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Refractive Indices, Dielectric Constants, and Order Parameter of Four Alkyl/Alkoxyphenylcyclohexanecarboxylate Liquid Crystals in the Nematic Phase

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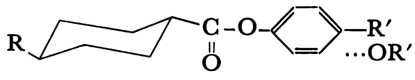
(Received October 2, 1984)

The extraordinary and ordinary refractive indices, n_e and n_o, and the densities of four liquid crystals 4-pentylphenyl *trans*-4′-pentylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4′-propylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4′-butylcyclohexanecarboxylate, and 4-methoxyphenyl *trans*-4′-pentylcyclohexanecarboxylate have been reported at different temperatures. The effective polarizabilities α_e and α_o in the nematic phase have been calculated using 1) Neugebauer and 2) Vuks methods. The order parameter S calculated from the two methods were comparable. The dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, parallel and perpendicular to the long axis of the molecules have been measured at 1 kHz at different temperatures. The order parameters for the liquid crystals were then evaluated from dielectric anisotropy $\Delta\varepsilon(=\varepsilon_{\parallel}-\varepsilon_{\perp})$, polarizability anisotropy $\Delta\alpha(=\alpha_e-\alpha_o)$ and dipole moment μ, using Maier and Meier equation and were found only slightly less than those obtained from refractive indices method. It was concluded that Maier and Meier equation also could be used to evaluate the order parameter of liquid crystals of molecules having dipole moments 2 Debye or less.

The knowledge of dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, parallel and perpendicular to the long molecular axis helps us to select a liquid crystal for a specific electrooptical display device. The values of dielectric anisotropy $\Delta\varepsilon(=\varepsilon_{\parallel}-\varepsilon_{\perp})$ and polarizability anisotropy $\Delta\alpha(=\alpha_e-\alpha_o)$ where α_e and α_o are the effective polarizabilities of the nematic medium and the dipole moment μ may be useful for the evaluation of order parameter of liquid crystals using Maier and Meier equation.[1] de Jeu and Lathouwers[2,3] observed that in the case of liquid crystals with zero or small dipole moment, the average dielectric constant $\bar{\varepsilon}=1/3\ (\varepsilon_{\parallel}+2\varepsilon_{\perp})$ practically coincides with the dielectric constant ε_{iso} in the isotropic phase. They pointed out that these results indicate that the Maier and Meier equation gives qualitatively the correct picture of dielectric properties of liquid crystals. But for the lack of information on molecular polarizabilities, dipole moments, and their angle with the long molecular axis, the model could not be tested for quantitative measurements. Recently Sen *et al.*[4] observed that in the case of liquid crystals of strongly polar molecules having dipole moments of 4—5 Debye,[†] the order parameter S obtained from Maier and Meier equation using dielectric anisotropy and polarizability anisotropy are much less than the values obtained from other methods. Sen *et al.*[4] pointed out that the short range antiferroelectric dipole correlation of permament dipole moment μ in strongly polar nematics as proposed by Madhusudana and Chandrasekhar[5] might cause a large decrease in $\varepsilon_{\parallel}$ thus decreasing the order parameter. The object of the present investigation is to evaluate the order parameter S of liquid crystals with dipole moments about 2 Debye from the measurements of refractive indices and densities, and to compare these S values with those obtained from dielectric anisotropy $\Delta\varepsilon$ and polarizability anisotropy $\Delta\alpha$, using the Maier and Meier equation.[1]

Experimental

The structural formulae and nematic-isotropic transition temperatures of four liquid crystals which were obtained from Merck are given below. The general formula for these compounds is



where R and R′=Alkyl and OR′=Alkoxy.

