Comparison of Dielectric Properties of Three Alkyl and Alkoxy Azoxybenzenes (*n*AOBs and *n*OAOBs, *n* = 5, 6, 7) in the Isotropic and Liquid Crystalline Phases

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Results of dielectric studies of three 4,4’-di-*n*-alkyl-azoxybenzenes (*n*AOB) and 4,4’-di-*n*-alkoxy-azoxybenzenes (*n*OAOB), $n = 5$, 6 and 7, are presented. The *n*AOB compounds exhibit positive, and the *n*OAOBs negative dielectric anisotropy in the nematic phase. In the smectic A phase of 7AOB the anisotropy changes its sign, whereas in the smectic C phase of 7OAOB it persists negative; moreover, in the latter case the perpendicular component of the permittivity increases with respect to the value of the nematic phase. This may be due to parallel dipole-dipole correlation of the perpendicular components involved by the layer arrangements in both smectic phases. For all substances a systematic decrease of the permittivity components with chain length was observed. Different types of smectic order in the 7th members of both series are discussed in relation to the mean-field theory developed recently by Govind and Madhusudana. The dielectric relaxation times and activation enthalpies characterizing the molecular rotation around the principal inertia axes are given.

Key words: Liquid Crystals; Dielectric Properties; Alkyl- and Alkoxy-Azoxybenzenes.

1. Introduction

Recently, Govind and Madhusudana [1] have developed the mean-field theory which relates the type of smectic order with the position of the dipole group(s) in rod-like molecules. The lateral component of the dipole moment in the molecule is essential for the medium to exhibit the smectic C (S_C) phase. Moreover, the lateral dipole moment must stand *off* of the long molecular axis. Otherwise the smectic A (S_A) order is favoured. The alkyl- and alkoxy-azoxybenzenes were treated as model substances for testing the predictions of the theory. However, the theory seems to fail if only a central azoxy group is present in the molecule. The heptyl-azoxybenzene exhibits N–S_A polymorphism, whereas the heptyloxy-azoxybenzene shows N–S_C polymorphism. The measurement of the dielectric permittivity tensor components in different phases should reflect the dipole structures of the molecules. Additionally, it seems interesting to check whether the molecular rotational motions around the principal inertia axes is sensitive to the, rather subtle, differences in molecular arrangements in the S_A and S_C phases.

Many experimental groups have studied the dielectric properties of LC substances having an azoxybenzene core and symmetric end groups (e.g. [2 – 17]). However, the dynamic properties established in the sixties and seventies [2 – 9] were based on experimental data consisting of a few points only in the broad frequency bands necessary for covering the particular relaxation processes observed in LC phases. Moreover, the frequencies in the range between 10 MHz – 900 MHz were hardly accessible in that time. Nowadays experimental techniques give permittivities at densities of frequencies that are as high as necessary.

The aims of the present studies are: (*i*) to compare the static and dynamic dielectric properties of representative members of two similar homologous series of LC compounds; (*ii*) to discuss the predictions of the Govind and Madhusudana theory; (*iii*) to check whether the information obtained in the past using a resonance bridge and wave-guide techniques is consistent with that yielded by the modern experimental techniques (impedance analyser and time domain spectrometer).

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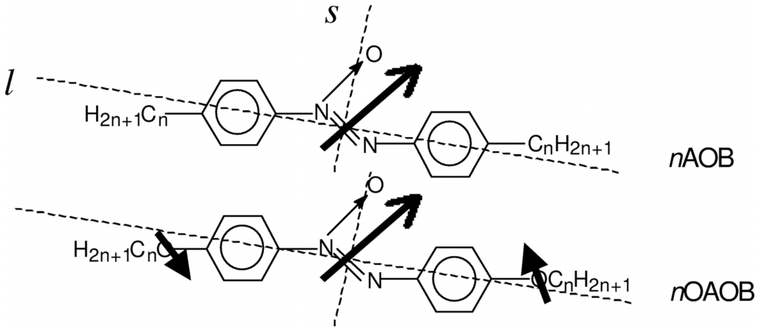

Fig. 1. Chemical structures of the two homologous series studied. The thick lines indicate the group dipole moments, and the broken lines show the postulated long (l) and short (s) rotation axes of the molecules.

