  Bull. Chem. Soc. Jpn., 61, 3681—3687 (1988) 

# Studies on Dielectric Permittivities, Refractive Indices for 1,1′-Bicyclohexyl Liquid Crystals in the Nematic and Isotropic Phases

Sushmita SEN, Krishnakoli KALI, and Subir K. ROY*
Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta 700032, India
(Received September 7, 1987)

The dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ and the refractive indices $n_e$, $n_o$ of five 4-cyano-4′-alkyl-1,1′-bicyclohexyls (CCH 2, CCH 3, CCH 4, CCH 5, CCH 7 where 2, 3, 4, 5, 7 means ethyl, propyl, butyl, pentyl, heptyl respectively) have been measured at different temperatures in the nematic and isotropic phases. The orientational order parameter from the refractive indices data, calculated from (1) Vuks' method and (2) Neugebauer's method were in good agreement. At any reduced temperature, the order parameter for CCH 2 is largest and that of CCH 7 is smallest and those for the others are in between them. Unlike for cyanobiphenyls or cyclohexylbenzenes, the dielectric permittivity $\varepsilon_{\parallel}$ is obtained for $\vec{E} \perp \vec{H}$ and $\varepsilon_{\perp}$ for $E \parallel H$, where $\vec{E}$ is the electric and $\vec{H}$ is the magnetic field, and has been explained as due to these molecules having negative diamagnetic anisotropy. The dielectric anisotropy, $\Delta\varepsilon$ and optical anisotropy $\Delta n$ for all the CCH's is much less than that of the corresponding CB or PCH molecules. All the CCH's show pretransitional permittivity just above the transition temperature $T_{NI}$.

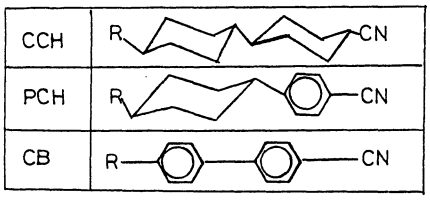
Dielectric permittivities and refractive indices of liquid crystals are required for their selection for practical uses. The data for dielectric permittivities and refractive indices for alkylcyanobiphenyls,[1-3] cyclohexylbenzenes,[4] phenylcyclohexanecarboxylates[5] have been reported earlier. Such data for CCH's are rather scanty. The object of the present investigations were to study how the dielectric properties and refractive indices change when both the phenyl rings are replaced by cyclohexyl rings.

Studies on the temperature dependence of dielectric permittivities in the isotropic phase for nematics with strong dipole moments show pretransitional effects while in nonpolar nematics pretransitional effect is absent.[5,6] It was thought worthwhile to study the pretransitional effects in dielectric permittivity in the isotropic phase of 1,1′-bicyclohexyl liquid crystals. The results are discussed in this paper.

## Experimental

Five CCH liquid crystals (CCH 2, CCH 3, CCH 4, CCH 5, CCH 7) procured from E. Merck, Germany were used in the investigations without further purification. Mesomorphic range of the samples,

| Sample | Nematic range/°C |
|---|---|
| CCH 2 (4-cyano-4′-ethyl-1,1′-bicyclohexyl) | 46—49 |
| CCH 3 (4-cyano-4′-propyl-1,1′-bicyclohexyl) | 50—80 |
| CCH 4 (4-cyano-4′-butyl-1,1′-bicyclohexyl) | 54—79 |
| CCH 5 (4-cyano-4′-pentyl-1,1′-bicyclohexyl) | 62—85 |
| CCH 7 (4-cyano-4′-heptyl-1,1′-bicyclohexyl) | 71—83 |



R=alkyl group

**Measurement of Refractive Indices.** The method of measurement of the refractive indices $n_e$, $n_o$ for the extraordinary and ordinary rays with the help of ABBE refractometer and density measurements by means of capillary tube were de-

Table 1. Refractive Indices, Density, Polarizabilities and Order Parameter for CCH

| $T$/°C | $\rho$/ g ml$^{-1}$ | $n_o$ | $n_e$ | $\bar{\alpha}$ | Vuks' method | | | Neugebauer's method | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Å$^3$ | $\alpha_o$/Å$^3$ | $\alpha_e$/Å$^3$ | $S$ | $\alpha_o$/Å$^3$ | $\alpha_e$/Å$^3$ | $S$ |
| (a) CCH 2 | | | | | | | | | | |
| 46 | 0.925 | 1.4661 | 1.4959 | 26.486 | 25.822 | 27.806 | 0.62 | 25.903 | 27.652 | 0.65 |
| 46.5 | 0.924 | 1.4661 | 1.4953 | 26.498 | 25.846 | 27.791 | 0.60 | 25.922 | 27.648 | 0.64 |
| 47 | 0.923 | 1.4662 | 1.4942 | 26.503 | 25.878 | 27.744 | 0.58 | 25.950 | 27.607 | 0.62 |
| 47.5 | 0.923 | 1.4663 | 1.4934 | 26.507 | 25.903 | 27.709 | 0.56 | 25.968 | 27.586 | 0.60 |
| 48 | 0.922 | 1.4668 | 1.4919 | 26.518 | 25.959 | 27.605 | 0.52 | 26.025 | 27.503 | 0.55 |
| 49 | 0.919 | 1.4748 | | | | | | | | |
| 49.5 | 0.918 | 1.4746 | | | | | | | | |
| 50 | 0.918 | 1.4742 | | | | | | | | |
| 50.5 | 0.917 | 1.4741 | | | | | | | | |
| 51 | 0.917 | 1.4740 | | | | | | | | |
| 53.5 | 0.915 | 1.4729 | | | $\alpha_{\perp}$= | $\alpha_{\parallel}$= | | $\alpha_{\perp}$= | $\alpha_{\parallel}$= | |
| 55.5 | 0.913 | 1.4720 | | | 25.532 | 28.726 | | 25.703 | 28.384 | |

