Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

X-Ray Studies on the Mesogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile(5OCB) in the Solid Crystalline State

P. Mandal [a] & S. Paul [a]
[a] Department of Physics, North Bengal University, Darjeeling, India, 734 430
Version of record first published: 19 Oct 2010.

To cite this article: P. Mandal & S. Paul (1985): X-Ray Studies on the Mesogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile(5OCB) in the Solid Crystalline State, Molecular Crystals and Liquid Crystals, 131:3-4, 223-235

To link to this article: http://dx.doi.org/10.1080/00268948508085045

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 223–235
0026-8941/85/1314–0223/$20.00/0

Printed in the United States of America

X-Ray Studies on the Mesogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile(50CB) in the Solid Crystalline State

P. MANDAL and S. PAUL

Department of Physics, North Bengal University, Darjeeling, India. 734 430

(*Received January 21, 1985; in final form June 7, 1985*)

The crystal and molecular structure of the nematogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile has been determined by direct methods. The crystals belong to the monoclinic system with space group $P2_1/n$. a = 21.378(5), b = 5.695(3), c = 12.789(2) Å, β = 106.074(17)° with four molecules per unit cell. Least-squares refinement leads to R = 0.050 (Rw = 0.038) for 1773 observed reflections. The molecules are in their most extended conformation, the rigid part lies parallel to a-axis while the chain part is inclined to it. Rigid part is also highly planar and is almost parallel to ab-plane. The molecules are stacked along c-axis. The molecules associate in pairs about the centre of inversion. In the unit cell the adjacent molecules are antiparallel to each other. The structure is of a common type for nematogens and could transform to the nematic state by means of a simple displacive transition.

INTRODUCTION

X-ray diffraction studies on 4′-n-Pentyloxy-4-biphenylcarbonitrile (50CB) in the liquid crystalline phase were carried out by Bhattacharjee et al.[1] These studies included measurements of transition temperatures, the orientational order parameters, intermolecular distances, apparent molecular length of magnetically aligned sample and texture studies by means of polarising microscope. Order parameters had also been calculated from refractive indices measurements.[1a]

In this paper we have reported the crystal and molecular structure of 50CB. This structure analysis is part of a programme aimed at investigating whether relation exists between the crystal and liquid crystal structures in compounds which form mesophases.

The structural formula of the compound is $CH_3 \cdot (CH_2)_4 \cdot O \cdot (C_6H_4)_2 \cdot CN$. This compound was supplied to us by M/s. F. Hoffmann-La-Roche and Co., Basel, Switzerland. According to their literature the transition temperatures of 50CB are as follows.

$$\text{Solid} \underset{}{\overset{47.5°C}{\rightleftharpoons}} \text{Nematic} \overset{67.5°C}{\rightleftharpoons} \text{Isotropic}$$

X-ray diffraction and Texture studies[1] also confirmed this only a supercooling effect was found in addition.

$$\text{Solid} \underset{\sim 31.5°C}{\overset{47.5°C}{\rightleftharpoons}} \text{Nematic} \overset{67.5°C}{\rightleftharpoons} \text{Isotropic}$$

EXPERIMENTAL

Crystal data

Transparent plate like crystals were obtained by slow evaporation from a solution of acetone. Lattice parameters and space group were determined by taking oscillation and Weissenberg photographs along different axes. The crystal belongs to monoclinic system. The space group $P2_1/n$ was uniquely determined from the observed systematic absences of hol reflections with $h + l = 2n + 1$ and oko reflections with $k = 2n + 1$. A crystal of dimension $.075 \times .275 \times .350$ mm^3 was mounted on a goniometer head and was used for intensity measurement.

Accurate cell parameters were determined by a least-squares fit of sin θ values of 25 reflections within $20° < 2\theta < 23°$ measured on an "Enraf Nonius" CAD-4 computer controlled diffractometer, CuK_α radiation monochromated by a graphite monochromator was used throughout. A total of 2224 reflections were collected in the interval $4° < 2\theta < 120°$ of which 1773 were classified as observed and had intensities greater than 2σ (I). The reflections were corrected for Lorentz and Polarisation factors, but no absorption correction was made [$\mu(CuK_\alpha) = 5.11$ cm^{-1}]. Data were collected on a $\omega - 2\theta$ scan mode. The important crystallographic data are given in Table I.

