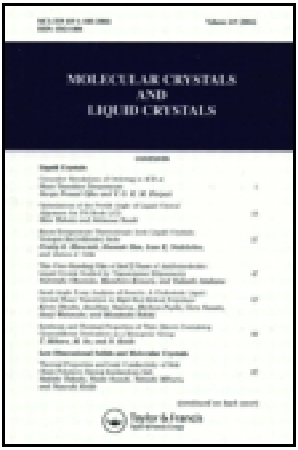

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# Determination of Orientational Order Parameter from Optical Studies for a Homologous Series of Mesomorphic Compounds

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# Determination of Orientational Order Parameter from Optical Studies for a Homologous Series of Mesomorphic Compounds

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We have measured the refractive indices ($n_o$, $n_e$) and densities of four members (nonyl, decyl, undecyl and dodecyl) of a homologous series cyanobiphenyl alkyl ether over their entire mesomorphic range and in their isotropic phases. The molecular polarizabilities have been calculated from refractive indices using both Vuks' and Neugebauer's relations. The additive rule of bond polarizabilities has also been employed to calculate the molecular polarizabilities of the four compounds assuming two different configurations of the alkyl chains. The orientational order parameter values at different temperatures for each compound have been calculated from these polarizability data. Since all the four compounds possess smectic A phases, we have compared our experimental order parameters with those calculated from the McMillan's model. Our experimental $\langle P_2 \rangle$ values for these four compounds show a pronounced odd-even effect.

*Keywords: mesogens, polarizabilities, order parameters*

## 1. INTRODUCTION

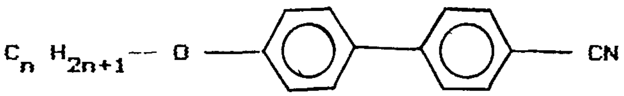
The study of optical birefringence is a useful and very simple technique to calculate the orientational order parameter in the liquid crystalline state. Until now a large number of papers have been published reporting optical birefringence studies in nematic medium to calculate order parameters.[1-10] But no systematic optical studies have been done on liquid crystals of a homologous series possessing smectic A phases. Keeping this in mind we have taken four compounds of a homologous series for study by the optical birefringence technique. All the four compounds possess smectic A phases with wide temperature ranges.

In this paper we report the refractive indices ($n_o$, $n_e$), densities ($\rho$), molecular polarizabilities ($\gamma_o$, $\gamma_e$) and orientational order parameters ($\langle P_2 \rangle$) of the four compounds at different temperatures. McMillan theory[11,12] has been utilized to obtain the orientational order parameter $\langle P_2 \rangle$, translational order parameter ($\tau$) and mixed order parameter ($\sigma$) values. Our experimental $\langle P_2 \rangle$ values have been compared with those obtained from the above theory.

## 2. EXPERIMENTAL

All the four samples were donated by British Drug House (BDH), U.K. in pure form. They were used without further purification.

The structural formulae and the names of the four compounds are given below:



(I) 1 cyano-biphenyl-nonyl-ether (9 OCB in short), $n = 9$
(II) 1 cyano-biphenyl-decyl-ether (10 OCB in short), $n = 10$
(III) 1 cyano-biphenyl-undecyl-ether (11 OCB in short), $n = 11$
(IV) 1 cyano-biphenyl-dodecyl-ether (12 OCB in short), $n = 12$

### 2.1 Texture Studies

The phase transitions of the compounds were studied by observing textures under crossed polarizers with a polarizing microscope of magnification 150X. The transition temperatures of the four compounds as observed by us agree well with the literature values during heating but during cooling we get supercooled smectic A phases for all the samples studied. The transition temperatures obtained by us are given below:

$$\text{I. Solid} \underset{\sim 43.5^\circ\mathrm{C}}{\overset{64^\circ\mathrm{C}}{\rightleftharpoons}} \text{Smectic A} \overset{77.5^\circ\mathrm{C}}{\rightleftharpoons} \text{Nematic} \overset{80^\circ\mathrm{C}}{\rightleftharpoons} \text{Isotropic}$$

