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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Influence of Molecular Structure on the Low Frequency Dielectric Relaxation of p-Cyano-substituted Liquid Crystals in Nematic Solution

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Version of record first published: 17 Oct 2011.

To cite this article: G. Heppke , J. Kayed & U. Müller (1983): Influence of Molecular Structure on the Low Frequency Dielectric Relaxation of p-Cyano-substituted Liquid Crystals in Nematic Solution, Molecular Crystals and Liquid Crystals, 98:1, 309-319

To link to this article: http://dx.doi.org/10.1080/00268948308073484

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Mol. Cryst. Liq. Cryst., 1983, Vol. 98, pp. 309–319
0026-8941/83/9804–0309/$18.50/0
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Printed in the United States of America

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Influence of Molecular Structure on the Low Frequency Dielectric Relaxation of *p*-Cyano-substituted Liquid Crystals in Nematic Solution†

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(Received February 28, 1983)

The dielectric properties of several *p*-alkyl-*p'*-cyano-substituted liquid crystals of different molecular length, dissolved in the nematic mixture ZLI 1275, have been investigated as a function of frequency and temperature. Low relaxation frequencies have been observed which decrease from 138 kHz to 1.5 kHz at 25°C roughly corresponding to the increase of molecular length. Arrhenius plots show good linear relations with the activation energies being found to increase with decreasing relaxation frequency.

INTRODUCTION

In nematic phases, the lowest frequency at which a dispersion of the dielectric constant $\varepsilon_{\parallel}$ occurs is drastically decreased compared with that in isotropic phases. In isotropic phases the corresponding relaxation time is mainly related to the geometry of the molecule and the viscosity of the surrounding fluid.[1,2] Additionally, in nematic phases the molecular ordering has to be taken into account.[3,4] This considerably slows down the process of reorientation of the permanent dipole moment parallel to the long molecular axis.

Several papers have reported on dielectric relaxation in pure nematic phases.[5] However, in these cases variation of the molecular structure influ-

†Presented at the Ninth International Liquid Crystal Conference, Bangelore, December 6–10, 1982.

ences all three main contributions to the relaxation process simultaneously. Therefore, the investigations of this paper are restricted to dilute solutions of strongly polar *p*-cyano-substituted compounds in the same (more or less) non-polar nematic solvent which exhibits no dielectric relaxation of $\varepsilon_\parallel$ in the frequency range in question.

Depending on the value of the dielectric constant $\varepsilon_\parallel$ of the nematic solvent, mixtures of this kind will generally change the sign of the dielectric anisotropy with frequency. Therefore, they are also of interest for electro-optical display device applications, e.g., for mixtures with high multiplexing capability or for fast modulators.[6,7] Moreover, these nematic mixtures promise to combine two properties which at first sight do not seem compatible; these are low relaxation frequency and low viscosity.

EXPERIMENTAL

To study the influence of molecular structure on the dielectric relaxation process, *p*-alkyl-*p'*-cyano-substituted liquid crystalline compounds of different molecular length were chosen (Table I). Compound **6** was supplied by BDH Chemicals (T15), and compound **7** by E. Merck (ZLI 1131); all others were synthesized by standard methods. As solvent, the nematic mixture ZLI 1275 (t_{NI} = 83°C) was used; this exhibits a negative dielectric anisotropy ($\varepsilon_\parallel$ = 3.2, $\varepsilon_\perp$ = 4.0 at 25°C and 1 kHz) almost independent of frequency. Solutions of equivalent molality were used (generally 0.1 mol/kg which corresponds to 4–6 wt.%). The dielectric measurements were performed as described elsewhere in detail.[8] The HP 4274A multi-frequency LCR meter used offers a frequency range from 100 Hz to 100 kHz. The temperature range was 1°C to 95°C.

