PHYSICAL REVIEW E **69**, 022701 (2004)

Static and dynamic dielectric behavior of mesogenic compounds of different polarity in the vicinity of the isotropic to nematic phase transition

Margarita Ginovska
Faculty of Electrical Engineering, University of Sts. Cyril-Methodius, P.O. Box 574, 91000 Skopje, Macedonia

Horst Kresse
Institute of Physical Chemistry, Martin-Luther-University Halle, Mühlpforte 1, 06108 Halle, Germany

Danuta Bauman
Faculty of Technical Physics, Poznań University of Technology, Nieszawska 13a, 60-965 Poznań, Poland

Grzegorz Czechowski and Jan Jadżyn*
Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland
(Received 24 September 2003; published 27 February 2004)

Mesogenic compounds belonging to the two well-known -cyanophenyl, and -isothiocyanatophenyl homologous series, which distinctly differ in the molecular polarity ($-C\equiv N$, 5D; $-N=C=S$, 2.5D), show an essential difference in the pretransitional dielectric behavior in the vicinity of the isotropic to nematic (I-N) phase transition. Taking into account the results presented in Phys. Rev. E **67**, 041705 (2003), the features of the I-N transition observed for the less polar mesogens are characteristic for the first order phase transition, whereas in the case of the strongly polar ones, the I-N transition is undoubtedly close to the second order.

DOI: 10.1103/PhysRevE.69.022701 PACS number(s): 64.70.Md, 72.20.Ht, 68.35.Rh

I. INTRODUCTION

The phase transition from the isotropic liquid to the nematic liquid crystal (I-N) is mostly classified as weakly first order or close to second order. That somewhat ambiguous attribution of the I-N transition results from the fact that in experiments one detects the molar volume jump and the latent heat at the transition, on the one hand, and the pretransitional effects in the isotropic phase when the temperature approaches to the transition, on the other hand [1]. However, in some papers the I-N transition is classified as first order because of a lack of prenematic effects in measured physical property.

The pretransitional effects in the vicinity of the I-N transition appear nearly exclusively in nonlinear studies, i.e., when an external stimulus is sufficiently strong. The experimental data are abundant and they are concerned with the static measurements of magnetic [2] and electric [3] birefringence, light scattering [4], and the nonlinear dielectric effect [5], as well as dynamic studies of molecular spin-lattice relaxation [6,7], dynamic light scattering [8], the transient grating optical Kerr effect [9,10], and the nonlinear dielectric relaxation [11–13]. The prenematic effects which appear in the linear dielectric properties as a peculiar temperature behavior of the static permittivity [14–16] are a rather exceptional case. The present paper shows that the peculiarity in the static permittivity behavior concerns the most polar mesogens only. The fact, of course, does not abate the significance of that peculiarity, which is still waiting for the theoretical description.

II. EXPERIMENT

The two compounds studied, 1-(4-*trans*-pentylcyclohexyl)-2-(4-isothiocyanatophenyl) ethane $C_5H_{11}CyHxCH_2CH_2Ph-N=C=S$, (5NCS), and 1-(4-*trans*-pentylcyclohexyl)-2 -(4-cyanophenyl)ethane $C_5H_{11}CyHxCH_2CH_2Ph-C\equiv N$, (5CN), are of a very similar molecular structure and differ in the polar group only. The temperatures of the phase transitions between the crystalline (Cr), nematic (N) and isotropic (I) phases were as follows: Cr *314.2K* N *321.3K* I, for 5NCS and Cr *310K* N *325.3K* I, for 5CN. Because of a relatively narrow temperature range of the nematic phase in 5NCS (7 K), if compared to 5CN (15 K), and a possible influence of that circumstance on the prenematic behavior, the third compound: 1-(*trans*-4-octylcyclohexyl)-4-isotiocyanatobenzene, $C_8H_{17}CyHxPh-N=C=S$ (8CHBT), Cr *301.9K* N *321.0K* I, with a large range of existence of the nematic phase (19 K), was studied, too. The compounds were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. Their purity, checked by chromatography, was better than 99%.

