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Influence of temperature and terminal chain length on helical pitch in homologue series *n*H6Bi

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The homologous series of three ring chiral esters with terminal chains, one 1-methylheptyl group and, one alkanoyloxyhexyloxy group, were studied. Compounds of these series are liquid crystals with smectic phases, that is, SmA, SmC* (ferroelectric phase) and SmC*_A (antiferroelectric phase). The helical pitch was measured by a spectrophotometric method of selectively reflected light. It was found that the helical pitch increases and then decreases with temperature in the SmC*_A phase for most homologues and in the SmC* phase for one homologue. The temperature characteristics of the helical pitch are related to the change in handedness of the helix.

Keywords: liquids crystals; ferroelectric phase; antiferroelectric phase; helical pitch; helical twist sense

1. Introduction

Different authors have shown that the temperature dependence of helical pitch in the ferroelectric and antiferroelectric phases is different for different materials. For example, many authors have presented results showing that the helical pitch of the antiferroelectric phase is stable with change of temperature [1, 2]. However, Li *et al.* [3] have shown that the helical pitch in the antiferroelectric phase can increase with temperature or increase and then decrease, or increase and then decrease with a discontinuity in between, depending on the material.

In the smectic SmC^* phase the helical pitch usually does not change with temperature [1, 2, 4]. Sometimes a decrease in the value of helical pitch is observed before transition to the SmA phase [5, 6].

It has already been proven that the helical structures of the SmC^{*} and SmC^{*}_A phases in the same substance have opposite handedness [1, 4, 7, 8]. Lagerwall *et al.* [9] have given a theoretical explanation for the fact that helix twisting sense reverses at this transition.

Results of helical pitch measurements can also be found in the literature showing that the sign of the helix changes in crossing transitions from SmC^{*} to SmC^{*} γ or from SmC^{*} γ to SmC^{*}_A [10, 11].

The change of helix handedness is not only observed between different phases but also within a phase. For example, it was found that the helix changes the twist sense within the SmC*_{β} phase [11] or the SmC* phase [12]. The same is also observed in the SmC*_A phase. The temperature dependence of selectively reflected light measured for MHPOBC in the antiferroelectric phase shows an increase and then a decrease of the selected band with a decrease in

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temperature [3], and it was proven that this is due to the change in handedness of the helix [10].

In this work we have determined the value of helical pitch and twist sense of compounds belonging to the homologous series nH6Bi [13]. These compounds are used in antiferroelectric multicomponent mixtures with high contrast [14]. The objectives of this work were to study the influence of temperature and length of terminal chain on the value of helical pitch in these compounds with special attention paid to the type of investigated phases. The increase and following decrease of helical pitch connected with a change of helix handedness in the SmC*_A and SmC* phases is reported. These basic studies show also that the helical pitch changes with temperature may be similar in the ferro- and antiferroelectric phases.

2. Experimental details

The structure and phase sequences [13] of the compounds of the homologous series nH6Bi studied here are shown in Scheme 1.

The textures were analysed with the use of a polarising optical microscope (POM) Olympus BX51. The microscopic glass plates used for the investigation were both untreated as well as covered with a surfactant, cetyl trimethylammonium bromide (CTAB) ensuring homeotropic alignment.

The helical pitch measurements were made based on the selective light reflection phenomenon. The measurements of light transmission were carried out on a Shimadzu UV-VIS-NIR spectrometer in the range 360–3000 nm. The tested compounds were placed on a glass plate with a CTAB layer without covering with



Scheme 1. The structure and phase sequences of the homologous series nH6Bi used in this work.

another glass plate. A MLW U7 controller of temperature with Peltier elements was used for changing the temperature; the temperature range of measurement was $5-105^{\circ}$ C. The temperature accuracy was 0.1° C. The presented results were obtained during the cooling cycle.

The results are presented as the wavelength of selectively reflected light λ_s versus temperature in all the figures. In order to obtain values for helical pitch, the values of λ_s should be divided by the double refractive index for the SmC* phase or by the refractive index for the SmC*_A phase (the value of the average refractive index for this class of materials is about 1.5 [15]).

