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Refractive Indices and Orientational Order Parameter of Five Liquid Crystals in Nematic Phase

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Refractive indices of bis-(4′-*n*-alkyloxy benzal)-2-chloro-1,4 phenylene diamine (alkyl = hexyl, octyl and decyl), RO-TN-101 and RO-CE-154 have been measured over the whole nematic ranges for different wave lengths. A prism method has been employed for these measurements. The samples were aligned by surface rubbing and by the application of magnetic field. For all the samples, the refractive index for the extra-ordinary ray (n_e) decreases and that for the ordinary ray (n_0) increases with increasing temperature. At the nematic isotropic transition there is a discontinuity in the refractive indices values. The principal molecular polarizabilities (α_e and α_0) for the samples have been calculated using Neugebauer's relation. The necessary density measurements have been made by us. The anisotropy of the molecular polarizabilities was calculated using Haller's extrapolation method. The orientational order parameters were calculated at different temperatures for the samples using principal polarizability and the molecular polarizability anisotropy values. The agreement with Maier–Saupe theory is quite good for all substances except RO-TN-101 which is a mixture.

1 INTRODUCTION

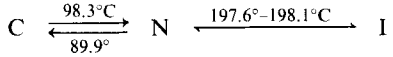
It is well known that nematic liquid crystals are birefringent. The birefringence studies on these substances provide an important means of determining their orientational order parameter. The well known Lorëntz–Lorentz formula cannot however be used in this system becuase of the anisotropy in molecular arrangements. It is generally replaced by Vuks formulae[1] or Neugebauer's relations.[2] It has been shown by Subramhanyam *et al.*[3] that the use of Neugebauer's relations lead to reasonable and consistent results. In the present work we have measured the refractive indices for five liquid crystal samples over a wide temperature range and have used Neugebauer's relations to calculate the orientational order parameters. The

orientational order parameters thus obtained have been compared with the predictions of the Maier–Saupe theory.[4]

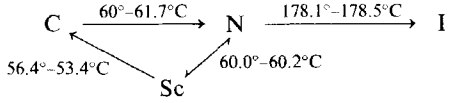
2 EXPERIMENTAL

The structural formula of the compounds for which the refractive index, density, polarizability and orientational order parameter reported here are listed below together with their transition temperatures.

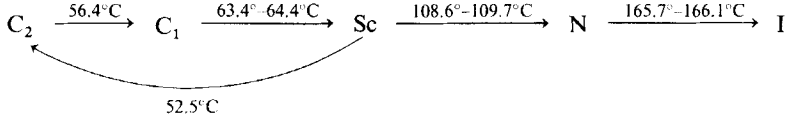
1) Bis-(4′-*n*-hexyloxy benzal)-2-chloro-1,4-Phenylenediamine (in short BHeCP)



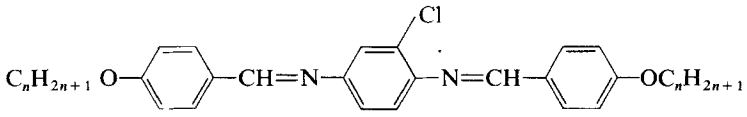
2) Bis-(4′-*n*-octyloxy benzal)-2-chloro-1,4 Phenylenediamine (in short BOCP)



3) Bis-(4′-*n*-decyloxy benzyli dene)-2-chloro-1,4 Phenylene diamine (in short BDeCP)



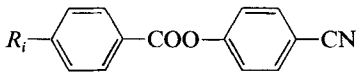
The structural formula for the above three compounds can be represented as follows:



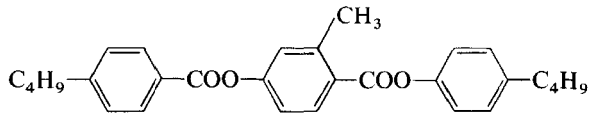
For BHe CP, $n = 6$; BOCP, $n = 8$; and for BDeCP, $n = 10$.

4) RO–TN–101

RO–TN–101 is an ester mixture consisting of the four components.



with $R_1 = n\text{-}C_4H_9$, $R_2 = n\text{-}C_6H_{13}$, $R_3 = n\text{-}C_8H_{17}$ and the diester

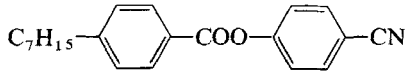


in molar proportions of 1:1:1:1.

$$C \xrightarrow{\sim 0°C} N \xrightarrow{71°C} I$$

5) RO-CE-154

It is an alkyl cyano ester whose structural formula is



$$C \xrightarrow{44.0\text{-}44.2°C} N \xrightarrow{56.5\text{-}56.6°C} I$$

The samples 1, 2 and 3 were sent to us as gift by Dr A. E. de Vries of Liquid Crystal Institute, Kent State, Ohio, U.S.A. They were prepared and purified by Dr Mary E. Neubert of the same institute. The samples 4 and 5 were also sent to us as gift by Dr M. Schadt of M/S. F. Hoffman, La Roche and Company Limited, Basle, Switzerland. The first three samples were further purified by recrystallization.

