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Dielectric Relaxation in the Nematic and Isotropic Phases of n-heptyl- and n- heptoxy-cyanobiphenyl

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Dielectric Relaxation in the Nematic and Isotropic Phases of *n*-heptyl- and *n*-heptoxy-cyanobiphenyl

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The dielectric spectrum of *n*-heptyl-cyanobiphenyl (7CB) and *n*-heptoxy-cyanobiphenyl (7OCB) are reported over a frequency range up to 18 GHz and over a temperature range well into the isotropic phase. Two relaxation processes are observed in the isotropic phase of both compounds, as well as in the nematic phase (when measurements are made parallel to the nematic director). Possible mechanisms for the two relaxation processes are discussed.

Some aspects of molecular reorientation in liquid crystals may be revealed by dielectric relaxation studies. In particular reorientation about the different molecular axes may be investigated using suitably aligned samples and intramolecular reorientations are often amenable to investigation. We wish to report the dielectric properties of *n*-heptoxy-cyanobiphenyl (7OCB) in the nematic and isotropic phases at frequencies up to 18 GHz and also an extension to 18 GHz of previous measurements made on *n*-heptyl-cyanobiphenyl (7CB) in order to further test the theories on dielectric relaxation in nematogens.

Three theories of dielectric relaxation in nematogens have been published.[2-4] The one due to Nordio *et al.*[2] applies generally to molecules whose resultant dipole moment lies at an angle to the long molecular axis, and predicts four relaxation processes in the nematic phase; two are observed in measurements made with the measuring electric field parallel with

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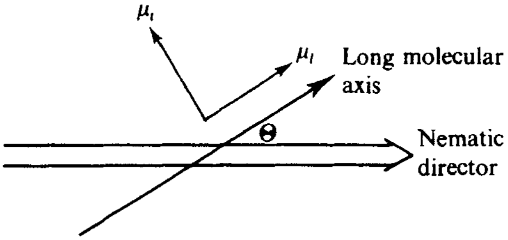

FIGURE 1 Schematic representation of dipole components in an aligned nematogen.

the uniformly aligned director (parallel alignment) and two with the measuring field perpendicular to the uniformly aligned director (perpendicular alignment). The situation may be schematically illustrated as in Figure 1, where μ_l and μ_t are the dipole components parallel and perpendicular to the long molecular axis inclined at an average angle θ (described by the nematic ordering potential S) to the nematic director. The overall dipole moment in the parallel alignment is given (in the mean field theory) by

$$\langle \mu_{11}^2 \rangle = \tfrac{1}{3}\mu_l^2(1 + 2S) + \tfrac{1}{3}\mu_t^2(1 - S) \tag{1}$$

and the dielectric spectrum reflects the relaxation of both dipolar contributions to $\langle \mu_{11}^2 \rangle$. The overall dipole moment in the perpendicular alignment is given by

$$\langle u_\perp^2 \rangle = \tfrac{1}{3}\mu_l^2(1 - S) + \tfrac{1}{3}\mu_t^2(1 + \tfrac{1}{2}S) \tag{2}$$

and again both components of $\langle \mu_\perp^2 \rangle$ contribute to the spectrum.

The Martin *et al.* theory[4] and that due to Pokrovsky[3] is restricted to nematogens with dipole moments parallel to the long molecular axis (e.g. 7CB with $\mu_t = 0$). One broad absorption is predicted in the perpendicular alignment, but two may occur in the parallel alignment if the nematic potential barrier is sufficiently high. The second absorption occurs at high frequencies and is much less intense than the lower frequency absorption arising from molecular reorientation about the short molecular axis.

EXPERIMENTAL

Both nematogens, *n*-heptyl-cyanobiphenyl (7CB) and *n*-heptoxy-cyanobiphenyl (7OCB), were supplied by Messrs. BDH Chemicals Ltd. and were used without further purification. The measured clearing points (7CB at 316 K and 7OCB at 347 K) agreed with the literative values.

