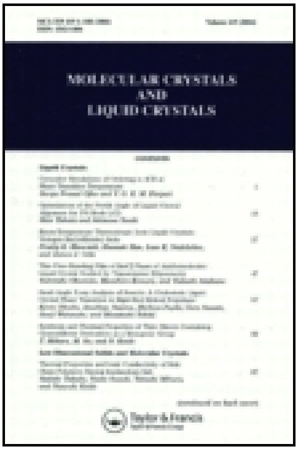

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Influence of Molecular Conformations on the Dielectric Relaxation Spectra of Liquid Crystals

S. Wróbel [a]

[a] Institute of Physics, Jagellonian University, 30-059 Kraków, Reymonta, 4, Poland

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Influence of Molecular Conformations on the Dielectric Relaxation Spectra of Liquid Crystals†

S. WRÓBEL

Institute of Physics, Jagellonian University, 30-059 Kraków, Reymonta 4, Poland

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Dielectric relaxation spectra observed for liquid crystals cannot be satisfactorily explained in terms of models which assume rod like molecules. Our investigations show that the low-frequency relaxation is in most cases a Debye-type process. On the other hand, the microwave relaxation region exhibits a distribution of the relaxation times, especially, for temperatures close to the clearing point. One can explain this effect by assuming intramolecular transitions between the conformational states of molecules. It is seen from the dielectric investigations that the relaxation rate for the intramolecular process ($\tau_{\mathrm{intra}}^{-1}$) fulfills the condition $\tau_{\perp}^{-1} \geqslant \tau_{\mathrm{intra}}^{-1} \gg \tau'^{-1}_{\parallel}$, where $\tau'_{\parallel}$ and $\tau_{\perp}$ are the relaxation times connected with the reorientations of the long and short axes, respectively. Our results also indicate that the molecules of such compounds as PAP, HOAB, and 7S5 have well defined conformations in the low temperature region of the nematic phases. For such conformations the moment of inertia tensors as well as the principal axes frames (p.a.f.) were found. These calculations enable us to analyze the dielectric data in terms of the Bauer model for molecular reorientations. The values of the energies and entropies connected with the two molecular motions were also obtained.

I. INTRODUCTION

Dielectric relaxation investigations of liquid crystals started in 1961 when Maier and Meier[1] discovered experimentally a low-frequency relaxation (l.f.r.) in the nematic phases of some 4,4′-di-n-alkoxy-

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azoxybenzenes:

$$H_{2n+1}C_nO—C_6H_4—N_2O—C_6H_4—OC_nH_{2n+1}.$$

They found that the critical frequency of the low frequency relaxation depends strongly on temperature as well as on the number of carbon atoms in the side chains.

First dielectric relaxation investigations of liquid crystals in the microwave frequency range were done by Carr *et al.* in 1962[2] who found a high frequency relaxation (h.f.r.) in the isotropic and nematic phases of PAA. More systematic investigations of the h.f.r. were performed by Axmann[3] for a few members of alkoxy-azo- and alkoxy-azoxy-benzenes. Axmann found that the relaxation times depended strongly on the molecular length. He also found that the h.f.r. exhibits a pronounced distribution of the relaxation times in both the isotropic and nematic phases.

These first investigations initiated further studies of the dielectric relaxation processes for liquid crystals with quite different molecular structures.[4-15] Now, there are many groups dealing with investigations of dielectric dispersion in liquid crystals as this method constitutes one of the best techniques for studying molecular dynamics in condensed matter. It is well established[10] that the l.f.r. is connected with the 180°-jumps around the short axis of the molecule, whereas the h.f.r. originates from the fast reorientations about the long axis (Figure 4). To a first approximation these two molecular motions can be treated as reorientations around two principal molecular axes, which can be determined by diagonalization of the inertia tensor calculated for the most stretched form of the molecules. Such calculations have been done for the molecules studied in our group.[8-10] The assumption that in the nematic phase the molecules reorient around the axes of the principal axes frame (p.a.f.) sheds more light upon the distribution of the relaxation times, as well as the dielectric spectra of the nematic phases of cyanobiphenyls (nCB)[4,6] with dipole moment parallel to the para-axis. Up to now some theories have been worked out[15-18] to understand more clearly the relation between the dielectric spectra and the molecular dynamics. All these theories assume that the molecules are rigid rods. In some cases a quantitative agreement between the theory and the experiment have been found.[4]

When one looks at the results of some recent dielectric relaxation studies of liquid crystals[4-14] the following questions may arise.

