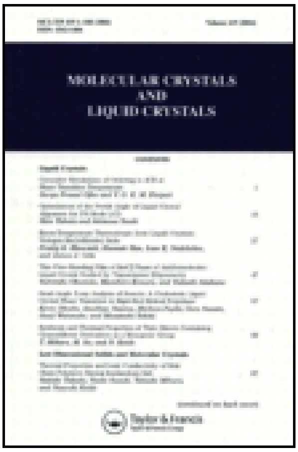

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X-ray Diffraction Studies on Solid and Mesomorphic Phases of Four Members of Alkoxy-Cyanobiphenyls

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X-ray Diffraction Studies on Solid and Mesomorphic Phases of Four Members of Alkoxy-Cyanobiphenyls

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X-ray diffraction studies of four alkoxy cyanobiphenyls (alkyl = nonyl, decyl, undecyl and dodecyl) have been undertaken to determine orientational order parameters, layer thickness, packing fraction and coefficients of HJL type potential. All these values show some odd-even effect with the number of chain carbon atoms. Powder X-ray patterns from these compounds in solid phase have also been indexed satisfactorily. Orientational order parameters have been fitted to those calculated from McMillan's theory by varying the parameters α and δ.

Keywords: Mesogens, order parameters, cyanobiphenyl, X-ray diffraction, packing fraction, layer thickness

1. INTRODUCTION

Mesophases of alkoxy cyanobiphenyls (*n*OCB) have been studied extensively and mixtures of these compounds have been used in display devices, since they can be prepared easily and are comparatively stable. X-ray diffraction studies[1,2] on mesophases of some of these compounds show formation of association of molecules in the smectic phase and even in the nematic phase. Octyl and nonyl members of this homologous series have both nematic and smectic phases, whereas higher members have only smectic phases. Though 8OCB has been studied quite thoroughly, not much work has been reported on higher homologues. Keeping this in mind, we decided to study X-ray diffraction from magnetically aligned samples of nonyl, decyl, undecyl and dodecyl members of this series using the X-ray set up described earlier.[3]

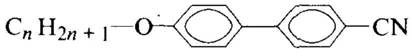
Refractive index and orientational order parameter (OOP) measurements on these four compounds have already been reported by us.[4] We have also fitted these OOP values to McMillan's theory[5] using δ and α in the potential as adjustable parameters and have obtained an odd-even effect in the values of α.[4] Hence, it is of interest to determine order parameters from X-ray studies and compare these with those found from refractive index data. Also, the layer thickness in the smectic phase can be determined easily from the X-ray diffraction pattern and this can give an idea about molecular association. Our results show that the order parameters obtained from X-ray studies are much smaller than those obtained from refractive index measurements. This may partly be due to inability to form good single domain samples of these smectogens in the magnetic field due to negative magnetic susceptibility anisotropy of the long alkyl chain of these compounds.[6] These OOP values cannot be fitted well to the theoretical values from McMillan's potential.

Molecular order and packing in the solid phase predetermines the structure of the mesophase. Hence a systematic study of the molecular and crystal structure of liquid crystalline compounds is of considerable interest for interpretation of some properties in mesomorphic state. In this context crystal structure analysis of the compounds of this homologous series was undertaken by our research group at University of North Bengal.[7] For 9OCB and 10OCB single crystals of good quality for analysis purposes could not be grown. For 11OCB and 12OCB, although trial structures were determined from single crystal diffraction data, the structures could not be refined.[8] We have tried to index the powder X-ray patterns obtained from all these compounds.

We have also calculated the angular part of the mean field potential from the experimentally derived distribution function. The coefficients of the potential show some odd-even effect.

2. EXPERIMENTAL METHODS AND DATA ANALYSIS

All the four compounds were provided as free gifts by British Drug House (at present E. Merck) Poole, U. K. and were used without further purification. The names, structural formula and transition temperature of all the four compounds are as follows.



I. $n = 9$, nonyloxycyanobiphenyl (9OCB).
II. $n = 10$, decyloxycyanobiphenyl (10OCB).
III. $n = 11$, undecyloxycyanobiphenyl (11OCB).
IV. $n = 12$, dodecyloxycyanobiphenyl (12OCB).

