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Crystal and Molecular Structure of the Nematogenic Compound 4-Cyanophenyl-4′-*n*-Heptylbenzoate (CPHB)

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INTRODUCTION

It is now well established that for a proper understanding and interpretation of several physical properties of liquid crystalline phases, a knowledge of the molecular arrangement in the crystalline state is very useful. A preliminary survey of the present knowledge of the solid-mesophase relationships has been given by Bryan.[1] The classical view is that in typical nematogen crystals the long narrow molecules lie more or less parallel and are interleaved giving what was described by Bernal and Crowfoot[2] as an *imbricated* packing and that the transformation from the solid to the nematic phase is characterised by the breakdown of the positional order of the molecules but not of the orientational order. Leadbetter[3] has however pointed out that although this is true of at least the majority of the small number of cases so far known, it is a generalisation which must at this stage be treated with caution. Hence the determination of the crystal and molecular structure of the title nematogenic compound was undertaken. Bhattacharjee *et al.*[4] have previously studied the transition temperatures of this compound by X-ray diffraction and optical microscopy and found as follows:

$$\text{Solid} \underset{\sim 33^\circ\text{C}}{\overset{43.5^\circ\text{C}}{\rightleftharpoons}} \text{Nematic} \overset{56^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$$

These transition temperatures were found to be identical to those reported by M/s. F. Hoffmann-La-Roche,[5] (the only additional feature being the supercooling). Bhattacharjee *et al.* also determined the orientational order parameters and distribution functions of magnetically aligned samples, intermolecular distances and apparent molecular lengths. In this paper we describe the crystal and molecular structure of CPHB and discuss the change in the molecular packing which accompanies the solid to nematic phase transition.

EXPERIMENTAL

Crystal data

Transparent plate-like crystals were obtained by slow evaporation from a solution in acetone. The unit cell dimensions and space group were determined from oscillation and Weissenberg photographs. The

TABLE I

Summary of crystallographic data

Molecular Formula	$C_{21}H_{23}N_1O_2$
Formula weight	321.42 g/mol.
Crystal system	Monoclinic
Space group	$P2_1/n$
Form/habit	Plate shaped
a = 23.692 (6) Å	
b = 5.986 (8) Å	
c = 13.399 (2) Å	
β = 105.146 (1)°	
V_c = 1834.3 Å^3	
D_c = 1.16 g.cm^{-3}	
D_0 = 1.15 g.cm^{-3}	
Z = 4	
$\lambda(\text{CuK}_\alpha)$ = 1.5418 Å	
Number of independent reflections	1872
Number of observed reflections	1227, $I > 2.5\sigma(I)$

crystals belong to the monoclinic system. Systematic absences occur for the $h0l$ reflections with $h + l = 2n + 1$ and the $0k0$ reflections with $k = 2n + 1$ indicating the space group $P2_1/n$. A crystal of dimensions .3 × .3 × .1 mm was used for intensity data collection.

Accurate cell parameters were determined by a least squares fit of $\sin\theta$ values of 20 reflections within the range $35.5° < \theta < 40.4°$ measured on an Enraf Nonius CAD-4 diffractometer, CuK_α radiation monochromatised by a graphite monochromator was used throughout. A total of 1872 reflections were collected on a $\theta - 2\theta$ scan mode, of which 1227 were treated as significant having intensities greater than 2.5σ (I). The data were corrected for Lorentz and polarisation factors, but no absorption correction was made. The principal crystallographic data are given in Table I.

