Dielectric relaxation study of 1-*n* hexyl-4-(4-isothiocyanatophenyl)bicyclo [2,2,2] octane in the nematic and isotropic phases

D. Bauman[a]; P. Kędziora[b]; C. Legrand[c]; J. Jadzyn[b]

[a] Institute of Physics, Poznań University of Technology, Poznań, Poland [b] Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland [c] Département Hyperfréquencies et Semiconducteurs, Institut d'Electronique et de Microelectronique du Nord, Villeneuve d'Ascq, France

PLEASE SCROLL DOWN FOR ARTICLE

Dielectric relaxation study of 1-n hexyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octane in the nematic and isotropic phases

by D. BAUMAN*†, P. KĘDZIORA‡, C. LEGRAND§ and J. JADŻYN‡

†Institute of Physics, Poznań University of Technology, Piotrowo 3,
60-965 Poznań, Poland
‡Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17,
60-179 Poznań, Poland
§Institut d'Electronique et de Microelectronique du Nord,
Département Hyperfréquencies et Semiconducteurs, F-59652 Villeneuve d'Ascq,
France

Dielectric relaxation investigations on the mesogen 1-n-hexyl-4-(4-isothiocyanato-phenyl)bicyclo[2,2,2]octane in the nematic and isotropic phases have been carried out in the frequency region from about 1 kHz to 1 GHz. Two relaxation processes have been observed in both the isotropic and nematic phases, when the measurements of the electric permittivity versus frequency are made parallel to the orientation axis of the liquid crystal. The possible mechanisms responsible for these two processes are discussed. The height of the potential barrier which hinders the rotation of the liquid crystal molecules around the short axis in the nematic state, and the order parameter of the liquid crystal under investigation have been estimated on the basis of the values for the relaxation times in the nematic and isotropic phases.

1. Introduction

Dielectric studies of nematic liquid crystals have proved to be a valuable source of information on molecular arrangement and molecular reorientations, as well as on specific intermolecular interactions in the mesomorphic and isotropic phases. Knowledge of the dielectric properties of liquid crystals is also important for technical reasons, because of the application of these substances in electro-optical display devices. Therefore, dielectric studies for a number of nematic liquid crystals have been carried out both experimentally [1] and theoretically [2–7].

For calamitic liquid crystals, if one neglects the precessional and librational movements, there exist two possibilities for relaxation of the electric dipole moments connected with the rotation of the rod-like molecules around two main molecular axes. If the sample is in the nematic phase and is macroscopically oriented, e.g. by means of a magnetic field, the dielectric relaxation occurs at very different frequency regions when the measuring electric field is parallel or perpendicular to the orientation axis of the liquid crystal. In the parallel condition, the relaxation process is observed in the megahertz range, whereas in the perpendicular situation, the relaxation occurs at higher frequencies in the gigahertz range. The presence of the low frequency relaxation region in the parallel component is characteristic for the liquid crystalline state and is connected with hindering of molecular rotation around the short axis in the presence of the nematic potential.

In this paper we have investigated the relaxation processes for the mesogen 1-n-hexyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octane (referred to from now on as I) in the nematic and isotropic phases. This compound and its homologues were discovered by Dąbrowski et al. [8] and, because of their low viscosity, low melting enthalpies, the occurrence of nematic phases only [8, 9] and strong positive dielectric anisotropy [10, 11], can be highly useful as components of technologically important liquid crystal mixtures.

2. Experimental

The nematogenic (I) has the following chemical structure:

$$C_6H_{13} - \langle bicyclooctane \rangle - \langle phenyl \rangle - NCS$$
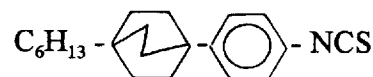
*Author for correspondence.

This was supplied by Professor R. Dąbrowski from the Military Academy of Technology in Warsaw and was used without further purification. The temperatures of the phase transitions were in the agreement with the literature [8] and were as follows:

$$Cr \ 324{\cdot}7\,K \quad N \quad 362{\cdot}9\,K \ I.$$

Permittivity (ε') and dielectric loss (ε'') were measured at different temperatures in both the nematic and isotropic phases. The measurements were made in the frequency region from about 1 kHz to 1 GHz using two impedence analyzers HP4192A (1 kHz–13 MHz) and HP4191A (1 MHz–1 GHz) connected with an HP87 computer. The measuring cell consisted of two parallel-plane capacitors located at the end of a coaxial line [12]. The homogeneous orientation of the molecules in the nematic phase was obtained by means of a magnetic field of 1·2 T and the measurements were carried out for a position of the cell in the electromagnet such that the magnetic field **B** was parallel to the electric field **E** ($\varepsilon_\parallel$). It was estimated that the overall uncertainty was better than 2% for ε' and 5% for ε''. The temperature of the sample was stable within $\pm 0{\cdot}1$ K.