Structure determination and refinement

The structure was determined by applying MULTAN package programme[2] to 200 room temperature structure amplitudes with E-values greater than 1.65. In normalising the structure factors planarity

TABLE I

Summary of Crystallographic data

Molecular Formula	$C_{18}H_{19}NO$
Formula weight	265.36 g/mol.
Crystal system	Monoclinic
Space group	$P2_1/n$
Form/habit	Rectangular Plates
a = 21.387(5) Å	
b = 5.695(3) Å	
c = 12.789(2) Å	
β = 106.074(17)°	
V_c = 1496.8 Å^3	
D_c = 1.17 gcm^{-3}	
D_m = 1.16 gcm^{-3}	
Z = 4	
λ (CuK_α) = 1.5418 Å	
Number of independent reflections 2224	
Number of observed reflections 1773, $I > 2\sigma(I)$	

of the rigid part of the molecule was taken into consideration and a least-square straight line through Debye Curve was used.

The positions of all the non-hydrogen atoms could be located from the E-map. But the peculiarity of the map was that two trial structures could be constructed in each of which two orientations of the pentyl chain were possible i.e. four possibilities altogether. Steriochemically best suited model was refined with overall isotropic temperature factor by full matrix least-squares method using the programme MAMIE of Vickery et al[3] after being modified for B6700 computer. This leads to a R-index 0.42 for observed data only which is not at all hopeful. Still it was decided to refine the structure with individual isotropic temperature factors since in mesogenic compounds thermal vibrations of the chain part are generally found to be much higher than those of the rigid part. With this Block-diagonal least squares refinement resulted a R-value 0.35. At this stage the temperature factor of the last carbon atom in pentyl-chain [C(18), Figure 1] was found to be too high (B = 18.3) compared to those of the nearby atoms (B~5). Assuming C(18) was in wrong position we excluded it and refined the remaining atomic parameters which converged R-value to 0.305. Then from Fourier and difference Fourier maps the correct position of C(18) was located. Five cycles of refinement of all non-hydrogen atomic parameters brought down the R-value to 0.176 and introduction of anisotropic temperature factors reduced R further to 0.139. At this stage positions of all the hydrogen atoms except the three in methyl group were calculated theoretically using programme HGEN

(Vickery et al.[3]) from the known geometry around the carbon atoms. These positions were also confirmed from the difference Fourier map. The hydrogen atoms were attributed isotropic temperature factors of the parent carbon atoms at the last cycle of isotropic refinement. Then the structure was refined first keeping hydrogen atoms fixed and non-hydrogen atoms vibrating anisotropically and then hydrogen atoms were allowed to vibrate isotropically keeping non-hydrogen atoms fixed. This resulted in R value 0.09.

A difference Fourier map was again computed to locate the methyl hydrogen positions. Three cycles of refinement in the above fashion with all atoms terminated the analysis at R value 0.059 with Rw as 0.054 and S as 0.996, the weight being done by $W = 1/\sigma^2(F_o)$ and S being the standard deviation of an observation of unit weight. The function minimised in the least-squares refinement process was $\Sigma\, w(|F_0| - |F_c|)^2$ and $Rw = [\Sigma\, w\,(|F_0| - |F_c|)^2/\Sigma\, w|F_0|^2]^{1/2}$. From the structure factor table four reflections—013, 012, 111, 103 were found to have secondary extinction effect. R value reduced to 0.050 (Rw = 0.038 and S = 0.716) when these reflections were excluded. A difference Fourier map at this stage showed no maxima greater than $0.2e\text{Å}^{-3}$ indicating the termination of refinement.† Neutral atom scattering factors were taken from Stewart et al.[4] for H atoms and from Cromer and Waber[5] for C, N and O atoms.

RESULTS AND DISCUSSION

Molecular conformation

Final positional and thermal parameters of all atoms are listed in Tables II, III and IV using the numbering scheme of the molecule as shown in Figure 1. The bond lengths and bond angles are given in Table V. Bond lengths and bond angles are comparable with those found in other mesogenic compounds.[6-9] The average C-C bond lengths in phenyl rings A and B are 1.383(4) Å and 1.387 (3) Å respectively (expected value is 1.395Å).[10] In the ring A,C(2)-C(7) has a value of 1.367 Å which is lower than the average of other bond lengths by 4σ where σ(= .004) is the e.s.d. of each bond. Such shortening has been found in other mesogenic compounds.[6,9] The average C-C single bond length in the chain part is 1.518(4) Å (expected value is 1.541 Å).[10] C(5)-C(8) bond length is 1.489 (3) Å and

†A list of observed and calculated structure factors is available from the authors on request.

