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Orientational Order Parameter in Alkoxy Benzoic Acids—Optical Studies

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Alkoxy benzoic acids are well-known liquid-crystalline compounds with nematic phase of long thermal ranges. The refractive indices measurements are carried out using a wedge-shaped cell with the help of a modified spectrometer. The birefringence ($\delta n = n_e - n_o$) is obtained directly by using the method developed by Kuczynski et al. *[10] in all the available compounds (alkoxy chain number $n = 3$ to 12 and 16). The higher homologues exhibit the smectic-C phase along the nematic phase. The molecular polarizabilities are calculated from the refractive indices and the density using the well-known internal field models. The molecular anisotropy is estimated from the Lippincott δ-function model and molecular vibration method. The order parameter, S, is estimated (a) using molecular polarizabilities and the molecular anisotropy for both the models, (b) from Haller's extrapolation using molecular polarizabilities, and (c) directly from the birefringence, a method developed by Kuczynski* et al. *[10] along with the nematic phase. Further, the order parameter from δn, without the consideration of any internal field model, to the nematic molecule is compared with S obtained from density due to Maier* et al. *[23]. The results are compared with one another and the advantages and disadvantages are discussed.*

Keywords Benzoic acids; birefringence; order parameter

Introduction

Alkoxy benzoic acids are well-known liquid crystals and are extensively studied in H-bonding [1,2]. These compounds exhibit a single variant nematic phase (the lower homologues with $n = 3$ to 6) and bivariant nematic and smectic-C phases (the higher homologues with $n = 7$ to 12 and 16) [3]. Further, these compounds exhibit long thermal ranges of nematic and smectic-C phases suitable for birefringence studies.

The orientational ordering makes the nematic phase of liquid crystals behave like a uniaxial crystal [4–6]. For a uniaxial system, the optical anisotropy has the form $\delta n = n_e - n_o$ (i.e., the difference between the extraordinary and ordinary refractive indices). A quantitative description of the ordering in the case when

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elongated nematic molecules behave like rigid rods can be done using the scalar order parameter, S, introduced by Tsvetkov [6].

$$S = \frac{1}{2} <3\cos^2\theta - 1>$$

where θ is the angle between the long molecular axis of the molecule and the optic axis, and the brackets denote averaging over all directions of the long molecular axes in a small, uniformly aligned macroscopic volume.

Recently, the authors have carried out systematic studies on a number of compounds with varying lengths of end aliphatic chains using two different techniques, viz. the wedge method to measure the refractive indices and Newton's rings technique to directly, measure the birefringence, $\delta n = n_e - n_o$ [7]. This article presents refractive indices and birefringence results on alkoxy benzoic acids homologous series to study the variation of order parameter, S, with temperature in the nematic phase.

Experimental

The refractive indices of the liquid crystal were measured with a wedge-shaped glass cell, similar to the one used by Haller *et al.* [8] with a modified spectrometer. In this a wedge-shaped glass cell was formed with two optically flat rectangular glass plates (50 mm × 25 mm) sandwiched with a glass plate (0.4 mm), which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge to get the alignment of the LC molecule. The cell is filled with the LC material. The LC in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block was ±0.10°C. The accuracy in the measured refractive indices was ±0.0005.

The other technique is the optical rings (known as Newton's ring) method, which directly gives the birefringence, $\delta n = n_e - n_o$, whose particulars are given elsewhere [9–11]. The p-n-alkoxy benzoic (99.9% purity; $n = 3$ to 12 and 16) were supplied by Frinton Laboratories, New Jersey, USA, and the compounds were used without further purification. The lower homologues $n = 3$ to 6 exhibit only the nematic phase, whereas the higher homologues with $n = 7$ to 12 and 16 show nematic

Table 1. Transition temperatures across different phases

Compound	I-N Transition temp. (°C)	N-C Transition temp. (°C)
3ObA	155.8 (154.9)	—
4ObA	160.0 (160.1)	—
5ObA	150.0 (151.4)	—
6ObA	154.0 (153.8)	—
7ObA	147.4 (146.8)	102.2 (98.3)[a]
8ObA	146.6 (147.5)	93.6 (97.8)
9ObA	144.9 (142.9)	117.5 (117.1)
10ObA	137.0 (138.3)	115.6 (115.6)
11ObA	140.7	119.8
12ObA	137.2 (137.2)	120.3 (128.9)
16ObA	150.3	120.3

[a]Taken from Swati *et al.* [3].

and smectic-C phases. The transition temperatures observed in the refractive index experiment are in good agreement with those supplied by the company. The transition temperatures are given in Table 1.