Table 1. (Continued)

| $T$/°C | $\rho$/ g ml$^{-1}$ | $n_o$ | $n_e$ | $\bar{\alpha}$ | Vuks' method | | | Neugebauer's method | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Å$^3$ | $\alpha_o$/Å$^3$ | $\alpha_e$/Å$^3$ | $S$ | $\alpha_o$/Å$^3$ | $\alpha_e$/Å$^3$ | $S$ |
| (b) CCH 3 | | | | | | | | | | |
| 58.5 | 0.915 | 1.4590 | 1.5056 | 28.416 | 27.303 | 30.644 | 0.65 | 27.479 | 30.291 | 0.66 |
| 62 | 0.912 | 1.4578 | 1.5029 | 28.407 | 27.326 | 30.569 | 0.63 | 27.492 | 30.238 | 0.64 |
| 64 | 0.910 | 1.4575 | 1.5014 | 28.431 | 27.375 | 30.537 | 0.61 | 27.528 | 30.239 | 0.63 |
| 66.5 | 0.908 | 1.4567 | 1.4991 | 28.422 | 27.401 | 30.461 | 0.59 | 27.556 | 30.154 | 0.61 |
| 68.5 | 0.906 | 1.4564 | 1.4968 | 28.428 | 27.453 | 30.375 | 0.56 | 27.597 | 30.090 | 0.58 |
| 70.5 | 0.905 | 1.4560 | 1.4949 | 28.442 | 27.499 | 30.317 | 0.54 | 27.622 | 30.081 | 0.57 |
| 73 | 0.902 | 1.4553 | 1.4930 | 28.452 | 27.538 | 30.275 | 0.53 | 27.669 | 30.020 | 0.55 |
| 76 | 0.900 | 1.4546 | 1.4900 | 28.452 | 27.594 | 30.171 | 0.50 | 27.731 | 29.895 | 0.51 |
| 78 | 0.898 | 1.4545 | 1.4878 | 28.469 | 27.658 | 30.084 | 0.47 | 27.776 | 29.854 | 0.49 |
| 80.5 | 0.896 | 1.4548 | 1.4834 | 28.464 | 27.764 | 29.855 | 0.40 | 27.865 | 29.662 | 0.42 |
| 82.5 | 0.889 | 1.4635 | | | | | | | | |
| 85 | 0.887 | 1.4625 | | | | | | | | |
| 87 | 0.885 | 1.4615 | | | $\alpha_\perp$= | $\alpha_\parallel$= | | $\alpha_\perp$= | $\alpha_\parallel$= | |
| 89 | 0.884 | 1.4605 | | | 26.910 | 32.093 | | 27.212 | 31.490 | |
| (c) CCH 4 | | | | | | | | | | |
| 56 | 0.9109 | 1.4650 | 1.5081 | 30.503 | 29.407 | 32.695 | 0.64 | 29.601 | 32.305 | 0.61 |
| 58 | 0.9092 | 1.4642 | 1.5070 | 30.517 | 29.418 | 32.692 | 0.64 | 29.572 | 32.409 | 0.64 |
| 60 | 0.9066 | 1.4635 | 1.5048 | 30.540 | 29.481 | 32.645 | 0.62 | 29.607 | 32.404 | 0.63 |
| 64 | 0.9041 | 1.4616 | 1.5026 | 30.516 | 29.466 | 32.606 | 0.61 | 29.576 | 32.394 | 0.63 |
| 68 | 0.9005 | 1.4600 | 1.4998 | 30.518 | 29.496 | 32.583 | 0.60 | 29.678 | 32.199 | 0.63 |
| 76 | 0.8928 | 1.4554 | 1.4973 | 30.573 | 29.477 | 32.744 | 0.61 | 29.605 | 32.507 | 0.57 |
| 78 | 0.8909 | 1.4558 | 1.4939 | 30.582 | 29.593 | 32.560 | 0.58 | 29.742 | 32.267 | 0.57 |
| 79 | 0.8858 | 1.4680 | | | | | | | | |
| 80 | 0.8850 | 1.4676 | | | | | | | | |
| 82 | 0.8836 | 1.4663 | | | | | | | | |
| 83 | 0.8826 | 1.4650 | | | | | | | | |
| 85 | 0.8812 | 1.4644 | | | | | | | | |
| 87 | 0.8799 | 1.4640 | | | | | | | | |
