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Stanislaw Urban; Roman Dabrowski; Jerzy Dziaduszek; Joanna Janik; Jozef K. Moscicki

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Phase transition and dielectric studies of a three-ring homologous series with the –NCS terminal group

STANISŁAW URBAN*, ROMAN DĄBROWSKI†, JERZY DZIADUSZEK†,
JOANNA JANIK, and JÓZEF K. MOŚCICKI

Institute of Physics of the Jagiellonian University, Reymonta 4, 30-059 Cracow,
Poland
†Institute of Chemistry, Military University of Technology, 01-489 Warsaw,
Poland

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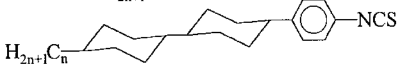
The synthesis route and phase properties for a new three-ring homologous series, 4-(*trans*,*trans*-4-alkylbicyclohexyl)benzene-isothiocyanates (*n*CCHBT) with $n = 2$–7, are presented. The substances exhibit very broad range nematic phases exceeding 200 K, and low viscosity with a low activation enthalpy. The dielectric properties of the *n*CCHBT materials are compared with those of their long known two-ring analogues (*n*CHBT). The static permittivity, $\varepsilon_{s\parallel}$ is considerably lower for the three-ring compounds. It is found that $\varepsilon_{s\parallel}$ decreases with n at temperatures as low as $T_r = T/T_{NI} = 0.7$. The relaxation time, $\tau_\parallel$ shows the odd–even effect, the amplitude of which reverses on going from $T_r = 0.7$ to 1. The activation enthalpy for molecular rotation about the short axis alternates with n practically in the same manner for the corresponding members of both homologous series. It is argued that the present results are at odds with models assuming that the activation enthalpy consists of the viscosity and nematic potential components.

1. Introduction

Technical applications of liquid crystals (LCs) stimulate the search for new classes of compounds having predetermined physical properties. The temperature range of existence of a given LC phase, the dielectric and optical anisotropy, the elastic constants, as well as a low viscosity are very important factors in this respect. Many homologous series with the isothiocyanato (–NCS) terminal group demonstrate such favourable properties. They were synthesized in the Institute of Chemistry, Military University of Technology, Warsaw [1–4] and studied in the past by different research groups, e.g. [5–9]. In this paper we present results of dielectric studies of two classes of very low viscosity materials: (**1**) the 4-(*trans*-4-alkylcyclohexyl)benzene-isothiocyanates (*n*CHBT), and (**2**) the 4-(*trans*,*trans*-4-alkylbicyclohexyl)-benzene-isothiocyanates (*n*CCHBT). The members with $n = 2$–12 of series *n*CHBT were synthesized many years ago [1, 2] while members of series *n*CCHBT with $n = 2$–7 were prepared by us recently.

1



2

The *n*CCHBTs give very broad temperature ranges (nearly 200 K) of the nematic phase (N), see figure 1 and table 1. On the other hand, the N phase of the *n*CHBT

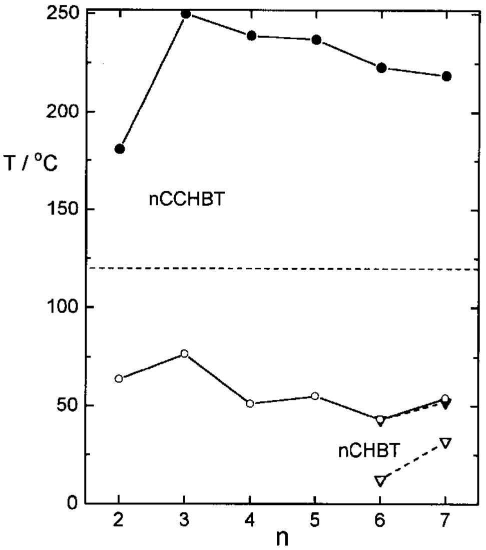


Figure 1. The phase transition points for the *n*CCHBT (circles) and *n*CHBT (triangles) homologous series: full points—clearing, T_{NI}; open points—melting, T_{Cr}. The horizontal dashed line indicates the upper limit of temperature accessible for the physical studies.

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

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Table 1. Phase transition temperatures (°C) (upper line) and *enthalpies* (kJ mol^{-1}) (lower line) for the compounds **2**, from DSC measurements.

