Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: N. K. Lokanath, D. Revannasiddaiah, M. A. Sridhar & J. Shashidhara Prasad (2000): Crystal Structure of 4-Octlyloxybenzoic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 348:1, 7-13

To link to this article: http://dx.doi.org/10.1080/10587250008024791

Mol. Cryst. Liq. Cryst., Vol. 348, pp. 7-13
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Crystal Structure of 4-Octlyloxybenzoic Acid

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(Received October 11, 1999; In final form February 08, 2000)

4-octyloxybenzoic acid, $C_{15}H_{22}O_3$, crystallises in the triclinic space group $P\bar{1}$ with lattice parameters $a = 12.207(3)$Å, $b = 13.424(3)$Å, $c = 4.8666(16)$Å, $\alpha = 91.26(2)°$, $\beta = 91.46(3)°$, $\gamma = 116.756(14)°$, $V = 711.4(3)$Å^3, $Z = 2$, $D_{(cal)} = 1.169$ Mg/m^3, $\mu = 0.08$ mm^{-1}, $F_{000} = 272$, GooF = 0.940, $R1 = 0.0563$ and $wR2 = 0.1512$.

Keywords: Crystal structure; liquid crystal; benzoic acid

INTRODUCTION

The crystal structure studies of mesogens provide better insight into the understanding of physical properties and phase behaviour. In view of this the crystal structure study of 4-octyloxybenzoic acid was undertaken. The crystal melts into smectic state at 101°C and smectic to nematic at 108°C and nematic to isotropic phase at 147°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. Crystal with approximate size of $0.1 \times 0.1 \times 0.1$ mm^3 was mounted on Rigaku AFC7S diffractometer equipped with a graphite monochromated Mo$K\alpha$ X-ray source

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($\lambda = 0.71069$Å). The unit cell parameters were obtained by using the method of short vectors followed by least squares refinement of 18 reflections. All reflections could be indexed with respect to a triclinic cell. Lorentz and polarization 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 showed the positions of all missing non-hydrogen atoms. The structure refined by full matrix least-squares using SHELXL-97 [3] with istropic temperatire factors for all non-hydrogen atoms converged the residual to 0.16. 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 done using SHELXL-97 based on 5326 reflections and 168 parameters which converged to $R = 0.056$ for 5119 observed reflections with $I > 2\sigma(I)$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.236 and $-0.285 e^{-}$Å^{-3} respectively.

RESULTS AND DISCUSSION

The final positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table I. Anisotropic parameters for non-hydrogen atoms are listed in Table II. Tables III and IV give the bond distances and angles. Figure 1 represents the ORTEP [4] diagram of molecule with thermal ellipsoids at 50% probability. Figures 2 and 3 show packing of molecules in the unit cell down *a* and *c* axes respectively. Two molecules are bound into dimers through well defined hydrogen bonds, as is observed in the case of crystalline aggregates of fatty acids [5]. These dimers are stacked in layers as can be seen from figure. Alkyl chains are in extended conformation. The torsion angles of the alkyl chain are given in Table V. The atoms in the alkyl chain are planar and the chain is bent at the oxygen (O10) position. The phenyl ring and the carbonyl group are planar. The plane of the alkyl chain makes an angle of 56.93(12)° with the phenyl ring.

The intermolecular hydrogen bond between atoms O1-H···O3 has length 2.631(3)Å and angle 173(3)° with symmetry code $1 - x, 1 - y, -2 - z$. The introduction of oxygen moiety of the molecule has drastic effect on the occurrence of liquid crystalline phases. The structure of octyl benzoic acid [6] indicates a packing that has layering down two axes but along the third axis does not show layering. Further, it has both cyclic and open dimer formation in the crystalline phase. Hence it does not show smectic phase inspite of dimer formation. The formation

of dimers has been discussed to account for the temperature variation of dipole moment [7–9]. This is confirmed by the present structural results. The dipole moment is almost zero due to antiparallel combination of molecules in the crystalline phase. However, as the two hydrogen bonds break down in steps open dimer and monomers will be formed consecutively. In the case of octyl benzoic acid there is a small dipole moment in the crystalline phase as the crystal is non-centrosymmetric, unlike in octyloxybenzoic acid.