1. Why in some cases the h.f.r. exhibits a distribution of the relaxation times?

2. Is this distribution related to the molecular structure and/or strong fluctuations of the nematic potential?
3. Do the relaxation times, activation energies and entropies show an odd-even effect or not?
4. Why in the case of cyanobiphenyls the h.f.r. shows up in the direction perpendicular to the director?

To answer all these questions one would need more systematic studies of the dependence of the dielectric relaxation parameters on temperature as well as side chain length. In our group such investigations are being performed for the alkoxyazoxybenzene and alkylphenylalkoxythiobenzoate homologous series. In this paper we shall analyze some of the data in terms of the Bauer model,[4,32] which seems to be the best for describing the dipolar reorientations. For this purpose the principal moments of inertia as well as p.a.f. have been found.

II. EFFECT OF CONFORMATIONS ON THE DIELECTRIC RELAXATION SPECTRA

All relaxation processes, showing up in liquid crystals, can be interpreted on the basis of Cole-Cole modification of the Debye equation. So, for a given direction of the nematic phase one can write down:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + \sum_j \frac{\epsilon_{oj} - \epsilon_{\infty j}}{1 + (i\omega\tau_{oj})^{1-\alpha_j}} \tag{1}$$

where τ_{oj} is the most probable relaxation time for the j-th process, α_j is a parameter accounting for the distribution of relaxation times, ϵ_{oj} and $\epsilon_{\infty j}$ are the static and high-frequence permittivities, respectively.

In the isotropic phases one observes a broad spectrum with $\alpha_{is} = 0.3$,[10] whereas in the nematic phase the spectra consists of two well separated relaxation regions: 1) *the l.f.r.*—characterized by $\tau'_\parallel$ and $\alpha'_\parallel$ and 2) *the h.f.r.*—described by $\tau_\perp$ and $\alpha_\perp$. However, there is a third relaxation process observed parallel to the director[3,5,10] but it will not be discussed in this paper as it is affected by many molecular processes. There are two important experimental facts which suggest that in the low temperature region of the nematic phase the molecules possess a well defined conformation. One of them is the behaviour of the principal relaxation times ($\tau'_\parallel$ and $\tau_\perp$) as function of the molecular length (Figure 1 and 2). There is a strong increase of both relaxation times with increasing number of carbon atoms in the side chains. It means that not only the viscosity and molecular volume[32] determine the magnitude of the relaxation times, but also inertial effects have great influence on them. The second important experimental fact is the temperature dependence of the $\alpha_\perp$ parameter presented in Figure 3 for PAP ($\alpha_\perp$) and 7S5 (α_o) as a function of reduced temperature: $T_{\text{red}} = (T/T_{N-1}$. As it is seen, at low temperatures of the nematic phase $\alpha_\perp$ (or α_o) goes to zero. It might mean that in both cases one has one single molecular process, i.e. the reorientation around the long molecular axis (Figure 4). A strong dependence of the α_o parameter with decreasing temperature was also observed in the vicinity of the clearing point for one of the substituted phenylbenzoates.[11]

On the other hand, the $\alpha'_\parallel$ parameter is always equal to zero. Only nematic mixtures exhibit[20] a distribution of the relaxation times at

