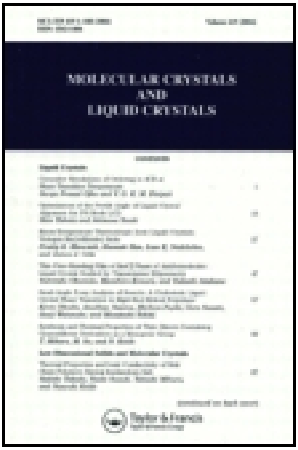

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DIELECTRIC ANISOTROPY IN NEMATIC OF p-CYANO-p'-ALKYLPHENYLCYCLOHEXANES

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Abstract Anisotropy of static electric permittivities of the homologous series of p-cyano-p'-alkylphenylcyclohexanes (PCH) have been measured as a function of temperature in isotropic and nematic phases. The mean square effective dipole moment components along the principal directions of a liquid crystal have been determined. The Kirkwood correlation factors $g_{(i)}$, obtained from Maier and Meier equations, exhibit the odd-even alteration within the studied series. The g-factors values have been interpreted in terms of an anti-parallel association.

INTRODUCTION

Molecular association is one of the dipolar forces manifestation, which results in an anti-parallel aggregation of molecules. The dipole-dipole interactions, together with the flexible aliphatic chain attached to the rigid rod-like mesogenic molecules, are essential for stabilization of nematic phase. Most macroscopic parameters of liquid crystals show a characteristic alteration as a function of the number of the aliphatic chain segments, i.e. the well-known odd-even effect[1-5].

In the paper we report the results of static dielectric polarization studies for the homologous series of PCH (C_nH_{2n+1}-C_6H_{10}-Ph-C≡N for n=3 to 9) in both isotropic and nematic phases. The aim of the paper is to analyze the odd-even effects of dielectric properties in terms of molecular quantities.

THEORETICAL BACKGROUND

For a liquid crystal with uniaxial symmetry, the effective dipole moment components ($\mu^2_{\mathrm{eff(i)}}$, $i = \parallel, \perp$) along the principal directions of the molecule are given by Maier and Meier's equations[6,7]

$$\mu^2_{eff(\parallel)} = \frac{3kT}{F}\left[\frac{(\varepsilon_\parallel-1)\,\varepsilon_0}{NhF} - \bar{\alpha} - \frac{2}{3}\Delta\alpha S\right] \tag{1a}$$

$$\mu^2_{eff(\perp)} = \frac{3kT}{F}\left[\frac{(\varepsilon_\perp-1)\,\varepsilon_0}{NhF} - \bar{\alpha} + \frac{1}{3}\Delta\alpha S\right] \tag{1b}$$

where $\epsilon_\parallel$ and $\epsilon_\perp$ are the principal permittivities, N is the number of molecules per cm^3, h is the cavity field factor, F is the reaction field factor, α and $\Delta\alpha$ are, respectively, the mean molecular polarizability and polarizability anisotropy, S is the order parameter and $\epsilon_0=8.85$ Pf/m. The meaning of different molecular dipole moment components is explained in Fig.1.

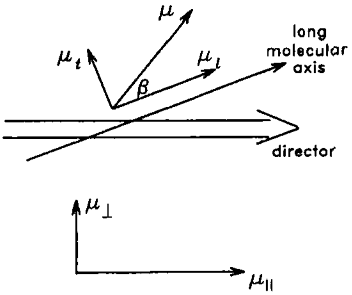

FIGURE 1 Dipole moment vector components of mesogens.

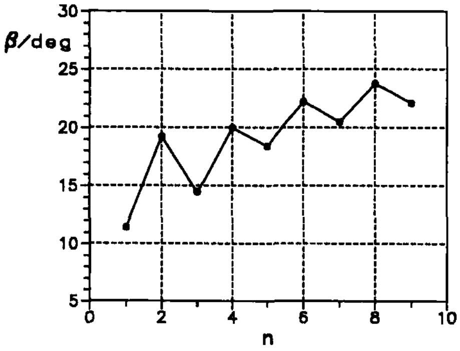

FIGURE 2 Odd-even effect for the β values in PCH series.