TABLE II

Final fractional positional coordinates of non-hydrogen atoms with e.s.d.s. in parentheses

Atom	x(σ)	y(σ)	z(σ)
O(1)	.0198(1)	.2139(3)	.6151(1)
N(1)	.5279(1)	.2541(4)	.5668(2)
C(1)	.4753(1)	.2424(5)	.5682(2)
C(2)	.4080(1)	.2328(5)	.5717(2)
C(3)	.3652(1)	.4084(5)	.5255(2)
C(4)	.3017(1)	.4011(5)	.5327(2)
C(5)	.2795(1)	.2208(4)	.5858(2)
C(6)	.3239(1)	.0460(5)	.6320(2)
C(7)	.3877(1)	.0527(5)	.6249(2)
C(8)	.2118(1)	.2164(4)	.5958(2)
C(9)	.1667(1)	.3935(4)	.5514(2)
C(10)	.1038(1)	.3889(4)	.5595(2)
C(11)	.0833(1)	.2051(4)	.6129(2)
C(12)	.1268(1)	.0292(5)	.6589(2)
C(13)	.1898(1)	.0369(5)	.6496(2)
C(14)	−0.0028(1)	.0220(5)	.6689(2)
C(15)	−0.0739(1)	.0609(5)	.6608(2)
C(16)	−0.0875(1)	.2748(5)	.7211(2)
C(17)	−0.1588(1)	.2773(5)	.7249(2)
C(18)	−0.1780(1)	.5011(6)	.7708(3)

TABLE III

Final anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms with e.s.d.'s in parentheses. The temperature factor is of the form $\exp -(h^2\beta_{11}^2 + k^2\beta_{22}^2 + l^2\beta_{33}^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

Atom	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
O(1)	21(1)	369(8)	99(2)	8(2)	19(1)	46(3)
N(1)	26(1)	535(12)	167(3)	9(3)	31(1)	28(5)
C(1)	27(1)	365(12)	100(3)	6(3)	19(1)	−2(5)
C(2)	20(1)	356(11)	81(2)	−1(2)	15(1)	−20(5)
C(3)	25(1)	462(14)	95(3)	−4(3)	17(1)	55(5)
C(4)	21(1)	439(13)	103(3)	7(3)	13(1)	73(5)
C(5)	21(1)	295(10)	63(2)	−4(2)	9(1)	−12(4)
C(6)	25(1)	316(12)	142(3)	14(3)	28(1)	57(5)
C(7)	26(1)	356(13)	160(3)	24(3)	29(1)	52(6)
C(8)	20(1)	271(10)	60(2)	−1(2)	9(1)	−6(4)
C(9)	25(1)	281(11)	97(3)	3(3)	20(1)	34(5)
C(10)	24(1)	290(11)	100(3)	15(2)	19(1)	38(5)
C(11)	20(1)	327(11)	72(2)	−2(2)	13(1)	1(4)
C(12)	23(1)	342(12)	90(2)	8(3)	15(1)	54(5)
C(13)	21(1)	328(11)	85(2)	10(2)	10(1)	43(4)
C(14)	24(1)	347(12)	104(3)	−3(3)	19(1)	32(5)
C(15)	21(1)	402(13)	97(3)	−12(3)	16(1)	4(5)
C(16)	22(1)	419(13)	91(2)	4(3)	15(1)	9(5)
C(17)	24(1)	524(15)	119(3)	−1(3)	24(1)	29(6)
C(18)	31(1)	578(17)	193(4)	22(3)	37(2)	−13(7)

TABLE IV

Final fractional positional coordinates and isotropic thermal parameters of the hydrogen atoms with e.s.d.'s in parentheses. Atoms are numbered according to the heavy atoms to which they are bonded