We prepared hollow glass prisms with refracting angle about 2°. The glass plates used in the hollow prism were optically flat and the two surfaces of the glass plates were perfectly parallel. The prisms were precalibrated by measuring the refractive indices of distilled water, glycerin, potasium chromate and ferric chloride solutions and the values were in good agreement with the results obtained with an Abbe refractometer. Before fabricating the prism the plates were rubbed parallel to one of their edges. Then the plates were treated with an aquous solution containing 1% poly vinyl alcohol and then dried. Again they were rubbed along the same direction as before. Then the prism was formed keeping the treated surfaces inside and the rubbing directions parallel to the refracting edge of the prism. Then the liquid crystal sample was allowed to flow in by melting a few crystals at the top. The prism was then kept in the field of an electromagnet. The refracting edge of the prism was kept parallel to the field. At first the sample was heated to the isotropic state and was then cooled very slowly in the presence of a magnetic field of strength ~ 5 K. Gauss. The combination of rubbing and flow together with the magnetic field produced a homogeneous nematic specimen with the optic axis parallel to the refracting edge of the prism. The prism was put inside a brass thermostat heated electrically and controlled manually to $\pm 0.5°$. The

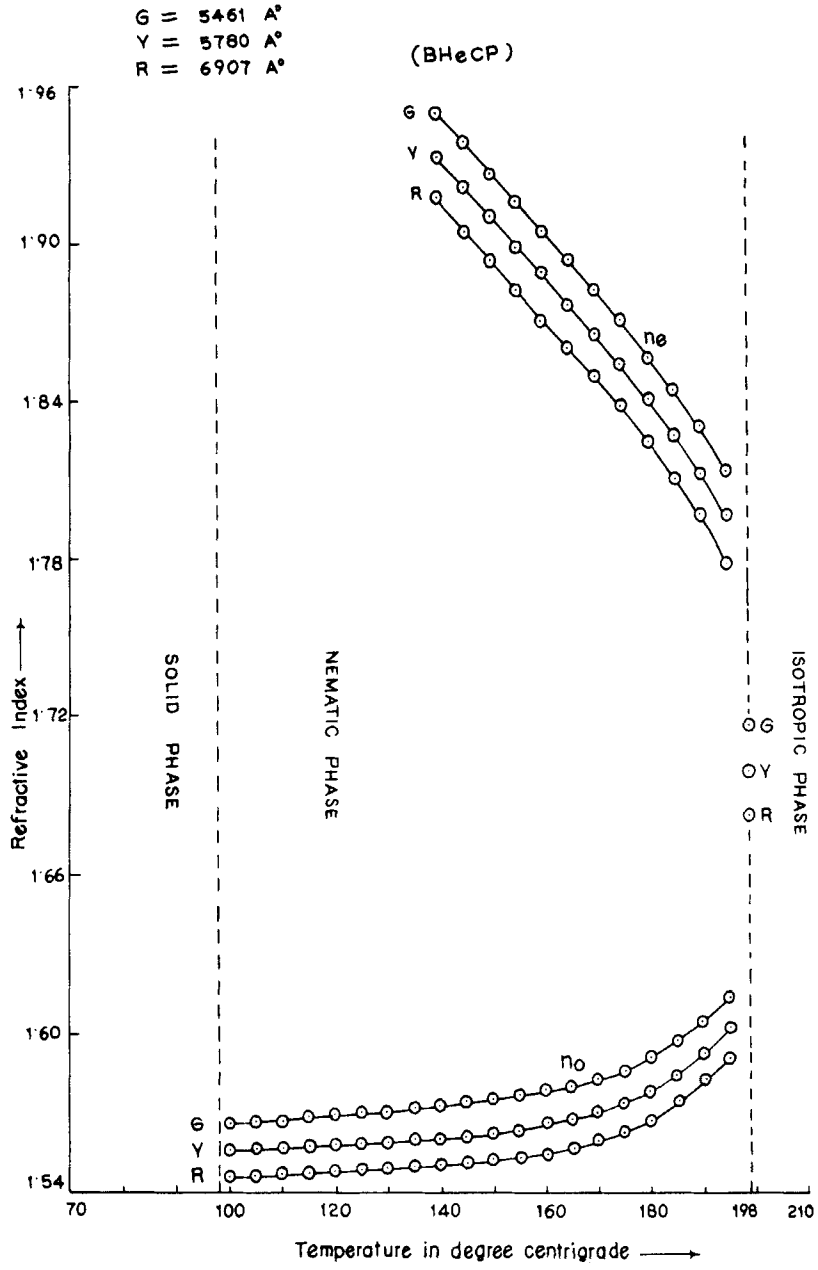


FIGURE 1 Refractive indices of BHeCP against temperature in degree centigrade.

temperature of the sample was measured by using a copper-constantan thermocouple which was precalibrated against the melting points of pure *p*-nitro toluene (m.p. 54°C), O-toluic acid (m.p. 102°C), cinnamic acid (m.p. 133°C) and adipic acid (m.p. 152°C). The angles of minimum deviation for ordinary and extra-ordinary rays and the angle of the prism were measured using a precision spectrometer and a Nicol Prism. The refractive indices were measured for three different wave lengths obtained from a mercury lamp. The densities of the samples in the nematic and the isotropic phases were determined by