3. Results and discussion

Figure 1 presents the permittivity, ε' and the dielectric loss, ε'' *versus* frequency for **I** in the nematic phase

(parallel component), whereas figure 2 shows ε' and ε'' as a function of frequency in the isotropic phase. It is seen that the relaxation strength in the nematic phase decreases as the temperature rises and simultaneously, the effective relaxation time, corresponding to the maximum of the absorption spectrum, shifts towards lower values. In the isotropic phase, the relaxation strength is significantly lower than in the nematic phase and remains almost constant. The position of the absorption maximum also changes only very slightly.

It was previously found by Buka *et al.* [13] that in the dielectric relaxation spectra measured in the frequency range up to 18 GHz for 4-alkyl-4'-cyanobiphenyls (*n*CB), both in the nematic and isotropic phases, two relaxation contributions of the Debye-type can be distinguished. Results obtained for other liquid crystals with strong longitudinal dipole moments [14–16] have shown that the dielectric spectra measured for both the nematic and isotropic phases can also be interpreted as a sum of two relaxation processes described by the Debye functions. Therefore, we too have tried to separate the relaxation spectra for the liquid crystal material under investigation into two Debye-type components by using the following equations:

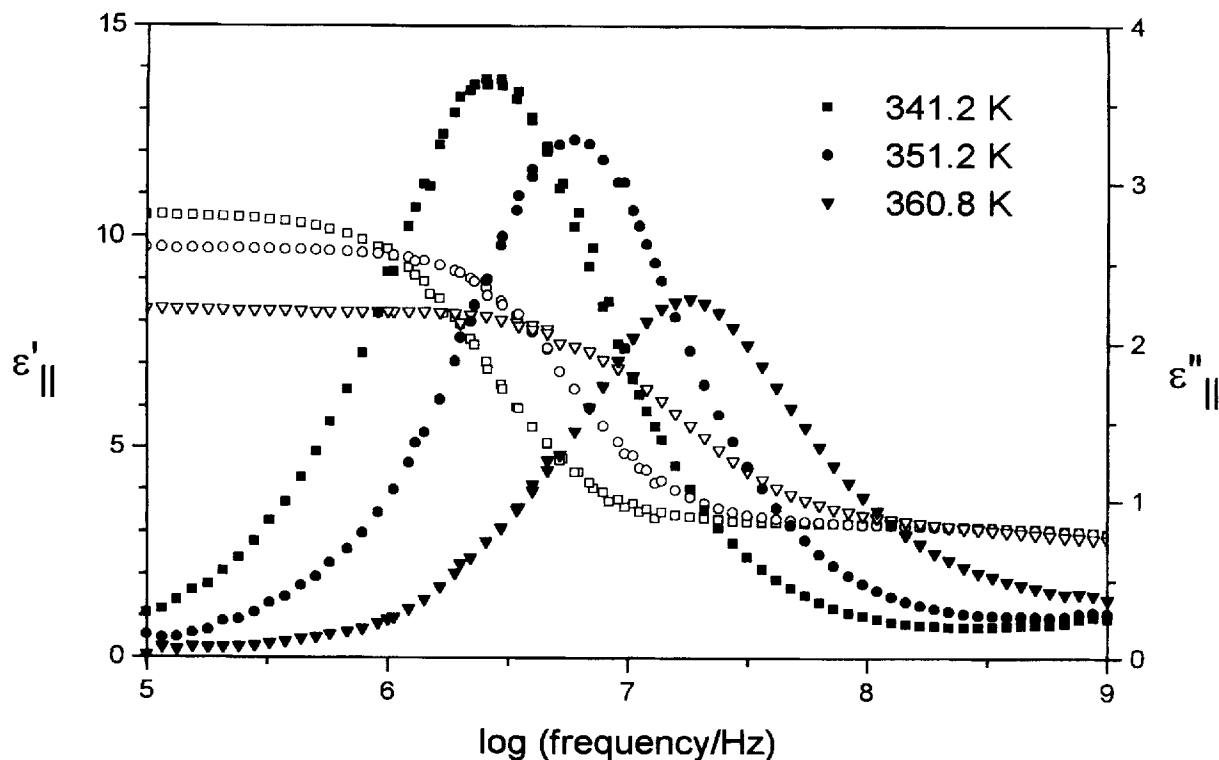$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{i=1}^{2} A_i \frac{1}{1 + \omega^2 \tau_i^2} \qquad (1)$$