Dielectric characteristics of the compounds were measured with a HP 4194A impedance/gain phase analyzer in the frequency range of 50 kHz–100 MHz. A high performance electrical heating of the plane measuring capacitor assured a temperature stabilization of better than 10^{-3} K and the possibility of a temperature change of 10^{-2} K [15].

The shear viscosity was measured with a Haake viscometer RV 20 with a measuring system CV 100. The system consists of a rotary beaker filled with the studied liquid and a cylindrical sensor of Mooney-Ewart type (ME 15), placed in the center of the beaker. The liquid gap was 0.5 mm. The studied liquids show a Newtonian behavior in the available

---

*Electronic address: jadzyn@ifmpan.poznan.pl

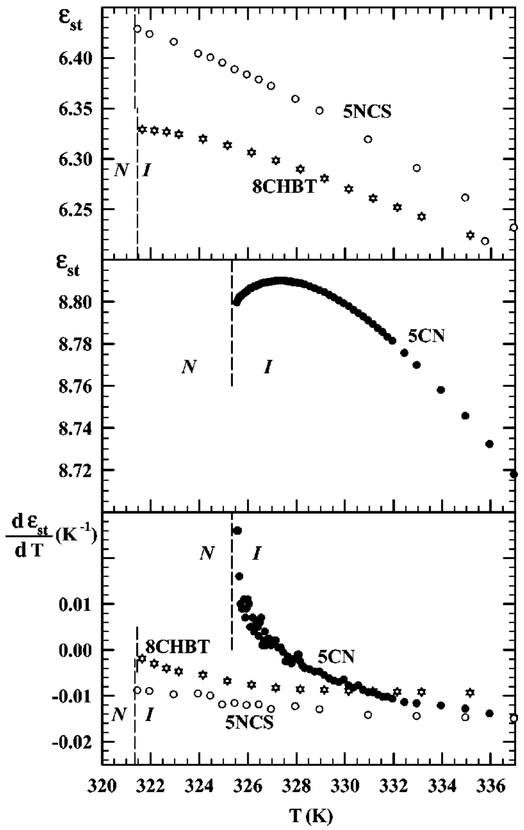

FIG. 1. Temperature dependences of the static permittivity and its temperature derivative for 5NCS, 8CHBT, and 5CN in the vicinity of isotropic to nematic phase transition.

range of the shear rates (30–300 s^{-1}). The accuracy of the viscosity determination was 0.5%. The temperature of the sample was controlled within $\pm 0.1\,^{\circ}\mathrm{C}$.

III. RESULTS AND DISCUSSION

Figure 1 presents temperature dependences of the static dielectric permittivity and its derivative for the compounds studied. A difference observed in the dielectric behavior of -NCS derivatives and 5CN is striking.

The results are quite similar to those presented in Ref. [15] for mesogenic pentylcyanobiphenyl (5CB) and nonmesogenic butylcyanobiphenyl (4CB). The former compound showed a critical-like behavior of the permittivity derivative as the temperature of isotropic to nematic phase transition approaches (like observed for 5CN in Fig. 1), what is characteristic for the transition *close to the second order*. The latter, nonmesogenic 4CB, showed no pretransitional effects, as expected for the first order phase transition from isotropic liquid to crystalline solid (I-Cr).

As seen in Fig. 1, for 5NCS there are no symptoms in the permittivity behavior of the coming up I-N phase transition, and for 8CHBT one observes only a slight increase in the permittivity derivative. The fact can suggest that the transition is *close to the first order*, the more so as the slope of $d\varepsilon_{\mathrm{st}}/dT$ on T dependences, equal to about $4\times10^{-4}\ \mathrm{K}^{-2}$, is very close to that obtained for nonmesogenic, strongly polar nCB, in the vicinity of the I-Cr phase transition [15].