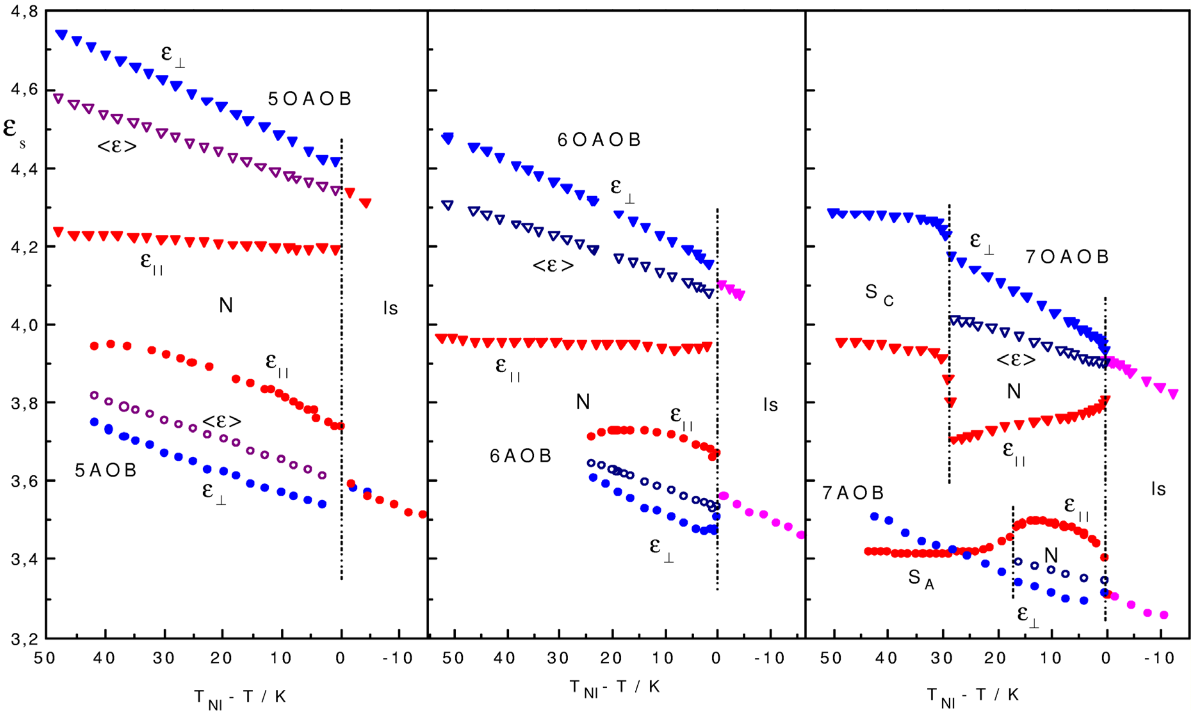

Fig. 2. Tensor permittivity components of the three pairs of compounds.

Table 1. Transition temperatures of the six substances studied.

Substance	Phase sequence
5AOB	Cr – 25.2 °C – N – 69.0 °C – Is
6AOB	Cr – 23 °C – N – 48.5 °C – Is
7AOB	Cr – 38.8 °C – S_A – 55.5 °C – N – 72.7 °C – Is
5OAOB	Cr – 77.3 °C – N – 124.0 °C– Is
6OAOB	Cr – 82.3 °C – N – 130.3 °C– Is
7OAOB	Cr – 74.6 °C – S_C – 95.0 °C – N – 124.0 °C – Is

2. Experimental

The substances studied belong to two homologous series: 4,4’-di-*n*-alkyl-azoxybenzenes (*n*AOBs in short) and 4,4’-di-*n*-alkoxy-azoxybenzenes (*n*OAOBs in short). The chemical and dipole structures of both series are presented in Figure 1. The members with $n = 5$, 6 and 7 of both series were chosen for the present studies. Their transition temperatures are gathered in Table 1. The members with $n = 5$ and 6 have only the nematic (N) phase, whereas the seventh members have both the N and a smectic phase (S_A for 7AOB and S_C for 7OAOB). The *n*AOB substances were synthesized in the Institute of Chemistry, Military University of Technology, Warsaw, and the *n*OAOBs come from the Institute of Chemistry, University of Podlasie, Siedlce, Poland (the authors wish to thank to Profes-