Short-range dipolar aggregation can be described by introducing the Kirkwood correlation factors $g_\parallel$ and $g_\perp$ for components of a dipole moment of the molecule along and perpendicular to the director, $\mu_\parallel$ and $\mu_\perp$, respectively

$$g_\parallel = \frac{\mu^2_{eff(\parallel)}}{\mu^2_\parallel}, \qquad g_\perp = \frac{\mu^2_{eff(\perp)}}{\mu^2_\perp} \tag{2}$$

The values of $\mu_\parallel$ and $\mu_\perp$ can be obtained with the following equations :

$$\begin{aligned}\mu_{\parallel}^2 &= \mu_l^2(1+2S) + \mu_t^2(1-S)\\ \mu_{\perp}^2 &= \mu_l^2(1-S) + \mu_t^2(1+\frac{1}{2}S)\end{aligned} \qquad (3)$$

where μ_l and μ_t are longitudinal and transverse molecular dipole components.

The angle value between long axis of molecule and direction of its dipole moment (β) was obtained from molecular mechanics calculations which were carried out for the seven members of PCH homologous series using the program MM2[8] (Fig.2).

From equations (2) and (3) one obtains :

$$\begin{aligned}g_{\parallel} &= \frac{\mu_{eff(\parallel)}^2}{\mu_l^2(1+2S) + \mu_t^2(1-S)}\\ g_{\perp} &= \frac{\mu_{eff(\perp)}^2}{\mu_l^2(1-S) + \mu_t^2(1+\frac{1}{2}S)}\end{aligned} \qquad (4)$$

Dielectric studies performed in oriented nematic sample give a unique opportunity for investigation of the dipolar correlations in two directions: parallel and perpendicular to the molecular alignment.

EXPERIMENTAL

The phase transition temperatures of the studied p-cyano-p'-alkylphenylcyclohexanes $C_nH_{2n+1}-C_6H_{10}-Ph-CN$ for n=3 to 9, (abbr. from PCH3 to PCH9) are shown in Fig.3. The compounds were synthesized and purified at the Institute of Chemistry, Military Technical Academy, Warsaw. The values of the nematic-isotropic phase transition temperature are in good agreement with those reported in literature[9-11].

The static electric permittivity was measured with a Wayne-Kerr B330 bridge at a frequency of 1.5 Khz with an accuracy of ±0.1 per cent. The samples were measured in a plane copper capacitor with gold-covered electrodes. The thickness of liquid layer was 1 mm. To orient the samples the O.6 T magnetic field was used. During measurement the temperature was stable within ±0.01°C.

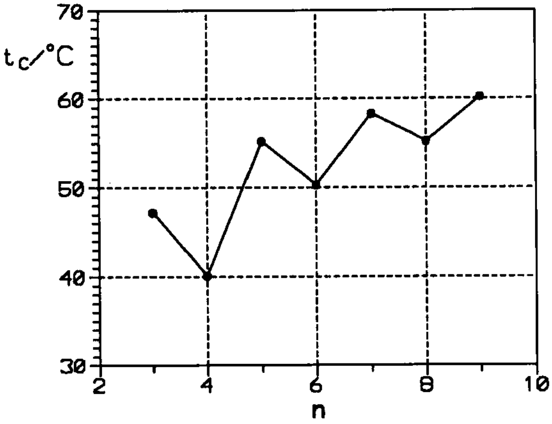

FIGURE 3 Nematic−isotropic phase transition temperatures of the PCH series.

RESULTS AND DISCUSSION

The temperature dependencies of the static electric permittivities for the homologous series of p-cyano-p'-alkylphenylcyclohexanes are shown in Fig.4.