Atom	x(σ)	y(σ)	z(σ)	B_{iso}(σ)
H(3)	.378(1)	.535(6)	.482(2)	5.5(1.0)
H(4)	.273(1)	.527(6)	.495(2)	5.6(9)
H(6)	.313(1)	−0.080(6)	.679(2)	5.1(9)
H(7)	.417(1)	−0.077(6)	.664(2)	5.3(9)
H(9)	.180(1)	.530(5)	.509(2)	3.4(8)
H(10)	.072(1)	.518(5)	.524(2)	3.3(8)
H(12)	.116(1)	−0.097(5)	.704(2)	2.5(7)
H(13)	.220(1)	−0.099(5)	.688(2)	3.1(8)
H(141)	.005(1)	−0.133(5)	.635(2)	4.2(9)
H(142)	.026(1)	.019(5)	.751(2)	2.7(7)
H(151)	−0.101(1)	.073(5)	.577(2)	3.2(8)
H(152)	−0.090(1)	−0.088(5)	.692(2)	4.3(9)
H(161)	−0.057(1)	.273(5)	.802(2)	4.3(9)
H(162)	−0.079(1)	.419(6)	.687(2)	5.4(9)
H(171)	−0.187(1)	.248(6)	.642(2)	5.3(9)
H(172)	−0.164(1)	.139(5)	.770(2)	5.5(9)
H(181)	−0.221(1)	.498(7)	.774(3)	8.7(1.1)
H(182)	−0.171(1)	.645(6)	.730(3)	10.2(1.2)
H(183)	−0.149(1)	.522(7)	.854(3)	11.0(1.3)

C(1)-N(1) is 1.132(3) Å which are close to the values found in other cyano-compounds.[7,9,11] The two kinds C-O bond lengths 1.367(2) Å and 1.443(3) Å are close to the expected values. The average internal bond angles in both the phenyl rings (C-C-C) are 120.0(.2)°. The two angles C(6)-C(5)-C(4) and C(13)-C(8)-C(9) in rings A and B are 116.9° and 116.3° respectively which deviate significantly from the average value so are the angles C(5)-C(4)-C(3) and C(8)-C(9)-C(10) which are 122° and 121.1° respectively. The external nonhydrogen bond angles in the rings range from 119.9° to 121.9° with very small variation but C(12)-C(11)-O(1) and C(10)-C(11)-O(1) have much different values—125° and 115.7°. This indicates a degree of strain in the phenyl rings which presumably arises due to the rigidness of this

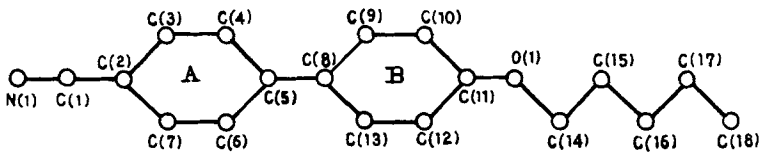

FIGURE 1 Lebelling of the 50CB molecule.

TABLE V

Bond lengths (Å) of the non-hydrogen atoms with e.s.d.'s in parentheses

N(1)	-	C(1)	1.132(3)	C(10)	-	C(11)	1.385(3)
C(1)	-	C(2)	1.452(3)	C(11)	-	C(12)	1.383(3)
C(2)	-	C(3)	1.375(4)	C(12)	-	C(13)	1.386(3)
C(2)	-	C(7)	1.367(4)				
C(3)	-	C(4)	1.387(3)	C(11)	-	O(1)	1.368(3)
C(4)	-	C(5)	1.386(4)	O(1)	-	C(14)	1.444(3)
C(5)	-	C(6)	1.390(3)	C(14)	-	C(15)	1.513(3)
C(6)	-	C(7)	1.391(3)	C(15)	-	C(16)	1.512(4)
C(5)	-	C(8)	1.489(3)	C(16)	-	C(17)	1.538(3)
C(8)	-	C(9)	1.402(3)	C(17)	-	C(18)	1.508(4)
C(8)	-	C(13)	1.385(3)				
C(9)	-	C(10)	1.379(3)				

Bond angles (°) of the non-hydrogen atoms with e.s.d.'s in parentheses.

N(1)	-	C(1)	-	C(2)	178.5(3)	C(7)	-	C(2)	-	C(1)	119.9(2)
C(1)	-	C(2)	-	C(3)	120.5(2)	C(4)	-	C(5)	-	C(8)	121.9(2)
C(2)	-	C(3)	-	C(4)	119.9(2)	C(6)	-	C(5)	-	C(8)	121.2(2)
C(3)	-	C(4)	-	C(5)	122.0(2)	C(5)	-	C(8)	-	C(9)	121.9(2)
C(4)	-	C(5)	-	C(6)	116.9(2)	C(8)	-	C(9)	-	C(10)	122.1(2)
C(5)	-	C(6)	-	C(7)	121.3(2)	C(9)	-	C(10)	-	C(11)	120.0(2)
C(6)	-	C(7)	-	C(2)	120.4(3)	C(10)	-	C(11)	-	C(12)	119.3(2)
C(7)	-	C(2)	-	C(3)	119.6(2)	C(11)	-	C(12)	-	C(13)	119.7(2)
C(12)	-	C(13)	-	C(8)	122.5(2)	C(11)	-	O(1)	-	C(14)	116.5(2)
C(13)	-	C(8)	-	C(9)	116.3(2)	O(1)	-	C(14)	-	C(15)	108.6(2)
C(5)	-	C(8)	-	C(13)	121.8(2)	C(14)	-	C(15)	-	C(16)	114.5(2)
C(10)	-	C(11)	-	O(1)	115.7(2)	C(15)	-	C(16)	-	C(17)	110.8(2)
C(12)	-	C(11)	-	O(1)	125.0(2)	C(16)	-	C(17)	-	C(18)	113.6(2)