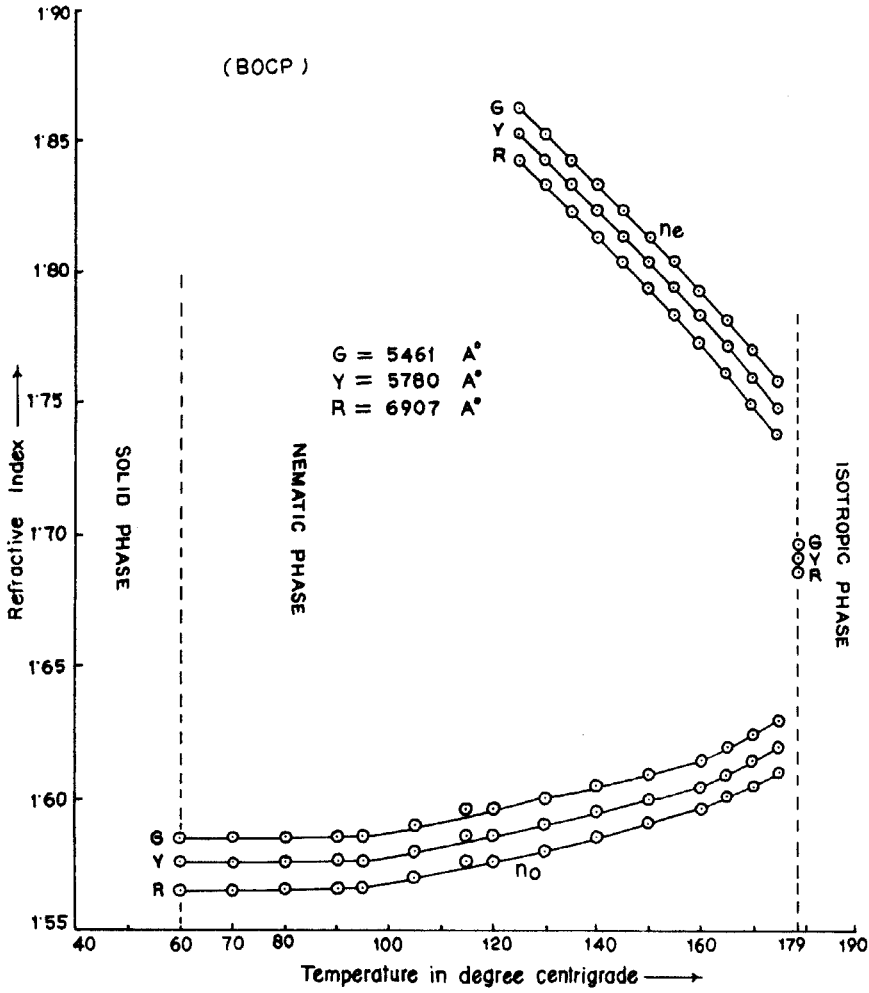


FIGURE 2 Refractive indices of BOCP against temperature in degree centigrade.

putting weighed samples inside a glass capillary tube which was placed in a thermostat. The length of the column was measured by a travelling microscope and the density calculated after correcting for the expansion of glass.

3 RESULTS AND DISCUSSION

The values of experimental refractive indices for BHeCP, BOCP, BDeCP, RO–TN–101 and RO–CE–154 are shown in Figure 1 to Figure 5 respectively.

