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Refractive Indices and Dielectric Studies of Three Phenylcyclohexane Liquid Crystals in the Nematic Phase

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The refractive indices n_e, n_0 and densities and the dielectric primittivities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of three P-cyano-P′-alkylcyclohexanes (PHC-3, PCH-5, PCH-7) have been measured at different temperatures. The order parameters calculated by using Neugebauer and Vuks' methods were comparable. A comparison of order parameters of the PCH with the corresponding alkylcyanobiphenyls at reduced temperatures τ ($= T - T_{NI}/T_{NI}$) shows that the replacement of a phenyl ring with a cyclohexyl ring decreases the order parameter appreciably. The experimental values of dielectric permittivities $\epsilon_{\parallel}$ in each of the PCHs are found to be less than half of the $\epsilon_{\parallel}$-value calculated from Maier and Meier equations using the polarizability and the order parameter obtained from refactive index measurements. This was explained as due to short range antiparallel ordering of strongly polar molecules in the nematic phase, as proposed by Chandrasekhar and Madhusudan, which was not taken into consideration in Maier and Meiers' theory.

INTRODUCTION

In a recent communication[1] the orientational order parameters of several alkyl and alkoxy cyanobiphenyls were determined from the refractive indices and density measurements using the methods due to Neugebauer,[2] Vuks[3] and Saupe and Maier.[4] The results obtained by Neugebauer and Vuks methods were comparable and agree with those reported from other methods. The object of the present investigations was to study how the order parameter changes with replacement of a phenyl ring in cyanobiphenyls by a cyclohexane ring. It was also intended to study the dielectric permittivities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ parallel and perpendicular to the long axes of PCH molecules and compare these experimental $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ values with the $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ values calculated from Maier and Meier equations using polarizability α and order parameter S obtained from refractive index measurements. The results are discussed in the paper.

EXPERIMENTAL

The transition temperatures of different mesophases of three P-cyano-P′-alkylcyclohexanes (PCH) obtained from Merck, Germany, are given below.

1. P-cyano-P′-propylphenylcyclohexane (PCH-3): $\xrightarrow{43°C}$ N $\xrightarrow{45°C}$ I
2. P-cyano-P′-Pentylphenylcyclohexane (PCH-5): C $\xrightarrow{30°C}$ N $\xrightarrow{55°C}$ I
3. P-cyano-P′-heptylphenylcyclohexane (PCH-7): C $\xrightarrow{30°C}$ N $\xrightarrow{57°C}$ I

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

The method of measurements of the refractive indices n_e, n_o for extraordinary and ordinary ray with the help of ABBE refractometer and the density measurements by means of a capillary tube method were described earlier.[1]

Measurements of delectric permittivities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were made with a GR-1620 capacitance bridge using a capacitor of stainless steel electrodes separted by 1 mm teflon spacer described earlier.[5] Alignment of molecules parallel and perpendicular to the electrode surfaces were made by 10 KG magnetic field. The cell was calibrated with freshly distilled toluene and chlorobenzene and values agreed to 0.1% of the standard value. The temperature of the cell was maintained constant by means of a thermostat.

RESULTS

The experimental values of refractive indices n_e, n_o and the densities of the liquid crystals at different temperatures are given in Tables (I–III). The refractive index anisotropy is shown in figure 1 (a, b, c). The effective polarizabilities α_e and α_o in the nematic phase were

TABLE I

Refractive indices, density and order parameter S for PCH-3

					Vuks Method			Neugebauer's Method		
T^0C	n_o	n_e	$\rho gm/cc$	$\bar{\alpha}(\mathrm{\AA}^3)$	$\alpha_o(\mathrm{\AA}^3)$	$\alpha_e(\mathrm{\AA}^3)$	S	$\alpha_o(\mathrm{\AA}^3)$	$\alpha_e(\mathrm{\AA}^3)$	S
42	1.4912	1.5852	0.9685	28.39	26.31	32.54	0.67	26.66	31.85	0.63
42.5	1.4913	1.5842	0.9678	28.40	26.35	32.50	0.66	26.69	31.82	0.63
43	1.4920	1.5820	0.9672	28.40	26.41	32.38	0.64	26.75	31.71	0.61
43.5	1.4920	1.5814	0.9666	28.41	26.43	32.36	0.64	26.76	31.70	0.60
44	1.4928	1.5787	0.9660	28.41	26.51	32.21	0.61	26.83	31.58	0.58
44.5	1.4930	1.5775	0.9652	28.42	26.55	32.16	0.60	26.86	31.54	0.57
45	1.4936	1.5755	0.9645	28.43	26.61	32.05	0.58	26.91	31.45	0.55
46iso	1.5208		0.9576							
46.5	1.5205		0.9571							
47	1.5201		0.9567							
47.5	1.5200		0.9560							
48	1.5197		0.9555							

$\alpha_{\parallel} = 34.82$ $\alpha_{\perp} = 25.49$ $\alpha_{\parallel} = 34.06$ $\alpha_{\perp} = 25.87$

calculated using two methods, Neugebauer and Vuks and are included in the Tables (I–III). The principal polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ parallel and perpendicular to the long axis of molecules in the crystalline state were obtained from Hallers' et al.[6] graphical method. The order parameter S calculated from the relation $S = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$, are also included in Tables (I–III).