Structure determination and refinement

The structure was determined by the direct methods program system SIMPEL83 (C. T. Kiers and H. Schenk),[6] using all reflections in order to employ all positive and negative quartet relationships, all sigma1 relations and all special two dimensional quartets apart from the triplets. The 300 strongest reflections were phased using 4 symbols. Two out of the 16 solutions had appreciably better FOM's than all others, combined FOM's of 74 and 75 respectively on a scale from 0 to 100. The highest CFOM revealed the complete structure, the lower one showed a superposition of two images of the structure, shifted by half a bond length in opposite directions along the long axis of the molecule. The trial structure was found to have an *R*-value of 18.6%, which, after four cycles of refinement by full-matrix least squares, reduced to 13.8% (using first an overall value and then individual values for isotropic temperature factors). The positions of hydrogen atoms were then calculated from the known geometry around the carbon atoms and these positions were subsequently confirmed on a difference Fourier map. The hydrogen atoms were given isotropic temperature factors of the parent carbon atoms for the last cycle of isotropic refinement. Then the structure was refined through several cycles by block-diagonal approximation, first keeping hydrogen atoms fixed and allowing non-hydrogen atoms to vibrate anisotropically and then with hydrogen atoms vibrating isotropically and non-hydrogen atoms fixed. This resulted in an *R*-value of 4.7%. Finally one cycle of refinement was carried out with the hydrogen atoms allowed to vibrate isotropically and non-hydrogen atoms to vibrate anisotropically. The final R-value was 4.5% with R_w, 5.0% and $S \approx 1.27$, using weighting $w = 1/\sigma^2$ and S being the standard deviation of an observation with unit weight. The function minimised in the least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ and

$$R_w = \left[\frac{\Sigma w(|F_0| - |F_c|)^2}{\Sigma w|F_0|^2}\right]^{1/2}$$

In the final cycle the shifts in the parameters were all less than their estimated standard deviations and a difference Fourier map showed no maxima greater than 0.1 eÅ^{-3}. All the calculations were carried out by means of the program package "X-RAY ARC" of B. L. Vickery *et al.*[7] modified for the B6700 computer. Neutral atom scattering factors were taken from Stewart *et al.*[8] for H atoms and from Cromer and Waber[9] for C, N and O atoms.

TABLE II

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

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
C1	.2960 (2)	.4060 (7)	1.2370 (3)
C2	.3095 (2)	.3646 (7)	1.1384 (3)
C3	.2972 (2)	.5239 (6)	1.0615 (3)
C4	.3090 (2)	.4786 (6)	.9671 (3)
C5	.3331 (2)	.2761 (6)	.9538 (2)
C6	.3467 (2)	.1178 (7)	1.0305 (3)
C7	.3342 (2)	.1622 (7)	1.1238 (3)
C8	.3191 (2)	.0595 (6)	.8010 (3)
C9	.3386 (2)	.0319 (6)	.7045 (2)
C10	.3688 (2)	.1967 (7)	.6674 (3)
C11	.3837 (2)	.1607 (7)	.5751 (3)
C12	.3703 (2)	−0.0352 (7)	.5204 (3)
C13	.3405 (2)	−0.2008 (7)	.5590 (3)
C14	.3252 (2)	−0.1681 (6)	.6513 (3)
C15	.3847 (2)	−0.0665 (7)	.4170 (3)
C16	.4253 (2)	−0.2604 (7)	.4159 (3)
C17	.4389 (2)	−0.2856 (7)	.3093 (3)
C18	.4706 (2)	−0.5002 (7)	.2994 (3)
C19	.4858 (2)	−0.5210 (8)	.1948 (3)
C20	.5161 (2)	−0.7413 (8)	.1849 (3)
C21	.5380 (3)	−0.7525 (10)	.0892 (4)
O1	.3459 (1)	.2367 (4)	.8586 (2)
O2	.2840 (1)	−0.0577 (4)	.8262 (2)
N1	.2870 (2)	.4347 (7)	1.3152 (2)

RESULTS AND DISCUSSIONS

Molecular conformation

Final positions and thermal parameters of all atoms are listed in Tables II, III and IV using the atom numbering scheme shown in Figure 1. Figure 2 shows a perspective drawing of the molecule viewed normal to the least squares plane. Bond lengths and bond angles are given in Table V. These are comparable with those found in other similar compounds.[10-14] The average C—C bond lengths in phenyl rings C2—C7 and C9—C14 are 1.380 (5) Å and 1.386 (5) Å respectively (expected value is 1.395 Å).[15] The average C—C single bond length in the chain part is 1.524 (6) Å (expected value is 1.541 Å).[15] The C1—N1 bond length is 1.144 (5) Å which is close to the values found in other cyano-compounds.[11,13,14] The bond lengths of the linkage carboxylic group are similar to those observed for 4'-cyanophenyl-4-*n*-pentylbenzoate[14] and 4'-cyanophenyl-4-*n*-pentoxybenzoate[11] and