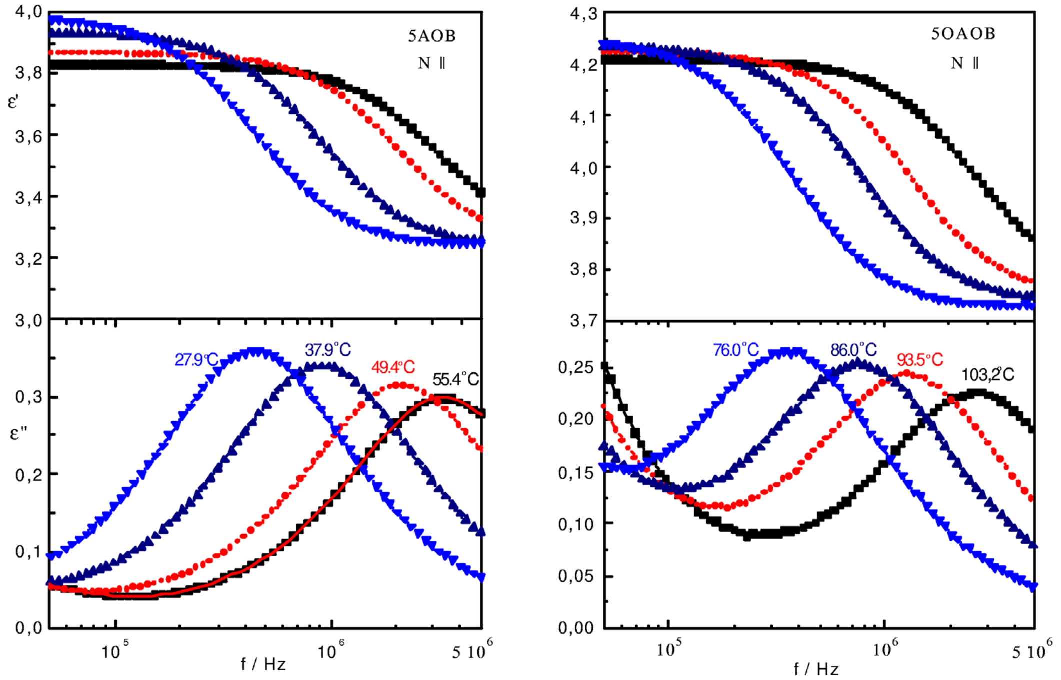

Fig. 3. Typical dispersion and absorption spectra measured for parallel oriented samples. The lines are fits of the Debye equation with the conductivity term (in the case of 5OAOB).

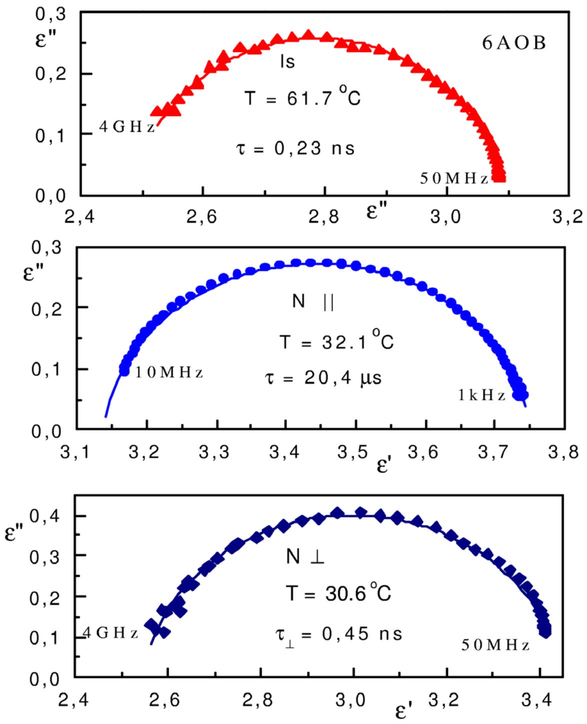

Fig. 4. Cole-Cole plots in the isotropic and nematic phases of 6AOB.

sors R. Dąbrowski and J. Chruściel for kind by supplying us with the samples).

The dielectric relaxation spectra, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, were collected with an HP 4192A analyzer (1 kHz – 10 MHz) and a time domain spectrometer (TDS) [18] (20 MHz – 3 GHz). In the LC phases the samples were oriented by a magnetic field of 0.7 T. Only *n*AOB compounds were studied by TDS in the isotropic phase, since the clearing temperatures of the *n*OAOBs are too high. All measurements were carried at decreasing temperatures, which enabled us to supercool the samples. During measurements the temperature was stabilized within ±0.2 °C above and within ±0.1 °C below 70 °C.

