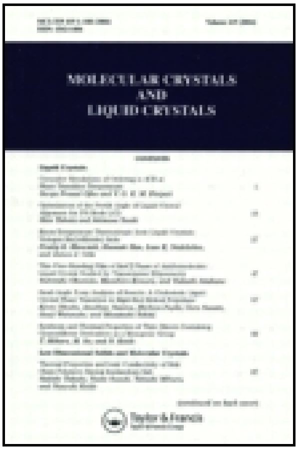

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Structural Analysis by X-Ray Diffraction of a Polar Mesogen 4-Cyanobiphenyl-4′-heptylbiphenyl Carboxylate

S. Haldar [a] , P. K. Mandal [a] , S. J. Prathap [b] , T. N. Guru Row [b] & R. Dabrowski [c]

[a] Physics Department, North Bengal University, Siliguri, India

[b] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India

[c] Institute of Chemistry, Military University of Technology, Warsaw, Poland

Version of record first published: 03 Jun 2009

To cite this article: S. Haldar, P. K. Mandal, S. J. Prathap, T. N. Guru Row & R. Dabrowski (2009): Structural Analysis by X-Ray Diffraction of a Polar Mesogen 4-Cyanobiphenyl-4′-heptylbiphenyl Carboxylate, Molecular Crystals and Liquid Crystals, 503:1, 99-111

To link to this article: http://dx.doi.org/10.1080/15421400902841411

Mol. Cryst. Liq. Cryst., Vol. 503, 99–111, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902841411

Structural Analysis by X-Ray Diffraction of a Polar Mesogen 4-Cyanobiphenyl-4′-heptylbiphenyl Carboxylate

S. Haldar[1], P. K. Mandal[1], S. J. Prathap[2], T. N. Guru Row[2], and R. Dabrowski[3]
[1]Physics Department, North Bengal University, Siliguri, India
[2]Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India
[3]Institute of Chemistry, Military University of Technology, Warsaw, Poland

Crystal and molecular structure of a compound 4-cyanobiphenyl-4′-heptylbiphenyl carboxylate (7CBB), which exhibit both monolayer smectic A and nematic phases, have been determined by direct methods using single crystal X-ray diffraction data. The structure is monoclinic with the space group $P2_1/c$ *and* $Z = 4$. *The unit cell parameters are* $a = 16.9550(5)$ Å, $b = 5.5912(18)$ Å, $c = 27.5390(9)$ Å, $\alpha = 90.000°$, $\beta = 93.986(6)°$, *and* $\gamma = 90.000°$. *Packing of the molecules is found to be precursor to SmC phase, although* SmA_1 *phase is observed on melting. Several strong van der Waals interactions are observed in the core part of the neighboring molecular pairs. Crystal to mesophase transition is probably of reconstitutive nature. Geometry, packing, and nature of crystal-mesophase transition are compared to those in 6CBB.*

Keywords: crystal and molecular structure; crystal-mesogen transition; molecular packing; reconstitutive transition; smectogen; van der Waals interaction

1. INTRODUCTION

Nematogenic cyanobiphenyls are of great interest because of their commercial use in liquid crystal devices (LCD) devices [1,2]. Two biphenyl moieties—one having terminal cyano group, and the other possessing terminal alkyl chain—when linked with carboxylate group give rise to an elongated core homologous series viz., 4-cyanobiphenyl-4′-n alkylbiphenyl carboxylate (nCBB, in short). These materials have also drawn much attention because they are first four-ring compounds

Address correspondence to Prof. P. K. Mandal, Physics Department, North Bengal University, Siliguri 734 013, India. E-mail: mandal_pradip@yahoo.com

higher homologues ($n = 8, 9$) of which exhibit reentrant nematic (N_{re}) phase as well as two types of smectic A phases, the monolayer (SmA_1) and the partially bilayer (SmA_d) smectics. On the other hand, the lower homologues ($n = 4$–7) form only SmA_1 and nematic phases [3,4]. Moreover, binary mixtures of four-ring nCBB compounds with two-ring nCB compounds exhibit induced or enhanced SmA_d phase. Induction or enhancement of the SmA_d phase takes place in the form of an "island" or "semi-island" surrounded by nematic sea. Reentrant nematic phase is also induced in some cases [5].

It has been observed that in mesogenic compounds knowledge of molecular geometry and packing of the molecules in the crystalline state often helps in explaining the observed phase behavior that depend on the subtle balance of intermolecular interactions [6–15]. With this aim the crystal structure of 6CBB was determined and the packing of the molecules in the crystalline state was found to be precursor to the smecticA phase structure [16]. In this article, we report results of structural analysis of the next member (7CBB) and compare the structure of the two compounds vis-à-vis their mesogenic properties. Observed phase sequence of 7CBB is Cr 123 SmA_1 136 N 350 I, and that of 6CBB is Cr 141.5 SmA_1 158.7 N 360 I (temperatures in °C) [3].