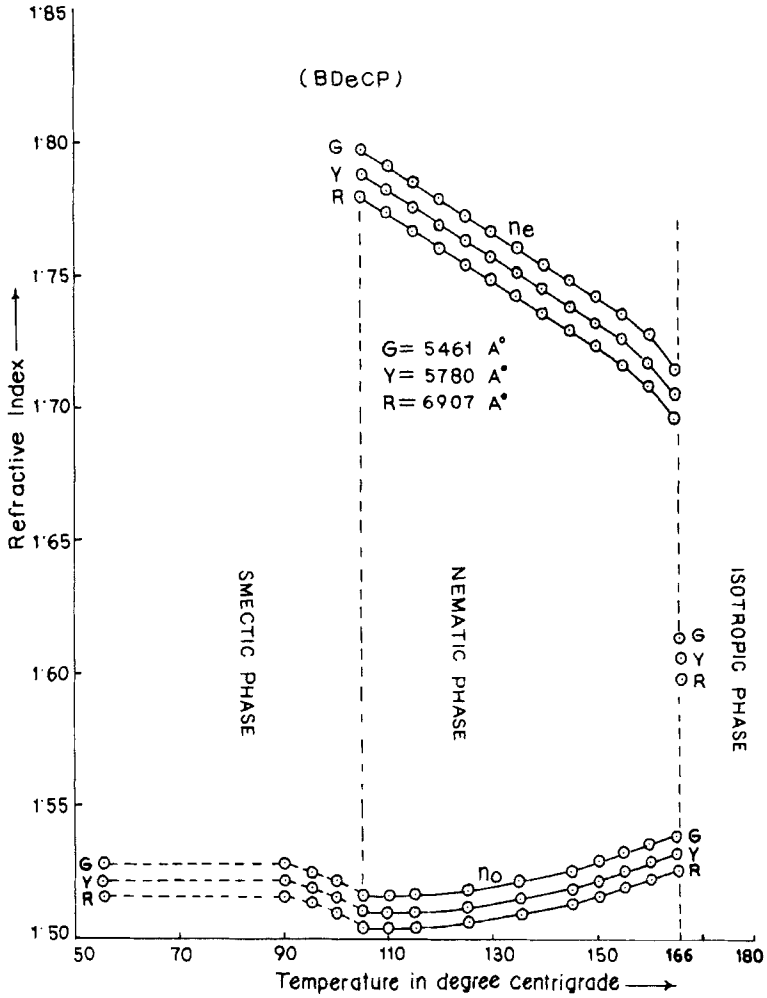


FIGURE 3 Refractive indices of BDeCP against temperature in degree centrigrade.

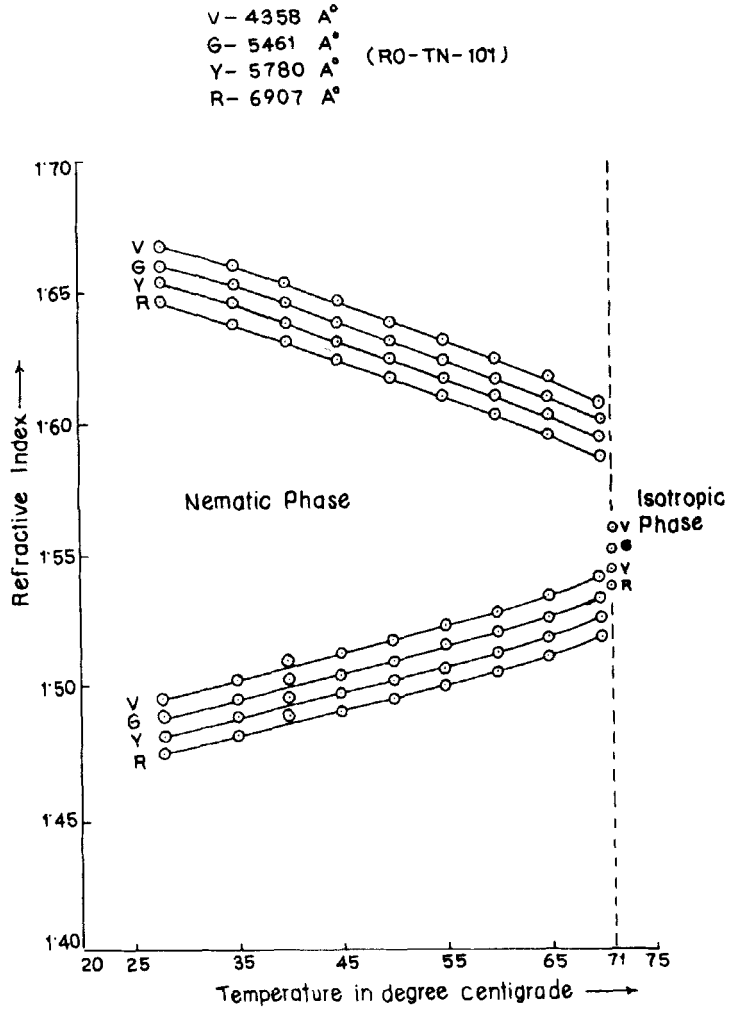


FIGURE 4 Refractive indices of RO-TN-101 against temperature in degree centigrade.

Due to the absorption of extra-ordinary rays in the solid phase and at the lower temperature range in the Nematic phase n_e data could not be taken below 140°C, 125°C and 105°C in the case of BHeCP, BOCP and BDeCP respectively. For RO-TN-101 sample, since its solid phase is below 0°C, we were unable to measure the n_0 and n_e data in solid phase and at temperatures below room temperature in the nematic phase. But in case of RO-CE-154 we were able to measure the n_e and n_0 data both in solid and nematic phase. Lefevre *et al.*[5] have measured the birefringence of BDeCP by texture