Bond lengths (Å) involving hydrogen atoms with e.s.d.'s in parentheses.

C(3)	-	H(3)	.99(3)	C(15)	-	H(151)	1.07(2)
C(4)	-	H(4)	.98(3)	C(15)	-	H(152)	1.03(3)
C(6)	-	H(6)	1.00(3)	C(16)	-	H(161)	1.06(2)
C(7)	-	H(7)	1.00(3)	C(16)	-	H(162)	.98(3)
C(9)	-	H(9)	1.03(3)	C(17)	-	H(171)	1.08(3)
C(10)	-	H(10)	1.02(2)	C(17)	-	H(172)	1.00(3)
C(12)	-	H(12)	0.99(3)	C(18)	-	H(181)	.92(3)
C(13)	-	H(13)	1.04(2)	C(18)	-	H(182)	1.01(3)
C(14)	-	H(141)	1.02(3)	C(18)	-	H(183)	1.08(3)
C(14)	-	H(142)	1.06(2)				

Bond angles (°) involving hydrogen atoms with e.s.d.'s in parentheses.

C(2)	-	C(3)	-	H(3)	120(1)	C(7)	-	C(6)	-	H(6)	116(1)
C(4)	-	C(3)	-	H(3)	119(1)	C(6)	-	C(7)	-	H(7)	115(1)
C(3)	-	C(4)	-	H(4)	116(1)	C(2)	-	C(7)	-	H(7)	124(.5)
C(5)	-	C(4)	-	H(4)	121(1)	C(8)	-	C(9)	-	H(9)	120(1)
C(5)	-	C(6)	-	H(6)	121(1)	C(10)	-	C(9)	-	H(9)	117(1)
C(9)	-	C(10)	-	H(10)	120(.5)	C(15)	-	C(16)	-	H(161)	109(1)
C(11)	-	C(10)	-	H(10)	119(1)	C(15)	-	C(16)	-	H(162)	111(.5)
C(11)	-	C(12)	-	H(12)	122(1)	C(17)	-	C(16)	-	H(161)	108(1.1)

TABLE V (continued)

C(13)	-	C(12)	-	H(12)	117(1)	C(17)	-	C(16)	-	H(162)	108(1)
C(12)	-	C(13)	-	H(13)	115(1.1)	H(161)	-	C(16)	-	H(162)	107(1)
C(8)	-	C(18)	-	H(13)	121(1)	C(16)	-	C(17)	-	H(171)	105(1)
O(1)	-	C(14)	-	H(141)	110(.5)	C(16)	-	C(17)	-	H(172)	106(1)
O(1)	-	C(14)	-	H(142)	108(.5)	C(18)	-	C(17)	-	H(171)	111(1)
C(15)	-	C(14)	-	H(141)	112(.5)	C(18)	-	C(17)	-	H(172)	110(1)
C(15)	-	C(14)	-	H(142)	111(1)	H(171)	-	C(17)	-	H(172)	108(.5)
H(141)	-	C(14)	-	H(142)	106(1)	C(17)	-	C(18)	-	H(181)	112(1)
C(14)	-	C(15)	-	H(151)	108(1)	C(17)	-	C(18)	-	H(182)	112(1)
C(14)	-	C(15)	-	H(152)	106(1)	C(17)	-	C(18)	-	H(183)	109(1)
C(16)	-	C(15)	-	H(151)	109(1)	H(181)	-	C(18)	-	H(182)	109(1)
C(16)	-	C(15)	-	H(152)	109(1)	H(181)	-	C(18)	-	H(183)	105(1)
H(151)	-	C(15)	-	H(152)	107(1)	H(182)	-	C(18)	-	H(183)	107(.5)

part of the molecule. The C-C-C bond angles in the chain range from 108.5° to 114.5° with a mean value of 111.9° which is quite normal. From the steriomodel of the molecule in its most extended conformation the length was found to be 17.5 Å whereas the calculated length of the molecule in the crystalline state is equal to 17 Å. This suggests that the chains are in their most extended conformation. The bond angle N(1)-C(1)-C(2) has a value 178.5°. This deviation from linearity of the cyanogroup was also found in other cyanocompounds.[7,11,12] The C-H distances range from 0.924 Å to 1.078 Å with a mean value 1.019 Å.

