Chapter VI

MOLECULAR STRUCTURE AND PACKING IN THE CRYSTALLINE STATE OF 4-n-ETHYL-4'-CYANOBIPHENYL (2CB) BY SINGLE CRYSTAL X-RAY DIFFRACTOMETRY

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6.1 INTRODUCTION

Both the homologous series; 4-n-alkyl-4′-cyanobiphenyl (*n*CB) and 4-n-alkoxy-4′-cyanobiphenyl (*n*OCB) are particularly interesting and useful family of mesogens. These systems have been studied extensively from different angles using various experimental techniques. Several of them are used as components in commercially available liquid crystal mixtures [1]. In both the series the first four homologous compounds show monotropic nematic phase whereas the eight higher ones form enantiotropic nematic and/or smectic phases. Knowledge of molecular conformation and packing in the crystalline state gives better insight in understanding their structure and properties in the mesophase [2,3] as has been discussed in Chapter II. With this view crystal and molecular structures of the 3rd, 4th, 6th and 7th members of the *n*CB-series [4-6] and first to eighth members of the *n*OCB-series[7-10] were reported earlier. Crystal and molecular structures of a large number of liquid crystal compounds including the 5th member of the nOCB series [8,11-17] have been determined by co-workers and mechanism of transition to mesomorphic phase has been tried to explain in relation to the molecular organization in the crystalline state. In continuation of this program the crystal and molecular structure of the second member of the *n*CB series (2CB) have been determined and described in this chapter.

6.2 EXPERIMENTAL

6.2.1 Crystal Data

Transparent needle shaped crystals were grown by slow evaporation technique from a solution in acetone. A single crystal of dimensions .23×.18×.28 mm was used to collect intensity data using Enraf-Nonious CAD4 diffractometer. MoK_α radiation, monocromated by graphite monocromator, was used for data collection. The unit cell parameters were obtained using the method of short vector followed by least-squares refinement of 25 reflections in the interval $8 < \theta < 18^\circ$. All the 25 reflections could be indexed with respect to a monoclinic cell. The reflections

0k0 with k=2n+1 were found to be systematically absent indicating that the space group is $P2_1$. All together 1153 independent reflections were measured in the interval $4 < 2\theta < 50^\circ$ of which 557 were taken as observed reflections with $I>2\sigma(I)$. Lorentz and polarization corrections were applied but no absorption correction was made. Data were collected in ω-2θ scan mode. Important crystallographic data of the compound are given in Table 6.1

6.2.2 Structure Determination and Refinement:

The structure was solved by direct methods using the PC version of the crystallographic package program SIR92 [18]. Details of the direct method have been described in Chapter II. In SIR92 package estimation of structure invariants and structure seminvariants is based on Representation Theory developed by Giacovazzo [19,20]. Stereochemically best suited model obtained from E-map was refined by full-matrix block least-squares method. Anisotropic thermal parameters for the non-hydrogen atoms were used during refinement while the hydrogen atoms were attributed isotropic thermal parameters of the parent C-atoms. Positions of hydrogen atoms were calculated theoretically. SHELXL-93 computer program [21] was used for refinement. The final residual structure factor R(F) is 0.079. A difference Fourier map at this stage showed no electron density maxima greater than ±0.3 Å^{-3}. The atomic scattering factors were taken from the International Table for Crystallography [22]. For brevity calculated and observed structure factors are not produced here and also in Chapter VII.

6.3 RESULTS AND DISCUSSIONS

6.3.1 Molecular Conformation

Perspective view of 2CB molecule is shown in figure 6.1. Final positional and anisotropic thermal parameters of all non-hydrogen atoms are listed in Tables 6.2 and 6.3 using the numbering scheme of atoms shown in figure 6.1. Their bond lengths and bond angles are given in Table 6.4. Positions of the hydrogen atoms with their isotropic temperature factors are given in Table 6.5. Average C-C bond distance in cyanophenyl ring is 1.375(11) Å and that in alkyl phenyl ring is 1.374(10) Å, about 0.02 Å less than the expected value [23]. Mean C-C bond lengths in the phenyl rings were found to be 1.383 Å and 1.40 Å in 3CB and 4CB molecules respectively [4,5]. Moreover, the C2-C3 bond distance is found to be 1.358(13) Å, quite less than the expected value. Such shortening of bond lengths has, however, been observed in other mesogens [8,24,25]. But average C-C-C bond angle in the phenyl rings is 120.0(7)° as expected. The distance C14-C15 in the ethyl chain is 1.390(13) Å, quite less than the expected value 1.541 Å [23]. In fact the terminal atom C15 is found to have a temperature factor almost double than that of other atoms. Hence we ignored the methyl hydrogen atoms in final stages of refinement. It is noted that 4CB molecule also showed [5] disordering in the last two C atoms of the butyl chain and such disordering in terminal chain was observed in other mesogenic structures [26-28] as well. The C1-N bond distance is found to be 1.159(7) Å somewhat larger than 1.142(5) Å in 3CB and 1.130(2) Å in 4CB and 1.132Å in 5OCB [4,8]. The angle N-C1-C2 is 179.6(8)° close to the value observed in other cyanophenyl compounds.

