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The molecular and crystal structure of a polar mesogen 4-cyanobiphenyl-4′-hexylbiphenyl carboxylate

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The crystal structure of the compound 4-cyanobiphenyl-4′-hexylbiphenyl carboxylate (6CBB), which exhibits both monolayer smectic A and nematic phases, has been determined by direct methods using single crystal X-ray diffraction data. The structure is triclinic with the space group *P*-1 and $Z=2$. The unit cell parameters are $a=9.3511(7)$ Å, $b=11.2456(7)$ Å, $c=13.1417(6)$ Å, $\alpha=85.872(4)^{\circ}$, $\beta=76.258(5)^{\circ}$ and $\gamma=70.697(5)^{\circ}$. The molecule is found to be slightly bow-shaped although the alkyl chain is in all-*trans* conformation. The phenyl rings in 6CBB are non-coplanar. The packing of the molecules in the crystalline state is found to be a precursor to the smectic A phase structure. Comparison of crystal structures and packing of the four-ring 6CBB with those of the two-ring *n*CB or *n*OCB compounds has been made to explain the observed phase behaviour.

1. Introduction

Strongly polar nematogenic cyanobiphenyl compounds are of great interest because of their commercial use in LCD technology [1, 2]. Two biphenyl moieties—one having a terminal cyano group and the other possessing a terminal alkyl chain—when linked with a carboxylate group give rise to an elongated core homologous series, 4-cyanobiphenyl-4′-alkylbiphenyl carboxylate (*n*CBB). These materials have drawn much attention because they are the first four-ring compounds whose higher homologues ($n=8,9$) exhibit a reentrant nematic (N_{re}) phase as well as two types of smectic A phase—monolayer (SmA_1) and partially bilayer (SmA_d) smectics [3]. On the other hand, the lower homologues ($n=4$–7) form only SmA_1 and nematic phases. For example, the title compound 6CBB exhibits the phase sequence Cr 141.5 SmA_1 158.7 N 360 I (°C), like $n=4,5,7$; the observed phase sequence for 8CBB is Cr 118 SmA_1 (108.5) N_{re} 160.5 SmA_d 298 N 343 I (°C), a similar phase behaviour being observed for $n=9$. It has been further observed [4–8] that:

(1) the thermal stability of monolayer SmA_1 decreases as the alkyl chain length increases;
(2) the ratio of SmA_d layer spacing (d) to the length of the molecule (l) is less than in a typical SmA_d phase created in short cyanobiphenyl molecules such as *n*CB or *n*OCB;
(3) the SmA_d layer spacing corresponds to anti-parallel side-by-side homodimers where the rigid cores of the molecules overlap;
(4) in binary mixtures of four-ring *n*CBB compounds with two-ring *n*CB compounds, the SmA_d phase is induced or enhanced substantially. Induction or enhancement of the SmA_d phase takes place in the form of an 'island' or 'semi-island' surrounded by nematic sea—a reentrant nematic phase is also induced in some cases.

It has been observed that in mesogenic compounds [9–18] knowledge of the molecular geometry and packing of the molecules in the crystalline state often helps in explaining the observed phase behaviour,

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which depends on a subtle balance of intermolecular interactions [9–18]. With this aim an attempt has been made to determine the crystal structures of the present compounds. But after repeated trials, single crystals suitable for X-ray study were obtained only for 6CBB; results of its structural analysis are presented here.