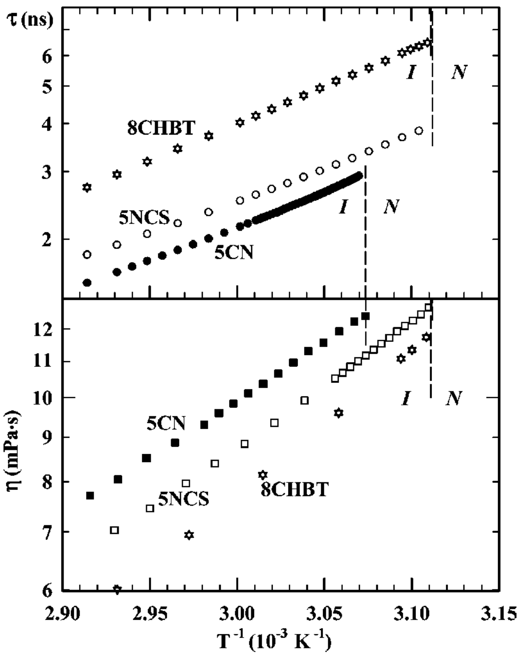

FIG. 2. Arrhenius plots for the dielectric relaxation time (τ) corresponding to the molecular rotation around the short axis and for the viscosity (η) measured in the isotropic phase of 5NCS, 8CHBT, and 5CN.

The above suggestion of the difference in the order of I-N phase transitions in -NCS derivatives and 5CN seems to find a support also in the dynamic dielectric properties of the compounds. Figure 2 presents temperature dependences (in form of the Arrhenius plots) of the dielectric relaxation time (τ) and the viscosity (η) of 5NCS, 8CHBT, and 5CN. The relaxation time corresponds to the molecular rotation around the short axis. For rotating molecules with the dipole moment directed, more or less, along their long axis, as in the case of compounds studied, the dielectric absorption band corresponding to the above mentioned mode of rotation, dominates in the spectrum and the evaluation of τ is quite reliable (the details of the procedure are described in Ref. [15]).

An analysis of the results presented in Fig. 2 shows that the dependences do not fulfill strictly the Arrhenius requirement for the constant activation energy E_A:

$$\ln\chi(T)=\ln\chi_A+\frac{E_A}{RT}, \tag{1}$$

i.e., the dependence $\ln\chi(T)$ on T^{-1} is not linear. χ denotes here the relaxation time or the viscosity, χ_A is the pre-exponential factor, R the gas constant, and T the absolute temperature. The most often the experimental data concerning the thermally activated physical processes, do not fulfill the Arrhenius relation (1) with the assumption of the temperature independent activation energy. As we discussed previously [15] there are no physical reasons for the assumption, as the basic physical properties of liquids, the number of molecules in unit volume, first of all, depend essentially

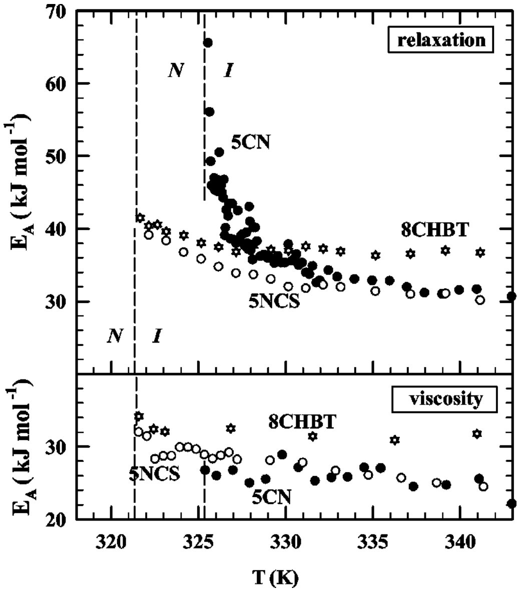

FIG. 3. Temperature dependences of the activation energy for the molecular rotation around the short axis and for the viscous flow of 5NCS, 8CHBT, and 5CN in the isotropic phase.

