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STRUCTURAL ANALYSIS AND LIQUID CRYSTALLINE PROPERTY OF 4, 4′-METHOXY BIS-HYDRAZONE

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The title compound, 4, 4′-methoxy bis-hydrazone, $C_{16}H_{16}N_2O_2$, has been characterized thus: monoclinic, Cc, $a = 17.418(3)\,\AA$, $b = 10.710(3)\,\AA$, $c = 8.435(3)\,\AA$, $\beta = 113.74(.02)^\circ$, $V = 1440.3(7)\,\AA^3$, $Z = 4$, $F.W. = 268.31$, $D_c = 1.237\,\mathrm{Mg.m^{-3}}$, $F_{000} = 568.00$, $\lambda(\mathrm{Mo}K_\alpha) = 0.71069\,\AA$, $\mu = 0.083\ \mathrm{mm^{-1}}$, *final R1 and* w*R2 are 0.0427 and 0.1413, respectively. The compound is a mesogen which exhibits nematic phase and also shows super cooling.*

Keywords: hydrazone; methoxy bis-hydrazone; mesogen; crystal structure

INTRODUCTION

Small molecules with geometrical anisotropy and high polarizability may exhibit one or more liquid crystalline phases besides the well-known crystalline and isotropic phases [1]. Incorporation of such moieties into the main chain or side group in a molecule can result in the formation of liquid crystalline phase at moderate or higher temperatures. The formation of such a phase, as well as its type, are closely related to the molecular structure [2–4].

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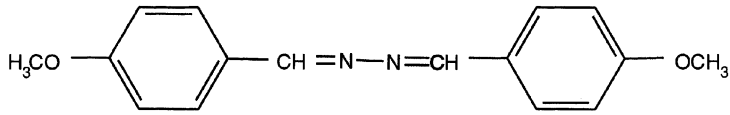


FIGURE 1 4, 4′-methoxy bis-hydrazone.

Typically, it has been found that liquid crystalline compounds have a rigid core, which serves as the mesogenic unit, and flexible alkyl chain(s) at the terminal end(s) [5]. This feature is of prime importance in the design and synthesis of new liquid crystalline compounds. These mesogens exhibit liquid crystalline behavior as a result of their high aspect ratio (length to breadth ratio). Some dihydrazides also show liquid crystalline properties at moderate and high temperatures [6].

We have synthesized a series of bis-hydrazones which show liquid crystalline property. This paper reports the synthesis and characterization of the liquid crystalline material, 4, 4′-methoxy bis-hydrazone. The structure of 4, 4′-methoxy bis-hydrazone is shown in Figure 1.

EXPERIMENTAL

Synthesis

4, 4′-methoxy bis-hydrazone (0.01 mol), prepared by refluxing diethylsuccinate and hydrazine hydrate, was dissolved in ethanol (30 ml) and was then treated with a solution of 4-methoxy benzaldehyde (0.02 mol) in ethanol. The mixture was heated under reflux on water bath for 2–3 h after the addition of a few drops of concentrated sulphuric acid. A solid mass was obtained on cooling the reaction mixture. It was collected by filtration and recrystallized from ethanol to yield yellow-colored crystals.

Characterization

^{1}H NMR and Mass Spectra

The structure of 4, 4′ bis-hydrazone was confirmed by ^{1}H NMR (see Figure 2) and mass spectra. The details are as given below:

^{1}H NMR(DMSO-d_6): (400 MHz): δ 3.85(s, 6H, 2*OCH_3), 1.58(s, 4H, 2*CH_3), 2.17(s, 4H, 2*p-ArH J = 8.8 Hz), 7.78(d, 4H, 2*p-ArH, J = 8.8 Hz), 8.61(s, 2H, 2*N = CH-)

Mass spectra: m/e (% abundance) : 268(90%), 161(100%), 134(45%), 107(10%).