| 90 | 0.8783 | 1.4620 | | | $\alpha_\perp$= | $\alpha_\parallel$= | | $\alpha_\perp$= | $\alpha_\parallel$= | |
| 92 | 0.8762 | 1.4616 | | | 29.013 | 34.152 | | 29.255 | 33.666 | |
| (d) CCH 5 | | | | | | | | | | |
| 68 | 0.906 | 1.4580 | 1.5093 | 32.516 | 30.796 | 34.960 | 0.64 | 31.018 | 35.514 | 0.64 |
| 72 | 0.902 | 1.4568 | 1.5061 | 32.198 | 30.861 | 34.876 | 0.62 | 31.076 | 34.440 | 0.61 |
| 76 | 0.898 | 1.4560 | 1.5020 | 32.218 | 30.963 | 34.726 | 0.58 | 31.151 | 34.353 | 0.58 |
| 78 | 0.897 | 1.4560 | 1.4991 | 32.226 | 31.048 | 34.580 | 0.54 | 31.223 | 34.231 | 0.55 |
| 81 | 0.894 | 1.4568 | 1.4931 | 32.238 | 31.231 | 34.259 | 0.46 | 31.396 | 33.923 | 0.46 |
| 83 | 0.892 | 1.4575 | 1.4823 | 32.252 | 31.378 | 33.999 | 0.40 | 31.511 | 33.733 | 0.41 |
| 85 | 0.884 | 1.4675 | | | | | | | | |
| 86 | 0.883 | 1.4665 | | | | | | | | |
| 87 | 0.883 | 1.4660 | | | | | | | | |
| 88 | 0.882 | 1.4655 | | | | | | | | |
| 89 | 0.881 | 1.4650 | | | $\alpha_\perp$= | $\alpha_\parallel$= | | $\alpha_\perp$= | $\alpha_\parallel$= | |
| 92 | 0.880 | 1.4640 | | | 30.327 | 36.850 | | 30.672 | 36.161 | |
| (e) CCH 7 | | | | | | | | | | |
| 71 | 0.893 | 1.4558 | 1.5009 | 35.858 | 34.487 | 38.600 | 0.52 | 34.713 | 38.157 | 0.54 |
| 72 | 0.892 | 1.4554 | 1.4997 | 35.843 | 34.500 | 38.539 | 0.51 | 34.716 | 38.103 | 0.53 |
| 73 | 0.891 | 1.4552 | 1.4980 | 35.843 | 34.542 | 38.449 | 0.49 | 34.751 | 38.026 | 0.52 |
| 74 | 0.890 | 1.4550 | 1.4966 | 35.842 | 34.573 | 38.374 | 0.48 | 34.758 | 38.009 | 0.51 |
| 75 | 0.889 | 1.4548 | 1.4952 | 35.840 | 34.607 | 38.302 | 0.47 | 34.786 | 37.948 | 0.50 |
| 76 | 0.888 | 1.4546 | 1.4936 | 35.838 | 34.652 | 38.220 | 0.45 | 34.849 | 37.816 | 0.47 |
| 77 | 0.887 | 1.4544 | 1.4919 | 35.822 | 34.678 | 38.114 | 0.43 | 34.859 | 37.748 | 0.45 |
| 78 | 0.886 | 1.4542 | 1.4905 | 35.826 | 34.717 | 38.102 | 0.43 | 34.894 | 37.689 | 0.44 |
| 79 | 0.885 | 1.4540 | 1.4891 | 35.840 | 34.764 | 37.987 | 0.40 | 34.915 | 37.689 | 0.44 |
| 80 | 0.884 | 1.4538 | 1.4874 | 35.841 | 34.810 | 37.902 | 0.39 | 34.959 | 37.605 | 0.42 |
| 81 | 0.883 | 1.4537 | 1.4859 | 35.851 | 34.862 | 37.828 | 0.37 | 35.004 | 37.547 | 0.40 |
| 82 | 0.880 | 1.4536 | | | | | | | | |
| 84 | 0.877 | 1.4625 | | | | | | | | |
| 87 | 0.875 | 1.4604 | | | $\alpha_\perp$= | $\alpha_\parallel$= | | $\alpha_\perp$= | $\alpha_\parallel$= | |
| 89 | 0.873 | 1.4592 | | | 33.311 | 41.229 | | 33.833 | 40.184 | |

