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LIQUID CRYSTALS, 1998, VOL. 24, NO. 5, 681–688

Dielectric studies of a 5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (*n*DBT) homologous series ($n=4$–10)

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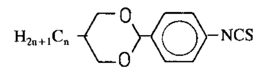
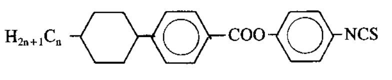
The results of dielectric studies of seven members of a 5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (*n*DBT) homologous series ($n=4$–10) in the isotropic and smectic A phases are presented. The complex dielectric permittivity, $\varepsilon^*(\nu)=\varepsilon'(\nu)-i\varepsilon''(\nu)$, was measured with the aid of two experimental set-ups: an impedance analyser (10 kHz–13 MHz) and a dielectric time domain spectrometer (TDS, 10 MHz–4 GHz). This allowed two main relaxation processes in both the phases studied to be separated: the low frequency (l.f.) process connected with molecular reorientations around the short axes, and the high frequency (h.f.) process connected with the rotations around the long axes. The measured dielectric increments enabled us to estimate the value and direction of the dipole moment of the *n*DBT molecules. The l.f. relaxation process in the isotropic and smectic A phases of the *n*DBT compounds exhibits some peculiar features which distinguish the materials from other similar substances. The observed decrease of the relaxation times and activation enthalpy with increasing *n* is discussed in relation to the molecular arrangements in the smectic layers.

1. Introduction



*n*DBT



*n*TPCHB

Liquid crystalline (LC) isothiocyanates such as *n*DBT [1] and *n*TPCHB [2] forming smectic A (SmA) phases are interesting for understanding molecular packing in smectic layers. Bi-ring compounds containing the isothiocyanatophenyl fragment (dipole moment 3·6 D) form quite different smectic layers from compounds containing the cyanophenyl fragment (dipole moment 4·05 D). The cyano compounds, such as *n*CBs or *n*OCBs, are nematics for small *n* and exhibit a smectic A_d phase for longer alkyl or alkoxy chains, whereas *n*DBTs form only a monolayer smectic A_1 phase [3]. However, in the *n*DBT series the layer spacings *d* are not strictly related to the molecular lengths *l* and increase weakly with increasing alkyl chain length (figure 1). The ratio d/l changes from 0·88 to 0·99 for $n=2$–12 for these bi-ring compounds, whereas in the three-ring compounds *n*TPCHB, this ratio changes from 1·0 to 1·09 for $n=4$–12 [4]. This suggests that the internal structure of the SmA layer in both the *n*DBT and the *n*TPCHB series must change and that this happens in a continuous way. This is not the case in cyano compounds where a transformation from the A_1 to the A_d smectic phases occurs rapidly and sometimes through a re-entrant nematic phase [3].

Difference in smectic layer organization between *n*DBTs and similar *n*CBs or *n*OCBs have also been seen in phase diagram studies [5, 6]. Bi-component mixtures containing one *n*DBT compound with small *n* and one *n*CB or *n*OCB compound give phase diagrams with a nematic gap between the A_1 phase of *n*DBT and the A_d phase of *n*CB or *n*OCB, whereas mixtures of *n*DBT with long alkyl chains give phase diagrams showing full miscibility of the A_1 and the A_d smectic phases [5, 6].

We suppose that the change in the molecular packing in the SmA_1 layer, with the length of the alkyl chain of the *n*DBT series, may influence the ability for molecular reorientation to occur, especially around the short axes,

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an effect which can be seen in dielectric relaxation studies.

*n*DBT compounds have a strong longitudinal dipole moment connected mainly with the terminal –NCS group and a smaller perpendicular component caused by the oxygens in the dioxane ring. Therefore, one can expect that both main relaxation processes present in the LC phases, the low frequency (l.f.) relaxation connected with molecular rotation around the short axis and the high frequency (h.f.) relaxation connected with the rotations around the long axis, will be observed in dielectric measurements. The same motions can also be detected in the isotropic (I) phase provided that a sufficiently broad frequency band is available. Using two experimental techniques, an impedance analyser and a time domain spectroscopy set-up (TDS), we were able to obtain the dielectric permittivities and relaxation times characterizing the molecular rotations around the long and the short axes in these phases. The results obtained allow us to estimate the values and direction of the net dipole moment of the molecules, and to study how lengthening of the alkyl chain influences the relaxation times and activation barriers for molecular rotations around the short axes in the isotropic and the SmA phases.

2. Experimental

The *n*DBT substances with $n=4$–10 were studied using their isotropic and smectic phases. Their transition temperatures are shown in figure 1. All substances were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw.

