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Crystal Structure of an Unsymmetrical Dimeric Liquid Crystal with a Wide Temperature Range Chiral Smectic A Phase

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Cholesteryl 6-{4-[4-(1S-methylheptyloxy)phenylethynyl]phenoxy} hexanoate, $C_{110}H_{160}O_8$, crystallises in the monoclinic space group $P2_1$ with $a = 18.710(12)$Å, $b = 9.740(14)$Å, $c = 27.865(16)$Å, $\alpha = 90.00°$, $\beta = 103.85(5)°$, $\gamma = 90.00°$, $V = 4931(8)$Å^3 $Z = 2$, $D_{(cal)} = 1.085$ Mg/m^3, $\mu = 0.066$ mm^{-1}, $F_{000} = 1768$, GooF = 0.83, $R1 = 0.07$ and $wR2 = 0.20$.

Keywords: Unsymmetrical; dimeric; smectic

INTRODUCTION

It is well known that arising from purely symmetry arguments, the chiral smectic A phase exhibits the phenomenon called the electroclinic effect [1]. The application of an electric field in the plane of the smectic layer induces the molecules to tilt with respect to the layer normal. The effect is of much interest because of the associated fast analog electro-optical response with promising applications in spatial light modulation having grey scale capabilities [2]. From the practical point of view, it is obviously an advantage to have material that exhibits a wide temperature range for the smectic A phase. To our knowledge, amongst the numerous chiral liquid crystalline compounds known, monomeric as well as

polymeric, the widest temperature range ($\sim$ 85°C) over which electroclinic effect has been observed is for a compound reported by Crawford et al. [3]. We have recently [4] found that linking two mesogenic entities, one of them being a cholesterol moiety, to form a dimesogen, leads to a very wide temperature range of 130°C for the cholesteric phase. The dimesogen called Cholesteryl 6-{4-[4-(1S-methylheptyloxy)phenylethynyl]phenoxy} hexanoate is shown schematically in Figure 1. It consists of two chiral mesogenic units viz., diphenylacetylene moiety with a chiral 2-octyloxy tail and a cholesteryl ester unit separated by a n-pentyl spacer. The temperature range of the smectic A phase is about 153°C, which is comparable to the value of $\sim$ 160°C obtained for a furanoside compound by Goodby et al. [5]. Thus it will be useful to obtain the crystal and molecular structure of the above said compound.

EXPERIMENTAL

Crystal with approximate size of $0.5 \times 0.3 \times 0.3$ mm^3 was mounted on Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromated Mo$K\alpha$ X-ray source ($\lambda = 0.71069$Å). The unit cell parameters were obtained by using the method of short vectors followed by least squares refinement of 25 reflections. All reflections could be indexed with respect to a monoclinic cell. Lorentz and polarisation corrections were applied. The trail structure could not be obtained in a straight forward manner using any one of the direct methods. A partial structure containing only one benzene ring and a couple of non-hydrogen atoms resulted using SHELXS-97 [6] for high angle reflections only. Then the structure was expanded by using PHASEX of DIRDIF-97 [7]. This gave almost all the atoms of the two molecules of the asymmetric unit. The structure was refined by full matrix least-squares using SHELXL-97 [8] with isotropic temperature factors for all non-hydrogen atoms which converged the residual to 0.19. 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 [8] based on 5677 reflections and 1190 parameters which converged to $R = 0.072$ with $I > 2\sigma(I)$. The maximum and minimum peaks on the fi-

nal difference Fourier map correspond to 0.140 and -0.116 $e^{-}.Å^{-3}$ respectively and goodness of fit is 0.830.

RESULTS AND DISCUSSION

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table 1. Figure 1 represents the schematic diagram of the molecule. Figure 2 represents the ORTEP [9] diagram of the molecule with thermal ellipsoids at 50% probability. Figure 3 shows packing of molecules in the unit cell down *b* axis. The packing of the molecules down *a* and *c* axes indicates strong layering of molecules which is a prerequisite for the occurrence of smectic phase. The bond lengths and bond angles do not show any large deviations from the standard values. Intermolecular hydrogen bond C19B-H···O31A of length 2.42(2)Å with 153(10)° and intramolecular hydrogen bond C26B–H···O31B of length 2.3865(1)Å with 151(1)° are observed. There are a large number of intermolecular contacts which are less than the van der Waal's radii, indicating that the intermolecular interactions are mainly due to van der Waal's forces. It may be summarised that intermolecular interactions of this type play a crucial role in the subtle behaviour of the mesogen.