Table 2. Dielectric Permittivities of CCH

| $T$/°C | $\varepsilon_{\parallel}$ | $\varepsilon_{iso}$ | $\varepsilon_{\perp}$ | $\bar{\varepsilon}$ |
|---|---|---|---|---|
| (a) CCH 2 | | | | |
| 46.5 | 9.85 | | 5.696 | 7.081 |
| 47 | 9.782 | | 5.757 | 7.099 |
| 47.5 | 9.760 | | 5.869 | 7.166 |
| 48 | 9.684 | | 5.892 | 7.156 |
| 48.5 | 9.440 | | 5.939 | 7.106 |
| 50 | | 7.503 | | |
| 51 | | 7.562 | | |
| 52 | | 7.603 | | |
| 53 | | 7.624 | | |
| 54 | | 7.607 | | |
| 55 | | 7.532 | | |
| 56 | | 7.503 | | |
| 60 | | 7.382 | | |
| (b) CCH 3 | | | | |
| 58 | 9.419 | | 4.673 | 6.255 |
| 60 | 9.598 | | 4.732 | 6.354 |
| 62 | 9.725 | | 4.863 | 6.484 |
| 64 | 10.015 | | 4.905 | 6.608 |
| 66.5 | 10.184 | | 5.099 | 6.794 |
| 68.5 | 10.112 | | 5.185 | 6.827 |
| 70.5 | 10.094 | | 5.385 | 6.955 |
| 73 | 9.998 | | 5.459 | 6.972 |
| 76 | 9.968 | | 5.593 | 7.051 |
| 78 | 9.953 | | 5.702 | 7.119 |
| 79 | 9.490 | | 5.722 | 6.978 |
| 80.5 | | 7.855 | | |
| 82.5 | | 7.916 | | |
| 83 | | 8.207 | | |
| 84 | | 8.024 | | |
| 85 | | 7.959 | | |
| 86 | | 7.554 | | |
| 88 | | 7.463 | | |
| 90 | | 7.340 | | |
| (c) CCH 4 | | | | |
| 56 | 8.871 | | 4.361 | 5.864 |
| 58 | 8.876 | | 4.404 | 5.895 |
| 60 | 9.119 | | 4.386 | 5.964 |
| 64 | 9.119 | | 4.592 | 6.101 |
| 68 | 9.120 | | 4.635 | 6.130 |
| 72 | 9.117 | | 4.893 | 6.301 |
| 76 | 9.037 | | 5.049 | 6.378 |
| 78 | 8.934 | | 5.467 | 6.623 |
| 79 | 8.869 | | 5.472 | 6.604 |
| 80 | 8.741 | | 5.474 | 6.563 |
| 82 | | 7.072 | | |
| 83 | | 7.108 | | |
| 85 | | 7.159 | | |
| 87 | | 7.152 | | |
| 90 | | 7.146 | | |
| 92 | | 7.110 | | |
| (d) CCH 5 | | | | |
| 51 | 8.586 | | 4.365 | 5.772 |
| 56 | 8.910 | | 4.371 | 5.884 |
| 60 | 8.992 | | 4.479 | 5.983 |
| 65 | 9.146 | | 4.631 | 6.136 |
| 69 | 9.214 | | 4.723 | 6.220 |
| 73 | 9.251 | | 4.753 | 6.252 |
| 77 | 9.279 | | 4.832 | 6.314 |
| 81 | 9.333 | | 4.951 | 6.412 |
| 84 | 8.752 | | 5.412 | 6.525 |
| 85 | | 6.596 | | |
| 87 | | 6.779 | | |
| 88 | | 7.173 | | |
| 89 | | 7.341 | | |
| 90 | | 7.337 | | |
| 91 | | 7.328 | | |
| 93 | | 7.319 | | |
| 96 | | 7.298 | | |
| (e) CCH 7 | | | | |
| 74 | 7.169 | | 3.888 | 4.982 |
| 75 | 7.181 | | 3.963 | 5.036 |
| 76 | 7.175 | | 4.020 | 5.072 |
| 77 | 7.182 | | 4.045 | 5.091 |
| 78 | 7.155 | | 4.067 | 5.096 |
| 79 | 7.132 | | 4.050 | 5.077 |
| 80 | 6.939 | | 4.037 | 5.004 |
| 82 | 6.919 | | 4.022 | 4.988 |
| 83 | 6.490 | | 4.036 | 4.854 |
| 84 | 6.444 | | 3.985 | 4.805 |
| 86 | 5.895 | | 4.246 | 4.796 |
| 87 | | 4.891 | | |
| 88 | | 4.919 | | |
| 89 | | 4.925 | | |
| 90 | | 4.873 | | |
| 91 | | 4.849 | | |
| 93 | | 4.821 | | |
| 94 | | 4.806 | | |
| 96 | | 4.799 | | |
| 98 | | 4.796 | | |

scribed elaborately in an earlier publication.[7]

**Measurement of Dielectric Permittivities.** The dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ polarized parallel and perpendicular to the long molecular axes of the liquid crystals were measured at 1 kHz with a GR-1620 capacitance bridge using a capacitor of stainless steel electrodes of radius 1 cm separated by a 1 mm thick Teflon spacer. A magnetic field of 1.0 T was used to allign the molecules of the liquid crystals parallel and perpendicular to the electrode surfaces. The temperature of the sample was measured with a thermocouple mounted directly on one of the electrodes. The temperature of the cell was maintained constant within ±0.02 °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.

## Results

The experimental values of refractive indices $n_e$, $n_o$ and the densities of the liquid crystals at different temperatures are given in Table 1. The effective polarizabilities $\alpha_e$ and $\alpha_o$ in the nematic phase calculated by using two methods Vuks[8] and Neugebauer[9] are included in Table 1. The principal polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ parallel and perpendicular to the long axis of the molecules in the crystalline state were obtained from Hallers' et al.[10] graphical method. The orientational order parameters $S$ were calculated from the relation $S=(\alpha_e-\alpha_o)/(\alpha_{\parallel}-\alpha_{\perp})$ and are included in Table 1.

Table 3a. Values of the Dielectric Anisotropy of CCH Compounds at Different Reduced Temperature

| CCH 2 | | CCH 4 | | CCH 7 | |
|---|---|---|---|---|---|
| $T/T_{NI}$ | $\Delta\varepsilon$ | $T/T_{NI}$ | $\Delta\varepsilon$ | $T/T_{TN}$ | $\Delta\varepsilon$ |
| 0.989 | 4.154 | 0.927 | 4.510 | 0.964 | 3.281 |
| 0.991 | 4.025 | 0.932 | 4.472 | 0.967 | 3.218 |
| 0.992 | 3.891 | 0.949 | 4.527 | 0.972 | 3.137 |
| 0.994 | 3.792 | 0.961 | 4.485 | 0.975 | 3.088 |
| 0.995 | 3.501 | 0.972 | 4.224 | 0.981 | 2.902 |
| | | 0.989 | 3.467 | 0.989 | 2.454 |
| | | 0.992 | 3.397 | 0.997 | 1.649 |
| | | 0.994 | 3.267 | | |

