This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric studies of the 4-*n*-alkyl-4'-thiocyanatobiphenyl (*n*BT) homologous series (*n*=2-10) in the isotropic and E phases

Stanislaw Urban; Krzysztof Czuprynski; Roman Dąbrowski; Bo Gestblom; Joanna Janik; Horst Kresse; Heiko Schmalfuss

Online publication date: 06 August 2010

To cite this Article Urban, Stanislaw , Czuprynski, Krzysztof , Dąbrowski, Roman , Gestblom, Bo , Janik, Joanna , Kresse, Horst and Schmalfuss, Heiko(2001) 'Dielectric studies of the 4-*n*-alkyl-4'-thiocyanatobiphenyl (*n*BT) homologous series (*n*=2-10) in the isotropic and E phases', Liquid Crystals, 28: 5, 691 — 696

To link to this Article: DOI: 10.1080/02678290010023343

URL: http://dx.doi.org/10.1080/02678290010023343

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 2001, VOL. 28, NO. 5, 691–696

Dielectric studies of the 4-*n*-alkyl-4′-thiocyanatobiphenyl (*n*BT) homologous series (*n* = 2–10) in the isotropic and E phases

STANISŁAW URBAN*, KRZYSZTOF CZUPRYŃSKI†,
ROMAN DĄBROWSKI†, BO GESTBLOM‡, JOANNA JANIK,
HORST KRESSE§, and HEIKO SCHMALFUSS§

Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland
†Institute of Chemistry, Military Technical Academy, 00-908 Warsaw, Poland
‡Institute of Physics, Uppsala University, S-75121 Uppsala, Sweden
§Institute of Physical Chemistry, Martin-Luther University, Halle/S, Germany

(*Received 8 June 2000; accepted 28 September 2000*)

Results of the dielectric studies of nine members of the *n*BT (4-*n*-alkyl-4′-thiocyanatobiphenyl, $n = 2$–10) homologous series in the crystal E (E) and isotropic (I) phases are presented. The dependence of the static permittivity ε_s in the isotropic phase, the longitudinal relaxation times τ_{is} and $\tau_{\|}$, and the activation enthalpies ΔH_{is} and $\Delta H_{\|}$ on the number of carbon atoms in the alkyl chain *n* are analysed. A considerable increase in the retardation factor $g = \tau_{\|}/\tau_{is}$ with decreasing *n* is observed. The results are compared with those obtained for similar two-ring homologous series. The parameters characterizing the molecular rotations around the short axis in the E phase ($\tau_{\|}$ and $\Delta H_{\|}$) indicate a hardening of this solid-like phase with shortening of the alkyl chain.

1. Introduction

Liquid crystalline (LC) substances with the isothiocyanato (−NCS) in the terminal position of the molecules exhibit phase sequences which differ considerably from those observed for their analogues with the −CN group [1, 2]. The 4-*n*-alkyl-4′-thiocyanatobiphenyl homologous series (*n*BT), figure 1, exhibits exclusively the crystal E (E) phase for $n = 2$–10, whereas the corresponding cyanobiphenyls (*n*CBs) and 4-alkoxy-4′-cyanobiphenyls (*n*OCBs) form the nematic phase for $5 \leqslant n \leqslant 7$, and the nematic–SmA$_d$ phase sequence for $n \geqslant 8$. Other two-ring isothiocyanato compounds, such as the 5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxans, *n*DBT [3, 4], exhibit exclusively the SmA$_1$ phase, but the 4-(*trans*-4′-alkylcyclohexyl)isothiocyanatobenzenes (*n*CHBT) show only the nematic phase for $n = 2$–12 [5].

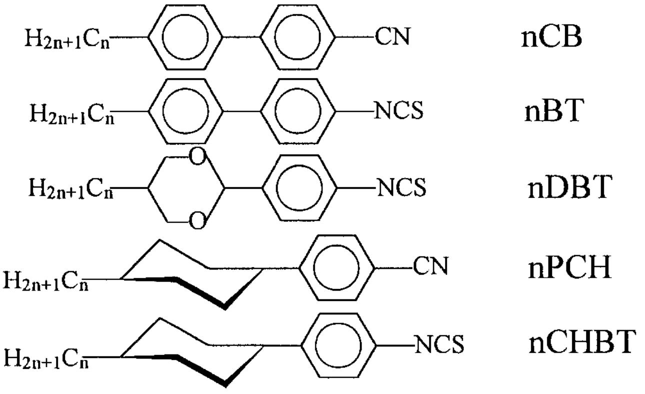


Figure 1. *n*-Alkyl two-ring homologous series discussed in the paper.