To get an idea about the conformation of the molecule least-squares planes through different fragments of 2CB and the dihedral angles between the planes have been calculated and given in Table 6.6. As expected both the phenyl rings are highly planar. The cyano group atoms C1 and N are displaced downward from the phenyl group by 0.10 Å and 0.18 Å respectively. The two phenyl rings are inclined to each other at an angle 1.46° unlike the 3CB and 4CB molecules where the angle is 40.5° and 42.8° respectively. Though few biphenyl mesogenic compounds [5,7] show the

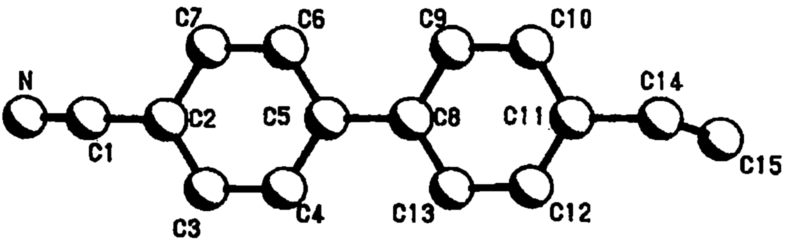

Figure 6.1: Perspective view of 2CB molecule along with atomic numbering scheme.

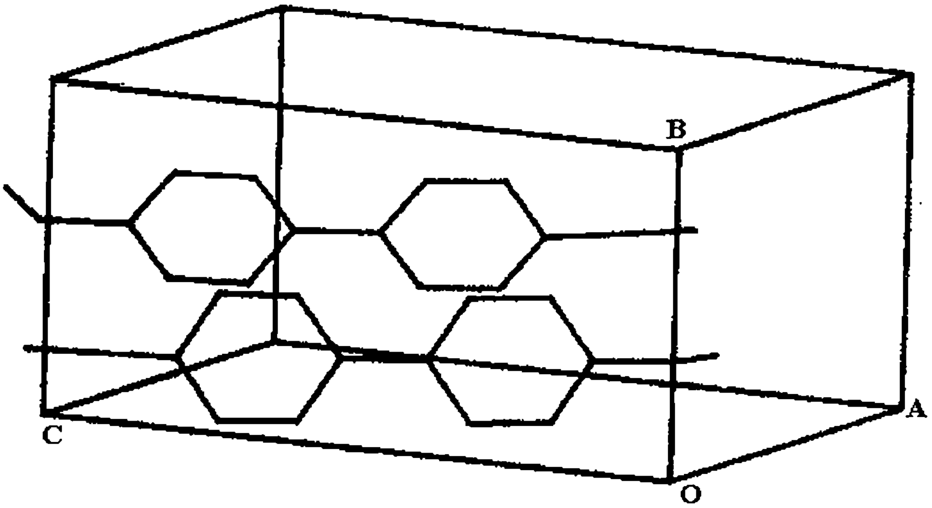

Figure 6.2: Packing of 2CB molecules in the unit cell.

above dihedral angle around 40° but a wide range of values namely 0-50° have also been observed [7]. Interestingly, all the first eight *n*OCB members show large dihedral angles only exception is 5OCB [8] where this angle was found to be 0.82°. Length of the molecule (N-C15) in the crystalline state is found to be 11.83 Å and when methyl group hydrogen bond length is included it becomes 12.85 Å in good agreement with the model length of the molecule in *all-trans* configuration.

6.3.2 Crystal Packing:

Different views of the packing of 2CB molecules in the crystalline state are shown in figures 6.2-6.4. The molecules are extended parallel to each other with their long axis making an angle of ~23° with [001] direction. Antiparallel pairs of molecules, related by the symmetry element two fold screw axis (2_1), are arranged in layers by translational symmetry along [100] and [010] and the layers are stacked along [001] direction. The thickness of these layers is equal to the length of crystallographic *c*-axis.