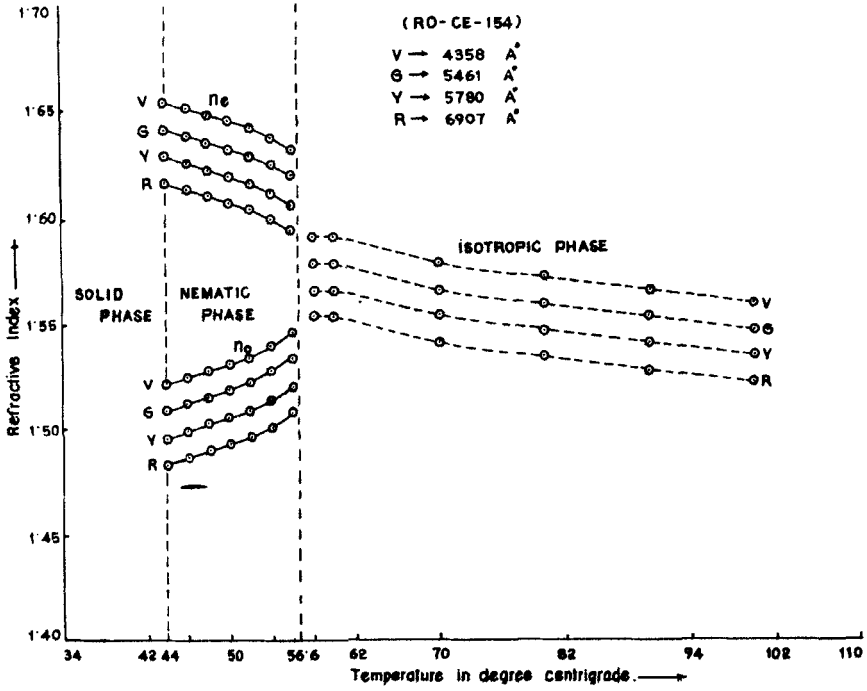


FIGURE 5 Refractive indices of RO-CE-154 against temperature in degree centigrade.

method. It is seen that our values are in quite good agreement with those of Lefevre (Figure 6). Tables I, II, III, IV, and VI give the polarizability values of BHeCP, BOCP, BDeCP, RO-TN-101 and RO-CE-154 calculated from our experimental results and Neugebauer's relations. Also given in the same table are the values of the density of these samples measured by us. Zhuk *et al.*[6,7] have also measured the density of RO-CE-154 which is consistent with our results. Due to the lack of data in the solid phase, except RO-CE-154, we could not calculate directly the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$, the molecular polarizabilities parallel and perpendicular to the long axis respectively. So to calculate the value of $\alpha_{\parallel}$ and $\alpha_{\perp}$, an extrapolation procedure following Haller *et al.*[8] was adopted. We plotted log $(\alpha_e - \alpha_0)$ versus log $(T_c - T)$ giving a straight line at lower temperatures which is extrapolated to log T_c. The limiting value of $(\alpha_e - \alpha_0)$ is assumed[8] to correspond to $(\alpha_{\parallel} - \alpha_{\perp})$. The orientational order parameter S may be calculated from

$$S = \frac{\alpha_e - \alpha_0}{\alpha_{\parallel} - \alpha_{\perp}}$$

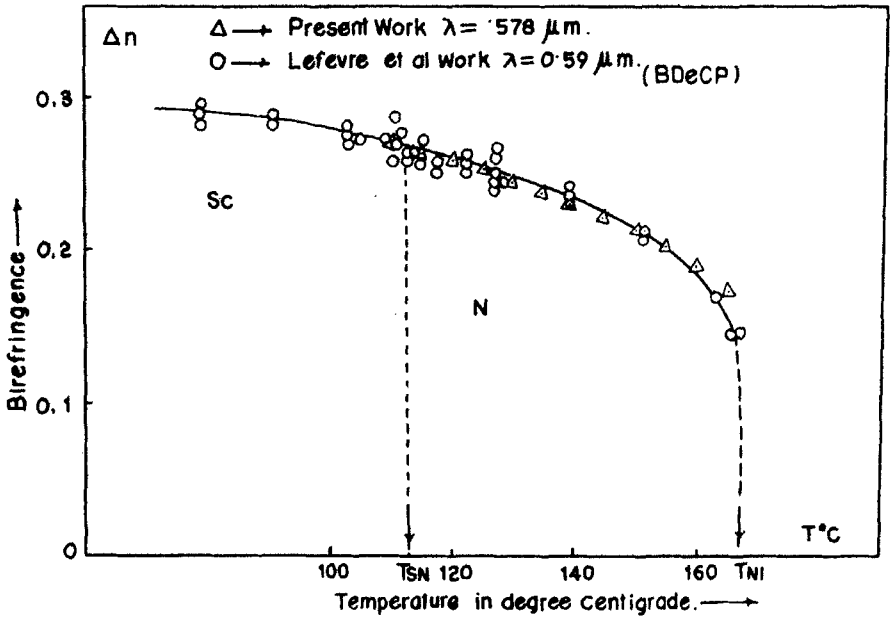


FIGURE 6 Comparison of the present work on the temperature dependence of the birefringence of BDeCP with that of Lefevre *et al.*