$$\text{II. Solid} \underset{\sim 46^\circ\mathrm{C}}{\overset{59.5^\circ\mathrm{C}}{\rightleftharpoons}} \text{Smectic A} \overset{84^\circ\mathrm{C}}{\rightleftharpoons} \text{Isotropic}$$

$$\text{III. Solid} \underset{\sim 55^\circ\mathrm{C}}{\overset{71.5^\circ\mathrm{C}}{\rightleftharpoons}} \text{Smectic A} \overset{87.5^\circ\mathrm{C}}{\rightleftharpoons} \text{Isotropic}$$

$$\text{IV. Solid} \underset{\sim 56.5^\circ\mathrm{C}}{\overset{70^\circ\mathrm{C}}{\rightleftharpoons}} \text{Smectic A} \overset{90^\circ\mathrm{C}}{\rightleftharpoons} \text{Isotropic}$$

### 2.2 Optical Studies

Refractive indices were measured using the thin prism technique. The experimental details of this procedure have been given by Zeminder *et al.*[13] We have measured the refractive indices ($n_o$, $n_e$) within ±0.001 for four different wavelengths. The experimental uncertainty of measuring density values is ±0.1%. Different internal field models[14–19] have been proposed to explain the molecular polarizabilities in liquid crystals. Of those models the Vuks' isotropic internal field model[14] and Neugebauer's anisotropic internal field model[15] are commonly used to calculate the polarizabilities ($\gamma_o$, $\gamma_e$). Here we used Vuks' and Neugebauer's methods.

The relation[20] we used to calculate the orientational order parameter $\langle P_2\rangle$ is as follows:

$$\langle P_2\rangle = (\gamma_e - \gamma_o)/(\gamma_{\parallel} - \gamma_{\perp})$$

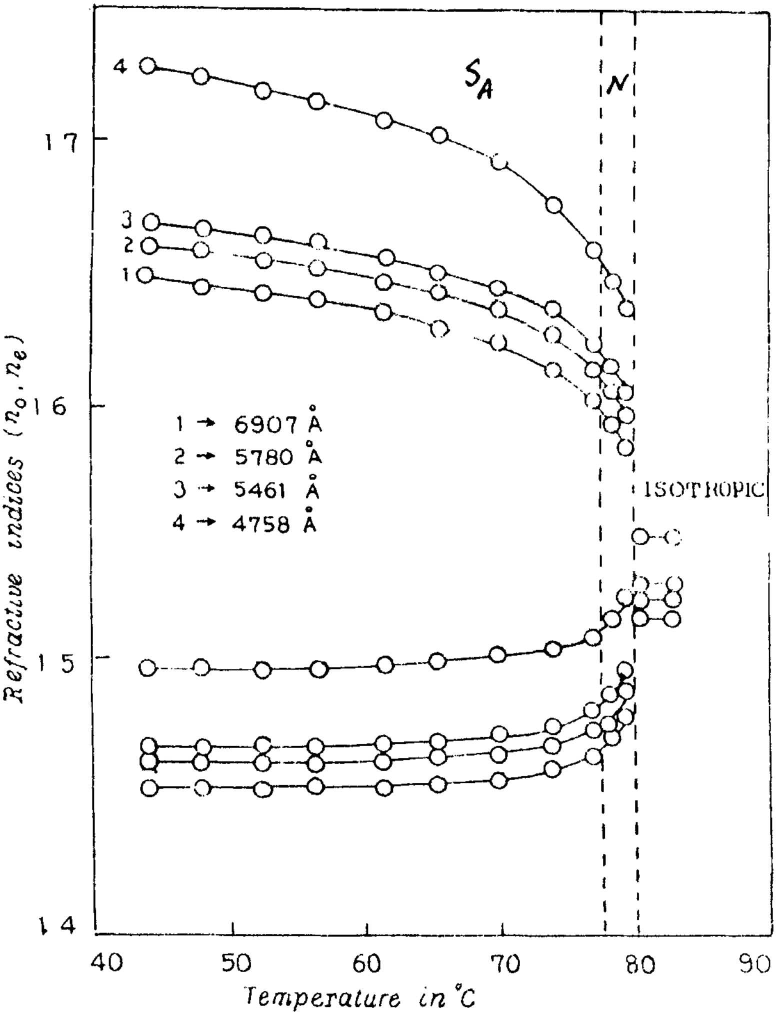


FIGURE 1 Variation of refractive indices ($n_o$, $n_e$) of 9 OCB with temperature.

