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Liquid Crystals

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To cite this Article Jadyn, J. , Czechowski, G. and Shonova, N. T.(1988) 'Odd-Even Effects in the Dielectric Properties of Nematics 4-(Trans-4'-*N*-Alkylcyclohexyl)Isothiocyanatobenzenes', Liquid Crystals, 3: 12, 1637 — 1641
To link to this Article: DOI: 10.1080/02678298808086626
URL: http://dx.doi.org/10.1080/02678298808086626

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Liquid Crystals, 1988, Vol. 3, No. 12, 1637–1641

Odd–even effects in the dielectric properties of nematics 4-(trans-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes

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(*Received 10 March 1988; accepted 27 June 1988*)

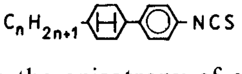
The anisotropy of the static electric permittivity and conductivity for the homologous series of nematics: 4-(trans-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes (*n*-CHBT) for $n = 3$–10 have been measured. It is shown that the odd–even effect in the dielectric anisotropy $\Delta\varepsilon$ is related to the perpendicular component $\varepsilon_\perp$ of electric permittivity. The odd–even effect is found in *n*-CHBT for both the anisotropy in the conductivity and the activation energy for ionic movement.

1. Introduction

The flexible aliphatic chain attached to the rigid rod-like group of typical mesogenic molecules is essential for stabilization of nematic phase. Most macroscopic parameters of liquid crystals, if compared at the same shifted temperature $T - T_c$ ($\equiv \Delta T$), show a characteristic alternation as a function of the number of chain segments, i.e. the well-known odd–even effect [1].

Although seemingly insignificant, in reality the differences in conformation of the even and odd membered alkyl chains strongly modify the molecular interactions. The odd–even effect seen in the phase transition temperatures (from the ordered to the isotropic phase) supports this conjucture. For compounds containing an even number of units in their terminal-chains, the transition temperature from the nematic to the isotropic phase is lower than the corresponding temperature for compounds containing ($n - 1$) units. This has been confirmed by many experimental and theoretical studies [1]. For even membered compounds lower values of the order parameter [2], the dielectric anisotropy [3], the jump in the molar volume [4], the entropy [4, 5], the self-diffusion coefficients [6], etc., are obtained than for their odd membered homologues.

Here, we present the results of measurements of the electric permittivity and the conductivity for the homologous series of 4-(trans-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes (*n*-CHBT):



$n = 3$–10.

It was shown that both the anisotropy of conductivity ($\sigma_\parallel/\sigma_\perp$) and the activation energy of ionic movement ($E_{A\parallel}$ and $E_{A\perp}$) undergo the same alternation as other physical quantities. Moreover, it was shown that the odd–even effect in dielectric anisotropy ($\Delta\varepsilon$) for the homologous series studied is related mainly to the perpendicular electric permittivity ($\varepsilon_\perp$).

2. Experimental

Materials. The *n*-CHBTs were synthetized according to the procedure described by Dąbrowski *et al.* [7]. Their nematic–isotropic transition temperatures are shown in figure 1.