I. 9OCB $\text{Solid} \underset{32.5^\circ\text{C}}{\overset{64^\circ\text{C}}{\rightleftharpoons}} \text{SM A} \overset{77.5^\circ\text{C}}{\rightleftharpoons} \text{N} \overset{80^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

II. 10OCB $\text{Solid} \underset{64^\circ\text{C}}{\overset{59.5^\circ\text{C}}{\rightleftharpoons}} \text{Sm A} \overset{84^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

III. 11OCB $\text{Solid} \underset{55^\circ\text{C}}{\overset{71.5^\circ\text{C}}{\rightleftharpoons}} \text{Sm A} \overset{87^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

IV. 12OCB $\text{Solid} \underset{56.5^\circ\text{C}}{\overset{70.0^\circ\text{C}}{\rightleftharpoons}} \text{Sm A} \overset{90^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

The experimental technique employed has been discussed in detail in our earlier publication.[3] Since we had to align the smectic phase without any nematic phase at higher temperatures in three of the four substances studied, we had to cool the sample slowly in a large magnetic field (6 Kilogauss) to obtain a well aligned sample. Sometimes we had to repeat the process several times for better alignment. Also to obtain better accuracy in the measurement of layer thickness, X-ray diffraction photographs of inner spots were taken with sample to film distance increased to about 9 cm. The details of analysis of data are also given in an earlier[2] publication, where the procedure for obtaining the orientational distribution function, order parameters, and layer thickness are mentioned.

The cell dimensions and the space group of the four compounds were determined from the powder diffraction data using the program PPLP of the NRCVAX package of White *et al.*[9] The trial cell dimensions were given on the basis of the single crystal data of 11OCB and 12OCB.[8] The density of each of the four compounds was calculated from the unit cell volume taking one molecule per asymmetric unit. This was compared with the experimental density value in the solid determined by the flotation method. The molecular packing coefficients were evaluated from the cell parameters of the crystals using the approach of Kitaigorodsky.[10] The packing coefficient is defined as the ratio of the geometric (Van der Walls') volume of the molecules to the volume occupied per molecule in the crystal. Single crystal studies on 11OCB and 12OCB show that both the compounds belong to space group $P2_1/a$. Powder X-ray photographs as well as powder diffraction scans were taken for all the four samples. We successfully indexed the observed diffraction lines of 9OCB and 10OCB using the above space group extinction conditions. Though not many lines were observed, the reliability factor M20 value indicate that the assignments of Miller indices to diffraction lines are reasonable.

3. RESULTS AND DISCUSSION

Orientational order parameters (OOP) $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as obtained from our X-ray data, have been plotted as function of temperature for 9OCB, 10OCB, 11OCB and 12OCB in Figures 1, 2, 3 and 4 respectively. It is seen from Figure 1 that the nematic - smectic transition is of first order, since the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ change abruptly in passing to the nematic phase from the smectic phase. It is clear that in all the four compounds the order parameters at first increase and then remains almost constant with decreasing temperature except for 11OCB in which case OOPs increase marginally with decreasing temperature. The reason for the anomaly may be due to the fact that while the biphenyl part of these molecules have positive magnetic susceptibility anisotropy, the chain parts have negative magnetic anisotropy.[6] Hence, in a strong magnetic field the chain parts of the molecules will tend to align themselves perpendicular to the magnetic field, while the cyanobiphenyl part will align parallel to the magnetic field. Since, such orientation of the chain may not be possible for steric reasons, the chain may, nevertheless, take gauche form. This effect will be more pronounced at lower temperatures, where thermal motion of the molecules are reduced. Since the order parameters obtained from the X-ray diffraction are the statistical average over the scattering from the nearest pair of molecules, such gauche configuration of the chain will reduce the observed order parameter. On the other