Results and Discussion

Order Parameter From Refractive Indices and Molecular Polarizabilities

The refractive indices of all the compounds were measured using a modified spectrometer attached with small angled prism that houses the LC sample. The cell was placed in a heating block for the measurement of refractive indices with temperature. The refractive index showed a slight change in the isotropic phase (n_{iso}) as expected. At the IN phase transformation, the isotropic value split into two, one higher and the other lower than isotropic value corresponding to extraordinary (n_e) and ordinary (n_o) refractive indices, respectively. This separation was clearly observed through the telescope of the modified spectrometer at the position of the angle of minimum deviation. In the nematic region, the n_e increased, whereas the n_o decreased with the decrease of temperature and both attained saturation in the deep nematic region in all the compounds except in the compound with chain length 12. The variation of refractive indices with temperature in the isotropic and nematic phases is illustrated for the compounds with $n = 3$, 9, and 16 in Figs. 1 to 3. The change in $\delta n = (n_e - n_o)$ value from compound to compound exhibits an odd–even effect and this is illustrated in Fig. 4.

The birefringence, $\delta n = n_e - n_o$, from the second method is obtained by the measurement of the ring radius.

Estimation of δn from the Optical Ring Diameter

The LC sample whose $\delta n = n_e - n_o$ was to be measured was placed between the lens and plate. A system of concentric rings was observed.

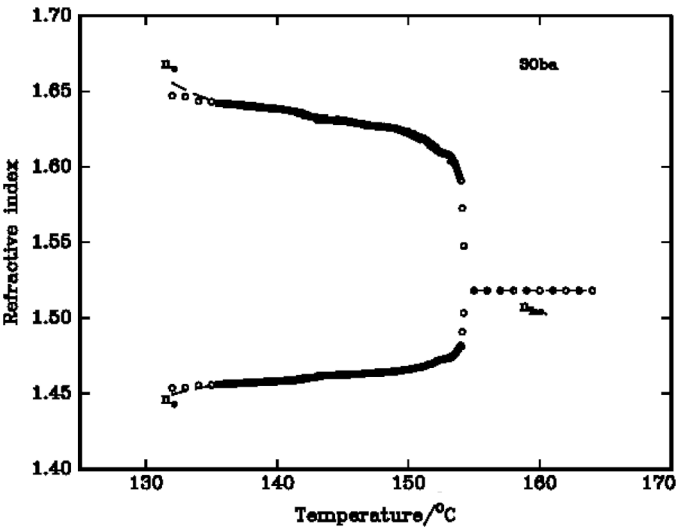

Figure 1. Variation of refractive indices with temperature in 3Oba.

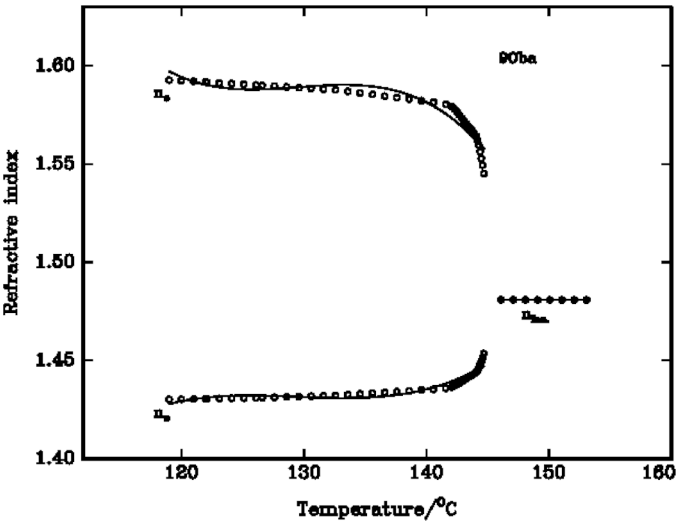

Figure 2. Variation of refractive indices with temperature in 9Oba.

The optical path difference between o-ray and e-ray is given by y. δn that corresponds to the bright ring is $k\lambda$ (y denotes the sample thickness in the middle of the ring, λ is the wavelength of the light, and k is the successive ring number). The thickness y can be calculated from

$$y = x^2/2R.$$

From the above,

$$\delta n = (2R\lambda)k/x^2$$

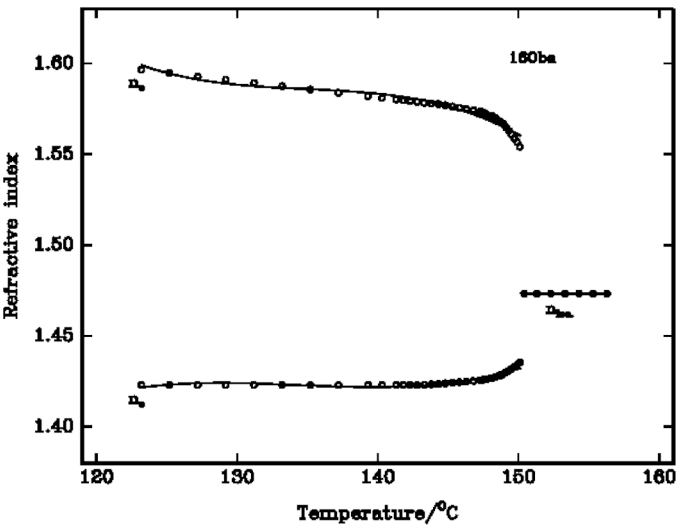

Figure 3. Variation of refractive indices with temperature in 16Oba.

