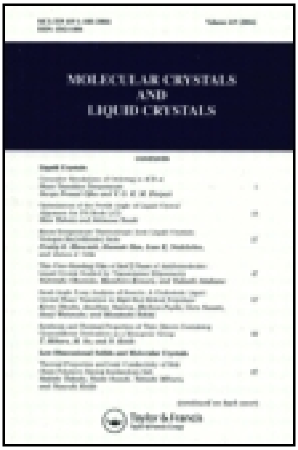

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The Influence of Hydrogen Bonding on Generation and Stabilization of Self-Assembled Layer Structure of 6-[4-(Trans -4-pentylcyclohexyl)phenoxy]hexane diol

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The Influence of Hydrogen Bonding on Generation and Stabilization of Self-Assembled Layer Structure of 6-[4-(*Trans*-4-pentylcyclohexyl)phenoxy]hexane-1,2-diol

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*The crystal structure of 6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexane-1,2-diol (hereafter, CP2OH) has been determined by X-ray diffraction techniques. The CP2OH molecule crystallizes in the monoclinic crystal system with space group* C2/c *(#15). The asymmetric unit consists of one crystallographically independent molecule of CP2OH, and the unit cell contains eight molecules of CP2OH. The CP2OH molecules crystallize in sheets of layered arrangement along the [010] direction. The unit distance of 30 Å exists between neighbouring layers along the [010] direction. In each sheet of the layered structure of CP2OH, the molecules are aligned in an inclined manner in which the terminal hydroxyl groups lie in a head-to-head fashion generated by hydrogen bonding interactions.*

The driving force behind the generation and stabilization of each sheet of the layered structure is attributed to the hydrogen bonded network between the terminal hydroxyl groups; $O1 \cdots O2$ *2.68(2) Å, and* $O1 \cdots O1$ *2.64(5) Å in the self-assembled driven interactions amongst the CP2OH molecules. The intermolecular interactions are generally driven by hydrogen bonding and are also orientation dependent. Analysis of the molecular geometry suggest that neither the packing of the rigid phenoxy moiety nor the cyclohexyl moiety affects the molecular geometry in the hexane-1,2-diol moiety and pentyl chain, respectively. The length of CP2OH molecule measured from O1 to C23 is 21.98 Å Intermolecular C…C contacts between neighboring alkyl chain molecules were not observed, and suggests that an influence of hydrophobic effects on the packing structure of the alkyl chain molecules are not strongly pronounced.*

Keywords: crystal structure; crystallography; hydrogen bonding; layered structures; self assembly

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1. INTRODUCTION

Intermolecular hydrogen bonds play an important role in the design and engineering of architectures of functional materials having useful applications as electro-optic materials, conductive materials, and biomaterials [1]. The use of molecular self-assembly processes is a useful strategy for the development of novel functional materials [2]. Therefore, molecules capable of forming self-assembled and self-organized structures have attracted a great deal of attention in materials chemistry. The concepts of self-assembly are concerned with manipulation of intermolecular interactions in the architecture of supramolecular assemblies. Self-assembly is widely believed to be the central issue to the utilization of functional materials in application of devices based on material science technology. Conceptually, self-assembly is used to design and form structures wherein specific intermolecular interactions form specific packing structures *via* van der Waals, electrostatic, and hydrophobic interactions [3,4].

Hydrogen bonding can affect the chain packing, flexibility, rigidity, and molecular order in self-assembled layer structures [5,6]. A systematic study of hydrogen bond driven self-assembled layered structures can address the fundamental question of probable best approaches to designing stable layered structures having suitable applications in liquid crystal studies. The understanding of intermolecular interactions in the context of crystal packing, and in the utilization of such understanding in the design of new solids with desired physical and chemical properties is important in development of novel functional materials through a knowledge of crystallography.

In our present studies, we are challenged to investigating the influence of hydrogen bonding on the generation and stabilization of self-assembled layered structures observed in the crystal structure studies of 6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexane-1,2-diol (hereafter, CP2OH) in respect to knowing how the conformation of a less rigid group (cyclohexyl moiety) affects the packing structure of the attached flexible alkyl chain as well as the effect of rigid group (phenoxy moiety) on the packing fashion of the attached less flexible moiety (hexane-1,2-diol), and also generation of hydrogen bonding network *via* the two terminal hydroxyl groups in hexane 1,2-diol in a self-assembled arrangement. The investigations will enhance research studies on design of novel functional materials such as liquid crystals.

