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# Dielectric and elastic properties of a nematic phase induced by charge transfer interaction in a binary system containing disc-shaped molecules

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The dielectric constants and the elastic coefficients for splay ($K_1$) and bend ($K_3$) of the charge transfer induced nematic ($N_c$) phase of tridecyl pentakis(phenylethynyl)phenyl ether (**1**) doped with different amounts of 2,4,7-trinitrofluorenone (**2**) were determined by studying the electric field induced bend deformation using the capacitance method. A negative dielectric anisotropy was observed. For the bend elastic constant $K_3$ values up to $22 \times 10^{-12}$ N are found which are one order of magnitude higher than the respective values of discotic nematic ($N_D$) phases. Values of 0·6–0·8 are obtained for the ratio $K_1/K_3$; these show a minimum for the equimolar complex.

## 1. Introduction

The formation of induced mesophases occurring in hybrid mixtures of rod-like molecules has been extensively studied in the past [1]. Generally, these mixtures consist of compounds with different terminal polarity and in a few cases charge transfer interactions have been demonstrated [2]. For electron donor-acceptor systems containing disc-shaped molecules the induction of liquid-crystalline phases has also been observed [3–7]. Mostly, a discotic columnar ($D_{ho}$) type of phase is formed in the polymeric and low molecular weight systems studied so far. However, recently the induction of nematic phases was also reported [4–7]. It has been proposed that an alternate stacking of donor and acceptor molecules leads to ordered columns which behave similarly to rod-like nematic mesogens forming a so-called nematic columnar ($N_c$) phase. This $N_c$ phase has been found in systems of non-liquid-crystalline alkyl pentakis(phenylethynyl)phenyl ethers [4] and of various other multiyne compounds [7] doped with 2,4,7-trinitrofluorenone (**2**) as well as in a system of liquid-crystalline hexakispentyloxytriphenylene doped with a long chain substituted derivative of **2** [4, 5].

Here we present the first results for the electric field-induced bend deformation of the type of nematic phase formed by mixing tridecyl pentakis(phenylethynyl)phenyl ether with different amounts of **2** as an acceptor. Preliminary experiments have shown that this induced nematic phase exhibits a negative dielectric anisotropy. Starting from a good homeotropic alignment, easily achieved in commercially glass cells (E.H.C.) a low threshold voltage for the bend deformation has been found as reported previously for

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the $N_D$ phase of the hexakis(4-alkylphenylethynyl)benzene derivatives [8]. Therefore, we could use the capacitance method to determine the dielectric constants ($\varepsilon_{\parallel}, \varepsilon_{\perp}$) and the elastic coefficients for bend and splay ($K_3, K_1$) [9]. An unusual behaviour of these elastic constants and their dependence on the composition of the mixture is reported.

## 2. Experimental

The synthesis of tridecyl pentakis(phenylethynyl)phenyl ether (**1**) is described elsewhere [4]. 2,4,7-Trinitrofluorenone (**2**) is commercially available and was dried in vacuum. The charge transfer complexes were prepared by mixing corresponding amounts of both materials dissolved in dichloromethane. The formation of the electron donor–acceptor complex was indicated by the appearance of a red colour. After removing the solvent in vacuum the samples were homogenized mechanically. The phase transition data of the mixtures of **1** with **2** are shown in figure 2.

The dielectric constants and elastic coefficients for bend and splay were determined by measuring the cell capacitance of initially homeotropic aligned samples as a function of the applied signal voltage as described in an earlier paper [9].

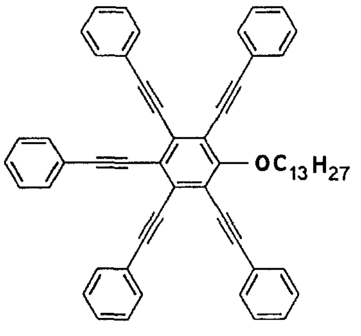
## 3. Results

The induced nematic phase formed by mixing **1** with **2** has a negative dielectric anisotropy. The dielectric constants are only slightly higher than those of the discotic nematic ($N_D$) phase of similar compounds. Figure 3 shows the temperature dependence of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ (parallel and perpendicular to the director) for the equimolar complex of **1** and **2**. The very small influence of the addition of **2** on the absolute values of the dielectric constants is in agreement with the small permanent dipole moment of this acceptor molecule.