TABLE I

Density (ρ), polarizabilities (α) and orientational order parameter (S) of BHeCP

λ T°C	ρ in gm/cm^3	6907 Å			5780 Å			5461 Å		
		α_0	α_e	S	α_0	α_e	S	α_0	α_e	S
140	0.755	82.71	151.40	0.641	83.48	156.03	0.647	84.67	159.67	0.638
145	0.752	83.08	150.66	0.631	83.90	155.19	0.635	85.24	158.53	0.624
150	0.750	83.28	150.26	0.625	84.11	154.77	0.630	85.51	157.99	0.617
155	0.748	83.53	149.76	0.616	84.54	153.91	0.618	85.78	157.45	0.610
160	0.745	83.92	148.98	0.601	85.16	152.67	0.602	86.29	156.43	0.597
165	0.743	84.31	148.20	0.596	85.53	151.93	0.592	86.57	155.87	0.589
170	0.742	84.67	147.48	0.586	85.71	150.57	0.570	86.95	155.11	0.580
175	0.741	85.21	146.40	0.558	86.18	150.63	0.564	87.30	154.41	0.571
180	0.740	85.40	146.02	0.538	86.57	149.85	0.544	87.90	153.21	0.550
185	0.739	86.47	143.88	0.530	87.31	148.37	0.524	88.68	151.65	0.531
190	0.738	87.55	141.72	0.516	88.26	146.47	0.502	89.56	149.89	0.511
195	0.737	88.32	140.18	0.470	89.48	144.03	0.480	90.43	148.15	0.480
198 (Liquid)	0.732									

α_e and α_0 are in units 10^{-24} cm^3.

TABLE II

Density (ρ), polarizabilities (α) and orientational order parameters (S) of BOCP

$\lambda \longrightarrow$ T°C	ρ in gm/cm^3	6907 Å			5780 Å			5461 Å		
		α_0	α_e	S	α_0	α_e	S	α_0	α_e	S
125	1.113	64.62	106.76	0.664	65.08	108.84	0.660	65.75	110.50	0.660
130	1.108	65.08	105.83	0.646	65.51	107.97	0.651	66.19	109.62	0.641
135	1.105	65.57	104.85	0.630	65.82	107.36	0.640	66.61	108.78	0.622
140	1.101	66.15	103.70	0.610	66.42	106.16	0.617	67.12	107.77	0.600
145	1.097	66.78	102.64	0.586	66.98	105.03	0.590	67.52	106.95	0.581
150	1.093	67.27	101.46	0.572	67.64	103.72	0.566	67.99	106.03	0.560
155	1.089	67.94	100.12	0.554	68.25	102.50	0.540	68.46	105.07	0.548
160	1.086	68.60	98.90	0.528	68.77	101.46	0.521	69.13	103.74	0.520
165	1.084	68.78	98.45	0.502	69.12	100.76	0.491	69.58	102.84	0.496
170	1.082	69.23	97.54	0.480	69.67	99.66	0.465	70.135	101.73	0.466
174	1.081	69.53	96.94	0.436	69.96	99.08	0.452	70.44	101.12	0.453
179 (Liquid)	1.073									

α_e and α_0 are in units 10^{-24} cm^3.

TABLE III

Density (ρ), polarizabilities (α) and orientational order parameters (S) of BDeCP

$\lambda \longrightarrow$ T°C	ρ in gm/cm^3	6907 Å			5780 Å			5461 Å		
		α_0	α_e	S	α_0	α_e	S	α_0	α_e	S
105	1.236	56.82	100.84	0.666	57.23	102.63	0.665	57.66	104.38	0.671
110	1.232	56.98	100.51	0.658	57.40	102.30	0.658	57.83	104.04	0.663
115	1.229	57.08	100.32	0.654	57.49	102.11	0.654	57.95	103.79	0.652
120	1.225	57.40	99.68	0.640	57.81	101.47	0.640	58.27	103.16	0.640
125	1.222	57.62	99.23	0.630	58.04	101.02	0.630	58.47	102.75	0.630
130	1.218	57.99	98.47	0.612	58.37	100.36	0.615	58.80	102.09	0.621
135	1.215	58.31	97.84	0.598	58.60	99.89	0.600	59.14	101.41	0.600
140	1.211	58.77	96.93	0.577	59.08	98.93	0.584	59.76	100.16	0.580
145	1.208	59.16	96.16	0.560	59.55	97.99	0.560	60.13	99.43	0.564
150	1.205	59.56	95.35	0.542	60.10	96.90	0.539	60.71	98.26	0.539
155	1.201	60.34	93.79	0.506	60.76	95.58	0.510	61.33	97.04	0.513
160	1.198	60.69	93.09	0.490	61.20	94.69	0.491	62.01	95.68	0.483
165	1.195	61.14	92.18	0.470	61.73	93.64	0.464	62.24	95.22	0.470
167 (Liquid)	1.193									

α_e and α_0 are in units 10^{-24} cm^3.

TABLE IV

Density (ρ), polarizability (α) and orientational order parameter (S) of RN-TN-101

$\lambda \longrightarrow$ T°C	ρ in gm/cm^3	6907 Å			5780 Å			5461 Å			4358 Å		
		α_0	α_e	S	α_0	α_e	S	α_0	α_e	S	α_0	α_e	S
26	1.022	30.87	103.33	0.601	31.24	104.14	0.594	31.62	104.92	0.596	31.97	105.90	0.596
35	1.018	31.26	102.55	0.592	31.66	103.31	0.584	32.03	104.09	0.586	32.39	105.10	0.586
40	1.016	31.50	102.07	0.586	31.88	102.86	0.578	32.21	103.73	0.581	32.61	104.66	0.581
45	1.013	31.72	101.63	0.580	32.07	102.47	0.573	32.44	103.26	0.576	32.85	104.17	0.575
50	1.011	31.94	101.19	0.575	32.31	101.99	0.568	32.68	102.78	0.570	33.08	103.71	0.569
55	1.008	32.13	100.83	0.570	32.51	101.60	0.563	32.82	102.51	0.566	33.27	103.31	0.565
60	1.006	32.41	100.26	0.563	32.78	101.06	0.556	33.19	101.76	0.557	33.60	102.68	0.557
65	1.004	32.65	99.79	0.559	33.02	100.59	0.551	33.45	101.25	0.551	33.86	102.16	0.551
70	1.001	32.99	99.09	0.548	33.39	99.84	0.541	33.83	100.50	0.542	34.17	101.54	0.543
72 (Liquid)	0.999												