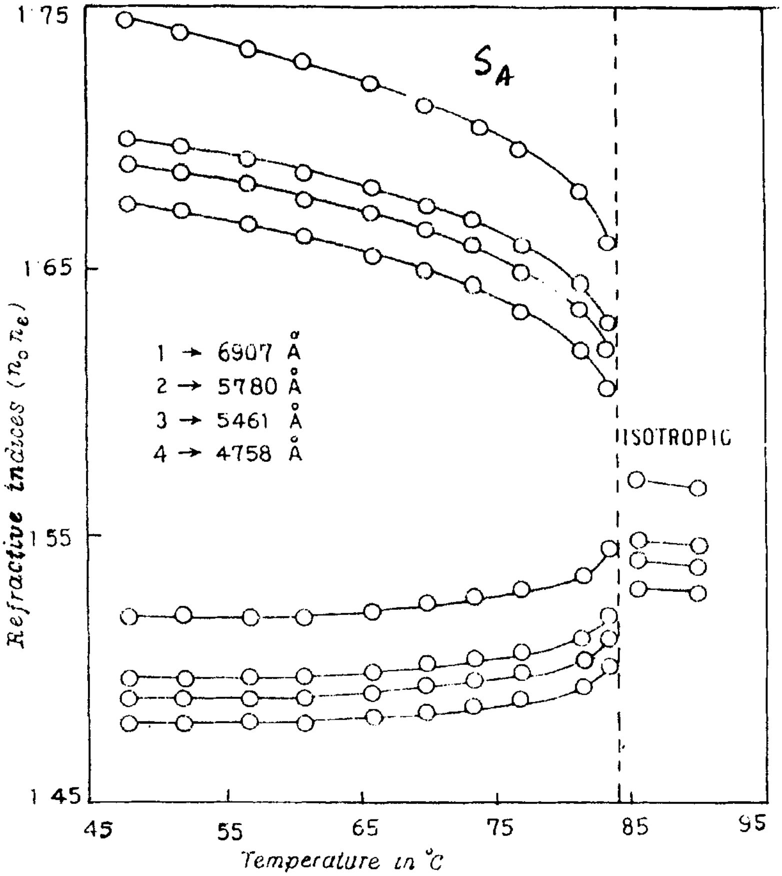


FIGURE 2 Variation of refractive indices ($n_o$, $n_e$) of 10 OCB with temperature. The sequence of the wavelength number is the same as in Figure 1.

where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the molecular polarizabilities parallel and perpendicular to the molecular long axis respectively.

## 3. McMILLAN THEORY FOR SMECTIC A PHASE

According to McMillan[11,12] the potential function for the smectic A phase is of the form

$$V_M(\cos\theta,z) = -\nu\{\delta\alpha\tau\cos(2\pi z/d) + [\eta + \alpha\sigma\cos(2\pi z/d)]P_2(\cos\theta)\}$$

where $d$ is the layer spacing along $z$-direction; $\theta$ is the angle made by the molecular long axis with the director, assumed to be in the $z$-direction; $\nu$, $\delta$ and $\alpha$ are three constants which depend on the characteristics of the molecules. $\eta$ is the orientational order parameter, $\tau$ is the translational order parameter and $\sigma$ is the mixed order parameter describing the correlation or coupling between the orientational and