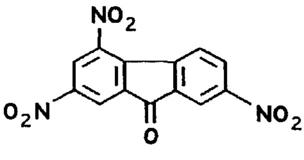
Threshold voltages between 3 and 7 V were observed for the bend deformation. From the threshold voltage $U_c$ and the dielectric anisotropy $|\varepsilon_a| = \varepsilon|_{\parallel} - \varepsilon_{\perp}|$ the bend elastic constant $K_3$ was calculated from

$$K_3 = \frac{1}{\pi_2} \varepsilon_0 |\varepsilon_a| U_c^2.$$

The values of $K_3$ up to $22 \times 10^{-12}$ N (cf. figure 4) are higher by about one order of magnitude than those for the discotic nematic ($N_D$) type of phase of the chemically



**1**



**2**

Figure 1. Structures of the tridecyl pentakis(phenylethynyl)phenyl ether (**1**) and of 2,4,7-trinitrofluorenone (**2**).

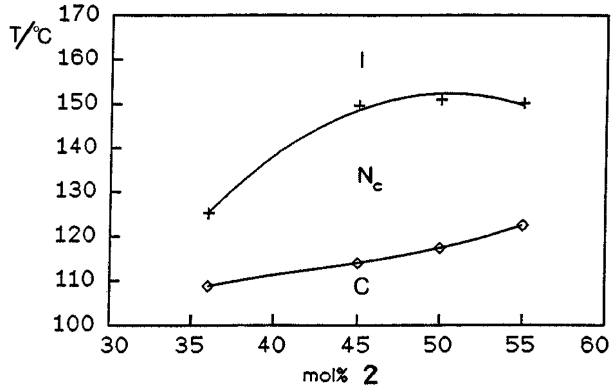


Figure 2. Transition temperatures for different compositions of tridecyl pentakis(phenylethynyl)phenyl ether (**1**) with **2** (C, crystalline; N$_c$, induced nematic; I, isotropic).

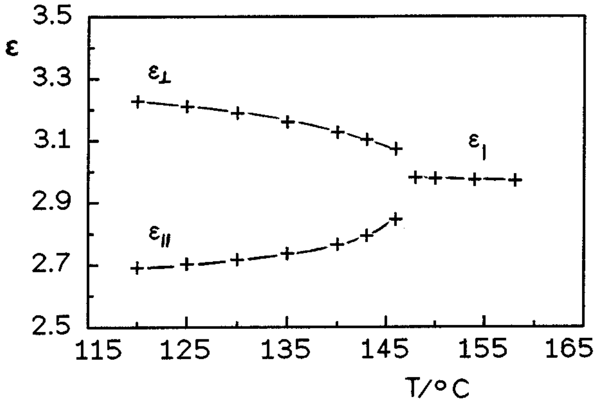


Figure 3. Temperature dependence of the dielectric constants parallel and perpendicular to the director ($\varepsilon_{\parallel}, \varepsilon_{\perp}$) for the equimolar complex of **1** and **2**.

