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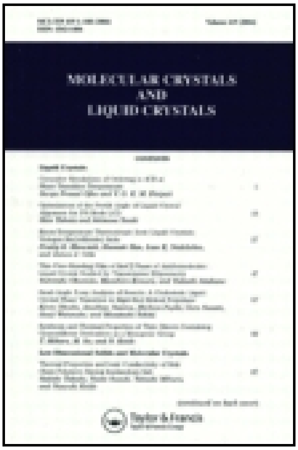

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Crystal and Molecular Structure of Nematogenic 4′- n-butyl-4-cyanobiphenyl (4CB)

G. V. Vani [a]

[a] Raman Research Institute, Bangalore, 560 080, India

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Crystal and Molecular Structure of Nematogenic 4′-*n*-butyl-4-cyanobiphenyl (4CB)[†]

G. V. VANI

Raman Research Institute, Bangalore 560 080, India

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The crystal and molecular structure of 4′-*n*-butyl-4-cyanobiphenyl (4CB), $C_{17}H_{17}N$, has been determined at room temperature. The compound, which exhibits a monotropic nematic phase, crystallizes in the monoclinic space group $P2_1/c$, $a = 12.198$, $b = 9.204$, $c = 14.746$ Å, $\beta = 123.38°$, with four molecules in the unit cell. The structure has been refined to $R = 0.136$ using photographically observed data. The terminal part of the butyl chain is disordered. The 4CB molecules pack in a sheet-like arrangement, with nearest neighbors oriented antiparallel to each other. The angle between the phenyl rings is 40°30′.

INTRODUCTION

As part of a program of X-ray structural investigations on liquid crystalline materials, the crystal and molecular structure of 4′-*n*-butyl-4-cyanobiphenyl (4CB) has been determined. 4′-*n*-alkyl-4-cyanobiphenyls have been extensively studied in recent years and a detailed knowledge of the structural features of these compounds in the crystalline phase would be of considerable value in understanding their structure and properties in the mesophase.

4CB (Figure 1) is a monotropic nematic liquid crystal exhibiting the following phase transitions:

$$\begin{tikzcd}
\text{Crystal} \arrow[rr, "46.5^\circ\text{C}"] & & \text{Isotropic} \arrow[dl, "16.5^\circ\text{C}"] \\
& \text{Nematic} \arrow[ul] &
\end{tikzcd}$$

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 1982.

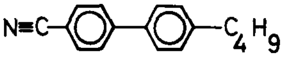

FIGURE 1

EXPERIMENTAL

Transparent white crystals of 4CB were kindly provided by Mr. M. R. Subrahmanyam and were cut and ground into suitable needles. From oscillation and Weissenberg photographs, the crystals were found to be monoclinic. Systematic absences of the type hol, *l* odd and oko, *k* odd fixed the space group to be $P2_1/c$. The crystal data are listed in Table I.

Three dimensional intensity data were collected photographically using Cu Kα radiation. The diffraction pattern was of poor quality and intensities were found to drop rapidly with increasing Bragg angle. As a result, only 872 independent reflections could be recorded. The intensities were estimated visually and corrected for Lorentz and polarization factors and spot shape effects. No absorption correction was applied.

STRUCTURE DETERMINATION

The crystal structure was determined by direct methods using the computer program MULTAN-80.[1] The E-map corresponding to the best solution of MULTAN revealed 16 out of the 18 non-hydrogen atoms in the molecule. Positions of C(17) and C(18), the two missing atoms at the end of the butyl chain, were determined with the help of a difference electron density

TABLE I

Crystal data.

Molecular Formula	$C_{17}H_{17}N$
Molecular Weight	235.3
a =	12.198 ± 0.009 Å
b =	9.204 ± 0.008 Å
c =	14.746 ± 0.009 Å
β =	123.38 ± 0.3°
Space Group	$P2_1/c$
V =	1382.52 $Å^3$
$F(000)$ =	504
μ(Cu Kα) =	4.28 cm^{-1}
Z =	4
D_c =	1.13 gm cm^{-3}
D_m(flotation) =	1.11 ± 0.03 gm cm^{-3}

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map. However, the peaks indicating these atomic positions were very diffuse. Four cycles of full-matrix least-squares refinement with isotropic thermal parameters using SHELX-76 program system[2] gave an R-factor ($\Sigma\,|\Delta F|/\Sigma\,|F_0|$) of 0.192. Two more cycles of refinement with anisotropic thermal parameters reduced the R-value to 0.158.