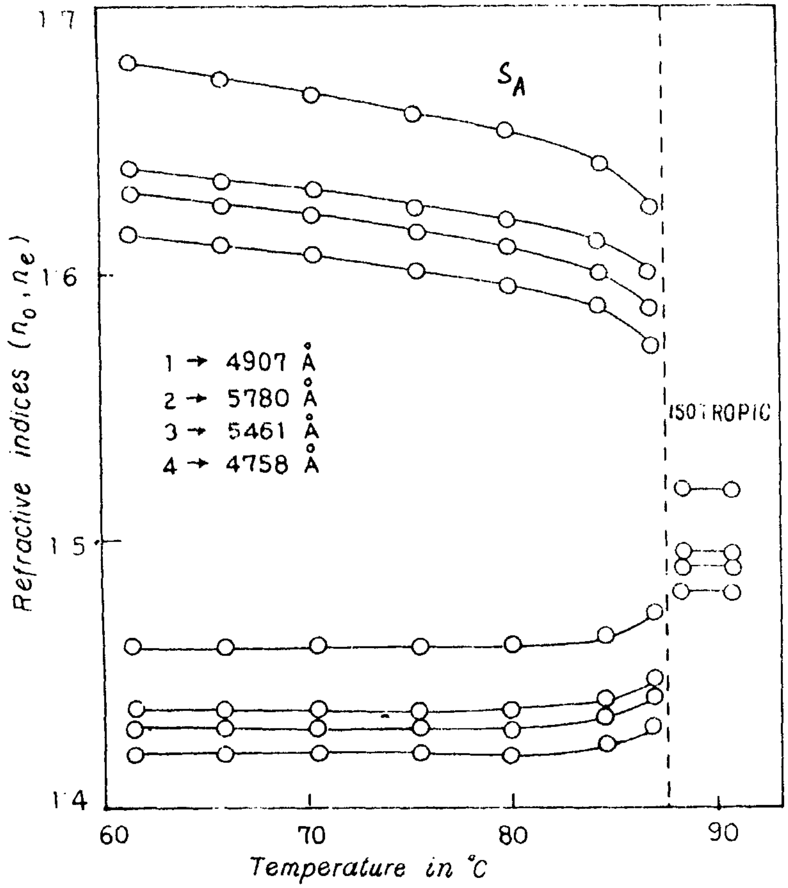


FIGURE 3 Variation of refractive indices ($n_o$, $n_e$) of 11 OCB with temperature. The sequence of the wavelength number is the same as in Figure 1.

translational orders. Lengthening the alkyl chains in a homologous series increases the spacing $d$ and hence is expected to increase the parameter $\alpha$.

Using the single molecule potential function in the mean field approximation, the single molecule distribution function has been obtained. The potential, $V_M$, contains the undetermined order parameters $\eta$, $\tau$ and $\sigma$. The three sets of self-consistent equations will give the expected values of $\eta$, $\tau$ and $\sigma$. In this paper we have replaced the symbol $\eta$ by the more commonly used $\langle P_2 \rangle$.

## 4. RESULTS AND DISCUSSIONS

The temperature dependence of refractive indices of the four compounds are shown in Figures 1–4. Table I contains our experimental density and polarizability data for both Vuks' and Neugebauer's models. Although we have calculated $\gamma_o$ and $\gamma_e$ for four different wavelengths, we have given their values corresponding to $\lambda$ = 5780 Å only, since the values at different wavelengths are quite close. Table I also