RESULTS AND DISCUSSION

Figure 1 shows the frequency dependence of the dielectric constants for a 0.1 mol/kg solution of the liquid crystalline compound **12** in ZLI 1275 at different temperatures. Similar results were obtained for all other compounds. The dielectric constants $\varepsilon_\perp$ are found to be independent of frequency; whereas, the dielectric constants $\varepsilon_\parallel$ show a characteristic step, the relaxation frequency markedly decreasing upon cooling. The high frequency values of $\varepsilon_\parallel^{HF}$ approach the dielectric constant $\varepsilon_\parallel$ of the nematic solvent ZLI 1275 and are nearly independent of temperature. The low frequency values $\varepsilon_\parallel^{LF}$, however, are enhanced with decreasing temperature due to the increase of the order parameter.[3,4]

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TABLE I

Structures of the compounds under investigation.

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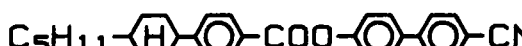
5	
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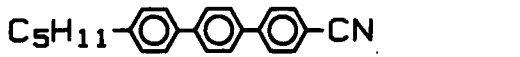
8	
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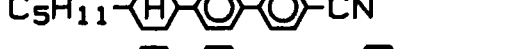
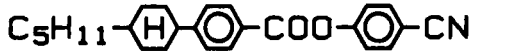
10	
11	
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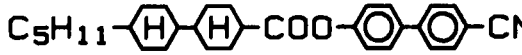
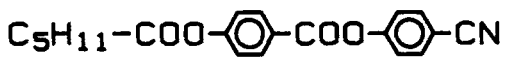
14	
15	

By the addition of the polar component, the dielectric anisotropy at low frequency is considerably increased compared with that of the solvent ((($\Delta\varepsilon = 0.8$ at 25°C and 1 kHz) as Figure 2 shows for the case of compound **12**.) Most of the components contain ester groups which contribute to the permanent dipole moment perpendicular to the long molecular axis. Mainly from this, the addition of the polar component also increases the value of $\varepsilon_\perp$. Thus, at low temperatures and high frequencies, i. e., in the situation where no reorientation of the molecule around its short axis is possible, the magnitude of the negative dielectric anisotropy is increased compared with that of the solvent.

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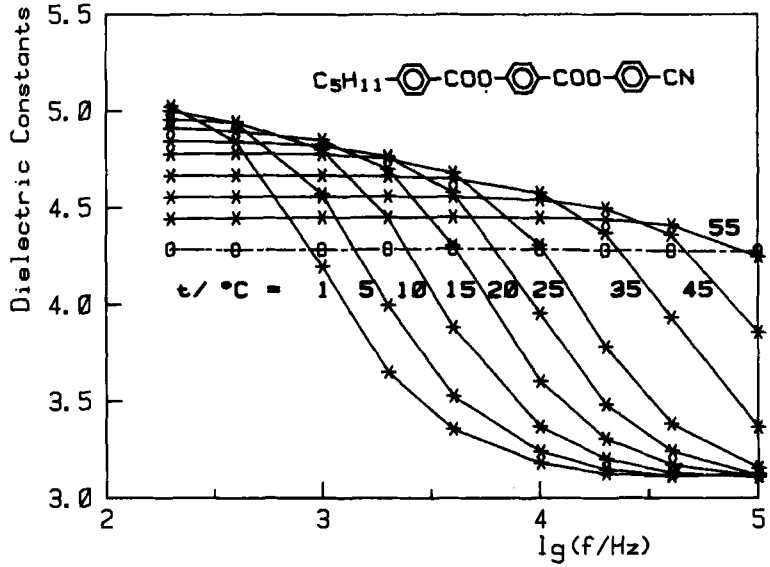

FIGURE 1 Dielectric constants $\varepsilon_{\parallel}$ (*) and $\varepsilon_{\perp}$ (0) as a function of frequency for compound **12** (0.1 mol/kg in ZLI 1275). The temperature increases from left to right for $\varepsilon_{\parallel}$ (*) and is 25°C for $\varepsilon_{\perp}$ (0).