2. EXPERIMENTAL, STRUCTURE DETERMINATION, AND REFINEMENT

Crystals were grown from a solution of dichloromethane and methyl alcohol by slow evaporation technique. A transparent plate-shaped crystal with suitable dimension was mounted on a glass fiber and transferred to a Bruker SMART CCD single-crystal diffractometer for data collection. Three-dimensional X-ray data were collected by the scan method using graphite-monochromated MoK_α radiation. A total of 4589 unique reflections were measured within the range $-20 \le h \le 20$, $-6 \le k \le 6$, $-32 \le l \le 32$. Of these, 2925 reflections were above the significance level of $2\sigma(I)$ and were treated as observed. The range of $(\sin\theta)/\lambda$ was 0.044–0.595 Å^{-1} ($1.80 \le \theta \le 25.00°$). The structure was solved by direct methods and difference Fourier synthesis. All the hydrogen positions were initially located in the difference Fourier maps and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out. The details of the data collection and refinement have been done using the following

TABLE 1 Important Crystallographic Data

Formula	$C_{33}H_{31}N_1O_2$
Formula weight	473.59 g/mol
T (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a	16.9546(53) Å
b	5.5912(18) Å
c	27.5387(86) Å
α	90.000°
β	93.986(6)°
γ	90.000°
V	2604.26(18) $Å^3$
Z	4
D_{cal}	1.208 g/cc
Radiation, $\lambda(MoK_\alpha)$	0.71073 (Å)
F(000)	1007.9
Independent reflections	4589
No. of observed reflections	2925 $[I > 2\sigma(I)]$
Refinement method	full-matrix least-squares on F^2
R	0.057
Rw	0.142

packages: data collection and cell refinement: Bruker SMART [17]; data reduction: SAINT [18]; absorption correction: SADABS [18]; structure solution: SHELXS–86 [18]; refinement: SHELXL97 [18]; molecular graphics: CAMERON [19]. Important crystallographic data and refinement parameters are given in Table 1. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 689871.

3. RESULTS AND DISCUSSIONS

A perspective drawing of the molecule with the atom numbering scheme is shown in Fig. 1. Final positional coordinates with equivalent temperature factors, anisotropic thermal parameters, bond lengths, and bond angles of the nonhydrogen atoms are listed in Tables 2–5.

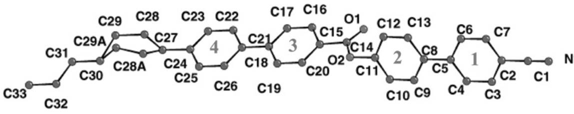

FIGURE 1 Perspective view of 7CBB molecule with atom numbering scheme.

TABLE 2 Fractional Coordinates and Equivalent Isotropic Parameters of the Non-Hydrogen Atoms with e.s.d's in Parentheses

Atom	x	y	z	U_{eq} (Å^2)
N(1)	0.97133(14)	0.56450(45)	0.78808(8)	0.096
C(1)	0.92812(14)	0.57812(44)	0.75450(9)	0.07
C(2)	0.87219(12)	0.59513(41)	0.71248(7)	0.057
C(3)	0.87025(13)	0.41956(45)	0.67735(8)	0.071
C(4)	0.81676(13)	0.43620(42)	0.63737(8)	0.066
C(5)	0.76431(11)	0.62456(34)	0.63072(7)	0.044
C(6)	0.76708(13)	0.79579(40)	0.66693(8)	0.065
C(7)	0.82015(14)	0.78225(43)	0.70713(8)	0.07
C(8)	0.70929(11)	0.64270(34)	0.58611(7)	0.045
C(9)	0.70825(14)	0.47245(40)	0.54961(8)	0.068
C(10)	0.66027(14)	0.49358(42)	0.50712(8)	0.07
C(11)	0.61207(11)	0.68652(39)	0.50088(7)	0.053
C(12)	0.60949(13)	0.85577(43)	0.53644(8)	0.066
C(13)	0.65788(12)	0.83259(41)	0.57866(8)	0.062
O(1)	0.63630(10)	0.99812(33)	0.43035(5)	0.085
O(2)	0.56232(8)	0.70323(27)	0.45781(5)	0.062
C(14)	0.58111(12)	0.86722(39)	0.42421(7)	0.053
C(15)	0.52487(11)	0.86135(34)	0.38061(7)	0.045
C(16)	0.52876(12)	1.04091(38)	0.34621(7)	0.056
C(17)	0.47724(12)	1.04380(37)	0.30520(7)	0.055
C(18)	0.42009(10)	0.86758(33)	0.29635(6)	0.042
C(19)	0.41775(11)	0.68736(36)	0.33115(7)	0.052
C(20)	0.46877(11)	0.68437(37)	0.37246(7)	0.053
C(21)	0.36378(10)	0.87103(35)	0.25228(7)	0.044
C(22)	0.36373(13)	1.05145(43)	0.21803(8)	0.067
C(23)	0.31045(14)	1.05358(48)	0.17762(8)	0.076
C(24)	0.25488(13)	0.87675(49)	0.16908(8)	0.065
C(25)	0.25600(14)	0.69676(49)	0.20244(9)	0.078
C(26)	0.30863(14)	0.69340(43)	0.24285(8)	0.07
C(27)	0.19432(16)	0.88295(63)	0.12610(9)	0.093
C(28)	0.1184(2)	0.9982(14)	0.1375(1)	0.081
C(28A)	0.1219(6)	0.8256(42)	0.1291(4)	0.062
C(29)	0.0502(5)	0.9958(16)	0.0985(4)	0.07
C(29A)	0.0647(10)	0.8943(67)	0.0854(6)	0.101
C(30)	0.00313(17)	0.75475(55)	0.09016(10)	0.088
C(31)	−0.05609(14)	0.75725(47)	0.04597(9)	0.076
C(32)	−0.10810(17)	0.54386(51)	0.04014(11)	0.093
C(33)	−0.16337(18)	0.54718(61)	−0.00522(11)	0.112