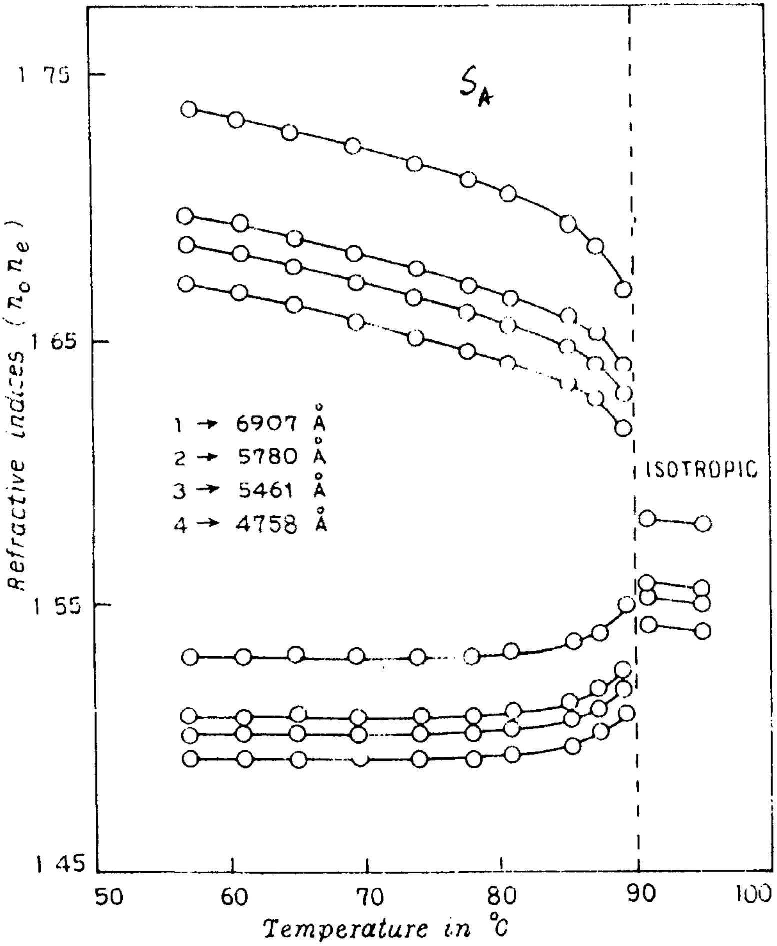


FIGURE 4 Variation of refractive indices ($n_o$, $n_e$) of 12 OCB with temperature. The sequence of the wavelength number is the same as in Figure 1.

contains the experimental $\langle P_2 \rangle$ values. We could not calculate directly the values of $\gamma_{\parallel}$ and $\gamma_{\perp}$ since solid phase data were not available and we adopted Haller's extrapolation procedure for this purpose.[21] Extrapolated $(\gamma_{\parallel} - \gamma_{\perp})$ values are taken in all calculations. It is clear from Table I that both Vuks' and Neugebauer's models give different absolute values of polarizabilities but the variation of order parameters is in reasonable agreement with both the models.

Estimation of polarizabilities of a molecule was also carried out using the additive rule of bond polarizability data.[22] Table II is given to show the experimental and calculated data of mean polarizability ($\gamma$) and molecular polarizability anisotropy $(\gamma_{\parallel} - \gamma_{\perp})$ values for the four compounds. $(\gamma_{\parallel} - \gamma_{\perp})$ was calculated for two configurations of the end chains of the molecules. The two configurations give different $(\gamma_{\parallel} - \gamma_{\perp})$ values. It is to be noted that only for the two even members of the series (10 OCB and 12 OCB) the molecular polarizability anisotropies $(\gamma_{\parallel} - \gamma_{\perp})$ obtained from the bond polarizability values (1st configuration: assuming

TABLE I

Density ($\rho$), polarizabilities ($\gamma_o$, $\gamma_e$) and order parameter ($\langle P_2 \rangle$) of the four compounds for $\lambda$ = 5780 Å