3. Results

Figure 2 presents the tensor components of the static permittivity in the isotropic (Is) and LC phases of all substances studied. As can be seen the azoxy group alone gives positive dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$, whereas the addition of the alkoxy groups leads to negative anisotropy. In the case of 7AOB the dielectric anisotropy changes sign within the smectic A phase [4, 14, 16], which was not observed for the smectic C phase of 7OAOB.

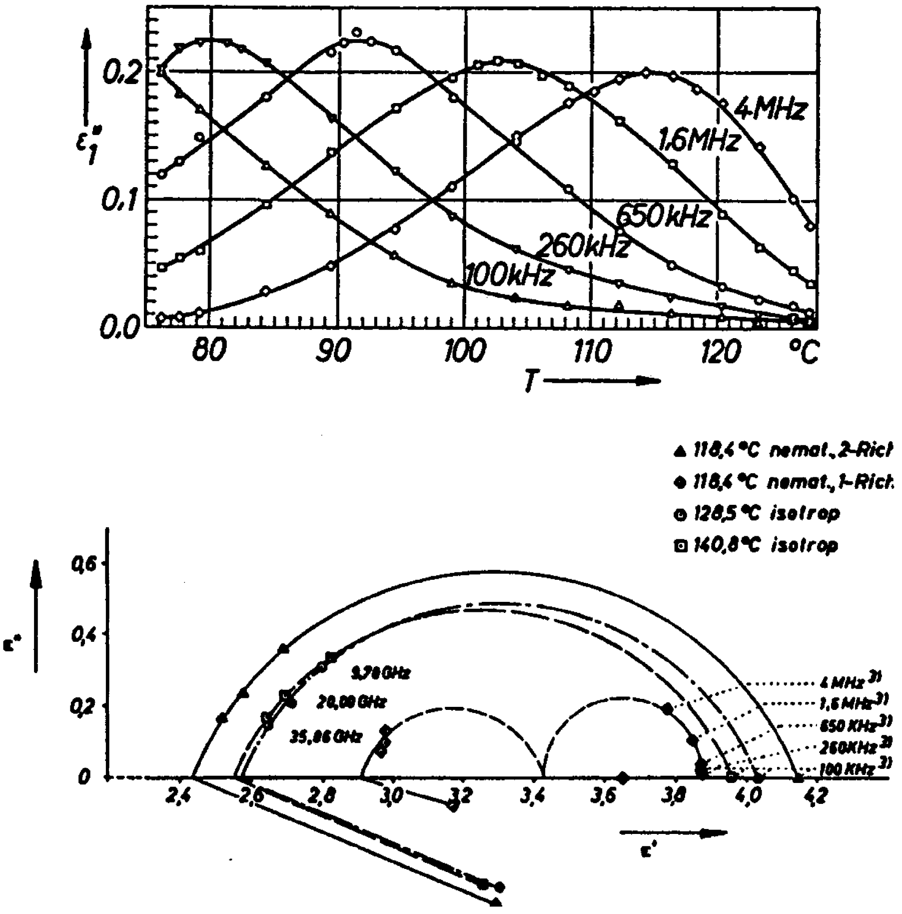

Fig. 5. Examples of dielectric relaxation spectra obtained for 6OAOB in the N phase in the sixties by Maier and Meier [3] (top) and Axmann [4] (bottom). The relaxation times derived from these data are shown in Figure 8.

Substance	5AOB	5OAOB	6AOB	6OAOB	7AOB		7OAOB	
Phase	N	N	N	N	N	S_A	N	S_C
l. f. process	62 ± 2	81 ± 2 (77) [10]	68 ± 2 (81.2) [16]	90 ± 2 (92) [10]	102 ± 3 (87,7 [16]	59 ± 2 63,1)	113 ± 3 (108) (116) [10]	103 ± 3 (113) [6]
h. f. process	–	28 ± 4	29 ± 2 (23,5) [16]	25 ± 5	25 ± 2 (32,3) [16]	25 ± 2 (24,6)	– (24)	26 ± 4 (17) [6]

Table 2. Activation enthalpy (in kJ/mol) for molecular motions around the principal inertia axes of *n*AOB and *n*OAOB substances in different phases (in parentheses: the data from other studies [6, 10, 16]).