Two carbon atoms (C28 and C29) of the alkyl chain are found to be in considerable disordered condition. Major occupancy factors for the two atoms are 78% and 66%, respectively. No such disordering is observed in 6CBB.

TABLE 3 Anisotropic Thermal Parameters of the Non-Hydrogen Atoms with the e.s.d's in Parantheses. The Temperature Factor is of the Form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+U_{13}hla^*c^*+2U_{23}klb^*c^*]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	0.097(2)	0.111(2)	0.077(1)	−0.017(1)	−0.041(1)	0.009(1)
C(1)	0.070(2)	0.076(2)	0.063(1)	−0.013(1)	−0.014(1)	0.006(1)
C(2)	0.053(1)	0.067(1)	0.050(1)	−0.012(1)	−0.008(1)	0.008(1)
C(3)	0.066(1)	0.076(2)	0.070(2)	0.019(1)	−0.019(1)	−0.002(1)
C(4)	0.070(1)	0.068(2)	0.059(1)	0.017(1)	−0.013(1)	−0.013(1)
C(5)	0.045(1)	0.046(1)	0.042(1)	−0.005(1)	0.001(1)	0.005(1)
C(6)	0.076(1)	0.055(1)	0.062(1)	0.010(1)	−0.016(1)	−0.008(1)
C(7)	0.087(2)	0.065(2)	0.056(1)	0.001(1)	−0.020(1)	−0.011(1)
C(8)	0.045(1)	0.046(1)	0.043(1)	−0.004(1)	0.001(1)	0.004(1)
C(9)	0.087(2)	0.050(1)	0.064(1)	0.015(1)	−0.021(1)	−0.008(1)
C(10)	0.093(2)	0.057(1)	0.057(1)	0.006(1)	−0.022(1)	−0.012(1)
C(11)	0.049(1)	0.061(1)	0.047(1)	−0.008(1)	−0.009(1)	0.006(1)
C(12)	0.062(1)	0.074(2)	0.059(1)	0.022(1)	−0.010(1)	−0.003(1)
C(13)	0.065(1)	0.069(1)	0.050(1)	0.018(1)	−0.007(1)	−0.010(1)
O(1)	0.087(1)	0.105(1)	0.061(1)	−0.046(1)	−0.024(1)	0.012(1)
O(2)	0.0610(9)	0.0726(10)	0.0510(9)	−.0132(8)	−.0168(7)	0.0124(8)
C(14)	0.053(1)	0.059(1)	0.046(1)	−0.005(1)	−0.002(1)	−0.003(1)
C(15)	0.044(1)	0.049(1)	0.041(1)	0.001(1)	0.000(1)	−0.004(1)
C(16)	0.060(1)	0.055(1)	0.053(1)	−0.018(1)	−0.005(1)	0.001(1)
C(17)	0.064(1)	0.052(1)	0.048(1)	−0.010(1)	−0.004(1)	0.009(1)
C(18)	0.041(1)	0.043(1)	0.040(1)	0.005(1)	0.003(1)	−0.003(1)
C(19)	0.053(1)	0.050(1)	0.053(1)	−0.011(1)	−0.008(1)	0.004(1)
C(20)	0.054(1)	0.052(1)	0.051(1)	−0.006(1)	−0.006(1)	0.010(1)
C(21)	0.041(1)	0.051(1)	0.041(1)	0.005(1)	0.004(1)	−0.002(1)
C(22)	0.063(1)	0.074(2)	0.063(1)	−0.012(1)	−0.009(1)	0.020(1)
C(23)	0.072(2)	0.095(2)	0.060(1)	−0.005(1)	−0.010(1)	0.030(1)
C(24)	0.054(1)	0.097(2)	0.045(1)	0.005(1)	−0.004(1)	0.001(1)
C(25)	0.079(2)	0.089(2)	0.065(2)	−0.023(1)	−0.024(1)	0.008(1)
C(26)	0.079(2)	0.069(2)	0.060(1)	−0.020(1)	−0.022(1)	0.013(1)
C(27)	0.076(2)	0.147(3)	0.055(2)	0.003(2)	−0.015(1)	0.006(2)
C(28)	0.083(3)	0.085(4)	0.073(2)	0.013(2)	−0.020(2)	−0.001(2)
C(28A)	0.052(7)	0.080(12)	0.053(7)	0.004(6)	−0.011(5)	0.003(7)
C(29)	0.069(3)	0.077(5)	0.062(4)	0.000(3)	−0.010(3)	0.009(3)
C(29A)	0.073(7)	0.174(18)	0.053(6)	0.030(9)	−0.025(5)	−0.020(8)
C(30)	0.077(2)	0.109(2)	0.076(2)	0.023(2)	0.004(1)	0.027(2)
C(31)	0.066(1)	0.083(2)	0.078(2)	0.004(1)	0.004(1)	0.017(1)
C(32)	0.104(2)	0.080(2)	0.096(2)	−0.002(2)	0.034(2)	0.000(2)
C(33)	0.103(2)	0.132(3)	0.102(2)	−0.034(2)	0.019(2)	−0.032(2)