The measurements of the complex dielectric permittivity, $\varepsilon^*(\nu)=\varepsilon'(\nu)-i\varepsilon''(\nu)$, for the smectic phase of all substances were performed in the frequency range ν of 1 kHz–13 MHz using an HP 4192A impedance analyser. A parallel-plate capacitor ($A\approx 2\,\mathrm{cm}^2$) was calibrated with the use of standard liquids. The distance between the electrodes was 0·2 mm. We tried to orient the samples parallel to the measuring field using both d.c. electric ($\mathbf{E}\approx 1500\,\mathrm{V\,cm}^{-1}$) and magnetic ($\mathbf{H}\approx 0{\cdot}7\,\mathrm{T}$) fields. However, these fields did not materially affect the smectic phase.

The experimental details of the time domain spectroscopy technique (TDS) can be found in preceeding papers [7–9]. Two time windows were used (10 ns and 100 ns) and then the spectra were spliced as described in ref. [9]. This allowed us to cover the frequency range from 10 MHz to *c.* 4 GHz. The temperature was stabilized within ±0·1 K in both experiments.

3. Results

Figure 2 shows the static permittivity ε_s as a function of temperature in the isotropic and smectic phases of

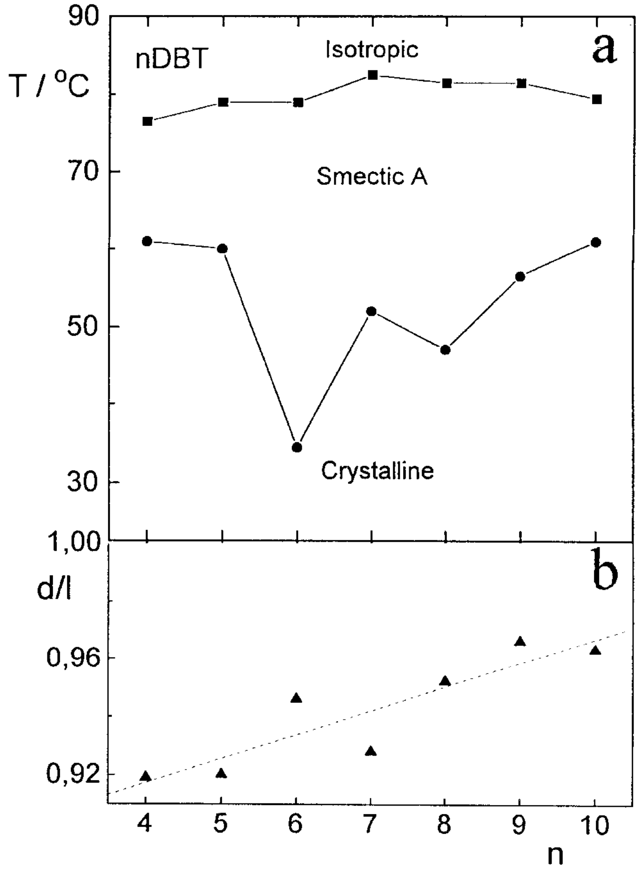

Figure 1. Transition temperatures (*a*) and the ratio of the layer spacing *d* to the length of molecules *l* in the SmA phase (*b*) versus the number of carbon atoms in the alkyl chain of the *n*DBT compounds.

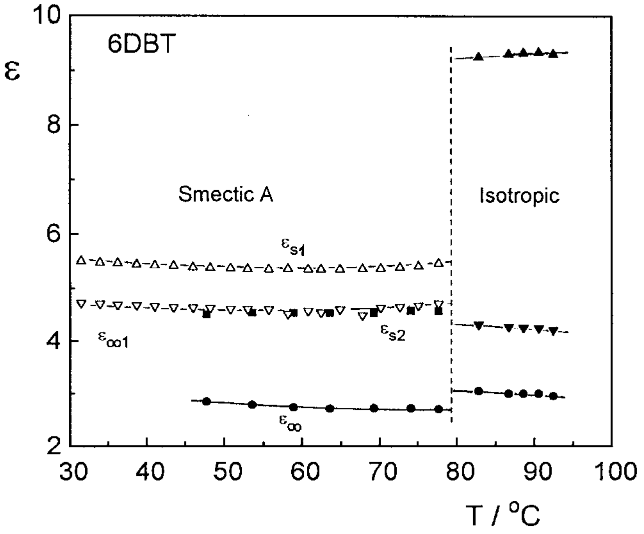

Figure 2. The static permittivities obtained from the fits of equations (1) and (2) to the spectra measured for 6DBT with the aid of both the experimental techniques used: TDS spectrometer (full symbols) and HP analyser (open symbols).

6DBT. The behaviour is typical for all substances studied. At the I–SmA phase transition a considerable drop in the permittivity was observed. Within the smectic phase the permittivities of all substances were practically constant down to the freezing point. The static permittivity of the isotropic phase decreases with an increasing number of carbon atoms *n* in the alkyl chain (compare figure 5).

