

Dielectric Studies of Smectogenic Members of the 4'-alkyl-4-cyanobiphenyl (*n*CB) Homologous Series

Joanna Czub, Urszula Gubernat, Bo Gestblom^a, Roman Dąbrowski^b, and Stanisław Urban

Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Cracow, Poland

^a Institute of Physics, Uppsala University, S-75121 Uppsala, Sweden

^b Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland

Reprint requests to Prof. S. U. E-mail: ufurban@cyf-kr.edu.pl; Fax: 0048-12-6337086

Z. Naturforsch. **59a**, 316 – 324 (2004); received March 3, 2004

Results of dielectric studies of smectogenic members of the *n*CB (4'-alkyl-4-cyanobiphenyl, $n = 9 \div 12$) homologous series are presented. The dielectric relaxation measurements were performed in the isotropic (Is) and smectic A (*S_A*) phases. The relaxation times characterizing the molecular rotations around the short axes (the low frequency, l.f., process) were established for both phases. In the Is phase the high frequency process connected with the molecular rotations around the long axes was also determined. The l.f. relaxation times were analysed using the Arrhenius and Bauer activation equations, which yielded the activation enthalpy ΔH and activation entropy ΔS . All results were analysed together with the literature data on the shorter members of the homologous series as well as on 14CB recently published. The ΔH and ΔS values show typical odd-even alternation that is especially well seen for the shorter members. In the Is phase the l.f. relaxation times are related to the viscosity data measured recently by Jadżyn et al.

Key words: Liquid Crystal; Smectic; Dielectric Relaxation; Cyanobiphenyls.

1. Introduction

4'-Alkyl-4-cyanobiphenyls (*n*CBs) belong to the liquid crystalline (LC) substances most interesting to study. The theoreticians treat them as model compounds for testing the models of LC phases, whereas good chemical stability and useful physical properties decide about their applications. First few *n*CBs were synthesized in the 1970s [1,2], the longest member, 14CB, was obtained quite recently [3]. The phase diagram for the members with $n = 5 \div 14$ (except $n = 13$) is presented in Figure 1. The first three members with $n = 5 \div 7$ show a nematic (N) phase, the members with $n = 8$ and 9 exhibit the nematic and smectic A (*S_A*) polymorphism, whereas those with $n \geq 10$ have exclusively the *S_A* phase. However, in the case of 10CB and 11CB the N phase appears again under elevated pressures [4]. *n*CBs have been studied previously, using a variety of experimental techniques. In particular, the dielectric relaxation studies of one or several members of this homologous series were reported in [4–24].

In this paper we present the results of dielectric investigations of the smectogenic members of the *n*CB series ($n = 9 \div 12$) for which such studies were not yet reported. The main information from the studies con-

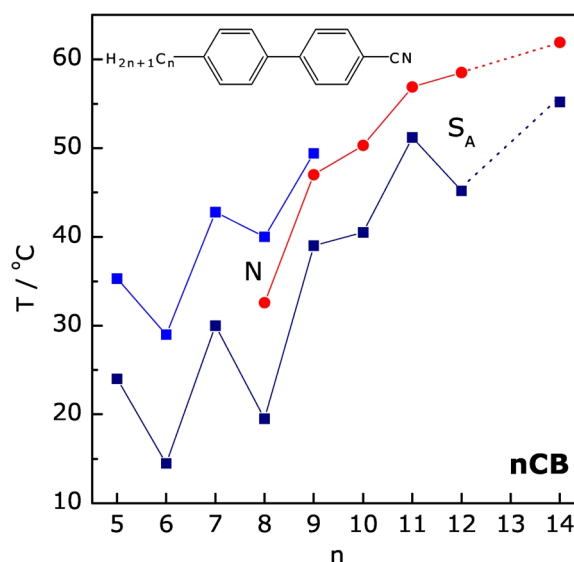


Fig. 1. Phase diagram of the *n*CB series.

cern the relaxation processes taking place in the liquid crystalline and the isotropic phases. Two main re-orientation motions can be distinguished: around the short molecular axes and around the long molecular axes. The corresponding relaxation processes fall into