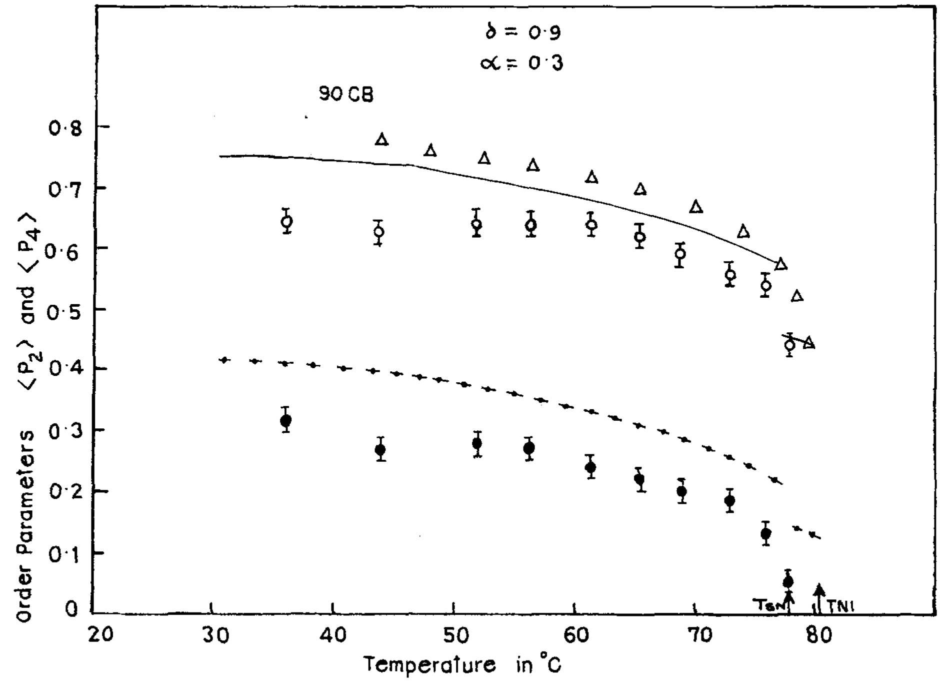


FIGURE 1 Temperature dependences of $\langle P_2\rangle$ and $\langle P_4\rangle$ for 9OCB. Δ = refractive index data for $\langle P_2\rangle$, o = X-ray data for $\langle P_2\rangle$, ● = X-ray data for $\langle P_4\rangle$, T_{NI} = nematic-isotropic transition temperature, T_{SN} = smectic-nematic transition temperature. The vertical bars indicate estimated errors. —— $\langle P_2\rangle$ values and .... $\langle P_4\rangle$ values from McMillan's theory.

hand, OOP from refractive index data depends more on the polarizability anisotropy of the molecules, i.e. the biphenyl part contributes mostly to it, hence, the 00P calculated from refractive index data are not expected to show such anomalous behaviour. Moreover, in refractive index measurements surface alignment was used to obtain mono domain samples instead of magnetic field. Even though, the $\langle P_2\rangle$ values from refractive index data have been obtained using Haller's extrapolation procedure,[11] which is of doubtful validity, any error in extrapolation can only shift all the $\langle P_2\rangle$ values by the same ratio. Thus, the two sets of $\langle P_2\rangle$ values cannot be reconciled by changing the method of refractive index data analysis.

Since a perfect fit over the complete temperature range was not possible, we have tried to fit the higher temperature (near smectic–isotropic) OOP values with those calculated from McMillan's theory[5] by varying the values of the α parameter in the potential (δ being kept the same for all the compounds). This was done since α depends on the molecular length, which varies with the chain length. The parameter δ, being the ratio of the translational to the orientational part of the potential, may be assumed to be almost constant for these four compounds.

The agreement of the experimental $\langle P_2\rangle$ and $\langle P_4\rangle$ values near the transition temperature with the theoretical values seems to be fair. (Figures 1–4). The values of δ and α used for calculations are also shown in the respective figures.