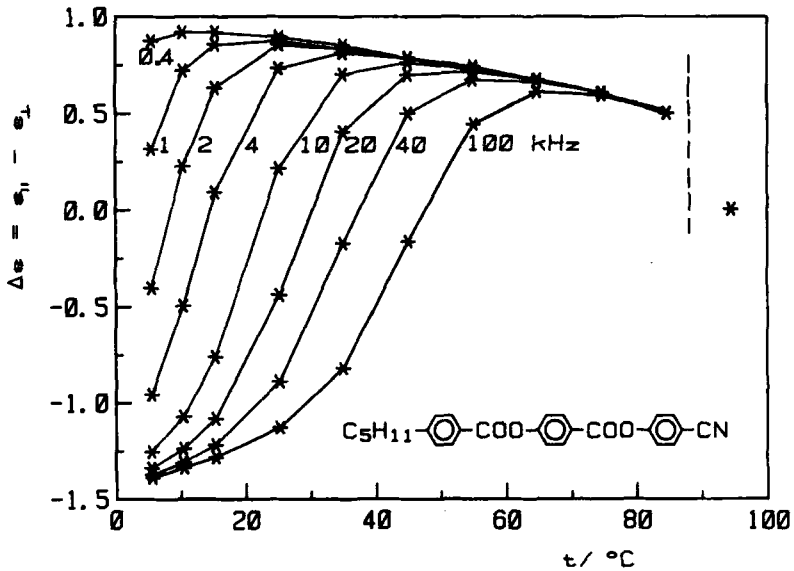

FIGURE 2 Dielectric anisotropy $\Delta\varepsilon$ as a function of temperature for compound **12** (0.1 mol/kg in ZLI 1275) at different frequencies. The dashed line indicates the clearing temperature.

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In Figure 3, the variation of the dielectric constants with the concentration of the polar component is studied. Usually for liquid crystal mixtures, a linear relationship to the molar fractions of the components has been found,[7,9] though this behavior does not seem to be fully established by theory. Indeed, for compound **12** a good linear relationship is obtained when plotting the values $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ vs the molality (Figure 3). This is remarkable considering the fact that the clearing temperature of the mixtures increases with the amount of the polar component (Table II) thereby

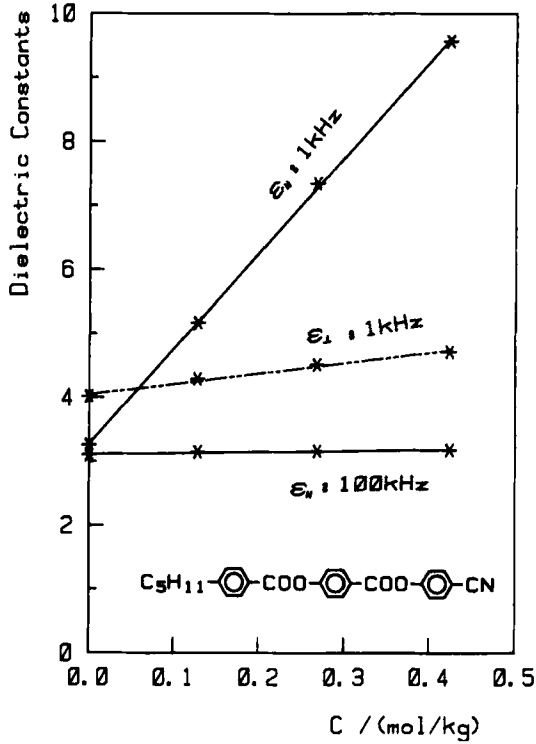

FIGURE 3 Dielectric constants as a function of concentration c of compound **12** in ZLI 1275 at 25°C.

TABLE II

Clearing temperature t_{NI} and relaxation frequency $f_{1/2}$ for different concentrations of compound **12** in ZLI 1275.

c/mol · kg^{-1}	t_{NI}/°C	$f_{1/2}$/kHz
0.13	89.6	14.6
0.27	98.6	9.1
0.42	104.4	7.4

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enhancing the order parameter. Further investigation into this problem is required.

At low temperatures, the nematic solvent ZLI 1275 itself exhibits a slight frequency dependence of $\varepsilon_\parallel$ which will affect the evaluation of the dispersion behavior of the solute. To eliminate the contribution of the solvent to the dielectric constants, the values of pure ZLI 1275 (according to its contribution by weight in the mixtures) are subtracted.