Permittivity (ε^1) and dielectric loss measurements (ε^{11}) were made over the frequency range of 10^5 to 18×10^9 Hz using a Wayne Kerr B201 bridge, a Boonton RX meter 250 A and the sweep frequency microwave dielectrometer.[5] A specially constructed parallel plate capacitor was used for measurements on the Wayne Kerr bridge and on the Boonton RX meter. Corrections for lead effects followed the method described by O'Konski and Edwards.[6] The uncertainties in permittivity measurements were estimated as ±0.02 and in dielectric loss as ±5 % or 0.02 (whichever was the greater).

The measuring cells were temperature controlled to within ±0.1 K. Magnetic field could be applied either parallel to the measuring electrodes (parallel alignment) or perpendicular to the electrodes (perpendicular alignment). A magnetic flux density of about 0.2 T was sufficient to establish near saturation conditions. A coaxial line operating in the TEM mode was used for measurements using the sweep frequency methods. The nematogens were aligned using a solenoid wound around the coaxial cell (for perpendicular alignment) or by a low frequency (1kHz) square wave applied across the inner and outer conductors (for parallel alignment).

Analysis of the results

The variation of the dielectric loss with logarithm of the frequency is often symmetrical about the frequency of maximum dielectric loss. Such absorptions are conveniently analysed using the Fuoss–Kirkwood[7] equation:

$$\cosh^{-1}\frac{\varepsilon''_m}{\varepsilon''} = \beta \ln \frac{f_m}{f} \tag{3}$$

where ε'' is the dielectric loss at frequency f (the subscript m indicating the parameters at maximum dielectric loss) and β is an empirical distribution factor describing the width of the absorption ($0 < \beta \leq 1$; $\beta = 1$ corresponds to the Debye equation). Values of ε''_m were selected iteratively to give the best linear fit for Eq. (3), and f_m $(=(2\pi\tau)^{-1}$ where τ is the relaxation time) is determined from such a plot.

In cases where two relaxation times appear the absorptions were analysed using two Fuoss–Kirkwood equations. Analysis into two absorptions gave a better fit to the experimental data than did the use of an asymmetric absorption equation such as that proposed by Cole and Davidson.[6]

The intensity of the absorption $(\varepsilon_0 - \varepsilon_\infty = 2\varepsilon''_m/(\beta))$ was related to a molecular dipole (μ) moment using the Onsager equation

$$\mu^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)\varepsilon 9\mathbf{k}T}{\varepsilon_0(\varepsilon_\infty + 2)^2 N} \tag{4}$$

where ε_0 and ε_∞ are the limiting permittivity at low frequency and at frequencies beyond the dispersion range and N is the number of molecules per unit volume.

TABLE I

Dielectric relaxation parameters for *n*-heptylcyanobiphenyl (7CB)

		Low frequency absorption					High frequency absorption					
	T/K	ε_{01}	$\varepsilon_{\infty 1}$	β_1	τ_1/ns	$10^{30}\ \mu_1$/Cm	ε_{02}	$\varepsilon_{\infty 2}$	β_2	τ_2/ns	$10^{30}\ \mu_2$/Cm	Ref.
Nematic	294	5.40	2.45	0.61	2.4	7.37						
(perpendicular)	313	6.42	2.30	0.66	2.2	9.21						
	294	5.40	2.60	0.65	2.5							1
Nematic	294	16.71	3.55	1	112	11.8	3.55	3.25	1	0.26	2.2	
(parallel)	313	14.81	3.55	1	21	11.5	3.55	2.55	1	0.26	4.6	
	293	17.51	3.30	1	110							1
Isotropic	321	10.05	3.50	1	4.0	9.20	3.50	2.70	1	0.14	4.1	
	321	9.75	3.76	1	3.8							1

RESULTS AND DISCUSSION

A *n*-heptyl-cyanobiphenyl (7CB)

The dielectric parameters for 7CB are listed in Table I, and illustrated for the parallel alignment (nematic phase) and for the isotropic phase in Figures 2 and 3. The static permittivities agree with those determined by Dunmer *et al.*[9] Extension of the frequency coverage to 18 GHz produced no new features in the perpendicular alignment over the previously published results;[1] the absorption is broad and centred at 66.3 MHz at 294 K. The results are also in agreement with those reported by Lippens *et al.*,[10] but we have insufficient evidence to allow of a reliable resolution into three relaxation processes. The dipole moment calculated from the absorption intensity is 9.21×10^{-30} Cm at 313 K, a value higher than the 6.0×10^{-30} Cm calculated from the mean field theory using Eq. 2.