Figure 1.   Parallel component of permittivity, $\varepsilon'_\parallel$ (open) and dielectric loss, $\varepsilon''_\parallel$ (filled) *versus* frequency for **I** in the nematic phase.
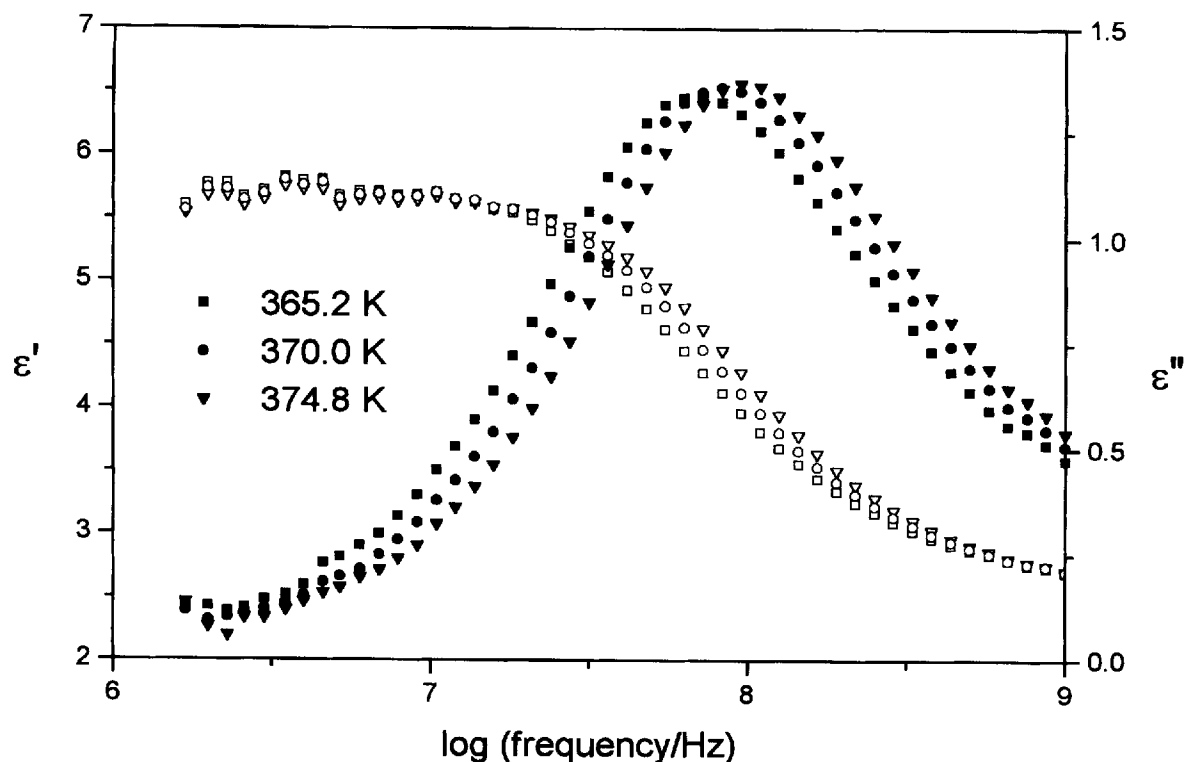
Figure 2. Permittivity, ε' (open) and dielectric loss, ε'' (filled) *versus* frequency for **I** in the isotropic phase.

$$\varepsilon''(\omega) = \sum_{i=1}^{2} A_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \qquad (2)$$

where A_i and τ_i denote the relaxation strength and the relaxation time, respectively. They are the adjustable parameters in the fitting procedure.