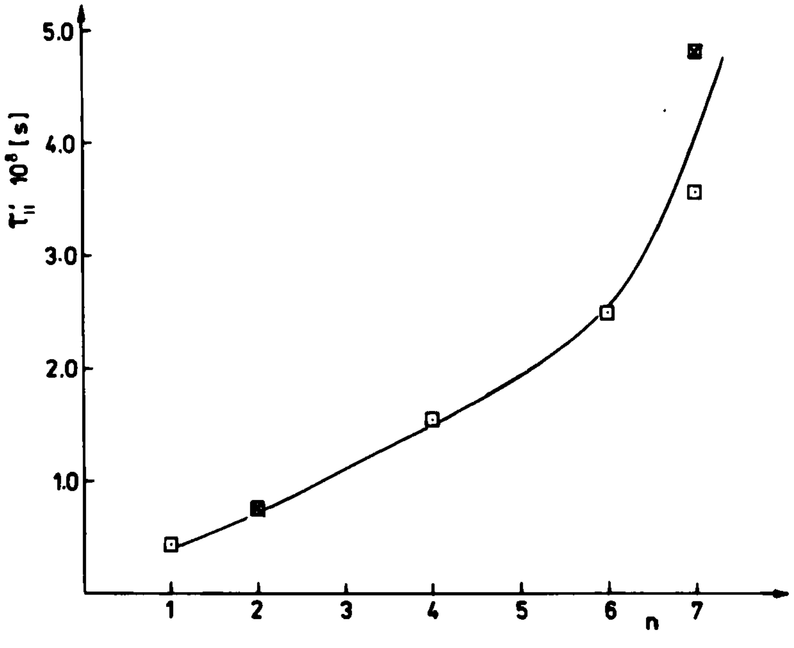

FIGURE 1 The relaxation time $\tau'_\parallel$, connected with the restricted reorientations around the S axis, versus the number of carbon atoms in the side chains for dialkoxyazoxybenzene homologous series.
⊡—experimental point obtained by Maier and Meier[1,3]
☒—experimental values obtained in our group.

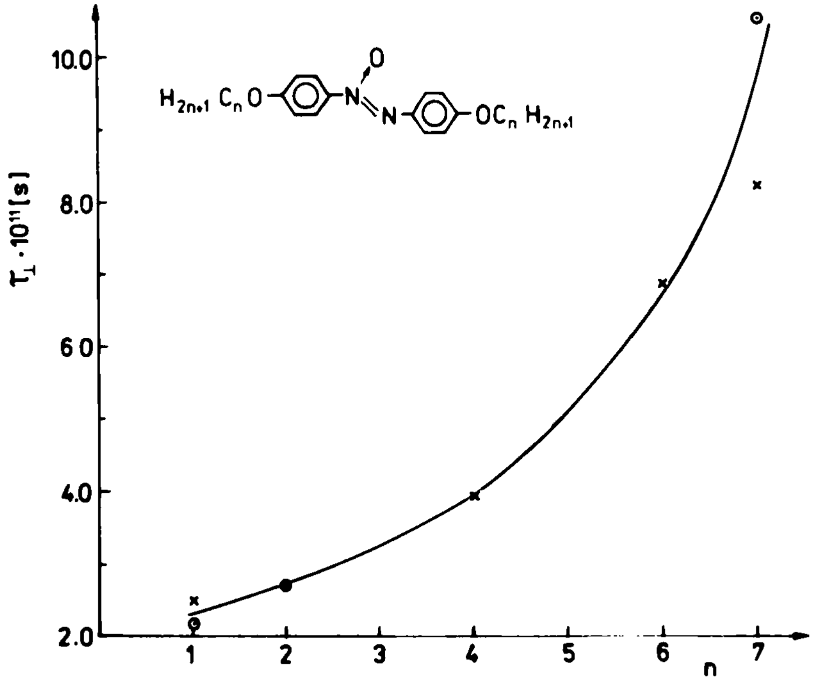

FIGURE 2 The relaxation times $\tau_\perp$ (or τ_0), connected with the fast reorientations about the long molecular axis, versus the number of carbon atoms in the side chains for alkoxyazoxybenzene homologous series. x—Axmann's data,[3] ⊙, ⊗—our results.