The E phase has an orthogonal structure with a ‘herring bone’ ordering of the molecules in the layers [6]. Figure 2 shows the change in the transition temperatures of the *n*BTs with the number of carbon atoms in the alkyl chain. We have undertaken dielectric studies of this series with the aim of detecting the influence of the length of the alkyl chain on the static permittivity and the low frequency (l.f.) relaxation process connected with molecular reorientations around the short axes in the isotropic (I) and E phases. The results can be compared with the dielectric data obtained recently for four other *n*-alkyl two-ring homologous series (figure 1): *n*CB [7], *n*PCH [7], *n*DBT [4], and *n*CHBT [4, 8]. Special attention will be paid to the changes in the dielectric relaxation times and activation enthalpies at the transitions from the isotropic to the different LC phases.

2. Experimental

The *n*BT samples were synthesized in the Institute of Chemistry, the Military University of Technology, Warsaw. Some members of the series have been prepared

---

*Author for correspondence; e-mail: ufurban@cyf-kr.edu.pl

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010023343

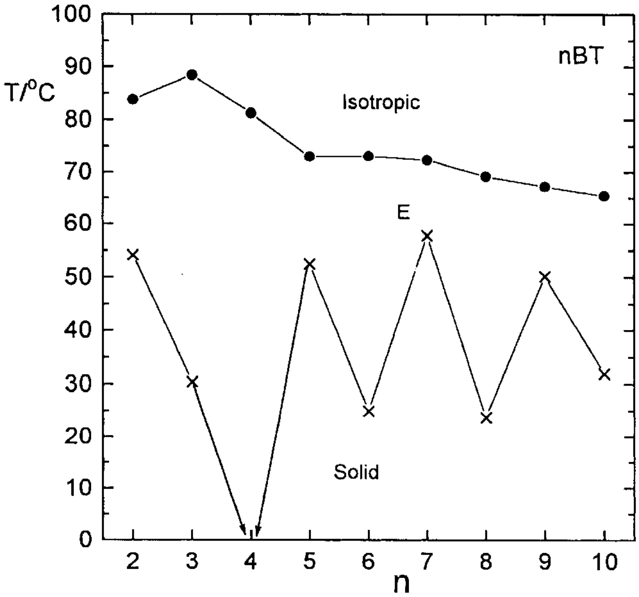


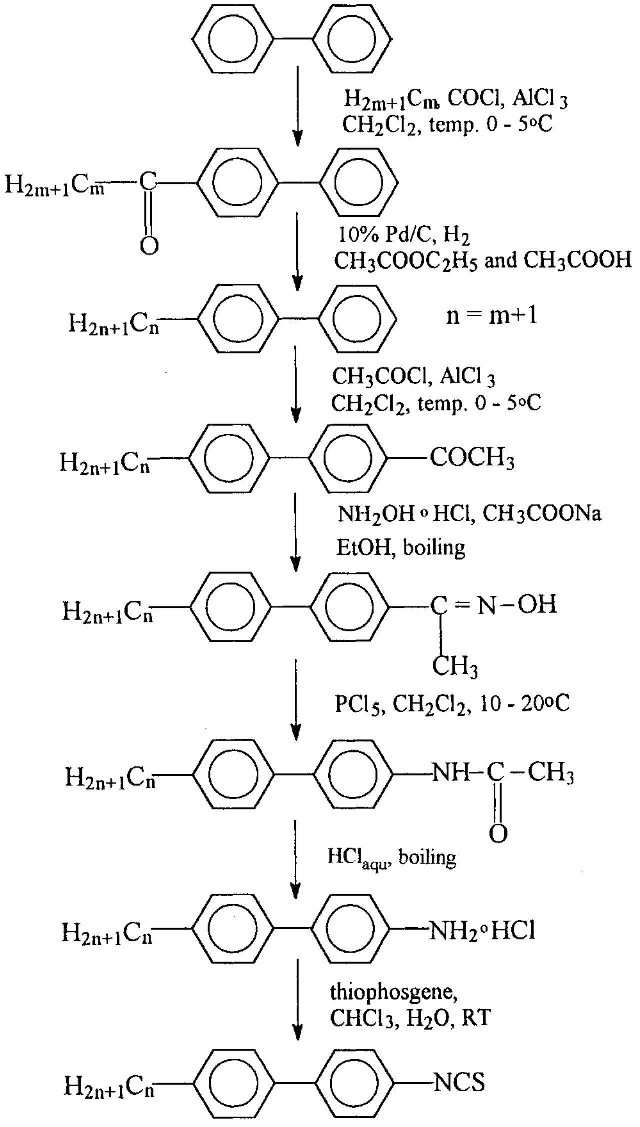
Figure 2. Phase transition points in the *n*BT homologous series.

