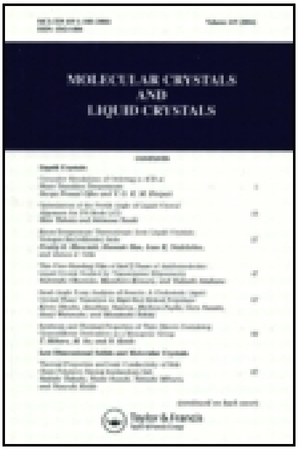

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Molecular Structure and Packing in the Crystalline State of 4-*n*-Ethyl-4′-Cyanobiphenyl (2CB) by Single Crystal X-ray Diffractometry

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Crystal and molecular structure of the compound 4-*n*-ethyl-4′-cyanobiphenyl (2CB), which exhibits nematic phase monotropically, is determined by direct methods from single crystal X-ray diffraction data. The crystal belongs to monoclinic system with space group $P2_1$, cell parameters being $a = 8.584(4)$, $b = 5.865(3)$, $c = 11.833(3)$ (Å) and $\beta = 92.30(3)°$ with 2 molecules per unit cell. Refinement led to $R = 0.079$ with $I > 2\sigma(I)$. The molecules are in the most extended conformation. The phenyl rings are highly planar, the dihedral angle between them is 1.46°. Antiparallel pairs of 2_1 symmetry related molecules are arranged in layers and the layers are stacked along [001]. The thickness of these layers is equal to the length of crystallographic *c*-axis. van der Waals' type of contact encompasses all the molecules within a layer. Molecular geometry and crystal packing are discussed in the context of geometry and packing of other known *n*CB and *n*OCB structures.

Keywords: Liquid crystals; crystal structure; molecular geometry; packing effects

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

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*Corresponding author. Tel.: 0353-450414, Fax: 0353-450546, e-mail: root@nbu.ernet.in different angles using various experimental techniques. Several of them are used as components in commercially available liquid crystal mixtures. In both the series first four homologous compounds show monotropic nematic phase whereas 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 [1]. With this view crystal and molecular structures of the 3rd and 4th members of the *n*CB-series [2, 3] and first to seventh members of the *n*OCB-series [4–6] were reported earlier. As a part of our program of X-ray structural investigations on liquid crystalline materials we report here the crystal and molecular structure of the second member of the *n*CB series (2CB).

EXPERIMENTAL

Crystal Data

Transparent needle shaped crystals were obtained by slow evaporation 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 with graphite monochromator 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 $8 < \theta < 18°$. All the 25 reflections could be indexed with respect to monoclinic cell. 1153 independent reflections were measured in the interval $4 < 2\theta < 50°$ of which 557 were taken as observed reflections with $I > 2\sigma(I)$. Lorentz and polarisation corrections were applied but no absorption correction was made. Intensity data were collected in ω-2θ scan mode. Important crystallographic data are given in Table I.

Structure Determination and Refinement

The structure was solved by direct methods using the PC version of the crystallographic package program [7] SIR92 based on Representation Theory developed by Giacovazzo [8, 9] for estimating structure invariants and structure seminvariants. Stereochemically best suited model obtained from *E*-map was refined by full-matrix block least-squares method using anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms attributing values of the parent

TABLE I 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	$\alpha = 90.00(3)$ deg.
$b = 5.865(3)$ Å	$\beta = 92.30(3)$ deg.
$c = 11.833(3)$ Å	$\gamma = 90.00(4)$ 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}

C-atoms. Positions of hydrogen atoms were calculated theoretically. SHELXL-93 computer program [10] was used for refinement. The final residual structure factor $R(F)$ is .079. A difference Fourier map at this stage showed no maxima greater than ± 0.3 Å^{-3}. The atomic scattering factors were taken from International Table for Crystallography [11]. The tables of thermal parameters and structure factors are available from the authors on request.

RESULTS AND DISCUSSIONS

Molecular Conformation

Perspective view of 2CB molecule is shown in Figure 1. Final positional parameters of all non-hydrogen atoms are listed in Table II using the numbering scheme of atoms shown in Figure 1. 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 [12]. 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 [2, 3]. 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 [5, 13, 14].