Recently, we succeeded in obtaining single crystals of CP2OH and the crystal structure was solved by X-ray diffraction techniques and analysed. The structural analyses have revealed how the layer structure is formed in CP2OH. Thus, in this manuscript, we present the crystal structure of 6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexane-1,2-diol, and how it addresses the aims of our research studies as per mentioned.

2. EXPERIMENTAL

2.1. Structure Solution and Refinement

The crystals of CP2OH suitable for single crystal structure determination by X-ray diffraction techniques were crystallized from solvent mixture of ethylacetate/acetone (2 ml/8 ml) for 36 hrs by slow evaporation method in IUCHI PCI-300 incubator at about 20°C. Data collection was performed on a MacScience DIP 2000 Image Plate system using MoK_α radiation ($\lambda = 0.7107$ Å) operating at 40 kV and 200 mA. The crystal was positioned at 70 mm from the Image Plate. Thirty frames were measured at 6° intervals with an exposure time of 600 s (10 mins) to give 5909 measured reflections. Data collection and processing was carried out with the DENZO software package [7], whilst the structure solution and refinement was performed using maXus program [8]. The crystal structure was solved by direct methods (SIR92) [9] and expanded using Fourier techniques (DIRDIF) [10]. The refinement of the crystal structure was made by full-matrix least-squares on F^2 [8]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the oxygen of the terminal hydroxyl groups could not find its position in the difference Fourier map, but were included at calculated positions , with O-H = 0.86 Å. The orientation of hydrogen atoms of hydroxyl oxygen atoms were determined as per the best hydrogen bond to oxygen atom. All other H atoms were placed in idealized positions with C-H distances of 0.99 Å for the secondary (CH_2) group and 1.00 Å for the tertiary (CH) group. The H atoms were treated using a riding model. All diagrams and calculations were performed using maXus program [8]. The final cycles of full-matrix least-squares refinement were based on 2778 observed reflections, 235 variable parameters. The goodness of fit, final crystallographic R-(calculated based on F) and R_w-factor (calculated based on F^2) were 1.183, 0.075, 0.124, respectively. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The atomic coordinates, bond lengths, bond angles, torsional anglesm and thermal parameters can be obtained upon request from the Director, Cambridge Crystallographic Data Centre, Cambridge, U.K. The deposit number is *680711*. Summary of crystal data and experimental parameters are shown in Table 1.

TABLE 1 Summary of Crystal Data and Experimental Parameters of the CP2OH

Molecular formula	$C_{23}H_{38}O_3$
Formula weight	362.55
Crystal system	Monoclinic
Space group	$C2/c$ (No.15)
Z	8
a/Å	59.7515(10)
b/Å	5.489(6)
c/Å	13.501(11)
$\beta/^\circ$	92.91(2)
V/Å^3	4422.0(6)
D_x/g cm^{-3}	1.089
μ(MoK$_\alpha$)/mm^{-1}	0.07
Temperature/K	298
F(000)	1600
Crystal dimensions/mm^3	$0.4 \times 0.5 \times 0.1$
h, k, l range	$0 \rightarrow 74$, $0 \rightarrow 6$, $-16 \rightarrow 16$
Colour, shape of crystal	Colourless, platelet
No. of measured reflections	5909
No. of unique reflections	3724
No. of reflections for R	2778 [$I > 2\sigma(I)$]
Restraints, parameters	0, 235
R, R_w	0.075, 0.124
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	−0.43, 0.30

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry and Conformation

The chemical and molecular structure of CP2OH with the numbering of atoms are shown in Fig. 1. Table 1 summarizes the crystal data for the crystal structure determination of CP2OH. The CP2OH molecule crystallizes in the monoclinic crystal system with space group $C2/c$ (#15). Its asymmetric unit consists of one crystallographically independent CP2OH molecule, whilst the unit cell contains eight molecules of CP2OH. The bond distances and angles in the cyclohexyl and phenoxy moieties are in the normal accepted range observed in 1-(4′-cyanophenyl)-2-(4″-pentylcyclohexyl)ethane [11] and 2-phenoxyethanol [12] and phenols [13–15]. The alkyl chain defined by C19, C20, ..., C23 has an extended structure of all *trans* conformation as evident in the normal values of the torsional angles (170.0(2)–178.2(4)°). However, the C-C chain defined by C1, C2, C3,........., C6 does not have all *trans* conformation but a *gauche* conformation along C3-C4 as evident in the torsional angle C2-C3-C4-C5 (67.8 (6)°). The bond angles and distances are within the normal accepted