previously: $n=5$ by van der Veen [9], $n=5$–7 by Dąbrowski *et al.* [10], and $n=5$ and 7 by Hird *et al.* [11]. Now the synthesis has been improved. The preparative route is shown in the scheme, and the phase transition temperatures and enthalpies of the carefully purified substances for n = 2–10 are gathered in the table.

Table. Phase transition temperatures (°C) and the enthalpies of the transitions (italics, kJ mol^{-1}) for the *n*BT homologous series.

n	CrI		Cr		E		I
2			*	56.3 *7.10*	*	84.1 *11.72*	*
3			*	31.7 *9.16*	*	88.2 *14.77*	*
4			*	[a]	*	82.2 *11.17*	*
5			*	53.1 *11.6*	*	73.6 *10.84*	*
6	*	10.4	*	33.9 *11.21*	*	73.8 *11.21*	*
7			*	57.8 *14.81*	*	72.4 *7.70*	*
8			*	30.4 *18.40*	*	69.4 *10.13*	*
9			*	50.2 *31.55*	*	67.2 *10.28*	*
10			*	32.2 *27.48*	*	64.9 *10.04*	*

[a] The compound did not crystallize even when kept for a long time at low temperature.



Scheme. Route for the synthesis of 4-alkyl-4′-isothiocyanatobiphenyls.

The measurements of the complex dielectric permittivity, $\varepsilon^*(\nu)=\varepsilon'(\nu)-i\varepsilon''(\nu)$, have been carried out in three laboratories. In the frequency range 100 Hz–13 MHz (HP4192A impedance analyser) the *n*BT substances with $4 \leqslant n \leqslant 10$ were studied in the temperature range 100–25°C in Kraków. A parallel-plate capacitor ($C_0 \approx 50$ pF) was calibrated with the use of standard liquids. Corrections to the capacitor constants due to increase in temperature were introduced. The measurements were carried out only on cooling the samples. During collection of the spectra the temperature was stabilised within ±0.1 K. These measurements gave the static permittivity values in the I phase for all the substances and the low frequency relaxation times for *n*BTs with $n \geqslant 4$ in the E phase. The relaxation process in the E phase of the two shortest compounds, 2BT and 3BT, was studied in Halle with the aid of a Solatron Schlumberger analyser in combination with a Chelsea Interface (0.1–10^7 Hz). A double plate capacitor (2 cm^2) with a distance between electrodes of 0.2 mm was used. The temperature was stabilized by Eurotherm equipment. The relaxation process in the isotropic phase of all nine substances was studied with the aid of a time domain spectrometer (TDS) in Uppsala. The details of the TDS set-up can be found elsewhere [12].

3. Results

Figure 3 presents the temperature dependence of the static permittivity, ε_s, in the isotropic phase (all substances) and in the E phase (three typical examples). At the I–E transition point ε_s drops markedly and within the E phase is remains almost constant; neither electric (up to 3500 V cm^{-1}) nor magnetic (*c.* 0.8 T) fields influenced the permittivity values.

Figure 4 presents the absorption spectra $\varepsilon''(\nu)$ collected for particular *n*BT substances in the E phase (at *c.* 7°C below the clearing point) and in the I phase (at *c.* 5°C above the clearing point). The spectra for the E phase can be described excellently by the monodomain Debye equation,

$$\frac{\varepsilon''(\omega)}{\varepsilon_o - \varepsilon_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2}$$

as shown in the figure (solid lines). In the I phase, an additional relaxation process could be observed at high frequencies which would reflect the fast reorientation motions of the molecules around the long axis (this was more pronounced for the longer homologous). However, we analysed the vicinity of the maximum loss only, which gave us the relaxation times characterizing the molecular motions around the short axes: $\tau_{is} = 1/(2\pi\nu_{max})$. The relaxation times calculated for both phases are presented in figure 5 in the form of Arrhenius plots. The slopes give the activation enthalpy, $\Delta H = R(\partial \ln \tau/\partial T^{-1})$, hindering the molecular motions around the short axes.

