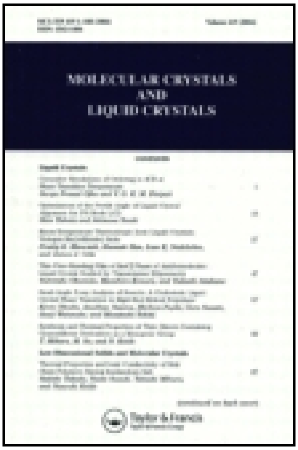

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An Influence of the Fluorosubstitution and the Spacer Length on the Phase Transitions and Helical Pitch Value in High Tilted Antiferroelectric Esters

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Phase transitions temperatures and temperature dependence of helical pitch p for S-(+)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[(4,4,4,3,3,2,2-heptafluorobutoxy)alkoxy] benzoates, and 3-fluoro-, and 2-fluoro-, 2,3-difluoro-benzoates upon length of alkoxy spacer were tested. For etoxy and propoxy spacer the pitch p in antiferroelectric phase is increasing with temperature to maximal value of about 1000 nm in high temperatures region. For pentoxy, hexoxy, and heptoxy spacer the pitch p is longer and reverse temperature dependence is observed. The compounds convenient for formulation of antiferroelectric orthoconic mixture with pitch length of about 2000 nm were selected.

Keywords: antiferroelectric; esters; helical pitch; high tilted; orthoconic

INTRODUCTION

Chiral three ring esters with perfluorinated alkanoyloxy unit in a terminal chain exhibit so called orthoconic liquid crystalline antiferroelectric phase (OAFLC) with saturated molecular cone angle of 90°.

So called “bookshelf structure” of an orthoconic antiferroelectric smectic liquid crystal (SSOAFLC) forms an optically uniaxial and optically negative medium with the optical axis normal to the surrounding

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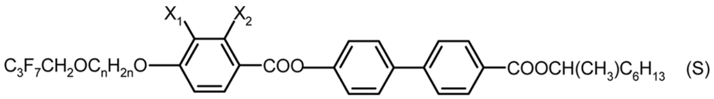
glass plates. When such a sample is placed between polarizers it provides perfect dark state for the normally incident light beam regardless the structure defects involving local disorientation of the smectic layer normal within OAFLC bookshelf structure [1].

Numerous compounds with the molecular rigid core containing biphenyl benzole unit were synthesized at MUT during last few years [2], and extensive studies of compounds exhibiting high tilted smectic phases were conducted [3,4]. Compounds with 1-methylheptyloxy chiral part are typically smectogenic and exhibit low temperature tilted phases. The helical pitch value registered for this kind of materials is rather low and its value is typically less than 1 μm. This is a twice lower than the thickness of the (anti-)ferroelectric LC slab used a typical cell for electrooptical applications. Such a short helical pitch is considered as a main factor of the parasitic effects such a "light leakage" deteriorating the performance of units with (anti-)ferroelectric materials as an optically active medium. Mentioned light leakage is caused by a graduate switching of the cell below the threshold electric field. The direct reason is unwinding of the remainder of the helical structure upon low electric field applied. This is considered as the most problematic effect at practical applications. Structure defect, which is the remainder of the helix within the SSOAFLC hampers the utilizing of OAFLC mixtures. It is supposed that the light leakage problem can be greatly limited when OAFLCs with pitch longer than the thickness of the OAFLC slab are used [5]. The motivation of this paper was to study the influence of the structure modification of unchiral molecular parts on the value of the helical pitch of high tilted smectogenic compounds. The subject or our interest was the molecular part opposite to this one comprising the chiral carbon atom. Two molecular parts were taken under study at this attempt. The first one was the length of the spacer at the aliphatic chain and the second one was the single benzene ring within the rigid molecular core. Those molecular parts were taken under study because their modifications were considered to affect the helical pitch without inducing other mesogenic phases. Due to this a liquid crystalline esters with partially fluorinated alkoxyalkoxy chain (see the template structure below) were synthesized.



where n = 2, 3, 5, 6, 7; $X_1 = X_2 = F$ (CH_2)nFphF; $X_1 = X_2 = H$ (CH_2)nHphH; $X_1 = F$ and $X_2 = H$ (CH_2)nFphH; $X_1 = H$ and $X_2 = F$ (CH_2)nHphF.