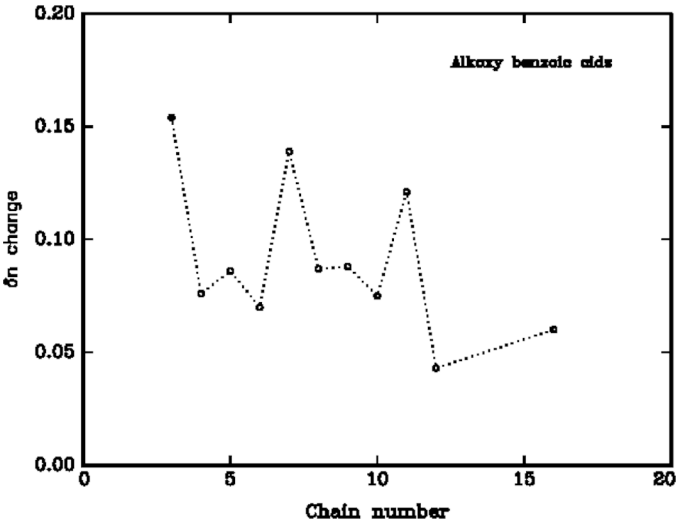

Figure 4. Change of δn with the chain number.

Since $2R\lambda = C$, the cell constant (c) for a given wavelength of light is

$$\delta n = Ck/x^2$$

where x is the radius of the ring and R is the radius of curvature of the lens used.

$\delta n = n_e - n_o$ can be measured with great accuracy by taking the slope of the straight line drawn between x^2 and the ring number, k, and the same is the case with the dark rings. As the temperature decreases, δn increases.

Figure 5 shows the square of the ring radius versus the ring number in the compound 9Oba as a representative case at different temperatures. The data evaluated

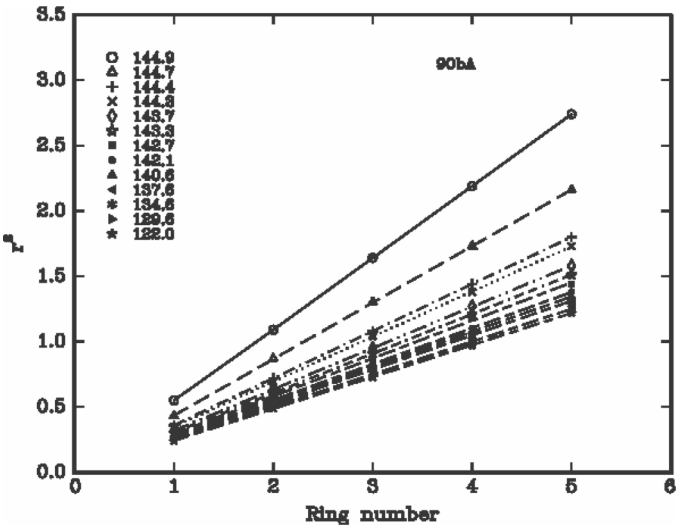

Figure 5. Square of the ring radius versus the ring number in compound 9Oba.

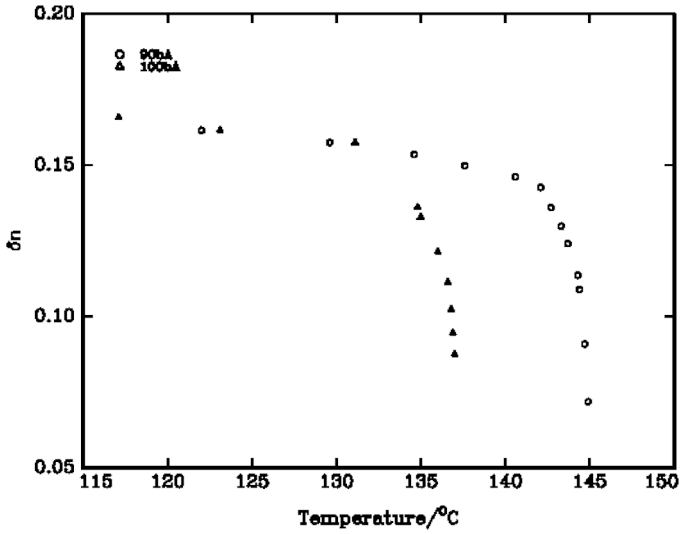

Figure 6. Variation of δn with temperature in 9ObA and 10ObA.

from this method reveal that agreement between the δn values obtained from this method and those estimated from $\delta n = (n_e - n_o)$ within experimental error. Figure 6 depicts the variation of δn with temperature in compounds 9Oba and 10Oba.

Molecular Polarizability Anisotropy and Mean Polarizability

The modified Lippincott δ-function model and the molecular vibration methods were used for the evaluation of the above parameters in the case of all compounds. Detailed descriptions of the methods are given in the literature [12–14]. In estimating the molecular anisotropy, the equations given in the above references and the procedure followed by Rama Murthy *et al.* [15] were adopted. The molecular polarizability anisotropy and the mean polarizability values calculated using the two methods for all compounds are presented in Table 2.