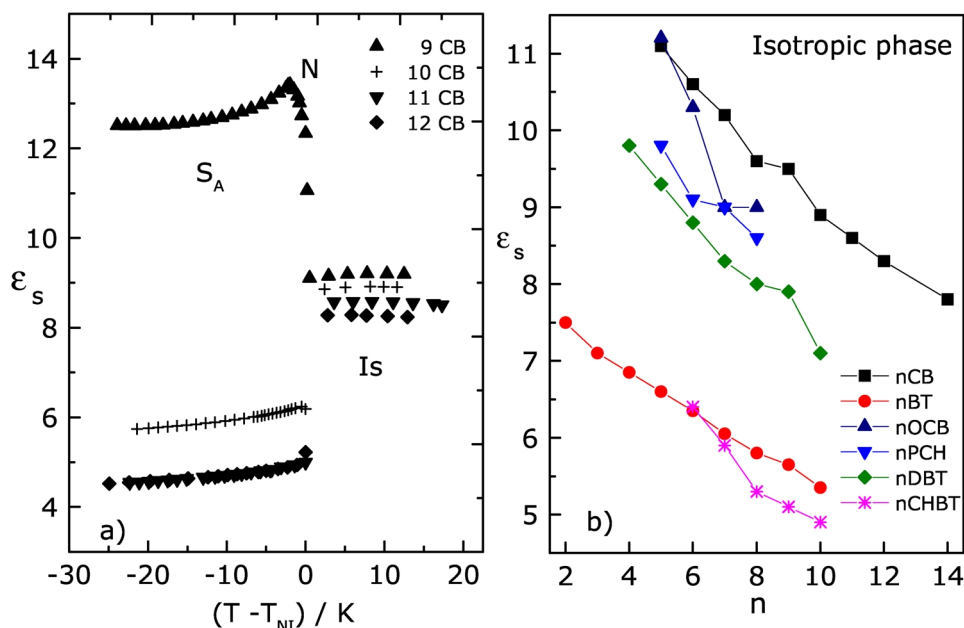


Fig. 2. a) Static permittivity in the *Is*, *N*, and *S_A* phases of *n*CBs. Only the 9CB sample was aligned. b) Static permittivity in the isotropic phase of several homologous series with one alkyl or alkoxy tail and the –CN or –NCS group at terminal positions.

megahertz frequencies (the low frequency, l. f., process) and hundreds of MHz or even GHz ranges (the high frequency, h. f., process), respectively. The aim of the studies was to investigate the influence of the length of the alkyl chain on the molecular dynamics in the LC and isotropic phases. The present results are compared and discussed with those obtained previously in our group [4, 13–20] on other *n*CBs. Some final comments on the dynamical properties of molecules in the isotropic, nematic and smectic A phases of the *n*CB series will be given.

2. Experimental

The substances studied were synthesized in the Institute of Chemistry, the Military University of Technology, Warsaw [3, 4]. The measurements of the complex dielectric permittivity, $\epsilon^*(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$, have been carried out in two frequency ranges. In the range of 1 kHz–10 MHz the measurements were performed with the aid of an HP 4192A impedance analyser. The parallel three-plate capacitor was used with the distance $d \sim 0.08$ mm between plates. Before each measurement the capacitor was calibrated with the use of four nonpolar liquids. The capacity of the empty cell was $C_0 \approx 50$ pF and the stray capacity was ~ 8 pF. The

capacitor was filled using capillary action. A magnetic field of c. 0.7 T and an electric bias field of 3000 V/cm were applied for orienting the samples. However, only in the case of 9CB the parallel alignment of the *N* and *S_A* phases were achieved by a bias field. The relaxation processes in the isotropic phase of all substances were studied with a time domain spectroscopy (TDS) in the frequency range 10 MHz–5 GHz at the Uppsala University. The experimental details of the TDS technique were described in [16, 20, 21]. All measurements were done in the temperature range 25–95 °C with decreasing temperature, which caused a considerable supercooling of the smectic samples. The temperature was stabilized within ± 0.2 K.

3. Results

Figure 2a presents the temperature dependence of the static dielectric permittivity ϵ_s in the isotropic and *S_A* phases of substances with $n = 9 \div 12$. In the isotropic phase the ϵ_s -values decrease with increasing chain lengths, as it was observed for other liquid crystalline substances – see Figure 2b. At the transition to the *S_A* phase the permittivity dropped considerably even if an orienting field (**E** and/or **B**) was applied. For 9CB a narrow nematic phase was sufficient to align the