The dielectric relaxation measurements performed for five substances in the isotropic phase (TDS method) revealed the existence of complex spectra which are presented in figure 3 in form of the Cole–Cole plots. These spectra were analysed with the assumption of two Debye-type processes

$$\varepsilon^* - \varepsilon_\infty = \frac{\delta_1}{1 + i\omega\tau_1} + \frac{\delta_2}{1 + i\omega\tau_2} \qquad (1)$$

where subscripts 1 and 2 correspond to the l.f. and h.f. relaxation processes, respectively; $\delta_1 = \varepsilon_{s1} - \varepsilon_{\infty 1}$, $\delta_2 = \varepsilon_{s2} - \varepsilon_\infty$ give the dielectric strengths (increments) of both relaxation processes. The fitting parameters of equation (1) are presented in figures 2, 5 and 6.

In the smectic phase of all substances, the measurements at MHz frequencies revealed a relaxation process with a small increment (δ_1 in figure 5) which can only be extended slightly by an external electric field ($\sim$1500 V cm^{-1}). The spectra of all substances have wings at the high frequency side of the Cole–Cole plot. However, within the frequency range 10 kHz–5·6 MHz the spectra can well be described by the Debye equation. The high value of the extrapolated $\varepsilon_{\infty 1}$ permittivity ($\sim$4·5, compare figure 4) suggested that a second relaxation process at high frequencies should exist. This stimulated us to perform the measurements with the aid of the TDS method, which effectively have revealed the high frequency relaxation process—see figure 4. The TDS spectra were analysed with the Cole–Cole equation

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}} \qquad (2)$$

where the parameter α characterizes the distribution of the relaxation times. The fitting parameters are presented in figure 2 (6DBT) and figures 5 and 6 for all substances studied. The α parameter is remarkable for 4DBT only ($\sim$0·12); for other samples it was close to zero.

The relaxation times characterizing the relaxation processes observed in all substances are presented in figure 6 in the form of activation plots. To avoid the shifts caused by different clearing points the abscissa was taken as $(1/T - 1/T_{\text{I-SmA}})$. The activation enthalpies calculated using the Arrhenius equation, $\tau = \tau_0 \exp(\Delta H/RT)$, are listed in the table together with the data for other similar compounds.

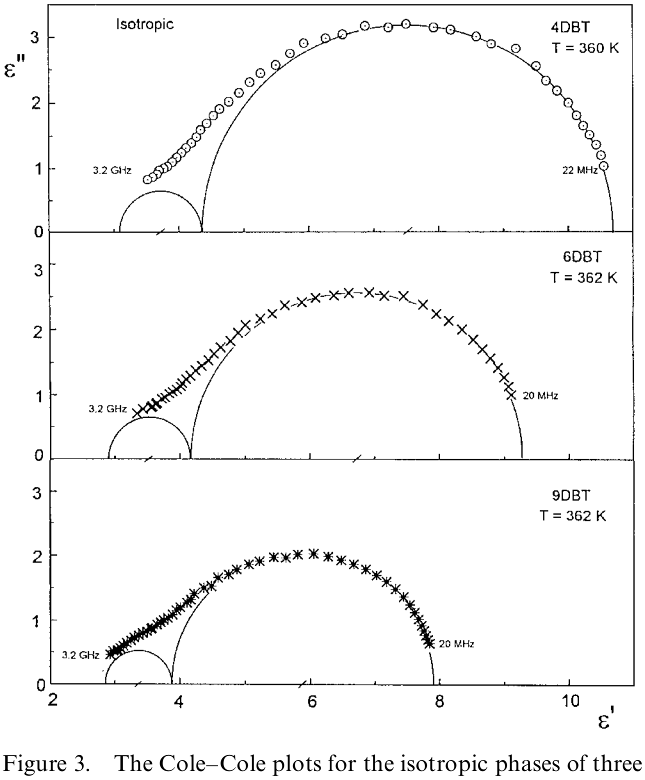

Figure 3. The Cole–Cole plots for the isotropic phases of three substances studied by the TDS method. The semi-circles correspond to the fits of equation (1) to the spectra.