Estimation of Order Parameter

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium, and the orientational order parameter S are determined from the birefringence of the LCs. For the calculation of the polarizabilities of the molecules and S from birefringence $(n_e - n_o)$, the Lorenz-Lorentz formula cannot be applied because its validity is restricted to the cases where there is spherical (or cubic) symmetry in connection with the molecular arrangement. According to Vuks's formula [16], the ratio of the average local electric field to the applied field is the same, when the applied field is either parallel or perpendicular to the optic axis of the medium. However, Neugebauer [17,18] has considered in detail the form of the polarization field in anisotropic media. As a result of the anisotropic distribution of the molecules, the average local field is of the form $E + YP$, where E is the applied field, P is the polarization, and Y is a factor that is different from the directions parallel and perpendicular to the optic axis in a medium. The molecular polarizabilities are evaluated from the refractive indices and density data using the equations from both the methods.

Table 2. Values of $(\alpha_{\|} - \alpha_{\perp}) \times 10^{-24}\,\mathrm{cm}^3$ used for the evaluation of order parameter S by different methods and from log-log plots extrapolated to absolute zero for Haller and Scaling factors

Compound	Lippincott $(\alpha_{\|} - \alpha_{\perp})$	Molecular vibration $(\alpha_{\|} - \alpha_{\perp})$	Haller $(\alpha_{\|} - \alpha_{\perp})$		Scaling factors	
			Vuks	Neug.	*Sc* Vuks	*fB* Neug.
3ObA	13.02	14.78	13.81	13.90	1.535	1.625
4ObA	14.58	15.05	14.90	15.00	1.535	1.525
5ObA	16.17	16.25	16.60	16.65	1.540	1.540
6ObA	17.59	17.46	17.60	18.00	1.500	1.512
7ObA	19.26	18.66	18.90	19.20	1.467	1.452
8ObA	20.82	19.86	20.77	20.48	1.431	1.410
9ObA	22.37	21.07	19.11	23.49	1.440	1.439
10ObA	23.92	22.27	22.47	23.98	1.414	1.399
11ObA	25.47	23.47	25.67	25.99	1.421	1.420
12ObA	27.04	24.67	26.06	26.74	1.423	1.421
16ObA	33.12	29.49	30.10	33.33	1.322	1.379

The data is taken from experimental values of refractive indices (present work) and density data [24].

In the present study the order parameter S was evaluated using both models from the estimation of molecular polarizabilities α_e and α_o. The S value is given as

$$S = (\alpha_e - \alpha_o)/(\alpha_{\|} - \alpha_1) \tag{1}$$

where $(\alpha_{\|} - \alpha_{\perp})$ is the molecular anisotropy obtained in different ways. In the present work, it is evaluated from the Lippincott δ-function method (described above) and the scaling procedure due to Haller *et al.* [8] and Murthy and Murthy [19], where $(\alpha_{\|} - \alpha_{\perp})$ to evaluate S are obtained with the assumption that if an LC could be cooled to absolute zero without undergoing any phase transitions, where S would become equal to unity.

For the evaluation of S from Vuks [16] and Neugebauer [17], the following equations are employed. In the Vuks model S is given by [21]

$$S = \left[\frac{\alpha}{\alpha_{\|} - \alpha_{\perp}}\right]\left[\frac{n_e^2 - n_o^2}{n - 1}\right] \tag{2}$$

where

$$n = \left[\frac{n_e^2 + 2n_o^2}{3}\right]$$

and α is the mean polarizability, and $\alpha_{\|}$ and $\alpha_{\perp}$ are the principal polarizabilities. Using this scaling factor, S can be calculated from Eq. (2).

In the Neugebauer method [17,18], S is given by

$$S = \left[\frac{\alpha}{\alpha_{\|} - \alpha_{\perp}}\right] f(B) \tag{3}$$

where

$$f(B) = \left(\frac{9}{4AB}\right)\left[\left(B^2 - \left(\frac{10}{3}\right)B + 1\right)^{1/2} + \frac{B}{3} - 1\right]$$

and

$$B = \frac{n^2 - 1}{n^2 + 1}\left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_o^2 + 2}{n_o^2 - 1}\right)$$

The scaling factors for the determination of order parameter were obtained in both the cases by plotting log-log plots between $\left[\frac{n_e^2 - n_o^2}{n-1}\right]$ and $f(B)$ in Vuks's [16] and Neugebauer's [17,18], methods, respectively, against $(1 - T/T_C)$, that is, the reduced temperature. The scaling factors due to Vuks and Neugebauer derived using the above equations and extrapolation technique are given in Table 1.

Using the two models, the molecular polarizabilities and the polarizability anisotropy ($\alpha_e - \alpha_o$) of all the liquid crystals were calculated at different temperatures and the values are presented in the case of 7Oba in Table 3. Not all temperatures are selected in the table. However, in the estimation of molecular polarizabilities or the order parameter, all the experimental values are considered.