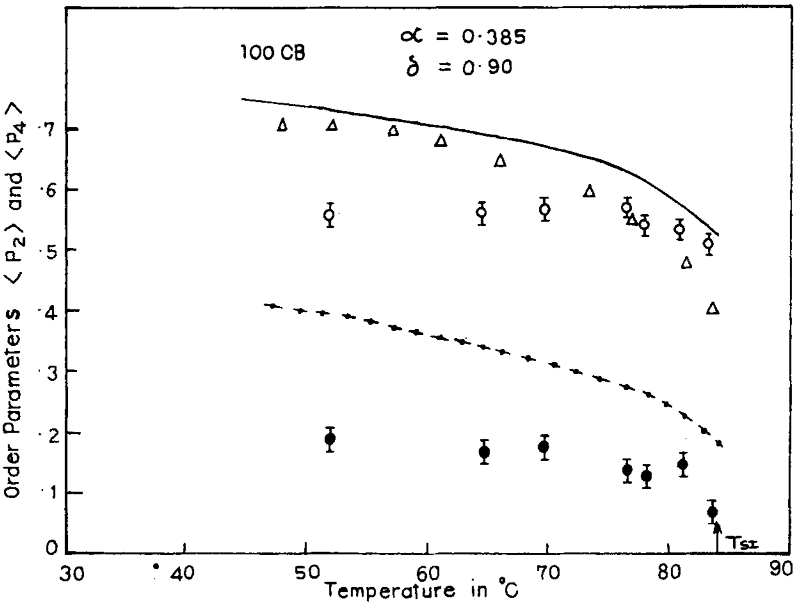


FIGURE 2 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 10OCB. Δ = refractive index data for $\langle P_2 \rangle$, o = X-ray data for $\langle P_2 \rangle$, ● = X-ray data for $\langle P_4 \rangle$, T_{SI} = smectic-isotropic transition temperature. The vertical bars indicate estimated errors. —— $\langle P_2 \rangle$ values and ..... $\langle P_4 \rangle$ values from McMillan's theory.

Layer thickness of all the compounds were determined over their mesomorphic temperature range. For all the four compounds the layer thickness remains almost constant throughout the mesomorphic range. The mean layer thickness of the oriented samples, as obtained from our measurements are 32.75 Å, 34.28 Å, 35.39 Å, and 37.5 Å for 9OCB, 10OCB, 11OCB and 12OCB respectively (Table I). So it is clear that the layers are partially bilayers, since the molecular lengths of the compounds in their most extended forms as determined by stereo model are 22.1 Å, 23.05 Å, 24.55 Å and 25.6 Å respectively. This is in accordance with earlier observations on cyanobiphenyls by Leadbetter *et al.*[1]

Table I gives the values of δ and α used in fitting our experimental data with those from McMillan's theory. As mentioned before the δ values were kept constant. The best fit α values increase gradually as the chain part increases, which is in accordance with the theoretical predictions.

The Miller indices of the observed diffraction lines for all the four compounds are shown in Table II along with the Qobs, Qcal and M20 values, where $Q_{hkl} = 1/d^2_{hkl} = (2\sin\theta/\lambda)^2$, θ and λ being the Bragg angle and wavelength of X-ray respectively. In all cases powder diffractometer values were used except for 9OCB where our X-ray powder photograph data were taken. All the compounds were assumed to have monoclinic unit cell, as single crystals of 11OCB and 12OCB have this form. Q_{obs} and Q_{cal} are the magnitudes of the observed and calculated Q values respectively. M20 gives the reliability of the indexing. The cell parameters of the compounds used for indexing are given in Table III. The calculated and measured