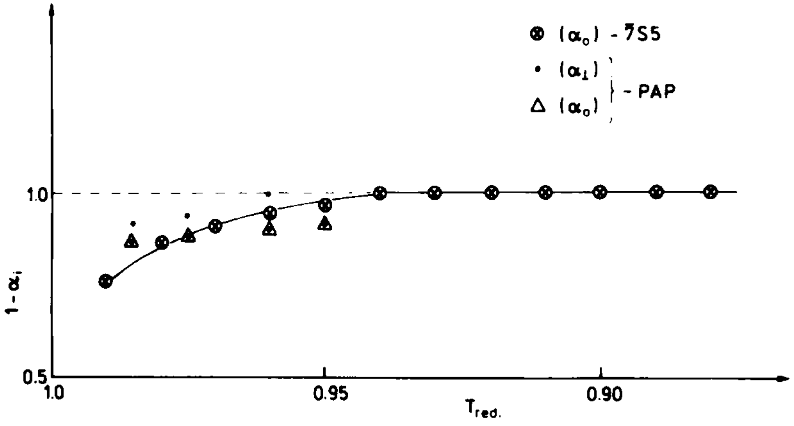

FIGURE 3 Temperature dependence of the distribution parameters obtained for different nematic liquid crystals (PAP and 7S5). Index "o" refers to the measurements done on unoriented samples.

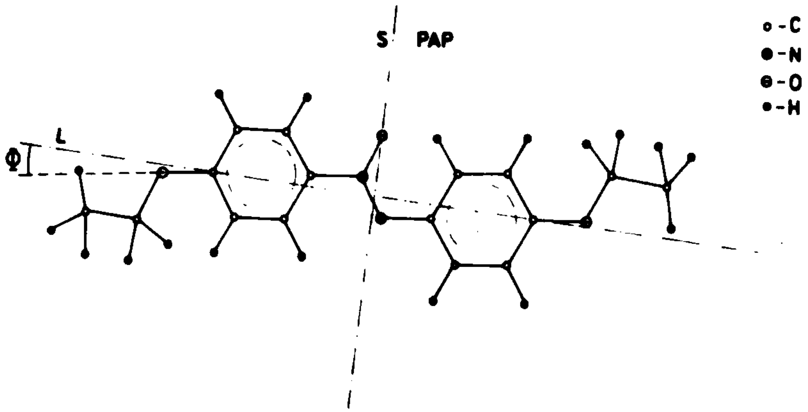

FIGURE 4 The principal axes frame (p.a.f.) of PAP molecule: S stands for the short molecular axis and L—for the long one.

low frequencies. In such cases the most probable relaxation times lie between the values of the relaxation times for pure components of the mixture. This result may be interpreted as follows: in the case of mixtures, different molecules relax with slightly different relaxation times. But a question arises how can one explain the existence of a distribution of the relaxation times observed in many liquid-crystalline systems at microwave frequencies? One can put forward a hypothesis that the molecules perform transitions—due to the collisions with phonons—between their conformational states. The life-time of such states is comparable with the correlation time connected with the reorientation around the long axis ($\tau_\perp \approx 10^{-11}$ s). If this hypothesis is true one can explain the dielectric relaxation spectra of alkoxyazoxybenzenes as follows: the low-frequency relaxation spectrum does not exhibit any distribution of the relaxation times because the conformational changes are so fast that they lead to an average conformation seen at radio frequencies. In other words at low frequencies the molecules are showing up as rigid rods. On the other hand, at microwave frequencies one sees different conformational states of the molecules because their life-time is comparable with the correlation time for the perpendicular component of the net dipole moment.