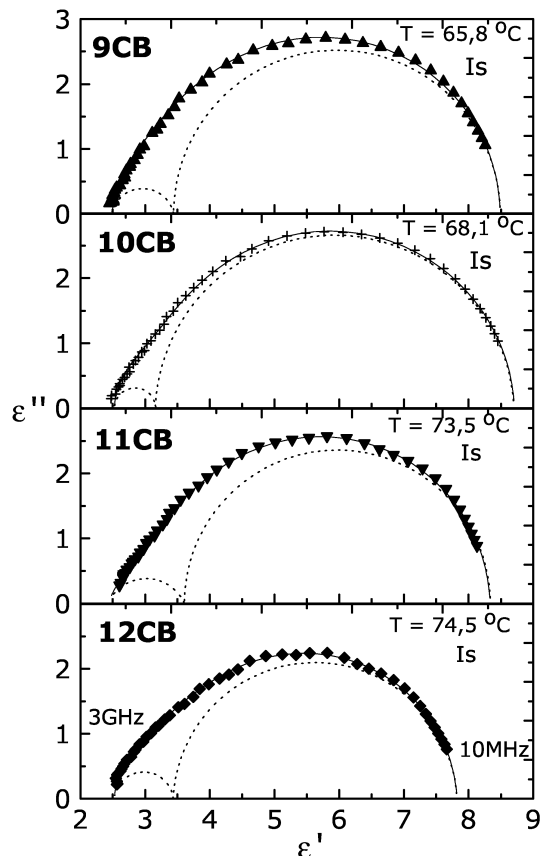


Fig. 3. Cole-Cole plots for the isotropic phase of *n*CBs. The spectra were analyzed assuming a superposition of two Debye-type processes, Eq. (1).

sample parallel to the measuring field, and this orientation could then be kept down to the smectic phase.

Figure 3 shows the dielectric spectra measured in the isotropic phase of four substances in form of Cole-Cole plots. The spectra of all substances reveal skewing at the high frequency part as was observed in other studies of *n*CBs [4, 5, 9–12, 20–24]. This can be considered as a consequence of the existence of two relaxation processes or as a result of an asymmetric distribution of relaxation times. In the former case a superposition of two Cole-Cole-type processes can be assumed:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon_{l.f.}}{(1 + i\omega\tau_{l.f.})^{1-\alpha_{l.f.}}} + \frac{\Delta\varepsilon_{h.f.}}{(1 + i\omega\tau_{h.f.})^{1-\alpha_{h.f.}}}, \quad (1)$$

where $\Delta\varepsilon = (\varepsilon_S - \varepsilon_\infty)$ is the dielectric increment, ε_S and ε_∞ being the static and high frequency permittiv-

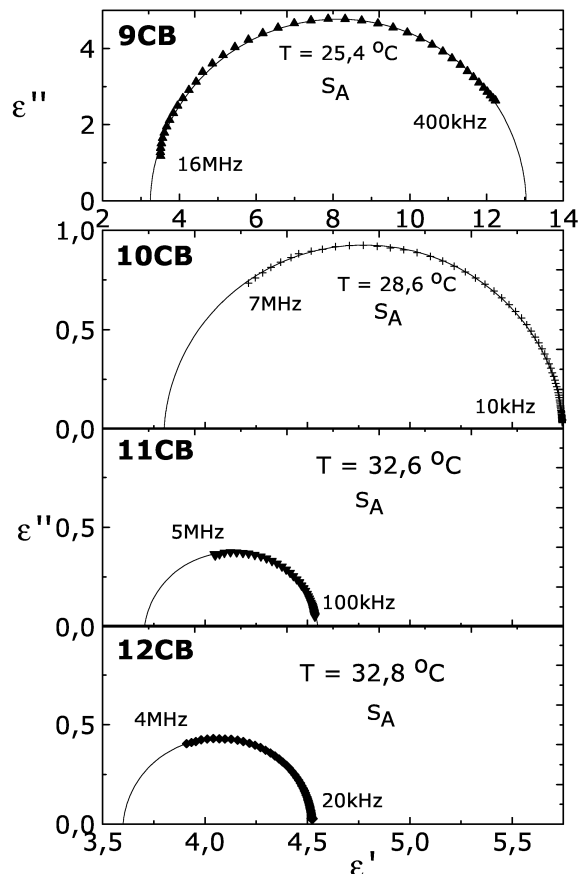


Fig. 4. Cole-Cole plots for the S_A phase of *n*CBs. The spectra were analyzed with the Cole-Cole equation (3).

ities, $\tau_{l.f.}$, $\tau_{h.f.}$ are the relaxation times of the low and high frequency relaxation processes, respectively, and $\alpha_{l.f.}$, $\alpha_{h.f.}$ describe the symmetric distribution of the relaxation times for both processes ($\alpha = 0$ corresponds to the Debye equation). In the latter case the Davidson-Cole [25] equation

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_S - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau_{DC})^{1-\beta}}. \quad (2)$$

can be applied to fit the results. The fits are very good (with $\beta \sim 0.8$), but the time parameter τ_{DC} and the distribution parameter β have not a simple physical interpretation [25]. Therefore we prefer to analyse the spectra with (1). The quality of fits is practically the same as for (2) with the α parameters close to zero. Würflinger [26] proposed the following relationship between τ_{DC} and the relaxation time derived from the Debye or Cole-Cole equations: $\tau = \tau_{DC} \arctan[(\pi/2)/(\beta + 1)]$. It was found that the l.f.