2. Experimental, structure determination and refinement

Transparent plate shaped crystals were grown from a solution of acetone and xylene by the slow evaporation technique. A crystal with dimensions $0.20 \times 0.75 \times 0.75\,\text{mm}^3$ (approximately) was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuK_α radiation and $\omega - 2\theta$ scan. A total of 5 197 unique reflections were measured within the range $-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 0$. Of these, 4 166 were above the significance level of $2.5\sigma(I)$. The range of $(\sin\theta)/\lambda$ was 0.039–$0.626\,\text{Å}^{-1}$ ($3.5^\circ < \theta < 74.7^\circ$). Two reference reflections ($0\,\bar{1}\,\bar{1}$; $2\,2\,\bar{1}$) were measured hourly and showed no decrease during the 67 h collecting time. Unit cell parameters were refined by a least-squares fitting procedure using 23 reflections with $39.99^\circ \leqslant \theta \leqslant 40.90^\circ$. Corrections for Lorentz and polarization effects were applied. The structure was solved by the program package CRUNCH [19]. The hydrogen atoms were placed at calculated positions using the known geometry around the carbon atoms. Full-matrix least-squares refinement on the structure factors (F), with anisotropic temperature factors for the non-hydrogen atoms and isotropic for the hydrogen atoms (restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.0Å) converged to $R = 0.076$, $R_w = 0.074$, $(\Delta/\sigma)_{\max} = 0.19$, $S = 0.88$. The secondary isotropic extinction coefficient [20, 21] refined to $g = 3717(225)$. A weighting scheme $w = [0.7 + 0.01^*(\sigma_{F\text{obs}}{}^2 + 0.01/(\sigma_{F\text{obs}})]^{-1}$ was used. A final difference Fourier map revealed a residual electron density between -0.25 and $0.28\,\text{eÅ}^{-3}$. Scattering factors were taken from Cromer and Mann [22] and International Tables for X-ray Crystallography [23]. All calculations were performed with XTAL3.7 [24], unless stated otherwise. Important crystallographic data and refinement parameters are given in table 1.

Table 1. Crystallographic data for 6CBB.

Formula	$C_{32}\ H_{29}\ N\ O_2$
Formula mass	$459.56\,\text{g mol}^{-1}$
Crystal system	Triclinic
Space group	P-1 (No. 2)
a, b, c	9.3511(7) Å 11.2456(7) Å, 13.1417(6) Å
α, β, γ	85.872(4)° 76.258(5)°, 70.697(5)°
V	$1266.91(14)\,\text{Å}^3$
Z	2
D_{cal}	$1.205\,\text{g cc}^{-1}$
$\text{Mu}(\text{CuK}_\alpha)$	$0.580\,\text{mm}^{-1}$
$F(000)$	488
Crystal size	$0.20 \times 0.75 \times 0.75\,\text{mm}^3$

3. Results and discussion

A perspective drawing of the 6CBB molecule with atom numbering scheme is shown in figure 1. Final positional coordinates with equivalent temperature factors, anisotropic thermal parameters, bond lengths and bond angles of the non-hydrogen atoms are listed in tables 2–5.

The average aromatic bond length in the phenyl rings A,B,C and D are respectively 1.387(5), 1.389(5), 1.386(6) and 1.386(6) Å (maximum and minimum value being 1.400(5) and 1.365(6) Å in D). The average observed bond angle in each of the four phenyl rings is 120.0(3)°. These values are in agreement with the geometry of other biphenyl moieties reported in the Cambridge structural database [25]. In particular the geometry of the biphenyl fragment of 6CBB agrees well with that of α,ω-bis(4-cyanobiphenyl-4′-yloxy)octane [10], 3-[4-(4′-ethylbiphenyl)]-1-propene [26] (average aromatic bond distance is 1.382 and 1.368 Å, respectively) and of related compounds [14, 27–31]. The alkyl chain is in the all-*trans* conformation with mean bond