α_e and α_0 are in units 10^{-24} cm^3.

TABLE V
Density (ρ), refractive indices (n) and polarizabilities (α) of RO-CE-154 in crystalline phase at 22°C

λ Å	ρ in gm/c.c.	n_e	n_0	$\alpha_\parallel$	$\alpha_\perp$
	1.15				
6907		1.616	1.432	62.75	25.18
5708		1.629	1.445	63.47	25.81
5461		1.641	1.457	64.45	26.40
4358		1.654	1.470	65.36	27.03

$\alpha_\parallel$ and $\alpha_\perp$ are in units 10^{-24} cm^3.

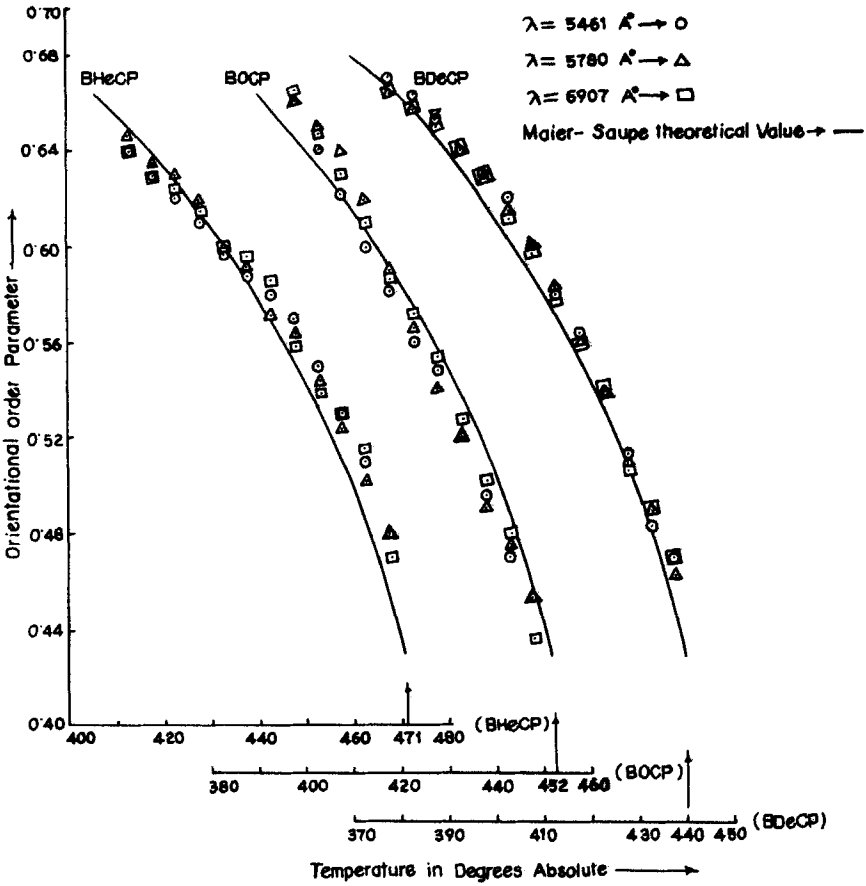


FIGURE 7 Orientational order parameter of BHeCP, BOCP and BDeCP against temperature in degree absolute.

TABLE VI

Density (ρ), polarizability (α) and orientational order parameter (S) of RO-CE-154

$\lambda \longrightarrow$		6907 Å				5780 Å				5461 Å				4358 Å			
T°C	ρ in gm/cm^3	α_0	α_e	S_c	S	α_0	α_e	S_c	S	α_0	α_e	S_c	S	α_0	α_e	S_c	S
44	1.095	30.51	52.08	0.574	0.567	31.16	52.78	0.574	0.569	31.87	53.54	0.569	0.570	32.52	54.37	0.570	0.574
46	1.093	30.79	51.52	0.552	0.545	31.43	52.23	0.552	0.547	32.20	52.89	0.553	0.544	32.80	53.82	0.548	0.553
48	1.091	31.04	51.03	0.532	0.526	31.78	51.54	0.525	0.520	32.45	52.38	0.523	0.524	33.08	53.26	0.526	0.531
50	1.090	31.29	50.53	0.512	0.506	31.94	51.22	0.512	0.507	32.70	51.88	0.504	0.504	33.30	52.82	0.509	0.513
52	1.088	31.55	50.00	0.491	0.485	32.29	50.51	0.484	0.479	33.06	51.16	0.475	0.476	33.60	52.22	0.486	0.489
54	1.087	31.95	49.20	0.459	0.454	32.66	49.77	0.454	0.450	33.50	50.29	0.441	0.442	34.04	51.32	0.451	0.454
56	1.085	32.46	48.18	0.418	0.413	33.09	48.92	0.420	0.416	33.98	49.32	0.403	0.403	34.52	50.37	0.413	0.417
57 (Liquid)	1.082																

α_e and α_0 are in units 10^{-24} cm^3.