As it can be seen (Figure 3) the conformation changes influence strongly the h.f.r. in the vicinity of the clearing point. At temperatures far from this point the molecules seem to reorient as rigid rods. To prove this, in section IV, a discussion of the principal relaxation processes is presented on the basis of the Bauer model. It is assumed that reorientations of the molecules take place around the principal

TABLE I

The principal values of the moments of inertia for PAP, HOAB, $\bar{7}$S5 and 7CB

Substance	$I_L \times 10^{38}$ [g cm^2]	$I_S \times 10^{37}$ [g cm^2]	Φ [°]
PAP	5.2	7.1	13.4
HOAB	13.2	40.0	25.9
$\bar{7}$S5	5.8	27.1	18.4
7CB	6.4	12.4	14.5

axes of the inertia tensor. Its principal values were calculated for the most stretched planar forms assuming standard values for the bond lengths.[22,23]

III. THE PRINCIPAL MOMENTS OF INERTIA

Calculations of the moment of inertia tensor I_{kl} have been done for some members of alkoxyazoxybenzene homologous series, for $\bar{7}$S5 and 7CB. The principal values of the I_{kl} tensor are gathered in table I. For the purpose of this paper two components of I_{kl}, connected with the respective short axes of the flat molecule, are averaged to one: $I_S = ½ (I_{xx} + I_{yy})$. The values of the angle Φ (Figure 4) the L axis makes with the para axis of the molecule, are given in the last column. As it is seen, for each substance the I_L component of I_{kl} is about one order of magnitude smaller than I_S component. In such a case the conformational changes will greatly influence the I_L component. Due to this fact the rotation around the long axis is sensitive to the conformational changes inside the end chains, which leads to the fluctuations of the principal axes frame. On the other hand these fluctuations do not effect the I_S component so much.

Calculations of the I_{kl} for 7CB have been performed to compare our analysis with the literature data.[4] One cannot rely so much on the scarce literature data of the moments of inertia[26,27] as the authors do not give the assumptions made in their calculations. In addition there are big differences in the values of I_{ii} computed by different authors.

IV. THE ENERGIES AND ENTROPIES OF ACTIVATION

Table II presents the values of energies and entropies of activation obtained for the two principal molecular motions in the nematic phases.

TABLE II

The energies and entropies of activation calculated on the basis of the Bauer equation for the nematic phases of PAP, HOAB, $\bar{7}$S5 and 7CB

Substance	ΔE_B^L [kJ/mol]	ΔE_B^S [kJ/mol]	ΔS_B^L [J/Kmol]	ΔS_B^S [J/Kmol]
PAP	11.62	91.05	8	155
HOAB	23.6	113.7	34	230
$\bar{7}$S5	14.9	75.7	8	152
7CB[a]	7.5 (6 ± 2)	63.0 (60 ± 8)	−30 (−22 ± 8)	140 (130 ± 16)

[a]The values of the relaxation times were taken from.[4] The values computed by M. Davies et al. are given in parenthesis.

They were calculated by fitting to the experimental data[8,9,10] the Bauer relaxation equation:

$$\tau_{oi} = \left(\frac{2\pi I_{ii}}{k_B T}\right)^{1/2} \exp\left(\frac{\Delta E_B^i}{RT}\right) \exp\left(-\frac{\Delta S_B^i}{R}\right) \tag{2}$$

where: τ_{io} is the most probable relaxation time for the respective molecular reorientation, I_{ii}—is an appropriate principal value of the inertia tensor, connected with the i-th axis of molecular reorientation, k_B is the Boltzmann constant, R—gas constant, T—absolute temperature, ΔE_B^i and ΔS_B^i are, respectively, the energy and entropy of activation for the given molecular (i-th) process. Figures 5, 6 and 7 present the Bauer plots obtained for the liquid-crystalline phases of PAP, HOAB and $\bar{7}$S5. In most cases the plots are rather good straight lines. Only close to the clearing points are there deviations from linearity. They also might be caused by the conformation changes of the molecules.