Figure 4 shows the $\varepsilon_\parallel$-values corrected in such a manner for three concentrations of compound **12**. The full lines have been calculated after the Debye formula

$$\varepsilon_\parallel(f) = \varepsilon_\parallel^{HF} + \frac{\varepsilon_\parallel^{LF} - \varepsilon_\parallel^{HF}}{1 + (f/f_{1/2})^2} \tag{1}$$

with $f_{1/2}$ denoting relaxation frequency. The coincidence of theoretical and measured values proves the validity of a single Debye relaxation mechanism. This agrees with recent observations of other authors.[7,10]

As Table II shows, the relaxation time $\tau = 1/(2\pi f_{1/2})$ grows with increasing concentration of the polar component. Theoretically the relation

$$\tau = g\tau_0 \tag{2}$$

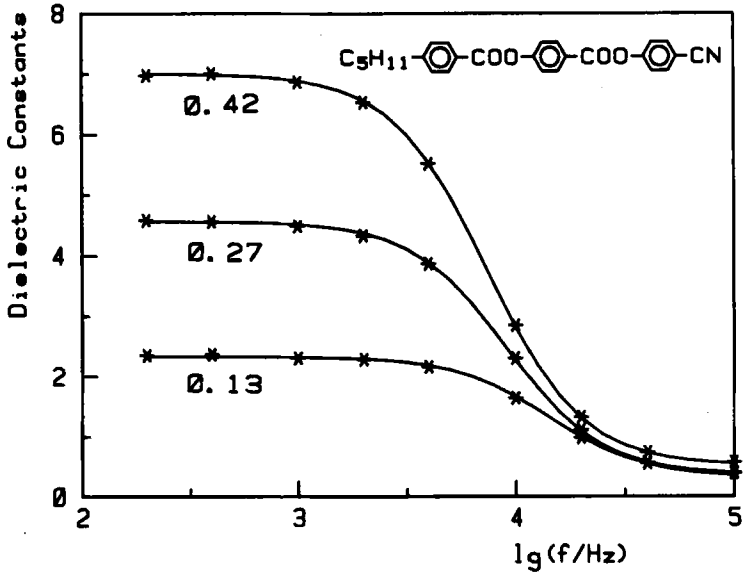

FIGURE 4 Frequency dependence of the corrected dielectric constants at different concentrations (in mol/kg) of compound **12** in ZLI 1275 at 25°C.

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is predicted,[3,4] where τ_0 is the relaxation time of a comparable isotropic liquid and g denotes the retardation factor which takes into account the influence of the nematic order. Considering this relation, two factors may be responsible for the increase of the relaxation times. Firstly, the addition of the polar component will generally increase the viscosity. Secondly, it will enhance the clearing temperature which with reference to constant temperature will result in an increase of the order parameter and thereby the retardation factor.

From the frequency dependences of $\varepsilon_\parallel$ at different temperatures, $f_{1/2}$-values were obtained for each of the compounds **1–15** at a standard concentration of 0.1 mol/kg. As is shown in Figure 5 for three examples (**6, 12** and **14**), very good linear relationships have been found between $\lg(f_{1/2})$ and $1/T$ (Arrhenius-behavior) in all cases. For comparison, the values of a flow viscosity η (Ubbelodhe-viscosity)[11] and of the rotational viscosity[12] γ_1 for the solvent ZLI 1275 are included in Figure 5. Contrary