| Temp. (°C) | $\rho$ (g/cm$^3$) | Vuks' approach |  |  | Neugebauer's approach |  |  |
|---|---|---|---|---|---|---|---|
|  |  | $\gamma_o$ | $\gamma_e$ | $\langle P_2 \rangle$ | $\gamma_o$ | $\gamma_e$ | $\langle P_2 \rangle$ |
| 9 OCB |  |  |  |  |  |  |  |
| 44.0 | 1.0842 | 30.94 | 47.39 | 0.7694 | 31.90 | 45.49 | 0.7765 |
| 48.0 | 1.0822 | 31.03 | 47.22 | 0.7575 | 31.97 | 45.35 | 0.7648 |
| 52.5 | 1.0800 | 31.12 | 47.08 | 0.7463 | 32.04 | 45.23 | 0.7537 |
| 56.5 | 1.0771 | 31.23 | 46.95 | 0.7356 | 32.13 | 45.14 | 0.7432 |
| 61.5 | 1.0740 | 31.47 | 46.78 | 0.7163 | 32.35 | 45.02 | 0.7237 |
| 65.5 | 1.0697 | 31.77 | 46.61 | 0.6945 | 32.62 | 44.90 | 0.7017 |
| 70.0 | 1.0585 | 32.27 | 46.63 | 0.6715 | 33.10 | 44.97 | 0.6789 |
| 74.0 | 1.0386 | 33.19 | 46.69 | 0.6313 | 33.97 | 45.14 | 0.6384 |
| 77.0 | 1.0184 | 34.18 | 46.50 | 0.5760 | 34.88 | 45.09 | 0.5830 |
| 78.5 | 1.0095 | 34.90 | 46.19 | 0.5242 | 35.54 | 44.83 | 0.5307 |
| 79.5 | 1.0060 | 35.81 | 45.29 | 0.4432 | 36.36 | 44.20 | 0.4483 |
| 10 OCB |  |  |  |  |  |  |  |
| 48.0 | 1.0355 | 35.32 | 53.71 | 0.7129 | 36.43 | 51.48 | 0.7097 |
| 52.0 | 1.0292 | 35.56 | 53.83 | 0.7082 | 36.66 | 51.62 | 0.7053 |
| 57.0 | 1.0221 | 35.85 | 53.78 | 0.6949 | 36.93 | 51.61 | 0.6924 |
| 61.0 | 1.0169 | 36.08 | 53.62 | 0.6800 | 37.14 | 51.51 | 0.6780 |
| 66.0 | 1.0132 | 36.45 | 53.13 | 0.6463 | 37.45 | 54.12 | 0.6447 |
| 70.0 | 1.0102 | 36.80 | 52.79 | 0.6197 | 37.76 | 50.87 | 0.6182 |
| 73.5 | 1.0067 | 37.14 | 52.50 | 0.5950 | 38.06 | 50.65 | 0.5938 |
| 77.0 | 1.0023 | 37.59 | 51.83 | 0.5520 | 38.44 | 50.12 | 0.5511 |
| 81.5 | 0.9915 | 38.52 | 50.97 | 0.4826 | 39.26 | 49.48 | 0.4823 |
| 83.5 | 0.9836 | 39.51 | 49.90 | 0.4024 | 40.13 | 48.66 | 0.4024 |
| 11 OCB |  |  |  |  |  |  |  |
| 61.5 | 1.1040 | 30.85 | 48.90 | 0.8130 | 31.84 | 46.93 | 0.8384 |
| 63.0 | 1.0927 | 32.20 | 49.08 | 0.8050 | 32.18 | 47.13 | 0.8305 |
| 70.5 | 1.0920 | 31.26 | 48.73 | 0.7870 | 32.21 | 46.83 | 0.8124 |
| 75.5 | 1.0845 | 31.52 | 48.58 | 0.7684 | 32.44 | 46.73 | 0.7937 |
| 80.0 | 1.0782 | 31.75 | 48.32 | 0.7461 | 32.65 | 46.53 | 0.7712 |
| 84.5 | 1.0720 | 32.21 | 47.85 | 0.7042 | 33.06 | 46.16 | 0.7281 |
| 87.0 | 1.0690 | 32.78 | 46.63 | 0.6237 | 33.52 | 45.14 | 0.6454 |
| 12 OCB |  |  |  |  |  |  |  |
| 57.0 | 1.0177 | 39.95 | 58.53 | 0.7371 | 41.09 | 56.25 | 0.7359 |
| 61.0 | 1.0165 | 40.03 | 58.25 | 0.7230 | 41.15 | 56.02 | 0.7220 |
| 65.0 | 1.0088 | 40.39 | 58.24 | 0.7080 | 41.48 | 56.06 | 0.7077 |
| 69.5 | 1.0043 | 40.63 | 57.99 | 0.6890 | 41.69 | 55.88 | 0.6891 |
| 74.0 | 0.9991 | 40.91 | 57.63 | 0.6632 | 41.92 | 55.60 | 0.6640 |
| 78.0 | 0.9943 | 41.16 | 57.43 | 0.6456 | 42.14 | 55.47 | 0.6468 |
| 81.0 | 0.9906 | 41.45 | 57.15 | 0.6228 | 42.40 | 55.26 | 0.6242 |
| 85.5 | 0.9853 | 42.07 | 56.65 | 0.5783 | 42.95 | 54.89 | 0.5797 |
| 87.5 | 0.9825 | 42.60 | 55.99 | 0.5313 | 43.40 | 54.37 | 0.5326 |
| 89.5 | 0.9765 | 43.50 | 55.07 | 0.4591 | 44.20 | 53.68 | 0.4605 |