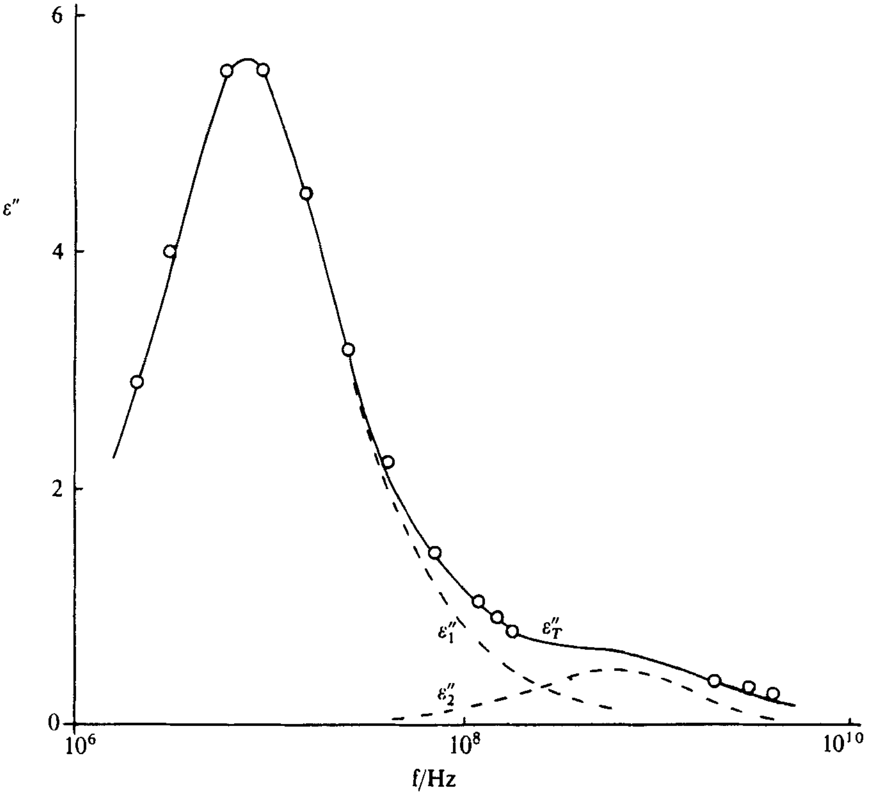

FIGURE 2 Dielectric absorption (ε'') as a function of frequency (*f*) in 7CB (nematic parallel alignment) at 313 K. ○, experimental points, - - - -, resolved components (ε''_1 and ε''_2); ———, calculated absorption ($\varepsilon''_T = \varepsilon''_1 + \varepsilon''_2$).