Table 3b. Values of the Dielectric Ansotropy of CB 7, PCH 7, and CCH 7 at Different Reduced Temperature

| CB 7 | | PCH 7 | | CCH 7 | |
|---|---|---|---|---|---|
| $T/T_{NI}$ | $\Delta\varepsilon$ | $T/T_{NI}$ | $\Delta\varepsilon$ | $T/T_{NI}$ | $\Delta\varepsilon$ |
| 0.930 | 12.1 | 0.930 | 8.12 | 0.964 | 3.28 |
| 0.955 | 11.7 | 0.954 | 7.84 | 0.972 | 3.14 |
| 0.970 | 11.1 | 0.967 | 7.41 | 0.975 | 3.09 |
| 0.980 | 10.3 | 0.980 | 6.92 | 0.980 | 2.90 |
| 0.995 | 8.6 | 0.990 | 6.03 | 0.992 | 2.46 |

Table 4a. Values of the Order Parameter of CCH Compounds at Different Reduced Temperature

| CCH 2 | | CCH 4 | | CCH 7 | |
|---|---|---|---|---|---|
| $T/T_{NI}$ | $S$ | $T/T_{NI}$ | $S$ | $T/T_{NI}$ | $S$ |
| 0.991 | 0.65 | 0.935 | 0.61 | 0.969 | 0.54 |
| 0.992 | 0.64 | 0.940 | 0.64 | 0.971 | 0.53 |
| 0.994 | 0.62 | 0.957 | 0.63 | 0.977 | 0.51 |
| 0.995 | 0.60 | 0.969 | 0.63 | 0.980 | 0.50 |
| 0.997 | 0.55 | 0.991 | 0.57 | 0.983 | 0.47 |
| | | | | 0.989 | 0.45 |
| | | | | 0.994 | 0.42 |

Table 4b. Values of the Order Parameter of CB 7, PCH 7, and CCH 7 at Different Reduced Temperature

| CB 7 | | PCH 7 | | CCH 7 | |
|---|---|---|---|---|---|
| $T/T_{NI}$ | $S$ | $T/T_{NI}$ | $S$ | $T/T_{NI}$ | $S$ |
| 0.950 | 0.62 | 0.948 | 0.50 | 0.969 | 0.54 |
| 0.959 | 0.58 | 0.954 | 0.49 | 0.971 | 0.53 |
| 0.968 | 0.56 | 0.967 | 0.46 | 0.977 | 0.51 |
| 0.978 | 0.52 | 0.979 | 0.41 | 0.980 | 0.50 |
| | | 0.985 | 0.39 | 0.983 | 0.47 |
| | | | | 0.989 | 0.44 |
| | | | | 0.994 | 0.42 |

## Discussion

The values of the dielectric anisotropy, $\Delta\varepsilon$, Table 3b, Fig. 4b for CB,[11] PCH,[4] and CCH compounds in the present paper shows that $\Delta\varepsilon$ gradually decreases from CB to PCH to CCH by the progressive replacement of one phenyl ring in PCH and both the phenyl rings in the CCH compounds by cyclohexyl groups. This may be attributed to the decrease in the degree of conjuga-

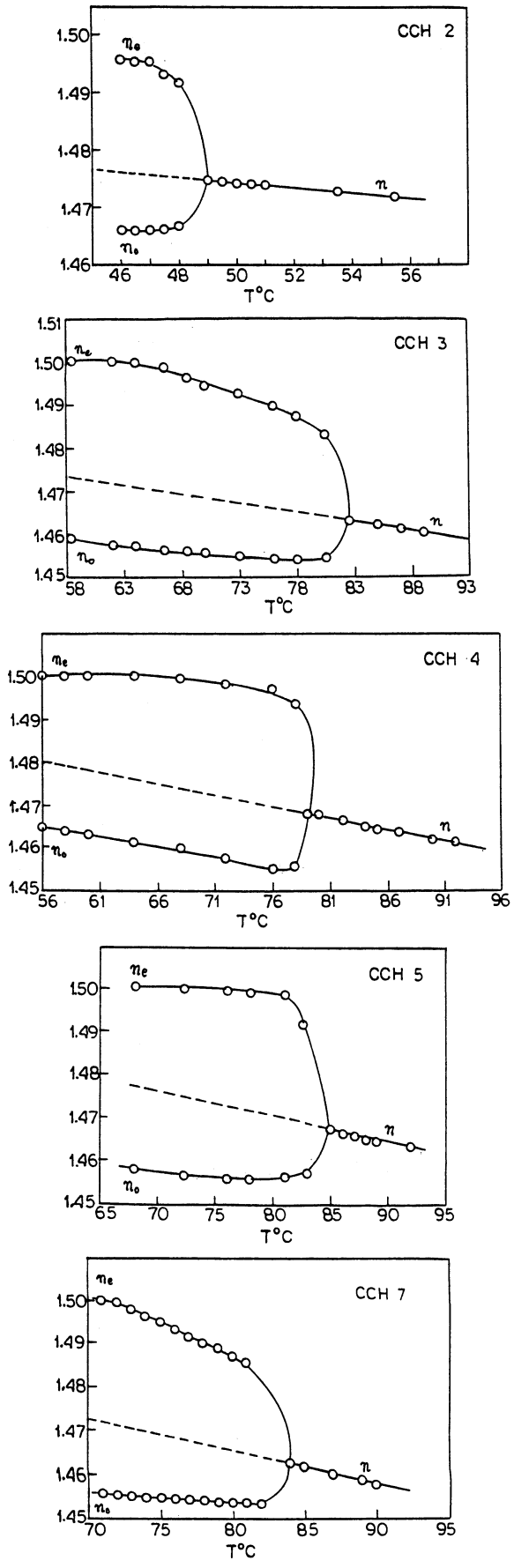



Fig. 1. Refractive index anisotropy plots for CCH 2, CCH 3, CCH 4, CCH 5, CCH 7 respectively.