	Heating							Cooling	
n	Cr_1		Cr		N		I	Temp. of crystallization	Purity
2	•	45[a]	•	66	•	190	•	30	B[b]
3			•	76.5	•	248.7	•	65.5[c] → 32.7	99.6
				10.45		*1.46*		*7.15* *1.67*	
4			•	49.1	•	239.4	•	21.1[c] → 12.5	99.6
				22.57		*1.67*		*5.43* *7.10*	
5	•	38.4	•	55.5	•	2.37	•	49.6[d] →	98.5
		12.5		*10.45*		*1.46*		*9.99*	
6			•	42.2	•	223.1	•	26.2[c] → 20.0	98.4
				26.33		*1.3*		*7.1* *16.3*	
7			•	54.9	•	217.8	•	52.0[c] → 23.5	99.3
				33.86		*1.67*		*12.96* *15.0*	

[a] Compound contains a small percentage of *cis*-isomer; this temperature is the melting point of the eutectic mixture of *cis*- and *trans*-isomers.

[b] B: *cis*- and *trans*-isomers are not separated by crystallization or during chromatographic analysis (capillary column HP; 5, 25 m lengths and 0.32 mm diameter), so the concentration of the *cis*-isomer is not known exactly.

[c] Unstable form.

[d] Transformation to the second polymorphic form after 3 h.

series exists in the vicinity of room temperature (figure 1, [1, 2]). Since molecules of both series differ only by the presence of an additional cyclohexyl ring in series *n*CCHBT, it seems interesting to compare their dielectric behaviour.

Because the clearing points of the *n*CCHBTs are rather high (figure 1) our dielectric studies had to be limited to the lower temperature range of N (below *c.* 120°C). In spite of this, some general observations can be made which seem to be applicable to the whole range of the phase.

2. Experimental

2.1. *Synthesis*

The preparative route for the CCHBTs is shown in figure 2. The bicyclohexylbenzene core was formed in stages a–d. The condensation of the Mannich salt with ethyl 2-alkylacetoacetate gave the cyclohexenone ring (step b), which was reduced first to the cyclohexanone ring (step c) and then to the cyclohexane ring. These procedures derive from our previous work [12]. The ratio of *trans*- to *cis*-isomers is increased after acetylation (step c). Therefore it was not necessary to separate the *trans*-isomer earlier than after step e. Pure 4-(*trans*-4-alkylcyclohexyl)-acetophenone was separated by crystallization for members with alkyl chains containing 3–7 carbon atoms, but not for $n = 2$. Since the acetophenone with $n = 2$ contained *cis*-isomer, the final product 2CCHBT was contaminated by it and this was not removable by crystallization. The preparative procedures for stages e–g were the same as those used for the CHBT series [2]. The purity of the compounds was tested by gas chromatography—(Hewlett-Packard 5890) with flame ionization and mass selective detector.

2.2. *Phase transition temperatures and enthalpies*

The transition temperatures and enthalpies of the compounds **2** were measured using a differential scanning calorimeter (DSC) SETARAM'92. The heating and cooling rate was 2°C min^{-1}. The phases were identified using a polarizing optical microscope (Biolar-PZO) equipped with a Linkam heating system.

2.3. *Viscosity studies*

A single compound of the *n*CCHBT series was dissolved (20 wt %) in a eutectic three component mixture of *n*CHBTs (mixture A: propyl, hexyl and octyl members in the weight ratio 40 : 42 : 18). Then the kinematic viscosity was measured by the capillary method in the temperature range from − 20°C to 50°C.

2.4. *Dielectric studies*

The measurements of the complex dielectric permittivity, $\varepsilon^*(\nu) = \varepsilon'(\nu) - \varepsilon''(\nu)$, were made in the frequency range ν from 0.1 kHz to 13 MHz using a HP 4192A impedance analyser. A parallel-plate capacitor of geometric capacitance $C_0 \approx 50$ pF and having a distance between the electrodes of 0.12 mm was calibrated with standard liquids. Due to the presence in the *n*CCHBT molecule of two cyclohexyl rings having a negative magnetic susceptibility [13], the accessible magnetic field ($\mathbf{B} = 0.8$ T) was not enough to