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	β_{11} (σ)	β_{22} (σ)	β_{33} (σ)	β_{12} (σ)	β_{13} (σ)	β_{23} (σ)
C1	32 (1)	339 (16)	74 (3)	−4 (4)	18 (2)	−19 (6)
C2	22 (1)	319 (15)	54 (2)	−1 (3)	14 (1)	−4 (5)
C3	26 (1)	258 (14)	68 (3)	8 (3)	13 (1)	1 (5)
C4	28 (1)	273 (14)	54 (2)	−9 (3)	10 (1)	4 (5)
C5	23 (1)	299 (14)	48 (2)	−7 (3)	13 (1)	−7 (5)
C6	30 (1)	311 (15)	62 (3)	20 (3)	19 (1)	13 (5)
C7	34 (1)	335 (16)	54 (3)	23 (4)	18 (1)	17 (5)
C8	23 (1)	267 (13)	54 (2)	13 (3)	11 (1)	20 (5)
C9	19 (1)	280 (14)	46 (2)	−1 (3)	9 (1)	3 (5)
C10	36 (1)	264 (14)	65 (3)	−10 (3)	22 (2)	−1 (5)
C11	41 (1)	301 (16)	70 (3)	−16 (4)	29 (2)	17 (6)
C12	26 (1)	338 (16)	52 (2)	18 (3)	14 (1)	27 (5)
C13	28 (1)	282 (14)	63 (3)	−3 (3)	18 (1)	−9 (5)
C14	22 (1)	269 (14)	63 (3)	−5 (3)	16 (1)	4 (5)
C15	40 (1)	333 (16)	58 (3)	14 (4)	24 (2)	21 (6)
C16	30 (1)	441 (17)	59 (3)	14 (4)	20 (1)	18 (6)
C17	31 (1)	403 (17)	60 (3)	13 (4)	23 (1)	26 (6)
C18	29 (1)	412 (17)	67 (3)	13 (4)	19 (2)	21 (6)
C19	31 (1)	441 (18)	67 (3)	15 (4)	23 (2)	17 (6)
C20	34 (1)	505 (21)	104 (4)	44 (4)	29 (2)	51 (8)
C21	45 (2)	679 (27)	124 (4)	36 (6)	37 (2)	−32 (10)
O1	31 (1)	320 (10)	54 (2)	−22 (2)	21 (1)	−15 (4)
O2	28 (1)	295 (9)	72 (2)	−10 (2)	23 (1)	3 (4)
N1	43 (1)	509 (16)	79 (3)	8 (4)	29 (1)	−25 (6)

TABLE IV

Final positional fractional 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 bounded

Atom	x (σ)	y (σ)	z (σ)	B_{iso} (σ)
H3	.278 (1)	.665 (6)	1.069 (2)	2.6 (8)
H4	.299 (1)	.579 (6)	.908 (2)	2.1 (8)
H6	.365 (1)	−0.032 (6)	1.019 (2)	2.9 (9)
H7	.345 (2)	.053 (6)	1.183 (3)	3.5 (1.0)
H10	.379 (1)	.330 (6)	.712 (2)	2.0 (8)
H11	.404 (2)	.277 (6)	.548 (3)	3.7 (9)
H13	.329 (2)	−0.341 (6)	.522 (2)	3.3 (9)
H14	.301 (1)	−0.287 (6)	.675 (2)	1.9 (8)
H151	.347 (1)	−0.079 (8)	.360 (3)	5.8 (1.1)
H152	.403 (2)	.083 (7)	.401 (3)	3.7 (1.0)
H161	.404 (2)	−0.408 (7)	.428 (3)	5.5 (1.0)
H162	.465 (2)	−0.238 (7)	.475 (3)	5.1 (1.1)
H171	.467 (2)	−0.156 (7)	.307 (3)	4.1 (1.0)
H172	.399 (2)	−0.272 (7)	.253 (3)	5.4 (1.1)
H181	.445 (2)	−0.642 (8)	.302 (3)	5.7 (1.1)
H182	.507 (2)	−0.514 (8)	.360 (3)	6.3 (1.2)
H191	.512 (2)	−0.384 (8)	.188 (3)	5.3 (1.1)
H192	.450 (2)	−0.500 (6)	.135 (3)	4.0 (1.0)
H201	.489 (2)	−0.866 (9)	.190 (3)	8.1 (1.3)
H202	.549 (2)	−0.766 (9)	.253 (3)	8.2 (1.4)
H211	.551 (2)	−0.904 (8)	.081 (3)	6.6 (1.2)
H212	.571 (2)	−0.629 (10)	.104 (4)	9.6 (1.6)
H213	.502 (2)	−0.727 (9)	.028 (3)	7.5 (1.3)