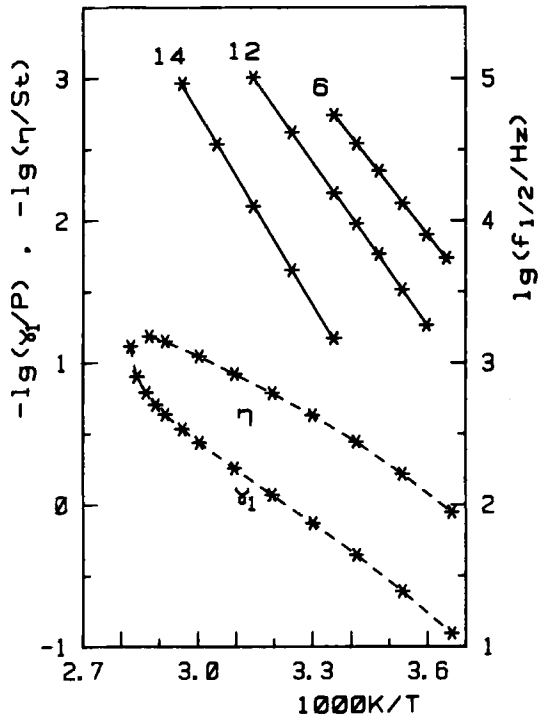

FIGURE 5 Arrhenius plots of the relaxation frequency (full line) for the compounds **6, 12** and **14** at a concentration of 0.1 mol/kg and the viscosities η and γ_1 (dashed line) for the solvent ZLI 1275.

to the linear behavior of the relaxation frequencies, curves are obtained for the viscosities. Taking into account the temperature dependence of the g-factor according to Eq. 2 an even more distinct bending is to be expected. Therefore the Arrhenius-behavior predicted by the earlier theory[3,5]

$$f_{1/2} \sim \exp(-E_a/kt) \tag{3}$$

is more likely to describe the experimental results on $f_{1/2}$.

Altogether the dielectric properties of the diluted nematic mixtures can be characterized by three parameters (Table III):

the relaxation frequency at one temperature (25°C) = $f_{1/2}$,

the activation energy = E_a,

the step height of the dielectric constant $\varepsilon_\parallel$ at a standard concentration (0.1 mol/kg) = $\varepsilon_\parallel^{LF} - \varepsilon_\parallel^{HF}$.

The theories of Debye and Perrin predict the dependence of the relaxation times on molecular size.[1,2,13] Therefore, the molecular lengths l obtained from Dreiding-models are included in Table III. Roughly, the $f_{1/2}$-frequency decreases with molecular length, but no linear relationship as predicted theoretically between $\lg(f_{1/2})$ and $\lg(l)$ is found. Obviously this dicrepancy reflects the influence of intermolecular forces and molecular rigidity varying with the respective structure. For example, the length of compound **11** is similar to that of **6** and **7**, but the value of the relaxation

TABLE III

Molecular length l for each of the compounds investigated. Clearing temperature t_{NI}, relaxation frequency $f_{1/2}$ at 25°C, activation energy E_a and step height $\varepsilon_\parallel^{LF} - \varepsilon_\parallel^{HF}$ at 25°C for 0.1 mol/kg solutions in ZLI 1275.

No.	l/nm	t_{NI}/°C	$f_{1/2}$/kHz	E_a/eV	$\varepsilon_\parallel^{LF} - \varepsilon_\parallel^{HF}$
1	2.61	93.4	6.74	0.79	1.16
2	2.73	94.1	3.16	0.89	1.09
3	2.86	93.9	3.32	0.85	1.05
4	2.99	95.0	2.50	0.87	1.04
5	3.24	94.2	1.87	0.89	1.04
6	2.31	86.9	55.3	0.86	0.71
7	2.33	86.6	61.1	0.69	0.65
8	2.57	87.8	27.3	0.72	1.02
9	3.03	94.0	2.86	0.85	1.03
10	2.99	95.9	2.37	0.88	0.80
11	2.35	82.6	138	0.67	0.97
12	2.76	88.0	15.6	0.76	1.52
13	2.81	88.6	15.6	0.75	1.06
14	3.44	95.1	1.48	0.89	1.60
15	2.97	89.4	7.69	0.80	1.62

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frequency is more than two times higher. The same difference is found for **15** with respect to **4, 9** and **10**. Presumably this is caused by the additional two ester groups which are contained in **11** and **15** as compared with **6, 7** or **4, 9** and **10** respectively.