Examples of the spectra collected in the isotropic (for *n*AOBs only) and LC phases of substances studied are presented in Figs. 3 and 4. The spectra in all phases can be described by the well known Cole-Cole equation with the addition, if necessary, of the term responsible for conductivity,

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} - i\frac{\sigma}{\varepsilon_0\omega}, \quad (1)$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and α characterizes the distribution of the relaxation times τ. The disturbing contribution of conductivity σ to the overall loss has been taken into account by the second term (ε_0 = free space permittivity). Generally, the alkoxy compounds exhibited a more pronounced conductivity than their alkyl partners. In the case of the low frequency process in LC phases, the α parameter is close to zero, indicating a Debye-type process.

The low frequency relaxation times $\tau_\parallel$ derived from the spectra are presented in Fig. 5 in the form of Arrhe-

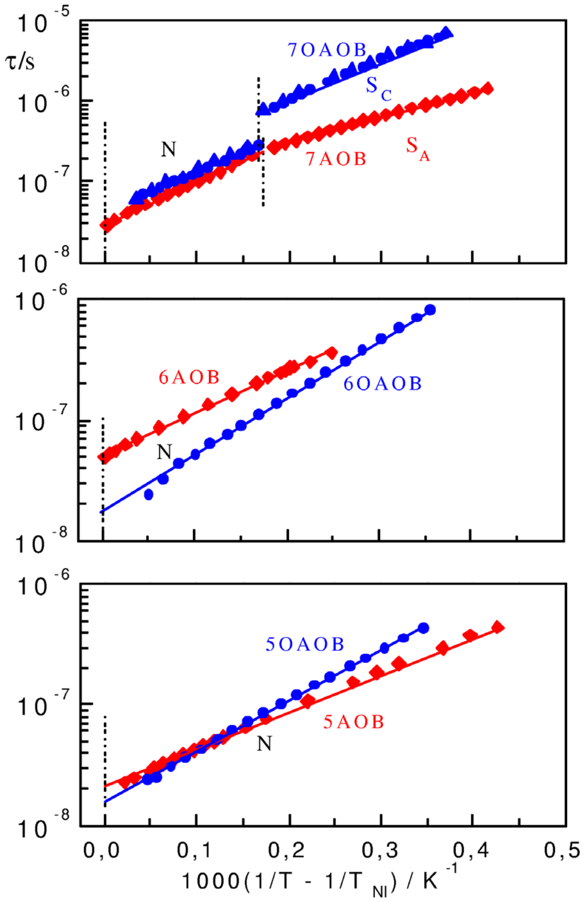

Fig. 6. The low frequency relaxation times obtained for particular substances in the LC phases. For a better clarity the term $(1/T - 1/T_{\mathrm{NI}})$ has been used instead of $1/T$.

nius plots using normalization to the clearing temperatures. The slopes of the lines fitted to the points gave the activation enthalpy $\Delta H = R(\partial \ln\tau/\partial(T^{-1}))$ ($R =$ gas constant). The obtained values are listed in Table 2.

In Figs. 6 – 8 the low frequency and high frequency relaxation times established for particular substances are shown. The data obtained by other authors are included (open symbols). Generally, they show satisfactory agreement with the present results.

4. Discussion

The following features should be pointed out if the results presented in Fig. 2 are considered: (*i*) In both series the permittivities systematically decrease with the lengths of terminal groups. (*ii*) The tensor permittivity components of *n*OAOB compounds are considerably greater than those characterising the *n*AOB substances. (*iii*) All *alkyl* compounds have positive dielectric anisotropy in the N phase, whereas their *alkoxy* counterparts exhibit negative anisotropy. (*iv*) The permittivity components in the smectic phases behave differently with temperature. The first feature was mentioned as typical for the isotropic phase of many homologous series (e.g. [19]), here it is clear that it holds for the N phase as well. The other properties can be discussed taking into account the Maier-Meier equations [20],