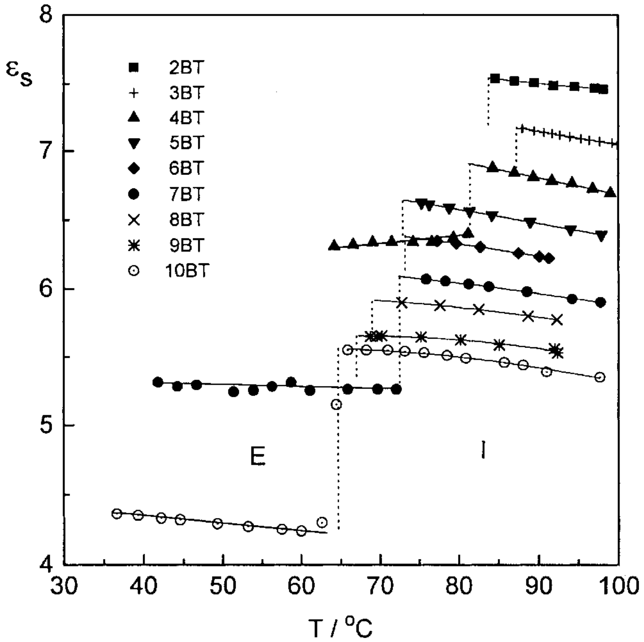


Figure 3. Static permittivity versus temperature in the isotropic (I) and E phases of the *n*BT series. To preserve clarity, the characteristic behaviour of ε_s in only three of the E phases is shown. Vertical dotted lines mark the clearing points.

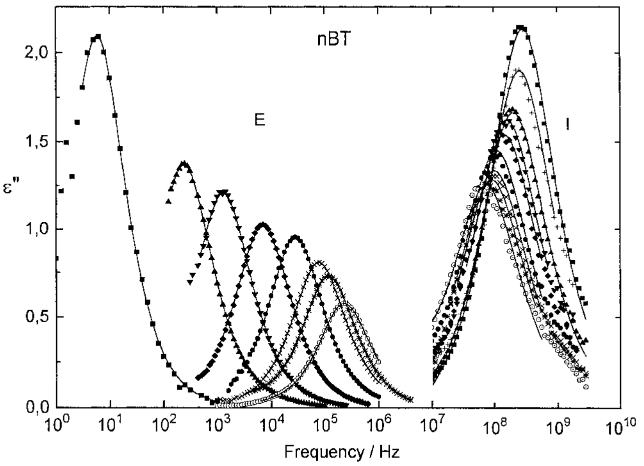


Figure 4. Absorption spectra collected for the *b*BTs in the E and isotropic (I) phases. The lines are fits of the imaginary part of the Debye equation. The symbols mean the same as in figure 3.

4. Discussion

In the isotropic phase of polar substances, the static permittivity is mainly determined by the factor μ^2/T, where μ corresponds to the total dipole moment of the molecules. In the case of the substances shown in figure 1, the dipole moments are determined by the strongly polar –CN ($\mu \approx 4.7$ D [13]) or –NCS ($\mu \approx 3.5$ D [14]) terminal groups. Their directions are slightly inclined from the *para*-axis of the benzene ring due to conformational motions of the alkyl tails and/or bending of the cyclohexyl ring [2, 4, 7]. Figure 6 presents the plots of the static permittivity ε_{is} extrapolated to the clearing point vs. *n* for five homologous series. Accordingly, the cyano compounds, *n*CB and *n*PCH, have considerably larger permittivities than the corresponding isothiocyanato analogues, *n*BT and *n*CHBT. However, larger permittivities are observed for the substances having two benzene rings. In the case of *n*DBTs the polar dioxan ring introduces an additional dipole moment [4] which results in an increase of the permittivity above the values observed for the other –NCS– compounds.