The least-squares planes for different parts of the molecule have been calculated. The equation of the planes and r.m.s. displacements of the atoms from the respective planes have been listed in Table VI. The dihedral angles of these planes are given in Table VII. As expected each of the phenyl rings shows high degree of planarity. Also the phenyl rings and the atoms N(1), C(1), and O(1) (the rigid part of the molecule) are found to be planar within experimental error. The dihedral angle between the least-squares planes of the chain part and the rigid part is 35.8° and that between the two phenyl ring planes is 0.82°.

Molecular packing

Molecular packing of 50CB in the ab plane is shown in Figure 2 and that in the ac plane is shown in Figure 3. From these it is observed that the rigid part of the molecule extends parallel to a-axis but the chain part is inclined to it by about 32°. The least squares plane of the rigid part is almost parallel to ab-plane and the molecules are stacked along c-axis. Thus for 50CB compound it is found to be true

TABLE VI

Coefficients p, q, r, s in the equation pX + qY + rZ = s of the least-squares planes and the r.m.s. displacements of the atoms from respective planes

	Plane	p	q	r	s	r.m.s. displacement (Å)
1.	Phenyl ring A	.0396	.5179	.8545	6.9574	.0009
2.	Phenyl ring B	.0530	.5135	.8565	7.0362	.0040
3.	N(1) to O(1)	.0425	.5158	.8557	7.0129	.0336
4.	O(1) to C(18)	.3320	−.0188	.9431	6.6075	.2262

TABLE VII

Angle between the normals to the planes of 50CB

Plane	Plane	Dihedral angles (°)
1	2	0.82
1	3	0.22
1	4	35.97
2	3	0.62
2	4	35.35
3	4	35.77

which many authors believe[13] that a parallel imbricated mode of molecular packing in the crystalline phase contiguous to the melt is a necessary condition for a compound to form nematic liquid crystal.

All intermolecular contact distances less than 4 Å (involving non-hydrogen atoms) have been listed in Table VIII. But only the cyanogroups of the neighbouring molecules are at a distance less than the sum of the van der Waals radii with a non-bonded contact distance of 3.30 Å existing between the C atom and the N-atom. This was also observed by Vani and Vijayan[11] in CBOOA. Thus the molecules associate in pairs about the centre of inversion to form a dimer. The adjacent molecules in the unit cell are antiparallel to each other.

The apparent length of the molecule in the nematic phase was found[1] to be 24.5 Å which is nearly 1.4 times the calculated length in the crystalline state. This is often found in cyanocompounds and to explain this bimolecular association is discussed.[1,9,14,15] Interaction between the dipoles induced by the cyanogroups to the easily polarisable biphenyl groups may result in this large overlapping. In the crystalline state this interaction is also assumed to be responsible for

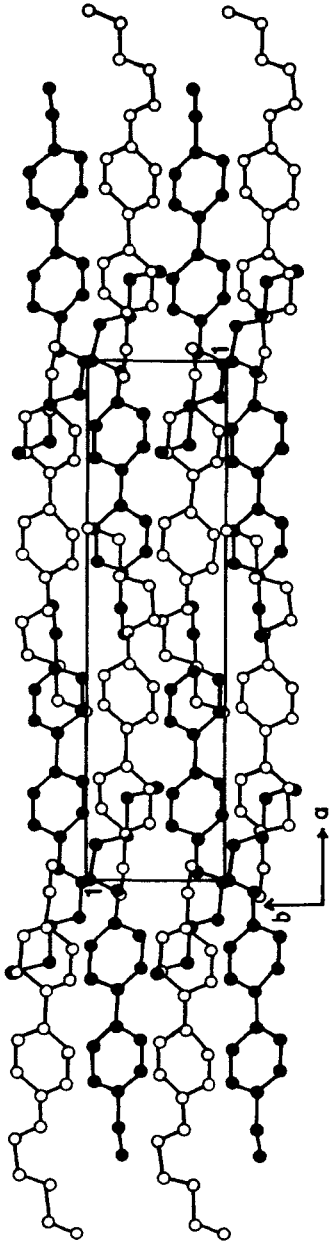

FIGURE 2 Projection of the crystal structure of 50CB along the c-axis.