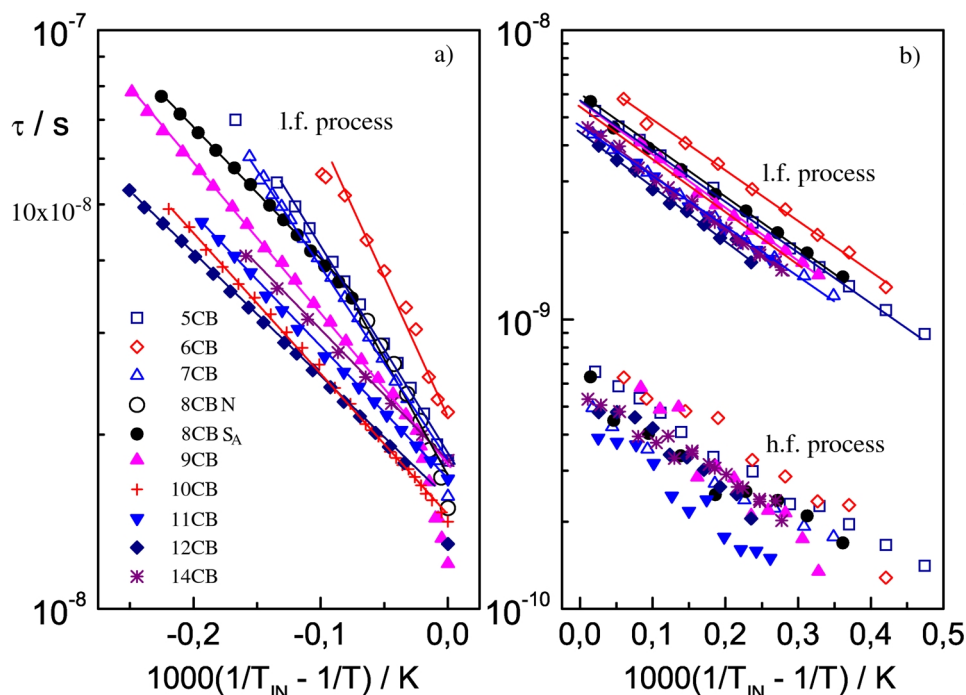


Fig. 5. Activation plots for the isotropic (a) and S_A (b) phases of *n*CBs. In order to avoid the shifts caused by different clearing points the $1000(1/T_{NI} - 1/T)$ abscissa is used. The lines are fits of the Arrhenius equation (4).

relaxation time derived from the fits of (1) agree very well with that calculated with Würflinger's formula.

The spectra obtained for the S_A phase are shown in Fig. 4 in the form of Cole-Cole plots. In this case only one relaxation process was observed in the frequency range available in the experiment. The dielectric spectra were analysed with the Cole-Cole equation

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_S - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}}. \quad (3)$$

The α parameter is of the order of $0.02 \div 0.05$, which means that practically one deals with a monodisperse relaxation process as in many other studies [4–24] of LC substances. Differences in the dielectric increment values $\Delta\varepsilon$ for particular compounds were caused by the fact that the orientation of the samples in the S_A phase could not be controlled.

The relaxation times obtained for all *n*CBs are presented in Fig. 5 in the form of activation plots, separately for the isotropic and LC phases. In order to avoid the shifts caused by different clearing points, the $1000(1/T_{NI} - 1/T)$ abscissa is used. The data for the members with $n = 5 \div 8$ were measured previously and

published in [19]. Traditionally, the Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{\Delta H_A}{RT}\right) \quad (4)$$

is used to fit the $\tau(T)$ results. The values of the enthalpy ΔH_A for all *n*CB compounds are presented in Fig. 7a (In the case of h.f. process in the isotropic phase the ΔH values were not calculated because of the rather large scatter of points, see Figure 5b).