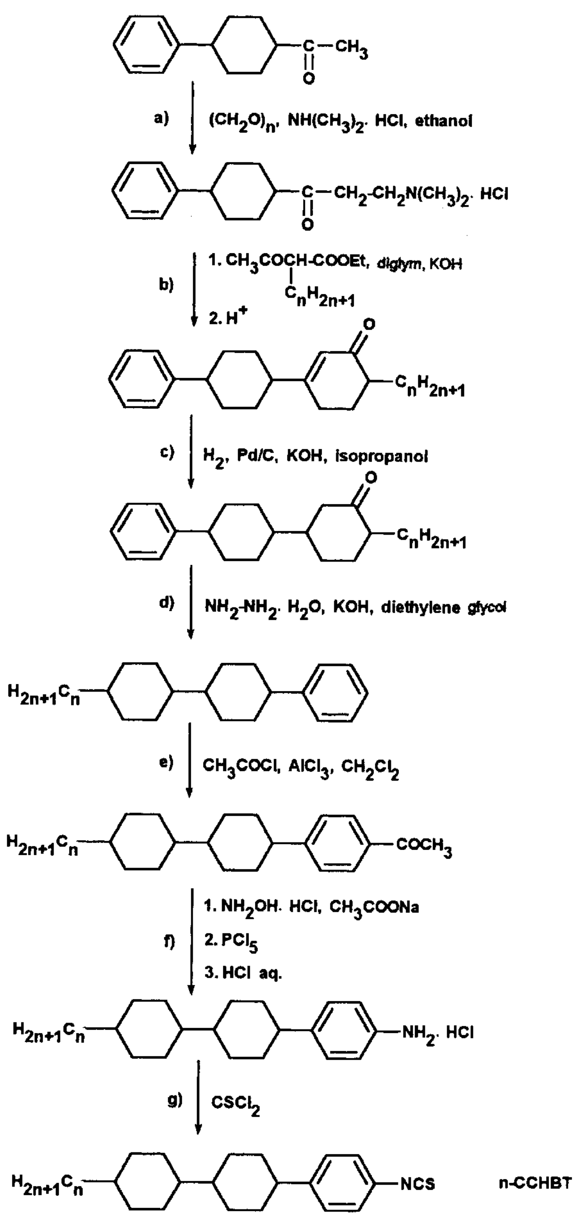

Figure 2. Route for the synthesis of members of homologous series *n*CCHBT.

achieve orientation saturation. This was possible for the *n*CHBTs, however. Therefore, we oriented our samples by using a d.c. electric field for which saturation was observed for **E** values larger than *c.* 1500 V cm^{-1}. The very high purity of the samples studied ensured that the dielectric spectra were free from conductivity effects down to 100 Hz. Only the parallel component of the dielectric permittivity, $\varepsilon_\parallel^*$, was measured. All measurements were carried out step by step on decreasing the temperature. In this way several samples could be supercooled considerably. The temperature stabilization was within ± 0.2°C above *c.* 90°C and ± 0.1°C below it.

3. Results

The phase transition temperatures and enthalpies of the *n*CCHBT homologous series are listed in table 1, and viscosity values for their 20 wt % solutions compared in table 2. The members $n = 2$–7 have a purity higher than 98 wt % except for $n = 2$ which is contaminated by *cis*-isomer. Their melting points are lower than the cyano or fluoro [14, 15] analogues and their clearing points are a little higher than cyano analogues [14] (about 5–10°C). In contrast to the cyano and fluoro compounds, no smectic phases are observed for any of the members investigated. The astonishingly low melting enthalpy of *c.* 10 kJ mol^{-1} is observed for the propyl homologue upon cooling, all the compounds crystallize to a metastable solid, which then transforms to another, more stable crystal form. Members with an even number of carbon atoms in the alkyl chain show a greater tendency to supercool than those with odd carbon chains. The presence of an *n*CCHBT in mixture A strongly increases its clearing point and its viscosity only a little, on increasing *n*—see table 2. The *n*CCHBTs are, therefore, convenient components for mixtures requiring low viscosity and a weak sensitivity to temperature. The viscosity activation energy is about 30 kJ mol^{-1}, values for the odd members being a little higher than for even members.