1) 4-Pentylphenyl *trans*-4′-pentylcyclohexanecarboxylate (D-55)

$$\mathrm{C}\xrightarrow{37\,^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{47\,^{\circ}\mathrm{C}}\mathrm{I}$$

2) 4-Ethoxyphenyl *trans*-4′-propylcyclohexanecarboxylate (D-302)

$$\mathrm{C}\xrightarrow{48\,^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{78\,^{\circ}\mathrm{C}}\mathrm{I}$$

3) 4-Ethoxyphenyl *trans*-4′-butylcyclohexanecarboxylate (D-402)

$$\mathrm{C}\xrightarrow{37\,^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{75\,^{\circ}\mathrm{C}}\mathrm{I}$$

4) 4-Methoxyphenyl *trans*-4′-pentylcyclohexanecarboxylate (D-501)

$$\mathrm{C}\xrightarrow{40\,^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{71\,^{\circ}\mathrm{C}}\mathrm{I}$$

The liquid crystals were used in the investigations without further purification.

Measurement of Refractive Indices. The refractive indices n_o and n_e for the ordinary and extraordinary refracted rays in the nematic phase and the refractive index n in the isotropic phase at different temperatures were measured by means of an Abbe refractometer. The glass prisms of the refractometer were first treated with an aqueous solution of 3% poly (vinyl alcohol) and dried. The prism was then rubbed with a lens paper along the length of prism several times. A little of the liquid crystal was dropped on the lower prism

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[†] 1D=3.3×10^{-30}cm.

and was spread with a spatula. These operations helped to align the liquid crystal along the length of the prism surface. The arrangement was complete when the upper prism was clamped in place.

Two positions of a nicol placed over the eyepiece allow distinct separation of bright and dark space corresponding to n_e and n_o (in the nematic $n_e > n_o$). The temperature was maintained constant within ±0.2 °C by means of a thermostat.

The densities of the liquid crystal in the nematic and isotropic phases were determined by introducing a weighed sample of the liquid crystal into a capillary tube placed in a thermostat. The length of the column in the capillary was measured at different temperatures with a travelling microscope. The density was calculated after correcting for the expansion of the glass tube.

Measurements of Dielectric Constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The static dielectric constants were measured at a frequency of 1 kHz using a GR-1620 capacitance bridge reading to an accuracy of 0.01%. A parallel plate capacitor with stainless steel electrodes of 2 cm×1 cm separated by a 1 mm teflon spacer, served as the sample holder. The temperature of the sample was measured with a thermocouple mounted directly on one of the electrodes. A magnetic field 1.0 T was used to align the liquid crystal molecules parallel and perpendicular to the electrode surfaces. The temperature of the sample holder was maintained constant within ±0.2 °C by means of a thermostat. The cell was calibrated with freshly distilled toluene and chlorobenzene and the values agree to 0.1% of the standard value.6)

Results

Refractive Indices and Polarizabilities. The experimental values of refractive indices n_e, n_o, and n and the densities of the liquid crystals are given in Tables 1 (a, b, c, d) and Fig 1. The effective polarizabilities α_e and α_o in the nematic state were calculated using two methods. 1) Neugebauer's7) method of anisotropic internal field given by

$$n^2_{e,c} - 1 = 4\pi N\alpha_{e,o}/(1 - N\alpha_{e,o} - \gamma_{e,o}), \tag{1}$$

where N is the number of molecules per 1 cm^3 and $\gamma_{e,o}$ are internal field constants. The relevant equations for calculating the polarizabilities are

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1} + \frac{2(n_o^2+2)}{(n_o^2-1)}\right], \tag{2}$$

$$\alpha_e + 2\alpha_o = \alpha_{//} + 2\alpha_{\perp} = \frac{9}{4\pi N}\left(\frac{n^2-1}{n^2+2}\right). \tag{3}$$