The parameter τ_0 in (4) is interpreted as the inversion of the oscillation frequency of a molecule in the potential well [27] and was assumed to be independent of the temperature and the moment of inertia I of the molecule. The dependence of τ_0 on the temperature was predicted in the Eyring theory which, however, treats the problem quantummechanically and is thus inappropriate for the classical relaxation process [25]. Therefore, the Bauer's equation

$$\tau = \left(\frac{2\pi I}{kT}\right)^{1/2} \exp\left(-\frac{\Delta S_B}{R}\right) \exp\left(\frac{\Delta H_B}{RT}\right) \quad (5)$$

seems to be worthy to consider for the present case, as it incorporates I and T in the pre-exponential

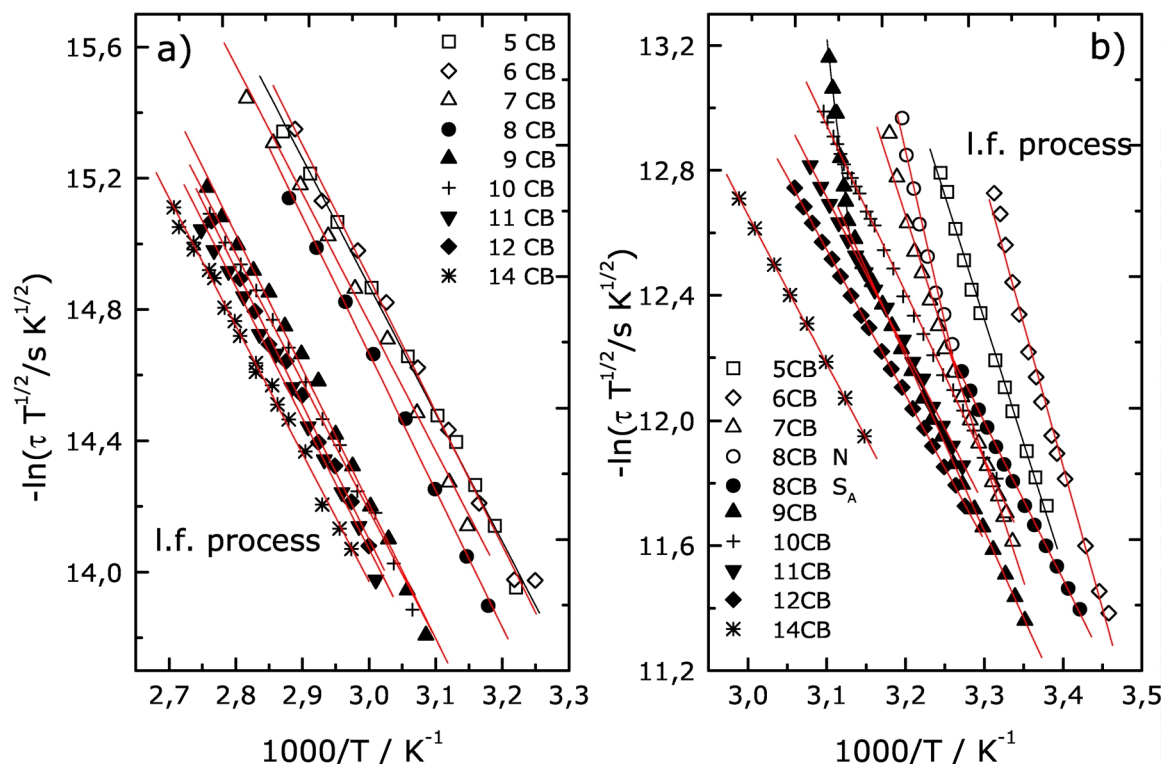


Fig. 6. Bauer plots for the l.f. relaxation times in the isotropic (a) and S_A (b) phases of *n*CBs. The lines are fits of the Bauer equation (5).

factor. ΔH_B is the Bauer activation enthalpy and ΔS_B is the activation entropy of a relaxation process. The appropriate value of the moment of inertia I must be calculated for the reorientation process around the short or long molecular axis. The I -values for the substances studied were calculated using the Chem3D 5.0 program for the all-*trans* conformers which are most stable (see insert of Fig. 8). Such conformations were obtained and published for others members of the *n*CB series in [28]. The corresponding lengths of the molecules are shown in Fig. 10 (open points).

Figures 6a and b present the Bauer plots, $-\ln(\tau \cdot T^{1/2})$ versus $1000(1/T_{NI} - 1/T)$, for the l.f. relaxation process for all *n*CBs, separately for the isotropic and liquid crystalline (*N* and S_A) phases. As one can see, the straight line can be fitted in both cases according to (5), yielding the values of ΔH_B and ΔS_B . These values are presented in Fig. 7a and b (open symbols) as dependent on *n*. From (4) and (5) can be deduced that the values of ΔH_B should be smaller than those of ΔH_A [25], as is also found.