Fig.5 shows the dependence on n for permittivities $\epsilon_{\|}$ and $\epsilon_{\perp}$ measured at $T-T_c=-4°C$ and for permittivity of isotropic phase measured at $T-T_c=+4°C$.

The effective dipole moment components along the principal directions of a liquid crystal calculated from eqs. 1a and 1b are given in Fig.6. The figures show the odd−even effect for components of the permittivity and effective dipole moment.

In Fig.6 the value of the squared dipole moment (μ_0^2) for free molecule is marked on the ordinate axis. The effective dipole moment components in the nematic phase ($\mu^2_{\mathrm{eff(i)}}$, $i=\|,\perp$) and in the isotropic phase ($\mu^2_{\mathrm{eff(iso)}}$) are of the lower values as compared with the value of μ_0^2 for the isolated molecule ($\sim$5D)[11]. This effect is undoubtedly related to the anti-parallel dipolar association of the rod-like molecules having large components of dipole moments along the molecular axis. For further analysis of these short-range correlation between dipoles, it is convenient to consider the Kirkwood correlation factors $g_{(i)}$ for the components of $\mu_{(i)}$ along and perpendicular to the director. These factors were calculated from eqs.4 and are shown in Fig.7.

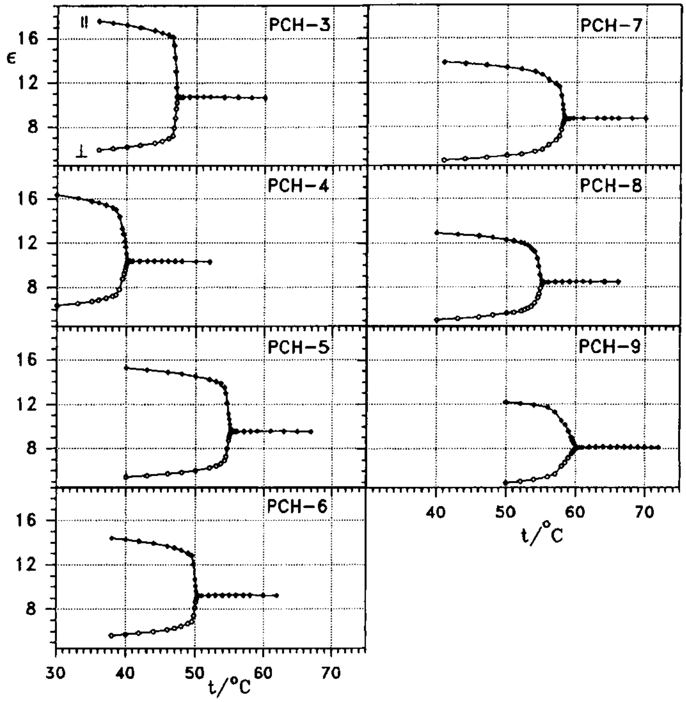

FIGURE 4 Electric permittivity of PCH as a function of temperature.

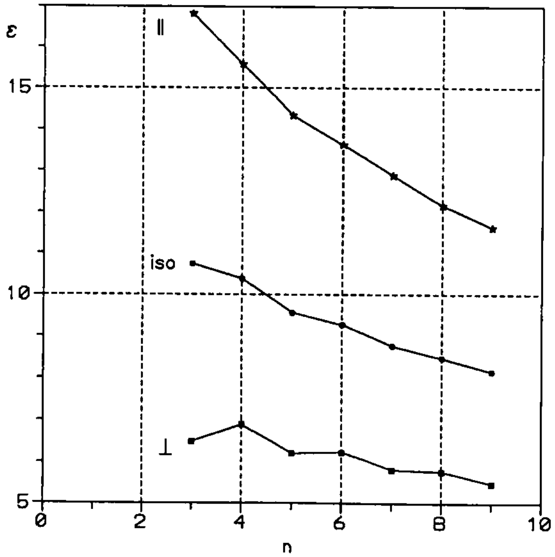

FIGURE 5 Odd−even effect for the electric permittivities of PCH (data for |ΔT| = 4°C from the nematic−isotropic transition).