Figures 3 and 4 show the examples of the decomposition of the dielectric loss spectra into two components at two temperatures: $T = 351 \cdot 2$ K (nematic phase) and $T = 370$ K (isotropic phase), respectively. The values of A_i and τ_i determined at each temperature are gathered in table 1, and figure 5 presents the temperature dependence of these quantities. It is seen that the significant changes at the nematic–isotropic phase transition and in the nematic phase occur only for A_1 and τ_1.

Previously it was found [10, 11] that the liquid crystal under investigation has a very strong positive dielectric anisotropy (e.g. at $T = 341 \cdot 2$ K, $\Delta \varepsilon = 6 \cdot 0$), indicating that the dipole moment component along the molecular long axis, $\mu_\parallel$ is considerably larger than the component perpendicular to this axis, $\mu_\perp$. This suggests that the main relaxation process, observed both in the parallel component of ε in the nematic phase and in the isotropic phase, is, as for other nematogens [1, 13–16], connected with rotation of the molecule around its short axis. In the mesomorphic phase, because of the existence of the nematic potential, this process is strongly hindered and

therefore it is observed at frequencies significantly lower than in the isotropic phase. The origin of the higher frequency relaxation is not clearly established. In the absence of a perpendicular dipole moment component, it cannot be associated with rotation about the molecular axis. Buka and Leyvraz [5] explained this high frequency process by a combination of the rotational diffusion and flip-flop model. However, in the case of **I**, the –NCS group does not need to be directed exactly along the molecular long axis and a small component of the dipole moment perpendicular to this axis may exist. A transverse dipole moment, different from zero, can also be connected with the flexibility of the alkyl chain and its influence on the direction of the overall molecular axis. Therefore, it seems that the high frequency relaxation process is related to molecular

Table 1. Relaxation strengths A_i, and relaxation times τ_i, in the nematic and isotropic phases for **I**.

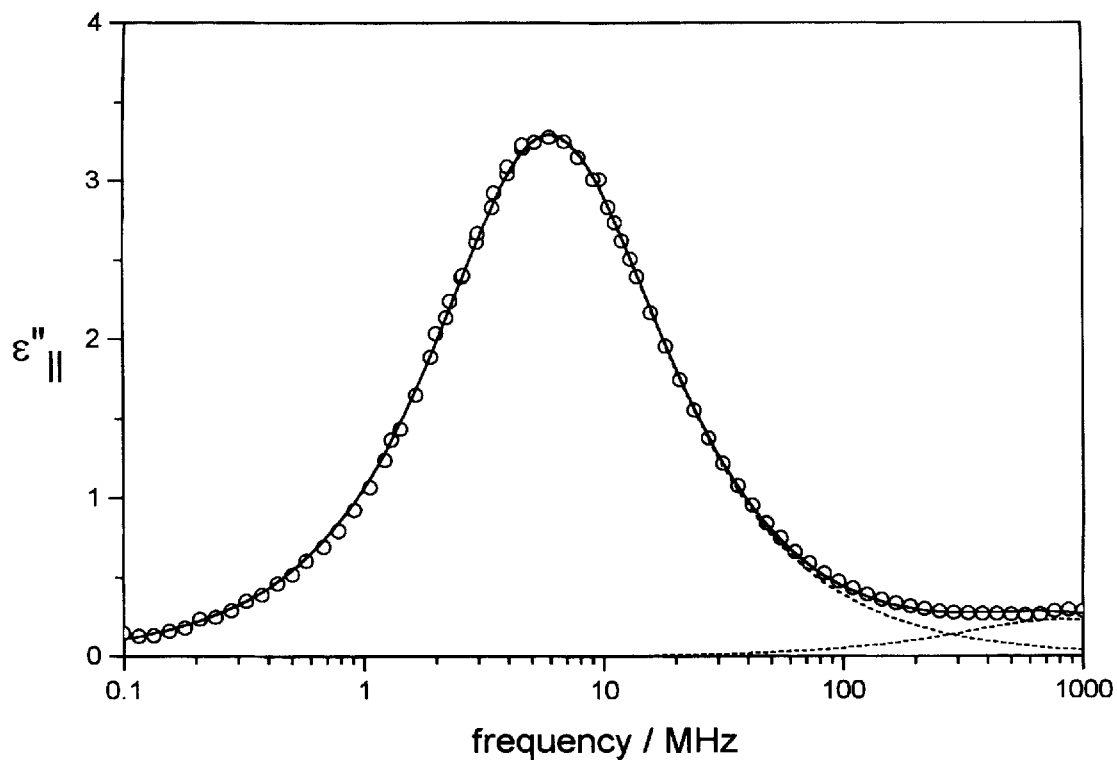| Phase	T/K	A_1	τ_1/ns	A_2	τ_2/ns
nematic	341·2	7·33	58·10	0·45	0·18
	351·2	6·63	26·50	0·47	0·18
	360·8	4·61	9·30	0·68	0·45
isotropic	365·2	2·51	2·59	0·74	0·36
	370·0	2·55	2·13	0·70	0·31
	374·8	2·56	1·80	0·66	0·27