The average aromatic bond lengths and bond angles in the phenyl rings shown in Table 6 for both the molecules. It is found that in the phenyl rings of 7CBB, average bond lengths are less by about 4σ compared to 6CBB values, however, average bond angles in both the cases

TABLE 4 Bond Distance (Å) of the Non-Hydrogen Atoms with Standard Deviations in Parentheses

C(1)	N(1)	1.142(4)
C(2)	C(7)	1.370(4)
C(2)	C(3)	1.377(4)
C(2)	C(1)	1.447(4)
C(3)	C(4)	1.380(4)
C(5)	C(4)	1.382(3)
C(6)	C(5)	1.381(3)
C(6)	C(7)	1.379(4)
C(8)	C(5)	1.493(3)
C(8)	C(9)	1.384(3)
C(8)	C(13)	1.380(3)
C(10)	C(9)	1.383(4)
C(11)	C(12)	1.365(4)
C(11)	C(10)	1.357(4)
C(12)	C(13)	1.382(4)
O(2)	C(11)	1.410(3)
O(2)	C(14)	1.356(3)
C(14)	O(1)	1.191(3)
C(15)	C(20)	1.380(3)
C(15)	C(14)	1.481(3)
C(15)	C(16)	1.385(3)
C(17)	C(16)	1.379(3)
C(18)	C(21)	1.491(3)
C(18)	C(19)	1.393(3)
C(18)	C(17)	1.391(3)
C(19)	C(20)	1.381(3)
C(21)	C(22)	1.381(4)
C(21)	C(26)	1.376(4)
C(22)	C(23)	1.384(4)
C(24)	C(23)	1.375(4)
C(24)	C(25)	1.362(4)
C(26)	C(25)	1.377(4)
C(27)	C(28)	1.492(6)
C(27)	C(28A)	1.277(13)
C(27)	C(24)	1.512(4)
C(28)	C(28A)	1.00(3)
C(29)	C(28)	1.522(12)
C(29)	C(29A)	0.72(4)
C(29A)	C(30)	1.32(3)
C(30)	C(31)	1.523(4)
C(31)	C(32)	1.486(4)
C(32)	C(33)	1.509(5)

are the same. These values are in agreement with the geometry of the other biphenyl moieties reported in Cambridge Structural database [20] and in other mesogenic compounds [7,21–25].