TABLE II

Refractive indices, density and order parameter S for PCH-5

					Vuks Method			Neugebauer's Method		
T^0C	n_o	n_e	$\rho gm/$cc	$\bar{\alpha}(\mathrm{\AA}^3)$	$\alpha_o(\mathrm{\AA}^3)$	$\alpha_e(\mathrm{\AA}^3)$	S	$\alpha_o(\mathrm{\AA}^3)$	$\alpha_e(\mathrm{\AA}^3)$	S
31	1.4870	1.6000	.9610	32.26	29.44	37.92	0.63	29.92	36.95	0.65
33	1.4864	1.5979	.9593	32.27	29.47	37.85	0.62	29.94	36.91	0.65
35	1.4860	1.5953	.9582	32.24	29.50	37.72	0.61	29.97	36.79	0.63
37	1.4860	1.5918	.9565	32.23	29.57	37.55	0.59	30.03	36.65	0.61
39	1.4860	1.5880	.9548	32.24	29.65	37.35	0.57	30.05	36.60	0.61
41	1.4860	1.5849	.9529	32.23	29.74	37.21	0.56	30.16	36.38	0.58
43	1.4860	1.5815	.9512	32.23	29.81	37.05	0.54	30.22	36.23	0.56
45	1.4860	1.5783	.9492	32.24	29.90	36.90	0.52	30.29	36.13	0.55
47	1.4860	1.5746	.9473	32.23	29.99	36.72	0.50	30.37	35.96	0.52
49	1.4860	1.5711	.9451	32.25	30.08	36.56	0.48	30.42	35.89	0.51
51	1.4870	1.5654	.9423	32.27	30.28	36.26	0.44	30.61	35.59	0.46
54	1.4898	1.5554	.9389	32.21				30.91	35.10	0.39
56iso	1.5105		.9336							
58	1.5095		.9317							
60	1.5081		.9300							
63	1.5075									

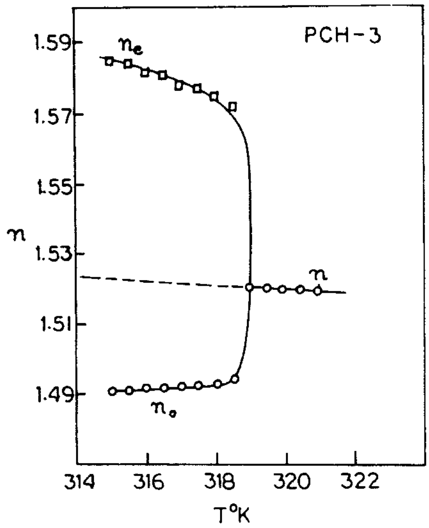
$\alpha_{\parallel} = 41.38$ $\alpha_{\perp} = 27.92$ $\alpha_{\parallel} = 39.60$ $\alpha_{\perp} = 28.81$

TABLE III

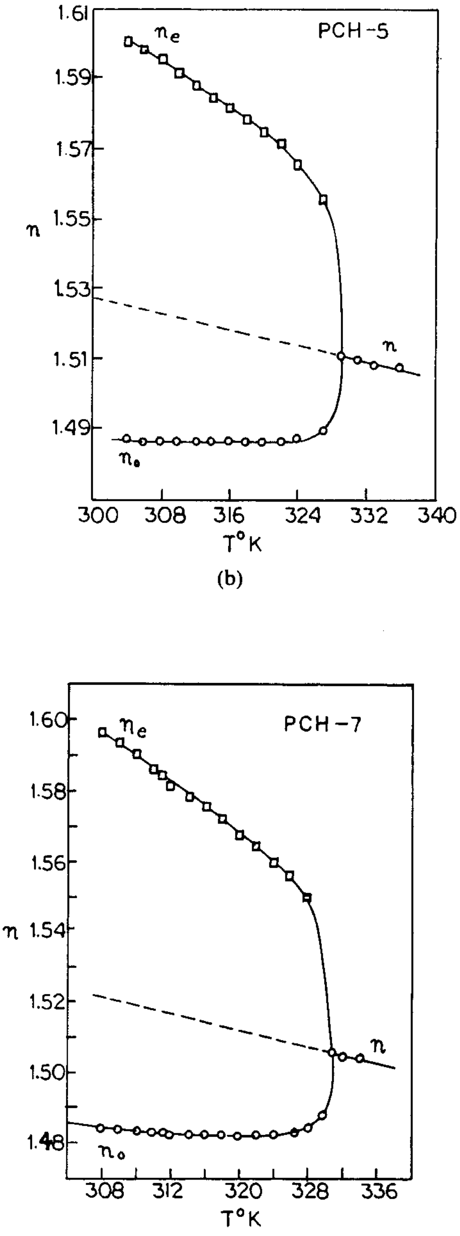
Refractive indices, density and order parameter S for PCH-7