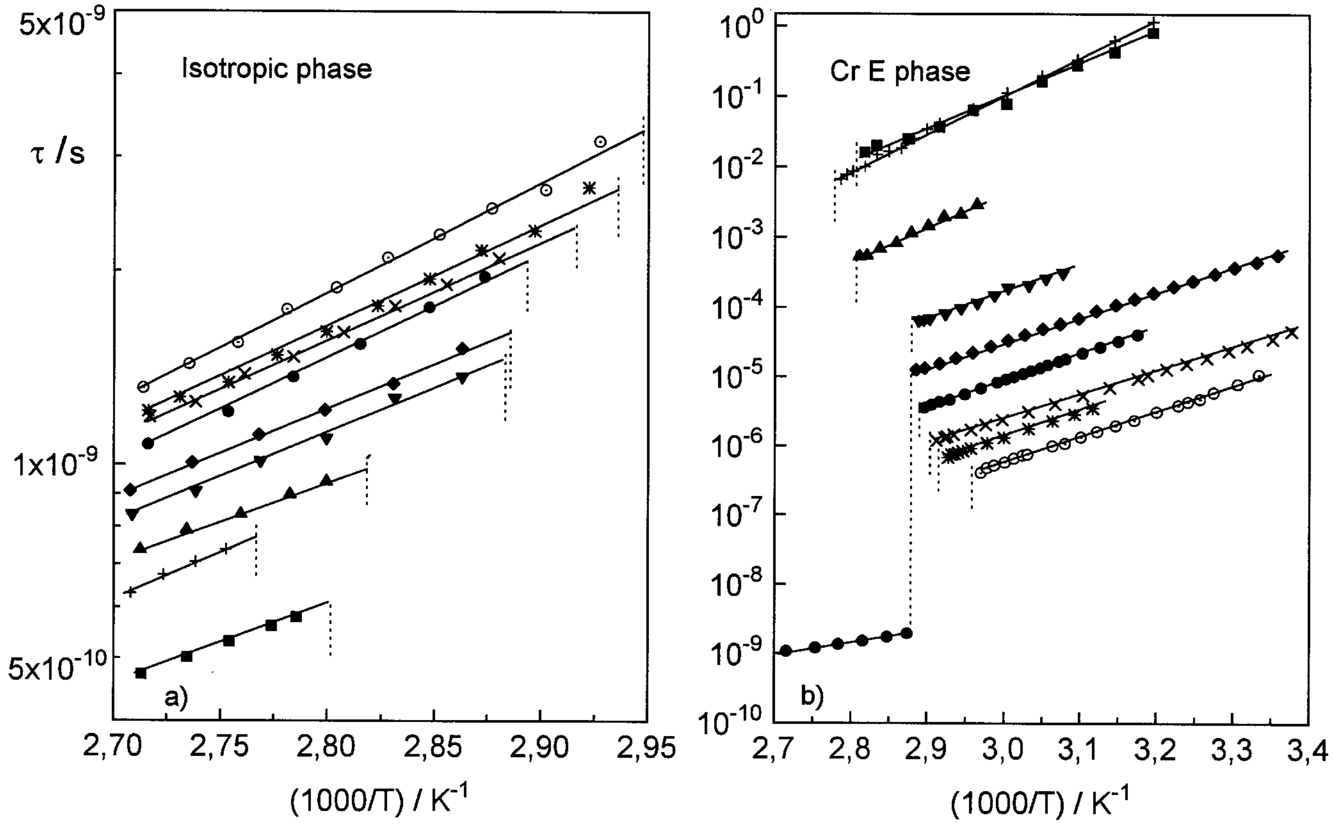


Figure 5. Arrhenius plots for the I (*a*) and E (*b*) phases of the *n*TBs. In (*b*) results for 7BT in the isotropic phase are shown in order to point out the difference in the scale of the τ-axes. The vertical dotted lines indicate the clearing points. The symbols mean the same as in figure 3.

The large dielectric increments $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ observed for all *n*BT substances in the I and E phases indicate that the corresponding relaxation process must be connected with large dipole moments, and thus with molecular reorientations around the short axes. Undoubtedly, the molecules arranged in the pseudo-crystal structure of the E phase have enough room for such voluminous motions which are typical for liquid-like phases (N, SmA, SmC). However, the motion under consideration is much more retarded on passing through the clearing point I–E in comparison with other I–liquid-like LC phase transitions. This is well characterized by the retardation factor $g = \tau_{LC}/\tau_{Is}$ displayed in figure 7 for the five homologous series (note the logarithmic scale of the *g*-axis). In the case of the I–N transition $g \approx 3$–5, for the I–SmA transition $g \approx 6$–19, whereas for the I–E transition it is 112 for 10BT and rapidly increases with *shortening* of the molecules up to *c.* 10^8.