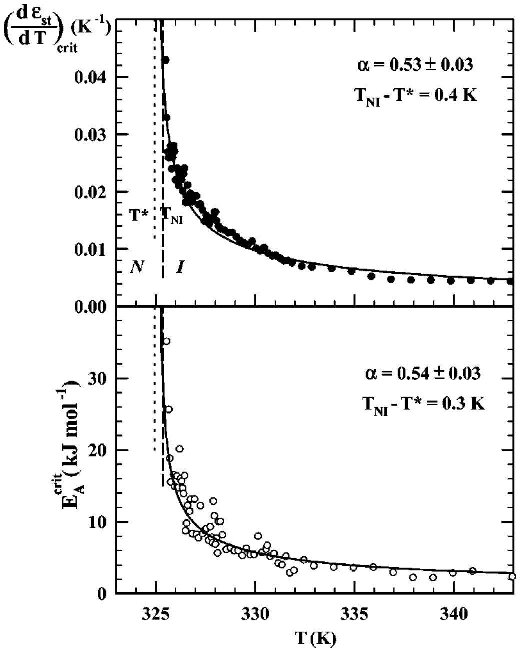

FIG. 4. Temperature dependence of the critical parts of the derivative of the static permittivity and the activation energy for the 5CN molecules rotation in the vicinity of the isotropic to nematic phase transition. The solid lines are the best fit of an equation of $(T-T^*)^{-\alpha}$ type to the experimental data.

on temperature. With decreasing temperature one should expect some increase of E_A, rather than its constant value.

As results from Eq. (1), the derivative $\partial \ln \chi(T)/\partial(T^{-1})$ gives directly E_A at a given temperature, so the temperature dependence of the activation energy can be analyzed. Of course, for the "Arrhenius processes" the value of E_A should be temperature independent.

Figure 3 presents temperature dependences of the activation energy for the rotation of 5NCS, 8CHBT and 5CN molecules and for the viscous flow of the compounds in the vicinity of I-N phase transition. We believe that the results are not trivial.

The viscous flow of the compounds of similar structure (5NCS and 5CB) can be described with the same value of the activation energy and shows only small deviation from the Arrhenius behavior: E_A weakly increases with the temperature decrease with the slope of about 0.24 kJ/mol per kelvin. For 8CHBT the viscosity activation energy is somewhat higher. There are no prenematic effects in the viscous properties of the compounds. The results presented in Fig. 3 show that for 5NCS and 5CN, in the temperature region of about 10° above the I-N transition and higher, the activation energy for the molecular rotation around the short axis behaves quite similarly to that of the viscosity: E_A for 5NCS and 5CN is equal to each other and its temperature dependence is analogous to that corresponding to the viscous flow. The value of the activation energy is only of about 6 kJ/mol higher than that of the viscosity. An analogous difference is observed for 8CHBT. All these experimental facts show that a relatively far from the I-N phase transition, the rotation of the mesogenic molecules in the isotropic phase is mainly governed by the viscosity of the medium.

In the temperature region close to the isotropic to nematic phase transition, the behavior of the activation energy for the molecular rotation strongly differentiates the $-$NCS derivatives and 5CN. Once more the prenematic effect in a form of the critical-like temperature dependence of the activation energy is observed for 5CN, while for the $-$NCS derivatives only a slight increase above the "normal" $E_A(T)$ dependence, i.e., parallel to that of the viscosity, is observed.

Figure 4 presents temperature dependence of the critical parts of the static permittivity derivative and the activation energy for the rotation of 5CN molecules. The critical part of a given quantity is taken as a difference between its experimental temperature dependence and the reference dependence of the quantity measured for nonmesogenic homologue in the vicinity of the first order phase transition (liquid-crystalline solid). As reference data, the results for 4CB, discussed in Ref. [15], were taken. The solid lines in Fig. 4 are the best fit of the equation of $(T-T^*)^{-\alpha}$ type to the experimental data. It is worth noticing that the critical behaviors of both the permittivity derivative and the activation energy can be consistently described with the same values of the critical exponent (α) and the distance between the temperature of the I-N phase transition (T_{NI}) and the virtual temperature of the second order phase transition (T^*).