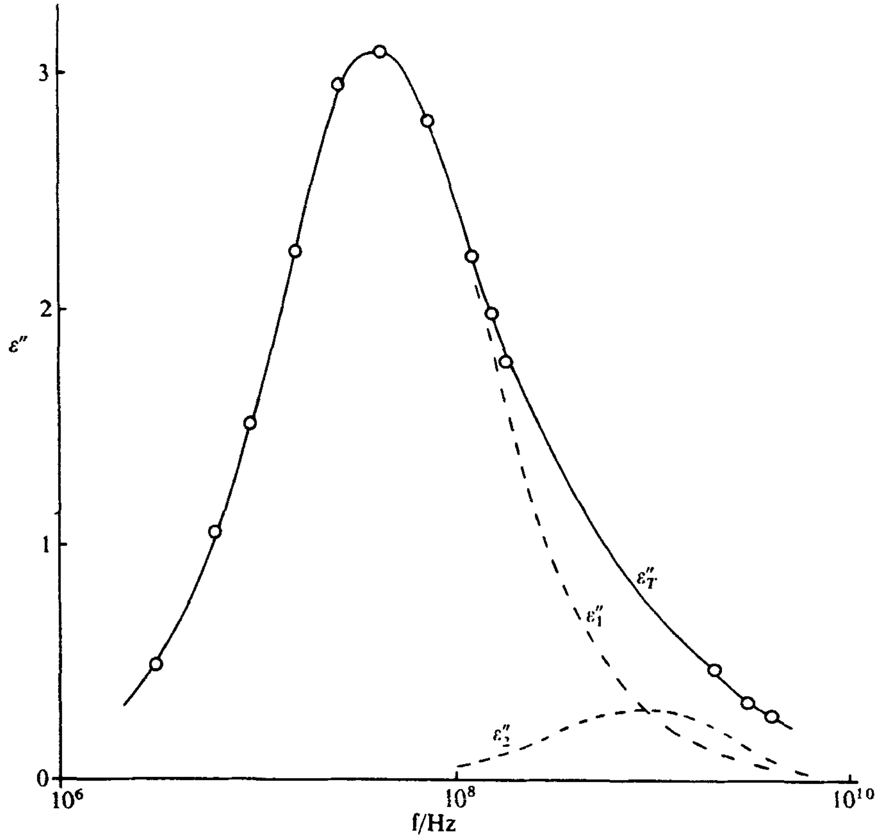

FIGURE 3 Dielectric absorption (ε'') as a function of frequency (f) in 7CB (isotropic phase) at 321 K. ○, experimental points, ----, resolved components (ε''_1 and ε''_2); ———, calculated absorption ($\varepsilon''_T = \varepsilon''_1 + \varepsilon''_2$).

However, extension of the frequency coverage to 18 GHz reveals a new absorption in both the nematic phase (parallel alignment) and in the isotropic phase. In the nematic phase the dielectric parameters for the low frequency, more intense absorption confirm previously published data.[1,10] The high frequency, low intensity absorption is a new feature which has not been previously reported. The parameters derived for this high frequency absorption are necessarily subject to a much higher uncertainty (± 10 to 15 per cent) than are those for the low frequency absorption. The total intensity of both absorptions corresponds to a dipole moment 12.1×10^{-30} Cm in good agreement with the 12.4×10^{-30} Cm calculated according to Eq. 1. In the isotropic phase the lower frequency absorption arises from a molecular reorientation similar to that found in "normal" isotropic liquids. The origin of the higher frequency absorption is not clearly established. It

TABLE II

Dielectric relaxation parameters for *n*-heptoxy-cyanobiphenyl (7OCB)

		Low frequency absorption					High frequency absorption				
τ/τ	T/K	ε_{01}	$\varepsilon_{\infty 1}$	β_1	τ_1/ns	$10^{30}\ \mu_1$/Cm	ε_{02}	$\varepsilon_{\infty 2}$	β_2	τ_2/ns	$10^{30}\ \mu_2$/Cm
Nematic (perpendicular)	331	6.50	2.35	0.6	1.42	9.61					
	335	6.66	2.35	0.6	1.38	9.85					
	339	6.88	2.35	0.7	1.42	10.1					
	342	7.12	2.35	0.7	1.45	10.5					
	346	7.52	2.35	0.7	1.57	10.9					
Nematic (parallel)	331	16.30	4.05	1	29.6	11.6	4.05	3.25	1	0.26	3.8
	335	15.90	4.05	1	23.0	11.5	4.05	3.05	1	0.25	4.4
	339	15.50	3.95	1	17.3	11.7	3.95	2.55	1	0.24	5.7
	343	14.85	3.85	1	12.9	11.6	3.85	2.45	1	0.23	5.9
	346	14.22	3.92	1	10.6	11.2	3.92	2.35	1	0.20	6.4
Isotropic	350	9.57	3.67	0.88	3.18	9.15	3.67	2.67	1	0.1	4.9
	355	10.20	3.62	0.90	2.55	9.74	3.60	2.60	1	0.1	5.0
	360	10.23	3.65	0.93	1.98	9.83	3.65	2.65	1	0.1	5.0