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

Atom	*x*	*y*	*z*	U_{eq}
O1	0.65292(12)	0.55621(11)	−0.8518(3)	0.0544(4)
C2	0.59057(16)	0.46717(14)	−0.7189(4)	0.0407(4)
O3	0.47782(11)	0.40781(11)	−0.7602(3)	0.0520(4)
C4	0.65952(15)	0.43585(13)	−0.5129(3)	0.0386(4)
C5	0.78698(16)	0.49504(14)	−0.4798(4)	0.0430(4)
C6	0.84995(16)	0.46182(14)	−0.2929(4)	0.0431(4)
C7	0.78720(14)	0.36852(13)	−0.1405(3)	0.0365(4)
C8	0.65945(15)	0.30948(14)	−0.1671(4)	0.0412(4)
C9	0.59751(15)	0.34448(15)	−0.3545(4)	0.0418(4)
O10	0.85799(10)	0.34045(10)	0.0319(3)	0.0444(3)
C11	0.79849(17)	0.24075(16)	0.1824(4)	0.0450(4)
C12	0.89701(17)	0.22440(16)	0.3416(4)	0.0472(4)
C13	0.98654(18)	0.20551(17)	0.1610(4)	0.0505(5)
C14	1.07326(18)	0.17375(17)	0.3246(4)	0.0517(5)
C15	1.16153(19)	0.15201(18)	0.1484(5)	0.0553(5)
C16	1.24337(18)	0.11484(17)	0.3104(4)	0.0537(5)
C17	1.3346(2)	0.0959(2)	0.1390(5)	0.0653(6)
C18	1.4112(2)	0.0528(2)	0.3025(6)	0.0734(7)

TABLE II Anisotropic thermal parameters of the non-hydrogen atoms (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0476(7)	0.0557(8)	0.0601(8)	0.0236(6)	−0.0094(6)	0.0157(6)
C2	0.0393(9)	0.0456(9)	0.0434(9)	0.0249(8)	−0.0044(7)	0.0030(7)
O3	0.0380(7)	0.0603(8)	0.0601(8)	0.0247(6)	−0.0101(6)	0.0107(6)
C4	0.0374(8)	0.0438(9)	0.0406(9)	0.0239(7)	−0.0058(7)	0.0014(7)
C5	0.0370(9)	0.0426(9)	0.0493(10)	0.0176(7)	−0.0033(8)	0.0097(8)
C6	0.0301(8)	0.0466(9)	0.0518(10)	0.0166(7)	−0.0038(7)	0.0079(8)
C7	0.0328(8)	0.0425(9)	0.0398(9)	0.0222(7)	−0.0038(7)	0.0006(7)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C8	0.0338(8)	0.0458(9)	0.0469(10)	0.0201(7)	–0.0002(7)	0.0103(7)
C9	0.0307(8)	0.0506(10)	0.0467(9)	0.0207(7)	–0.0030(7)	0.0053(7)
O10	0.0334(6)	0.0513(7)	0.0523(7)	0.0225(5)	–0.0063(5)	0.0110(6)
C11	0.0393(9)	0.0503(10)	0.0518(10)	0.0254(8)	–0.0001(8)	0.0123(8)
C12	0.0455(10)	0.0550(10)	0.0503(10)	0.0307(9)	–0.0020(8)	0.0116(8)
C13	0.0480(10)	0.0601(11)	0.0551(11)	0.0346(9)	–0.0039(9)	0.0085(9)
C14	0.0472(10)	0.0584(11)	0.0613(12)	0.0341(9)	–0.0027(9)	0.0101(9)
C15	0.0475(11)	0.0631(12)	0.0651(13)	0.0333(10)	0.0009(9)	0.0119(9)
C16	0.0407(10)	0.0590(12)	0.0689(13)	0.0287(9)	0.0016(9)	0.0107(10)
C17	0.0543(12)	0.0752(14)	0.0796(16)	0.0403(11)	0.0073(11)	0.0085(12)
C18	0.0546(13)	0.0747(16)	0.1069(19)	0.0438(12)	–0.0015(13)	0.0004(13)