TABLE 5 Bond Angles (°) Involving Non-Hydrogen Atoms with Standard Deviations in Parentheses

C(2)	C(1)	N(1)	179.0(3)
C(2)	C(3)	C(4)	119.7(3)
C(3)	C(2)	C(1)	119.8(3)
C(5)	C(6)	C(7)	121.9(3)
C(5)	C(8)	C(9)	121.8(2)
C(5)	C(8)	C(13)	121.8(2)
C(5)	C(4)	C(3)	122.6(3)
C(6)	C(5)	C(8)	122.3(2)
C(6)	C(5)	C(4)	116.3(2)
C(6)	C(7)	C(2)	120.5(3)
C(7)	C(2)	C(3)	119.0(2)
C(7)	C(2)	C(1)	121.2(3)
C(8)	C(5)	C(4)	121.3(2)
C(8)	C(9)	C(10)	122.2(3)
C(8)	C(13)	C(12)	122.0(3)
C(9)	C(8)	C(13)	116.4(2)
C(11)	O(2)	C(14)	117.6(2)
C(11)	C(12)	C(13)	119.5(3)
C(11)	C(10)	C(9)	119.3(3)
C(12)	C(11)	C(10)	120.6(2)
C(14)	C(15)	C(16)	118.7(2)
C(15)	C(14)	O(1)	125.7(2)
C(15)	C(16)	C(17)	120.7(2)
C(18)	C(21)	C(22)	122.4(2)
C(18)	C(21)	C(26)	122.2(2)
C(18)	C(19)	C(20)	122.0(2)
C(18)	C(17)	C(16)	121.9(2)
C(19)	C(18)	C(17)	116.4(2)
C(19)	C(20)	C(15)	120.7(2)
C(20)	C(15)	C(14)	123.1(2)
C(20)	C(15)	C(16)	118.3(2)
C(21)	C(18)	C(19)	121.5(2)
C(21)	C(18)	C(17)	122.1(2)
C(21)	C(22)	C(23)	121.7(3)
C(21)	C(26)	C(25)	122.4(3)
C(22)	C(21)	C(26)	115.5(2)
C(22)	C(23)	C(24)	122.2(3)
C(23)	C(24)	C(25)	116.0(3)
C(24)	C(25)	C(26)	122.2(3)
C(27)	C(28)	C(29)	118.2(6)
C(27)	C(28)	C(28A)	57.7(7)
C(27)	C(28A)	C(28)	81.1(13)
C(27)	C(24)	C(23)	122.5(3)
C(27)	C(24)	C(25)	121.4(3)
C(28)	C(27)	C(28A)	41.2(11)
C(28)	C(27)	C(24)	113.2(3)
C(28)	C(29)	C(29A)	95.3(16)

(*Continued*)

TABLE 5 Continued

C(28A)	C(27)	C(24)	123.2(6)
C(29)	C(28)	C(28A)	83.2(9)
C(29)	C(29A)	C(30)	96.6(18)
C(29A)	C(30)	C(31)	113.4(9)
C(30)	C(31)	C(32)	115.6(3)
C(31)	C(32)	C(33)	114.2(3)

The CO double bond and single bonds in carboxylate group are almost same in the two compounds as shown in Table 6. However, appreciably different values were observed in cholesteryl 6[4-(4-pentyloxyphenylethynyl) phenoxy] hexanoate [22], the respective bonds being 1.130(15) Å and 1.367 Å (mean value). A value of 1.385(2) Å for the single bond was observed in α,ω-bis(4-cyanobiphenyl-4′-yloxy) octane [7]. The CN triple bond (C1–N1) is found to be 1.142(4) Å, and the angle C2–C1–N1 is 179.0(3)°, and corresponding values in 6CBB are 1.137(5) Å and 178.3(4)°, respectively. Observed values in the above octane compound [7] are, respectively, 1.141(2) Å and 178.9°, in 5OCB these are 1.132(3) Å and 178.5°. Thus the observed bond distances and angles in 6CBB and 7CBB mostly agree with the values reported for other similar mesogenic materials.

TABLE 6 Comparison of Selected Bond Lengths (Å) and Bond Angles (°) in 6CBB and 7CBB

	Average bond lengths		Average bond angles	
Phenyl rings	6CBB	7CBB	6CBB	7CBB
1	1.387(5)	1.378(4)	120.0(3)	120.0(3)
2	1.389(5)	1.375(4)	120.0(3)	120.0(3)
3	1.386(6)	1.385(3)	120.0(3)	120.0(3)
4	1.386(6)	1.376(6)	120.0(3)	120.0(3)
	Bond lengths		Bond angles (C–C–N)	
Cyano group	6CBB	7CBB	6CBB	7CBB
C≡N (C1–N1)	1.137(5)	1.142(4)	178.3(4)°	179.0(3)°
	Bond lengths			
Carboxyl group	6CBB	7CBB		
C=O (C13=O1)	1.197(3)	1.191(3)		
C–O (C13–O2)	1.358(3)	1.356(3)		
C–O (O3–C14)	1.412(3)	1.410(3)		