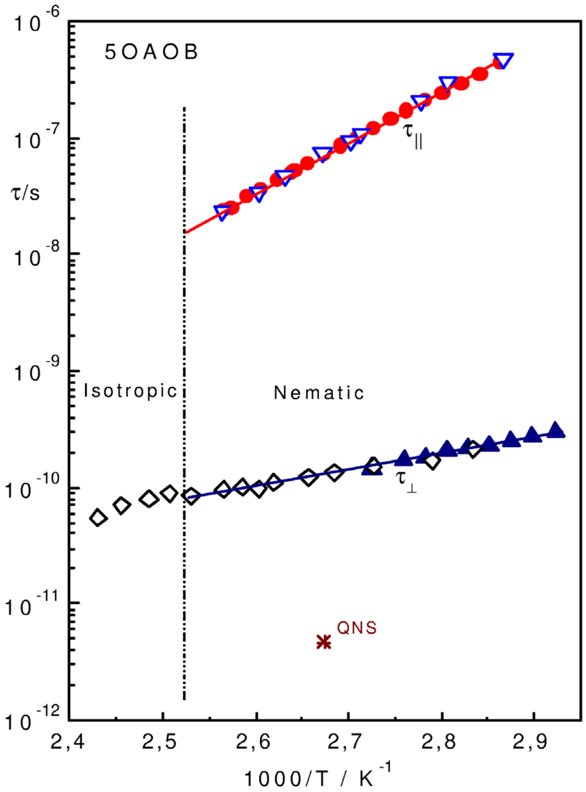

Fig. 7. The relaxation times obtained for 5OAOB in the present experiment (full points) and those established in the past by Nguyen et al. [11 – 13, 16] (open points). The point determined from the neutron scattering experiment (QNS) [11] is also shown for comparison.

$$(\varepsilon_{\|} - 1) = \varepsilon_0{}^{-1} N F h \tag{2}$$

$$\cdot\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu^2{}_{\mathrm{eff}}}{3kT}\left[1-(1-3\cos^2\beta)S\right]\right\}$$

$$(\varepsilon_{\perp} - 1) = \varepsilon_0{}^{-1} N F h \tag{3}$$

$$\cdot\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha S + F\frac{\mu^2{}_{\mathrm{eff}}}{3kT}\left[1+\frac{1}{2}(1-3\cos^2\beta)S\right]\right\},$$

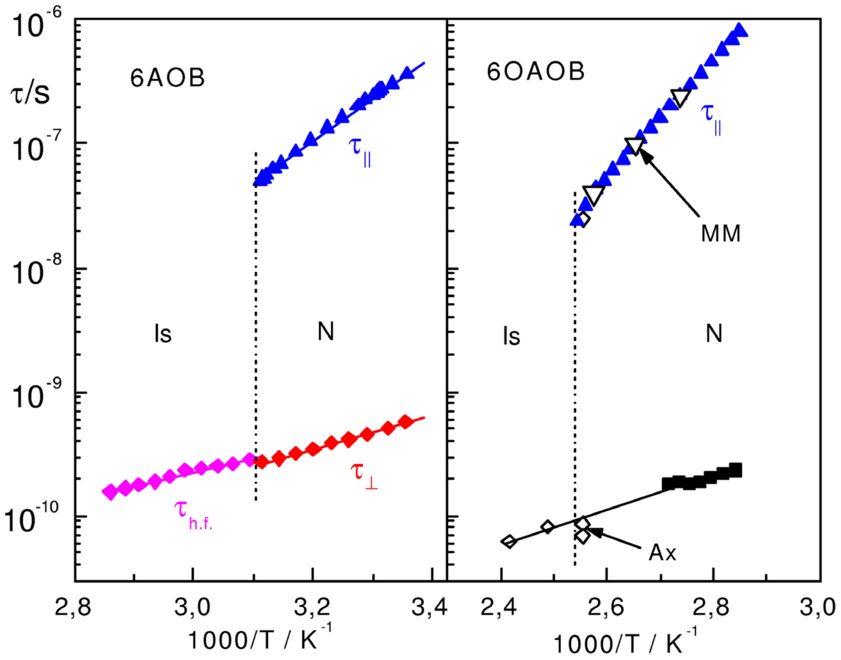

Fig. 8. The relaxation times obtained for the sixth member of both series in the present experiment (full points) and those established in the past (open points) by Maier and Meier (MM) [3] and Axmann (Ax) [4].

$$\Delta\varepsilon = (\varepsilon_\parallel - \varepsilon_\perp) = \varepsilon_0{}^{-1} N F h \left[\Delta\alpha - F\frac{\mu^2{}_{\mathrm{eff}}}{2kT}(1-3\cos^2\beta)\right] S, \qquad (4)$$

where $N = N_A\rho/M$ (N_A = Avogadro's number, ρ = density, M = molar mass), ε_0 is the permittivity of free space, $\Delta\alpha = \alpha_l - \alpha_t$ is the anisotropy of the molecular polarisability and $\bar{\alpha} = (\alpha_l + 2\alpha_t)/3$. The local field parameters F and h are expressed by the mean polarisability $\bar{\alpha}$ and mean permittivity $\bar{\varepsilon} \cdot S = \langle 3\cos^2\theta - 1\rangle/2$ is the order parameter. μ_{eff} is the effective dipole moment of a molecule, that may differ from the molecular dipole moment μ due to dipole-dipole correlations; the ratio $\mu_{\mathrm{eff}}/\mu = g_K$ is the Fröhlich-Kirkwood correlation factor. All quantities on the right hand side of the above equations are available from experiments [21]. Thanks to that, the angle β, which the dipole moments form *s* with the long molecular axis of *a* particular compound, can be estimated.