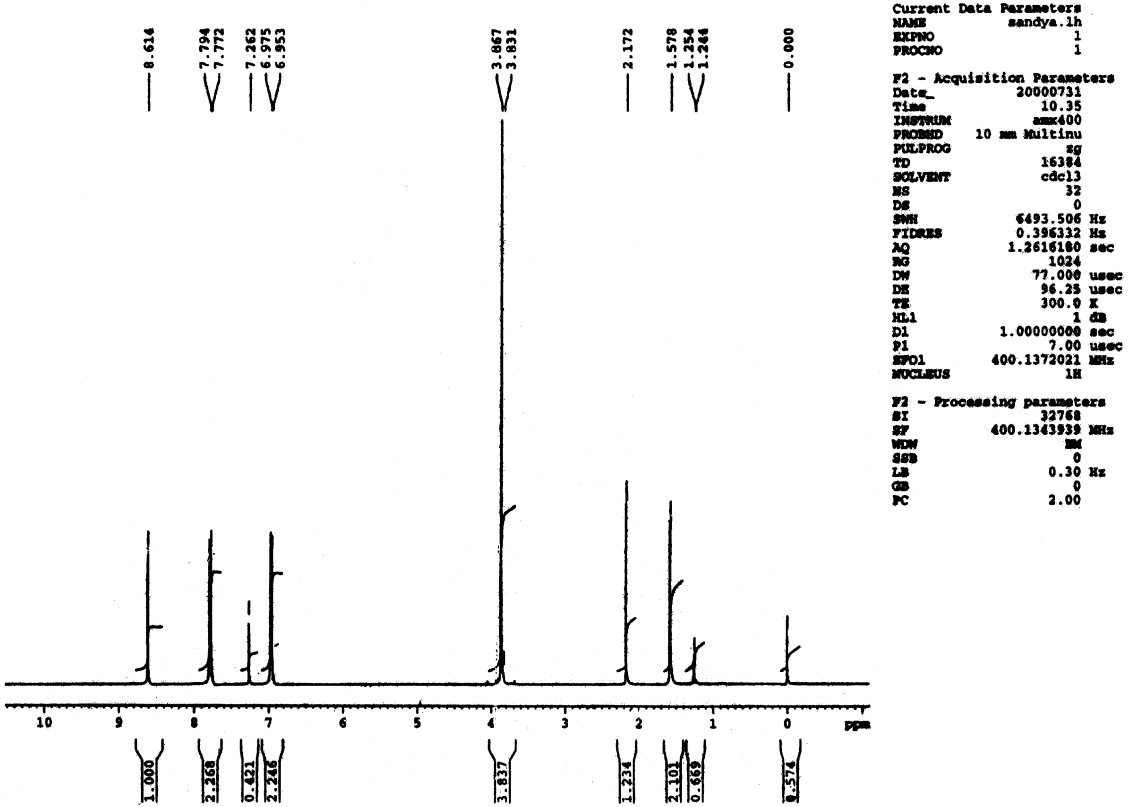


FIGURE 2 NMR spectra.