Table 3. Molecular polarizabilities and polarizability anisotropy ($\alpha_e - \alpha_o$) in 7ObA

	Vuks			Neugebauer		
Temp.	α_e	α_o	$\alpha_e - \alpha_o$	α_e	α_o	$\alpha_e - \alpha_o$
147.4	31.890	27.763	4.127	31.123	28.078	3.046
147.3	32.241	27.566	4.675	31.643	27.818	3.825
147.2	32.520	27.406	5.113	32.037	27.621	4.416
147.0	32.748	27.270	5.478	32.379	27.450	4.929
146.8	32.981	27.138	5.843	32.663	27.308	5.356
145.0	34.091	26.544	7.546	33.736	26.771	6.965
143.4	34.568	26.315	8.252	34.053	26.613	7.440
143.2	34.627	26.287	8.340	34.093	26.593	7.500
143.0	34.687	26.258	8.428	34.133	26.573	7.560
142.8	34.746	26.230	8.516	34.173	26.553	7.620
141.8	35.044	26.088	8.957	34.374	26.452	7.921
138.2	36.076	25.717	10.359	34.539	26.370	8.169
129.4	36.771	25.248	11.523	35.642	25.818	9.824
125.4	36.875	25.085	11.789	36.162	25.558	10.603
123.4	36.926	25.004	11.921	36.409	25.435	10.975
116.4	37.104	24.724	12.380	37.223	25.028	12.195
115.4	37.130	24.684	12.445	37.334	24.972	12.361
110.4	37.256	24.487	12.769	37.868	24.705	13.162
109.4	37.281	24.448	12.833	37.971	24.654	13.318
104.4	37.406	24.253	13.153	38.473	24.403	14.071
103.4	37.431	24.214	13.217	38.571	24.354	14.217

This data is taken from experimental values of refractive indices (present work) and density data [24].

Order Parameter from Birefringence Studies

It is well known that any physical properties of a nematic liquid crystal and the orientational order parameter S are closely connected to one another. Further, de Gennes [4] pointed out that the anisotropy of any physical quantity can be a measure of orientational order. In the case of uniaxial liquid crystal, this parameter can be defined as

$$Q = \frac{\delta A}{\Delta A} \tag{4}$$

where δA is the anisotropy of any arbitrary physical quantity A, and ΔA is the hypothetical anisotropy of A in the case of perfect order. Among many anisotropic physical quantities that could be used for the determination of the order parameter Q, the dielectric anisotropy for optical frequencies $\delta\varepsilon + n_e^2 - n_o^2$ is useful. Thus, $\delta\varepsilon$ can be used [4] for the determination of S if a particular local field is applied for the liquid-crystal molecule. Further, de Jeu [22] showed that birefringence δn can be used for this purpose. Based on this, Zywncki and Kuczynski [9] and Kuczynski *et al.* [10] proposed a simple procedure for the determination of order parameter S from the birefringence δn without considering the local field experienced by the molecule in a liquid-crystal phase. The birefringence δn, which is a function of temperature, is fitted to the following equation:

$$\delta n = \Delta n \cdot \left(1 - \frac{T}{(T^*)}\right)^{\beta} \tag{5}$$

where T is the temperature and T^* and β are constants. (T^* is about 0.1–4°C higher than the clearing temperature ($T_{\text{I-N}}$) and the exponent β is close to 0.20). This procedure enables one to extrapolate δn to the absolute zero temperature. In practice, the three adjustable parameters T^*, Δn, and β were obtained by fitting the experimental data for δn to the following equation written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta \cdot \log\left(\frac{T^* - T}{T^*}\right) \tag{6}$$

In the present investigations, the values of $\log \Delta n$ and β were calculated by the linear regression method. The parameter $T^* = (T_{\text{IN}} + X)$, where X is varied from 0.1 to 4°C to obtain the best correlation coefficient of the linear regression. Thus, S is given by

$$S = \frac{\delta n}{\Delta n} \tag{7}$$

The linear fits for the compounds propyl and hexadecyl benzoic acids are presented in Figs. 7 and 8, respectively. For the rest of the compounds, the Δn values, birefringence in perfect order, along with X values are given in Table 4.

Order Parameter, S

The order parameter, S, estimated from two models using different methods are compared with S calculated from Δn, the birefringence in perfect order. The reason

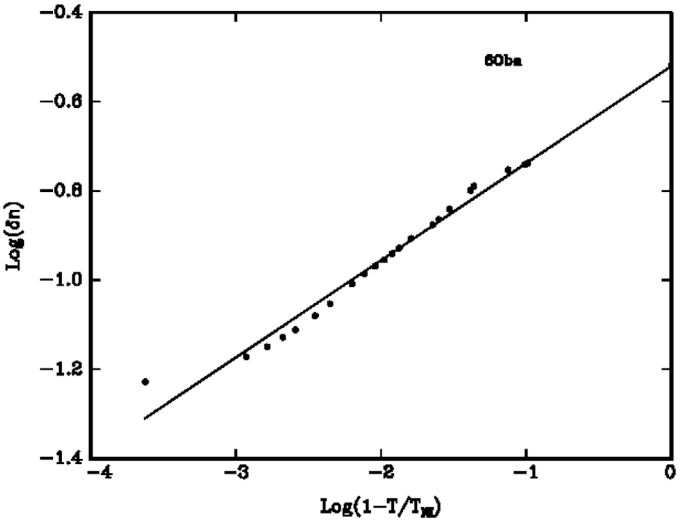

Figure 7. The log-log plot of δn versus reduced temperature for compound 6Oba.