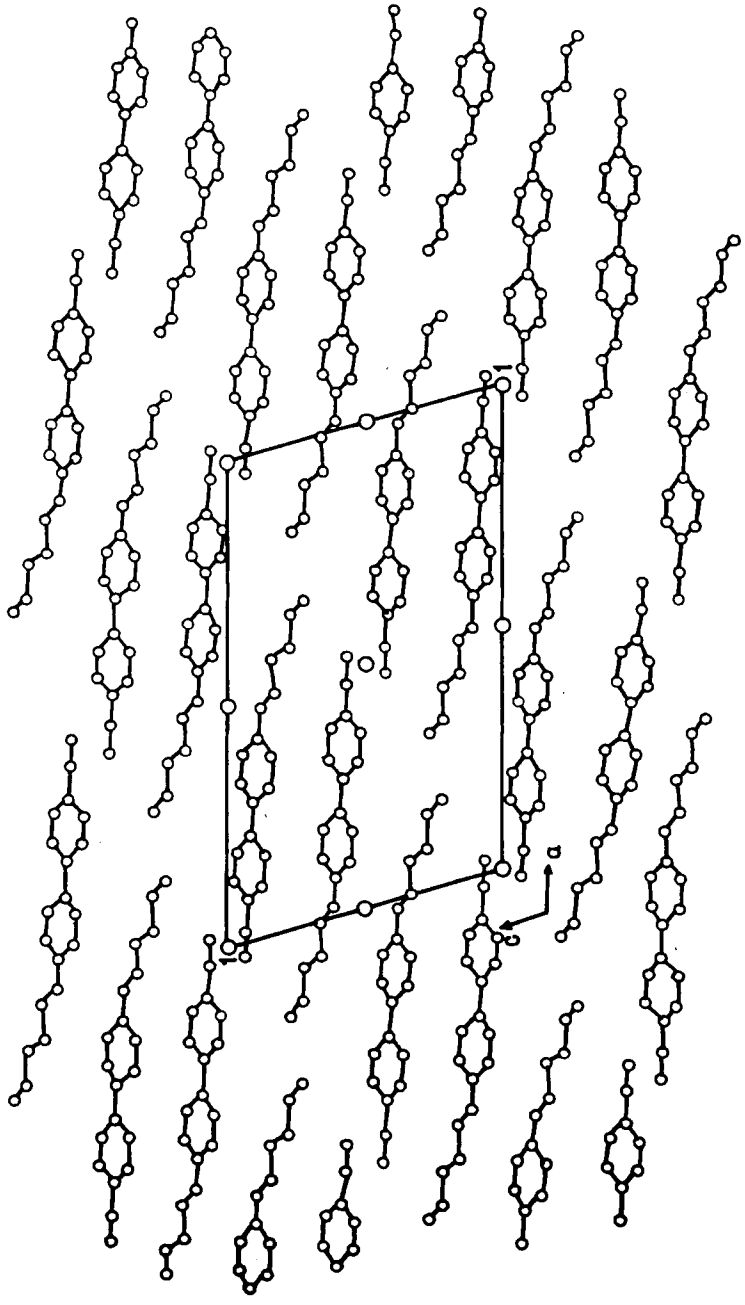

FIGURE 3 Projection of the crystal structure of 50CB along the b-axis.

TABLE VIII

Intermolecular contact distances less than 4 Å (involving non-hydrogen atoms)

C(1) - C(1)[a]	3.579	C(11) - C(6)[c]	3.843
C(1) - C(1)[b]	3.713	C(11) - C(7)[c]	3.794
C(1) - C(15)[c]	3.963	C(11) - C(14)[g]	3.767
C(1) - N(1)[b]	3.338	C(11) - C(15)[g]	3.768
C(1) - N(1)[a]	3.304	C(12) - C(6)[f]	3.779
C(2) - C(14)[c]	3.755	C(12) - C(6)[c]	3.920
C(2) - N(1)[b]	3.861	C(12) - C(7)[f]	3.947
C(2) - N(1)[a]	3.749	C(12) - C(10)[i]	3.848
C(3) - C(7)[d]	3.870	C(12) - C(15)[g]	3.962
C(3) - N(1)[b]	3.437	C(13) - C(9)[i]	3.794
C(3) - C(17)[c]	3.882	C(14) - C(1)[c]	3.618
C(3) - C(18)[e]	3.903	C(14) - C(10)[g]	3.897
C(4) - C(12)[c]	3.885	C(14) - N(1)[f]	3.879
C(4) - C(6)[d]	3.872	C(15) - N(1)[f]	3.776
C(5) - C(12)[c]	3.761	C(17) - C(18)[i]	3.844
C(5) - C(13)[c]	3.728	O(1) - O(1)[g]	3.733
C(6) - C(10)[f]	3.922	O(1) - C(7)[c]	3.880
C(7) - N(1)[a]	3.845	O(1) - C(10)[h]	3.717
C(8) - C(13)[c]	3.818	O(1) - C(14)[g]	3.794
C(9) - C(15)[g]	3.875	N(1) - N(1)[a]	3.404
C(9) - C(16)[h]	3.913	N(1) - N(1)[b]	3.326
C(9) - C(17)[h]	3.961	N(1) - C(16)[c]	3.983
C(10) - C(15)[g]	3.730	N(1) - C(16)[i]	3.810
C(10) - C(16)[h]	3.997	N(1) - C(18)[f]	3.606
C(11) - O(1)[g]	3.937		