Table 1a. Refractive indices, density and order parameter S for D-55

T/°C	n_o	n_e	ρ/g cm^{-3}	$\bar{\alpha}$/Å^3	Vuks' Method			Neugebauer's Method		
					α_o/Å^3	α_e/Å^3	S	α_o/Å^3	α_e/Å^3	S
36	1.4730	1.5304	0.9508	41.632	39.683	45.532	.70	39.995	44.908	.69
37	1.4724	1.5301	0.9501	41.623	39.664	45.550	.70	39.989	44.900	.69
39	1.4724	1.5272	0.9468	41.623	39.757	45.357	.67	40.058	44.753	.66
41	1.4720	1.5250	0.9486	41.629	39.818	45.241	.65	40.090	44.708	.65
43	1.4722	1.5217	0.9449	41.643	39.867	45.020	.61	40.206	44.518	.60
45	1.4736	1.5163	0.9431	41.652	40.190	44.571	.52	40.413	44.132	.52
47	1.4870		0.9416							
48.5	1.4862		0.9389							
51.5	1.4848		0.9357							
					$\alpha_{\perp}$= 38.869 (Å)^3	$\alpha_{\parallel}$= 47.2717 (Å)^3		$\alpha_{\perp}$= 39.310 (Å)^3	$\alpha_{\parallel}$= 46.398 (Å)^3	

Table 1b. Refractive indices, density and order parameter S for D-302

T/°C	n_o	n_e	ρ/g cm^{-3}	$\bar{\alpha}$/Å^3	Vuks' Method			Neugebauer's Method		
					α_o/Å^3	α_e/Å^3	S	α_o/Å^3	α_e/Å^3	S
51	1.4705	1.5448	1.0118	33.1706	31.1645	37.1733	.75	31.4817	36.5486	.75
54.5	1.4700	1.5417	1.0093	33.1730	31.2352	37.0442	.72	31.5438	36.4314	.72
57	1.4693	1.5401	1.0074	33.1790	31.2605	37.0092	.71	31.5646	36.4078	.71
60	1.4684	1.5384	1.0048	33.1960	31.2950	36.9931	.71	31.5954	36.3972	.71
63	1.4680	1.5356	1.0024	33.2063	31.3670	36.8800	.69	31.6581	36.3028	.69
66	1.4677	1.5327	1.0000	33.2183	31.4441	36.7570	.66	31.7181	36.2188	.66
69	1.4677	1.5289	0.9974	33.2293	31.5552	36.5697	.62	31.8137	36.0606	.63
72	1.4674	1.5263	0.9947	33.2550	31.6408	36.4781	.60	31.8919	35.9812	.61
75	1.4677	1.5222	0.9921	33.2713	31.7757	36.2608	.56	32.0104	35.7932	.56
77	1.4680	1.5198	0.9900	33.2956	31.8844	36.1550	.53	32.1633	35.5604	.50
78	1.4698	1.5146	0.9888	33.3126	32.0789	35.7753	.46	32.2666	35.4048	.46
79	1.4845		0.9849							
80	1.4842		0.9841							
84.5	1.4824		0.9804							
88	1.4810		0.9776							
					$\alpha_{\perp}$= 30.7379 (Å)^3	$\alpha_{\parallel}$= 38.7851 (Å)^3		$\alpha_{\perp}$= 31.1611 (Å)^3	$\alpha_{\parallel}$= 37.9387 (Å)^3	