exists at similar frequencies and intensity in both the nematic (parallel alignment) and isotropic phases and could well arise from the same mechanism. The existence of significant short range order leading to "swarms" in the isotropic phase has been well established by e.g. far infra-red spectroscopy,[12,13] Kerr effect[14] and X-ray diffraction,[15] and the observed high frequency relaxation process could arise from a process involving partial reorientation within these localized ordered regions ("swarms").

B 7OCB

The dielectric parameters for 7OCB are listed in Table II, and the dielectric loss (ε'') for the parallel alignment and isotropic liquid is plotted as a function of the frequency in Figures 4 and 5.

The temperature variation of the permittivity of 7OCB in the nematic and isotropic phases is illustrated in Figure 6. The anisotropy of the permittivity is 9.8 at 331 K which is less than that for 7CB. This is expected since 7OCB has a resultant dipole moment at an angle to the long molecular axis. The mean permittivity ($\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$) suffers a discontinuity at the ne-

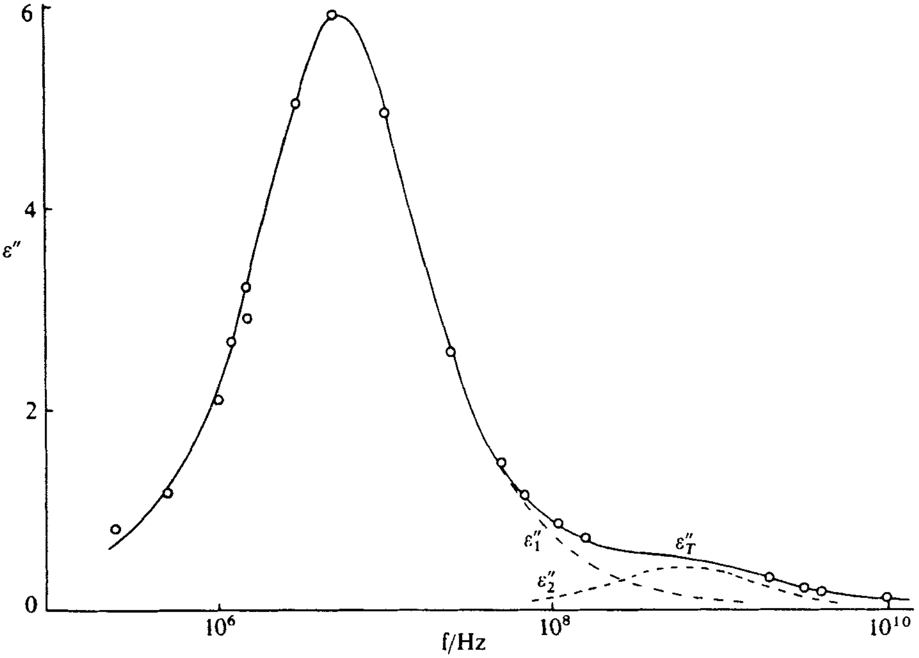

FIGURE 4 Dielectric absorption (ε'') as a function of frequency (f) in 7OCB (nematic, parallel alignment) at 331 K. ○, experimental points; - - - -, resolved components (ε''_1 and ε''_2); ———, calculated absorption ($\varepsilon''_T = \varepsilon''_1 + \varepsilon''_2$).