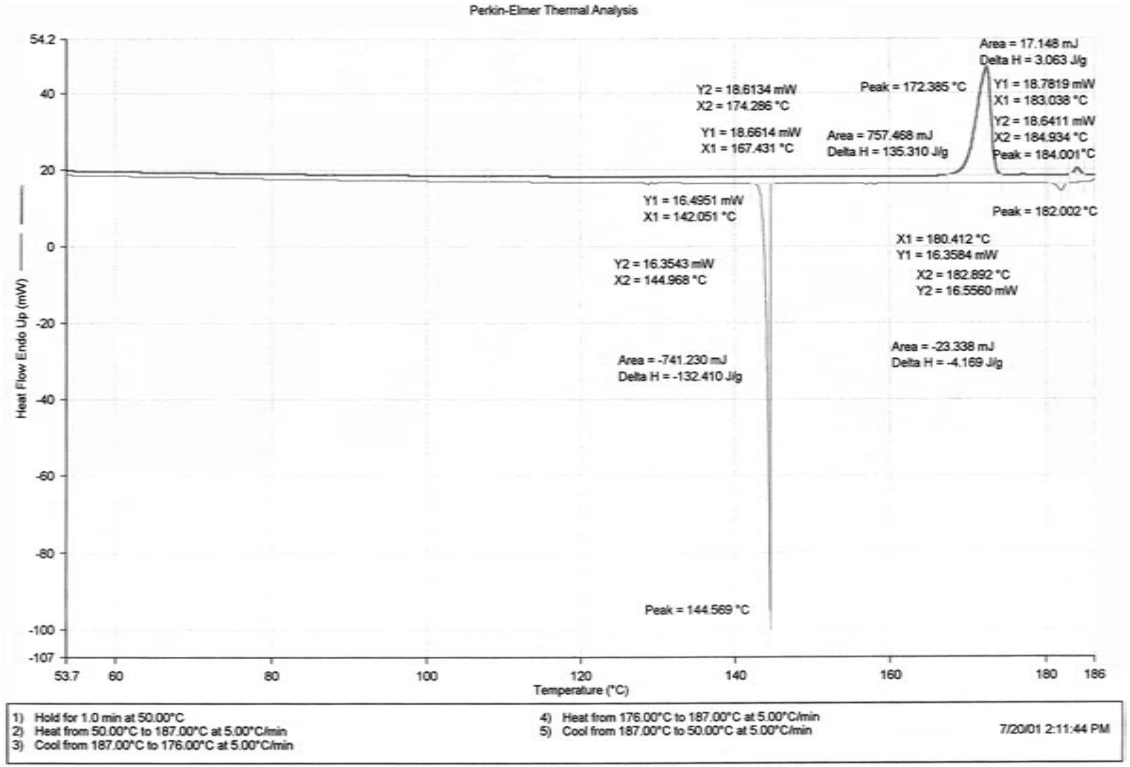
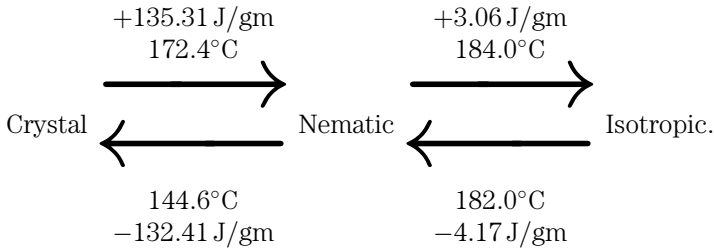


FIGURE 3 DSC curves for the title compound.

Differential Scanning Calorimetry and Microscopic Study

The transition temperatures and enthalpies of transition were determined using DSC, details of which are given in Figure 3.



The heating and cooling curves obtained at a rate of 5°C/min indicated peaks at the phase transitions. The transition temperatures were in agreement with those observed using a hot-stage on a polarizing microscope. The compound exhibits nematic phase, and texture of nematic phase is shown in Figure 4.

Crystal Structure Analysis

Single crystals of 4,4′-methoxy bis-hydrazone suitable for X-ray diffraction were obtained by the method of slow evaporation of a mixture of acetone and ethanol. All measurements were made on a Rigaku AFC7S

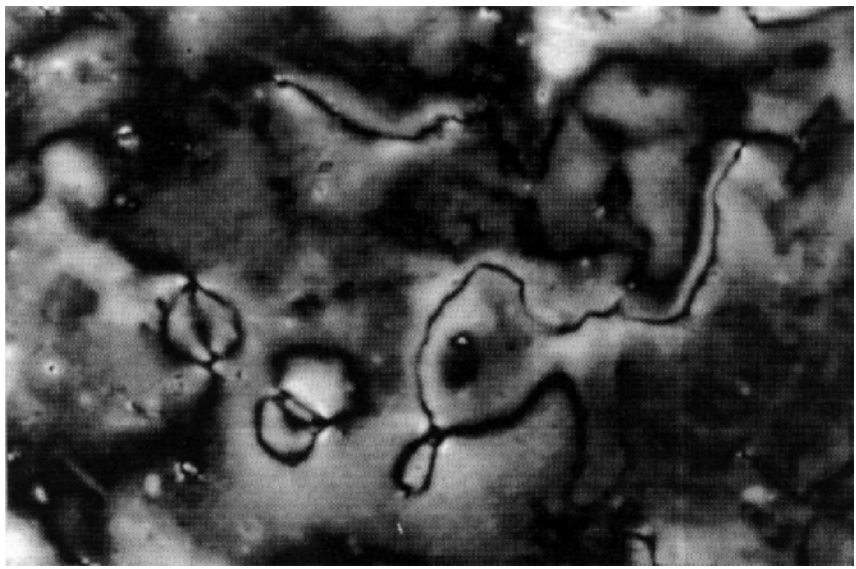


FIGURE 4 Photograph showing the nematic phase.