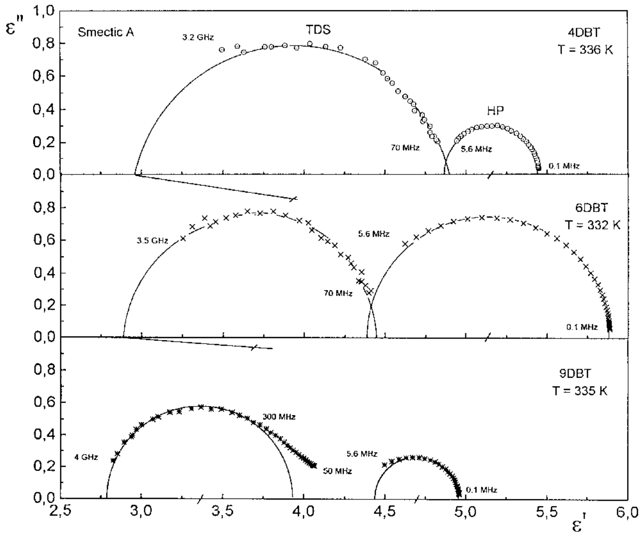

Figure 4. The Cole–Cole plots for the SmA phases of three substances studied with the aid of an impedance analyser (HP) and using the TDS method. The semi-circles are the fits of equation (2) to the spectra (separately for each spectrum). The measurements were carried out on unoriented samples and therefore a joining of the two relaxation bands cannot be expected.

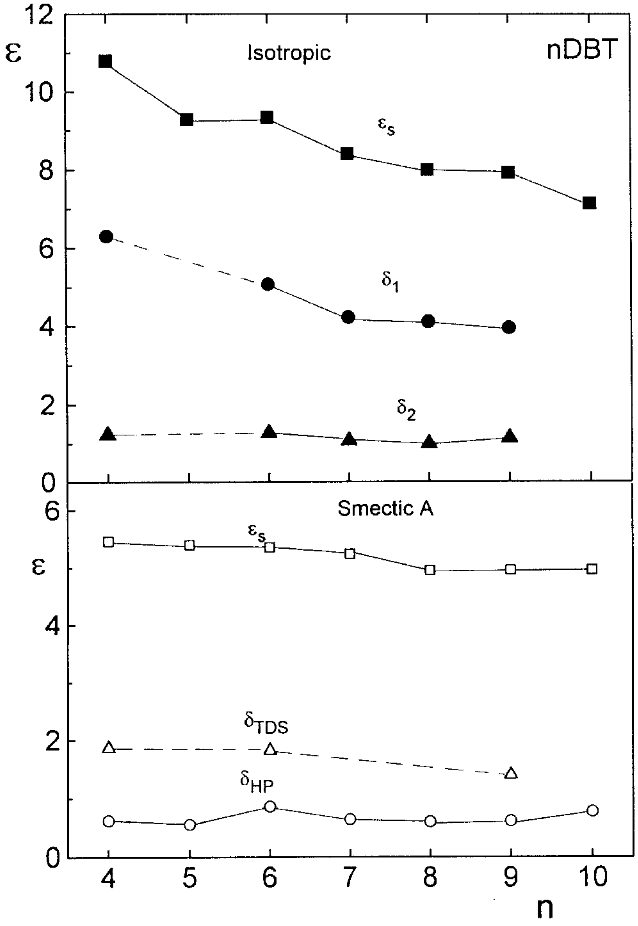

Figure 5. The fitting parameters of equation (1) (isotropic phase) and equation (2) (SmA phase) to the dielectric spectra as a function of the number of carbon atoms in the alkyl chain of the *n*DBT compounds.

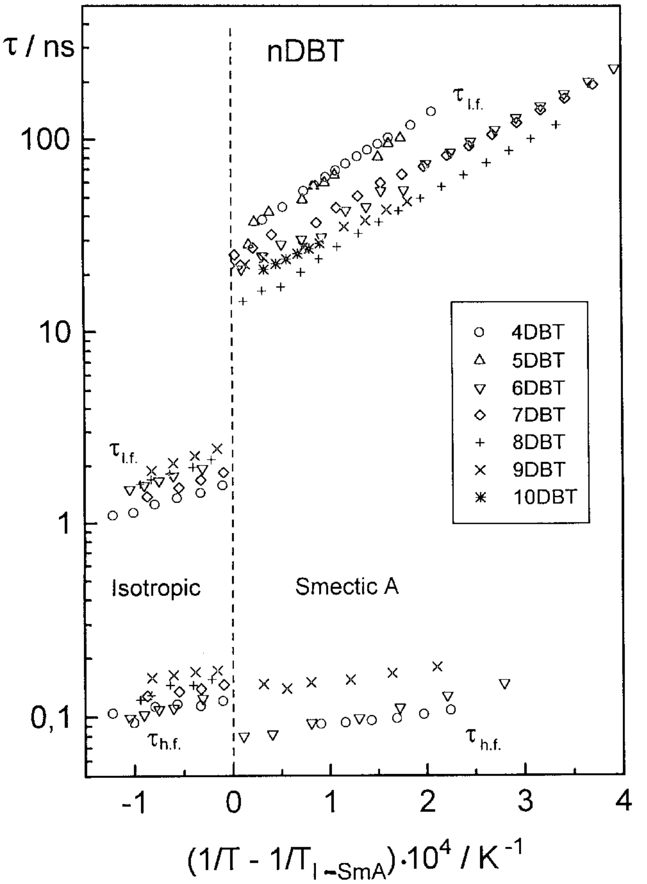

Figure 6. Log τ versus $(1/T - 1/T_{\text{I-SmA}})$ for different relaxation processes in the *n*DBT compounds where $T_{\text{I-SmA}}$ is the clearing temperature (l.f.=low frequency process, h.f.=high frequency process). In the SmA phase (l.f. process) the data come from at least two measurement runs.