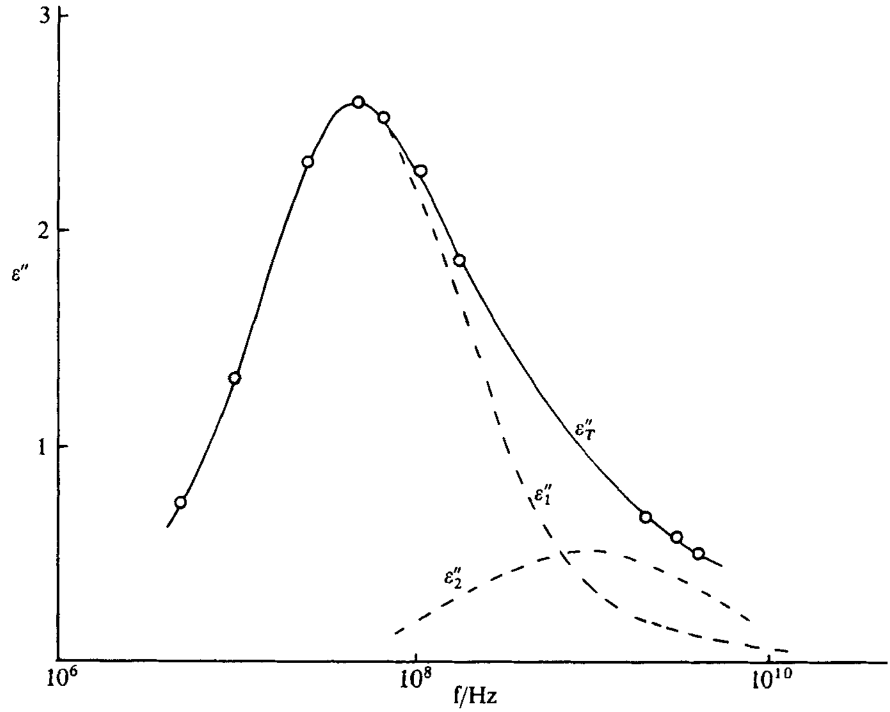

FIGURE 5 Dielectric absorption (ε'') as a function of frequency (f) in 7OCB (isotropic phase) at 350 K. O, experimental points; ----, resolved components (ε_1'' and ε_2''); ———, calculated absorption ($\varepsilon_T'' = \varepsilon_1'' + \varepsilon_2''$).

matic to isotropic transition temperature. Such a discontinuity is not predicted in the mean field theory and its occurrence indicates a limitation of the theory. The permittivity in the isotropic phase is reasonably independent of temperature and shows the presence of significant molecular association. This is confirmed from dipole moment measurements, where a dipole moment of 12.6×10^{-30} is calculated from the permittivity of the isotropic phase at 360 K. Measurements in cyclohexane solution yield a dipole moment of 17.0×10^{-30} Cm. These results yield a Kirkwood "g" factor of 0.55, indicating a high degree of antiparallel dipole association. Group moment calculations yield a resultant dipole moment of 15.1×10^{-30} Cm for 7OCB, in reasonable agreement (bearing in mind the limitations of such group moment calculations) with the measured value in cyclohexane. The corresponding dipole components parallel (μ_l) and perpendicular (μ_t) to the long molecular axis are calculated as 14.5 and 4.0×10^{-30} Cm respectively.

The resultant dipole moment in 7OCB lies at an angle to the long molecular axis and the Martin, Meier and Saupe theory of dielectric relaxation is no