Table 1c. Refractive indices, density and order parameter S for D-402

$T/°C$	n_o	n_e	$\rho/g\,cm^{-3}$	$\bar{\alpha}/Å^3$	Vuks' Method			Neugebauer's Method		
					$\alpha_o/Å^3$	$\alpha_e/Å^3$	S	$\alpha_o/Å^3$	$\alpha_e/Å^3$	S
40	1.4730	1.5508	1.0106	35.0349	32.8309	39.4324	.73	33.1803	38.7443	.73
44	1.4723	1.5469	1.0072	35.0449	32.9238	39.2740	.70	33.2561	38.6227	.70
45.5	1.4712	1.5473	1.0063	35.0406	32.8772	39.3628	.72	33.2233	38.6752	.71
52	1.4703	1.5408	1.0012	35.0499	33.0334	39.0702	.67	33.3455	38.4589	.67
55.5	1.4695	1.5380	0.9986	35.0513	33.0898	38.9691	.65	33.4004	38.3531	.65
59.5	1.4686	1.5345	0.9958	35.0389	33.1471	38.8183	.63	33.4507	38.2154	.62
64	1.4685	1.5288	0.9923	35.0433	33.3030	38.5099	.57	33.5646	38.0007	.58
67	1.4682	1.5256	0.9897	35.0539	33.3974	38.3626	.55	33.6578	37.8462	.55
69	1.4680	1.5234	0.9879	35.0629	33.4629	38.2637	.53	33.7192	37.7505	.53
71	1.4680	1.5207	0.9860	35.0756	33.5470	38.1216	.50	33.7745	37.6779	.51
73	1.4690	1.5164	0.9841	35.0939	33.7161	37.8363	.45	33.9132	37.4554	.46
74	1.4698	1.5137	0.9832	35.1016	33.5238	37.6430	.45	34.0195	37.2659	.42
75.5	1.4840		0.9815							
76.5	1.4835		0.9791							
78	1.4828		0.9778							
80	1.4820		0.9761							
					$\alpha_\perp=$ 32.1041 (Å)^3	$\alpha_\parallel=$ 41.1670 (Å)^3		$\alpha_\perp=$ 32.5785 (Å)^3	$\alpha_\parallel=$ 40.2182 (Å)^3	

Table 1d. Refractive indices, density and order parameter S for D-501

$T/°C$	n_o	n_e	$\rho/g\,cm^{-3}$	$\bar{\alpha}/Å^3$	Vuks' Method			Neugebauer's Method		
					$\alpha_o/Å^3$	$\alpha_e/Å^3$	S	$\alpha_o/Å^3$	$\alpha_e/Å^3$	S
40	1.4772	1.5445	1.0164	34.870	32.975	38.646	.73	33.270	38.070	.73
50	1.4742	1.5389	1.0087	34.900	33.065	38.561	.71	33.355	37.990	.71
60.5	1.4725	1.5302	1.0068	34.720	33.084	37.993	.63	33.354	37.452	.63
65	1.4723	1.5256	0.9970	34.956	33.430	38.005	.59	33.665	37.540	.59
70	1.4732	1.5180	0.9924	34.996	33.710	37.570	.50	33.921	37.148	.49
72.5	1.4752	1.5112	0.9896	35.033	34.000	37.107	.40	34.186	36.728	.39
74.5	1.4865		0.9861							
75.5	1.4860		0.9854							
					$\alpha_\perp=$ 32.533 (Å)^3	$\alpha_\parallel=$ 40.283 (Å)^3		$\alpha_\perp=$ 32.936 (Å)^3	$\alpha_\parallel=$ 39.477 (Å)^3	