On the basis of Table II as well as Figures 5, 6 and 7 the following conclusions can be drawn:

1. The energies and entropies of activation obtained for the two principal molecular reorientations are much different, and they depend strongly upon the molecular structure.
2. Both quantities depend strongly on the number of carbon atoms in the side chains for alkoxyazoxybenzenes. At the moment it is difficult to say whether they show an odd-even effect or not.

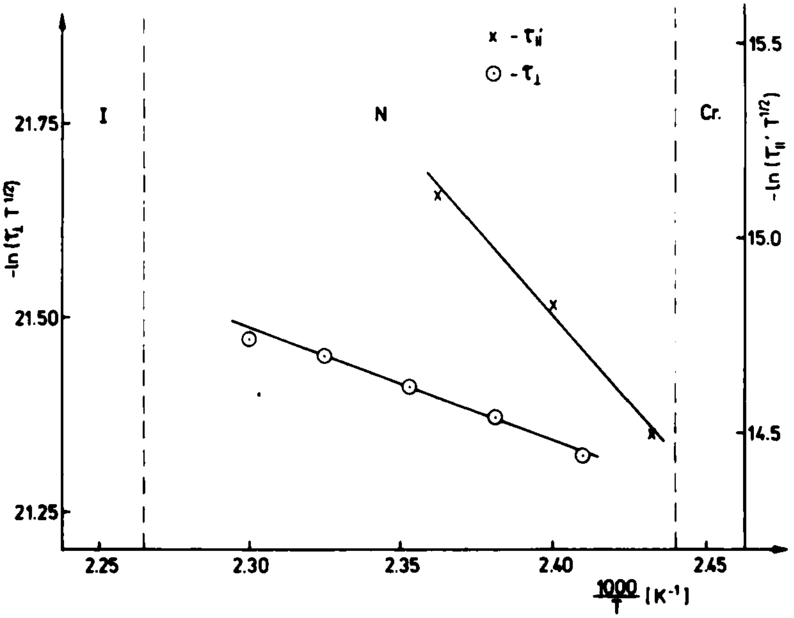

FIGURE 5 The Bauer plots for 4,4'-di-ethoxyazoxybenzene (PAP). $\tau'_{\parallel}$ and $\tau_{\perp}$ are the relaxation times connected with the two principal molecular motions in the nematic phase.

3. In most cases the Bauer plots deviate from the straight lines (Figures 5, 6, 7) close to the clearing points. This may indicate that there is an influence of molecular conformations on the relaxation processes observed. As it is known from earlier discussion, in the vicinity of the clearing point there is a temperature dependent distribution of the relaxation times connected with the rotation around the *L* axis. This process is most probably caused by conformational changes.

V. DISCUSSION

It is a very well established fact in the dielectric studies of condensed systems that molecular conformations cause a distribution of the relaxation times.[29,29] Taking into account the dielectric results obtained for liquid crystalline systems one can come to a conclusion that the conformation changes are very fast in comparison with the reorien-