for this is that in the latter case no internal field is considered. For the sake of clarity, for each compound two figures are drawn; one belongs to Vuks's model [16] along with S obtained from birefringence and the other is due to Neugebauer's model [17,18]. The data are presented in Figs. 9 and 10 for compounds 8Oba and 10Oba as representative cases.

The abbreviations used in the graphs are $\Delta n - S$ from Δn, sVukslip $- S$ from the Vuks-Lippincott method sVUksvib $- S$ from Vuks's vibration method, sVukshal $- S$ from the Vuks-Haller method, and sVukssc $- S$ from Vuks's scaling factor. In the case of Neugebauer model [17,18] the abbreviations used in the figures are: $\Delta n - S$ from Δn, sNeugip $- S$ from the Neug-Lippincott method, sNeugvib $- S$ from Neug

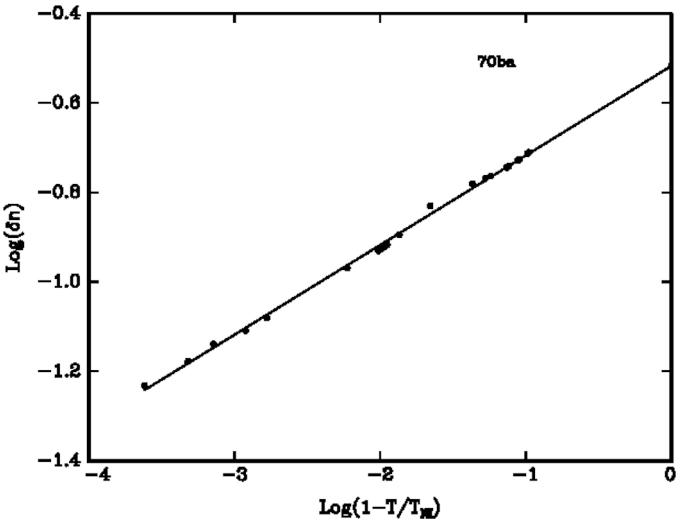

Figure 8. The log-log plot of δn versus reduced temperature for compound 7Oba.

Table 4. Parameters for the best fit through linear regression for the equation $\log \delta n = \log \Delta n + \beta \cdot \log\left(\frac{T^* - T}{T^*}\right)$

Compound	X	β	Log(Δn)	Δn	R
3ObA	0.001	0.185	−0.539	0.290	0.9758
4ObA	0.400	0.202	−0.448	0.357	0.9965
5ObA	0.050	0.160	−0.525	0.298	0.9938
6ObA	0.700	0.238	−0.485	0.330	0.9995
7ObA	0.100	0.202	−0.508	0.310	0.9986
8ObA	0.800	0.209	−0.563	0.273	0.9967
9ObA	0.050	0.133	−0.587	0.260	0.9856
10ObA	0.300	0.150	−0.556	0.278	0.9890
11ObA	1.000	0.199	−0.509	0.310	0.9954
12Oba	0.500	0.140	−0.537	0.250	0.9927
16ObA	4.000	0.170	−0.551	0.280	0.9744

vibration method, sNeughal $- S$ from the Neug-Haller method, and sNeugfB $- S$ from NeugfB parameter.

Before comparing the variation of S with temperature for two models with the S value from birefringence, it is worthwhile to mention the error involved in the determination of S from Δn. Here, in the linear regression analysis, a best fit has to be arrived at in between three different parameters involved in Eq. (6), viz. β, T^*, and R. The values suggested by Kuczynski *et al.* [10] are $\beta \sim 0.200$, $T^* = (T_{IN} + X)$, where X is adjusted to 0.01 to 4°C above the clearing temperature and $R \geq 0.99$. Except in a few compounds, the best fits were obtained for the above values (Table 3). However, Kuczynski *et al.* [10] stated that the error occurring in the S value estimated from molecular polarizabilities is around 20%. In the present study the results differ with this observation because in some compounds the S value calculated from polarizability data is in agreement with the value of S from birefringence.