$\gamma_o$ and $\gamma_e$ are in $10^{-24}$ cm$^3$ units.

the whole molecule to be planar) are very close to the values obtained from Vuks' formulae. On the other hand, for the two odd members (9 OCB and 11 OCB) the ($\gamma_{\parallel} - \gamma_{\perp}$) values calculated from additive rule of bond polarizabilities (2nd configuration: assuming the chain part to be planar but perpendicular to the planar rigid cyanobiphenyls of the molecules) are quite close to the Vuks' model. But for

TABLE II

Mean polarizability ($\gamma$) and molecular polarizability anisotropy ($\gamma_\parallel - \gamma_\perp$) of the four compounds

| | $\gamma \times 10^{24}$ cm$^3$ | | $(\gamma_\parallel - \gamma_\perp) \times 10^{24}$ cm$^3$ | | | |
|---|---|---|---|---|---|---|
| | | | Calculated from bond polarizability | | Haller's process | |
| Compounds | Calculated from bond polarizabilities | Vuks' or Neugebauer's approach (Iso. liq.) | (a) | (b) | Vuks' formula | Neugebauer's formula |
| I | 46.46 | 38.40 | 25.19 | 22.94 | 21.38 | 17.50 |
| II | 48.57 | 42.80 | 25.69 | 23.57 | 25.80 | 21.12 |
| III | 50.69 | 37.40 | 25.93 | 23.31 | 22.20 | 18.00 |
| IV | 52.80 | 47.60 | 26.47 | 23.96 | 25.20 | 20.60 |

(a) Calculated considering the whole molecule to be planar.

(b) Calculated assuming the chain part is planar but perpendicular to the planar rigid part (cyanobiphenyl) of the molecule.

Neugebauer's relations these values are significantly lower for all the compounds. It may be due to unjustifiable Haller's extrapolation procedure. Besides the additive rule of the bond polarizabilities is not free from limitations. This may explain the differences between experimental and calculated mean polarizability values.

In Figure 5 we have plotted the variation of our experimental $\langle P_2 \rangle$ values with reduced temperature $T^*$. Here $T^* = T/T_{NI}$ for 9 OCB and $T^* = T/T_{SI}$ for the other three compounds, $T_{NI}$ and $T_{SI}$ being nematic-isotropic and smectic A-isotropic transition temperatures respectively. The continuous curves are those obtained from McMillan theory for smectic A phase, which are best fitted by our experimental data. This was done by changing $\delta$ and $\alpha$ and calculating $\langle P_2 \rangle$ using the self-consistent relations. The four compounds show an odd-even effect in their $\langle P_2 \rangle$ values (see Table I). As the chain length increases the value of $\alpha$ should also increase, which is borne out in our calculations if we consider odd and even members separately. In this particular case we have to take two values of $\delta$, being equal to 0.5 for odd members and 0.9 for even members of the series for the best fit with our experimental $\langle P_2 \rangle$ values. This has happened due to odd-even effect in order parameters among the compounds. Table III shows the $\delta$ and $\alpha$ values required to calculate order parameters for the four compounds from McMillan theory. We have also studied another even member of this series (8 OCB) sometime ago.[23] So we have included the $\delta$ and $\alpha$ values for 8 OCB in Table III. The calculated reduced transition temperatures $T^*_{SN} (= k\, T_{SN}/v)$, $T^*_{NI} (= k\, T_{NI}/v)$ and $T^*_{SI} (= k\, T_{SI}/v)$ values have also been given in Table III; where $k$ is the Boltzmann constant; $T_{SN}$, $T_{NI}$ and $T_{SI}$ are the smectic A-nematic, nematic-isotropic and smectic A-isotropic transition temperatures respectively. Although we have calculated the translational and mixed order parameters for the compounds we do not produce these data here because we do not have experimental data to compare with these values. Except for 11 OCB, all our experimental values are very well reproduced from McMillan theory (Figure 5). We are unable to explain the discrepancy in the case of 11 OCB. In our laboratory we have also obtained $\langle P_2 \rangle$ values of these compounds from X-ray diffraction studies which will be reported subsequently.[24]