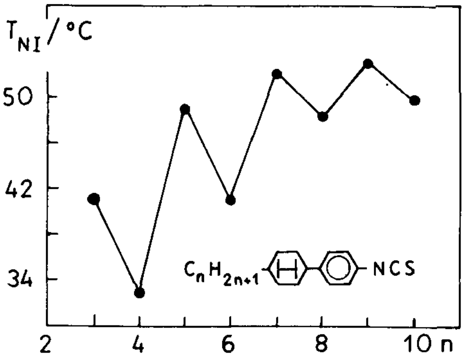


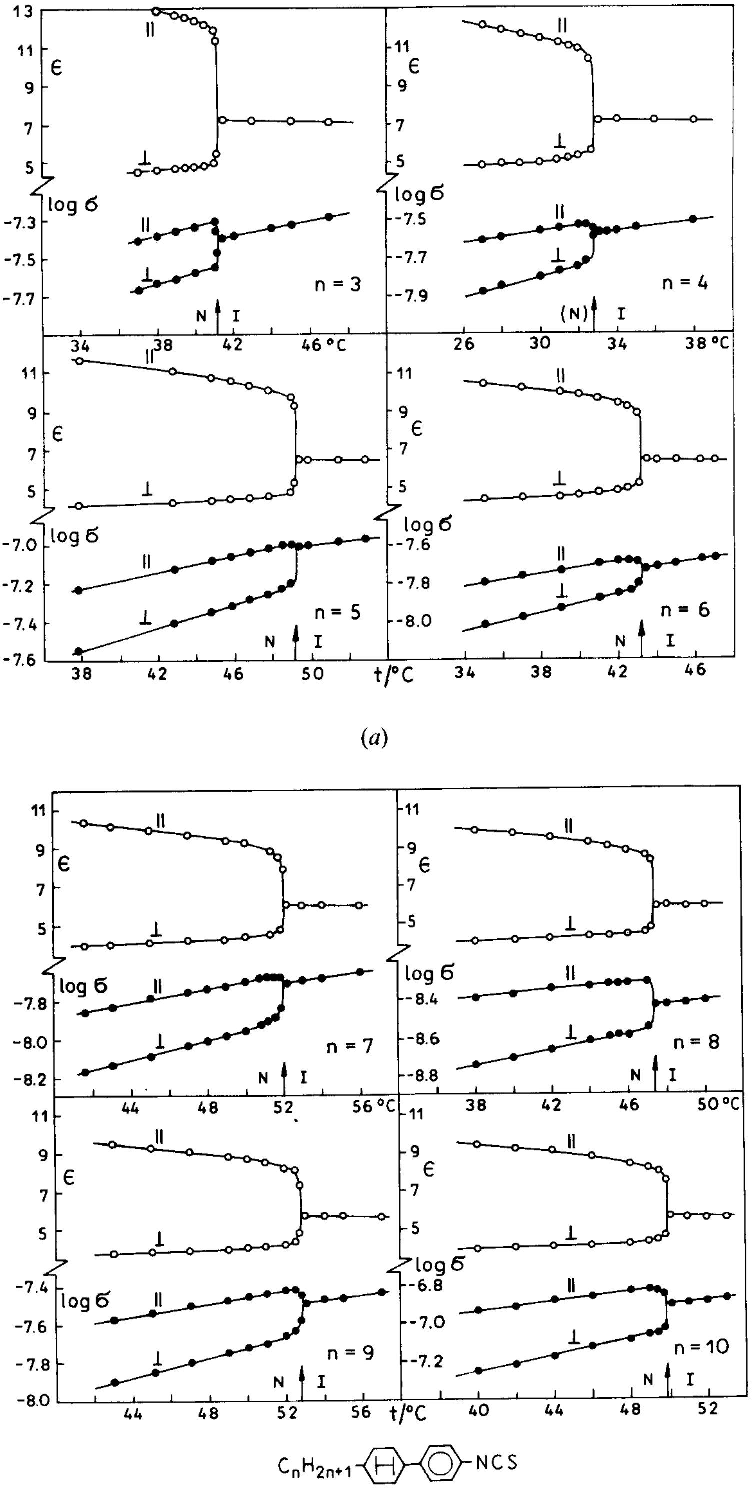
Figure 1. The nematic–isotropic transition temperatures of the *n*-CHBT series.

Apparatus. The static electric permittivity and conductivity were measured with a Wayne-Kerr B 330 bridge at 1·5 kHz. The liquid crystal samples (0·6 mm thick) were placed within a plane copper capacitor with gold covered electrodes. A magnetic field (1 T) was used to orient the samples. The temperature was stabilized with an accuracy of ±0·01°C. The electric permittivity and conductivity were measured with an accuracy of 0·05 and 0·1 per cent, respectively. The conductivity measurements were carried out for pure samples, that is without any special ionic additives.

3. Results and discussion

Figure 2 shows the results for the electric permittivity and conductivity for the *n*-CHBTs performed parallel and perpendicular to the director. The dielectric anisotropy of these compounds is positive and, as in most nematics, the conductivity along the direction of molecular orientation is higher than in the direction perpendicular to the latter, thus $\sigma_\parallel/\sigma_\perp > 1$.

The dielectric anisotropy, $\Delta\varepsilon$, reveals only a weak odd–even effect, see the upper part of figure 3. However, since this anisotropy is the difference between the values of the parallel and the perpendicular permittivity, it is possible that there is a compensation effect, resulting from the different dependencies of $\varepsilon_\parallel$ and $\varepsilon_\perp$ on the alkyl chain length. The middle part of figure 3 proves that this is indeed the case. The permittivity measured along the director decreases monotonically with increasing *n*; this reflects merely the effect of the dilution of the N=C=S dipoles within the non-polar medium. The distinct odd–even effect is not observed here. On the other hand, the perpendicular component of the permittivity, $\varepsilon_\perp$, reveals a distinct odd–even effect; higher values of $\varepsilon_\perp$ occurring for molecules containing an even number of units within the alkyl chain.