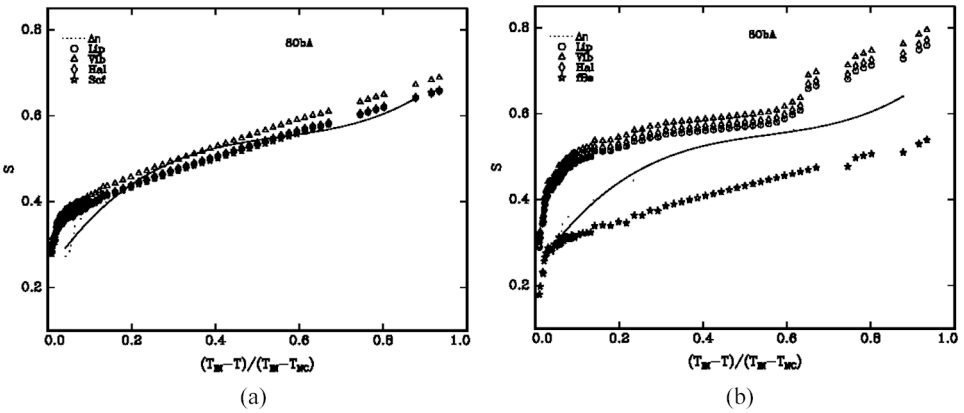

Figure 9. (a) Order parameter S versus the normalized nematic range for compound 8ObA (Vuks's model [16]); (b) Order parameter S versus the normalized nematic range for compound 8ObA (Neugebauer's model [17,18]).

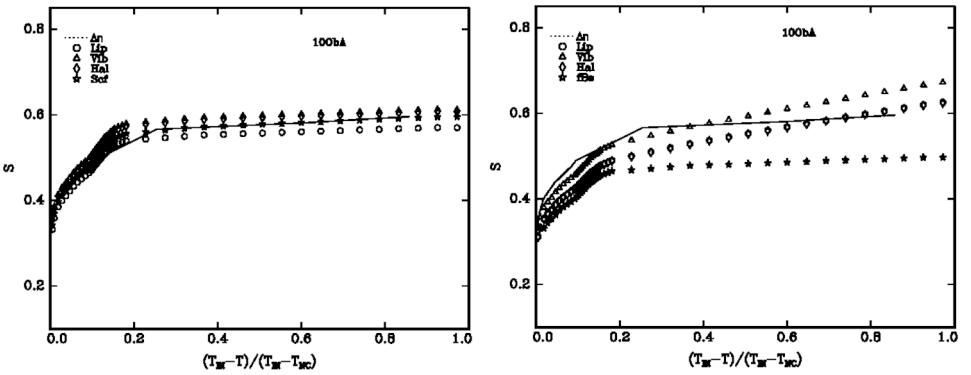

Figure 10. (a) Order parameter S versus the normalized nematic range for compound 10ObA (Vuks's model [16]); (b) Order parameter S versus the normalized nematic range for compound 10ObA (Neugebauer's model [17,18]).

For the sake of comparison of S from different methods for the two field models, with S from Δn, the percentage deviation of the S value from all methods to that calculated from Δn is presented in Table 5. The error in the value of S from Δn is about 10%. If the deviation is $\leq$10%, the values are shown in bold so that they can be considered in agreement with S from Δn within the experimental error.

From the results, the salient features are as follows:

- The S value obtained from Lippincott δ-function from Vuks's model agrees for the compounds with $n = 7$, 8, 9, 10, and 16, and the lower homologues

Table 5. Percentage of deviations of order parameter S estimated assuming the two field models and using different methods from that obtained using Δn, the birefringence in perfect order in alkoxy benzoic acids

	Vuks				Neugebauer			
Compound	Lip	Vib	Hal	**Sc**	Lip	Vib	Hal	**fB**
3ObA	+16.3	**+2.4**	**+9.5**	**+4.7**	**+6.1**	**−6.3**	**−0.6**	**−6.3**
4ObA	+41.0	+32.5	+33.1	+30.4	+45.0	+40.8	+41.0	**−7.6**
5ObA	+11.6	+11.5	**+9.0**	**+9.6**	+11.8	+11.7	**+9.6**	**−8.8**
6ObA	+22.2	+23.2	+22.2	+17.9	+26.9	+27.8	+26.9	**+0.6**
7ObA	**+9.2**	+12.8	+14.7	**+6.7**	**+4.8**	**+8.1**	**+5.0**	−12.0
8ObA	**0.0**	**+5.2**	**+0.6**	**+0.6**	+14.0	+19.4	+15.6	−20.0
9ObA	**−7.0**	**−1.5**	**+8.4**	**−4.4**	**+5.4**	+12.0	**+0.3**	−19.6
10ObA	**−5.3**	**+1.6**	**+0.6**	**−1.5**	**+1.0**	**+8.3**	**+0.6**	−17.8
11ObA	−10.8	**−3.2**	−11.5	**−7.8**	**−4.8**	**+3.3**	**−5.5**	−22.9
12ObA	−15.5	**−7.4**	−12.0	−12.0	**−8.1**	**+0.9**	**−7.2**	−26.0
16ObA	**−8.3**	**+3.4**	**+1.0**	**−7.4**	**−2.0**	**+10.0**	**−2.4**	−18.8

The data is taken from experimental values of refractive indices (present work) and density data [24].

show higher values; that is, $n = 3$ to 6. However, in Neugebauer's model [17,18], the agreement is in the case of $n = 3$, 7, 9, 10 to 16.