Geometry of the 7CBB molecules may be described in terms of the four phenyl ring planes, and their numbering scheme is shown in Fig. 1. All the phenyl rings are found to be planar (highest displacement of C8 from benzene ring **2** being 0.012 Å) as was observed in 6CBB. The C1 and N1 atoms of the cyano group are displaced downward by 0.005 Å and upward by 0.14 Å, respectively, from the nearest phenyl ring **1**. The atoms of the – COO group lie, as in 6CBB, closer to the plane of ring **3** than the ring **2**. Like the two ring cyanobiphenyl compounds, the two biphenyl rings in 7CBB are almost coplanar. For example, in 4′-n-pentyloxy-4-biphenyl carbonitrile (5OCB) [15], the dihedral angle between the two benzene rings is 0.8°, and in 3-[4-(4′-ethylbiphenyl)]-1-propene [21] it is 1.5°. On the other hand, in 7CBB, the angles between the planes of the rings **1&2**, **1&3**, **1&4**, **2&3**, **2&4**, and **3&4** are, respectively 4.6°, 63.6°, 61.7°, 63.5°, 61.7°, and 2.3°. In 6CBB, the corresponding angles are respectively 33.2°, 79.9°, 62.2°, 46.7°, 84.6°, and 38.0°. Thus the rigid core geometry is quite different in the two molecules. However, this is not quite unusual. In 4-cyanophenyl-4′-heptylbenzoate [14], where the two phenyl rings are linked by the spacer carboxylate group, the observed dihedral angle is 47.5°. Similar values are found in other phenyl benzoates [26–28], though coplanar benzene rings along with the carboxylate group has also been reported [29].

Calculated length of the 7CBB molecule in the crystalline state is found to be 28.47 Å (N1-H29B) whereas the model length in the most extended form is 31.8 Å. Disordering in alkyl chain and slightly bow-shaped nature of the molecule may be responsible for this difference in lengths. The corresponding lengths for 6CBB are 27.83 Å and 30.6 Å, respectively.

Packing of the 7CBB molecules in the unit cell is shown in Fig. 2. The direction cosines of the molecular long axis, defined as the best fitted line through all the atoms, are found to be 0.61, −0.042, and 0.79. Thus the

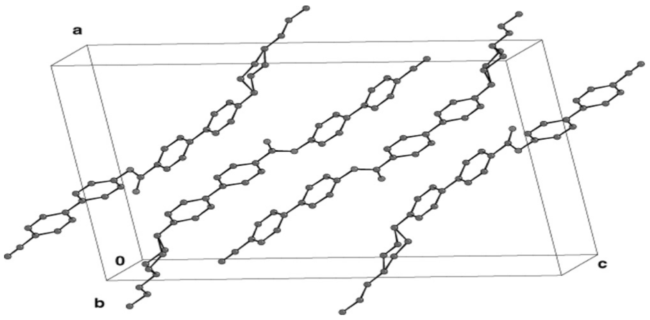

FIGURE 2 Partial packing of 7CBB molecule in the unit cell.

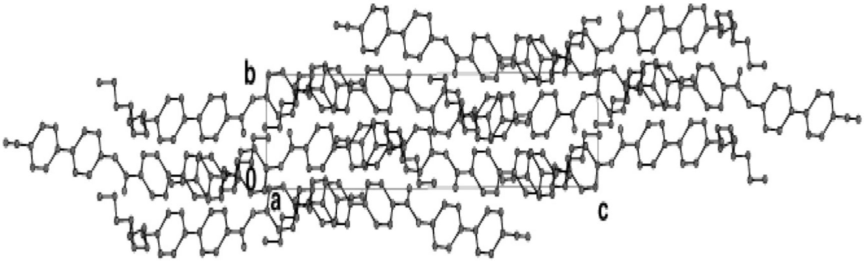

FIGURE 3 Crystal structure of 7CBB projected along a-axis.

long axis of the 7CBB molecules is inclined to the orthogonal **X**, **Y**, and **Z** axes at angles 53.4°, 92.4°, and 37.8°, respectively. The corresponding direction cosines of the molecular long axis of 6CBB found to be 0.31, -0.58, and 0.75, and the angles are 72°, 125°, and 41°, respectively.

Projection of the crystal structure along the **a**, **b**, and **c** axes are shown, respectively, in Figs. 3–5. From these figures it is evident that the pair of molecules related by the center of inversion are arranged in parallel manner although the space group is $P2_1/c$. These pairs of molecules are packed in interpenetrating layers and within a layer the molecules are tilted. Thus packing of the 7CBB molecules in the crystalline state is precursor to SmC phase structure rather than the observed SmA phase. In 6CBB, however, the nature of packing was precursor to the SmA phase structure. Crystal to SmA transition should therefore be of "reconstitutive" nature [30], where in addition to the translational motion, a rotation about an axis other than the molecular long axis is also necessary for the transition. In 6CBB, "displasive" type transition was observed.