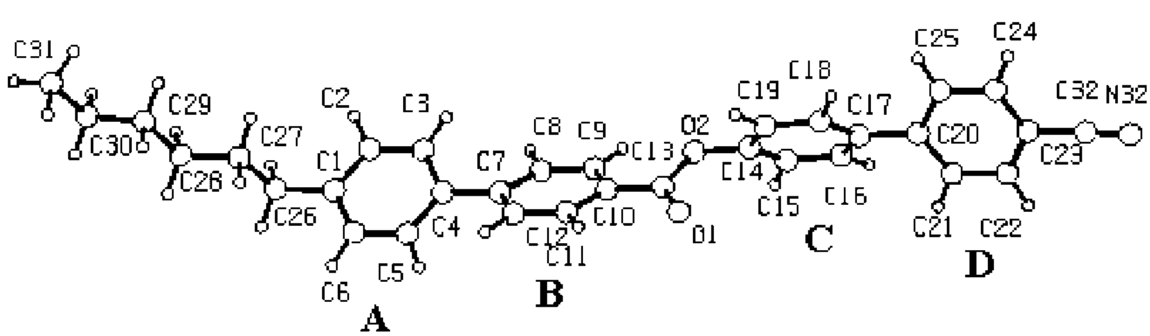

Figure 1. Perspective view of the 6CBB molecule with atom numbering scheme.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms with e.s.d. values in parentheses.

Atom	x	y	z	U_{eq} Å^2
O1	0.7316(3)	0.3107(3)	−0.1443(2)	0.0799(10)
O2	0.4772(3)	0.3355(2)	−0.08442(18)	0.0667(9)
N32	0.1691(5)	0.9777(3)	−0.7315(3)	0.1002(19)
C1	0.7725(4)	−0.2381(3)	0.4223(3)	0.0572(11)
C2	0.6277(4)	−0.1514(3)	0.4215(3)	0.0607(12)
C3	0.6051(4)	−0.0714(3)	0.3373(3)	0.0570(11)
C4	0.7269(4)	−0.0744(3)	0.2519(2)	0.0488(10)
C5	0.8719(4)	−0.1614(3)	0.2526(3)	0.0572(11)
C6	0.8938(4)	−0.2419(3)	0.3372(3)	0.0606(12)
C7	0.7020(4)	0.0139(3)	0.1628(2)	0.0500(10)
C8	0.5605(4)	0.0542(3)	0.1325(3)	0.0604(12)
C9	0.5351(4)	0.1406(3)	0.0527(3)	0.0617(12)
C10	0.6528(4)	0.1877(3)	0.0003(2)	0.0525(10)
C11	0.7953(4)	0.1455(3)	0.0280(3)	0.0575(12)
C12	0.8192(4)	0.0609(3)	0.1085(3)	0.0562(11)
C13	0.6303(4)	0.2823(3)	−0.0841(3)	0.0572(11)
C14	0.4363(4)	0.4229(3)	−0.1638(3)	0.0566(11)
C15	0.3576(4)	0.3944(3)	−0.2287(3)	0.0623(12)
C16	0.3123(4)	0.4782(3)	−0.3065(3)	0.0600(12)
C17	0.3403(4)	0.5935(3)	−0.3168(2)	0.0498(10)
C18	0.4164(4)	0.6214(3)	−0.2472(3)	0.0582(11)
C19	0.4636(4)	0.5371(3)	−0.1695(3)	0.0626(12)
C20	0.2977(3)	0.6795(3)	−0.4048(2)	0.0490(10)
C21	0.3128(4)	0.6303(3)	−0.5013(3)	0.0551(11)
C22	0.2774(4)	0.7082(3)	−0.5856(3)	0.0571(11)
C23	0.2239(4)	0.8372(3)	−0.5704(3)	0.0546(11)
C24	0.2056(4)	0.8885(3)	−0.4753(3)	0.0594(11)
C25	0.2415(4)	0.8097(3)	−0.3911(3)	0.0557(11)
C26	0.7964(6)	−0.3247(4)	0.5150(3)	0.0718(14)
C27	0.8349(5)	−0.2685(4)	0.6009(3)	0.0690(14)
C28	0.8536(6)	−0.3573(4)	0.6950(3)	0.0787(17)
C29	0.8845(6)	−0.3001(4)	0.7838(3)	0.0790(17)
C30	0.8905(7)	−0.3835(5)	0.8801(4)	0.0923(2)
C31	0.9263(11)	−0.3240(9)	0.9666(6)	0.1288(4)
C32	0.1925(5)	0.9176(3)	−0.6602(3)	0.0682(14)