Recently Jadzyn *et al.* [22, 29, 30] have noted that the activation enthalpy for the molecular rotation around the short axis and that of viscous flow in the isotropic phase are quite close to each other. This stimulated them to discuss the appropriateness of the Debye relation between $\tau_{l.f.}^{iso}$ and the viscosity coefficient η^{iso} ,

$$\tau_{l.f.}^{iso} = \frac{4\pi\eta^{iso}a^3}{kT}, \quad (6)$$

where the rotating dipolar molecule is represented by a sphere of a radius *a*. The authors have found quite good proportionality between $\tau_{l.f.}^{iso}/\eta^{iso}$ and $1/T$ in a broad range of temperature of the isotropic phase of 6CB [22] and calculated the radius of rotation of the molecule around the short axis $2a \approx 13$ Å. Now we extend this approach to all members of the *n*CB homologous series, using our $\tau_{l.f.}(T)$ data and Jadzyn's *et al.* $\eta^{iso}(T)$ data [31]. Then the effective lengths $l = 2a$ of molecules can be compared with those calculated for the all-*trans* conformers.

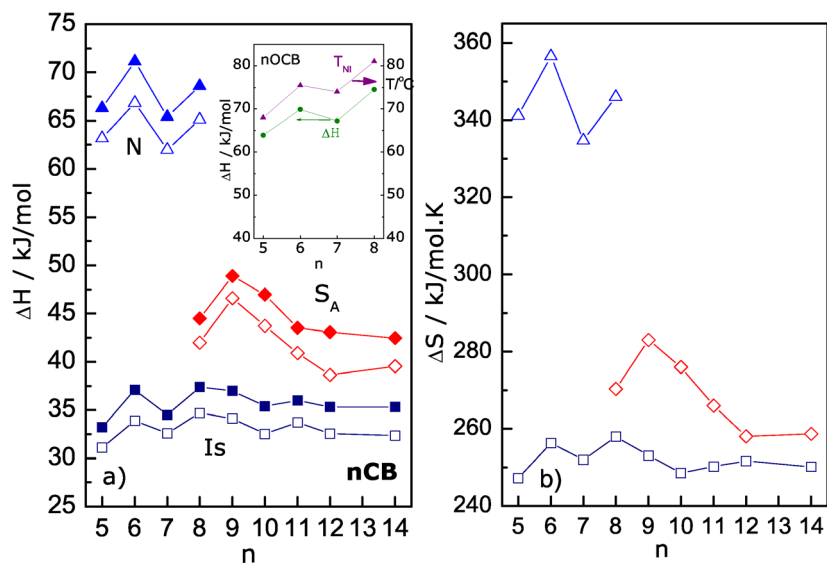


Fig. 7. The activation parameters, determined with the aid of the Arrhenius (full symbols) and Bauer (open symbols) equations. In the *N* phase of *n*CBs the alternations of ΔH and T_{cl} (compare Fig. 1) are opposite, whereas for *n*OCBs (see insert) the alternations of both quantities are the same.

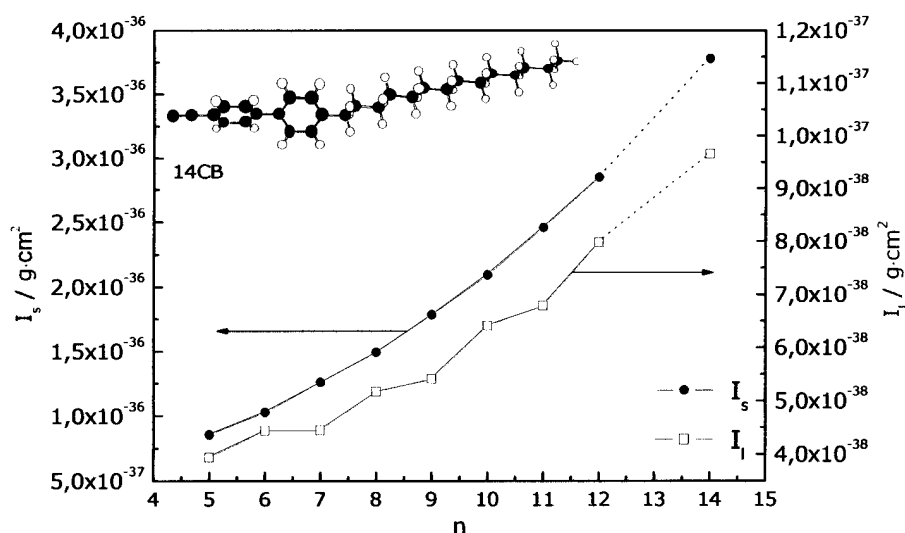


Fig. 8. The principal inertia moments determined with the Chem3D 5.0 program for the all-*trans* conformers.