Figure 8 presents the values of the activation enthalpy calculated from the slopes of the lines fitted to the relaxation times (figure 5). They are compared with the ΔH values obtained for other homologous series [4, 7]. In the I phase ΔH for the *n*BTs is the smallest in relation to the other series and slightly diminishes with decrease in the alkyl chain length. Rather unexpectedly, in the E phase the ΔH values calculated for $n \geqslant 5$ do not differ strongly from those obtained for other series in the N phase! Only for the short members of the series does the activation enthalpy increase considerably. In contrast, the ΔH values for the SmA phase of the *n*DBTs are markedly less than those obtained for other phases, a behaviour which is typical for this orthogonal phase (e.g. [15, 16]).

Other dielectric studies of the E phase have concerned substances in which this phase is separated from the isotropic phase by several other LC phases [17–24]. Apart from [22], dealing only with the high frequency relaxation process connected with molecular rotations around the long axis, the other studies revealed additionally the l.f. process which was found to be of the Debye-type. In the case of the three ring 4-*n*-alkoxybenzylideneamino-4′-cyanobiphenyls, an activation barrier

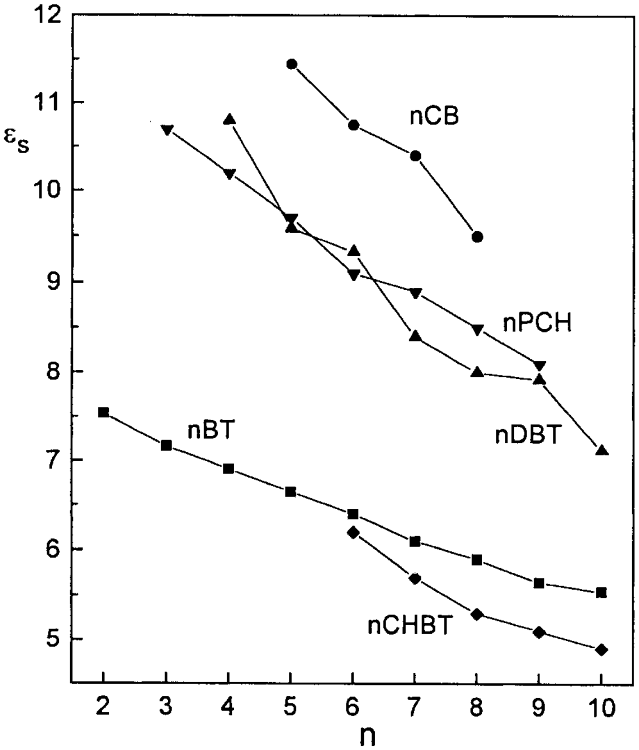


Figure 6. Static permittivity at the clearing point versus n in the isotropic phase of several alkyl two-ring homologous series with the −CN and −NCS terminal groups.

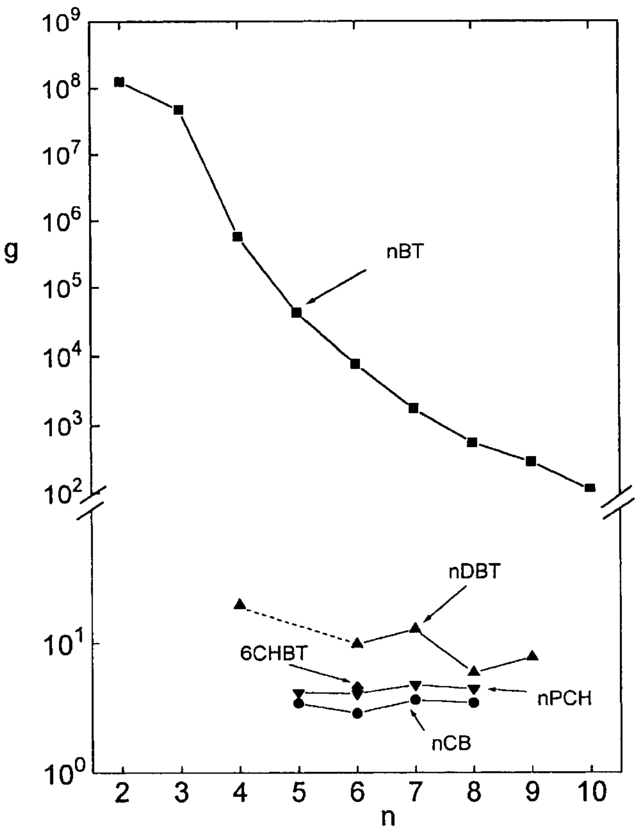


Figure 7. Retardation factor $g = \tau_{LC}/\tau_{Is}$ versus n for several alkyl two-ring homologous series (N–I for *n*CB, *n*PCH and 6CHBT, SmA–I for *n*DBT and E–I for *n*BT).