TABLE 1 Crystal Data and Structure Refinement for 4, 4′-methoxy bis-hydrazone

Empirical formula	$C_{16}\ H_{16}\ N_2\ O_2$
Chemical moiety	$H_3COC_6H_4CHNNCHC_6H_4OCH_3$
Formula weight	268.31
Temperature	293(2)K
Wavelength	0.71069Å
Reflns. for cell determination	25
θ range for cell determination	$13.76 - 24.87^\circ$
Crystal system	Monoclinic
Space group	*Cc*
Cell dimensions	$a = 17.418(3)$ Å, $b = 10.710(3)$ Å, $c = 8.435(3)$ Å, $\beta = 113.742(2)^\circ$
Volume	1440.3(7) Å^3
Z	4
Density(calculated)	1.237 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F_{000}	568
Crystal size	0.2 × 0.2 × 0.3 mm
θ range for data collection	2.29° to 28.28°
Index ranges	$0 \le h \le 23$ $0 \le k \le 14$ $-11 \le l \le 10$
Reflections collected	2810
Independent reflections	2616 [R(int) = 0.0171]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1852/2/182
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0442, wR2 = 0.1225$
R indices (all data)	$R1 = 0.0816, wR2 = 0.1503$
Extinction coefficient	0.0038(12)
Largest diff. peak and hole	0.212 and −0.220e.Å^{-3}

diffractometer with graphite monochromated radiation (MoK_α). The data were collected using the $w - 2\theta$ scan technique and were reduced by teXsan [7] data reduction program. Lorentz and polarization corrections were applied. The structure was solved using direct methods (SHELXS-97) [8] and refined by least squares method (SHELXL-97) [9]. The details are listed in Table 1.

RESULTS AND DISCUSSION

The final coordinates with equivalent isotropic temperature factors for all atoms are given in Table 2. Anisotropic thermal parameters (U_{ij}) for the nonhydrogen atoms are listed in Table 3. Tables 4 and 5 give bond distances and angles of nonhydrogen atoms, respectively.

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters (Å^2) of the Nonhydrogen Atoms

Atom	x	y	z	U_{eq}
C1	0.1812(3)	0.2664(4)	0.4066(6)	0.0796(9)
O2	0.1365(1)	0.1551(3)	0.3363(3)	0.0610(7)
C3	0.0579(2)	0.1402(3)	0.3345(4)	0.0503(8)
C4	0.0145(2)	0.0351(3)	0.2467(4)	0.0555(9)
C5	−0.0662(2)	0.0146(3)	0.2322(4)	0.0558(9)
C6	−0.1046(2)	0.0976(3)	0.3063(4)	0.0500(8)
C7	−0.0607(2)	0.2008(3)	0.3939(4)	0.0562(9)
C8	0.2010(2)	0.2228(3)	0.4082(4)	0.0539(8)
C9	−0.1909(2)	0.0727(4)	0.2857(4)	0.0577(9)
N10	−0.2282(2)	0.1395(3)	0.3588(4)	0.0636(7)
N11	−0.3115(2)	0.0983(3)	0.3133(4)	0.0627(7)
C12	−0.3495(2)	0.1664(4)	0.3818(4)	0.0576(8)
C13	−0.4375(2)	0.1449(3)	0.3502(4)	0.0518(9)
C14	−0.4863(2)	0.0513(3)	0.2412(4)	0.0560(9)
C15	−0.5693(2)	0.0344(3)	0.2129(4)	0.0590(9)
C16	−0.6050(2)	0.1117(3)	0.2962(4)	0.0541(9)
C17	−0.5590(2)	0.2051(3)	0.4041(4)	0.0595(9)
C18	−0.4758(2)	0.2220(3)	0.4307(4)	0.0568(9)
O19	−0.6866(2)	0.1028(3)	0.2794(4)	0.0714(8)
C20	−0.7374(3)	0.0072(5)	0.1701(7)	0.0910(9)