Typical dispersion and absorption spectra observed for the $n = 7$ members of both series studied are presented in figure 3. The striking feature of these plots is the very large shift of the relaxation frequency $\nu_R = 1/(2\pi\tau)$ corresponding to the maximum losses for the three-ring compound with respect to the two-ring analogue, both measured at similar temperatures. All spectra obtained are well fitted by the Debye equation

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau} \tag{1}$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and τ is the relaxation time. Figures 4 and 5 present the static permittivity $\varepsilon_{s\parallel}$ versus temperature for all the substances studied. The relaxation times $\tau_\parallel$ are shown in figure 6 in the form of activation plots. More than two orders of magnitude separate both groups of substances at comparable temperatures. The points lie nicely on straight lines (except in the vicinity of the clearing temperatures in the case of the *n*CHBTs) that can be described by the Arrhenius equation

$$\tau_\parallel = \tau_0 \exp(\Delta H_\parallel / RT) \tag{2}$$

where R is the gas constant. The values of the activation enthalpy $\Delta H_\parallel$ calculated from the slopes of the lines are presented in figure 7. The odd–even alternation typical for many properties of substances belonging to homologous series can be seen.

Table 2. Kinematic viscosity ($mm^2\ s^{-1}$) of mixtures containing 80 wt % of A and 20 wt % of *n*CCHBT at different temperatures.

		n					
Temp/°C	A	2	3	4	5	6	7
50		6.3	5.3	5.7	5.7	6.1	6.0
40	8.9	8.0	6.8	7.2	7.1	7.6	7.4
30	9.9	10.5	9.4	9.8	9.7	10.2	10.0
20	13.1	15.0	13.5	14.1	13.8	14.3	14.3
10	19.0	23.4	21.4	22.2	21.8	22.3	22.2
0	30.3	40.7	37.5	38.4	37.6	38.4	38.2
− 10	55.3	80.7	75.2	76.2	73.9	75.2	74.7
− 20	118.4	188.9	179.1	176.6	170.6	172.0	—
[a] ΔH_A/kJ mol^{-1}	31	30.6	31.7	31.1	30.8	30.3	30.5
T_{NI}/°C	41	63	76	74	74.7	73	75

[a] Calculated from the equation $\nu = \nu_0 \exp(-\Delta H_A/RT)$.

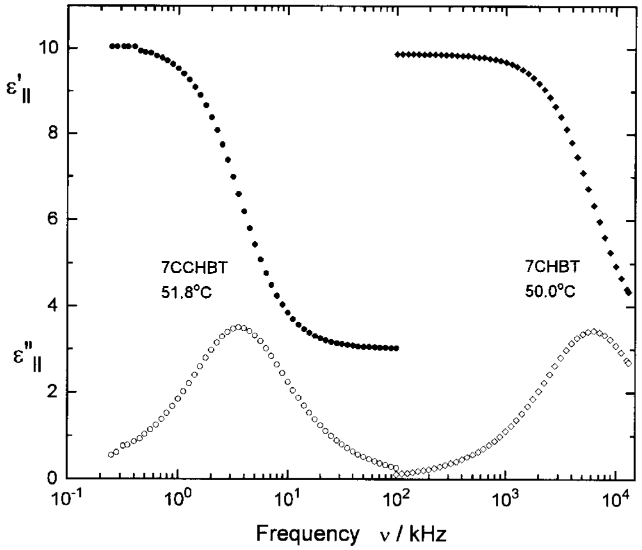

Figure 3. The dispersion (full points) and absorption (open points) spectra measured for 7CCHBT and 7CHBT.

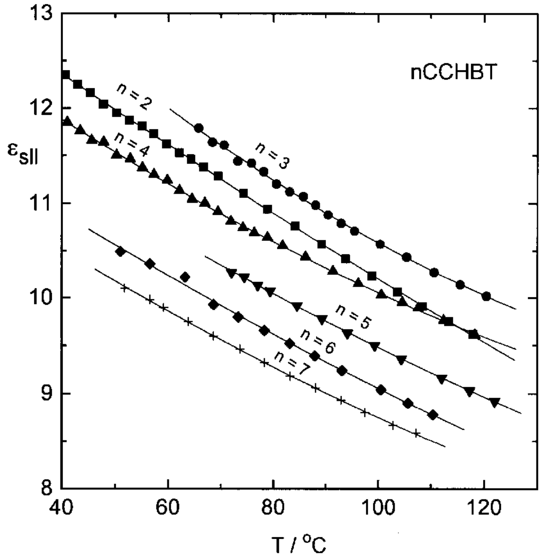

Figure 4. Static permittivity $\varepsilon_{s\parallel}$ as a function of temperature for six members of the *n*CCHBT homologous series.