The helical twist sense for chiral phases was determined by two methods. The first method was by comparison with a material of known twist sense in a contact preparation. Contact samples were prepared on microscopic glass plates coated with CTAB. The second method was based on a polarimetry technique for chiral compounds. The homeotropically aligned sample was viewed in transmission between crossed polarisers and the top polariser was rotated relative to the bottom one. The analysis of transmitted light was made under POM as well as more precisely in the spectrophotometer for a wavelength lower than λ_s to ensure that the same branch of optical rotation was viewed. According to the convention described in Shtykov and Vij [16], a clockwise rotation of the analyser in order to produce a darker state or minimum transmission when observation is made towards the incoming beam, indicates a dextro or left-handed helix and anticlockwise rotation indicates a laevo or right-handed helix.

3. Results and discussion

3.1 Temperature dependence of helical pitch of nH6Bi (n = 2-7)

Plots of wavelength of selectively reflected light λ_s versus temperature for compounds belonging to the

homologous series *n*H6Bi (n = 2-7) are presented in Figure 1(b)–(g). The selective reflection was measured in the SmC* and SmC*_A phases in the temperature range accessible in the setup. The SmA phase does not have a helical structure, thus it does not reflect the light.

In the SmC* phase, the helical pitch does not depend on temperature for homologues where n = 2, 3 and 5. The slight increase in pitch with decreasing temperature in this phase for homologues where n = 4, 6 and 7, is caused by the formation of the helical structure after crossing the phase transition from the SmA to SmC* phase. The jump in values of λ_s is observed crossing the phase transition from SmC* to SmC*_A. It shows that the structure is completely changing during this phase transition.

In the SmC*_A phase, the noteworthy result is the change in value of λ_s on temperature for compounds having carbon atoms in an alkyl chain equal to n = 2, 3and 4 (Figure 1(b)–(d)). At first the values increase, then they are over the measurement range and they decrease with the increase in temperature. The observation of microscopic textures of homeotropically aligned 2H6Bi shows the increase in brightness followed by a decrease with increasing temperature in the SmC_A^* phase (Figure 2). The brightest texture, indicating the unwound structure, appears at 69°C. The same change in brightness was observed for other members of the nH6Bi series; not only for members (n = 3 and 4) having two branches of λ_s in Figure 1, but also for members (n = 5, 6 and 7) having only values of λ_s at higher temperatures. The maximum brightness occurs, for example, at about 69°C for 5H6Bi and 64°C for 6H6Bi. Thus for these homologues, the lower temperature curve of λ_s is over the measurement range of the spectrophotometer so only the higher temperature part of the curve is visible (Figure 1(e)–(g)).

The helical twist sense of compound 2H6Bi was established by a contact method using compound 4F6Bi (C₄F₉COO(CH₂)₆OPhPhCOOPhCOOC*H $(CH_3)C_6H_{13}$ [17], which has a helical pitch in SmC*_A increasing with temperature over the whole measurement range where 2H6Bi has values of λ_s increasing and then decreasing. At lower temperatures (e.g. 45°C), at which both compounds have characteristics of λ_s increasing with temperature, the texture, observed in the POM between crossed polarisers, is continuously dark. At higher temperatures (e.g. 94°C), at which the characteristics of λ_s decrease for compound 2H6Bi and increase for 4F6Bi with temperature, between dark textures corresponding to pure compounds, a bright stripe appears indicating the unwinding of the helix in their mixtures (Figure 3(b)). Thus at lower temperatures the handedness of the helix of both compounds is the same and at higher



Figure 1. Wavelength of selectively reflected light λ_s versus temperature for homologous series *n*H6Bi (*n* = 1–7); the character of the curves is the same in all compounds, but the maximal temperature of phase SmC*_A is lower for 1H6Bi (48°C) compared with other homologues (between 85 and 95°C)



Figure 2. Textures of 2H6Bi in a homeotropically aligned SmC_A^* phase at different temperatures (°C) (colour version online).