TABLE 3 Anisotropic Thermal Parameters of the Non-hydrogen Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.056(2)	0.082(2)	0.103(3)	−0.011(2)	0.034(2)	−0.020(2)
O2	0.045(1)	0.072(1)	0.071(1)	−0.001(1)	0.029(1)	−0.004(1)
C3	0.046(2)	0.060(2)	0.047(2)	0.006(2)	0.021(2)	0.005(2)
C4	0.055(2)	0.056(2)	0.056(2)	0.002(2)	0.027(2)	−0.006(2)
C5	0.061(2)	0.054(2)	0.055(2)	−0.002(2)	0.026(2)	−0.006(2)
C6	0.046(2)	0.056(2)	0.049(2)	−0.001(2)	0.020(1)	0.006(2)
C7	0.058(2)	0.058(2)	0.063(2)	0.005(2)	0.035(2)	0.001(2)
C8	0.049(2)	0.057(2)	0.057(2)	−0.007(2)	0.023(2)	−0.006(2)
C9	0.049(2)	0.066(2)	0.055(2)	−0.001(2)	0.018(2)	0.002(2)
N10	0.048(2)	0.078(2)	0.067(2)	−0.004(1)	0.026(1)	−0.000(2)
N11	0.047(1)	0.076(2)	0.067(2)	−0.003(1)	0.024(1)	−0.004(1)
C12	0.052(2)	0.066(2)	0.060(2)	−0.007(2)	0.028(2)	−0.002(2)
C13	0.048(2)	0.059(2)	0.053(2)	0.003(2)	0.026(2)	0.004(2)
C14	0.051(2)	0.059(2)	0.064(2)	0.003(2)	0.029(2)	−0.005(2)
C15	0.058(3)	0.061(2)	0.064(2)	0.001(2)	0.031(2)	−0.009(2)
C16	0.051(2)	0.061(2)	0.055(2)	0.003(2)	0.027(2)	0.004(2)
C17	0.066(2)	0.062(2)	0.063(2)	0.003(2)	0.040(2)	−0.008(2)
C18	0.059(2)	0.060(2)	0.057(2)	−0.006(2)	0.029(2)	−0.006(2)
C19	0.053(1)	0.083(2)	0.089(2)	−0.004(1)	0.040(1)	−0.015(2)
C20	0.054(2)	0.112(3)	0.114(3)	−0.014(2)	0.040(2)	−0.034(3)

TABLE 4 Bond Lengths (Å)

Atoms	Length	Atoms	Length
C1-O2	1.416(4)	N11-C12	1.269(5)
O2-C3	1.373(4)	C12-C13	1.465(4)
C3-C8	1.380(5)	C13-C14	1.393(5)
C3-C4	1.391(5)	C13-C18	1.397(5)
C4-C5	1.378(5)	C14-C15	1.379(5)
C5-C6	1.403(5)	C15-C16	1.386(5)
C6-C7	1.377(5)	C16-O19	1.372(4)
C6-C9	1.466(4)	C16-C17	1.372(5)
C7-C8	1.400(5)	C17-C18	1.387(5)
C9-N10	1.279(5)	O19-C20	1.423(5)
N10-N11	1.414(3)		

TABLE 5 Bond Angles (°)

Atoms	Angle	Atoms	Angle
C3-O2-C1	118.7(3)	C12-N11-N10	111.3(3)
O2-C3-C8	124.3(3)	N11-C12-C13	121.7(4)
O2-C3-C4	115.2(3)	C14-C13-C18	117.6(3)
C8-C3-C4	120.5(3)	C14-C13-C12	123.2(3)
C5-C4-C3	119.5(3)	C18-C13-C12	119.2(3)
C4-C5-C6	120.8(3)	C13-C14-C15	121.8(3)
C7-C6-C5	119.1(3)	C16-C15-C14	119.2(3)
C7-C6-C9	122.0(3)	O19-C16-C17	115.0(3)
C5-C6-C9	118.9(3)	O19-C16-C15	124.3(3)
C6-C7-C8	120.5(3)	C17-C16-C15	120.7(4)
C3-C8-C7	119.7(3)	C18-C17-C16	119.7(3)
N10-C9-C6	122.5(4)	C17-C18-C13	121.1(3)
C9-N10-N11	111.1(3)	C16-O19-C20	117.7(3)