Figure 9 shows the dependence of $\tau_{l.f.}^{iso}/\eta^{iso}$ on $1000/T$ for *n*CBs except 14CB, for which viscosimetric data are not available. As can be seen from the figure, straight lines yielding a^3 could be drawn through practically all points of the smectogenic compounds, whereas in the case of nematogenic ones only high temperature points lie on the lines. In Fig. 10 (full points) the effective lengths $l = 2a$ of the molecules are compared with those determined using the Chem3D 5.0 program for the all-*trans* conformations. The large difference between both estimates of the molecular lengths indicates the role of conforma-

tional motions of the alkyl chains in the formation of the molecules.

4. Discussion

The present dielectric studies of smectogenic cyanobiphenyls extend the hitherto obtained results to all known *n*CBs. This allows to point out some common features which seem to be characteristic for this class of LC substances.

Looking at Fig. 2b one can easily confirm that the static dielectric permittivity ϵ_s in the isotropic phase

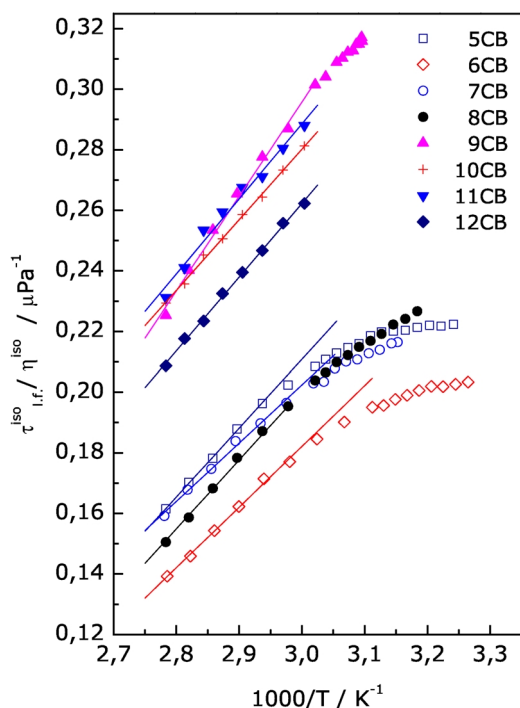


Fig. 9. The plots of the ratio $\tau_{l.f.}^{iso} / \eta^{iso}$ versus $1/T$ according to the Debye equation (6).

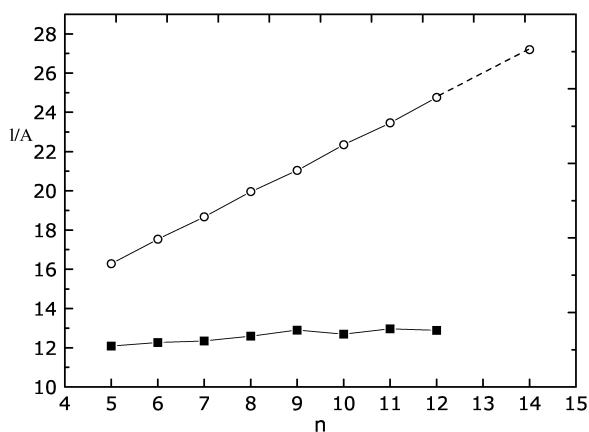


Fig. 10. Molecular lengths for *n*CBs from the Chem3D 5.0 program for the all-*trans* conformers (open points) and determined from the plots presented in Fig. 8 (full points).

diminishes with increasing length of the alkyl chain. This effect is known as a 'solvation' of the dipole moment with lengthening of the alkyl chain [32]. On the other hand, the kinks in the alkyl chain lead to divergence of the long molecular axes from the *para*-axis of the benzene ring which results in the appearance of the high frequency relaxation process observed in the

isotropic (compare Fig. 3) as well as in the nematic phase [5, 9–12] (the dipole moment of the –CN group reaches a non-zero transverse component).

The even-odd effect, revealed in the dependence of the activation enthalpy on the length of the alkyl chain, shows an opposite alternation of that observed for the clearing temperature (compare Figs. 2 and 7a). The latter effect was theoretically explained by Marčelja [33] as resulting from the dependence of the ordering process on the addition of subsequent carbon atoms to the chain. In the case of the alkyl chain the odd atoms help the ordering process, whereas the even atoms hinder the ordering. According to the mean field theory of Maier and Saupe [34] the anisotropic part of the intermolecular potential (the nematic potential q) is proportional to the order parameter S . One would expect that the activation barrier hindering the flip-flop molecular rotation should reflect the changing of q , which, however, is not the case! Contrary to that, the *n*OCB series exhibits the same alternation of both these quantities (see insert in Figure 7a).