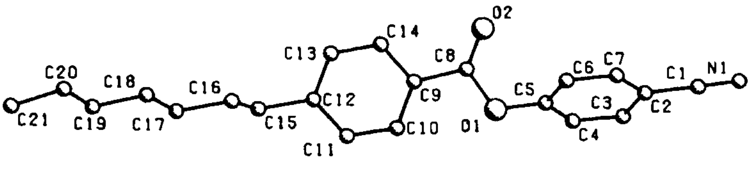

FIGURE 1 Numbering scheme of CPHB molecule.

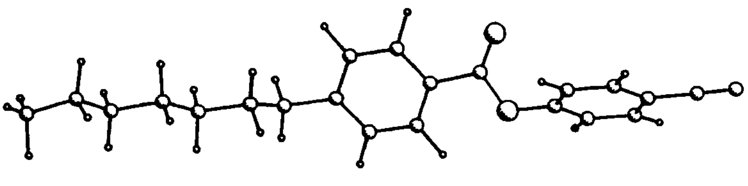

FIGURE 2 CPHB molecule looking down the normal to the least squares plane.

TABLE V

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

C1—C2	1.459 (5)	C9—C14	1.387 (5)
C1—N1	1.144 (5)	C10—C11	1.389 (5)
C2—C3	1.378 (5)	C11—C12	1.376 (6)
C2—C7	1.382 (6)	C12—C13	1.388 (6)
C3—C4	1.391 (5)	C12—C15	1.526 (5)
C4—C5	1.371 (5)	C13—C14	1.392 (5)
C5—C6	1.373 (5)	C15—C16	1.510 (6)
C5—O1	1.407 (4)	C16—C17	1.551 (5)
C6—C7	1.384 (5)	C17—C18	1.511 (6)
C8—C9	1.492 (5)	C18—C19	1.541 (5)
C8—O1	1.367 (4)	C19—C20	1.525 (7)
C8—O2	1.202 (5)	C20—C21	1.506 (7)
C9—C10	1.384 (5)		

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

C3—H3	0.97 (4)	C17—H171	1.02 (4)
C4—H4	0.98 (3)	C17—H172	1.04 (4)
C6—H6	1.03 (4)	C18—H181	1.05 (4)
C7—H7	1.01 (4)	C18—H182	1.03 (4)
C10—H10	0.99 (3)	C19—H191	1.04 (4)
C11—H11	0.97 (4)	C19—H192	1.01 (4)
C13—H13	0.98 (4)	C20—H201	0.99 (5)
C14—H14	1.02 (3)	C20—H202	1.03 (5)
C15—H151	1.02 (4)	C21—H211	0.98 (5)
C15—H152	1.04 (4)	C21—H212	1.05 (6)
C16—H161	1.05 (4)	C21—H213	1.04 (5)
C16—H162	1.06 (4)		