Figure 3. The homeotropically aligned contact sample of compounds, 4F6Bi on the left and 2H6Bi on the right, in the SmC*_A phase at temperature 94°C. A bright texture is observed in the middle corresponding to the unwound structure (b); rotation of the polariser anticlockwise causes a brightening of the texture of 2H6Bi (a); clockwise rotation of the polariser causes brightening of the texture of 4F6Bi (c) (colour version online).

temperatures the handedness is opposite. In the latter situation, the clockwise rotation of an analyser causes the appearance of a darker view in compound 2H6Bi and a brighter view in compound 4F6Bi (Figure 3(c)), while an anticlockwise rotation causes the appearance of a brighter view in compound 2H6Bi and a darker view in compound 4F6Bi (Figure 3(a)). It means that compound 2H6Bi has a left-handed structure and compound 4F6Bi has a right-handed structure. As 4F6Bi has the same handedness of helix over the whole temperature range, compound 2H6Bi has a right-handed helix at lower temperatures.

Next, more precise measurements of optical rotation were made using a spectrophotometer. The values of λ_s for 2H6Bi were over 1000 nm and the optical rotation was measured at 550 nm, thus at the same branch of optical rotation. The results of measurements of optical rotation are presented in Figure 4, where the positive values of angle rotation indicate the clockwise rotation of the analyser and negative values indicate the anticlockwise rotation, when measurement was made towards the incoming beam. Measurements were performed at temperatures 99°C in SmC*, 85°C and 50°C in SmC*_A. The helix in the SmC* phase and SmC*A at lower temperatures is right-handed but the helix in SmC*A at higher temperatures is left-handed, as for MHPOBC [11]. The helical twisting sense was also established for other compounds of the *n*H6Bi series (n = 3-7), and the same results were obtained.



Figure 4. Transmittance of the homeotropically aligned sample 2H6Bi between crossed polarisers versus angle rotation of the analyser at temperature 99°C SmC*, 85° C SmC*_A and 50° C SmC*_A.

All these measurements indicate that in compounds *n*H6Bi (n = 2-7) the change of helix handedness appears twice: in the crossing transition from SmC* to SmC*_A and within the SmC*_A phase.

3.2 Temperature dependence of the helical structure of 1H6Bi

An interesting situation was observed for the compound 1H6Bi. The results of helical pitch measurements obtained by spectrophotometry showed that the characteristic on temperature is the same as for homologue 2H6Bi (see Figure 1(a) and (b)). One might expect that the temperature of phase transition from SmC*_A to SmC* is around 100°C. Miscibility studies presented on phase diagrams for the mixture 1H6Bi-2H6Bi show that the phase transition from SmC*A to SmC* in 1H6Bi in fact occurs at 48°C (see Figure 5(a)). Also the results of phase identification with the standard SmC*A phase (we used 7H6B -C7H15COO(CH2)6OPhCOOPhPhCOOC*H(CH3)C6- H_{13} [13]) proved that transition (Figure 5(b)). Thus for 1H6Bi, only the branch of λ_s increasing with temperature is observed in the antiferroelectric phase (Figure 1(a)). The branch decreasing with temperature observed for this compound is actually in the ferroelectric phase, unlike other homologues (n = 2-7)(Figure 1(b)–(g)).

The handedness of the helix in 1H6Bi was established from miscibility studies with 2H6Bi. We found that the helix in both the SmC* and SmC*_A phases, for which the values of λ_s were possible to measure by spectrophotometry, is right-handed. As this contradicts the theory of the change of helix handedness [9], we looked for an additional branch of λ_s of the opposite handedness. The observation of a homeotropic texture of 1H6Bi showed that the unwound structure



Figure 5. Phase diagrams of the system (a) 1H6Bi-2H6Bi and (b) systems 1H6Bi-7H6B and 2H6Bi-7H6B.



Figure 6. Transmittance of the homeotropically aligned sample 1H6Bi between crossed polarisers versus angle rotation of the analyser at temperatures 90°C SmC*, 51°C SmC* and 47°C SmC*_A.