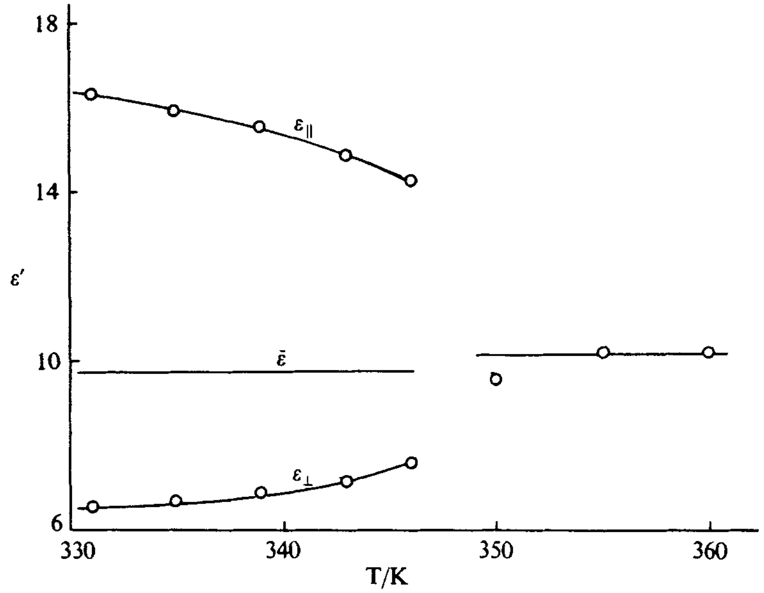

FIGURE 6 Temperature variation of the permittivity of 7OCB ($\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$) is the mean permittivity in the nematic phase).

longer applicable. The Nordio *et al.* theory of dielectric relaxation in nematogens predicts two relaxation mechanisms in the parallel alignment and two in the perpendicular alignment. The intensities of these absorptions may be given approximately by the two terms on the right hand side of Eqs. 1 and 2. A fifth relaxation process is also possible by the internal rotation of the terminal heptoxy-group.

The experimental results show that only one broad symmetrical absorption is observed in the perpendicular alignment. If two absorptions are present then the relative intensities would be expected to be in the approximate ratio of 5 : 1 [calculated from $\mu_l^2(1 - S)/u_t^2(1 + \frac{1}{2}S)$ see Eq. (2)], at 339 K and would yield an asymmetric absorption, contrary to observation. Consequently no attempt was made to resolve the absorption. Furthermore the dipole moment calculated from the peak intensity is 10.1×10^{-30} Cm at 339 K. This dipole moment is higher than the 6.4×10^{-30} Cm calculated for $\langle\mu_{\perp}^2\rangle^{1/2}$ from equation 2. Again this discrepancy may reflect the inadequecies of the mean field theory. The activation enthalpy for the relaxation in the perpendicular alignment is less than about 4 kJ mol^{-1} which is of the same order of magnitude as found for 7CB (1). These results obtained for 7OCB are very similar to those found for 7CB and do not present any new features which could be attributed to a relaxation process arising from the internal rotation of the heptoxy-group.

However, two relaxation processes are resolvable in the parallel alignment. The low frequency, high intensity absorption has an activation enthalpy of 65 ± 5 kJ mol^{-1} as expected from a reorientation about the short molecular axis and involving the nematic potential barrier. The dipole moment calculated from the intensity of the absorption is 11.8×10^{-30} Cm at 339 K, in agreement with the value calculated from the first term of Eq. (1). The low frequency absorption in the isotropic phase again arises from a molecular reorientation similar to that found in "normal" isotropic liquids and has an activation enthalpy of 49 ± 5 kJ mol^{-1}. As for 7CB, a second high frequency absorption is detected in both the nematic (parallel alignment) and in the isotropic phase. In the nematic phase the intensity of such an absorption should [in the mean field theory, Eq. (1)] correspond to a dipole moment of 1.6×10^{-30} Cm and is lower than the observed values (μ_2 of Table II) which range from 3.8 at 331 K to 6.4×10^{-30} Cm at 346 K. The possibility exists that this high frequency absorption contains a further component arising from a relaxation mechanism similar to that proposed in 7CB, and that the second absorption found in the isotropic phase again arises from a relaxation process within localized ordered regions ("swarms") (c.f. 7CB). Again there is no specific evidence for the presence of a relaxation process arising from the internal rotation of the heptoxy group. Both 7CB and 7OCB seem to have the same degree of molecular flexibility.

CONCLUSIONS

The dielectric relaxation spectrum of 7CB and 7OCB in the nematic (parallel alignment) and isotropic phases show two resolved absorptions. The high frequency absorption is believed to arise from a relaxation process occurring within localized ordered regions. Such ordered regions persist at temperatures well above the nematic to isotropic transition. The results for 7CB are in quantitative agreement with the theory proposed by Martin, Meier and Saupe (4). There is no evidence for internal rotation of the heptoxy-group in 7OCB.

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