4. Discussion

The physical properties of the nematic phase depend primarily on the actual value of the order parameter *S*. It is well known that *S* changes rapidly at temperatures close to the clearing point, whereas its value becomes practically constant below *c.* $T_{NI} - 40$ K [13, 16–18]. Our studies of the *n*CCHBT substances are limited to temperatures markedly lower than this value (see figure 1). Therefore it seems interesting to verify whether properties derived from the experimental data are still sensitive to temperature this far from T_{NI}.

4.1. *Static permittivity*

According to the Maier–Meier theory based upon the Onsager model of the local field adopted to the anisotropic medium [19], the parallel component of the static permittivity is given by

$$(\varepsilon_\parallel - 1) = \varepsilon_0^{-1} NFh\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu^2}{3kT}[1 - (1 - 3\cos^2\beta)S]\right\} \tag{3}$$

where ε_0 is the free space permittivity, *N* is the number density, *F* and *h* are the local field factors, $\bar{\alpha}$ and $\Delta\alpha$ are the mean polarizability and the polarizability anisotropy of the molecule, respectively, and the dipole moment μ makes an angle β with the major inertia axis of the molecule. From figure 5, one finds a strong decrease of the permittivity on approaching the clearing point in the case of the CHBTs, and a moderate decrease with

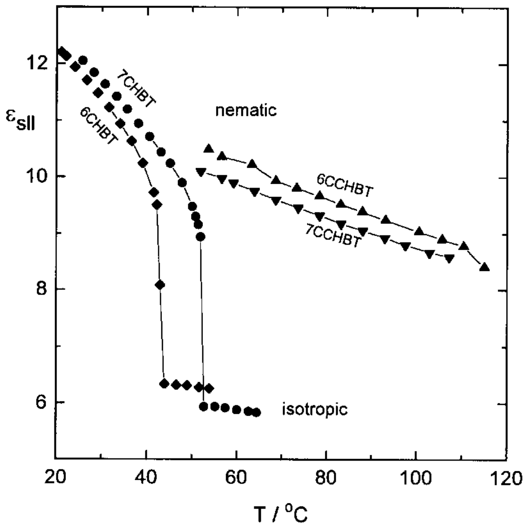

Figure 5. Static permittivity $\varepsilon_{s\parallel}$ as a function of temperature for two pairs of homologous from the *n*CCHBT and *n*CHBT series.

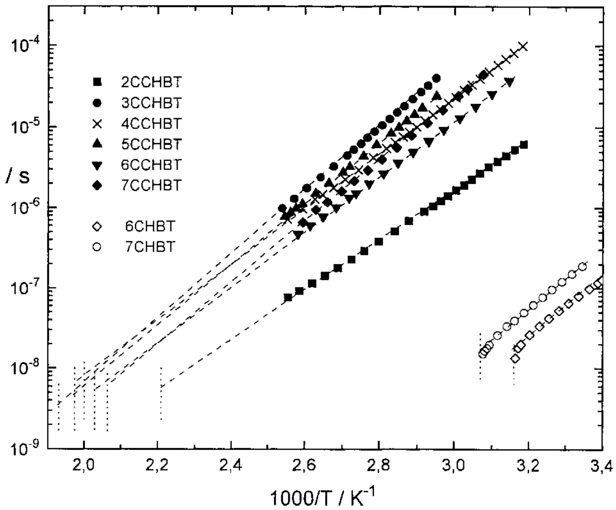

Figure 6. Activation plots for all substances studied. The vertical dotted lines mark the clearing points.