In both series of compounds the net dipole moments are inclined from the long molecular axis, treated as the lowest inertia moment axis (Fig. 1). The dipole moment of the azoxy N_2O group equals to 1.70 D and forms with the *para*-axis of the benzene ring the angle 60°, being thus larger than the "magic angle" 54.7° for which the dielectric anisotropy should be zero, compare (4). Because $\Delta\varepsilon > 0$ one can conclude that $\beta < 54.7°$. Thus, the long molecular axes deviate from the *para*-axis of the benzene ring. Using (4) and the data from [21] and Fig. 2, we obtained for 6AOB (at $T_{\mathrm{NI}} - T = 10$ K) the value $\beta \approx 45°$, which agrees well with the Parneix estimation for 7AOB [24] (named there as HEPTAB). The dipole moments of the alkoxy –OC_nH_{2n+1} groups equal 1.28 D and are inclined from the *para*-axis by 108° [22]. In principle, their longitudinal components, μ_l, should cancel due to symmetry, but in fact some contribution to the middle dipole moment seems to be essential because the parallel permittivities for *n*OAOBs are markedly larger than those for *n*AOBs (Fig. 2). (This holds also if the permittivities are normalized to 1 mole [23]). For the *n*OAOBs the transverse dipole moment, μ_t, is of course markedly greater than the longitudinal one, and this results in the negative dielectric anisotropy.

In the S_A phase of 7AOB the dielectric anisotropy changes its sign. This effect was first observed by de Jeu and Lathouvers [4] and then by other authors [14, 16]. This is explained by an increased dipole-dipole correlation due to the formation of the smectic planes (antiparallel correlation for $\mu_\parallel$ with $g_K^\parallel < 1$ and parallel correlation for $\mu_\perp$ with $g_K^\perp > 1$). However, the transition from the N to S_C phase of 7OAOB is accompanied by an increase of both permittivity components, that do not change within the smectic phase. Usually, at the nematic – smectic transition point the orienta-

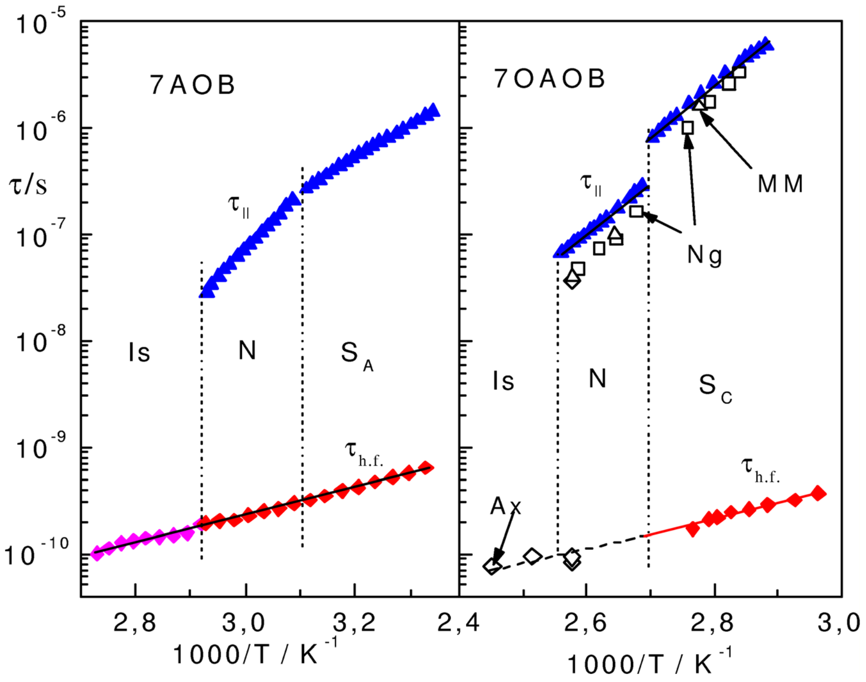

Fig. 9. The relaxation times obtained for the seventh member of both series in the present experiment (full points) and those established in the past (open points) by Maier and Meier (MM) [3], Axmann (Ax) [4] and Nguyen et al. (Ng) [9, 10].