distance 1.515(8) Å and bond angle 112.6(5)°, as found in other mesogenic compounds [15–18]. The CO double bond (C13–O1) is found to be 1.197(5) Å whereas the CO single bonds are 1.358(4) Å (C13–O2) and 1.412(4) Å (O3–C14). In cholesteryl 6[4-(4-pentyloxyphenylethynyl)phenoxy]hexanoate [27] the respective bonds are found to be 1.130(15) Å and 1.367 Å (mean value). A value of 1.385(2) Å for the single bond is observed in α,ω-bis(4-cyanobiphenyl-4′-yloxy)octane [10]. The CN triple bond (C23–N32) is found to be 1.137(5) Å and the angle C23–C32–N32 is 178.3(4)°. The corresponding observed values in the above octane compound 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 agree well with values reported for similar mesogenic materials.

The geometry of the 6CBB molecule may be described in terms of the four phenyl ring planes and the plane of the alkyl chain. All the phenyl rings are planar (highest displacement of the atom C14 from the benzene ring C being 0.02 Å). The atoms C32 and N32 are displaced downward from the nearest phenyl ring by 0.06 and 0.10 Å, respectively. The atoms of the–COO group lie closer to the plane of ring B than of ring C. The alkyl chain is also almost planar; r.m.s. displacement of the atoms is 0.05 Å. However, unlike the shorter cyanobiphenyl compounds, the phenyl rings in 6CBB are not coplanar, the dihedral angles between the planes being quite large. In 5OCB [18] the dihedral angle between the two benzene rings is 0.82° and in 3-[4-(4′-ethylbiphenyl)]-1-propene [26] it is 1.5°. On the other hand, in 6CBB the angles between the planes of the rings AB, AC, AD, BC, BD and CD are, respectively, 33.2°, 79.9°, 62.2°, 46.7°, 84.6° and 38.0°. The least value of the dihedral angle (25.5°) is observed between the planes of the hexyl chain and the phenyl ring furthest from it. However this is not quite unusual: in 4-cyanophenyl-4′-heptylbenzoate [17], where the two phenyl rings are linked by a carboxylate spacer, the observed dihedral angle is 47.5°. Similar values are found in other phenyl benzoates [32–34], though coplanar benzene rings along with the carboxylate group have also been reported [35].

The calculated length of the 6CBB molecule in the crystalline state is found to be 27.83 Å whereas the model length in the most extended form is 30.6 Å. Thus, although the alkyl chain is in the all-*trans* conformation, the molecule is slightly bow-shaped.

The packing of 6CBB molecules in the unit cell is shown in figure 2. The direction cosines of the molecular long axis, defined as the best fitted line through all the atoms, are found to be 0.31, −0.58 and 0.75. Thus the long axis of the 6CBB molecules is inclined to the orthogonal X, Y and Z axes at angles 72°, 125° and 41° respectively. If, however, the long axis is defined excluding the chain atoms, the corresponding angles change slightly to 71°, 131° and 47°.

Projections of the crystal structure along the a, b and c axes are shown, respectively, in figures 3–5. From these figures it is evident that the pairs of molecules related by the centre of inversion are arranged in a parallel manner. These pairs of parallel molecules are packed in interpenetrating layers. Figure 5 suggests that, on heating, the opposite shift of pairs parallel to each other by half the b axis may give rise to a SmA layer structure. Thus packing of the 6CBB molecules in the crystalline state is precursor to the SmA phase structure, which on further heating may adopt a nematic structure. The crystal to SmA transition is, therefore, 'displacive' rather than 'reconstitutive' [36]