- The above statement holds good for S obtained from the molecular vibration method except in one or two compounds in both field models.
- S calculated from the Haller extrapolation method of Vuks's model [16] agrees in the compounds with $n = 3$, 5, 8 to 10, and 16, and the agreement is with $n = 3$, 5, 7, 9 to 12, and 16 in the case of Neugebauer's model [17,18].
- S value estimated using the Vuks's [16] scaling factor agrees with most of the compounds except with $n = 4$, 6, and 12.
- S calculated using the fB parameter from Neugebauer shows lower values than that of S from Δn in all compounds but agrees within the limits for compounds with $n = 3$ to 6. However, in the higher homologues the difference in the S values is quite large (-12 to 26%). The percentage of deviations are estimated compared to the S value obtained from Δn to those calculated from different methods.

From these observations, it may be concluded that there is a broad agreement of S from Δn with S from other methods in the case of higher homologues than with lower ones.

In order to obtain a better conclusion, the S from Δn was compared with the S obtained from the following equation due to Maier and Saupe [23].

$$S = \left\{1 - 0.98(T/T_{\mathrm{IN}})(V_n/V_{n(\mathrm{IN})})^2\right\}^{0.22}$$

where T and T_{IN} are the temperature and the isotropic nematic transition temperature, respectively, and V_n and $V_{n(\mathrm{IN})}$ are the molar volumes at a temperature T and at IN transition. The S values estimated from the density data [24] using the above equation are plotted along with the S data from Δn in Fig. 11 for compounds 5Oba and 12Oba as a representative case. The results reveal that the S values from the two methods are in agreement for the compounds with $n = 3$, 8, 9, 10, 11, 12, and 16, whereas there is disagreement in the case of compounds with $n = 4$ and 6. The disagreement in compound with $n = 7$ is more just below the transition and decreases to about 7% deep in the nematic region.

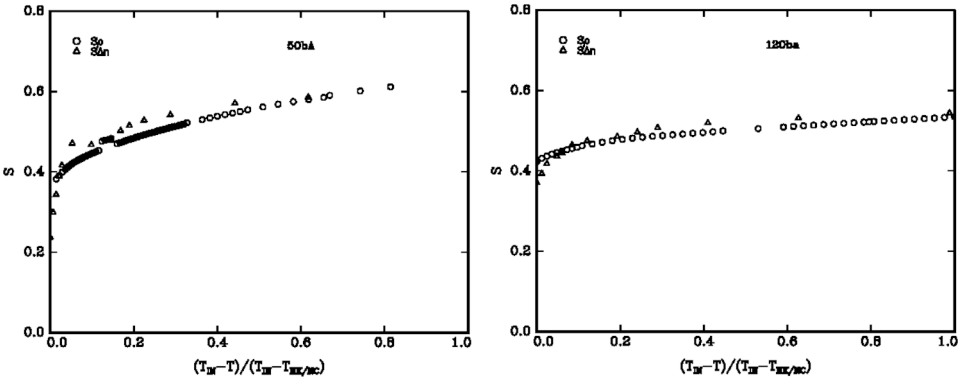

Figure 11. (a) Variation of S in 5ObA; (b) Variation of S in 12ObA.

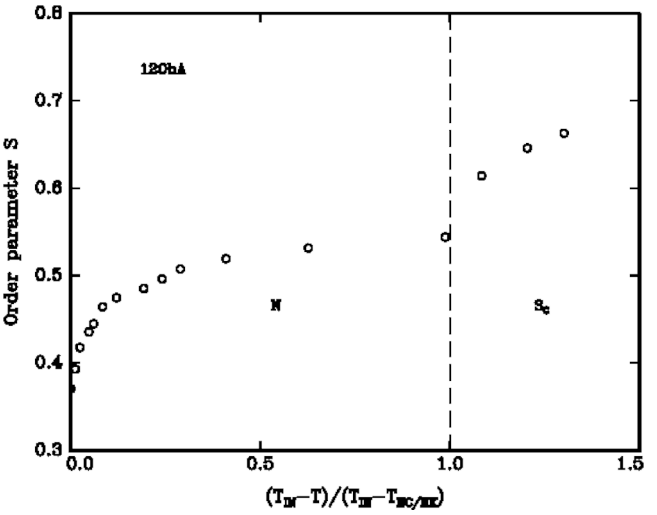

Figure 12. Order parameter variations with normalized nematic and smectic range in 12ObA.

The agreement between S values estimated from two independent methods (without considering any internal field to the molecule) was found to be good within the experimental error. Hence, it can be concluded that the S values obtained from birefringence can be considered as reference in comparing with the S values obtained from the two field models using different methods.

Figure 12 represents the variation of S with temperature for compound 12Oba, calculated from δn where the authors were able to get the Newton rings even in the case of the smectic-C phase (which is not possible in other compounds even though they exhibit the smectic-C phase). This may be due to the short range of the nematic phase in the case of 12Oba where S has not saturated in nematic phase. The jump in the order parameter S can be seen at the nematic–smectic-Cs interface.

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