Figure 7a shows that the values of the activation enthalpy in the nematic phase are distinctly higher than those in the smectic A phase. This is a common feature of substances having both these phases [8, 10, 18, 35]. This effect has been explained by Madhusudana *et al.* [36, 37] as the anisotropic packing effect. The volume expansion leads to an expansion within the smectic layer, whereas the layer spacing hardly varies with temperature. It is a unique opportunity to verify this model in the case of the S_A phase of 14CB, for which the data on the temperature dependence of the layer spacing d [3] and density ρ [38] are available. Figure 11 presents a comparison of $d(T)$ and the third root of the density within the S_A phase of 14CB. The larger slope of $\rho^{1/3}(T)$ seems to support the model.

The dependence of the activation entropy ΔS_B also exhibits the even-odd effect, which is presented in Figure 7b. The activation entropy in the isotropic phase and in the liquid crystalline phases (N and S_A) takes positive values. However, Brot [27] mentioned that the only meaningful quantities are the differences in entropies of the activation for the same molecule at the same temperature in different environments. However, the entropy-changes for the same motion in different phases are also discussed. ΔS_B describes a change of entropy between two orthogonal orientations of the molecules that take place during motion around their principal axes. The activation entropy ΔS_B for 7CB in nematic and isotropic phases was analysed by Davies

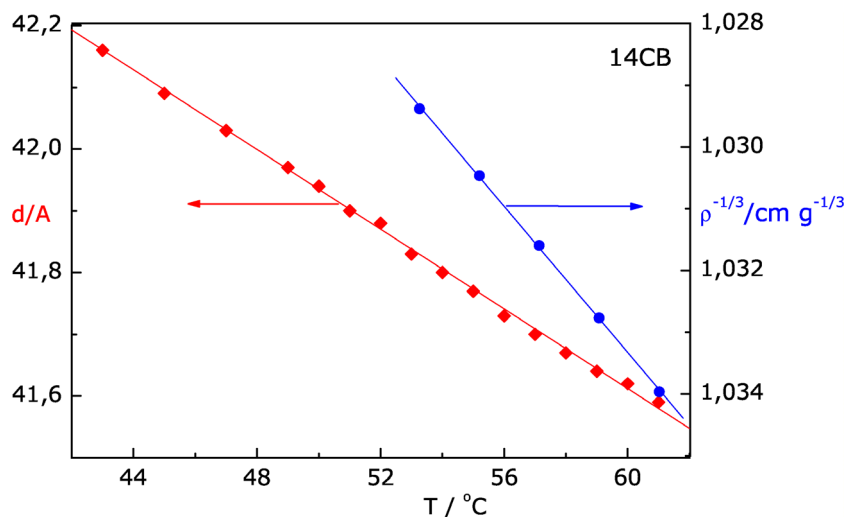


Fig. 11. Temperature dependences of the layer spacing d and the third root of the density $\rho^{1/3}$ in the S_A phase of 14CB.

et al. [5]. The ΔS_B values in the nematic phase are larger than those in the smectic A phase and in the isotropic phase. The differences between ΔS_B in the N and the I_s phase were explained by Hikmet and Zwerver [39]. The effect is considered to be due to the larger disruption of the local order during reorientation around short molecular axes in the nematic phase than in the isotropic phase.

The lengths of 8CB, 10CB and 12CB molecules calculated using Chem3D 5.0 for the all-*trans* conformers are similar to those obtained from the X-ray diffraction measurements performed by Leadbetter *et al.* [40, 41]. The length of the 6CB molecule obtained from equation (6) agrees with that calculated by Jadżyn *et al.* [22]. The differences between lengths of the *n*CB molecules obtained from Chem3D 5.0 and calculated on the basis of the viscosity measurements can be explained as resulting from the conformational motions of the alkyl chain. With increasing n , many different conformers become possible, which leads to a shortening of the molecular lengths. Therefore the activation enthalpy for the l. f. process in the S_A phase is practically the same for as different substances as 8CB and 14CB [3].

5. Conclusions

The results of dielectric studies of the *n*CB series in the isotropic and LC (N and S_A) phases allow us to point out the following:

1. In the isotropic phase two well separated relaxation bands are observed (Figure 3). The low frequency band is connected with the molecular rotations around the short axes whereas the high frequency band corresponds to the molecular rotations around the long axes.
2. In the S_A phase of substances with $n = 9 \div 12$ only one relaxation process relating to the molecular rotations around the short axes was observed (Figure 4).
3. The Bauer equation seems to be appropriate to analyse the temperature dependence of the relaxation times in the isotropic and LC phases.
4. Activation enthalpies and activation entropies reveal an even-odd alternation (Figure 7).
5. The activation barrier hindering the flip-flop molecular motion is markedly lower in the S_A phase than in the N phase. The model proposed by Madhusudana for explaining this effect is positively verified by the experimental facts.

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