Figure 3. Decomposition of the dielectric spectrum into two Debye-type absorption bands for **I** in the nematic phase at $T = 351 \cdot 2$ K.
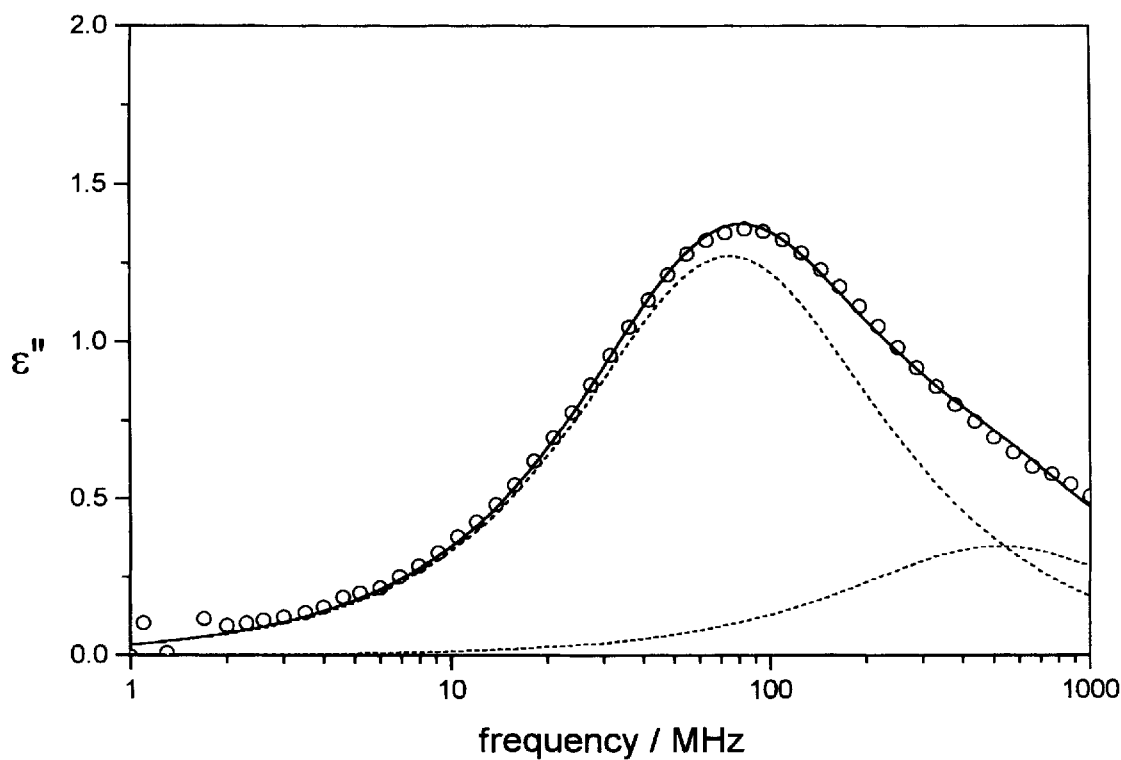