As is found for the $f_{1/2}$-values, the activation energies E_a increase more or less monotonously with molecular length. This effect may be mainly explained by the increase of the order parameter which on its part enhances the retardation factor. Figure 6 demonstrates a close correlation between $\lg(f_{1/2})$ and E_a indicating that both quantities are influenced by the same factors. This is in agreement with recent results obtained on rather different mixtures.[10]

Since the step height $\varepsilon_{\parallel}^{LF} - \varepsilon_{\parallel}^{HF}$ refers to the same number of molecules (0.1 mol/kg), this value is a measure for the longitudinal component of the molecular dipole moment. Three groups of molecules can be distinguished (Tables I, III),

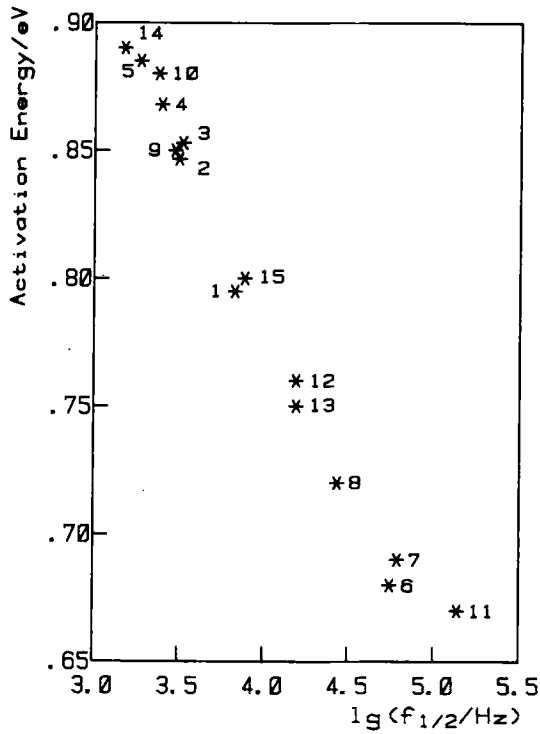

FIGURE 6 Activation energy *vs* the logarithm of the relaxation frequency for 0.1 mol/kg solutions of the compounds **1–15** in ZLI 1275.

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compounds **6**, **7** and **10**: $\varepsilon_{\parallel}^{LF} - \varepsilon_{\parallel}^{HF} \leq 0.8$,

compounds **1**, **5**, **8**, **9**, **11**, **13**: $\varepsilon_{\parallel}^{LF} - \varepsilon_{\parallel}^{HF} \approx 1$,

compounds **12**, **14**, **15**: $\varepsilon_{\parallel}^{LF} - \varepsilon_{\parallel}^{HF} \geqq 1.5$.

Obviously the main contributions to the total longitudinal dipole moment arise from the *p*-cyano-phenyl group and the ester linkage, especially when it is part of a phenyl benzoate group.

CONCLUSIONS

The results show that blending a low viscous nematic solvent with a small amount of a liquid crystalline cyano-compound leads to mixtures exhibiting a dispersion of the parallel dielectric constant $\varepsilon_{\parallel}$ at low frequencies. The relaxation frequencies for the mixtures under investigation are found to vary by two orders of magnitude, mainly depending on the molecular length of the polar additive.

The frequency dependence of $\varepsilon_{\parallel}$ is well described by a simple Debye relaxation mechanism. The dependence of relaxation frequency on temperature can be very well characterized by an Arrhenius-behavior. This result is remarkable with respect to the behavior of viscosity, retardation factor, and order parameter. Therefore, further theoretical and experimental investigations are required.

Obviously, viscosity and relaxation frequency are not strictly correlated, so that, regarding electro-optical device application, the development of dual-frequency materials with low relaxation frequency and at the same time low viscosity seems possible.[7,10,14]

A close correlation between the relaxation frequencies and the activation energies is found to hold for all compounds studied, denoting that both quantities are influenced by the same factors. With respect to dual-frequency mixtures this is a disadvantage, which may only be reduced by using optimized nematic solvents.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Gesellschaft der Freunde der Technischen Universität for financial support.

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