Table 3. Anisotropic thermal parameters of the non-hydrogen atoms with the e.s.d. values 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}
O1	0.0682(16)	0.0891(19)	0.0733(17)	0.0268(14)	−0.0103(13)	−0.0230(14)
O2	0.0642(15)	0.0761(16)	0.0623(14)	0.0238(12)	−0.0228(12)	−0.0249(12)
N32	0.1496(4)	0.0863(3)	0.0852(3)	0.0313(2)	−0.0520(3)	−0.0537(3)
C1	0.0735 (2)	0.0518(18)	0.0559(19)	0.0018(15)	−0.0260(17)	−0.0252(17)
C2	0.0630 (2)	0.0623(2)	0.0567(2)	0.0019(16)	−0.0115(17)	−0.0219(17)
C3	0.0533 (19)	0.0573(2)	0.0586(19)	0.0006(15)	−0.0150(16)	−0.0140(16)
C4	0.0533 (17)	0.0487(17)	0.0490(16)	−0.0026(13)	−0.0167(14)	−0.0183(14)
C5	0.0517 (19)	0.0596(2)	0.0584(2)	0.0009(16)	−0.0135(16)	−0.0148(16)
C6	0.0575 (2)	0.0572(2)	0.0701(2)	0.0018(17)	−0.0263(18)	−0.0144(17)
C7	0.0540 (18)	0.0485(17)	0.0494(17)	−0.0030(13)	−0.0158(14)	−0.0156(14)
C8	0.0586 (2)	0.0690(2)	0.0646(2)	0.0153(17)	−0.0250(17)	−0.0303(17)
C9	0.0591(2)	0.0707(2)	0.0654(2)	0.0140(17)	−0.0281(17)	−0.0272(18)
C10	0.0583 (19)	0.0533(18)	0.0464(17)	−0.0011(14)	−0.0149(14)	−0.0165(15)
C11	0.0551(19)	0.0646(2)	0.0529(19)	0.0051(16)	−0.0109(15)	−0.0211(16)
C12	0.0502(18)	0.0639(2)	0.0551(19)	0.0009(16)	−0.0157(15)	−0.0166(16)
C13	0.0642(2)	0.0569(2)	0.0487(18)	−0.0013(14)	−0.0121(16)	−0.0172(17)
C14	0.0601(2)	0.0615(2)	0.0503(18)	0.0099(15)	−0.0178(15)	−0.0205(16)
C15	0.0735(2)	0.0585(2)	0.0663(2)	0.0073(17)	−0.0264(18)	−0.0304(18)
C16	0.0740(2)	0.0577(2)	0.0637(2)	0.0083(16)	−0.0322(18)	−0.0313(17)
C17	0.0533(18)	0.0483(17)	0.0508(17)	−0.0010(13)	−0.0150(14)	−0.0178(14)
C18	0.0719(2)	0.0533(19)	0.0585(19)	−0.0007(15)	−0.0255(17)	−0.0245(17)
C19	0.0765(2)	0.0649(2)	0.0575(2)	0.0004(16)	−0.0288(18)	−0.0279(18)
C20	0.0449(16)	0.0513(17)	0.0521(17)	−0.0041(13)	−0.0119(13)	−0.0156(14)
C21	0.0594(19)	0.0482(19)	0.0574(19)	−0.0051(15)	−0.0163(15)	−0.0136(15)
C22	0.0578(19)	0.0631(18)	0.0512(18)	−0.0033(15)	−0.0156(15)	−0.0177(16)
C23	0.0509(18)	0.0590(19)	0.0576(19)	0.0056(15)	−0.0148(15)	−0.0219(15)
C24	0.0662(2)	0.0487(19)	0.0677(2)	0.0006(16)	−0.0185(17)	−0.0220(16)
C25	0.0619(2)	0.0523(18)	0.0554(19)	−0.0071(15)	−0.0139(16)	−0.0199(16)
C26	0.0992(3)	0.0602(2)	0.0660(2)	0.0095(19)	−0.0333(2)	−0.0308(2)
C27	0.0832(3)	0.0650(2)	0.0632(2)	0.0081(18)	−0.0271(2)	−0.0238(2)
C28	0.0921(3)	0.0819(3)	0.0674(3)	0.0148(2)	−0.0310(2)	−0.0289(3)
C29	0.0821(3)	0.0892(3)	0.0679(3)	0.0143(2)	−0.0213(2)	−0.0307(3)
C30	0.1057(4)	0.1033(4)	0.0679(3)	0.0227(3)	−0.0304(3)	−0.0310(3)
C31	0.1630(7)	0.1588(7)	0.1001(4)	0.0286(5)	−0.0680(5)	−0.0778(6)
C32	0.0835(3)	0.0647(2)	0.0675(2)	0.0119(19)	−0.0268(2)	−0.0340(2)

where, in addition to the translational motion, rotation about an axis other than the molecular long axis is also necessary for the transition.