Figure 4. Decomposition of the dielectric spectrum into two Debye-type absorption bands for **I** in the isotropic phase at $T = 370$ K.
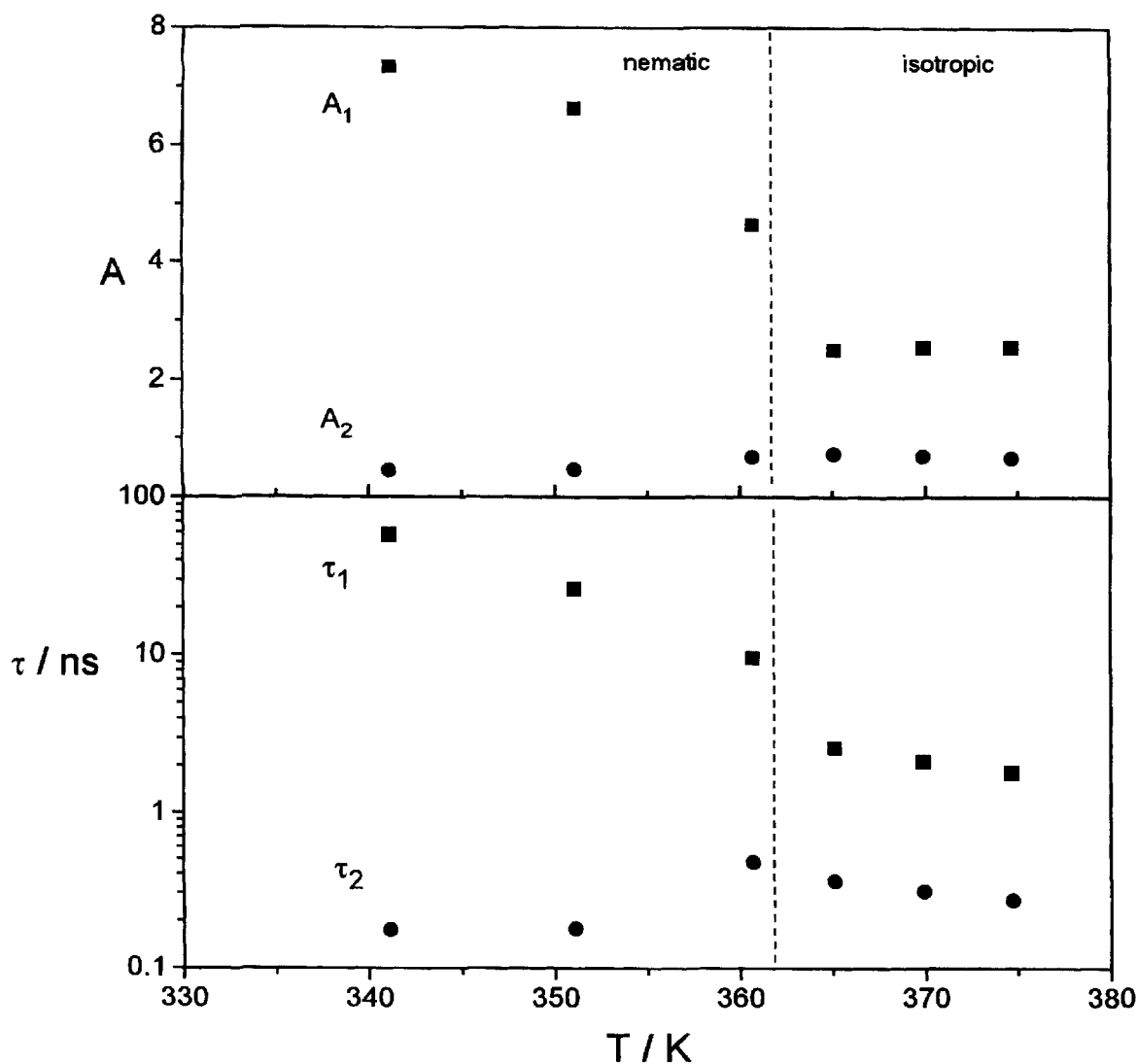
Figure 5. Relaxation strengths A_1 and A_2, and relaxation times τ_1 and τ_2 as a function of temperature in the nematic and isotropic phases for I.

rotation around the long axis. This can be confirmed by the fact that the relaxation time τ_2 in the nematic state (at temperatures 341·2 K and 351·2 K) is lower than in the isotropic phase. The alignment of the molecules in the nematic phase favours rotation around the long axis and this rotation becomes faster than in the isotropic liquid, where the rod-like molecules of the mesogen are randomly distributed.