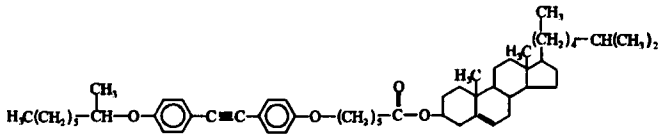

Figure 1: Schematic diagram of the molecule.

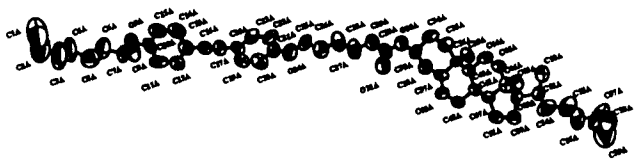

Figure 2: ORTEP of one of the molecule at 50% probability.

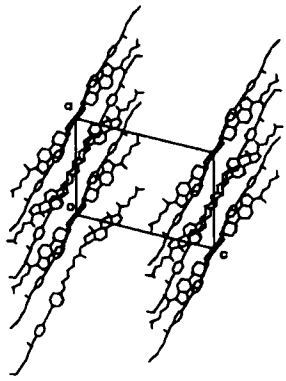

Figure 3: Packing of molecules down *b* axis.

Table 1: Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms.

Atom	x	y	z	U_{eq}
C1A	-1.8144(18)	-0.034(7)	-0.4876(9)	0.48(5)
C2A	-1.8063(17)	-0.015(5)	-0.4426(11)	0.304(19)
C3A	-1.7397(14)	0.049(4)	-0.4144(12)	0.300(18)
C4A	-1.6846(10)	-0.049(3)	-0.3921(9)	0.217(12)
C5A	-1.6132(12)	0.020(2)	-0.3614(7)	0.172(8)
C6A	-1.5508(9)	-0.072(2)	-0.3507(8)	0.169(8)
C7A	-1.4765(8)	-0.015(2)	-0.3258(7)	0.133(6)
C8A	-1.4496(9)	0.090(2)	-0.3565(7)	0.168(8)
O9A	-1.4287(7)	-0.1264(13)	-0.3184(5)	0.147(4)
C10A	-1.3567(10)	-0.114(2)	-0.2916(9)	0.121(6)
C11A	-1.3335(14)	-0.028(2)	-0.2550(8)	0.129(7)
C12A	-1.2586(12)	-0.031(2)	-0.2279(6)	0.114(6)
C13A	-1.2117(10)	-0.117(2)	-0.2418(7)	0.108(5)
C14A	-1.2371(13)	-0.208(2)	-0.2803(9)	0.134(7)
C15A	-1.3140(13)	-0.202(2)	-0.3044(6)	0.125(6)
C16A	-1.1348(9)	-0.1210(17)	-0.2175(5)	0.098(5)
C17A	-1.0736(9)	-0.1303(16)	-0.1968(5)	0.094(5)
C18A	-0.9989(9)	-0.1446(15)	-0.1710(7)	0.087(4)
C19A	-0.9826(10)	-0.1614(19)	-0.1202(8)	0.115(5)
C20A	-0.9116(13)	-0.1726(19)	-0.0937(6)	0.113(5)
C21A	-0.8546(9)	-0.1645(15)	-0.1169(9)	0.102(5)
C22A	-0.8682(11)	-0.149(2)	-0.1673(7)	0.112(6)
C23A	-0.9409(11)	-0.1440(16)	-0.1922(6)	0.098(5)
O24A	-0.7880(7)	-0.1781(14)	-0.0858(4)	0.139(4)
C25A	-0.7260(8)	-0.1681(17)	-0.1027(5)	0.107(5)
C26A	-0.6614(9)	-0.178(2)	-0.0586(6)	0.158(7)
C27A	-0.5911(9)	-0.174(2)	-0.0649(6)	0.136(6)
C28A	-0.5294(8)	-0.187(2)	-0.0177(5)	0.154(8)
C29A	-0.4553(7)	-0.1797(18)	-0.0206(5)	0.111(5)
C30A	-0.4023(9)	-0.193(2)	0.0270(6)	0.117(6)
O31A	-0.4168(6)	-0.1744(16)	0.0660(4)	0.156(5)
O32A	-0.3350(6)	-0.2062(11)	0.0252(3)	0.105(3)
C33A	-0.2781(8)	-0.2130(18)	0.0711(5)	0.096(5)
C34A	-0.2100(8)	-0.2819(14)	0.0595(5)	0.101(5)
C35A	-0.1483(8)	-0.2883(15)	0.1066(5)	0.101(5)
C36A	-0.1246(7)	-0.1462(14)	0.1306(5)	0.076(4)
C37A	-0.1950(7)	-0.0766(14)	0.1360(5)	0.075(4)
C38A	-0.2568(7)	-0.0716(17)	0.0898(5)	0.103(5)