The calculation of intermolecular distance between molecules related by centre of symmetry reveals the existence of numerous van der Waals interactions. Selected contact distances which are less than 3.65 Å are shown in table 6. Three different types of molecular associations in head-to-tail configuration are observed: (i) molecules of the pair overlap almost completely so that the cyano groups lie at opposite ends (related by symmetry operation 'a' having pair length 28.2 Å, and symmetry operation 'd' having pair length 30.8 Å); (ii) molecules of the pair overlap almost completely but the three end atoms of the hexyl chain lie at opposite ends (related by symmetry operation 'b' having associated length 33.3 Å); (iii) only the core regions of the two molecules of the pair overlap, but not the hexyl chains (related by symmetry operation 'c' having associated length 44.8 Å). Of these, pairs of the second type may easily give rise to a SmA$_1$ structure as noted above. Although the length of the pair of the first type is nearer to the observed smectic layer spacing (28.5 Å [6]) than the length of the second type, it is easier to obtain a smectic layer structure by translations of the second type pair than of the first type. The difference between the smectic layer and associated pair lengths may be due to a change in conformation of the molecules, change of extent of overlap of the pairs, or disorder in the chain part. On the other hand, in cyanobiphenyls (*n*CB or *n*OCB), bimolecular association is found to exist in both solid and mesophases involving cyano–cyano interactions [18, 31, 37, 38]. Thus a subtle difference in the interaction between neighbouring molecules as a result of a steric effect might be the origin of development of a monolayer SmA$_1$ phase in the four-ring cyano compound 6CBB, and a partially bilayer SmA$_d$ phase in two-ring cyano compounds

Table 4. Bond distance (Å) of the non-hydrogen atoms with standard deviations in parentheses.

O1–C13	1.198(5)	C14–C15	1.366(6)
O2–C13	1.358(5)	C14–C19	1.383(5)
O2–C14	1.412(4)	C15–C16	1.384(5)
N32–C32	1.136(5)	C16–C17	1.397(5)
C1–C2	1.384(5)	C17–C18	1.392(5)
C1–C6	1.383(6)	C17–C20	1.496(4)
C1–C26	1.516(5)	C18–C19	1.391(5)
C2–C3	1.386(5)	C20–C21	1.378(5)
C3–C4	1.390(5)	C20–C25	1.391(5)
C4–C5	1.386(5)	C21–C22	1.395(5)
C4–C7	1.490(4)	C22–C23	1.382(5)
C5–C6	1.392(5)	C23–C24	1.364(5)
C7–C8	1.394(5)	C23–C32	1.460(5)
C7–C12	1.396(5)	C24–C25	1.400(5)
C8–C9	1.385(5)	C26–C27	1.500(6)
C9–C10	1.392(5)	C27–C28	1.538(6)
C10–C11	1.386(5)	C28–C29	1.500(6)
C10–C13	1.483(5)	C29–C30	1.521(7)
C11–C12	1.379(5)	C30–C31	1.514(11)

such as 8OCB. Structural analysis of other *n*CBB compounds, especially 8CBB and 9CBB, might help in understanding the origin of developing SmA_d and N_{re} phases in these compounds. Unfortunately, as noted earlier, due to the lack of single crystals suitable for X-ray analysis this cannot be done at present.

Table 5. Bond angles (°) involving non-hydrogen atoms with standard deviations in parentheses.