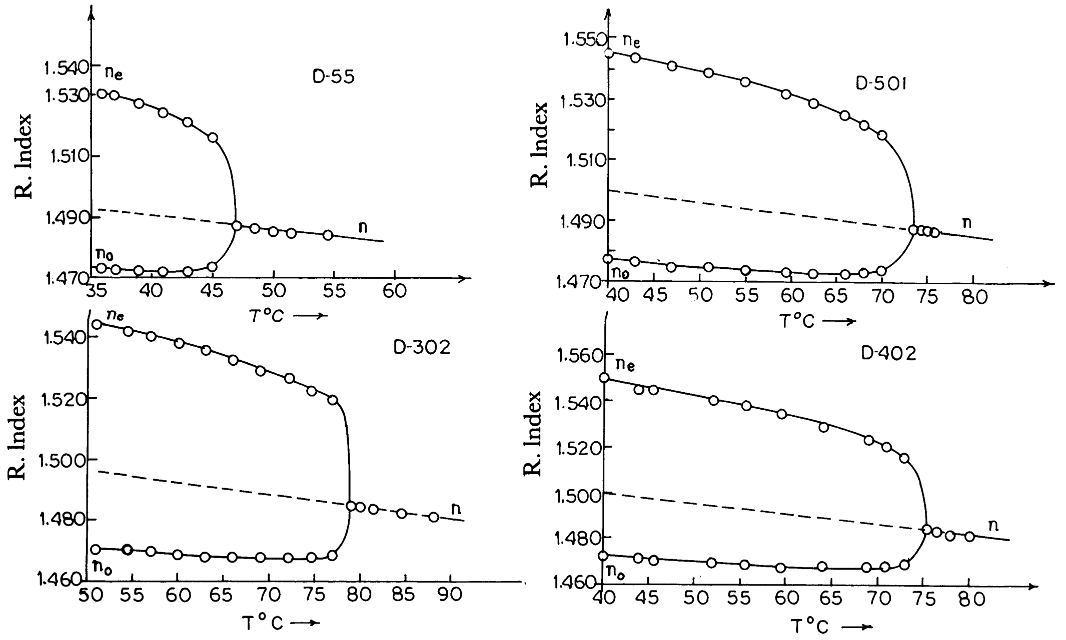

Fig. 1. Refractive index anisotropy plots for D-55, D-501, D-302, and D-402.

2) Vuks'method[8] of isotropic internal field given by

$$\frac{n_{e,o}^2-1}{\overline{n^2}+2}=\frac{4\pi N\alpha_{e,o}}{3}, \tag{4}$$

where $\overline{n^2}=1/3\ (n_e^2+2n_o^2)$.

The values of effective polarizabilities α_e and α_o obtained from the two methods are included in Tables 1 (a, b, c, d). Since the principal polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$, parallel and perpendicular to the long axis of the molecules in the crystalline state, were not available, the method of Haller *et al.*[9] was adopted. Graphs were plotted with log α_e/α_o *vs.* log (T_c-T) where T_c is the nematic-isotropic transition temperature. These plots are straight lines at lower temperatures and intersect the log α_e/α_o axis at 0 K assumed to correspond to log $\alpha_{\parallel}/\alpha_{\perp}$ in the crystalline state. From Eq. 3 the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ are obtained. The order parameter S was then calculated from the relation $S=\alpha_e-\alpha_o/\alpha_{\parallel}-\alpha_{\perp}$.

Dielectric Constants $\varepsilon_{\parallel}$ *and* $\varepsilon_{\perp}$ *and the Order Parameter.* The experimental values of dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of the liquid crystals in nematic state and that in the isotropic phase ε_{iso} are given in Table 2. The dielectric anisotropy is shown in Fig. 2. The order parameter was calculated using the Maier and Meier equation,[1]

$$\Delta\varepsilon = 4\pi NhF\left[\Delta\alpha-\frac{F\mu^2}{2kT}(1-3\cos^2\beta)\right]S, \tag{5}$$

where N is the number of molecules per 1 cm³, $h=3\bar{\varepsilon}/(2\bar{\varepsilon}+1)$, the cavity field factor, $F=1/(1-\bar{\alpha}f)$, the reaction field factor, and $f=4\pi N(2\bar{\varepsilon}-2)/3(2\bar{\varepsilon}+1)$, μ the dipole moment of the molecule, $\Delta\alpha$=polarizability anisotropy $=\alpha_e-\alpha_o$, and $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$ dielectric anisotropy.

The dipole moments μ of the liquid crystal molecules were determined in dilute solutions in benzene and included in Table 2. The angle between the resultant moment and the long axis of the molecules of the liquid crystals (β) was calculated from the alkoxyl

TABLE 2. VALUES OF DIELECTRIC PERMITTIVITIES|$\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, AND ε_{iso}