Calculation of intermolecular distance reveals existence of several stronger van der Waals interactions compared to 6CBB. Selected

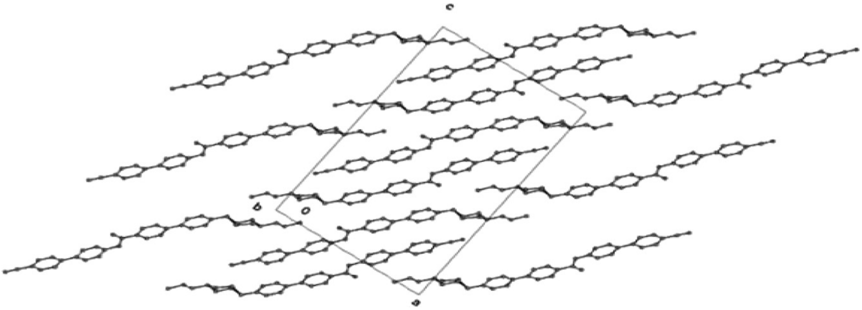

FIGURE 4 Crystal structure of 7CBB projected along b-axis.

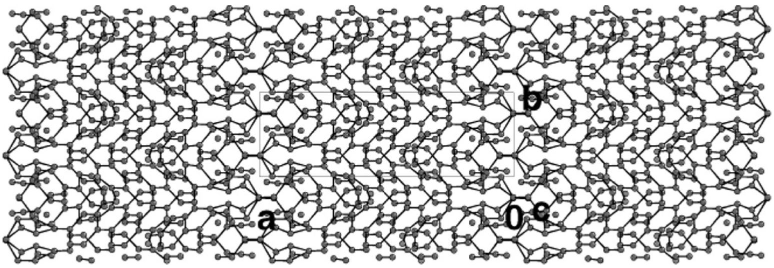

FIGURE 5 Crystal structure of 7CBB projected along c-axis.

contact distances less than 2.7 Å are shown in Table 7, all the short contacts are found to be in the rigid core portion of the molecules as shown in Fig. 6. Length of such a "dimer" is found to be 35.87 Å. Ratio of the associated length to model length is 1.13 in 7CBB while that in 6CBB is 1.09, thus molecular overlap is slightly less in 7CBB compared to 6CBB. In 7CBB, the smectic layer thickness is observed to be 30 to 31 Å, from X-ray study suggesting monolayer structure [3,29,31]. Centro-symmetrically related "dimmers" in the crystalline state probably overlap more in mesogenic state after melting to correspond to the observed smectic layer spacing.

TABLE 7 Selected Intermolecular Short Contact Distances Less Than 2.7 Å

Atom	Atom[a]	Distance
C6	C18	2.543
C6	C17	2.589
C18	C6	2.543
C21	C7	2.607
O2	C12	2.674
C15	C13	2.434
C17	C6	2.589
C14	C12	2.378
C16	C13	2.643
O1	C12	2.644
C7	C21	2.607
C7	C22	2.680
C12	O2	2.634
C12	C14	2.378
C12	O1	2.644
C13	C15	2.434
C13	C16	2.643
C22	C7	2.680

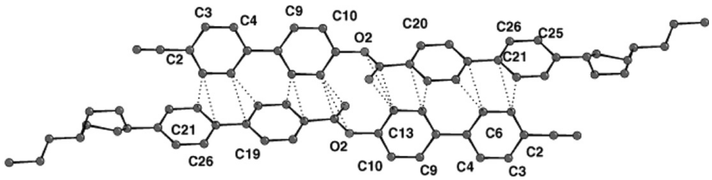

FIGURE 6 Molecular association observed in the crystal structure of 7CBB.

4. CONCLUSIONS

In continuation of our studies on nCBB series of compounds in the mesogenic as well as in the crystalline states, crystal and molecular structures of the seventh member of the series (7CBB) have been determined. Geometry of the rigid core and packing of the molecules in the crystalline state are found to be different from the lower homologue 6CBB. Molecules are packed in parallel manner, but in interpenetrating layers and within a layer the molecules are tilted. Packing of the molecules is, therefore, precursor to the SmC phase, whereas observed packing in 6CBB was found to be precursor to the SmA phase. Crystal to mesophase transition is probably of reconstitutive nature in this case, whereas it was of displacive type in 6CBB, although in both cases, the SmA_1 phase is observed on melting. Several stronger van der Waals interactions are observed in the core part of the neighbouring molecular pairs compared to 6CBB.