(i.e. the brightest texture) appears at 59°C in SmC*. In the temperature range between 48 and 59°C, a decrease in brightness of the homeotropic texture appears. The helical pitch in this temperature region is over the measurement range of the spectrophotometer but the measurements of optical rotation proved that the handedness of this helix is left; see results at temperatures of 90°C in SmC*, 48 and 51°C in SmC*_A for which the lowering of transmittance is for a left, right and left rotation of the analyser, respectively (Figure 6). It means that for compound 1H6Bi the change of the helix handedness appears twice, once within the SmC* phase and then in the crossing transition to the SmC*_A phase.

3.3 Influence of alkyl chain length on the helical pitch of nH6Bi (n = 2-7)

The results of λ_s for the homologue series *n*H6Bi (n = 2-7), presented in Figure 1, were compared with temperature related to the transition from the antiferroelectric to the ferroelectric phase $T - T_{C^*A-C^*}$ in Figure 7(a). We have not shown homologue n = 1 because of its different dependence of helical pitch on temperature compared with the other homologues. The results of λ_s versus terminal chain length at several set relative temperatures $T - T_{C^*A-C^*}$ are presented in Figure 7(b) for the SmC* phase (+2°C) and SmC*_A phase (-5 and -50°C).



Figure 7. Wavelength of selectively reflected light for homologous series *n*H6Bi (from n = 2 to n = 7) versus: (a) related temperature T–T_{C*A-C*}; (b) chain length at related temperature +2°C (SmC* phase), -5 and -50 °C (SmC*_A phase); (c) for homologous series *n*F6Bi at related temperature -70°C (SmC*_A phase) [18].

The increase in the number of carbon atoms in an alkyl chain causes at first a decrease and then an increase of values of λ_s in the SmC* phase (see the results indicated by squares in Figure 7(b)). It can be seen that this dependence is minimum for the homologue where n = 4. Thus for compounds that have a very short or very long terminal chain, the helical pitch is larger than for compounds with a medium chain.

In the SmC*_A phase, the values of λ_s in temperatures below $T - T_{C*A-C*} = -40^{\circ}$ C (Figure 7(a)) increase with increase in alkyl chain length (see results indicated by open triangles in Figure 7(b); results presented versus alkyl chain length for set related temperature $T - T_{C*A-C*} = -50^{\circ}$ C). Higher temperature curves for homologues n = 2-7 do not change linearly with the number of carbon atoms. They change in a stepwise way: for homologues n = 2-3, the curve decreases, for 4 it strongly increases, for homologues 4 - 6 it decreases again and for 7 it strongly increases (see results marked with open circles in Figure 7(b); results presented versus alkyl chain length for set related temperature $T - T_{C*A-C*} = -5^{\circ}$ C).

For comparison we have presented the dependence of λ_s in the SmC*_A phase on alkyl chain length (at temperature $T-T_{C^*A-C^*} = -70^{\circ}C$ for compounds belonging to homologous series with similar structures to *n*H6Bi, but with a perfluorinated part of the chain, C_nF_{2n+1}- instead of C_nH_{2n+1}- (homologous series nF6Bi) (Figure 7(c) [18]. In this case the helical pitch does not change with the increase in terminal chain length as much as for its protonated analogue in the SmC*_A phase but rather as in the SmC* phase. This behaviour is similar to the ferroelectric phase in compounds belonging to homologous series nH6Bi. It suggests two possibilities: for series *n*H6Bi, the same order of reflection may not be observed, which is why the results are not continuous with the increase in alkyl chain length; or the dependence of the helical pitch versus the number of carbon atoms in the achiral chain is not always the same in different homologous series.