between 80 and 130 kJ mol^{-1} was found [18, 19]. Kresse and Gajewska [19] used the retardation of the relaxation time characterizing molecular rotations around the short axes to distinguish between solid-like and liquid-like LC phases. Steps in τ of one decade were found at the transition into a solid-like modification. There are practically no changes in the dielectric increment indicating that the nature of the process did not change at phase transitions up to E. Schacht *et al.* [23] have studied two isomeric compounds, 4-undecyloxy-4′-carboxyethyl-*trans*-stilbene and 4-dodecyloxy-4′-carboxymethyl-*trans*-stilbene, exhibiting SmA, B and E polymorphism. A distinct jump in the relaxation frequency by approximately one order of magnitude occurs at the first order E to B phase transition. Nevertheless, the activation enthalpy in both these solid-like phases is approximately the same (~74 kJ mol^{-1}) and becomes slightly lower in the SmA phase. However, there is a temperature dependence of the activation energy within the E phase of the methyl derivative, which was assigned to a slight change in the axis for reorientation due to inequivalency of the *a* and *b* periods in the biaxial E phase.

5. Conclusions

Dielectric relaxation studies of nine members of the 4-*n*-alkyl-4′-thiocyanatobiphenyl homologous series in the isotropic and E phases allow us to point out the following. (i) The relaxation process observed is caused by molecular rotations around the short axes; this low frequency relaxation process was observed for other smectic phases, including solid-like phases (B, G, SmF) [17–24]. (ii) The motion is much more retarded at the I–E phase transition than at isotropic–liquid-like LC phase transitions. (iii) The retardation factor increases considerably with decrease in the alkyl chain length which indicates the importance of conformational motions of the tails in creation of the rotational freedom of the molecules in this crystal-like phase. (iv) The above comment is additionally supported by a considerable increase of the activation barrier for the shortest homologues in the E phase.

Undoubtedly, the molecular motions around the short axes depend significantly on molecular packing and the structure of the mesophase. The rotational freedom in the crystal-like E phase depends also on the conformational motions of the alkyl chains; a shortening of

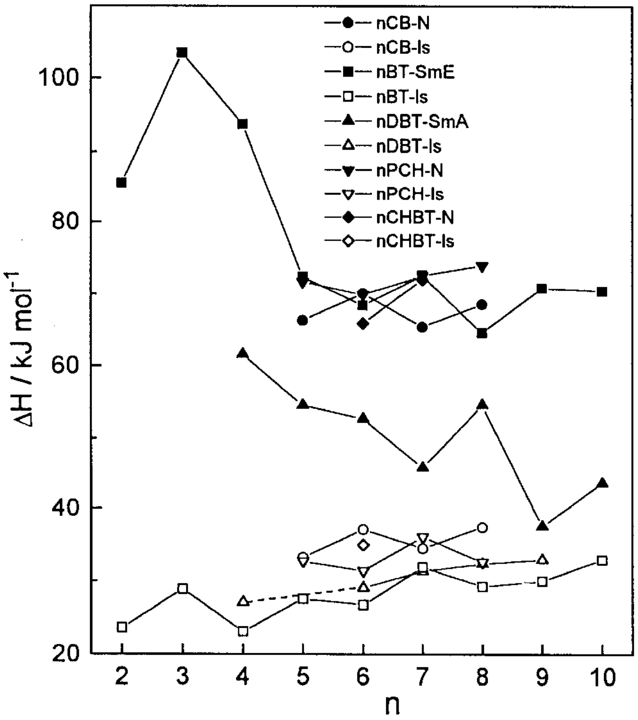


Figure 8. Activation enthalpy versus n in the isotropic (open symbols) and LC phases (full symbols) for several homologous series.

the chain below $n = 5$ results in a hardening of the quasi-crystal and consequently a considerable increase in the barrier for the rotation is observed. This corresponds well with the conclusion reached by Rzoska *et al.* [25, 26] on the basis of results from studies of the non-linear dielectric effect in the *n*BT series: increase in the length of the alkyl chain may decrease the degree of order in the E phase.

Similarly to other authors [20, 23], we can conclude that the reorientation of the molecules around the short axes is a cooperative process. This means that neighbouring molecules must make the room necessary for the flip-flop rotational jump of a given molecule. By analogy with the rotation-translation coupling model developed for the ODIC phases [27] one can suppose that this happens due to density fluctuations within the smectic layers. More ordering of the molecules in the layers reduces the frequency of the jumps. The fact that Δ*H* values for the l.f. process are similar in different LC phases seems to indicate that the barrier is determined mainly by the anisotropy of the molecular interactions, dependent upon the molecular shapes and dimensions.