					Vuks Method			Neugebauer's Method		
T^0C	n_o	n_e	$\rho gm/cc$	$\bar{\alpha}(\text{Å}^3)$	$\alpha_o(\text{Å}^3)$	$\alpha_e(\text{Å}^3)$	S	$\alpha_o(\text{Å}^3)$	$\alpha_e(\text{Å}^3)$	S
31	1.4840	1.5964	.9499	36.68	33.46	43.10	0.60	34.01	42.01	0.58
33	1.4838	1.5934	.9489	36.64	33.51	42.91	0.59	34.04	41.85	0.57
35	1.4836	1.5903	.9467	36.66	33.60	42.77	0.57	34.12	41.74	0.55
37	1.4832	1.5867	.9445	36.65	33.68	42.60	0.56	34.18	41.60	0.54
38	1.4830	1.5842	.9429	36.66	33.74	42.48	0.55	34.23	41.51	0.53
39	1.4825	1.5814	.9411	36.65	33.80	42.35	0.53	34.34	41.26	0.50
41	1.4822	1.5783	.9394	36.64	33.87	42.19	0.52	34.34	41.24	0.50
43	1.4820	1.5752	.9375	36.64	33.95	42.03	0.50	34.40	41.12	0.49
45	1.4820	1.5720	.9355	36.65	34.05	41.87	0.49	34.49	40.97	0.47
47	1.4820	1.5679	.9335	36.65	34.15	41.63	0.47	34.56	40.83	0.46
49	1.4820	1.5645	.9316	36.65	34.43	41.45	0.44	34.66	40.63	0.43
51	1.4822	1.5598	.9293	36.65	34.39	41.17	0.42	34.77	40.40	0.41
53	1.4830	1.5559	.9268	36.70	34.57	40.96	0.40	34.93	40.23	0.39
55	1.4842	1.5498	.9205	36.87	34.94	40.72	0.36	35.26	40.08	0.35
57	1.4876									
58iso	1.5055									
59	1.5040									
61	1.5035									

$\alpha_{11} = 47.64$ $\alpha_{\perp} = 31.62$ $\alpha_{11} = 46.14$ $\alpha_{\perp} = 32.36$



(a)



(b)

(c)

FIGURE 1a, 1b, 1c Refractive index anisotropy plots for PCH-3, PCH-5, PCH-7 respectively.

TABLE IV

Values of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and order parameter S from dielectric anisotropy values

	T^0C	$\epsilon_{\parallel}$	$\bar{\epsilon}$	$\epsilon_{\perp}$	$\Delta\epsilon$	S from $\Delta\epsilon$ values
	43	16.58		6.90	9.68	0.20
	43.5	16.21		7.02	9.19	0.19
PCH-3	44	15.98		7.06	8.92	0.18
	44.5	15.74		7.25	8.49	0.18
$\mu_D = 4.98$	45	15.51		7.49	8.02	0.17
	45 iso		10.62			
	47		10.65			
	49		10.71			
	33	14.74		4.81	9.93	0.32
	35	14.51		4.97	9.54	0.31
PCH-5	39	14.38		5.20	9.18	0.30
$\mu_D = 4.27$	43	14.23		5.40	8.83	0.29
	48	13.92		5.69	8.23	
	52	13.32		6.08	7.24	
	56 iso		8.93			
	58		9.02			
	60		9.06			
	31	12.85		4.18	8.67	0.31
	35	12.63		4.30	8.33	0.30
PHC-7	39	12.53		4.41	8.12	0.29
	43	12.37		4.53	7.84	0.29
$\mu_D = 4.39$	48	12.21		4.80	7.41	
	52	12.03		5.11	6.92	
	56	11.74		5.71	6.03	
	59 iso		8.69			
	61		8.76			
	63		8.82			