3.4 Concentration dependence of the helical pitch in the system 1H6Bi–2H6Bi

The helical pitch measurements made for different compositions of the mixtures 1H6Bi–2H6Bi (0.2, 0.5, 0.8 and 0.9 molar fraction of 2H6Bi) show that the values of λ_s increase in the SmC* phase and decrease in the SmC*_A phase with a decrease in temperature (Figure 8). To be able to compare the influence of concentration of compound 1H6Bi on helix change, the values of λ_s were plotted against the temperature related to the transition from the SmC* to SmA phase $(T-T_{C^*-A})$ (Figure 9(a)), which is often used for comparison of results, for example, tilt angle or spontaneous polarisation. It is not convenient to use this scale because just below $T-T_{C^*-A} = 0$, the results of SmC^{*}_A are mixed with the results of SmC*. Thus, we have also presented the results of λ_s versus temperature related to transition from SmC^{*}_A to SmC^{*} phase $(T-T_{C^*A-C^*})$ showing that the increase in concentration of compound 1H6Bi causes the decrease of helical pitch in the SmC*A phase and an increase in the SmC* phase (Figure 9(b)).

Remembering the situation of helix handedness in both pure compounds, namely the change of helical twist sense within SmC* for compound 1H6Bi and within SmC*_A for compound 2H6Bi, we checked the handedness of their mixtures by establishing the sign of optical rotation under POM. For a mixture of 0.1 molar fraction of 2H6Bi, the situation was the same as for pure 1H6Bi except the brightest texture indicating the unwound helix is 3° above the transition to the SmC_A^* phase (for 1H6Bi it was 11°). On the other hand, for mixtures of 0.9 and 0.8 molar fraction of 2H6Bi, the situation was the same as for pure 2H6Bi, but the brightest texture indicating the unwound helix is 10° and 5° below the transition to the SmC* phase, respectively. For mixtures from 0.2-0.7 molar fraction of 2H6Bi, it was not possible to observe the unwinding and following rewinding of the helix either in the



Figure 8. Wavelength of selectively reflected light on temperature for the system 1H6Bi–2H6Bi at different concentrations.



Figure 9. Wavelength of selectively reflected light for the system 1H6Bi–2H6Bi versus temperature related to the transition (a) $T-T_{C^*-A}$ and (b) $T-T_{C^*-A-C^*}$.

SmC* or SmC*_A phases. Probably the competition between the two compounds 1H6Bi and 2H6Bi with different helix dependence on temperature in the middle temperature range means that this behaviour cannot appear there. Thus the transition from SmC* to SmC*_A is not connected with the change in helix handedness for these mixtures. Only the sharp change in homeotropic texture from red to very bright for composition 0.2 and from very bright to red for composition 0.7 during transition from SmC*_A to SmC* occurs. Such a situation appearing in the mixture has been reported previously by Lagerwall *et al.* [9].

4. Conclusions

We measured the helical pitch in compounds belonging to the homologous series nH6Bi in the SmC* and SmC*_A phases. The results provided evidence that the dependence of the helix on structure is more complicated than expected. In the case of results presented for compounds 1H6Bi and 2H6Bi, it was found that these compounds have the same dependence of helical pitch on temperature but it occurs in different phases. The helical pitch increases and then decreases in both compounds, although in the case of 1H6Bi the increase is observed in the SmC*A phase and decreases in the SmC* phase, while in the case of 2H6Bi both the increase and decrease are observed in the same SmC*A phase. Taking into account only the results of helical pitch measurements for compounds 1H6Bi and 2H6Bi is not a technique for establishing phase transition temperatures in these compounds, although in many cases the discontinuity in temperature dependence of the pitch is characteristic for phase transition. The miscibility studies and helical pitch measurements of bicomponent mixtures showed that there is a smooth change in the transition SmC*A-SmC* from 2H6Bi to 1H6Bi.

In all the tested compounds the helix twisting sense changed twice: once according to the theory of crossing the transition from the ferroelectric to antiferroelectric phase and the second time depending on the length of compounds of the *n*H6Bi series, for n = 1 in the SmC* phase and for n = 2-7 in the SmC*_A phase. In the mixtures of compounds 1H6Bi and 2H6Bi having the change of helix handedness in different phases, it is possible to find, for the medium concentrations, that the transition SmC*_A-SmC* is not connected with change in helix handedness.

Helical structure is characterised by the parameters of helical pitch and helical twisting sense, it depends on the structure of the material and its temperature dependence can be different even for homologues of the same series.

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