tion of the sample is lost, which leads to an increase of the smaller component (here $\varepsilon_{\|}$) and a decrease of the larger component (here $\varepsilon_{\perp}$) of the permittivity (powdering effect). Therefore the observed increase of $\varepsilon_{\perp}$ at the N-S_C phase transition may mean that in the tilted smectic layers the molecules show a tendency to parallel dipole-dipole correlation too ($g_K^{\perp} > 1$). Unfortunately, more detailed analysis of this behavior could not be carried out because the permittivity components in the S_C phase were slightly different in two measurement runs, thus indicating a non-perfect orientation of the sample by the accessible magnetic field.

Summarizing, one can say that 7AOB, contrary to 7OAOB, does not fulfil the necessary conditions for the creation of the S_C phase, demanded in the Govind and Madhusudana model [1], because the perpendicular component of the dipole moment is too small in this case.

The relaxation processes observed in the LC phases can certainly be ascribed to molecular rotations around the principal inertia axes. Possible internal rotations of the alkoxy groups in *n*OAOBs should lie at much higher frequencies [10], not accessible in the present experiment. Oka et al. [16] have separated yet another relaxation process for 6AOB and 7AOB, which was ascribed to the precession of the dipole moment around the director. However, in our measurements this subtle effect could not be separated (compare Fig. 4).

The low frequency (l. f.) process connected with the rotation of molecules around the short axes is especially sensitive to the molecular arrangements in a given phase. This is well described by the Debye equation in all LC phases (Figs. 3, 4). This process is strongly retarded at the isotropic – LC phase transition point [25]. However, in the TDS spectra of the isotropic phase of *n*AOBs the l. f. process is hardly visible because a contribution of the high frequency (h. f.) process connected with the much faster molecular rotations around the long axes is dominating (compare Fig. 4). As is shown in Fig. 5a, the values of the relaxation times $\tau_{\|}$ normalized to the clearing points are close for the substances with the same *n*. Comparison (Fig. 5b) of the l. f. relaxation times for molecules with approximately the same lengths ($-C_nH_{2n+1}$ with $-OC_{n-1}H_{2n-1}$ indicates faster molecular rotations around the short axes in the case of *n*OAOB compounds; this might results in part from higher temperatures of the N phase (compare Table 1).

It seems interesting to note that the transition from the N to the S_A phase of 7AOB causes considerable diminishing of the activation enthalpy, but the relaxation time changes continuously (Fig. 8, Table 2). Contrary, the transition N–S_C in 7OAOB is accompanied by jump-wise lengthening of the relaxation time without marked change in the barrier. The first behavior is well known from dielectric studies of many substances with the N–S_A polymorphism (e.g. [25 – 30]) and can be treated as a common feature of substances having N–S_A polymorphism. Madhusudana et al. [27] have suggested that such lowering of the activation barrier is due to anisotropic packing effects: the volume expansion causes mainly an expansion within the smectic layer, whereas the layer spacing hardly varies with temperature; this favors a lowering of the activation energy in the S_A phase. Recently, we have checked for the S_A phase of 14CB [31], that really the thermal expansion of the volume is greater than the expansion of the layer spacing, indicating a small anisotropy of the thermal expansivity. In the case of the N–S_C polymorphism a step-wise behaviour of $\tau_{||}$ is commonly observed [29], but no rule concerning the relations between activation barriers in the two phases could be formulated. In this context it seems interesting to add that for 6OPB8, exhibiting the N–S_A–S_C polymorphism, it was found [30] that $\Delta H(\mathrm{N}) \gg \Delta H(\mathrm{S_A})$ but $\Delta H(\mathrm{S_A}) > \Delta H(\mathrm{S_C})$!

The molecular rotations around the long axes are not sensitive to the phase transitions, and the activation barriers are practically unchanged for both series of compounds. It is worthy to mention that the correlation time established for 5OAOB from QNS studies [11] is 25 times shorter than the h. f. relaxation time (Fig. 7). This means that the two experimental methods detect different molecular processes: the overall molecular rotations are observed in the dielectric relaxation measurements, and internal rotations of molecular moieties around $\varnothing$–N axes ($\varnothing$ stands for the benzene ring) in the QNS experiment [10].

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