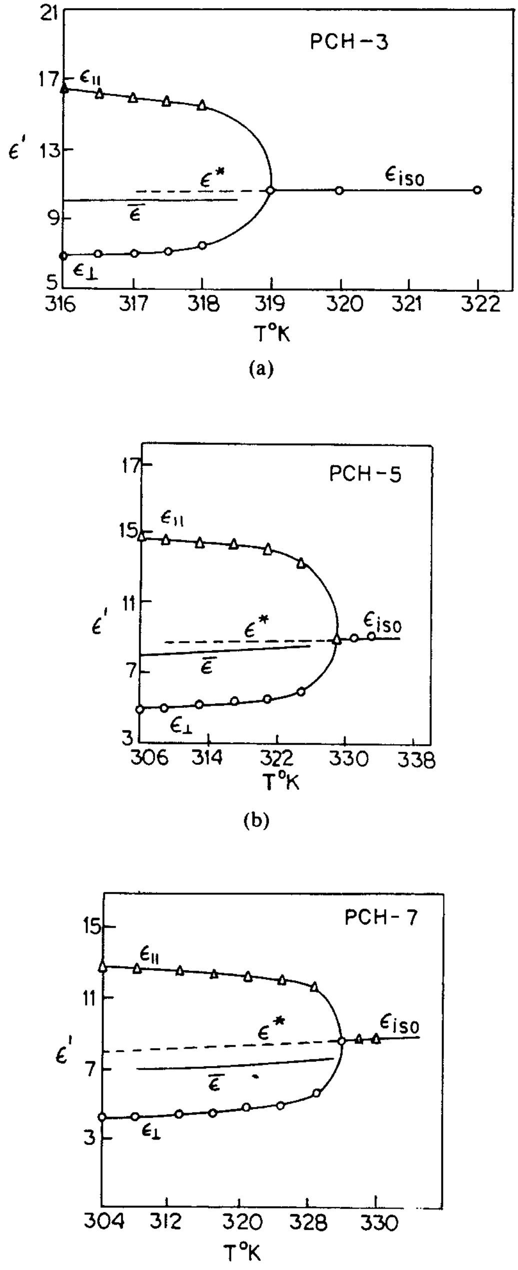
The experimental values of the dielectric permittivities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of the liquid crystals in the nematic phase are given in Table IV. The calculated values $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ obtained from the Maier and Meier equations[7] are included in Table IV.

Maier and Meiers' equations are

$$\epsilon_{\parallel} = 1 + 4\pi NhF\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1 - \left(1 - 3\,\mathrm{Cos}^2\beta\right)\right\}S\right] \qquad (1)$$

$$\epsilon_{\perp} = 1 + 4\pi NhF\left[\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1 + \frac{1}{2}\left(1 - 3\,\mathrm{Cos}^2\beta\right)\right\}S\right] \qquad (2)$$

$$\Delta\epsilon = 4\pi NhF\left[\Delta\alpha - \frac{F\mu^2}{2kT}\left(1 - 3\,\mathrm{Cos}^2\beta\right)\right]S \qquad (3)$$



(a)

(b)

(c)

FIGURE 2a, 2b, 2c Dielectric anisotropy plots for PCH-3, PCH-5, PCH-7 respectively.

where N is the number of molecules per c.c.; $h = 3\bar{\epsilon}/2\bar{\epsilon} + 1$, cavity field factor; $F = 1/1 - \bar{\alpha}f$, Reaction field factor; $f = 4\pi N(2\bar{\epsilon} - 2)/3(2\bar{\epsilon} + 1)$; μ is the dipole moment of free molecule; $\Delta\alpha$ = polarizability anisotropy; $\Delta\epsilon$ = dielectric anisotropy.

The dipole moment μ of the liquid crystals were determined in dilute solution in benzene and are included in Table IV. Dielectric anisotropy is shown in figure 2 (a, b, c).