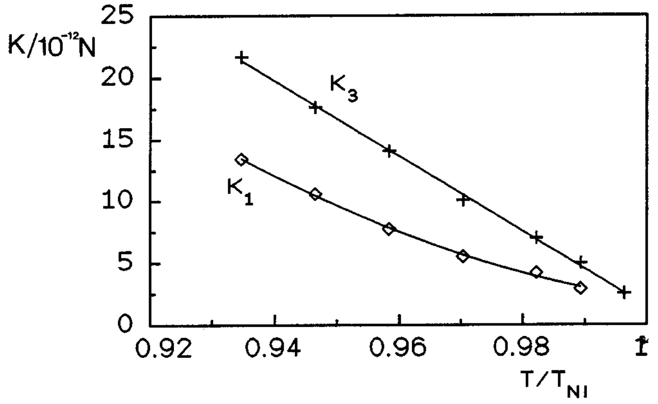


Figure 4. The bend elastic constant $K_3$ and the splay elastic constant $K_1$ as a function of the reduced temperature $T/T_{NI}$ for the equimolar complex of **1** and **2**.

similar hexakis(4-alkylphenylethynyl)benzene compounds [9]. The splay elastic constant $K_1$ was determined by fitting the measured field dependence of the capacitance to a theoretical curve [10]. A ratio $K_1/K_3$ of about 0·6–0·8 was obtained for all mixtures of **1** and **2**.

The induced nematic phase exists over a concentration range of between about 30 and 60 mol% of **2**. The influence of the acceptor (**2**) concentration on the properties of this nematic phase was studied by observing the elastic deformation in four different mixtures of **1** with **2**. The temperature for the nematic–isotropic transition varies with composition and has a maximum of 151°C at the equimolar complex of **1** and **2**. Therefore, we compare the results (see figure 5) for a constant reduced temperature $T/T_{NI}$ of 0·98. The absolute value of the dielectric anisotropy $\varepsilon_a$ increases when approaching the equimolar composition from low concentrations of **2**. Considering the dependence of $\varepsilon_a$ on the density and the orientational order parameter, this behaviour can be attributed to the charge transfer interaction between the electron donor and acceptor molecules (see figure 5 (*a*)). Even more clearly, the concentration dependence of $K_1$ and $K_3$ (see figure 5(*b*)) makes the equimolar composition stand out. The maximum of the elastic coefficients at this concentration indicates extraordinarily high intermolecular correlations. Not only do the values of $K_1$ and $K_3$ at a constant reduced temperature show a maximum at this concentration but their temperature coefficients $dK_1/d(T/T_{NI})$ and $dK_3/d(T/T_{NI})$ do also. Incidentally, the temperature coefficients of $K_1$ and $K_3$ become equal at the equimolar concentration of **1** and **2** so that $d(K_1/K_3)/d(T/T_{NI})$ exhibits a minimum at this composition.

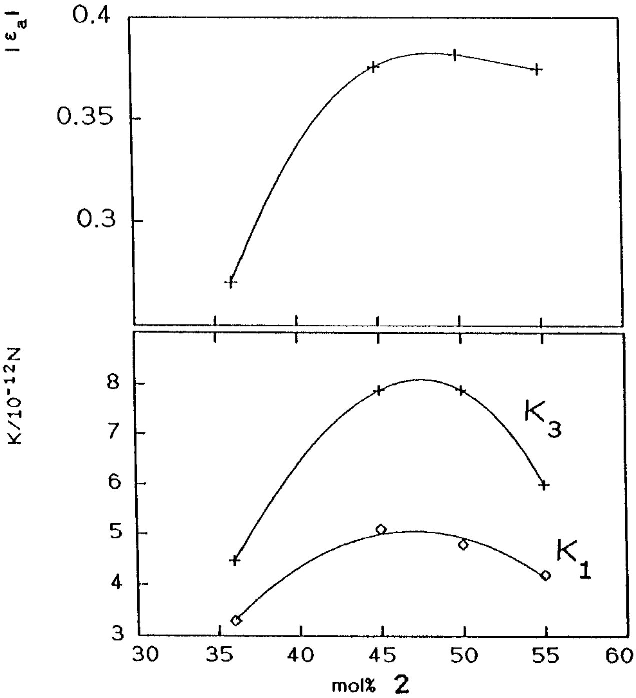


Figure 5. (*a*) Upper part: the absolute values of the dielectric anisotropies in the nematic phase of different mixtures of **1** with **2** at constant reduced temperature $T/T_{NI}$ of 0·98. (*b*) Lower part: the bend and splay elastic constants ($K_3$, $K_1$) of the different compositions of the mixtures of **1** with **2** at a reduced temperature of 0·98.