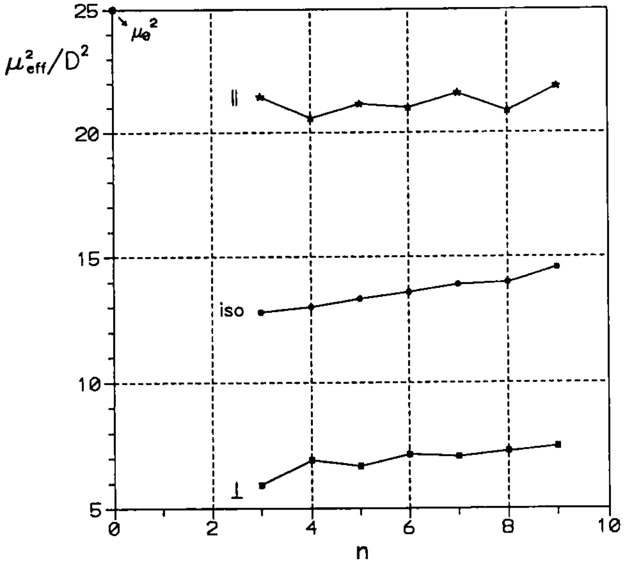

FIGURE 6 Effective squared dipole moment as a function of n within the PCH series.

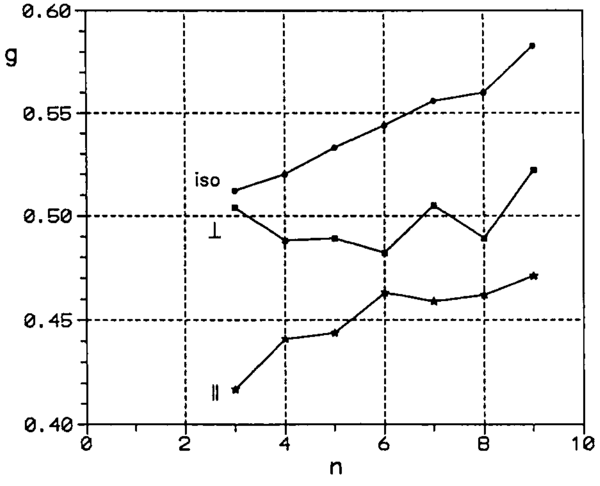

FIGURE 7 Kirkwood correlation factors g_{iso}, $g_{\parallel}$ and $g_{\perp}$ as a function of n for the PCH series.

The following conclusions result from our dielectric studies :

a) – The correlation factors $g_{(i)}$ in the nematic phase reveal an odd-even effect, whereas in the isotropic phase the effect is very small. It means that the odd-even effect found in the orientational order parameter S of n-PCH[12] is decisive here.

b) – The values of all g-factors are much less than unity, indicating local anti-parallel dipole-dipole correlation.

c) – Similar values of $g_{\|}$ and $g_{\perp}$, (close to 0.5), indicate that in nematic phase of PCHs the dipole-dipole interactions energy has a minimum for anti-parallel orientation of the dipole components both $\mu_{\|}$ and $\mu_{\perp}$.

d) – The data show that the dipole-dipole anti-parallel association degree decrease with increasing length of aliphatic chain. These effects can be explained by packing constraints and chain/core interactions for molecules with longer aliphatic chains[13].

e) – Going down from the isotropic to the nematic phase there is a decrease in the values of the Kirkwood correlation factors i.e. an increase in the tendency for anti–parallel orientation of molecules. It has been shown[13] that mesomorphic molecules undergo a change in shape and become more elongated in the nematic phase, and this will promote anti–parallel dipole association.

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