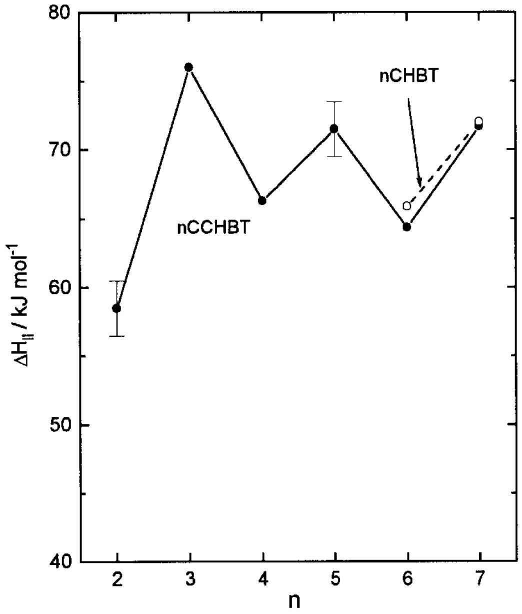

Figure 7. Activation enthalpy $\Delta H_{\parallel}$ versus the number of carbon atoms in the alkyl groups for the *n*CCHBT (full points) and *n*CHBT (open points) homologous series. The error bars are ± 3 kJ mol^{-1}.

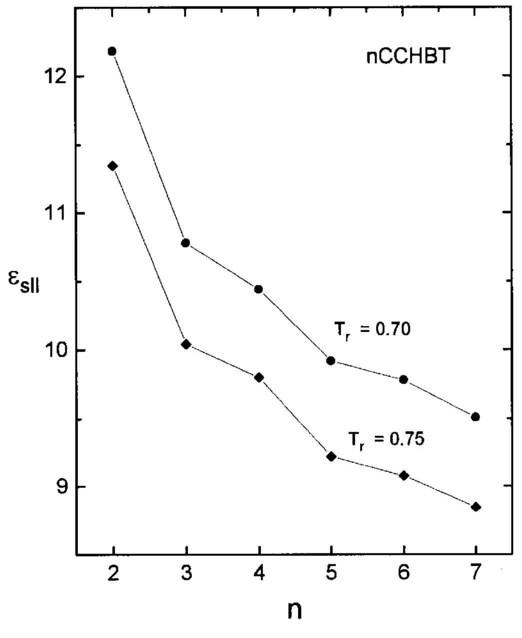

Figure 8. Static permittivity versus the number of carbon atoms in the alkyl chain of the *n*CCHBT compounds at two reduced temperatures $T_r = T/T_{\rm NI}$.

temperature for the CCHBTs having $T_{\rm NI}$ above 220°C. It follows from equation (3) that in the former case $\varepsilon_{\parallel} \propto S(T)/T$, whereas in the latter case this should rather be limited to $\varepsilon_{\parallel} \propto 1/T$ in the light of the above remarks concerning the $S(T)$ behaviour. The plots of $\varepsilon_{s\parallel}$ vs. T presented in figure 4 are roughly parallel to each other and the permittivity value increases with shortening of the alkyl chain, except for the shortest side chains. This exception correlates with a large difference between the clearing temperature of 2CCHBT and the other *n*CCHBTs (figure 1, table 1). It is instructive to compare the permittivity values at the same relative distance from $T_{\rm NI}$. Figure 8 shows a dependence of $\varepsilon_{s\parallel}$ on n at two reduced temperatures $T_r = T/T_{\rm NI}$: 0.75 and 0.70. A systematic decrease in the permittivity with lengthening of the molecules is clearly visible. A similar behaviour has already been observed for other homologous series having distinctly narrower ranges of the nematic or smectic phases, as well as for the isotropic phase [9, 20]. This is attributed to a 'solvation' of the dipole moment in the longer alkyl chains. The permittivity of the two-ring compounds is markedly larger than that of the three-ring analogues in spite of the very different temperature separation from the clearing points in both cases, see figure 5. This means that the effective dipole moments responsible for the relaxation domain are considerably larger for the shorter compounds. This can be explained as resulting from the increased flexibility of the bicyclohexyl molecule, making the molecule more bent. Consequently, the inclination of the major inertia axis of the molecule from the *para*-axis of the benzene ring is larger, and the same applies to the angle β.