Symmetry Code
None) x, y, z

[a] $1 - x, \bar{y}, 1 - z$
[b] $1 - x, 1 - y, 1 - z$
[c] $\frac{1}{2} - x, \frac{1}{2} + y, 1 + \frac{1}{2} - z$
[d] $x, y + 1, z$
$1 \quad 1 \quad 1$
[e] $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z - 1$
[f] $\frac{1}{2} - x, \frac{1}{2} + y - 1, 1 + \frac{1}{2} - z$
[g] $\bar{x}, \bar{y}, 1 - z$
[h] $\bar{x}, 1 - y, 1 - z$
[i] $x, y - 1, z$
[j] $\frac{1}{2} - x - 1, \frac{1}{2} + y - 1, 1 + \frac{1}{2} - z$

dimer formation. However, in this state molecular packing energy prohibits large overlapping. In the nematic state intermolecular attractive forces relax due to increased thermal energy and the large overlapping can be achieved only by a shift of the associated molecules with respect to each other along the crystal a-axis.

In the nematic state the interatomic distance was found[1] to be 5 Å which is close to the value of crystal b-axis. This suggests that during transition the molecular stacking along c-axis breaks down completely. A transformation into the liquid crystalline state can thus be attained only by transitional motion of the molecules without any drastic change in their orientations (only rotation along the molecular long axis may occur). The transition is thus of displacive type.[16]

Acknowledgments

We are very much grateful to Dr. Siddhartha Roy of Indian Association for the Cultivation of Science, Calcutta for his valuable guidance throughout the work. Thanks are due to University Grants Commission for granting a fellowship to P. Mandal and financial assistance for computational work.

References

1. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **89**, 181 (1982).
1a. M. Mitra, K. Bhattacharjee and P. Mandal, communicated for publication.
2. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. DeClercq and M. M. Woolfson, MULTAN-78, A system of computer programme for the Automatic Solution of Crystal Structures from X-ray Diffraction Data (University of York, England and Louvain, Belgium, 1978).
3. B. L. Vickery, D. Bright and P. R. Mallinson, "X-RAY ARC" IBM 1130 Programme System for Crystallography (1971).
4. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
5. D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).
6. A. J. Leadbetter and M. A. Mazid, *Mol. Cryst. Liq. Cryst.*, **51**, 85 (1979).
7. U. Baumeister, H. Hartung, M. Gdaniec and M. Jaskolski, *Mol. Cryst. Liq. Cryst.*, **69**, 119 (1981).
8. P. A. C. Gane and A. J. Leadbetter, *Mol. Cryst. Liq. Cryst.*, **78**, 183 (1981).
9. W. Haase, H. Paulus and H. T. Muller, *Mol. Cryst. Liq. Cryst.*, **97**, 131 (1983).
10. International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, (1962).
11. G. V. Vani and K. Vijayan, *Mol. Cryst. Liq. Cryst.*, **42**, 249 (1977).
12. U. Baumeister, H. Hartung and M. Jaskolski, *Mol. Cryst.*, **88**, 167 (1982).
13. R. F. Bryan, Proceedings of the Pre-Congress Symposium on Organic Crystal Chemistry, Poznan, Poland, Page 105 (1979).
14. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys.* (Paris), **36**, 37 (1975).
15. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Phys.*, **44**, 1391 (1981).
16. R. F. Bryan and P. G. Forcier, *Mol. Cryst. Liq. Cryst.*, **60**, 133 (1980).