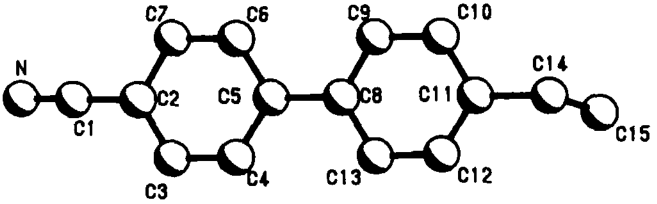

FIGURE 1 Perspective view of 2CB molecule along with atomic numbering scheme.

TABLE II Atomic co-ordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) 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 U_{ij} 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)

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 [12]. 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 [3] disordering in the last two C atoms of the butyl chain and such disordering in terminal chain was observed in other mesogenic structures [15–17] 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. The angle N—C1—C2 is 179.6(8)° close to the value observed in other cyanophenyl compounds.

Least-squares planes through different fragments of 2CB and the dihedral angles between the planes have been calculated. 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 many biphenyl mesogenic compounds [3, 4] show the above dihedral angle around 40° but a wide range of values namely 0–50° have also been observed [4]. Interestingly, all the first seven *n*OCB members show large dihedral angles only exception is 5OCB where this angle was found to be 0.82°. Length of the molecule (N—C15) in the crystalline state is 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.

Crystal Packing

Different views of molecular packing in the crystalline state are shown in Figure 2. Molecules are extended parallel to each other with their longest axis making an angle of ~23° with [001]. Antiparallel pairs of 2_1 symmetry related molecules are arranged in layers by translational symmetry along [100] and [010] and the layers are stacked along [001]. 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 have calculated the intermolecular distance between the atoms of the neighbouring molecules. No dipole–dipole contact is observed in this case. However van der Waals' 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 2_1 symmetry related molecules. Thus the neighbouring molecules overlap almost completely. Lengths of such paired molecules is 14.47 Å as against the single molecule length 12.85 Å.

Due to van der Waals' 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 centrosymmetric molecule. In 4CB overlapping is between the cyano group of one molecule either with 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 *n*OCB series, which also show monotropic nematic phase, the overlapping of neighbouring molecules is either of 3CB type or of 4CB type except in 4OCB where no cyano–cyano or cyano-phenyl interaction is observed.

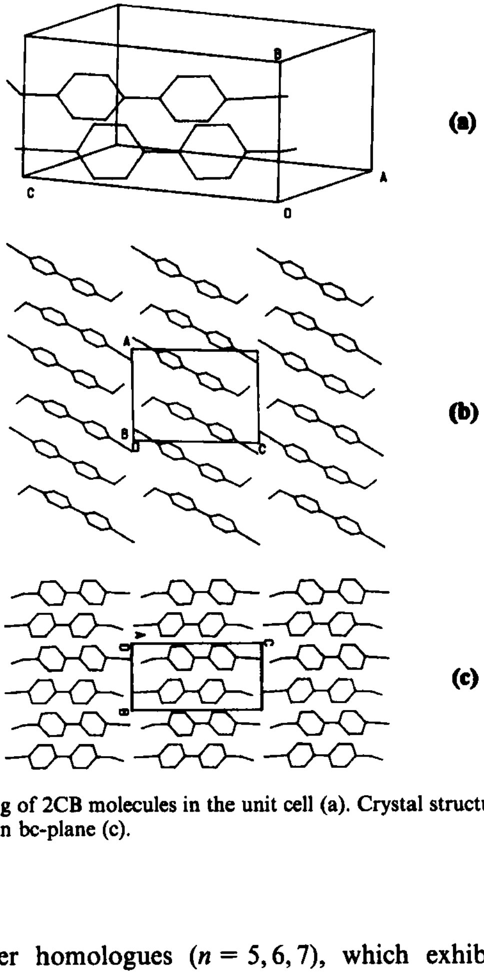

FIGURE 2 Packing of 2CB molecules in the unit cell (a). Crystal structure of 2CB projected in ac-plane (b) and in bc-plane (c).

The three higher homologues ($n = 5, 6, 7$), which exhibit enantiotropic nematic phase, show dipole–dipole interaction and overlapping is between opposing cyano groups.

Finally some comment might be made on the appearance of monotropic nematic phase in 2CB. Though the 2CB molecules are arranged in parallel fashion but the packing is not imbricated type, as is assumed necessary precursor to nematic phase, rather tilted smectic type. Moreover van der Waals' 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 resulting in a nematic phase as observed in the fifth member onwards of *n*OCB series of compounds.

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