4.2. *The relaxation process*

Debye-type dielectric spectra were observed everywhere in the temperature range studied for all substances. This indicates that the molecular rotation around the short axis, responsible for this process, is not accompanied by any other relaxation processes over the whole range of the nematic phase. The activation plots are straight lines except in the close vicinity of the clearing point of the *n*CHBTs, see figure 6. Taking into consideration the results of dielectric studies on other substances with a broad range of the nematic phase (e.g. [21, 22]) one can suppose that a similar behaviour would be observed for the *n*CCHBTs as well. We therefore extrapolated the Arrhenius plots up to the clearing temperature. Surprisingly, the relaxation times at T_{NI} for the *n*CCHBT compounds become visibly shorter than those obtained for the two-ring analogues (see figure 9; compare the same symbols corresponding to the reduced temperature $T_r = 1.00$, 0.95 and 0.90 and note the logarithmic scale in the abscissa axis). Notably, the odd–even alternation of $\tau_{\|}$ observed for the *n*CCHBTs becomes inverted at low temperatures with respect to the situation observed at T_{NI}.

The small curvature of the activation plots observed for the *n*CHBT compounds close to T_{NI} can be attributed to a rapid change in the nematic potential q assumed to be proportional to the order parameter S [23–25]. It is commonly assumed [25–27] that the activation enthalpy $\Delta H_{\|}$ consists of two parts: $\Delta H_{\|} = W_{\eta} + q$, where W_{η} accounts for viscosity effects. It has been proved experimentally [9, 24, 28] that $q \propto S$, so its value increases when the temperature is lowered. Because $\Delta H_{\|} =$ constant, this means that W_{η} is a decreasing function of temperature! This physically doubtful conclusion indicates a necessity for revision of the above model to take account of other factors determining the activation barrier hindering molecular rotations around the short axes. This is additionally clear on considering the fact that the two- and three-ring compounds have the same activation enthalpies (figure 7).

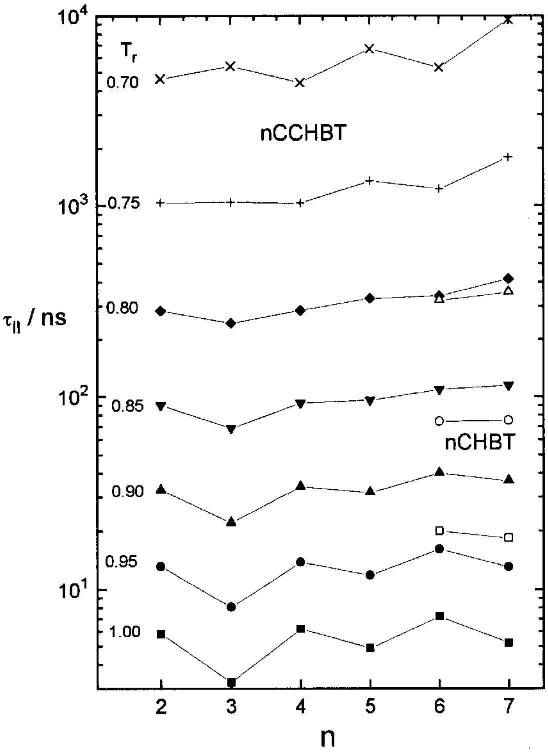

Figure 9. Relaxation times versus the number of carbon atoms in the alkyl chain of the *n*CCHBT series and *n*CHBT series (open symbols) taken at several reduced temperatures T_r.

5. Conclusions

The recently synthesized homologous series of *n*CCHBTs exhibits very broad temperature ranges of the nematic phase exceeding 200 K. The materials have low viscosity and low activation energy for this process, high purity and high thermal stability. For this reason the substances are convenient components of mixtures for display technology. Dielectric studies have shown that the static permittivity of the three-ring compounds (CCHBT) is considerably lower than that measured for two-ring analogues (CHBT). In spite of the fact that measurements had to be made far from the clearing point, the permittivity still seems to be sensitive to the value of T_{NI} due probably to its dependence on the order paramater S. The dielectric relaxation spectra $\varepsilon^*_{\|}(\nu)$ of the CCHBTs are of the Debye-type, even 200 K below the clearing point. The relaxation time $\tau_{\|}$ shows odd–even alternation at the clearing point as well as close to the freezing point, although it becomes inverted. Astonishingly the activation enthalpies for the same members of both homologous series are practically the same. It is argued that models assuming that the activation enthalpy consists simply of viscosity and nematic potential parts should be revised in the light of the results obtained.

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