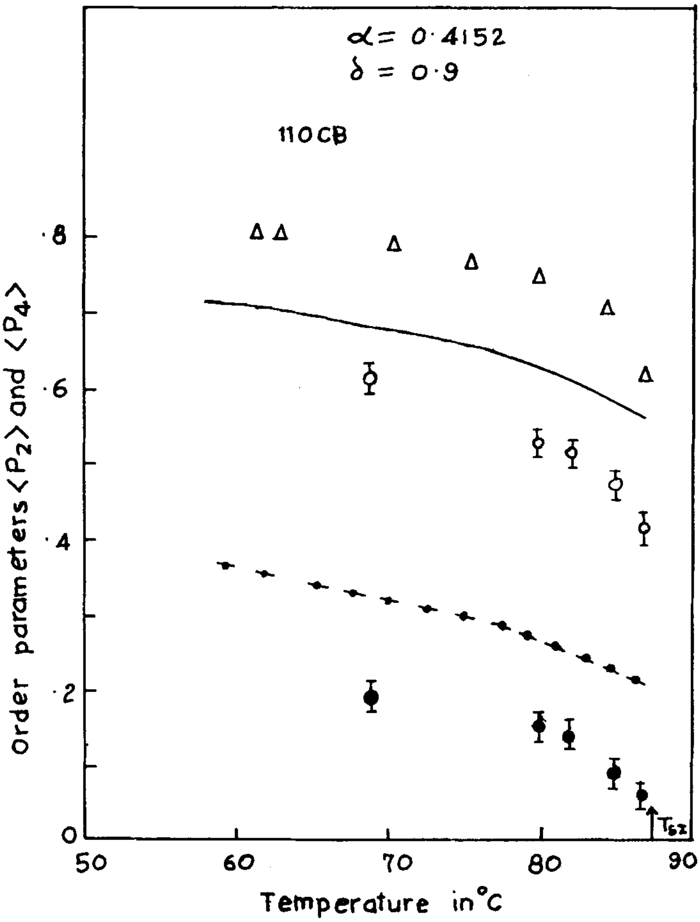


FIGURE 3 Temperature dependences of $\langle P_2\rangle$ and $\langle P_4\rangle$ for 11OCB. Δ = refractive index data for $\langle P_2\rangle$, o = X-ray data for $\langle P_2\rangle$, ● = X-ray data for $\langle P_4\rangle$, T_{SI} = smectic-isotropic transition temperature. The vertical bars indicate estimated errors. —— $\langle P_2\rangle$ values and ....$\langle P_4\rangle$ values from McMillan's theory.

densities along with the calculated packing fraction for these compounds are given in Table IV. The measured density values are accurate within ± 0.001 gm/c.c. The *c* values (the longest cell axis) determined by the PPLP program are quite accurate since we are using a number of (001) lines. From Table III it is found that the cells are almost orthogonal. The bimolecular association which exists in the smectic phase is most probably retained in the crystal phase as well, since the longest axis (*c*-axis) length is almost equal to the layer thickness in the smectic phase (Table I), the molecular long axis being almost parallel to the *c* axis. The near orthogonality of the cells may explain the occurrence of orthogonal smectic A phase. From Table III it is apparent that the increment in c with chain carbon number shows a strong odd- even effect. Not only in *c*, odd-even effect exists also in the solid phase values of densities (Figure 5) and packing fraction (Table IV). The packing fractions were calculated using the standard pro-

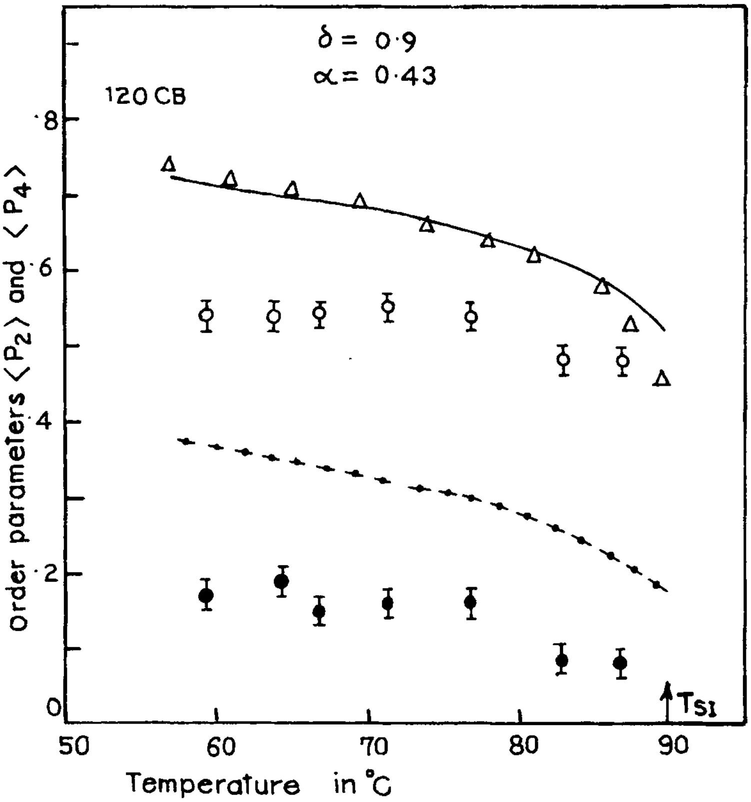


FIGURE 4 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 12OCB. Δ = refractive index data for $\langle P_2 \rangle$, o = X-ray data for $\langle P_2 \rangle$, ● = X-ray data for $\langle P_4 \rangle$, T_{SI} = smectic-isotropic transition temperature. The vertical bars indicate estimated errors. —— $\langle P_2 \rangle$ values and ..... $\langle P_4 \rangle$ values from McMillan's theory.