(a)

C_nH_{2n+1}–(H)–⟨○⟩–NCS

(b)

Figure 2. The electric permittivity and conductivity of *n*-CHBT as a function of temperature.

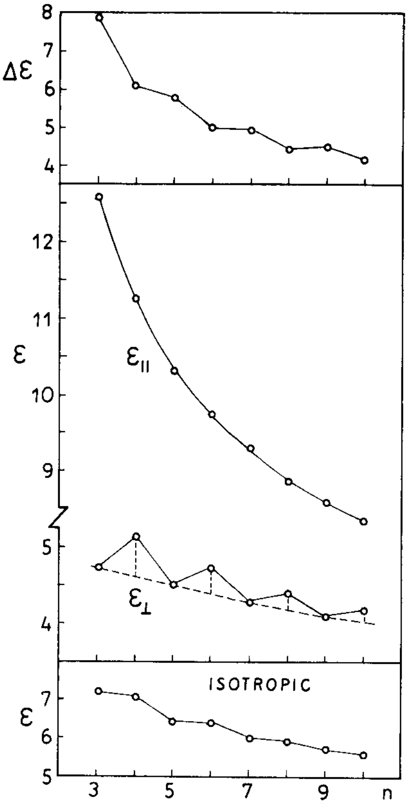


Figure 3. The odd–even effect in the electric permittivity of *n*-CHBT. Data for $|\Delta T| = 2°C$ from the nematic–isotropic transition.

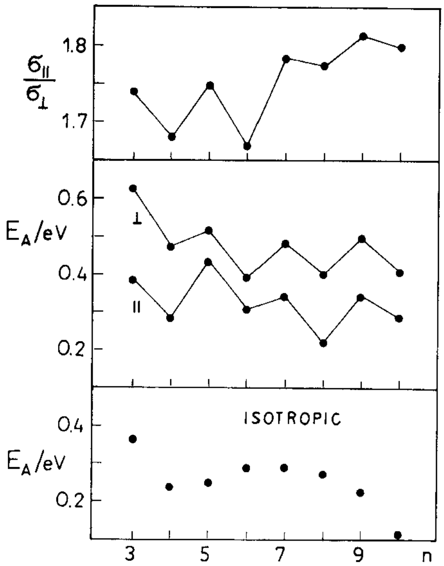


Figure 4. The odd–even effect in the anisotropy of the electric conductivity and the activation energy for ionic movement in oriented *n*-CHBT samples. $\sigma_{\parallel}/\sigma_{\perp}$ data for $\Delta T = 2°C$ from the nematic–isotropic transition.

The different behaviour of the components of the electric permittivity results mainly from the odd–even effect of the second rank orientational order parameter S and can be derived directly from the Maier–Meier theory [8]. Thus for linear dipolar molecules the contribution of dipole moment μ to $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ is proportional to $\mu^2(2S + 1)$ and $\mu^2(1 - S)$, respectively. The typical change in the order parameter S on going from odd to even homologues amounts to about 10 per cent (for example from 0·66 to 0·60) and leads (for the dipole moment value of the NCS-group of about 3 D) to variations in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of about 5 and 18 per cent, respectively. The effect is enhanced by the perpendicular component of dipole moment appearing in the even alkyl chains as a consequence of the deviation of the terminal methyl group from the long axis of molecules [9]. However, the low dipole moment of the $-CH_3$ group (*ca.* 0·4 D) makes this effect small.

Figure 4 shows the dependence of the electric conductivity anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ and activation energies for the conductivities $E_{A\parallel}$ and $E_{A\perp}$ (determined from a $\ln \sigma$ versus T^{-1} plot) on the number of segments in the *n*-CHBT aliphatic chain. Both the $\sigma_{\parallel}/\sigma_{\perp}$ ratio and the activation energy reveal an odd–even effect which is analogous to that observed for many other physical, i.e. for even homologues of the studied series the values of $\sigma_{\parallel}/\sigma_{\perp}$ and activation energy for ion movement are lower.

We are greatly indebted to Professor R. Dąbrowski for the high purity samples. This work was supported by the Polish Academy of Sciences within the framework of Project CPBP 01.12.

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