References

[1] Dąbrowski, R., Dziaduszek, J., and Szczuciński, T., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102,** 155.

[2] Baran, J. W., Raszewski, Z., Dąbrowski, R., Kędzierski, J., and Rutkowska, J., 1985, *Mol. Cryst. liq. Cryst.*, **123,** 237.

[3] Dąbrowski, R., Ważyńska, B., and Sosnowska, B., 1986, *Liq. Cryst.*, **1,** 415.

[4] Urban, S., Gestblom, B., and Bąbrowski, R., 1998, *Liq. Cryst.*, **24,** 681.

[5] Dąbrowski, R., Dziaduszek, J., and Szczuciński, T., 1985, *Mol. Cryst. liq. Cryst.*, **124,** 241.

[6] Demus, D., 1994, in *Liquid Crystals*, edited by H. Stegemeyer (Darmstadt, Steinkopf Verlag), p. 1.

[7] Urban, S., Gestblom, B., and Würflinger, A., 1999, *Mol. Cryst. liq. Cryst.*, **331,** 113.

[8] Urban, S., Dąbrowski, R., Dziaduszek, J., Janik, J., and Mościcki, J. M., 1999, *Liq. Cryst.*, **26,** 1817.

[9] Van der Veen, J., 1976, *J. Phys. (Paris)*, **37,** 13.

[10] Dąbrowski, R., Dziaduszek, J., and Szczuciński, T., 1984, *Bull. WAT,* **33,** (9), 33 (in Polish); Dąbrowski, R., Dziaduszek, J., and Szczuciński, T., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102,** 105.

[11] Hird, M., Seed, A. J., Toyne, K. J., Goodby, J. W., Gray, G. W., and McDonnell, D. G., 1993, *J. mater. Chem.*, **3,** 851.

[12] Urban, S., Gestblom, B., and Dąbrowski, R., 1999, *Phys. Chem. chem. Phys.*, **1,** 4843.

[13] Kędziora, P., and Jadżyn, J., 1990, *Liq. Cryst.*, **8,** 445.

[14] Kędziora, P., and Jadżyn, J., 1990, *Acta Phys. Polon.*, **A77,** 605.

[15] Urban, S., Novotna, E., Kresse, H., and Dąbrowski, R., 1995, *Mol. Cryst. liq. Cryst.*, **262,** 257.

[16] Markwick, P., Urban, S., and Würflinger, A., 1999, *Z. Naturforsch.*, **54a,** 275.

[17] Kresse, H., and Gajewska, B., 1981, *Phys. Status Solidi*, **A67,** K21.

[18] Gajewska, B., Kresse, H., and Weissflog, W., 1982, *Cryst. Res. Technol.*, **17,** 897.

[19] Kresse, H., and Gajewska, B., 1983, *Cryst. Res. Technol.*, **18,** 281.

[20] Kresse, H., 1983, *Adv. Liq. Cryst.*, **6,** 109.

[21] Buka, A., Bata, L., Pinter, K., and Szabon, J., 1982, *Mol. Cryst. liq. Cryst. Lett.*, **72,** 285.

[22] Druon, C., and Wacrenier, J. M., 1984, *J. Physique Lett.*, **45,** L169.

[23] Schacht, J., Buivydas, M., Gouda, F., Komitov, L., Stebler, S., Lagerwall, S. T., Zugenmaier, P., and Horii, F., 1999, *Liq. Cryst.*, **26,** 835.

[24] Kresse, H., Selbmann, Ch., Demus, D., Buka, A., and Bata, L., 1981, *Cryst. Res. Technol.*, **16,** 1439.

[25] Hensel-Bielòwka, S., Rzoska, S. J., Drozd-Rzoska, A., Burian, W., Czachor, M., Zioło, J., and Czupryński, K., 2000, *J. Phys. Condens. Matter*, **12,** 1677.

[26] Drozd-Rzoska, A., Rzoska, S. J., and Czupryński, K., 2000, *Phys. Rev. E*, **61,** 5355.

[27] Michel, K. H., and Naudts, J., 1977, *J. chem. Phys.*, **67,** 547; Michel, K. H., and Naudts, J., 1987, *J. chem. Phys.*, **68,** 216.