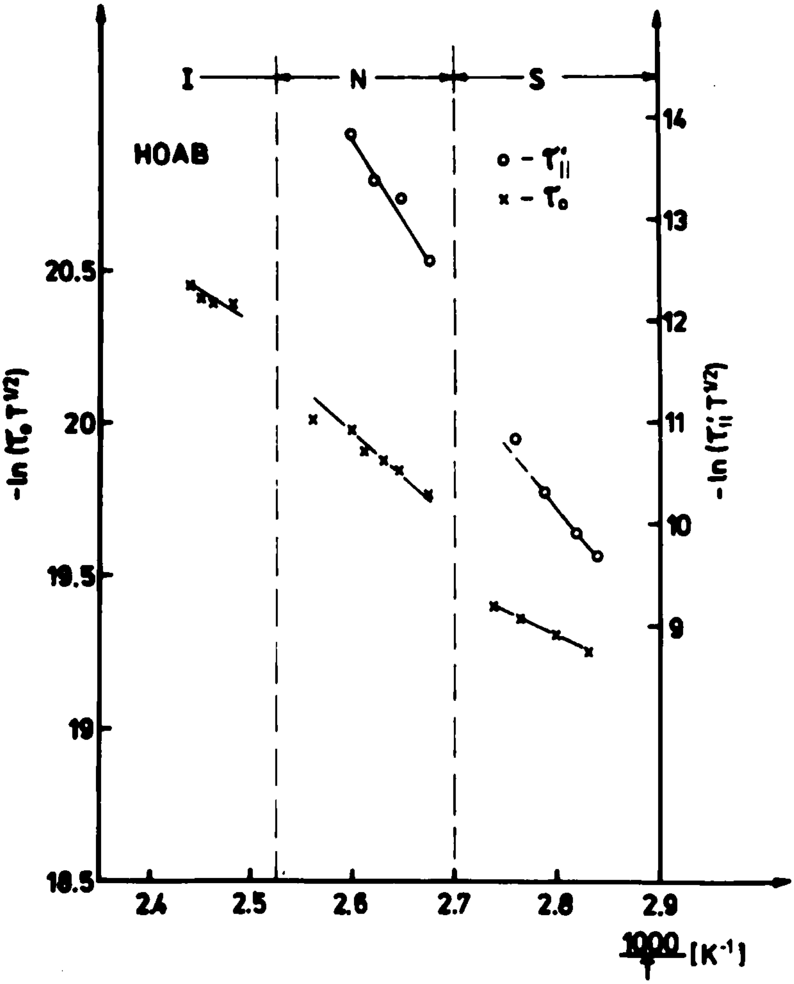

FIGURE 6 The Bauer plots for 4,4′-di-heptyloxyazoxybenzene (HOAB).

tation around the short axis (S), i.e. $\tau_{\text{intra}}^{-1} \gg \tau_{\|}^{-1}$. If this conclusion is true the conformations do not introduce any distribution of the relaxation time $\tau'_{\|}$. Additionally, due to the fast rotation about the L axis the molecular shape is averaged out and the molecules show up as "rigid rods" on the radio-frequency time scale ($\tau \sim 10^{-4}-10^{-9}$ s). The end-over-end exchange of such molecules gives a Debye-type dielectric relaxation process at low frequencies.

On the other hand, the molecular conformations take place on the same time scale as the reorientations about the L axis, i.e., $\tau_{\perp}^{-1} \geqq$