D-55			D-302			D-402			D-501		
T/°C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	T/°C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	T/°C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	T/°C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
37.5	2.940	3.419	51	3.2816	4.5447	40	3.2720	4.4947	43	3.4125	4.4595
40	2.958	3.396	54.5	3.2798	4.5150	52	3.2355	4.3607	47	3.3583	4.4137
42	2.958	3.382	60	3.2952	4.4732	59.5	3.2483	4.2246	51	3.3685	4.2837
44	2.984	3.351	66	3.3024	4.4155	69	3.3229	4.0941	55	3.3182	4.2423
46	2.997	3.313	72	3.3369	4.2613	73	3.3572	4.0179	60.5	3.3372	4.1875
50 iso	3.226		77	3.3566	4.1899	77 iso	3.7435		65	3.3560	4.1244
52	3.217		80	3.4673	4.0482	80	3.7143		70	3.4083	3.9952
54	3.208		84.5 iso	3.8518		85	3.6798		74 iso	3.8101	
			88	3.8308		88	3.6548		76	3.7936	
			90	3.8208					78	3.7727	
									80	3.7563	
									85	3.7110	
μ=1.99 D, β=66°			μ=2.17 D, β=72°			μ=2.08 D, β=72°			μ=2.23 D, β=68°		

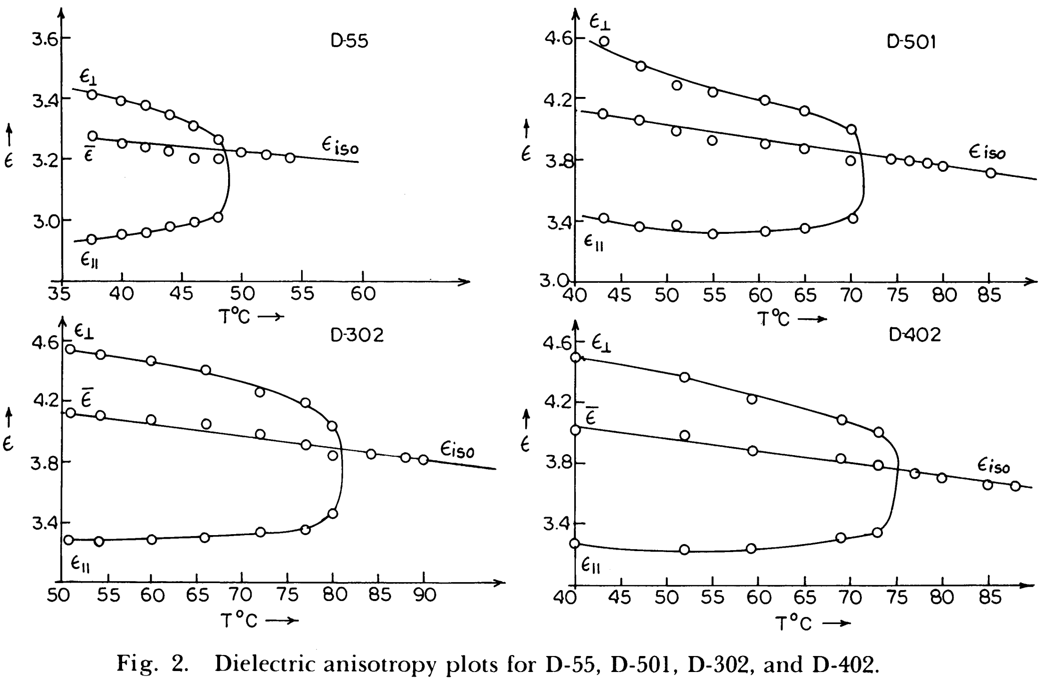

Fig. 2. Dielectric anisotropy plots for D-55, D-501, D-302, and D-402.