At this stage, the butyl chain atoms, particularly C(17) and C(18), were found to have strikingly high thermal parameters compared to the rest of the atoms. Also, the molecular dimensions involving C(17) and C(18) were very different from standard values. These disconcerting features suggested the presence of disorder in that part of the molecule. Hence, a difference Fourier map was computed after removing the contributions from C(17) and C(18). The difference electron density distribution was highly diffuse, but it was possible to fix two alternate positions for C(18). The occupancy factors for these two positions, *viz.*, C(181) and C(182), refined to 0.58 and 0.42 respectively. The diffuse nature of the map rendered any further analysis of the disorder difficult. However, it is possible that multiple alternate sites occur for C(18) and also perhaps for C(17). This type of disorder in the terminal chain of the molecule is found to occur in several mesogenic crystal structures (see, *e.g.*, Ref. 3–5). It is interesting to note that the presence of disorder resulted in the failure of the MULTAN to reveal the atoms C(17) and C(18) in the E-map.

In the subsequent least-squares refinement, the bond lengths involving the atoms C(17), C(181) and C(182) were constrained. The contributions from hydrogen atoms in their theoretically calculated positions were included in the structure factor calculations, but their positions were not refined due to paucity of reflection data. The final R-factor was 0.136. The tables of structure factors and the atomic parameters of the hydrogen atoms used in the structure factor calculations are available with the author and will be supplied on request.

All the computations were done on the DEC-1090 system at Indian Institute of Science, Bangalore.

RESULTS AND DISCUSSION

The final positional and thermal parameters of all the non-hydrogen atoms are listed in Tables II and III respectively. Table IV lists the bond lengths and angles. The molecular dimensions involving atoms N(1) to C(16) are normal within the limits of experimental error. In the phenyl rings, the average C-C distance is 1.40 (0.02) Å and the C-C-C angles average to 120 (1)°. The lengths and angles involving C(17) and the two positions of C(18) are not reliable due to the presence of disorder.

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TABLE II

Final fractional positional coordinates ($\times 10^3$) with e.s.d.'s in parentheses.

Atom	x	y	z
N(1)	521(1)	100(1)	410(1)
C(2)	412(2)	75(1)	358(1)
C(3)	271(1)	47(2)	291(1)
C(4)	211(2)	−50(1)	324(1)
C(5)	75(1)	−75(1)	257(1)
C(6)	3(1)	−5(1)	157(1)
C(7)	63(1)	95(1)	126(1)
C(8)	201(1)	121(1)	192(1)
C(9)	−141(1)	−42(1)	82(1)
C(10)	−186(1)	−184(1)	68(1)
C(11)	−318(1)	−216(1)	−8(1)
C(12)	−407(1)	−108(2)	−72(1)
C(13)	−361(1)	−39(2)	−56(1)
C(14)	−227(1)	71(1)	19(1)
C(15)	−549(1)	−153(2)	−150(1)
C(16)	−638(1)	−31(2)	−222(2)
C(17)	−784(2)	−77(3)	−293(2)
C(181)	−865(3)	−29(5)	−407(2)
C(182)	−815(5)	−153(4)	−388(3)

TABLE III

Final anisotropic thermal parameters ($\times 10^3$) with e.s.d.'s in parentheses.
The temperature factor is of the form
$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^*U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{13} + 2hka^*b^*U_{12})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	74(10)	107(10)	107(10)	4(8)	39(8)	−5(8)
C(2)	97(15)	65(9)	88(12)	13(8)	49(11)	2(9)
C(3)	49(10)	79(9)	66(9)	−19(8)	25(8)	2(7)
C(4)	92(13)	66(9)	79(10)	10(8)	48(10)	1(9)
C(5)	50(9)	78(9)	82(9)	3(8)	34(8)	−10(7)
C(6)	52(9)	67(8)	68(9)	−5(7)	34(7)	4(7)
C(7)	85(12)	66(8)	62(8)	6(7)	37(8)	−1(8)
C(8)	71(11)	76(9)	58(8)	−6(7)	27(8)	−21(7)
C(9)	59(9)	84(10)	63(8)	2(7)	38(6)	8(7)
C(10)	73(10)	52(8)	85(9)	9(7)	41(8)	−3(7)
C(11)	72(10)	61(9)	87(9)	5(7)	36(8)	−3(7)
C(12)	66(10)	89(10)	81(9)	−7(8)	36(7)	−12(8)
C(13)	77(11)	75(10)	85(10)	5(8)	32(8)	13(8)
C(14)	62(10)	65(9)	94(10)	−8(8)	38(8)	−4(7)
C(15)	59(10)	129(13)	90(10)	−6(11)	15(9)	−7(9)
C(16)	24(11)	239(23)	120(12)	−9(17)	18(9)	−27(12)
C(17)	132(20)	260(29)	157(18)	68(22)	58(17)	−19(18)
C(181)	70(25)	120(34)	117(32)	−30(25)	35(20)	−33(23)
C(182)	248(44)	135(29)	119(29)	−28(25)	102(29)	2(29)