Atom	x	y	z	U_{eq}
C39A	-0.0883(6)	-0.0611(15)	0.0971(4)	0.096(5)
C40A	-0.0733(7)	-0.1745(14)	0.1823(5)	0.073(4)
C41A	-0.0661(6)	-0.0493(15)	0.2142(5)	0.076(4)
C42A	-0.1399(7)	-0.0119(14)	0.2228(5)	0.094(4)
C43A	-0.2008(7)	-0.0130(15)	0.1767(5)	0.085(4)
C44A	0.0003(8)	-0.2320(14)	0.1778(5)	0.091(4)
C45A	0.0566(7)	-0.2512(15)	0.2282(5)	0.093(4)
C46A	0.0674(7)	-0.1166(16)	0.2558(5)	0.088(4)
C47A	-0.0097(7)	-0.0747(14)	0.2616(5)	0.079(4)
C48A	0.0984(7)	-0.0051(16)	0.2285(5)	0.104(5)
C49A	0.1098(6)	-0.1214(14)	0.3101(4)	0.081(4)
C50A	0.0814(7)	0.0028(17)	0.3352(5)	0.116(5)
C51A	0.0052(7)	0.0412(15)	0.2999(5)	0.103(5)
C52A	0.1952(7)	-0.1195(17)	0.3228(6)	0.102(5)
C53A	0.2254(8)	-0.237(2)	0.2986(6)	0.144(7)
C54A	0.2255(10)	-0.117(2)	0.3775(6)	0.190(10)
C55A	0.3088(11)	-0.095(4)	0.3916(9)	0.30(2)
C56A	0.3409(11)	-0.050(3)	0.4296(11)	0.261(16)
C57A	0.427(2)	-0.050(5)	0.4468(15)	0.31(3)
C58A	0.4475(14)	0.081(4)	0.4342(13)	0.31(2)
C59A	0.4452(14)	-0.027(6)	0.4990(11)	0.42(3)
C1B	-1.334(2)	-0.019(7)	-0.4775(14)	0.43(4)
C2B	-1.286(2)	-0.105(6)	-0.4513(16)	0.37(3)
C3B	-1.232(2)	-0.030(5)	-0.4193(15)	0.36(3)
C4B	-1.1707(15)	-0.124(3)	-0.3995(10)	0.224(14)
C5B	-1.1044(17)	-0.042(5)	-0.3714(13)	0.35(3)
C6B	-1.0486(9)	-0.061(5)	-0.3622(11)	0.29(2)
C7B	-0.9785(10)	0.026(3)	-0.3388(8)	0.164(8)
C8B	-0.9631(12)	0.122(3)	-0.3724(6)	0.221(13)
O9B	-0.9250(7)	-0.0776(14)	-0.3279(4)	0.145(5)
C10B	-0.8585(10)	-0.047(2)	-0.2985(6)	0.102(5)
C11B	-0.8385(9)	0.070(2)	-0.2716(7)	0.108(5)
C12B	-0.7699(9)	0.0908(18)	-0.2417(6)	0.095(5)
C13B	-0.7161(8)	-0.013(2)	-0.2384(5)	0.093(5)
C14B	-0.7378(10)	-0.131(2)	-0.2629(8)	0.128(7)
C15B	-0.8065(15)	-0.143(2)	-0.2929(8)	0.142(8)
C16B	-0.6440(8)	0.0012(16)	-0.2086(5)	0.098(5)
C17B	-0.5822(8)	0.0116(16)	-0.1864(5)	0.100(5)
C18B	-0.5089(9)	0.0252(17)	-0.1569(5)	0.086(4)
C19B	-0.4843(9)	0.126(2)	-0.1233(6)	0.102(5)