TABLE I

δ, α, different reduced transition temperature values for best fit with McMillan's theory ($T^* = kT/v$) for nOCB ($n = 9$, 10, 11 and 12). The last column indicates mean layer thickness

Sample	T^*_{SN}	T^*_{NI}	δ	α	Mean Layer thickness d (Å)
9OCB	0.2186	0.2202	0.90	0.375	32.75
10OCB	0.2230	–	0.90	0.385	34.28
11OCB	0.2270	–	0.90	0.415	35.39
12OCB	0.2318	–	0.90	0.430	37.50

cedure given by Kitaigorodsky[10] and taking the density values from our earlier work. One of the density values (of 11OCB) was miscalculated in the previous paper and we have determined the density of 11OCB again and have taken the fresh density value for the packing fraction calculations. We have included the density values of 5OCB, 6OCB, 7OCB and 8OCB (in solid phase measured by us) in Figure 5 to confirm the odd-even

TABLE II

Miller indices of the diffraction lines along with the calculated interplanar distance D_{cal}, the Q_{obs}, Q_{cal} and M20 values for nOCB ($n = 9$, 10, 11 and 12). DQ is the difference between the observed and the calculated Q values, $Q = (2\sin\theta/\lambda)^2$

D_{calc}	h	k	l	Q_{calc} $Å^{-2}$	Q_{obs} $Å^{-2}$	$DQ \times 10^{-5}$ $Å^{-2}$
			9OCB			
30.370	0	0	1	.00108	.00109	0
15.190	0	0	2	.00430	.00432	2
6.680	0	1	2	.02243	.02314	70
4.850	−1	1	3	.04248	.04263	15
4.485	−1	1	4	.04972	.04961	11
3.995	2	0	0	.0625	.06264	0
3.717	0	2	0	.07239	.07221	17
3.381	0	1	8	.08748	.08744	3
				M20 = 5.9		
			10OCB			
33.510	0	0	1	.00089	.00090	1
16.750	0	0	2	.00356	.00363	6
11.170	0	0	3	.00802	.00814	11
8.380	0	0	4	.01425	.01417	8
5.580	0	0	6	.03207	.03208	1
4.695	1	1	3	.04536	.04565	28
4.353	1	1	4	.05277	.05264	12
4.018	1	1	5	.06195	.06181	13
3.670	0	2	0	.07424	.07424	0
3.373	2	1	2	.08792	.08790	1
2.112	3	1	7	.22427	.22426	0
2.400	2	0	10	.17357	.17359	2
				M20 = 7.7		
			11OCB			
35.330	0	0	1	.00080	.00079	1
17.660	0	0	2	.00320	.00304	16
11.780	0	0	3	.00721	.00734	13
8.830	0	0	4	.01282	.01246	35
5.890	0	0	6	.02884	.02895	10
4.638	−1	1	4	.04649	.04668	18
4.318	−1	1	5	.05364	.05364	0
4.039	2	0	0	.06130	.06140	9
3.666	0	2	0	.07440	.07439	1
3.395	−2	1	3	.08673	.08660	13
3.140	2	0	7	.10143	.10143	0
				M20 = 5.9		
			12OCB			
38.570	0	0	1	.00067	.00068	0
19.280	0	0	2	.00269	.00273	3
12.860	0	0	3	.00605	.00614	8
9.640	0	0	4	.01076	.01065	11
5.190	1	1	2	.03718	.03698	19
4.664	1	1	4	.04597	.04572	25
4.528	−1	1	5	.04877	.04862	14
4.369	1	1	5	.05238	.05264	25
4.056	2	0	0	.06079	.06085	5
3.669	0	2	0	.07427	.07424	3
3.094	−1	2	5	.10447	.10459	12
				M20 = 8.5		