Table. Activation enthalpies (in kJ mol^{-1}) for particular *n*DBT compounds (and the mixture 4DBT+12DBT) in different phases. τ_{LC}/τ_{is} is the ratio of the relaxation times for the l.f. process extrapolated to the clearing temperature from the LC phase side and the isotropic phase side, respectively. $\Delta H_{LC}/\Delta H_{is}$ is the ratio of the activation enthalpies for the l.f. process in the LC and isotropic phases, respectively. For comparison, the data obtained for four similar compounds (see text) are listed.

	isotropic		nematic		smectic			
Substance	l.f.	h.f.	l.f.	h.f.	l.f.	h.f.	τ_{LC}/τ_{is}	$\Delta H_{LC}/\Delta H_{is}$
4DBT	27±2	19±4			62±2	10±4	19·07	2·28
5DBT					55±3			
6DBT	29±2	25±3			53±2	20±2	9·76	1·82
7DBT	31±2	17±3			46±2		12·6	1·46
8DBT	32±2	25±3			55±2		5·92	1·69
9DBT	33±3	11±3			38±3	13±4	7·77	1·14
10DBT					44±3			
(4+12)DBT [10]			78		51			
6CHBT	35		68	19			4·55	1·88
6BcBT [11]	43	34	95				2·91	2·21
8CB	41		64		44		2·54	1·55/1·07[a]
8OCB	50		75		56		2·46	1·49/1·12[a]

[a] Concerns the N/I and Sm/I phases.

4. Discussion

In order to discuss the dielectric properties of the *n*DBT compounds one must consider the electric structure of the molecules. The substances have two polar parts: one connected with the isothiocyanato group, and the second with the dioxane ring (figure 7). The former is mostly directed along the *para*-axis of the benzene ring [12]. However, dielectric studies of similar substances, one having the cyclohexyl (*n*CHBT) [13] and the other the bicyclo-octane (*n*BcBT) [11] ring instead of the dioxane ring, have shown separately the l.f. relaxation and also the h.f. relaxation with small increments in both the isotropic and nematic phases. This indicates that small perpendicular components of the dipole moments are effective in these substances. In the case of the 6CHBT molecule, the molecular long axis (treated as the axis of minimum moment of inertia) deviates from the *para*-axis of the benzene ring by *c.* 20° (figure 7). The dipole moment of 6CHBT is $\mu = 3{\cdot}48$ D [14] and can be considered as characteristic for all isothiocyanatobenzenes. In order to estimate the angle between μ and the molecular long axis, TDS measurements for the isotropic phase of 6CHBT have been performed. As can be seen in figure 8(*a*), the spectrum consists of two relaxation bands with the increments $\delta_{\text{l.f.}} = \varepsilon_s - \varepsilon_2 \approx 3{\cdot}04$ and $\delta_{\text{h.f.}} = \varepsilon_2 - \varepsilon_\infty \approx 0{\cdot}43$ which are practically independent of temperature—figure 8(*b*). (The l.f. relaxation times calculated from the spectra correspond very well with those obtained previously [13].) The dielectric permittivity values can be discussed taking into account the Onsager equation (we neglect here an evident difference in the shapes of the present and model molecules)

$$\mu^2 = \frac{9kT\epsilon_0}{N}\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} \qquad (3)$$

where k = Boltzmann constant, ϵ_0 = free space permittivity, N = number of dipoles in unit volume. With the assumption that the l.f. and h.f. processes are connected with the longitudinal (μ_l) and transverse (μ_t) components, respectively, of the dipole moment of the 6CHBT molecule, we can estimate the ratio of both components $\mu_t/\mu_l = \text{tg}\,\beta$. The value obtained for $\beta \approx 24°$ seems to be consistent with the above model considerations.

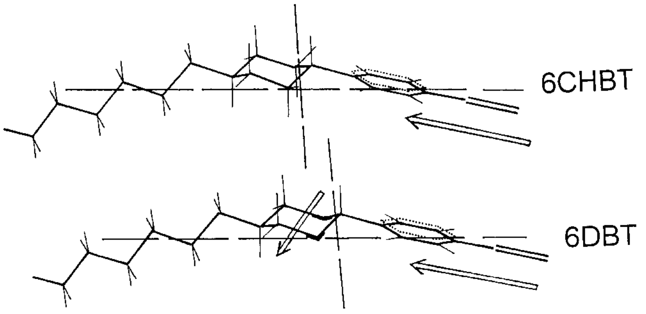

Figure 7. Molecular structures of 6CHBT and 6DBT molecules. The positions of the dipole moments are indicated schematically. The dashed lines show the molecular short and long axes.