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TABLE IV

(a) Bond lengths (Å) with standard deviations in parentheses.

Atoms	Distance	Atoms	Distance
N(1)–C(2)	1.13(2)	C(10)–C(11)	1.39(2)
C(2)–C(3)	1.46(2)	C(11)–C(12)	1.39(2)
C(3)–C(4)	1.40(2)	C(12)–C(13)	1.43(2)
C(4)–C(5)	1.40(2)	C(13)–C(14)	1.41(2)
C(5)–C(6)	1.40(2)	C(14)–C(9)	1.41(2)
C(6)–C(7)	1.39(2)	C(12)–C(15)	1.52(2)
C(7)–C(8)	1.42(2)	C(15)–C(16)	1.52(2)
C(8)–C(3)	1.40(2)	C(16)–C(17)	1.55(2)
C(6)–C(9)	1.52(2)	C(17)–C(181)	1.48
C(9)–C(10)	1.39(2)	C(17)–C(182)	1.43

(b) Bond angles (°) with standard deviations in parentheses.

Atoms	Angle	Atoms	Angle
N(1)–C(2)–C(3)	178(2)	C(6)–C(9)–C(14)	118(2)
C(2)–C(3)–C(4)	121(1)	C(9)–C(10)–C(11)	120(1)
C(2)–C(3)–C(8)	116(2)	C(10)–C(11)–C(12)	121(1)
C(3)–C(4)–C(5)	120(1)	C(11)–C(12)–C(13)	118(1)
C(4)–C(5)–C(6)	118(2)	C(12)–C(13)–C(14)	120(1)
C(5)–C(6)–C(7)	121(1)	C(13)–C(14)–C(9)	119(1)
C(6)–C(7)–C(8)	122(1)	C(14)–C(9)–C(10)	120(1)
C(7)–C(8)–C(3)	116(1)	C(11)–C(12)–C(15)	117(1)
C(8)–C(3)–C(4)	122(1)	C(13)–C(12)–C(15)	124(1)
C(5)–C(6)–C(9)	118(1)	C(12)–C(15)–C(16)	114(1)
C(7)–C(6)–C(9)	121(1)	C(15)–C(16)–C(17)	113(2)
C(6)–C(9)–C(10)	122(1)	C(16)–C(17)–C(181)	119
		C(16)–C(17)–C(182)	112

The two phenyl rings in the 4CB molecule make an angle of 40°30′ with one another. This value compares well with the inter-ring angles of 38° and 42° found in the two independent molecules of 4,4′-dibromobiphenyl,[6] 42° and 42° in 4-bromo-4′-cyanobiphenyl,[7] 36° and 40° in *p*,*p*′-bitolyl[8] and the gas phase value of 42° obtained for biphenyl from electron diffraction experiments.[9] NMR studies have shown that in the nematic phase of 4′-*n*-pentyl-4-cyanobiphenyl the dihedral angle is 32°.[10] Figure 2 shows the perspective view of the 4CB molecule, where only one of the two positions of C(18), corresponding to an occupancy factor of 0.58, has been indicated.