Atom	x	y	z	U_{eq}
C20B	-0.4119(8)	0.1437(16)	-0.0973(6)	0.091(4)
C21B	-0.3626(8)	0.0475(18)	-0.1029(5)	0.087(4)
C22B	-0.3822(8)	-0.0605(17)	-0.1361(6)	0.100(5)
C23B	-0.4566(9)	-0.0673(16)	-0.1629(6)	0.099(5)
O24B	-0.2922(6)	0.0670(11)	-0.0770(4)	0.117(4)
C25B	-0.2389(9)	-0.0273(19)	-0.0724(6)	0.144(7)
C26B	-0.1676(7)	0.0258(18)	-0.0418(6)	0.121(6)
C27B	-0.1262(8)	0.1033(17)	-0.0716(5)	0.108(5)
C28B	-0.0561(7)	0.1682(15)	-0.0381(5)	0.096(5)
C29B	-0.0019(7)	0.0628(14)	-0.0116(5)	0.087(4)
C30B	0.0640(8)	0.1211(19)	0.0208(6)	0.090(5)
O31B	0.0760(6)	0.2367(13)	0.0296(5)	0.137(5)
O32B	0.1149(5)	0.0251(9)	0.0374(3)	0.092(3)
C33B	0.1833(6)	0.0662(14)	0.0708(5)	0.076(4)
C34B	0.1762(6)	0.0548(15)	0.1246(5)	0.098(4)
C35B	0.2492(6)	0.0809(15)	0.1605(4)	0.089(4)
C36B	0.3110(6)	-0.0158(14)	0.1527(4)	0.068(3)
C37B	0.3132(7)	-0.0069(13)	0.0994(5)	0.078(4)
C38B	0.2412(6)	-0.0294(15)	0.0631(4)	0.085(4)
C39B	0.2950(6)	-0.1638(14)	0.1646(4)	0.088(4)
C40B	0.3860(5)	0.0282(15)	0.1866(4)	0.077(4)
C41B	0.4513(6)	-0.0253(15)	0.1686(4)	0.075(4)
C42B	0.4493(5)	0.0289(13)	0.1185(4)	0.075(4)
C43B	0.3739(8)	0.0184(18)	0.0851(5)	0.091(5)
C44B	0.3943(6)	-0.0064(16)	0.2407(4)	0.094(4)
C45B	0.4685(6)	0.0338(14)	0.2738(4)	0.087(4)
C46B	0.5306(6)	-0.0345(15)	0.2577(4)	0.073(4)
C47B	0.5227(5)	0.0153(13)	0.2038(4)	0.069(3)
C48B	0.5277(8)	-0.1896(16)	0.2610(5)	0.125(6)
C49B	0.6115(6)	0.0145(14)	0.2805(4)	0.083(4)
C50B	0.6528(6)	-0.0156(16)	0.2405(4)	0.099(5)
C51B	0.5939(6)	-0.0276(17)	0.1916(4)	0.104(5)
C52B	0.6505(7)	-0.0379(17)	0.3312(5)	0.103(5)
C53B	0.6093(7)	-0.016(2)	0.3707(4)	0.141(7)
C54B	0.7273(7)	0.0300(16)	0.3478(4)	0.109(5)
C55B	0.7799(8)	-0.024(2)	0.3931(6)	0.176(9)
C56B	0.8525(8)	0.049(2)	0.4024(5)	0.159(8)
C57B	0.9007(12)	0.039(4)	0.4526(11)	0.269(17)
C58B	0.9723(14)	0.107(4)	0.4525(9)	0.33(2)
C59B	0.916(2)	-0.096(5)	0.4672(16)	0.45(4)

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