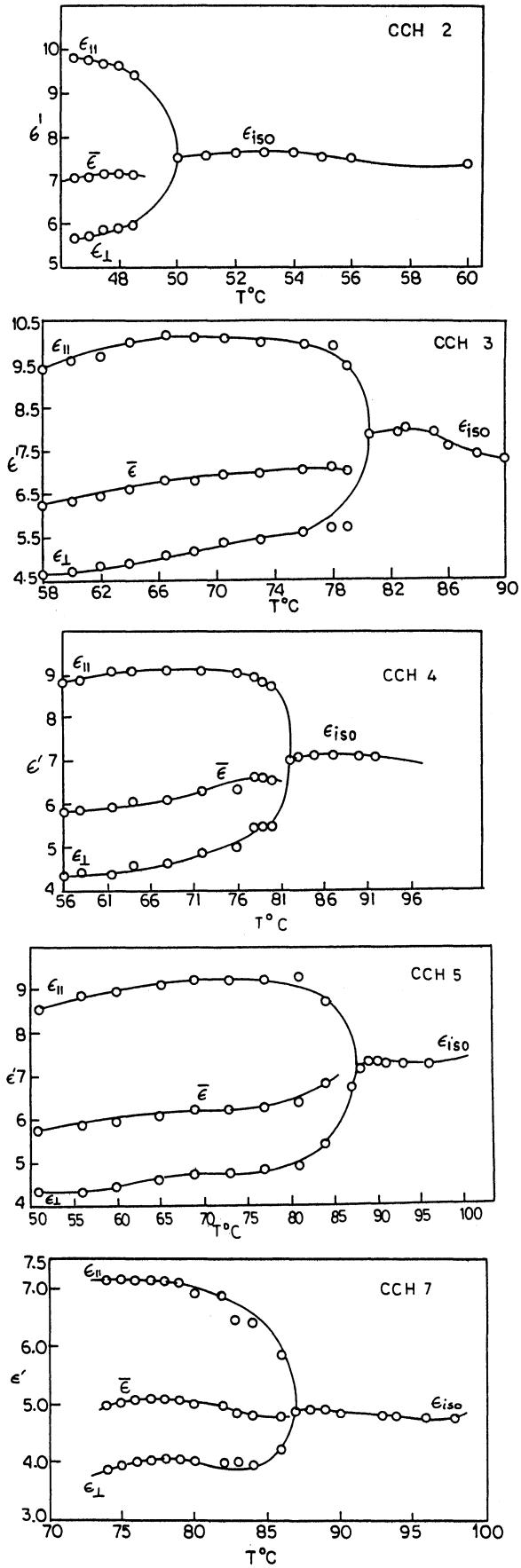



Fig. 2. Dielectric anisotropy plots for CCH 2, CCH 3, CCH 4, CCH 5, CCH 7 respectively.

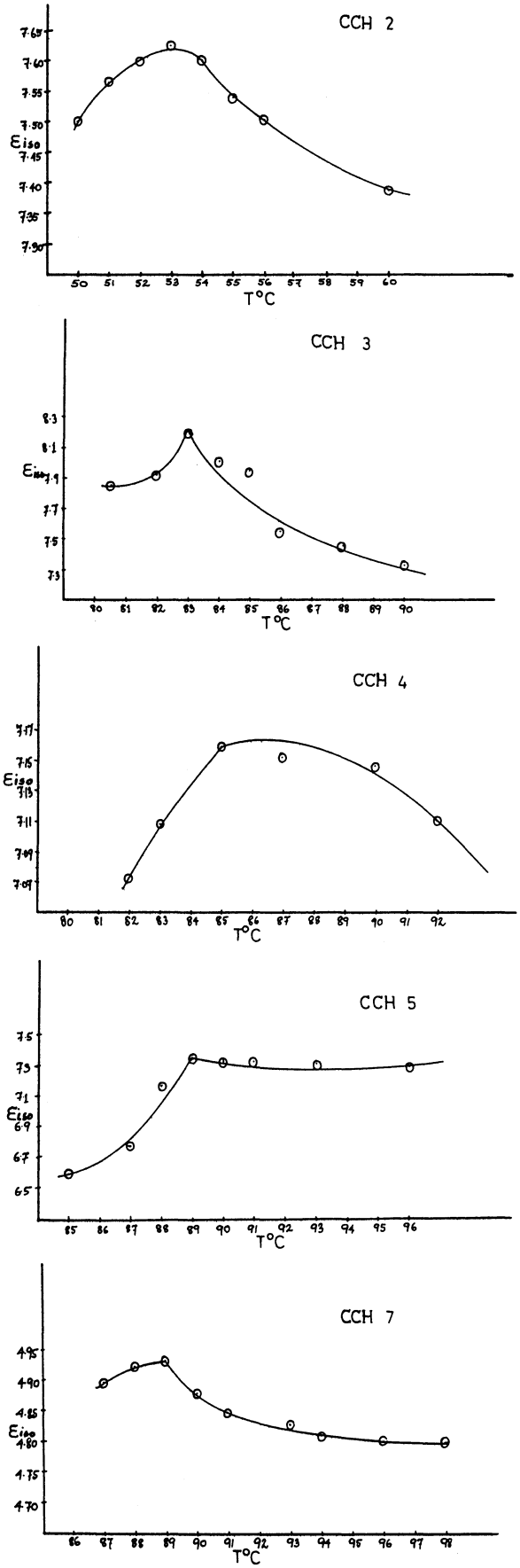



Fig. 3. Pretransition effect plots for CCH 2, CCH 3, CCH 4, CCH 5, CCH 7 respectively.

tion by progressive replacement of phenyl rings. This decrease of conjugation is more pronounced in the CCH compounds which are completely lacking in free $\pi$ electrons.