C13–O2–C14	118.3(3)	O2–C14–C19	121.0(3)
C2–C1–C6	118.1(3)	C15–C14–C19	121.6(3)
C2–C1–C26	120.4(4)	C14–C15–C16	119.4(3)
C6–C1–C26	121.4(4)	C15–C16–C17	121.0(3)
C1–C2–C3	120.8(4)	C16–C17–C18	118.2(3)
C2–C3–C4	121.2(3)	C16–C17–C20	120.0(3)
C3–C4–C5	118.0(3)	C18–C17–C20	121.8(3)
C3–C4–C7	120.8(3)	C17–C18–C19	121.2(3)
C5–C4–C7	121.3(3)	C14–C19–C18	118.6(4)
C4–C5–C6	120.5(3)	C17–C20–C21	120.1(3)
C1–C6–C5	121.3(3)	C17–C20–C25	121.1(3)
C4–C7–C8	121.3(3)	C21–C20–C25	118.8(3)
C4–C7–C12	120.8(3)	C20–C21–C22	121.4(3)
C8–C7–C12	117.9(3)	C21–C22–C23	118.6(3)
C7–C8–C9	121.2(3)	C22–C23–C24	121.2(3)
C8–C9–C10	120.0(4)	C22–C23–C32	118.0(3)
C9–C10–C11	119.1(3)	C24–C23–C32	120.7(3)
C9–C10–C13	122.0(3)	C23–C24–C25	119.8(3)
C11–C10–C13	118.8(3)	C20–C25–C24	120.1(3)
C10–C11–C12	120.6(3)	C1–C26–C27	113.6(4)
C7–C12–C11	121.0(4)	C26–C27–C28	112.2(4)
O1–C13–O2	123.3(3)	C27–C28–C29	113.0(4)
O1–C13–C10	125.6(4)	C28–C29–C30	113.1(4)
O2–C13–C10	111.2(3)	C29–C30–C31	111.4(5)
O2–C14–C15	117.2(3)	N32–C32–C23	178.4(4)

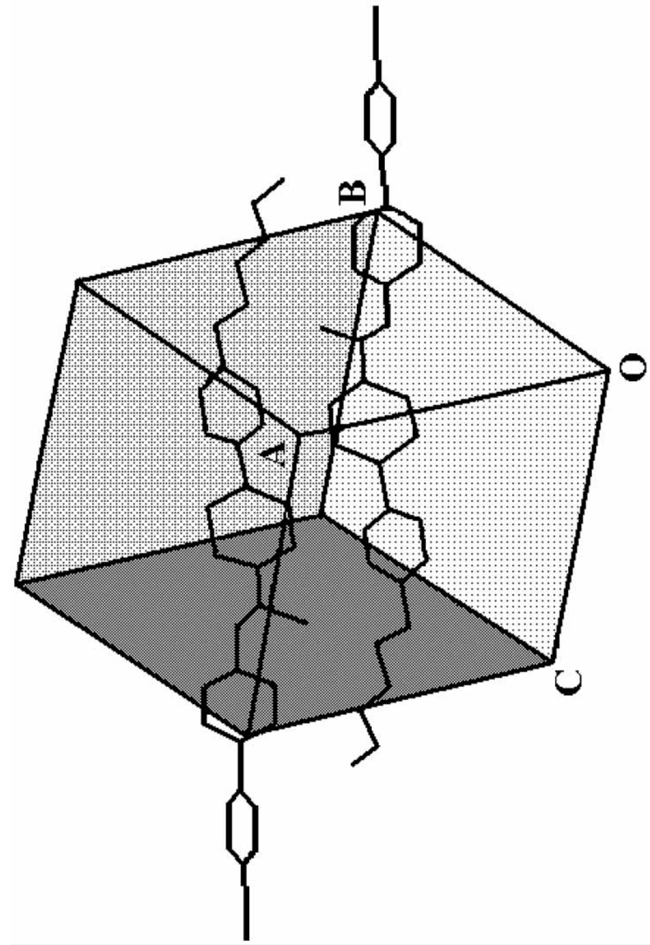

Figure 2. Partial packing of 6CBB molecules in the unit cell.