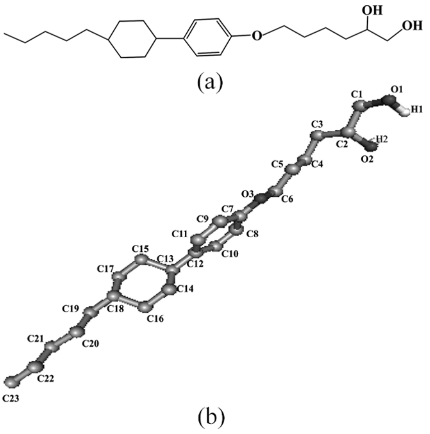
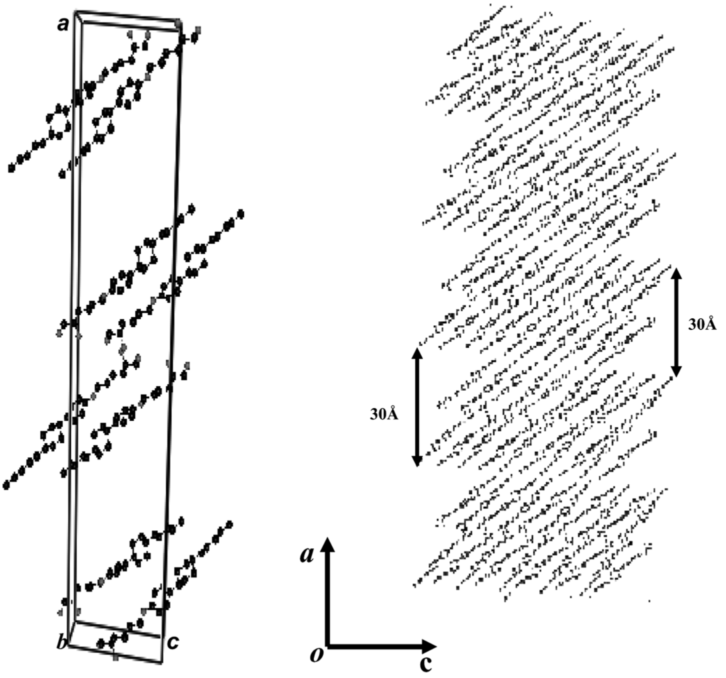


FIGURE 1 (a) The chemical structure of the CP2OH molecule. (b) The molecular structure and atomic numbering of the CP2OH molecule. The terminal hydroxyl groups are shown, whilst the remaining hydrogen atoms are omitted for clarity purpose.

range of values observed in alkyl chains [16]. The C1-O1 and C2-O2 distances are 1.42(6) Å and 1.43(4) Å respectively, whilst in C6-O3 and C7-O3, the bond distances are 1.43(7) Å and 1.36(9) Å, and are in agreement with the values observed in 25 crystal structures retrieved from Cambridge Structure Database (CSD) [17–21]. The phenoxy moiety is not coplanar with the cyclohexyl moiety as per evident in the dihedral angles observed in C10-C12-C13-C14 ($-73.7(4)^\circ$), C10-C12-C13-C15 ($-51.0(6)^\circ$), and C11-C12-C13-C14 ($-103.3(7)^\circ$), C11-C12-C13-C15 ($131.9(4)^\circ$). However, the carbon atoms in the phenoxy group are in the same plane whilst those of cyclohexyl moiety are not in the same plane. Calculating the Cremer–Pople ring puckering parameters Q and θ, where Q is the total amplitude of ring puckering, and θ is the degree of chair ($\theta = 0^\circ$ or 180°) [22], the value of $Q = 0.711(4)$ Å and $\theta = 178(7)^\circ$ for the cyclohexyl ring suggests the chair conformation. The cyclohexyl moiety lies perpendicular to the side of the plane of the phenoxy moiety. The C12-C19 bond linking the cyclohexyl group and phenoxy group is 1.49(4) Å. The dihedral angle observed in O1-C1-C2-O2; $-68.1(2)^\circ$ suggests that the hydroxyl groups point in different directions. However, all the other O-C-C-C dihedral angles are normal and lie in the normal range observed in 25 crystal structures retrieved from Cambridge Structure Database (CSD) [17–21]. The results of the molecular geometry suggest that neither the packing of the rigid phenoxy group nor the cyclohexyl group affects the molecular geometry (C-C chains) of the hexane-1, 2-diol moiety, and pentyl chain, respectively. The length of CP2OH molecule measured from O1 to C23 is 21.98 Å.