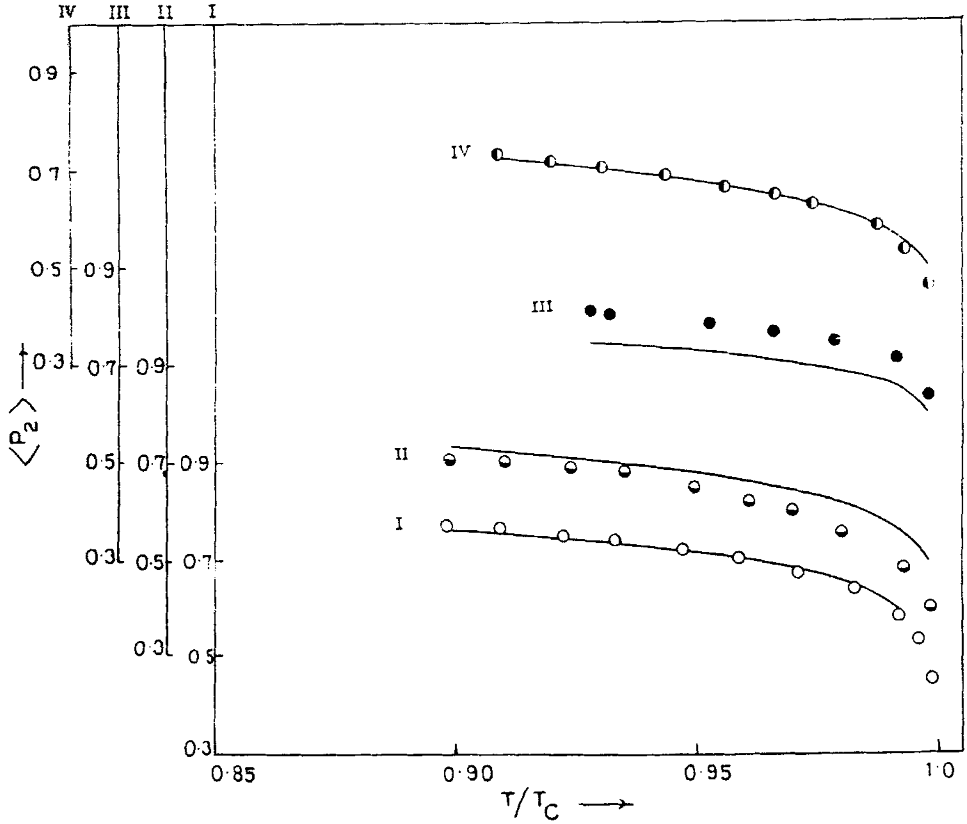


FIGURE 5 Plot of orientational order parameter $\langle P_2 \rangle$ with reduced temperature. Continuous curves correspond to McMillan theory with; $\delta = 0.5$ and $\alpha = 0.530$ for 9 OCB, (I); $\delta = 0.9$ and $\alpha = 0.385$ for 10 OCB, (II); $\delta = 0.5$ and $\alpha = 0.580$ for 11 OCB, (III) and $\delta = 0.9$ and $\alpha = 0.430$ for 12 OCB (IV).

TABLE III

$\delta$, $\alpha$ and different reduced temperature values for best fit with McMillan theory ($T^* = k\ T/V$)

| Compounds | Values of | | | | |
|---|---|---|---|---|---|
| | $\delta$ | $\alpha$ | $T^*_{SI}$ | $T^*_{SN}$ | $T^*_{NI}$ |
| 8 OCB | 0.9 | 0.350 | — | 0.2134 | 0.22019 |
| 9 OCB | 0.5 | 0.530 | — | 0.2186 | 0.22019 |
| 10 OCB | 0.9 | 0.385 | 0.2230 | — | — |
| 11 OCB | 0.5 | 0.580 | 0.2270 | — | — |
| 12 OCB | 0.9 | 0.430 | 0.2318 | — | — |

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