The low frequency relaxation process can be analysed in terms of theories given by Martin, Meier and Saupe [3, 17]. They extended the Debye theory [18] of dielectric relaxation in liquids and showed that the relaxation time in the presence of the nematic potential, τ is larger than the relaxation time τ_0 for $q = 0$ (no nematic

potential) by a factor:

$$g = \frac{\tau(q \neq 0)}{\tau_0(q = 0)}, \qquad (3)$$

called the retardation factor. Here q is the height of the potential barrier. According to the Maier–Saupe mean field theory of nematics [19], the nematic potential has the following form:

$$U(\theta) = qP_2(\cos\theta), \qquad (4)$$

where $P_2(\cos\theta)$ is the second Legendre polynomial and θ is the angle between the molecular long axis of the liquid crystal and the direction of the orientation, described by the director **n**.

The intermolecular forces, leading to the potential barrier, cause the orientation of the liquid crystal molecules, and thus it is clear that there is a relationship between q and the order parameter $\langle P_2 \rangle$. This order parameter is defined by [20]:

$$\langle P_2 \rangle = \frac{1}{2}(3\langle \cos^2 \theta \rangle - 1), \tag{5}$$

where:

$$\langle \cos^2 \theta \rangle = \frac{\int_0^{\pi/2} \cos^2 \theta f(\theta) \sin \theta d\theta}{\int_0^{\pi/2} f(\theta) \sin \theta d\theta}. \tag{6}$$

Here $f(\theta)$ is the undisturbed distribution function of the nematic order. Its simplest form is [3, 18]:

$$f(\theta) = f(0) \exp\left(-\frac{q}{kT} \sin^2 \theta \right). \tag{7}$$

It is clear that when the degree of order increases, the rotation of the permanent electric dipole around the molecular short axis becomes more and more hindered, which means that the dielectric relaxation frequency associated with $\varepsilon_\parallel$ shifts to lower frequencies. This effect is seen in figure 1.

The relaxation time τ_0 in equation (3) is a hypothetical value for the nematic state without the existence of the nematic potential. In our experiment we have determined this through the extrapolation of the temperature dependence of the relaxation times τ_1 measured in the isotropic phase to the temperature of interest in the nematic phase. Hence the retardation factor, g, for the rotation of the liquid crystal molecule around its short axis has been calculated. Next, the barrier height of the nematic potential, q, using the plots given by Martin *et al.* [3], has been obtained. The values of τ_0, q and g determined at three temperatures in the nematic phase are presented in table 2. For easier comparison of the results with data given in the literature, the q values are given in two different units. Knowing q, the distribution function, $f(\theta)$ and the order parameter, $\langle P_2 \rangle$ have

Table 2. Relaxation time τ_0, retardation factor $g_\parallel$, height of the potential barrier q for rotation around the molecular short axis, and the order parameter $\langle P_2 \rangle$ for I.

T/K	τ_0/ns	$g_\parallel$	q eV	q kJ mol^{-1}	$\langle P_2 \rangle$
341·2	4·57	12·71	0·140	13·47	0·63
351·2	3·74	7·09	0·112	10·80	0·53
360·8	2·94	3·16	0·078	7·50	0·37

Table 3. Comparison of the order parameters of I obtained from the different experiments.

T/K	$\langle P_2 \rangle^a$	$\langle P_2 \rangle^b$	$\langle P_2 \rangle^c$	$\langle P_2 \rangle^d$
341·2	0·63	0·53	0·55	0·50
351·2	0·53	0·46	0·48	0·45
360·8	0·37	0·35	0·39	0·32

[a] This paper.
[b] From Δn [10, 11].
[c] From $\Delta \varepsilon$ [10, 11].
[d] From R [10, 11].

been calculated from equations (7) and (5), respectively. It has been estimated that the uncertainty in the determination of the order parameter was ± 0.01.

Now let us compare the values of the order parameter obtained for I from the dielectric relaxation time measurements with those determined using other methods: the optical birefringence, Δn, the dielectric anisotropy, $\Delta \varepsilon$, as well as from the anisotropy of absorption, R, measured for a dichroic dye dissolved in the liquid crystalline host ('guest–host' effect [21]). The data are taken from references [10, 11] and are gathered, together with the results obtained in this paper, in table 3.

It is seen, that the values of $\langle P_2 \rangle$ determined from the relaxation time measurements differ from those estimated by using other experimental methods and the discrepancy increases as the temperature rises. The difference, within 20%, between the order parameter values obtained with various methods has been noticed previously by many authors [22–25]. The discrepancy between the results obtained in this paper and those presented in references [10, 11] for I may arise additionally from the fact that the dielectric relaxation processes are dominated by the short range order and are strongly affected by molecular association [24, 26–28], whereas measurements of anisotropic properties reflect the long range orientational order.