ACKNOWLEDGMENT

Authors thankfully acknowledge financial support for the work under the Indo-Polish Bilateral cooperation scheme.

REFERENCES

[1] Gray, G. W., Harrision, K. J., & Nash, J. A. (1973). *Electron Lett.*, *9*, 130.
[2] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor & Francis: London, UK, 53.
[3] Dabrowski, R., Pyc, K., Przedmojski, J., & Pura, B. (1985). *Mol. Cryst. Liq. Cryst.*, *129*, 169.
[4] Brodzik, M., Dabrowski, R., & Przedmojski, J. (1995). *J. Phys II France*, *5*, 1805.
[5] Brodzik, M., & Dabrowski, R. (1996). *Liq. Cryst.*, *20*, 99.
[6] Haase, W., & Athanassopoulou, M. A. (1999). *Stuct. and Bonding*, *94*, 140.
[7] Malpezzi, L., Bruckner, S., Ferro, Dino, R., & Luckhurst, G. R. (2001). *Liq. Cryst.*, *28*, 357.
[8] Sarkar, P., Paul, S., & Mandal, P. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 535.

[9] Sarkar, P., Sarkar, P., Mandal, P., & Manisekaran, T. (1998). *Mol. Cryst. Liq. Cryst.*, *325*, 91.

[10] Nath, A., Gupta, S., Mandal, P., Paul, S., & Schenk, H. (1996). *Liq. Cryst.*, *20*, 765.

[11] Mandal, P., Paul, S., Goubitz, K., & Schenk, H. (1995). *Mol. Cryst. Liq. Cryst.*, *258*, 209.

[12] Mandal, P., Paul, S., Schenk, H., & Goubitz, K. (1992). *Mol. Cryst. Liq. Cryst.*, *210*, 21.

[13] Gupta, S., Mandal, P., Paul, S., Goubitz, K., Wit, M. de., & Schenk, H. (1991). *Mol. Cryst. Liq.Cryst.*, *195*, 149.

[14] Mandal, P., Paul, S., Schenk, H., & Goubitz, K. (1986). *Mol. Cryst. Liq. Cryst.*, *135*, 35.

[15] Mandal, P., & Paul, S. (1985). *Mol. Cryst. Liq. Cryst.*, *131*, 223.

[16] Jaishi, B. R., Mandal, P. K., Goubitz, K., Schenk, H., Dabrowski, R., & Czuprynski, K. (2003), *Liq. Cryst.*, *30*, 1327.

[17] Bruker (1998). SMART. Version 5.054. Bruker AXS Inc. Madison, Wisconsin, USA.

[18] Sheldrick, G. M. SHELXS86 (1986) and SHELXL97 (1987), University of Göttingen, Germany.

[19] Walkin, D. M., Pearce, L., & Prout, C. K. (1993). *Cameron—A Molecular Graphics Package, Chemical Crystallographic Laboratory*, University of Oxford.

[20] Allen, F. H., & Kennard, O. (1993). *Chem. Des. Autom. News*, *8*, 31.

[21] Gupta, S., Chang-Chien, Gou-Ping, Lee, Wei-Shan, Centore, R., & Sen Gupta, S. P. (2002). *Liq. Cryst.*, *29*, 657.

[22] Sridhar, M. A., Lokanath, N. K., Shashidhara Prasad, J., Yelammagad, C. V., & Varshney, S. K. (2001). *Liq. Cryst.*, *28*, 45.

[23] Allouchi, H., Cotrait, M., Canlet, C., & Bayle, J. P. (2001). *Liq. Cryst.*, *28*, 1175.

[24] Lokanath, N. K., Sridhar, M. A., Revannasiddaiah, D., & Shasidhara Prasad, J. (2000). *Liq. Cryst.*, *27*, 767.

[25] Zugenmaier, P., & Heiske, A. (1993). *Liq. Cryst.*, *15*, 835.

[26] Baumeister, U., Hartung, H., & Jaskolski, M. (1982). *Mol. Cryst. Liq. Cryst.*, *88*, 167.

[27] Adams, J. M., & Morsi, S. E. (1976). *Acta cryst.*, *B32*, 1345.

[28] Kaiser, J., Richter, R., Lemke, G., & Golic, L. (1980). *Acta Cryst.*, *B36*, 193.

[29] Baumeister, U., Hartung, H., Gdaniec, M., & Jaskolski, M. (1981). *Mol. Cryst. Liq. Cryst.*, *69*, 119.

[30] Bryan, R. F., & Forcier, P. G. (1980). *Mol. Cryst. Liq. Cryst.*, *60*, 133.

[31] Brownsey, G. J., & Leadbetter, A. J. (1980). *Physical Review Letters*, *44*, 1608.