The values of $\Delta\varepsilon$ within the CCH compounds, Table 3a, Fig. 4a, decreases with the increase of chain length which is also found in the case of PCH compounds by Schad et al.[11]

Schad[11] found that the experimental data for the PCH compounds hold the relation $\Delta\varepsilon(t_r) \alpha S(t_r)$, considering only the contribution of the predominant dipolar part of the dielectric polarization to $\Delta\varepsilon$, though one would expect that $S(t_r)/T$ should depend on $\Delta\varepsilon$. A possible explanation of the result was given[1] by a model of antiparallel dipole correlation.

In the case of the CCH compounds (Fig. 5a) the decrease of order parameter at any reduced temperature, with the increase of alkyl chain length may also be explained from the above relation.

From Table 1a—e, it can be seen that the order parameter $S$ for each of the CCH liquid crystals evaluated from refractive indices and density data using Vuks' and Neugebauer's methods are in good agreement. Figure 5a, a comparison of the order parameter of the CCH liquid crystals at any common reduced temperature, $t_r=T/T_{NI}$, shows that the order parameter of CCH 2 is the largest and that for CCH 7 is the smallest and those for others are in between them. It appears that the larger the alkyl chain length the smaller is the order parameter.

The values of the order parameters at any reduced temperature $t_r$ in CB, is the largest and in PCH is the smallest, Fig. 5b. But in the case of CCH compounds it is nearer to that of the CB compounds but greater than that for PCH. This cannot be explained from the above relation.[11]

The antiparallel local ordering in CCH compounds found by X-ray measurement[12] corresponds to the overlap of cyano group, which is quite different from

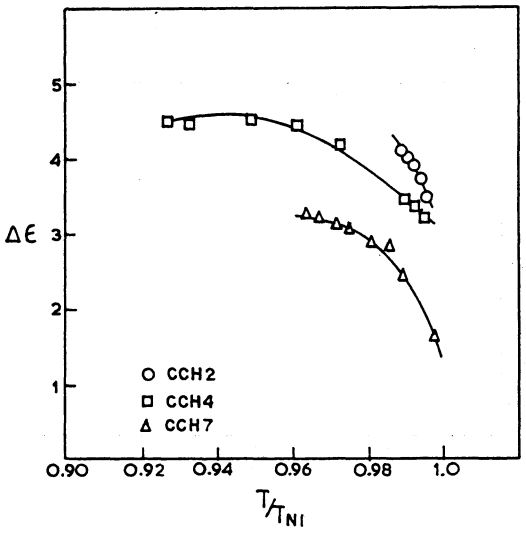



Fig. 4(a). Plots of $\Delta\varepsilon$ vs. $T/T_{NI}$ for CCH 2, CCH 4, CCH 7.

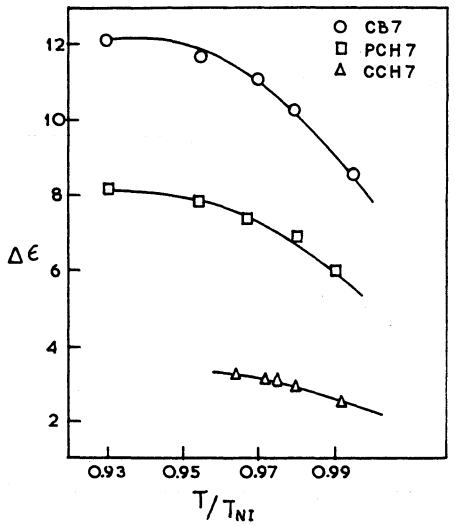



Fig. 4(b). Plots of $\Delta\varepsilon$ vs. $T/T_{NI}$ for CB 7, PCH 7, CCH 7.

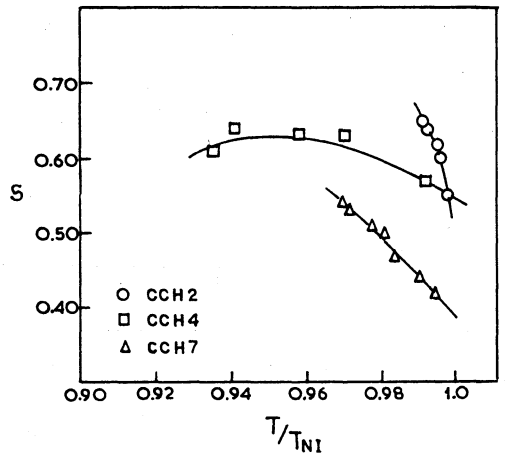



Fig. 5(a). Plots of $S$ vs. $T/T_{NI}$ for CCH 2, CCH 4, CCH 7.