TABLE III Bond Lengths (Å)

Atoms	*Length*	*Atoms*	*Length*
O1-C2	1.291(2)	C8-C9	1.388(2)
C2-O3	1.250(2)	O10-C11	1.432(2)
C2-C4	1.478(2)	C11-C12	1.514(2)
C4-C9	1.381(2)	C12-C13	1.523(3)
C4-C5	1.395(2)	C13-C14	1.521(2)
C5-C6	1.381(2)	C14-C15	1.517(3)
C6-C7	1.382(2)	C15-C16	1.515(3)
C7-O10	1.3650(18)	C16-C17	1.514(3)
C7-C8	1.396(2)	C17-C18	1.521(3)

TABLE IV Bond Angles (°)

Atoms	*Angle*	*Atoms*	*Angle*
O3-C2-O1	123.11(15)	C9-C8-C7	118.72(16)
O3-C2-C4	120.18(15)	C4-C9-C8	121.42(16)
O1-C2-C4	116.70(15)	C7-O10-C11	118.04(13)
C9-C4-C5	119.02(15)	O10-C11-C12	107.69(14)
C9-C4-C2	119.65(15)	C11-C12-C13	114.07(15)
C5-C4-C2	121.31(15)	C14-C13-C12	112.71(15)
C6-C5-C4	120.30(16)	C15-C14-C13	113.69(16)
C5-C6-C7	120.16(16)	C16-C15-C14	113.48(17)
O10-C7-C6	115.72(14)	C17-C16-C15	114.20(18)
O10-C7-C8	123.94(15)	C16-C17-C18	113.4(2)
C6-C7-C8	120.34(14)		