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

N1—C1—C2	177.8 (5)	C8—C9—C10	122.6 (3)
C1—C2—C3	120.4 (4)	C8—C9—C14	117.3 (3)
C1—C2—C7	118.6 (4)	C10—C9—C14	120.1 (3)
C3—C2—C7	121.0 (4)	C9—C10—C11	119.0 (4)
C2—C3—C4	119.4 (4)	C10—C11—C12	121.8 (4)
C3—C4—C5	118.7 (4)	C11—C12—C13	118.8 (4)
C4—C5—C6	122.5 (4)	C11—C12—C15	120.7 (4)
C4—C5—O1	117.5 (3)	C13—C12—C15	120.4 (4)
C6—C5—O1	119.9 (3)	C12—C13—C14	120.3 (4)
C5—C6—C7	118.6 (4)	C9—C14—C13	120.0 (3)
C2—C7—C6	119.7 (4)	C12—C15—C16	113.6 (3)
C9—C8—O1	111.8 (3)	C15—C16—C17	111.7 (3)
C9—C8—O2	125.0 (3)	C16—C17—C18	113.0 (3)
O1—C8—O2	123.2 (3)	C17—C18—C19	112.8 (3)
C5—O1—C8	117.6 (3)	C18—C19—C20	112.2 (4)
		C19—C20—C21	112.8 (4)

Bond angles in degrees involving hydrogen atoms with e.s.d.'s in parentheses.

C2—C3—H3	123 (2)	C16—C17—H171	104 (2)
C4—C3—H3	118 (2)	C16—C17—H172	107 (2)
C3—C4—H4	124 (2)	C18—C17—H171	108 (2)

TABLE V

(*continued*)

C5—C4—H4	117 (2)	C18—C17—H172	112 (2)
C5—C6—H6	121 (2)	H171—C17—H172	113 (3)
C7—C6—H6	120 (2)	C17—C18—H181	112 (2)
C2—C7—H7	119 (2)	C17—C18—H182	109 (2)
C6—C7—H7	121 (2)	C19—C18—H181	104 (2)
C9—C10—H10	116 (2)	C19—C18—H182	112 (2)
C11—C10—H10	125 (2)	H181—C18—H182	106 (3)
C10—C11—H11	119 (2)	C18—C19—H191	107 (2)
C12—C11—H11	119 (2)	C18—C19—H192	112 (2)
C12—C13—H13	122 (2)	C20—C19—H191	112 (2)
C14—C13—H13	118 (2)	C20—C19—H192	111 (2)
C9—C14—H14	121 (2)	H191—C19—H192	103 (3)
C13—C14—H14	119 (2)	C19—C20—H201	109 (3)
C12—C15—H151	109 (2)	C19—C20—H202	108 (3)
C12—C15—H152	107 (2)	C21—C20—H201	113 (3)
C16—C15—H151	112 (3)	C21—C20—H202	114 (3)
C16—C15—H152	111 (2)	H201—C20—H202	100 (4)
H151—C15—H152	104 (3)	C20—C21—H211	109 (3)
C15—C16—H161	109 (2)	C20—C21—H212	102 (3)
C15—C16—H162	110 (2)	C20—C21—H213	106 (3)
C17—C16—H161	107 (2)	H211—C21—H212	115 (4)
C17—C16—H162	110 (2)	H211—C21—H213	106 (4)
H161—C16—H162	110 (3)	H212—C21—H213	118 (4)

agree well with the standard dimensions based on an analysis of appropriate structural data in the Cambridge Crystallographic Database.[16] The average internal (C—C—C) bond angles in both phenyl rings are 120.0 (4)°. From Table V we note that the angles C3—C4—C5, C4—C5—C6 and C5—C6—C7 of the phenyl ring C2—C7 deviate by nearly 5σ from the average value and a similar deviation occurs for the angles C10—C11—C12 and C11—C12—C13 of the phenyl ring C9—C14. Of the external non-hydrogen bond angles in the rings C4—C5—O1, C8—C9—C10 and C8—C9—C14 differ significantly from the mean value 119.7°. This indicates a degree of strain in the phenyl rings arising from the presence of the carboxylic linkage groups between them. The C—C—C bond angles in the alkyl chain range from 111.7° to 113.6° with a mean value of 112.7° which exceeds the tetrahedral angle by more than 3° (but such values have been reported for mesogenic compounds). The length of the fully extended molecule estimated from a stereomodel is found to be 21 Å and the length of the molecule in the crystalline state is 20.8 Å. This suggests that the molecule is actually in its most extended conformation. The bond angle N1—C1—C2 is found to be 177.8°. This deviation from linearity was also found in other cyano-compounds.[14,17] The C—H distances range from 0.97 Å to 1.06 Å with a mean value of 1.02 Å.