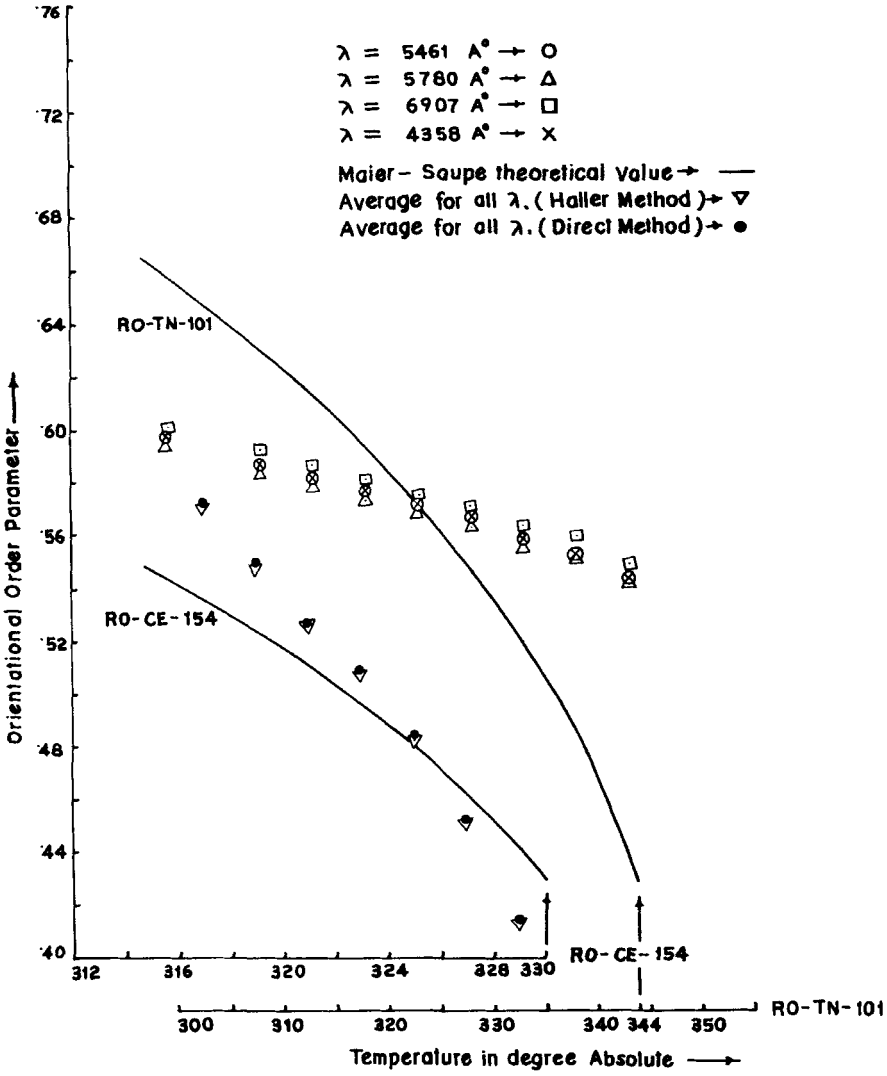


FIGURE 8 Orientational order parameter of RO–TN–101 and RO–CE–154 against temperature in degree absolute.

$\alpha_{\parallel}$ and $\alpha_{\perp}$ could be calculated only in the case of RO–CE–154 from the refractive index data in the crystalline phase. The values of refractive indices, density and molecular polarizabilities of RO–CE–154 in the crystalline phase are given in Table V. The orientational order parameter was calculated using the above relation and is given in Table VI under S_c. For comparison, the

values obtained by Haller's method are also given for RO-CE-154 in the same table under *S*.

These values of the order parameter are given in Tables I, II, III, IV, and VI. The values of the experimental orientational order parameter obtained by us are shown in Figures 7 and 8, together with the theoretical values of Maier and Saupe.[4] From Figure 7 it is seen that the agreement of the experimental values with the theoretical values is quite good in the case of BOCP, BDeCP and BHeCP. However Figure 8 shows that the experimental order parameter values for the samples RO-TN-101 and RO-CE-154 are not in good agreement with the Maier-Saupe[4] values with disagreement being very pronounced in the case of RO-TN-101. Since the Maier-Saupe theory may not be valid for mixtures, the discrepancy in the case of RO-TN-101 is not surprising. We plan to use an X-ray diffraction method to measure the order parameter of all the substances reported in this paper and compare with the values obtained here to test the internal consistency of the theory.

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