## 4. Conclusion

Our most striking result is that both $K_1$ and $K_3$ are, by one order of magnitude, higher than the respective values in a usual discotic nematic ($N_D$) phase [9]. This behaviour confirms the existence of an extraordinarily high correlation between neighbouring molecules as assumed in [4]. The dependence of $K_1$ and $K_3$ on the acceptor concentration indicates that this interaction is strongest for the equimolar composition. It is of interest to note the analogy to hybrid mixtures consisting of polar and non-polar nematic liquid crystals in which the tendency to form an injected (induced) smectic phase leads to the enhancement of a smectic-like local ordering. For these prolate molecules the ratio $K_3/K_1$ is observed to decrease on approaching the equimolar concentration (outside the pretransitional region) [11]. This corresponds to a decrease of the ratio $K_1/K_3$ in our system of oblate molecules [9, 12]. With respect to the unusual behaviour of the elastic constants it is of high priority to look for charge transfer induced nematic phases ($N_c$) in systems where the pure compound also shows a nematic phase ($N_D$). Furthermore, the pretransitional behaviour of the elastic constants on approaching a columnar phase should be studied for both pure discotic compounds as well as for charge transfer stabilized systems.

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## References

[1] (a) Engelen, B., Heppke, G., Hopf, R., and Schneider, F., 1978, *Ann. Phys.*, **3**, 403. (b) Domon, M., and Billard, J., 1979, *J. Phys.*, *Paris*, **C40**, C3. (c) Cladis, P. E., 1981, *Molec. Crystals liq. Crystals*, **67**, 177.

[2] Demus, D., Pelzl, G., Sharma, N. K., and Weissflog, W., 1981, *Molec Crystals liq. Crystals*, **76**, 241.

[3] (a) Ringsdorf, H., Wüstefeld, R., Zerta, E., Ebert, M., and Wendorff, J. H., 1989, *Angew. Chem.*, **101**, 934; 1989, *Angew. Chem. Int. Ed. Engl.*, **28**, 914. (b) Bengs, H., Ebert, M., Karthaus, O., Kohne, B., Praefcke, K., Ringsdorf, H., Wendorff, J. H., and Wüstefeld, R., 1990, *Adv. Mater.*, **2**, 141.

[4] Praefcke, K., Singer, D., Kohne, B., Ebert, M., Liebmann, A., and Wendorff, J. H., 1991, *Liq. Crystals*, **10**, 147.

[5] Bengs, H., Karthaus, O., Ringsdorf, H., Baehr, C., Ebert, M., and Wendorff, J. H., 1991, *Liq. Crystals*, **10**, 161.

[6] Ebert, M., Frick, G., Baehr, C., Wendorff, J. H., Wüstefeld, R., and Ringsdorf, H., 1992, *Liq. Crystals*, **11**, 293.

[7] Praefcke, K., Singer, D., Langner, M., Kohne, B., Ebert, M., Liebmann, A., and Wendorff, J. H., 1992, *Molec. Crystals liq. Crystals*, **215**, 121.

[8] Heppke, G., Kitzerow, H., Oestreicher, F., Quentel, S., and Ranft, A., 1988, *Molec. Crystals liq. Crystals Lett.*, **6**, 71.

[9] Heppke, G., Ranft, A., and Sabaschus, B., 1991, *Molec. Crystals liq. Crystals Lett.*, **8**, 17, and references therein.

[10] Schad, Hp., Scheuble, B., and Nehring, J., 1979, *J. chem. Phys.*, **71**, 5140, and references therein.

[11] Bradshaw, M. J., and Raynes, E. P., 1983, *Molec. Crystals liq. Crystals*, **99**, 107.

[12] Sokalski, K., and Ruijgrok, Th. W., 1982, *Physica* A, **113**, 126.