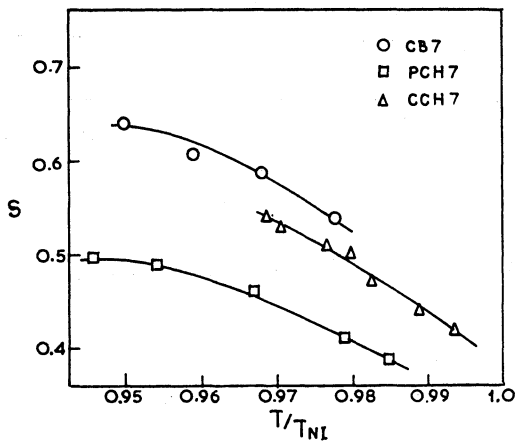



Fig. 5(b). Plots of $S$ vs. $T/T_{NI}$ for CB 7, PCH 7, CCH 7.

the core overlap in the case of CB and PCH compounds. This type of different local ordering in CCH compounds must affect the value of the order parameter and this may be the cause of the unexpected value of the order parameter in the CCH compound.

This type of unexpected observation of the ratio of Bend/splay ($k_{33}/k_{11}$) value of the elastic constant of the CCH compounds was found by Bradshaw et al.[5]

It is to be noted that for all the CCH liquid crystals, the dielectric permittivity $\varepsilon_{\parallel}$ is obtained for $\vec{E} \perp \vec{H}$ and $\varepsilon_{\perp}$ is obtained when $\vec{E} \parallel \vec{H}$ unlike the cyanobiphenyls, cyclohexylbenzenes, and other thermotropic liquid crystals, all of which have positive diamagnetic anisotropy. 1,1′-Bicyclohexyls have got negative diamagnetic anisotropy as was shown by Schad[11] in CCH 7 ($\Delta\chi=-2\times10^{-8}$ cm$^3$ g$^{-1}$). The negative diamagnetic anisotropy in CCH 5 was also confirmed by Pohl et al.[12] from the studies of the dependence of electric threshold voltage and switching time of a twisted layer of CCH 5, with the strength of the magnetic fleld.

Because of the negative anisotropy of the susceptibility, the CCH molecules orient themselves with the long molecular axis perpendicular to the magnetic field and this is why dielectric permittivity $\varepsilon_{\parallel}$ is obtained when $\vec{E} \perp \vec{H}$.

The anisotropy of the dielectric permittivity of the CCH's are shown in Fig. 2a—e. The average value of the dielectric permittivities $\bar{\varepsilon}$; shown in Table 2a—e in each case is found to increase with increase in temperature and is discontinuous with the isotropic value $\varepsilon_{iso}$ at $T_{NI}$, Fig. 2a—e. This indicates the presence of strong antiparallel local ordering of the CCH molecules in the nematic phase in strongly polar molecules as reported earlier.[13]

Temperature dependence of dielectric permittivity $\varepsilon_{iso}$ for the CCH liquid crystals in the isotropic phase is shown in Fig. 3a—e. It can be clearly seen that there is a peak in $\varepsilon_{iso}$, a little above the transition temperature $T_{NI}$. Such pretransition effects in dielectric permittivity in nematics with cyano end groups were reported by Bradshaw and Raynes,[5] Theon and Menu,[6] and recently by Krishnakoli et al.[14] The reduced contribution to dielectric permittivity $\varepsilon_{iso}$ from dipole moment $\mu$ was attributed to apparent reduction in $\mu$-values due to formation of dimers in antiparallel local ordering.[15] The pretransition in $\varepsilon_{iso}$ near $T_{NI}$ showing a maximum was explained as due to appreciable concentration of dimers in a dynamic dimer-monomer equilibrium.

## References

1) S. Sen, P. Brahma, S. K. Roy, D. K. Mukherjee, and S. B. Roy, *Mol. Cryst. Liq. Cryst.*, **100**, 327 (1983).
2) S. Sen, P. Brahma, S. K. Roy, and S. B. Roy, *Acta Physica Polonica*, **A65**, 47 (1984).
3) B. R. Ratna and R. Sashidhar, *Pramana*, **6**, 278 (1976).
4) S. Sen, K. Kali, S. K. Roy, and S. B. Roy, *Mol. Cryst. Liq. Cryst.*, **126**, 269 (1985).
5) M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **L72**, 73 (1981).
6) J. Theon and G. Menu, *Mol. Cryst. Liq. Cryst.*, **97**, 163 (1983).
7) K. Kali, S. Sen, and S. K. Roy, *Bull. Chem. Soc. Jpn.*, **58**, 3576 (1985).
8) M. F. Vuks, *Opt. Spectrosk*, **20**, 361 (1966).
9) H. E. J. Neugebauer, *Can. J. Phys.*, **32**, 1 (1954).
10) I. Haller, H. A. Huggins, H. R. Lilienthal, and T. R. McGuire, *J. Phys. Chem.*, **77**, 950 (1973).
11) Hp. Schad, G. Baur, and G. Meier, *J. Chem. Phys.*, **71**, 3174 (1979).
12) L. Pohl, R. Eidenchink, J. Krause, and G. Weber, *Phys. Lett.*, **65A**, 169 (1978).
13) N. V. Madhusudan and S. Chandrasekhar, Proc. International Conf. Liq. Cryst, Bangalore (1973), p. 427.
14) K. Kali, S. Sen, and S. K. Roy, *Acta Physica Polonica*, in press (1987).
15) L. Longa and W. H. de Jeu, *Phys. Rev. A*, **26**, 1632 (1982).