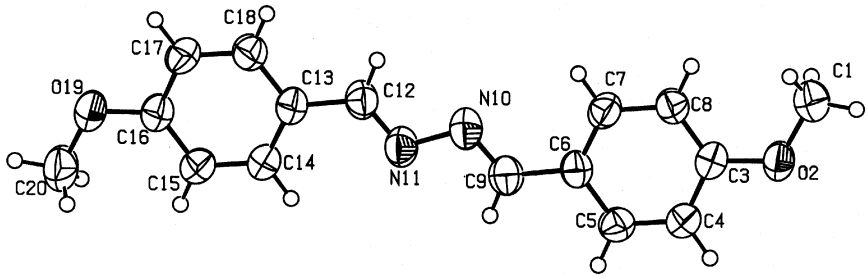


FIGURE 5 ORTEP of the molecule at 50% probability.

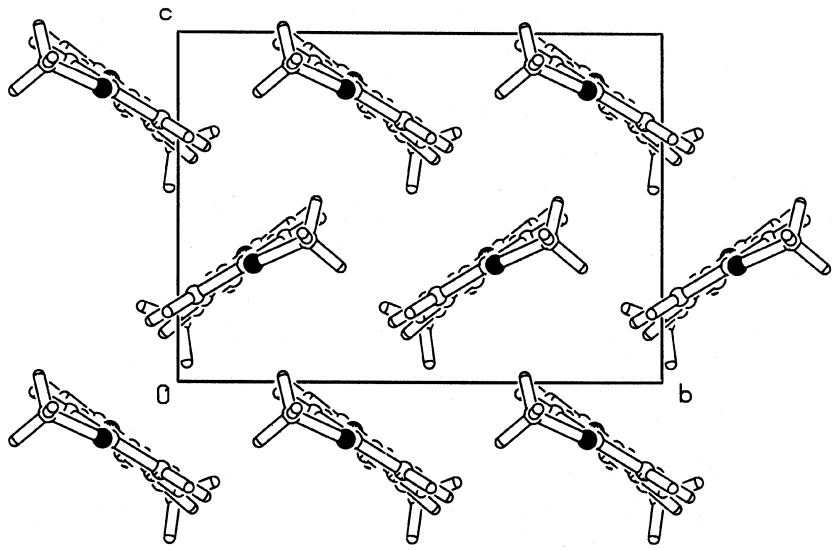


FIGURE 6 Packing of molecules down *a* axis.

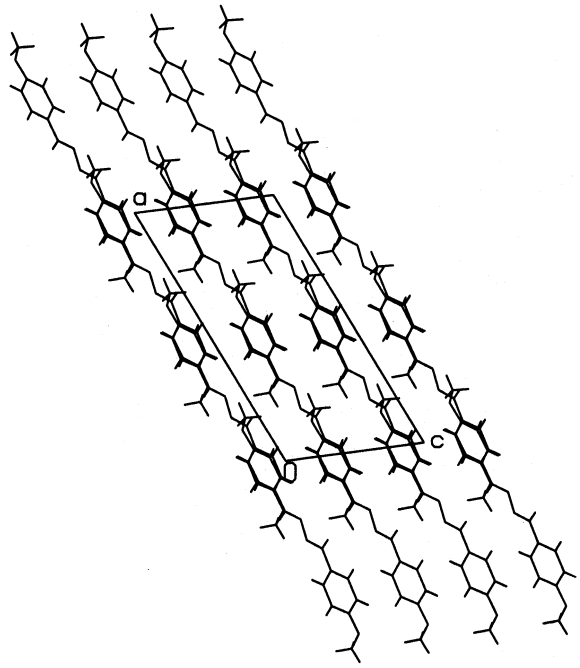


FIGURE 7 Packing of molecules down *b* axis.

Figure 5 represents the ORTEP [10] of the molecule. Figure 6 shows the packing of the molecules in the unit cell projected down the *a* axis. The crystalline cohesion is due to Van der Waal's interaction. No hydrogen bonding between the molecules is observed. The molecules are highly planar with a maximum deviation of 0.33 Å for the atom C1. The molecules are stacked when viewed down the *a* axis (Figure 6). The layering of molecules can be seen down the *b* axis (Figure 7).

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