DISCUSSION

It can be seen from Tables (I–III) that the order parameter S of the liquid crystals PCH-3, PCH-5 and PCH-7 obtained from the refractive indices data using the Neugebauer and Vuks methods are comparable. The order parameter for PCH-7 obtained in the present investigation agrees well with that obtained from dimagnetic susceptibility reported earlier.[8] It can be seen from fig. 3(a, b) that the order parameter of PCH-5 and PCH-7 at any reduced temperature $\tau = (T - T_{NI})/T_{NI}$ is less than the S-value of the corresponding Pentyl and heptylcylanobiphenyl at the same reduced temperature. It is therefore concluded that the replacement of a phenyl ring in cyanobiphenyls by a cylohexyl ring reduces the order parameter appreciably. The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ obtained in this study are fairly in agreement with those obtained by Pohl et al.[9]

From fig. 2(a, b, c) it can be seen that the average dielectric constant $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ is always less than the dielectric constant ϵ^*_{is} at $T < T_{NI}$ extrapolated in the nematic range from ϵ_{iso} at $T \geqslant T_{NI}$ in all

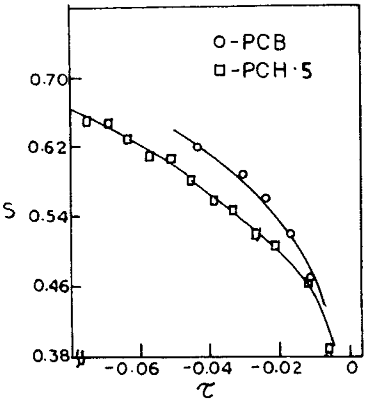


FIGURE 3a Plots of order parameter S vs. τ for PCB and PCH-5.

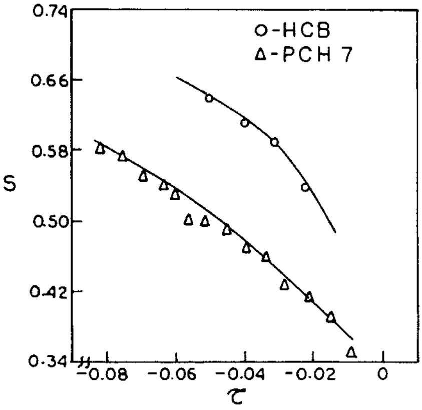


FIGURE 3b Plots of order parameter S vs. τ for HCB and PCH-7.

the PCH liquid crystals. These results are in agreement with the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ reported earlier for alkyl cyanobiphenyl,[10] P-alkoxybenzilidiene, P-aminobenzonitriles[11] which have got strong dipole moment. For liquid crystals, having small and zero dipole moment it was shown by de Jeu et al.[12] that $\bar{\epsilon}$ coincides with dielectric constant ϵ_{is} at the clearing temperature.

From these results it appears that though Maier and Meiers' theory gives qualitatively correct representation of dielectric properties in nematic liquids having small or zero dipole moment, it fails to do so in the case of strongly polar liquid crystals.

From Table V is can be seen that the experimental values of $\epsilon_{\parallel}$ is nearly half of the values of $\epsilon_{\parallel}$, calculated from Maier and Meiers' equation (1) using Polarizability α and order parameter S obtained from refractive index measurements. Similarly the value of the order parameter S calculated from experimental values of dielectric anisotropy $\Delta\epsilon$, using Maier and Meier equation (3) comes out much less than that obtained from birefringence or other methods. Similar results were also reported earlier in the case of cyanobiphenyls,

TABLE V

Comparison of $\epsilon_{\parallel}$ values obtained experimentally with $\epsilon_{\parallel}$ values calculated from birefringence data

T^0C	Expt. $\epsilon_{\parallel}$ values	$\epsilon_{\parallel}$ values calculated from birefringence data
PCH-3 43	16.58	38.60
PCH-5 33	14.74	26.80
PCH-7 31	12.85	23.10

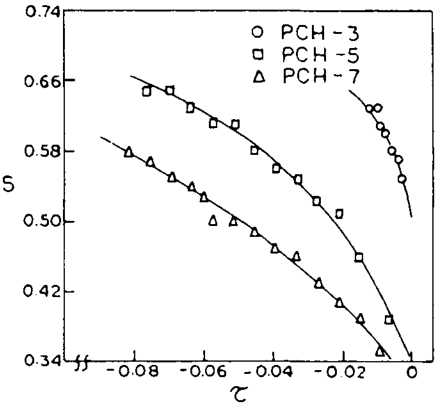


FIGURE 4 Order parameter S vs. τ for PCH-3, PCH-5, PCH-7.

cyanophenylheptylbenzoate.[5] Thus the results show that Maier and Meiers' theory for dielectric constants in anisotropic media of strongly polar molecules fails to give consistent results with the experimental values. This is due to the fact that only long range order was considered in Maier and Meiers's theory, existence of short range order was completely ignored. Madhusudan and Chandrasekhar[13] in their theory proposed the existence of antiferroelectric short range order in nematic phase of strongly polar molecules. Such short range antiparallel ordering in strongly polar nematic liquid crystals might cause a large decrease in $\epsilon_{\parallel}$, resulting in a decrease in dielectric anisotropy $\Delta\epsilon$ and thus a decrease on order parameter.

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