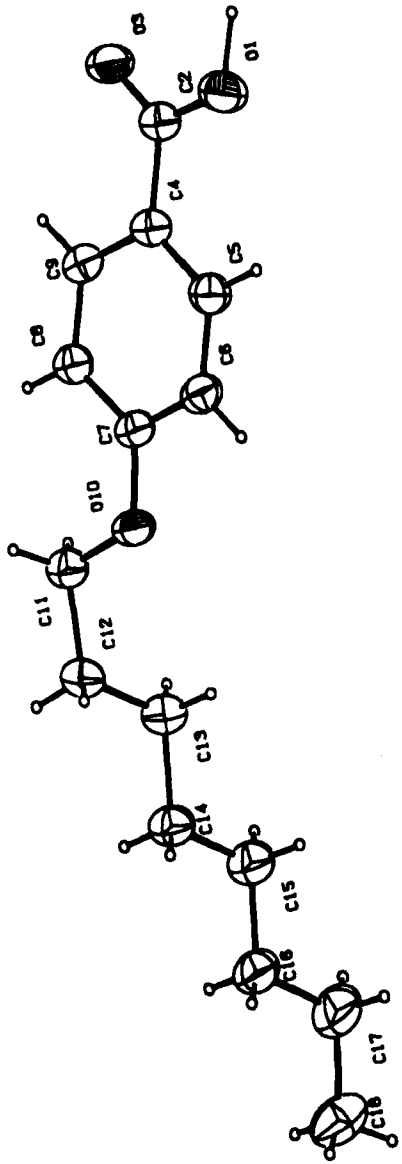

FIGURE 1 ORTEP of the molecule at 50% probability

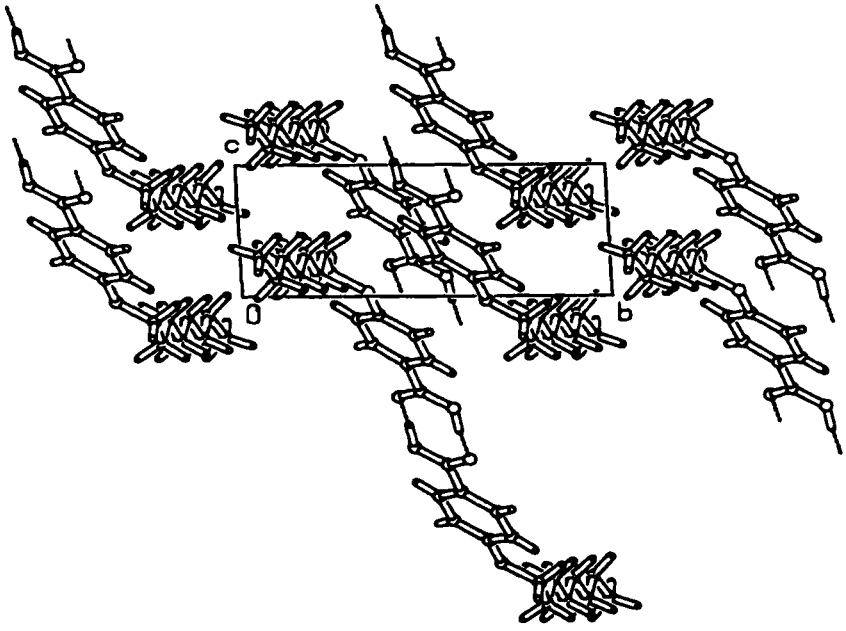

FIGURE 2 Packing of molecules down *a* axis

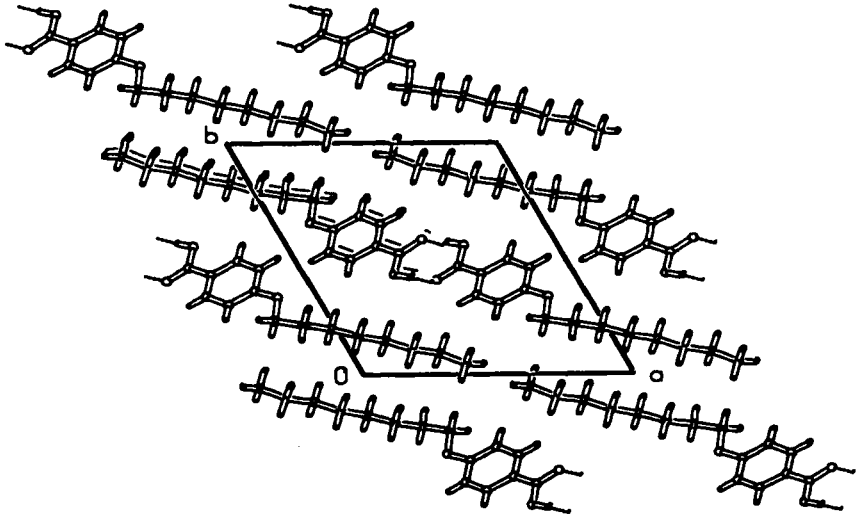

FIGURE 3 Packing of molecules down *c* axis

TABLE V Torsion Angles (°)

Atoms	*Angle*
C11-C12-C13-C14	−172.1(2)
C12-C13-C14-C15	178.7(2)
C13-C14-C15-C16	−177.1(2)
C14-C15-C16-C17	−178.2(2)
C15-C16-C17-C18	−177.0(2)

Acknowledgements

The authors would like to express their thanks to DST and CSIR, Government of India for financial assistance under the DST project SP/I2/FOO/93. NKL and DR would like to thank CSIR for finacial assistance under the project 03 (0821)/97/EMR-II.

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