The least squares planes for different parts of the molecule have been calculated to check the planarity of the molecule. The equation of the planes, individual and r.m.s. displacements of the constituent atoms along with some neighbouring 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 a high degree of planarity. Also the linkage part (plane 3) and the heptyl chain part (plane 5) are planar within experimental error. The dihedral angle between the phenyl ring planes is 47.5°. The cyano-group atoms are displaced slightly upward (.03 Å) from the cyanophenyl ring plane (plane 1), whereas the 01 atom is displaced slightly downward (.02 Å). The cyanophenyl ring makes an angle 7.2° with the heptyl chain plane and 62.1° with the linkage plane. On the other hand the carboxylic phenyl ring (plane 2) makes an angle 53.4° with the heptyl chain plane and 14.7° with the linkage plane. Thus we see that the molecule has a conformation similar to those of its lower homologue CPPB[14] and of the other two phenyl benzoates PB[18] and NPOOB.[19] Only CPPOB[11] is an exception.

Molecular packing

Diagrams of the molecular arrangement in the crystal are given in Figure 3 and Figure 4. The molecules are arranged in a head-to-tail fashion in imbricated rows (Figure 3). The molecular long axis (taken as the line connecting the two benzene ring centres) makes an angle of 18.5° with the *c*-axis and the inter-axial angle of the neighbouring molecules is 37°. With the benzene ring C2—C7 nearly parallel to the *bc*-plane, the molecule lies in an almost fully extended form in this plane. Figure 4 shows the molecular packing in *c* projection. If a pair of molecules related by a centre of symmetry is taken to be one unit, the arrangement of these units in the *ab*-plane could be described as a herringbone-like pattern. Along the *b*-direction these units are related by a simple translation whereas along the *a*-direction they are related by a two fold screw axis and an *n*-glide plane.

The pattern of molecular orientation in the crystal may be expressed in terms of the familiar orientational order parameter,

$$\langle P_2 \rangle = \frac{1}{2}(3\langle \cos^2\theta \rangle - 1)$$

by choosing the crystal *c*-axis as the director axis. The angle made by the molecular long axis with *c* is 18.5° giving a value of this order

TABLE VI

Equations of various least-squares planes and the individual and r.m.s. displacements (Δ) of the atoms from them

Equations of the planes	Atoms	Δ in Å	r.m.s. Δ in Å
	In plane		
1) .8531 X +	C2	.0053	
.3917 Y +	C3	−0.0066	
.3446 Z =	C4	.0001	
8.7895	C5	.0067	.0059
	C6	−0.0094	
	C7	.0023	
	Other atoms		
	O1	−0.0190	
	C1	.0357	.0306
	N1	.0343	
	In plane		
2) .7659 X −	C9	.0084	
.3908 Y +	C10	−0.0072	
.5106 Z =	C11	−0.0005	.0054
8.8414	C12	.0034	
	C13	.0004	
	C14	−0.0066	
	Other atoms		
	C8	.0491	.0606
	C15	.0703	
	In plane		
3) .6356 X −	C5	−0.0236	
.6078 Y +	O1	.0149	
.4760 Z =	O2	.0033	.0142
7.7384	C8	.0007	
	C9	−0.0147	
	In plane		
4) .8134 X −	N1	−0.0630	
.3502 Y +	C1	−0.0474	
.4646 Z =	C2	−0.0822	
8.7163	C3	0.7317	
	C4	0.7079	
	C5	−0.1393	
	C6	−0.9754	
	C7	−0.9360	
	O1	−0.1671	
	O2	0.5109	.4274
	C8	0.1604	
	C9	0.0309	
	C10	−0.0868	
	C11	−0.1584	
	C12	−0.1331	
	C13	−0.0334	
	C14	0.0392	
	C15	−0.1538	
	In plane		
5) .7870 X +	C15	0.0918	
.4954 Y +	C16	−0.0877	
.3677 Z =	C17	−0.0531	
7.9009	C18	0.0121	.0720
	C19	−0.0002	
	C20	0.1065	
	C21	−0.0766	