TABLE III

Lattice constants in solid phases of the substances

Cell consts.	9OCB	10OCB	11OCB	12OCB
a (Å)	8.00 ± 0.03	8.19 ± 0.02	8.08 ± 0.02	8.13 ± 0.03
b (Å)	7.43 ± 0.03	7.34 ± 0.02	7.33 ± 0.01	7.34 ± 0.02
c (Å)	30.40 ± 0.10	33.93 ± 0.07	35.33 ± 0.07	38.63 ± 0.12
β (deg)	92.40 ± 0.28	98.54 ± 0.10	90.52 ± 0.05	93.24 ± 0.09

TABLE IV

Experimental and calculated density values in the solid phase and calculated Packing fraction values in the three different phases

Samples	Density values (solid)		Packing fraction		
	Experimental	Calculated	Solid	L.C.	Isotropic
9OCB	1.103	1.195	0.754	0.678	0.646
10OCB	1.090	1.128	0.709	0.650	0.628
11OCB	1.088	1.120	0.717	0.646	0.631
12OCB	1.053	1.060	0.681	0.635	0.630

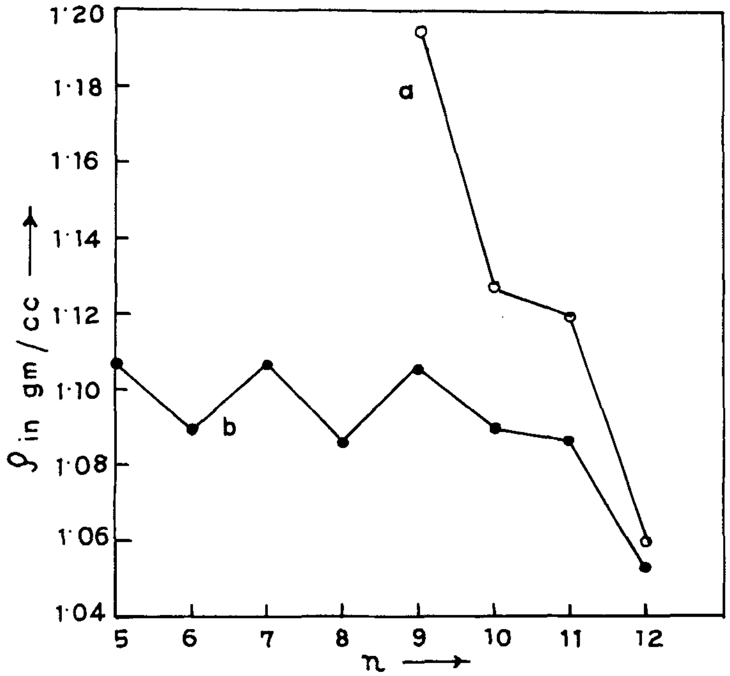


FIGURE 5 Density values in the solid phase for *n*OCB (*n* = 5, 6, 7, 8, 9, 10, 11 and 12). *a* calculated values using crystallographic data, *b* experimental values.

TABLE V

Mean values of the coefficients b_1 and b_2 for *n*OCB ($n = 9, 10, 11$ and 12)

Sample	b_1/k	b_2/k
9OCB	2223 ± 143	2429 ± 632
10OCB	2331 ± 125	3267 ± 412
11OCB	2185 ± 77	2917 ± 352
12OCB	2348 ± 123	3881 ± 243

trend. However, for 10OCB and 11OCB the odd-even effect is almost absent. It may be a coincidence that starting from 10OCB the higher homologues have smectic phase only.

Assuming the angular part of the mean field potential to be given by,[2,12]

$$V(\cos\theta) = -b_1\langle P_2\rangle P_2(\cos\theta) + b_2\langle P_4\rangle P_4(\cos\theta), \tag{1}$$

the normalised distribution function can be written as

$$f(\cos\theta) = c\exp[-V(\cos\theta)/kT], \tag{2}$$

where c is the normalising constant and k is the Boltzmann constant.

We have tried to fit our experimental $f(\cos\theta)$ values at different temperatures with those calculated from Equation 2 by changing the coefficients b_1 and b_2 of the potential (Equation 1). The mean values of the coefficients together with the standard deviations are given in Table V. Both the coefficients b_1 and b_2 show a marked odd even effect. However, this is not surprising since, odd-even effect in compounds having alkyl chains is well known and well understood.[13]

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