Figures 3 and 4 show the molecular packing in the *ab*- and *bc*-planes respectively. 4CB molecules associate in antiparallel pairs about centers of inversion. The molecules pack in sheets parallel to the *ac*-plane at $y = 0$ and ½. Molecules within a sheet are related by translational symmetry and

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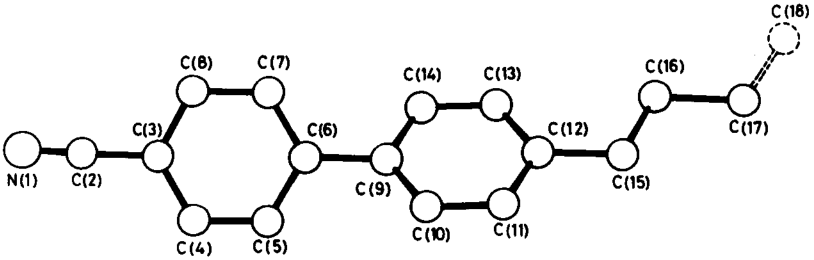

FIGURE 2 Perspective view of the 4 CB molecule, indicating the atom numbering scheme. Dotted lines correspond to the disordered region of the molecule. Only one of the two alternate positions of C(18), corresponding to an occupancy factor of 0.58, is shown.

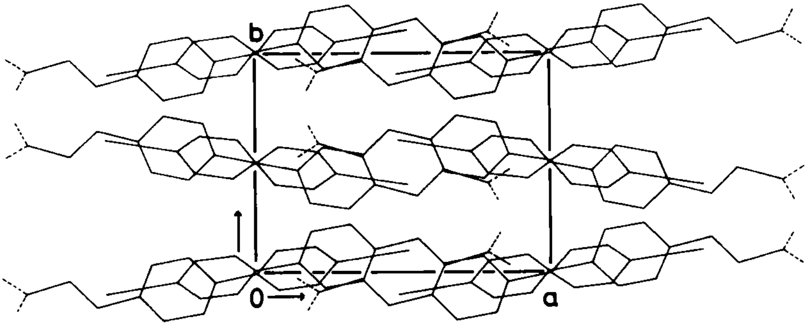

FIGURE 3 Molecular arrangement in the *ab*-plane.

inversion center, and those in the neighboring sheets by the 2_1 screw axis and the *c*-glide. Molecules in the adjacent sheets are inclined at an angle of about 20° to one another, showing a weak tendency towards a herringbone-like packing. The interactions between neighboring molecules are of the van der Waals' type. A list of intermolecular contacts is given in Table V.

TABLE V

Intermolecular contacts.

From atom at x, y, z	To Atom	At	Distance (Å)
N(1)	N(1)	$1 - x, -y, 1 - z$	3.50
C(2)	N(1)	$1 - x, y, 1 - z$	3.45
C(4)	N(1)	$1 - x, y, 1 - z$	3.50
C(13)	N(1)	$x - 1, \frac{1}{2} - y, z - \frac{1}{2}$	3.55
C(11)	C(2)	$-x, \frac{1}{2} + y, 1\frac{1}{2} - z$	3.56
C(11)	C(3)	$-x, \frac{1}{2} + y, 1\frac{1}{2} - z$	3.65
C(7)	C(7)	$-x, -y, -z$	3.59

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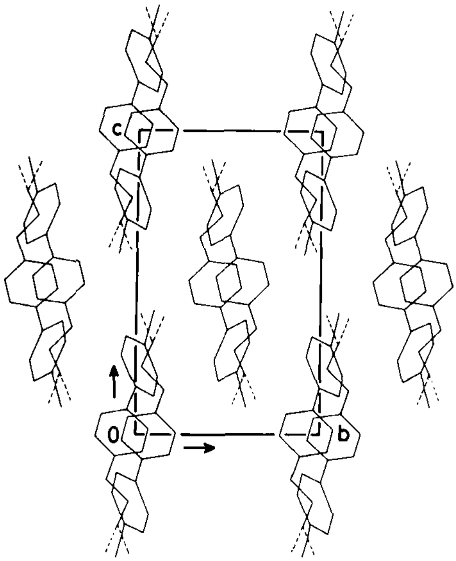

FIGURE 4 Molecular arrangement in the *bc*-plane.

An imbricated mode of molecular arrangement in the crystalline phase is considered to be a necessary pre-requisite for a compound to form a nematic liquid crystal. Though the 4CB molecules pack in an approximately parallel arrangement (which is conducive to mesophase formation), the degree of imbrication is low. This feature could perhaps be related to the monotropic behavior of the compound.

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I want to thank Professor S. Chandrasekhar for suggesting the study of this compound, Mr. M. R. Subrahmanyam for synthesizing the compound, and Dr. Ramesh Narayan for several useful discussions.

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