The structure variation of the template structure was done by incorporating of different number of –(CH_2)– units in the terminal chain and by the fluorosubstitution at the protonated single benzene ring. As it was expected obtained compounds with structural modifications described above, exhibit the low temperature, broad range antiferroelectric SmC_A^* phase. Their mesogenic behavior, layer spacing, helical pitch and molecular tilt were investigated by combined method including polarizing optical microscopy, DSC and spectroscopic investigations.

EXPERIMENTAL

The synthesis of investigated compounds was described elsewhere [6]. Purity and structures of obtained liquid crystalline esters were confirmed using Shimazu prominence chromatograph with HPLC MS (API-ESI) detector 2010EV. The methanol was used as an eluent. Phase sequences and phase transition temperatures of obtained esters were investigated by means of combined method utilizing the texture observation of a LC sample placed between two bar glass plates placed on the table of Biolar PI polarizing microscope (PZO Poland). The temperatures of the phase transitions were verified and their enthalpies were detected by using of DSC “Setaram 141” microcalorimeter upon subsequent heating and cooling cycles at the temperature rate of 2 K/min.

The helical pitch p of investigated compounds was studied by the method of the selective reflection of the light. The Shimazu UV-3600 Spectrophotometer was used where the spectral range from 360 nm to 3000 nm was analyzed. The cooling of the studied compounds was done within the spectrometer’s Peltier cells. Tested compounds were placed on glass plates. The surface of each substrate glass was covered by silane coupling agent inducing the homeotropic orientation of molecules of the studied mesogenic compounds. The other surface of the slab was a free one which promotes homeotropic orientation as well. Due to this the helical structure was formed upon sample cooling from the isotropic phase. The temperature variation of the maximum wavelength λ_{max} of selective reflection of the unpolarized light was observed on slow cooling from the isotropic state. The full helical pitch was calculated using well known formula:

$$p = x\lambda_{max}/n \tag{1}$$

where $x = 1$ for synclinic SmC^* phase and $x = 2$ for anticlinic SmC_A^* phase, n is the medium refractive index. For synthesized esters the average refractive index for the light traveling along the axis of the helix was taken n = 1.50 [7].

MESOMORPHIC PROPERTIES

In Figures 1–4 mesomorphic properties examined upon heating cycle are presented.

The mesogenic behavior of compounds with fully protonated benzene ring within the rigid molecular core and varying number of –(CH_2)– methylene groups (abbreviated here (CH_2)nHphH) one can observe in the Figure 1. One should notice that for the varying methylene spacer length an odd-even effect can be observed. The mesomorphic temperature range is larger for their representatives with even number of –(CH_2)– groups in the spacer, however the diagram is not fully complete because the series with n = 4 of –(CH_2)– groups has not been prepared yet. The antiferroelectric phase seems to be more stable for compounds with the terminal substituent comprising odd number of –(CH_2)– methylene groups. One can observe also that the synclinic ferroelectric phase is present for all members of the homologues series but the compound with n = 3 of –(CH_2)– spacers.

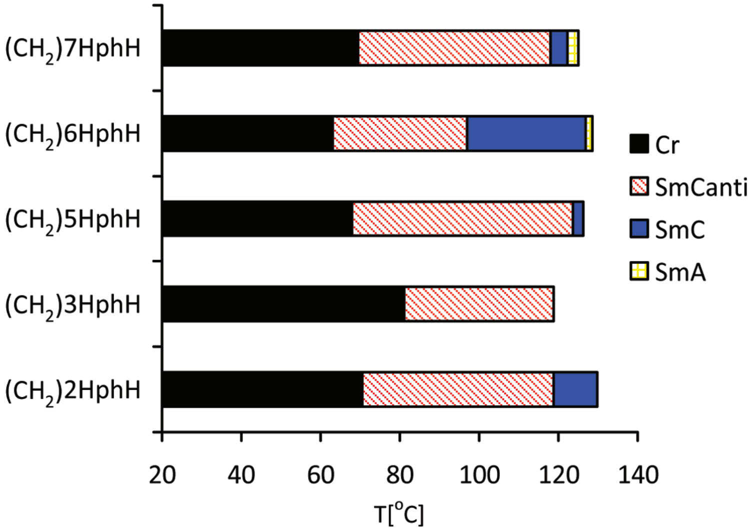


FIGURE 1 The mesogenic behavior of compounds with fully protonated molecular rigid core (CH_2)nHphH vs. the number n of –(CH_2)– methylene spacer within the terminal substituent.