In order to discuss the molecular association in the crystalline state, which might be interpreted either as a precursor or as a result of liquid crystalline state, we

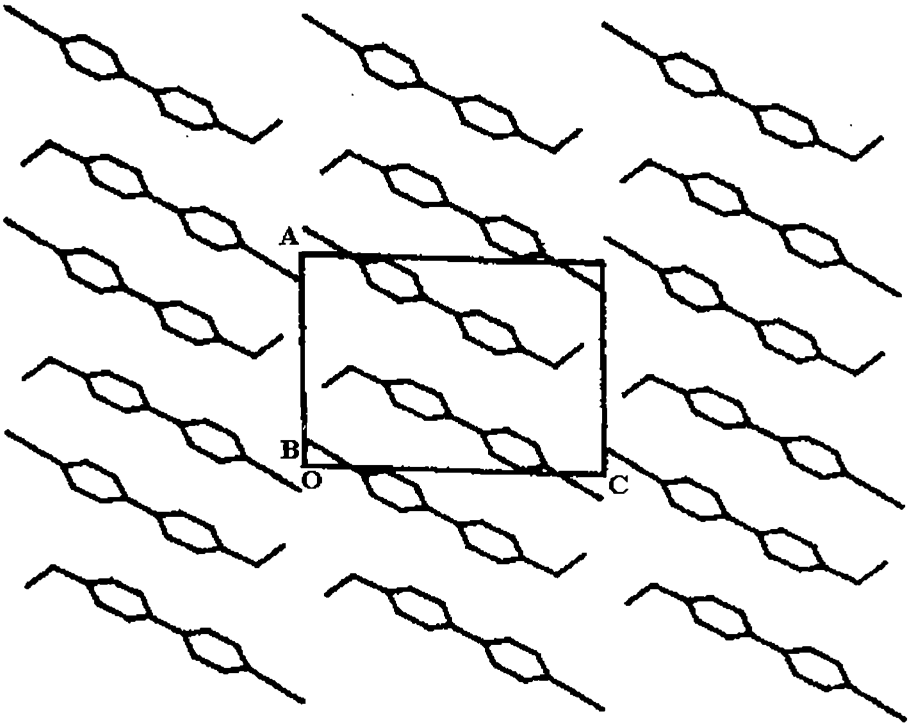

Figure 6.3: Crystal structure of 2CB projected in ac-plane.

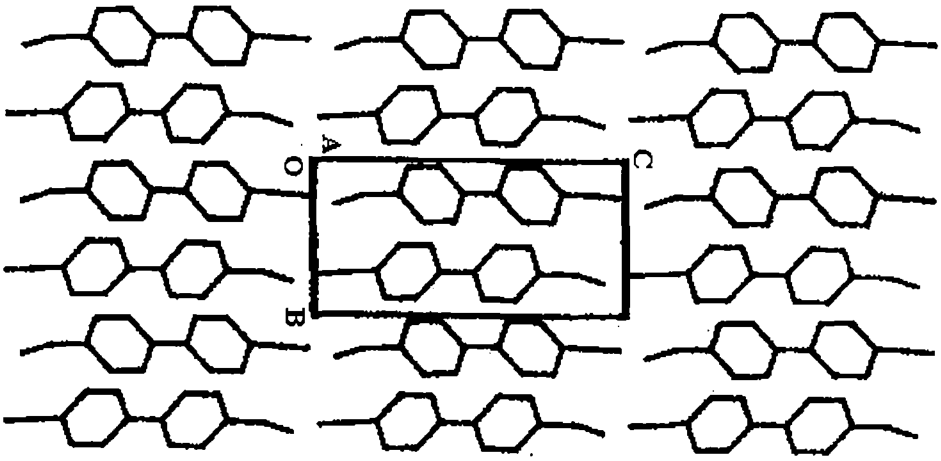

Figure 6.4: Crystal structure of 2CB projected in bc-plane.

have calculated the intermolecular distance between the atoms of the neighbouring molecules. No dipole-dipole contact is observed in this case. However van der Walls' type of contact is found to exist between atoms N-C15 (3.52 Å), C4-C8 (3.74

Å) and C12-C2 (3.79 Å) of the 2_1 symmetry related molecules. The length of such paired molecules is found to be 14.47 Å which is 1.13 times the single molecule length (L=12.85 Å). Thus the neighbouring molecules overlap almost completely. Due to van der Walls' type or dipole-induced dipole type contact, however, both the 3CB and 4CB molecules show different type of overlapping. In 3CB the overlapping is between cyano group of one molecule with the phenyl ring of the neighbouring molecule related by inversion symmetry. On the other hand, in 4CB overlapping is between the cyano group of one molecule with either the cyanophenyl group of centrosymmetric molecule or with the alkyl phenyl group of 2_1 symmetry related molecule. In case of the first four members of nOCB series, which also exhibit monotropic nematic phase, the overlapping of the neighbouring molecules is either of 3CB type or of 4CB type. In 4OCB no cyano-cyano or cyano-phenyl interaction is observed as in 2CB. The three higher homologues (n = 5,6,7), which exhibit enantiotropic nematic phase, show dipole-dipole interaction and overlapping is between opposing cyano groups. The length of the paired molecules, often called dimmer, is found to be in the range $L \leq l \leq 2L$. In the nematic or smectic phase l is found to be 1.4 times L [29,30].