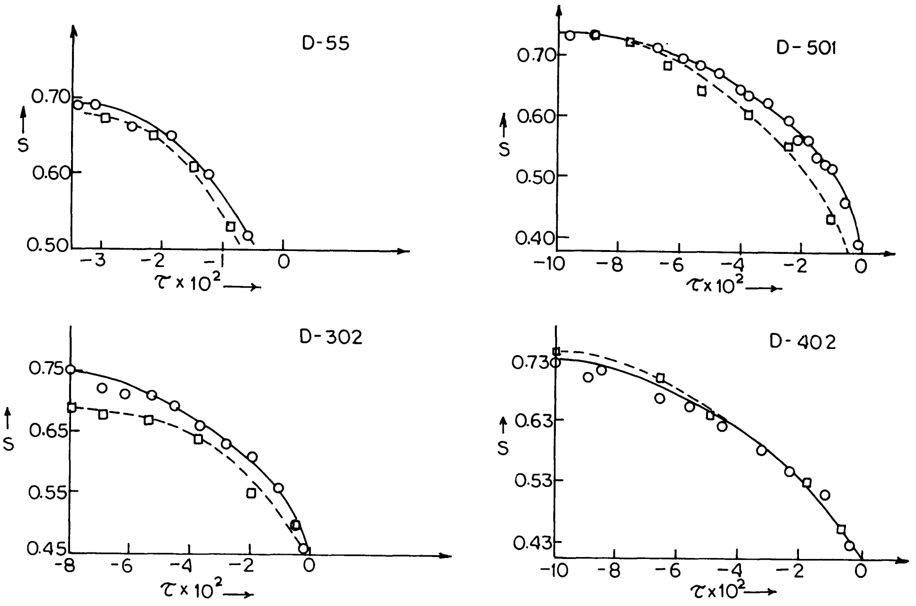

Fig. 3. Plots of order parameter S *vs.* $\tau=(T-T_{NI})/T_{NI}$.
By ○—Neugebauer's method, and □—Maier and Meier's method.

group moment and ester group moment reported in the literature.[10] The angle β for the different samples is given in Table 2.

Discussion

It can be seen from Tables 1 (a, b, c, d) that the order parameters S for the liquid crystals under study, obtained from the refractive indices using 1) Neugebauer and 2) Vuks methods are comparable. The S value decreases with increase of temperature till it suddenly vanishes at the clearing temperature. The order parameters for these liquid crystals have not been reported so far.

From Fig. 2, it can be seen that the average dielectric constants $\bar{\varepsilon}=(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3$ in the nematic phase practically coincide with the dielectric constants ε_{iso} in the isotropic phase. These results are similar to those reported by de Jeu[3] in the case of liquid crystals of very small or zero dipole moment but unlike to the case of liquid crystals having large dipole moment (μ=4—5 Debye) of which the average dielectric constant ε_{iso} in the isotropic phase reported by different workers.[11,12]

From Table 2, it can be seen that the values of the order parameter S, calculated from the values of the dielectric anisotropy $\Delta\varepsilon$, polarizability anisotropy $\Delta\alpha$ and dipole moment μ using the Maier and Meier equation for the alkoxyphenyl *trans*-4′-alkylcyclohexanecarboxylates, compare very well at all temperatures with those obtained from refractive index methods. Similarly for alkylphenyl *trans*-4′-alkylcyclohexanecarboxylates, the order parameters S from the Maier and Meier equation also agree well with those obtained from the refractive index methods, though the former values are only slightly less than the latter. The slight discrepancy may be due to the estimation of the angle β made by the resultant moment with the long axis of the molecule. So, it appears that for liquid crystals having dipole moment of about 2 D, or so, the Maier and Meier equation with dielectric anisotropy $\Delta\varepsilon$, provides another method for the determination of the order parameter.

The inapplicability of the Maier and Meier theory[1] for dielectric constants in strongly polar nematics might be due to short range antiferroelectric dipole correlation of the permament dipole moment as proposed by Madhusudana and Chandrasekhar,[5] which might cause a large decrease in $\varepsilon_{\parallel}$ in strongly polar nematics (μ>4 D); Such a decrease in $\varepsilon_{\parallel}$ in less polar nematics ($\mu\approx$2D) might not affect the dielectric anisotropy and hence the order parameter very effectively.

Of course some more liquid crystals having moments of more or less 2 D should be studied before drawing definite conclutions.

Our sincere thanks to Dr. S. B. Roy for his guidance.

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