The critical phenomena observed in the vicinity of isotropic to nematic phase transition result from a formation of the pseudonematic domains in the isotropic liquid. The domains are statistically distributed and show strong fluctuations in size and shape with time. Thus one can expect still a weak influence of the "nematic potential" on the short range behavior in the isotropic liquid. However, in case of the strongly polar mesogenic molecules, the potential reduces the dielectric permittivity via the tendency toward an antiparallel orientation of the molecules within the domains, on the one hand, and an increase of the molecular relaxation time (observed as a critical-like temperature dependence of the activation energy), on the other hand. The same physical reason for these two effects results in the same values of the critical parameters depicted in Fig. 4. The viscosity, as a quantity which concerns the bulk property of the liquid, cannot reflect a short range molecular ordering.

In case of a small tendency to antiparallel dipole-dipole correlation, as in -NCS derivatives, the molecular organization in the pseudonematic domains are not so efficient as in case of -CN derivatives, and the pretransitional effects are hardly observed in the linear dielectric properties. The conclusions arising from the presented results are following:

(i) The mesogenic compounds composed of the molecules of the same structure and different polarity can behave quite differently in the vicinity of the isotropic to nematic phase transition. On the basis of the static and dynamic linear dielectric properties, one can classify the I-N phase transition in the less polar compounds as close to first order and as close to the second order for the strongly polar compound.

(ii) A somewhat different look at the Arrhenius equation, allowing for the temperature dependence of the activation energy, which seems to have physical reasons, gives quite interesting and important data concerning the phase transition studied.

ACKNOWLEDGMENT

The work was supported by the Centre of Excellence for Magnetic and Molecular Materials for Future Electronics within the European Commission Contract No. G5MA-CT-2002-04049.

---

[1] P. G. de Gennes, *Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974).
[2] J.D. Litster and T.W. Stinson III, J. Appl. Phys. **41**, 996 (1970).
[3] J.C. Filippini and Y. Poggi, Phys. Lett. **65A**, 30 (1978).
[4] T.D. Gierke and W.H. Flygare, J. Chem. Phys. **61**, 2231 (1974).
[5] A. Drozd-Rzoska, S.J. Rzoska, and J. Ziolo, Phys. Rev. E **54**, 6452 (1996).
[6] B. Cabane and G. Clarke, Phys. Rev. Lett. **25**, 91 (1970).
[7] S. Gosh, E. Tettamanti, and E. Indovina, Phys. Rev. Lett. **29**, 638 (1973).
[8] T.W. Stinson III and J.D. Litster, Phys. Rev. Lett. **25**, 503 (1970).
[9] F.W. Deeg, S.R. Greenfield, J.J. Stankus, V.J. Newell, and M.D. Fayer, J. Chem. Phys. **93**, 3503 (1990).
[10] J.J. Stankus, R. Torre, C.D. Marshall, S.R. Greenfield, A. Sengupta, A. Tokmakoff, and M.D. Fayer, Chem. Phys. Lett. **194**, 213 (1992).
[11] P. Kedziora, J. Jadzyn, and L. Hellemans, Phys. Rev. E **66**, 031702 (2002).
[12] P. Kedziora, J. Jadzyn, and L. Hellemans, Phys. Rev. E **66**, 021709 (2002).
[13] P. Kedziora, J. Jadzyn, and L. Hellemans, J. Phys. Chem. A **107**, 5650 (2003).
[14] S.J. Rzoska, J. Ziolo, W. Sulkowski, J. Jadzyn, and G. Czechowski, Phys. Rev. E **64**, 052701 (2001).
[15] J. Jadzyn, G. Czechowski, C. Legrand, and R. Douali, Phys. Rev. E **67**, 041705 (2003).
[16] H. Kresse and F. Kremer, Phys. Status Solidi A **118**, K119 (1990).