Finally, some comment might be made on the appearance of virtual monotropic nematic phase in 2CB. Though the 2CB molecules are arranged in parallel fashion but the packing is not of imbricated type as is assumed necessary for a precursor to nematic phase. Observed packing is in fact precursor to the tilted smectic type. Moreover van der Walls' type of contact encompasses all the molecules within a layer. So the melting point is well above the range of thermal stability of the nematic phase. However, while cooling from isotropic melt, dipole-dipole interaction may give rise to parallel imbricated mode of packing as observed in the fifth member onwards of *n*OCB series of compounds and this in turn may sets in nematic phase.

TABLE 6.1

Important Crystallographic Data

Identification code	2CB
Empirical formula	$C_{15}H_{13}N$
Formula weight	207.26 g/mol
Crystal system	Monoclinic
Space group	$P2_1$
Form/habit	Needle shaped
a = 8.584(4) Å	α = 90.00(3) deg.
b = 5.865(3) Å	β = 92.30(3) deg.
c = 11.833(3) Å	γ = 90.00(4) deg.
Volume	595.3(4) $Å^3$
Z	2
Density (calculated)	1.156 Mgm^{-3}
Absorption coefficient	0.067 mm^{-1}
F(000)	220
Wavelength	0.71073 Å
Data collected within θ	2.37° to 24.98°
Index ranges	$0 \leq h \leq 10$, $0 \leq k \leq 6$, $-14 \leq l \leq 14$
Independent reflections	1153
Refinement method	Full-matrix-block least-squares on F^2
Final R index [$I>2\sigma(I)$]	R = 0.0787
Largest diff. peak and hole	0.265 and -0.179 $e.Å^{-3}$

TABLE 6.2

Atomic co-ordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) with e.s.d's in parentheses for the non-hydrogen atoms. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
N	-1173(8)	2280(24)	9871(6)	137(3)
C1	-496(8)	2177(24)	9045(6)	107(3)
C2	350(7)	2053(18)	8031(5)	85(2)
C3	124(9)	343(16)	7268(7)	107(3)
C4	863(9)	351(14)	6266(6)	100(2)
C5	1840(6)	2110(12)	5960(4)	64(2)
C6	2033(8)	3842(17)	6736(6)	100(3)
C7	1304(9)	3878(19)	7736(6)	111(3)
C8	2619(6)	2123(13)	4862(4)	68(2)
C9	3598(7)	3871(15)	4575(5)	82(2)
C10	4273(8)	3946(16)	3536(6)	94(2)
C11	4076(7)	2197(18)	2770(5)	88(2)
C12	3144(8)	466(17)	3064(6)	104(3)
C13	2434(8)	372(15)	4093(6)	93(2)
C14	4827(9)	2250(23)	1619(6)	123(3)
C15	3838(15)	2829(40)	705(9)	226(10)

TABLE 6.3

Anisotropic displacement parameters ($Å^2 \times 10^3$) for the non-hydrogen atoms with e.s.d's in parentheses. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}$ U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
N	137(5)	154(7)	124(5)	40(6)	52(4)	10(6)
C1	101(5)	125(7)	96(4)	25(6)	23(4)	-4(6)
C2	72(4)	101(6)	82(4)	17(5)	11(3)	-5(5)
C3	101(5)	100(6)	122(6)	-13(6)	39(5)	-33(6)
C4	108(5)	87(5)	107(5)	-15(6)	23(4)	-24(6)
C5	55(3)	69(4)	68(3)	4(5)	0(2)	-3(5)
C6	94(5)	113(6)	95(5)	-26(6)	22(4)	-39(6)
C7	113(5)	124(7)	100(5)	-33(6)	33(4)	-34(7)
C8	54(3)	69(4)	81(4)	-3(5)	-3(3)	3(5)
C9	77(4)	83(5)	85(4)	-9(5)	8(3)	-14(6)
C10	82(4)	98(6)	104(5)	-3(6)	10(4)	-9(6)
C11	68(4)	111(6)	85(4)	-4(6)	7(3)	-4(6)
C12	101(5)	115(7)	97(5)	-30(6)	7(4)	0(7)
C13	102(5)	85(5)	92(4)	-14(5)	15(4)	-15(6)
C14	135(6)	156(9)	78(4)	-3(7)	10(4)	23(9)
C15	196(10)	327(30)	159(9)	102(14)	42(8)	59(16)

TABLE 6.4

Bond lengths (Å) and bond angles (°) involving non-hydrogen atoms with e.s.d's in parentheses.