3.2. Effect of Hydrogen Bonding on Packing Structure in CP2OH

Molecular packing of CP2OH viewed along *b*-axis is shown in Fig. 2a and b. In Fig. 2b, the CP2OH molecules crystallize in sheets of layer arrangement along [010] direction. The unit distance between two neighboring layers was measured between two terminal carbon atoms from one layer to the other layer's terminal carbon atom (Fig. 2b) or from one terminal oxygen atom in one layer to the other terminal oxygen atom and was 30 Å between neighbouring layers along the [010] direction. In each sheet of the layered structure (Fig. 3), the CP2OH molecules are oriented in an inclined manner in which the terminal



(a) (b)

FIGURE 2 (a) The crystal structure of the CP2OH molecule. (b) The layer structure observed in the CP2OH along the [010] direction.

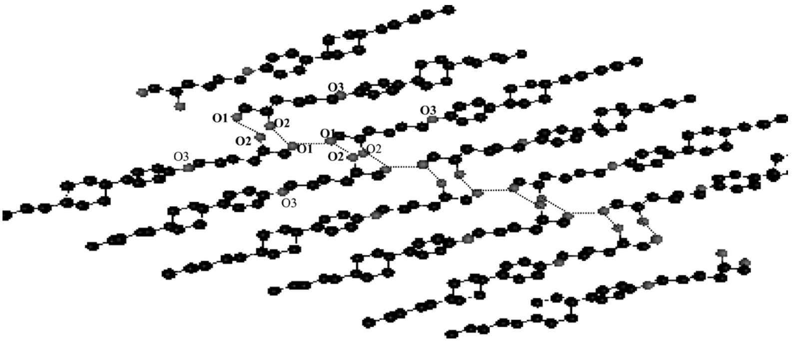


FIGURE 3 The sheet of the layered structure in the CP2OH with hydrogen bonding network existing between *O1 ⋯ O2* 2.68(2) Å, and *O1 ⋯ O1* 2.64(5) Å in the self-assembled driven interactions amongst the CP2OH molecules. The H-bond network in the crystal structure of the CP2OH viewed along *b*-axis. The broken lines depict H-bonds.

hydroxyl groups lie in a head-to-head fashion generated by hydrogen bonding interactions (Fig. 3). Since the hydrogen atoms of terminal hydroxyl groups were not located in the Fourier difference map, the criterion for hydrogen bonding was based on the short contact distances between two O ⋯ O atoms with values less than the sum of their van der Waals radii (3.04 Å) [23]. The driving force behind the generation and stabilization of each sheet of the layered structure is attributed to the hydrogen bonded network (Fig. 3) between the terminal hydroxyl groups; O1 ⋯ O2 2.68(2) Å, and O1 ⋯ O1 2.64(5) Å in the self-assembled driven interactions amongst the CP2OH molecule. The intermolecular interactions and formation of the layered structure are generally driven by hydrogen bonding and are also orientation dependent. The positions of the terminal hydroxyl groups is favorable for strong hydrogen bonding network which keeps each sheet of a layer strongly connected and stable. The hydrogen bonding network also regulates the arrangement of the alkyl chains in a fashion that is effected by the presence of adjacent hydroxyl groups in the *ac*-plane (Fig. 3). The flexible chair conformation of the cyclohexyl moiety has no significant effect on the packing structure of the attached alkyl chain. Similarly, the phenoxy group has no significant effect on the packing structure of the attached hexane-1,2-diol chain as evident in the molecular geometry analyses. Intermolecular C ⋯ C contacts between neighboring alkyl chain molecules as well as those between the cyclohexyl moieties and those between the phenoxy moieties were not observed. In all cases, the $CH_2 \cdots CH_2$

contact distances were more than the accepted sum of van der Waals values of 3.6 Å [23,24]. This suggests that an influence of hydrophobic effects on the packing structure of the alkyl chains, cyclohexyl, and phenoxy moieties are not strongly pronounced.

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