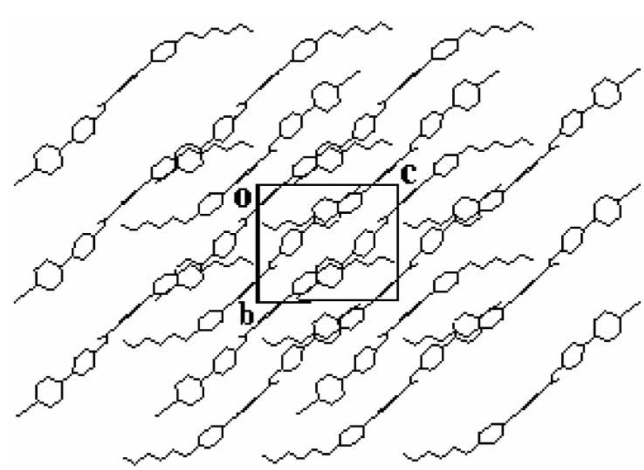

Figure 3. Crystal structure of 6CBB projected along the *a*-axis.

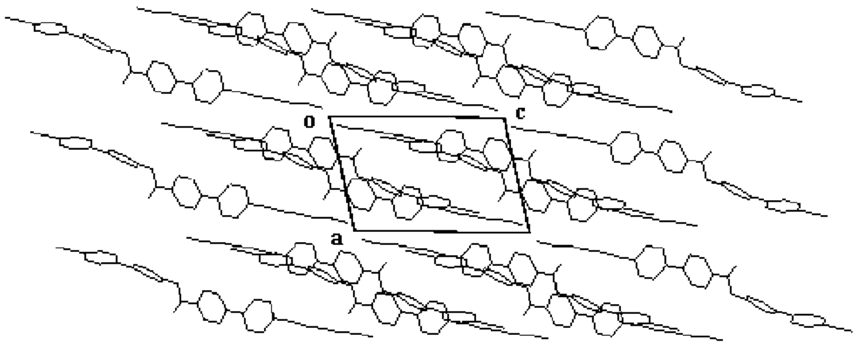

Figure 4. Crystal structure of 6CBB projected along the *b*-axis.

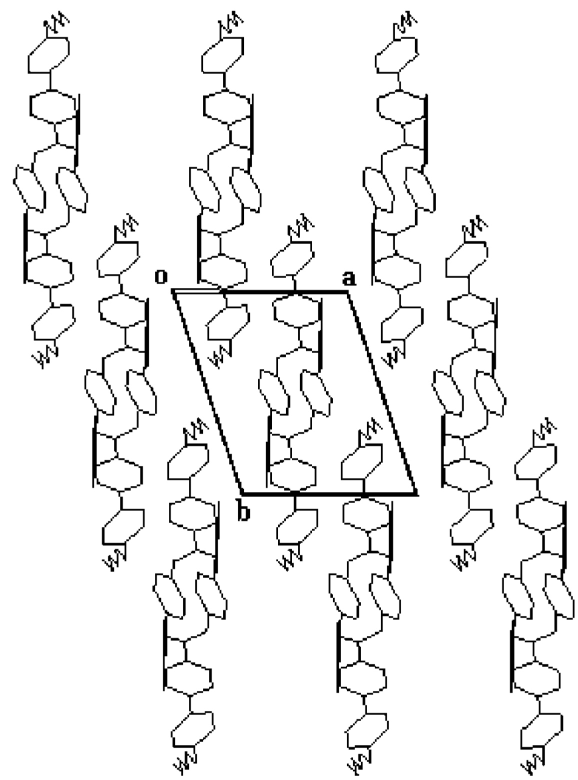

Figure 5. Crystal structure of 6CBB projected along the *c*-axis.

Table 6. Selected intermolecular short contact distances less than 3.65 Å.

Atoms		Distance/Å	Atoms		Distance/Å
C1	C16[a]	3.580	O1	C22[c]	3.592
C10	C19[b]	3.650	O1	C32[c]	3.546
C15	C22[c]	3.574	O1	N32[c]	3.478
C13	N32[c]	3.630	O1	C5[d]	3.509

[a]Atom at 1-*x*, 2-*y*, 2-*z*.
[b]Atom at $1-x$, $1-y$, $2-z$.
[c]Atom at $1-x$, $1-y$, $3-z$.
[d]Atom at $-x$, $2-y$, $2-z$.

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