References

[1] (a) DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach Science Publishers), Chap. 5; (b) BLINOV, L. M., 1983, *Electro-optical and Magneto-optical Properties of Liquid Crystals* (J. Wiley & Sons), pp. 49–68; (c) KRESSE, H., 1983, *Advances in Liquid Crystals*, Vol. 6, edited by G. H. Brown (Academic Press), pp. 109–172.
[2] MAIER, W., and MEIER, G., 1961, *Z. Naturforsch. A*, **16**, 470.
[3] MARTIN, A. J., MEIER, G., and SAUPE, A., 1971, *Symp. Faraday Soc.*, **5**, 119.
[4] NORDIO, P. L., RIGATTI, R., and SERGE, U., 1973, *Mol. Phys.*, **25**, 129.

[5] Buka, A., and Leyvraz, F., 1982, *Phys. Stat. Sol. B*, **112**, 289.

[6] Kozak, A., Mościcki, J. K., and Williams, G., 1991, *Mol. Cryst. liq. Cryst.*, **201**, 1.

[7] Kalmykov, P., 1991, *Liq. Cryst.*, **10**, 519.

[8] Dąbrowski, R., Dziaduszek, J., Drzewiński, W., and Czupryński, K., 1990, *Mol. Cryst. liq. Cryst.*, **191**, 171.

[9] Dąbrowski, R., 1990, *Mol. Cryst. liq. Cryst.*, **191**, 17.

[10] Herba, H., Żywucki, B., Czechowski, G., Bauman, D., Wąsik, A., and Jadżyn, J., 1995, *Acta Phys. Polon. A*, **87**, 985.

[11] Czechowski, G., Żywucki, B., Bauman, D., and Jadżyn, J., 1995, *Liquid Crystals: Materials Science and Applications*, edited by J. Żmija, Z. Raszewski and J. Zieliński, Proc. SPIE, **2372**, 163.

[12] Legrand, C., Parneix, J. P., Huutinh, N., and Destrade, C., 1985, *Mol. Cryst. liq. Cryst.*, **124**, 277.

[13] Buka, A., Owen, P. G., and Price, A. H., 1979, *Mol. Cryst. liq. Cryst.*, **51**, 273.

[14] Bose, T. K., Campbell, B., Yagihara, S., and Thoen, J., 1987, *Phys. Rev. A*, **36**, 5767.

[15] Jadżyn, J., Czechowski, G., Żywucki, B., Legrand, C., Bonnet, P., and Dąbrowski, R., 1993, *Z. Naturforsch A*, **48**, 871.

[16] Jadżyn, J., Hellemans, L., Stockhausen, M.,

[17] Legrand, C., and Czechowski, G., 1994, *Z. Naturforsch A*, **49**, 1077.

[17] Meier, G., and Saupe, A., 1967, *Liquid Crystals* (Gordon and Breach Science Publishers), pp. 195–205.

[18] Debye, P., 1929, *Polar Molecules* (New York: Chemical Catalogue Co.).

[19] Maier, W., and Saupe, A., 1960, *Z. Naturforsch A*, **14**, 882; **15**, 287.

[20] Saupe, A., 1964, *Z. Naturforsch A*, **19**, 161.

[21] Heilmeier, G. H., and Zanoni, L. A., 1968, *Appl. Phys. Lett.*, **13**, 91.

[22] Leadbetter, A. J., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 13.

[23] Żywucki, B., Kuczyński, W., and Czechowski, G., 1995, *Liquid Crystals: Materials Science and Applications*, edited by J. Żmija, Z. Raszewski and J. Zieliński, Proc. SPIE, **2372**, 151.

[24] Bauman, D., 1990, *Habilitation Dissertation*, Poznań.

[25] Urban, S., Gestblom, B., Brückert, T., and Würflinger, A., 1995, *Z. Naturforsch A*, **50**, 984.

[26] Madhusudana, N. V., and Chandrasekhar, S., 1975, *Pramana, Suppl.*, **1**, 57.

[27] Bauman, D., and Haase, W., 1989, *Mol. Cryst. liq. Cryst.*, **168**, 155.

[28] Bauman, D., 1989, *Mol. Cryst. liq. Cryst.*, **174**, 1.