TABLE VII

Angles between the normals to the planes of CPHB

Plane	Plane	Dihedral angles (°)
1	2	47.45
1	3	62.08
1	4	44.21
1	5	7.18
2	3	14.67
2	4	4.45
2	5	53.36
3	4	18.02
3	5	68.03
4	5	50.40

parameter of .84. The order parameter in the nematic phase calculated[4] for a magnetically aligned sample at about 36° is .61 giving an average value of θ, of 30°. The relation between the structure of the liquid crystal phase and crystalline solid could perhaps have been better illustrated by taking a photograph of a single domain liquid crystal

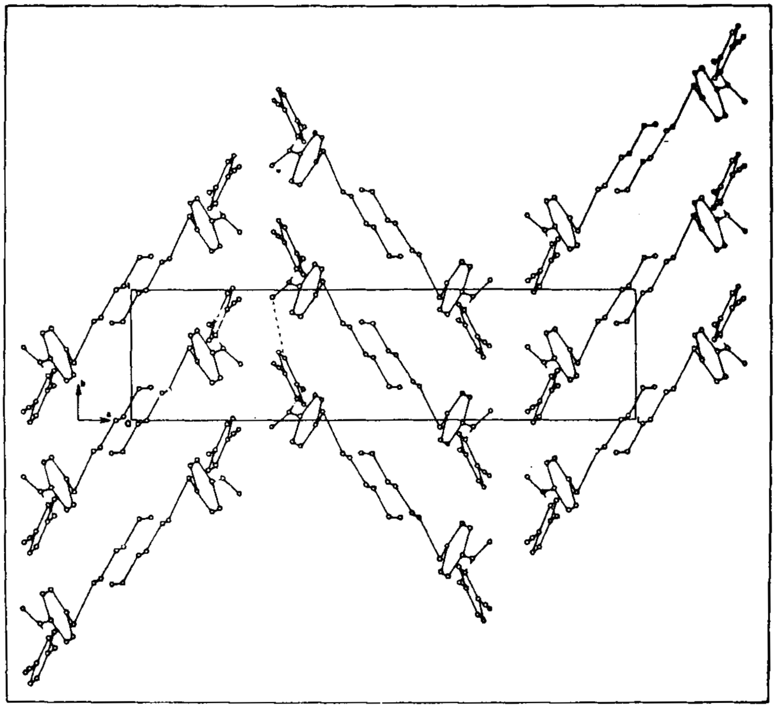

FIGURE 3 Imbricated rows of CPHB molecules in *bc* plane.