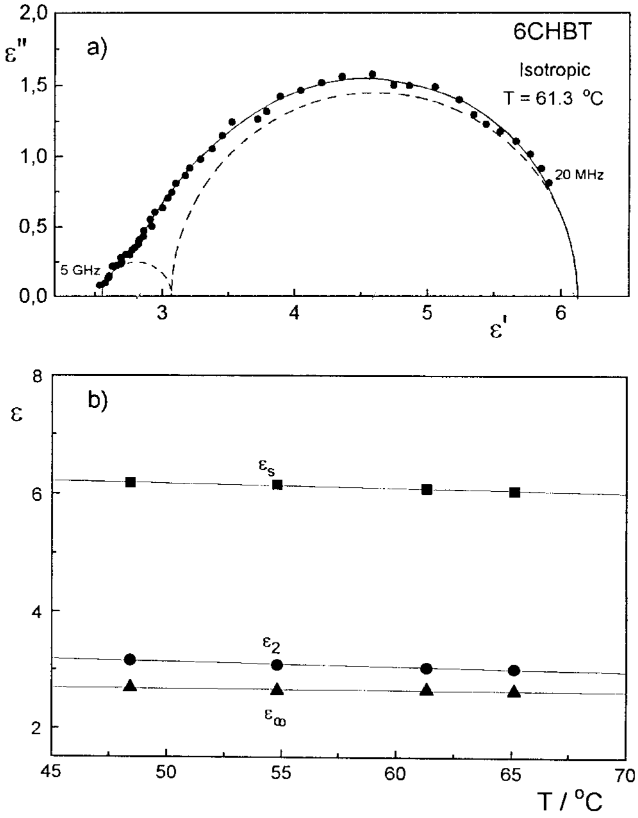

Figure 8. (*a*) TDS spectrum of the isotropic phase of 6CHBT in form of the Cole–Cole plot. The semi-circles show the separation into two Debye-type processes according to equation (1). (*b*) The permittivities characterizing both relaxation processes as a function of temperature.

The static permittivity values of the *n*DBT compounds in the isotropic phase are larger than those measured for the respective *n*CHBT and *n*BcBT substances. For example, in the case of the sixth member of these series we have $\varepsilon_{is} = 9{\cdot}3$, $6{\cdot}3$ and $5{\cdot}7$, respectively (see figure 2 and [11, 13]), indicating the greatest polarity for 6DBT. Taking separately the increments in both observed relaxation processes in the isotropic phase of particular *n*DBT compounds and equation (3), we obtained the following β values: 30°, 34°, 34° and 33° for $n = 4$, 6, 7 and 8, respectively.

In order to estimate the dipole moment of the 6DBT molecule we take advantage of its similarity to the 6CHBT molecule (figure 7). Let us assume that equation (3) is adequate to separate the description of both increments, $\delta_{\text{l.f.}}$ and $\delta_{\text{h.f.}}$, and that the densities of 6CHBT and 6DBT do not differ in the isotropic phase. Taking the experimental data shown in figure 2 and 8, we obtained $\mu_l(6DBT)/\mu_l(6CHBT) \approx 1{\cdot}08$ and $\mu_t(6DBT)/\mu_t(6CHBT) \approx 1{\cdot}50$. Knowing the components for 6CHBT ($\mu_l = 3{\cdot}2$ D, $\mu_t = 1{\cdot}4$ D) we have for 6DBT $\mu_l \approx 3{\cdot}5$ D and $\mu_t \approx 2{\cdot}1$ D, which leads to the effective dipole moment $\mu \approx 4{\cdot}1$ D inclined at *c.* 31° to the molecular long axis, in excellent agreement with the above mentioned β-values. The larger dipole moments of the *n*DBT compounds arise from the polar dioxane group (figure 7). The experimental dipole moment of 1,3-dioxane is 2·17 D [15], and *ab initio* calculations [16] show that it forms an angle of 40·5° with the axis placed on the symmetry plane and passing through the C2 and C5 atoms of the chair-shaped molecule.

As can be seen in figure 5, the static permittivity ε_{is} diminishes with the length of the alkyl chain in the *n*DBT series. This mainly affects the longitudinal δ_1 component of the dipole moment, as the increment δ_2 for the h.f. relaxation process is independent of *n* (figure 5). This effect can be attributed to a 'solvation' of the dipole moment in the longer alkyl chains.