N-C1	1.159(7)	N-C1-C2	179.6(8)
C1-C2	1.429(9)	C3-C2-C7	117.9(6)
C2-C3	1.358(13)	C3-C2-C1	122.1(10)
C2-C7	1.401(13)	C7-C2-C1	119.5(11)
C3-C4	1.367(9)	C2-C3-C4	121.0(8)
C4-C5	1.387(10)	C3-C4-C5	122.4(8)
C5-C6	1.375(10)	C6-C5-C4	115.6(5)
C5-C8	1.485(6)	C6-C5-C8	122.3(6)
C6-C7	1.360(9)	C4-C5-C8	122.1(6)
C8-C13	1.377(10)	C7-C6-C5	123.1(8)
C8-C9	1.377(10)	C6-C7-C2	119.9(9)
C9-C10	1.380(8)	C13-C8-C9	116.6(5)
C10-C11	1.375(12)	C13-C8-C5	122.0(6)
C11-C12	1.347(13)	C9-C8-C5	121.4(6)
C11-C14	1.530(8)	C8-C9-C10	121.7(7)
C12-C13	1.385(9)	C11-C10-C9	121.2(8)
C14-C15	1.390(13)	C12-C11-C10	116.8(6)
		C12-C11-C14	121.4(9)
		C10-C11-C14	121.8(9)
		C11-C12-C13	122.9(8)
		C8-C13-C12	120.5(8)
		C15-C14-C11	115.6(8)

TABLE 6.5

Hydrogen co-ordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) with e.s.d's in parentheses for the non-hydrogen atoms.

Atom	x	y	z	U(eq)
H14A	5944	3523	1576	59
H14B	5344	459	1424	91
H3	-545(9)	-852(16)	7429(7)	128
H4	706(9)	-868(14)	5772(6)	120
H6	2692(8)	5044(17)	6570(6)	120
H7	1440(9)	5113(19)	8223(6)	134
H9	3810(7)	5032(15)	5094(5)	98
H10	4873(8)	5203(16)	3352(6)	113
H12	2968(8)	-719(17)	2552(6)	125
H13	1827(8)	-884(15)	4267(6)	112

TABLE 6.6

Equations of the least-squares planes, distances (Å) of the atoms from them and dihedral angles (°) between them.

Plane no.	Equation of the plane	Atom	Distance	Atom	Distance
1	6.56111X - 2.82276Y + 4.70957Z	C2	.0153	C5	.0015
	= 3.41708	C3	-.0096	C6	.0047
		C4	.0011	C7	-.0129
	Other atoms	C1	-.0972	N	-.1815
2	6.67844X - 2.80266Y + 4.45162Z	C8	-.0167	C11	.0044
	= 3.33514	C9	.0195	C12	-.0021
		C10	-.0133	C13	.0082
	Other atoms	C4	-.0678	C14	-.0213
3	6.59860X - 2.81335Y + 4.63595Z	C2	.0025	C8	.0109
	= 3.37398	C3	-.0192	C9	.0321
		C4	.0016	C10	-.0253
		C5	.0096	C11	-.0183
		C6	.0094	C12	-.0100
		C7	-.0182	C13	.0250
	Other atoms	C1	-.1205	N	-.2133
		C14	-.0713	C15	-1.3105
4	7.09265X - 2.95778Y + 2.57269Z	C8	-.2174	C12	.1825
	= 2.69782	C9	-.1138	C13	-.0285
		C10	.0754	C14	.4768
		C11	.2560	C15	-.6310
5	6.42531X - 2.81915Y + 5.04445Z	N	-.0468	C4	-.0134
	= 3.62978	C1	.0005	C5	-.0359
		C2	.0675	C6	-.0087
		C3	.0195	C7	.0172

Dihedral angles between planes:

1 & 2, 1 & 3, 1 & 4, 1 & 5, 2 & 3, 2 & 4, 2 & 5, 3& 4, 3 & 5 and 4 & 5 are respectively 1.462°, .437°, 10.908°, 1.828°, 1.027°, 9.542°, 3.279°, 10.512°, 2.254° and 12.710°.

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