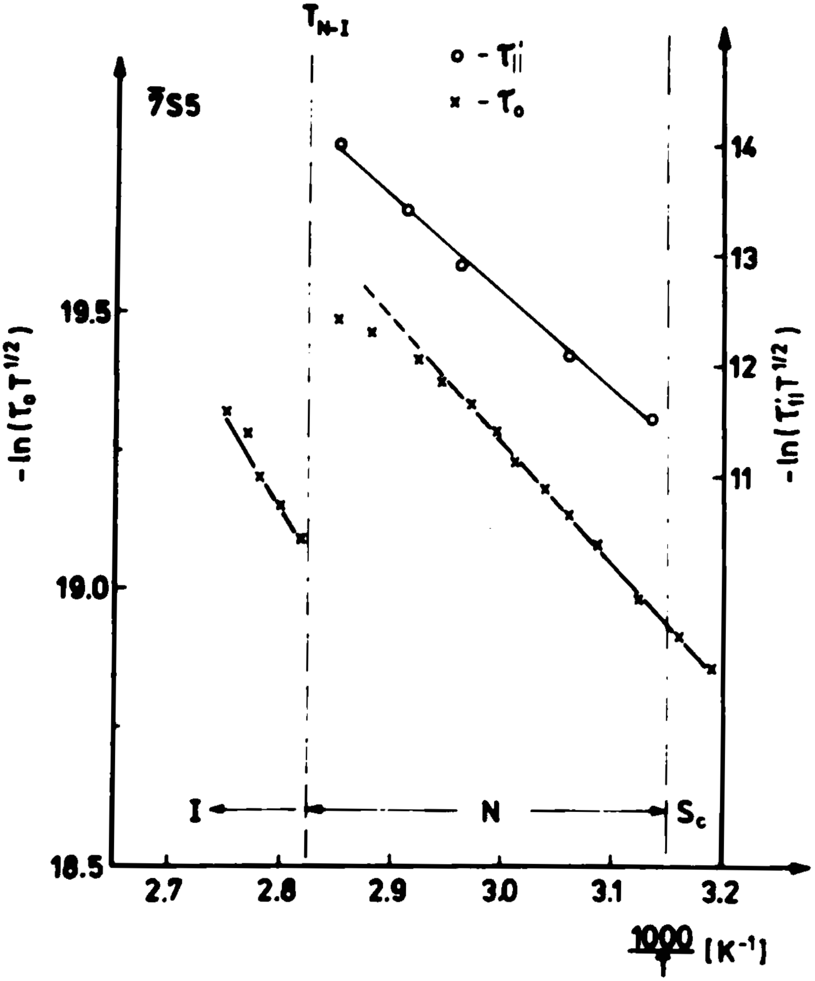

FIGURE 7 The Bauer plots for 4-n-pentylphenyl-4′-n-heptyloxytiobenzoate ($\bar{7}$S5).

τ_{intra}^{-1}. So, this could be a reason for the distribution of the relaxation times. In other words at microwave frequencies ($\tau \sim 10^{-10} - 10^{-11}$ s) different molecular conformers give contributions to the electric polarization. It is worth noting that conformations cannot be much faster ($\tau_{\text{intra}}^{-1} \gg \tau_{\perp}^{-1}$) than the reorientations around the long axis as until now nobody has observed clearly a separate relaxation process in perpendicular direction.

The picture presented above is characteristic for the region just below the clearing point, where the distribution parameter, $\alpha_{\perp}$, reaches its minimum value ($\alpha_\perp = 0$, see Figure 3). As it is very well known from NMR investigations[21,23-25] the nematic order parameter S_{zz} also exhibits a considerable change in the region discussed. From the dielectric standpoint both effects are of the same origin—i.e., the change of molecular conformations. They lead to the distribution of $\tau_\perp$, and they are also partly responsible for the strong temperature dependence of S_{zz} in the vicinity of the clearing point. In the low temperature region of the nematic phase the molecules seem to have stretched alkyl chains (trans-conformation). That is why the principal axes frame has been introduced to describe the molecular reorientations. The strong temperature dependences of $\alpha_\perp$ and S_{zz} below the clearing points can be then discussed in terms of fluctuations of the *L* axis of this frame.

As it is well known from the literature,[26] in the isotropic phase alkyl chains have different trans and gauche conformations, but the liquid crystalline ordering restricts to a certain extent the conformational freedom of the alkyl chains. So it is consistent with the dielectric data,[3,5,8-10] where for all isotropic phases there is a pronounced distribution of the relaxation times $\alpha_{\mathrm{is.}}$ ($\alpha_{\mathrm{is.}} = 0.2 \div 0.3$).

In the case of nCB molecules the conformation changes cause the *L* axis to coincide with the para axis due to the complete disorder in the alkyl chains in the isotropic phase. In such a case only the reorientation around the *S* axis influences the dielectric relaxation spectrum. In the nematic phase both the reorientations about the *S* and *L* axis affect the dielectric spectrum, because—due to the ordering of the chains—the L axis makes an angle with the para axis. In this sense there is a change of molecular conformation at the I-N transition point. In other words there is a change of molecular principal axes frame.

VI. CONCLUSIONS

1. In the low-temperature region of the nematic phase there is a well defined principal axes frame of the molecule and there is no distribution of the relaxation times.

2. The distribution of the relaxation times in the vicinity of the clearing point is most probably due to the fluctuations of the long molecular axis caused by the molecular conformational changes.

3. The low frequency relaxation process is not sensitive to the conformations because the fast rotation around the long molecular axis as well as the conformations of the alkyl chains average the molecular shape.

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