The transition from the isotropic to the SmA phase is always accompanied by a considerable decrease in the permittivity (figures 2 and 5). We believe that this effect is connected with the lack of alignment of the samples. That statement is corroborated by the fact that different fillings of the capacitor gave different values for the static permittivity in the SmA phase, whereas the values for the isotropic phase were very reproducible. Unfortunately, the available electric or magnetic fields did not enable us to attain a proper alignment of smectic samples. It should be pointed out, however, that in spite of differences in the permittivity values in the SmA phase, that l.f. relaxation times obtained from different runs were very consistent (figure 6). The same behaviour has also occurred in other studies of smectics [17, 18].

Looking at figures 2–5, one can easily confirm that the relaxation spectra of the isotropic and smectic phases are similar. They consist of two relaxation processes. The high frequency process has practically the same increments (δ_2 and δ_{TDS}) in both phases (a brief comparison of figures 3 and 4 may be misleading unless the reader notes the changes in the units on the axes). Additionally, the relaxation times (figure 6) and the activation barriers (table) for this process are close in both phases. In fact, they are even lower in the SmA phase in comparison with the isotropic phase. This is a typical behaviour of the relaxation process connected with the rotations of rod-like molecules around their long axes [9, 11, 13, 19] (in the nematic phase, this is observed for perpendicularly oriented samples).

The low frequency relaxation process observed in the isotropic and smectic phases of the *n*DBT compounds (and their mixture with the nematic gap [10]) is undoubtedly connected with the molecular rotations around the short axes. This conclusion arises from the following facts: (1) large increments in δ_1 for this process in the isotropic phase indicate that it must be connected with the large dipole moment directed along the main molecular axis; (2) a distinct increase in the l.f. relaxation time at the I–SmA phase transition (figures 6 and 9, and the table) which is typical for other LC substances [7–11, 17, 20]; (3) large activation barriers are characteristic for this motion (table and figure 9).

There are, however, some peculiarities which distinguish these substances from the others previously studied.

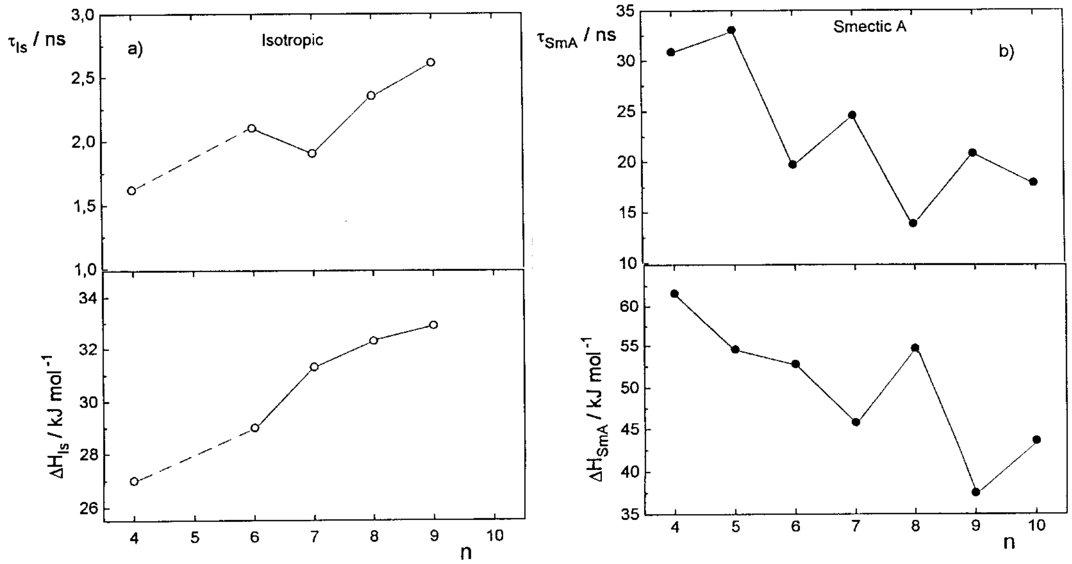

Figure 9. Relaxation times and the activation enthalpies for the l.f. relaxation process in the isotropic (*a*) and smectic (*b*) phases of *n*DBT compounds. All τ-values are extrapolated to the I–SmA transition point from the isotropic (*a*) and smectic (*b*) sides.

