyloxybenzoic acid, leads to structural changes in the crystalline phase. The molecules assume bent conformation and the dimers form bilayered structures that give rise to smectic phase on heating. On further heating the molecules tend to straighten up by the formation of open dimers to give a nematic phase. Thus we see that the molecular conformations and arrangements in the crystalline phase of the mesogen play an important role in the behaviour of liquid crystalline phases.

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