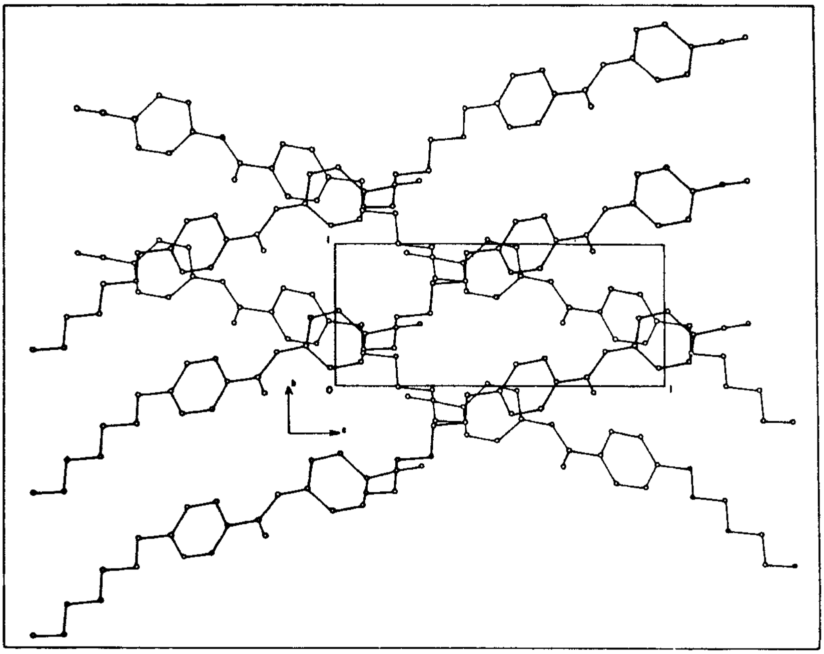

FIGURE 4 Crystal structure of CPHB in *c*-axis projection.

sample at the transition temperature. In the event, however, the crystal order parameter is sufficiently high to make it probable that the transition to the nematic phase is accomplished by a simple relaxation of the intermolecular attractive forces with increasing thermal energy in such a way that translational motion of the molecules becomes possible and is accompanied by rotation about the large molecular axes. Rotations of individual molecules about other axes cannot take place without the creation of much larger local free volumes and cooperative motions of similar type are also restricted.

A value of 27 Å was obtained for the apparent length of the molecules in the nematic phase from X-ray measurements. This is 1.3 times the calculated length in the crystalline state. This is often found in cyanocompounds and to explain this a bimolecular association resulting from an interaction between cyanogroups is invoked.[13,17,20] In CPHB no such dipole-dipole interaction has been observed as in the two other cyanocompounds CPPB[14] and CPPOB.[11] However, from the list of intermolecular contact distances given in Table VIII, it is evident that there is a close contact between C4 and O2 atoms of neighbouring molecules. Thus it appears that a different type of interaction exists between the neighbouring molecules of this cyano-

TABLE VIII

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

C1—C1[a]	3.773	C10—C13[f]	3.881
C1—N1[b]	3.407	C10—C19[g]	3.967
C2—C13[c]	3.856	C10—O2[c]	3.928
C2—N1[b]	3.600	C10—C14[f]	3.932
C3—C12[c]	3.841	C11—C13[d]	3.948
C3—C13[c]	3.509	C11—C18[g]	3.981
C3—C14[c]	3.679	C11—N1[h]	3.981
C3—N1[b]	3.801	C13—N1[i]	3.850
C4—C6[d]	3.970	C14—C20[e]	3.865
C4—C9[c]	3.663	C14—O2[a]	3.553
C4—C13[c]	3.630	C15—C18[j]	3.878
C4—C14[c]	3.280	C15—N1[i]	3.803
C4—O2[c]	3.978	C17—N1[i]	3.989
C4—O2[d]	3.322	C21—C21[k]	3.935
C5—C14[c]	3.661	C21—C21[l]	3.981
C7—N1[b]	3.450	C21—O1[e]	3.930
C8—C14[c]	3.986	O1—O2[c]	3.625
C8—C21[e]	3.795	O2—O2[a]	3.743
C9—C20[e]	3.794	O2—O2[c]	3.743
C9—C21[e]	3.842	N1—N1[b]	3.679
C10—C20[e]	3.996		

None x, y, z

[a] $1/2 - x, 1/2 + y - 1, 1/2 - z + 1$

[b] $1/2 - x, 1/2 + y - 1, 1/2 - z + 2$

[c] $1/2 - x, 1/2 + y, 1/2 - z + 1$

[d] $x, y + 1, z$

[e] $1 - x, \bar{y} - 1, 1 - z,$

[f] $x, 1 - y, z$

[g] $1 - x, \bar{y}, 1 - z$

[h] $x, y, z - 1$

[i] $x, y - 1, z - 1$

[j] $x, \bar{y}, z$

[k] $1 - x, \bar{y} - 2, z$

[l] $1 - x, \bar{y} - 1, \bar{z}.$

compound which play a role in stabilising the mesophase organisation. We therefore assume that bimolecular association generally occurs. The length of this associated pair in the crystalline state is 23 Å and in the nematic state this becomes 27 Å due to relaxation of the intermolecular attractive forces at the higher temperature.

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