The experimental evidence for the l.f. relaxation process in the isotropic phase of LC compounds is rather poor [7–9, 11, 13, 20–24], especially where homologous series are concerned [20, 21, 23]. Figure 9 (*a*)—top, shows that the relaxation times $\tau_{\rm is}$ extrapolated to the clearing point increase with lengthening of the *n*DBT molecules. The same applies to the activation enthalpies $\Delta H_{\rm is}$ [figure 9 (*a*)—bottom]. Figure 10 shows $\Delta H_{\rm is}$ values versus *n* obtained for different LC substances. These values should be related to the shapes and dimensions of the molecules, and to the activation enthalpy ΔH_{η} for the viscosity coefficient for particular substances which seem not to differ substantially in the isotropic phase [25]. It is clear from the figure that the activation barriers for *n*DBT molecules are considerably lower than those obtained for other similar compounds, and this may result from the differences in the shapes of the molecular cores in particular homologous series.

In the smectic phase of the *n*DBT compounds, the l.f. relaxation time extrapolated to the clearing point and the activation enthalpy for this motion [figure 9 (*b*)] show a remarkable odd–even effect with a rather systematic decrease with *n* which is just the opposite to the trend observed for the isotropic phase [figure 9 (*a*)]. In consequence, the activation barriers in the SmA and I phases almost become equal for large *n*.

These astonishing effects ought to be considered in the light of other experimental facts. It has been found that the activation energies hindering molecular rotations around the short axes in the orthogonal smectic phases (SmA and B) are smaller than those in the preceding nematic phase [17, 18, 20, 26]. The substances now under study show no N phase, but their mixtures do, and for the mixture 4DBT + 12DBT such an effect has been found recently [10] (see the table). The conclusion seems to be justified that the smectic A order facilitates flip-flop molecular rotations. Additional freedom for this motion may arise from a looser packing of molecules with longer tails.

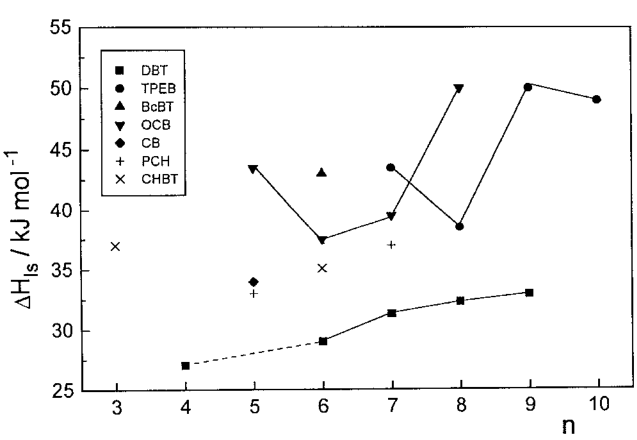

Figure 10. Activation enthalpy for molecular reorientations around the short axes in the isotropic phase of the *n*DBTs and other similar substances versus the number of carbon atoms in the alkyl or alkoxy chains.

The ratio of the layer thickness to the molecular length, *d*/*l*, slightly increases with *n* [1, 4] (figure 1). In fact, the length *l* was calculated assuming the most stretched all-*trans*-conformation of the alkyl chains. However, other conformations become more probable with increasing *n* which effectively shortens the molecular length. On the other hand, a linear expansion of the layer thickness with *n* is observed [4] and this can partly be caused by antiparallel side by side dimers. Both these trends lead to an increase with *n* of the rotational freedom of molecules around the short axes in the smectic A phase. A puzzling behaviour is exhibited by 8DBT which shows the shortest l.f. relaxation times and a relatively high activation enthalpy in the SmA phase (see figures 6 and 9).

5. Conclusions

The results of dielectric studies of seven members of the *n*DBT homologous series in their isotropic and smectic A phases allow us to point out the following:

(1) The *n*DBT compounds are strongly polar with the dipole moment $\mu \approx 4{\cdot}1$ D inclined at *c.* 31° from the molecular long axis.

(2) In both the isotropic and smectic A phases, two well separated relaxation bands are observed (figures 2 and 3). The low frequency band is connected with the molecular rotations around the short axes, and the high frequency band relates to the rotations around the long axes.

(3) The smectic order seems to facilitate the molecular rotations around the long axes (table and figure 6).

(4) The molecular rotations around the short axes change jump-wise at the I–SmA transition (figure 6). The relaxation times show more distinct increases at this transition than in the case of the isotropic–nematic transition for similar compounds. At the same time, the increase in the activation enthalpy is comparable with that observed for nematics (table).

(5) The l.f. relaxation process in the *n*DBT substances exhibits some peculiar properties: (a) in the isotropic phase, the activation enthalpies are markedly lower than for other similar compounds (figure 10 and table); (b) in the smectic A phase, the relaxation times and activation enthalpy show an odd–even alternation with a tendency to decrease with lengthening of the alkyl tail, in contradistinction to the behaviour in the isotropic phase (figure 9).

(6) The increase of relative molecular rotational freedom with n in the smectic A phase may be caused by a shortening of molecules due to conformational motions of the alkyl chain and by a small expansion of the layer thickness due to weak antiparallel side by side molecular arrangements.

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