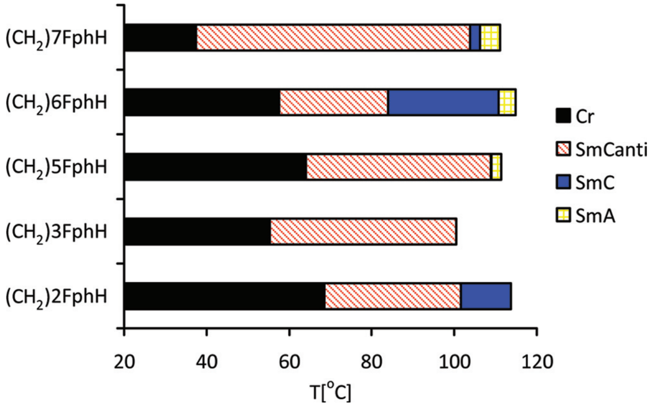


FIGURE 2 The mesogenic behavior of compounds $(CH_2)nFphH$ with a single fluoro substituted molecular rigid core in the position far from the chiral centre vs. the number n of CH_2 methylene spacer within the terminal substituent.

The compound with $n = 6$ of $–(CH_2)–$ spacers exhibits the widest range of the synclinic ferroelectric phase. The orthogonal SmA* phase is promoted for two compounds with the longest spacer comprising $n = 6$ and 7 $–(CH_2)–$ spacers.

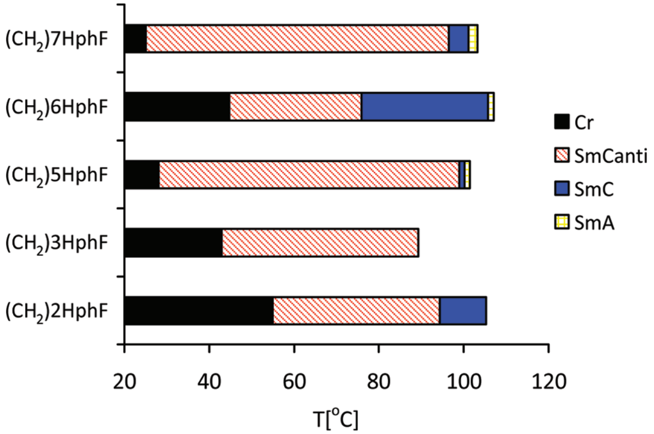


FIGURE 3 The mesogenic behavior of compounds $(CH_2)nHphF$ with a single fluoro substituted molecular rigid core in the position closer to the chiral centre vs. the number n of CH_2 methylene spacer within the terminal substituent.

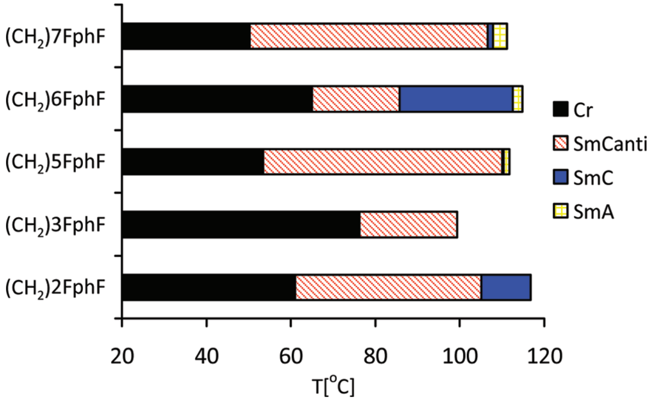


FIGURE 4 The mesogenic behavior of difluorosubstituted compounds (CH$_2$)nFphF vs. the number n of CH$_2$ methylene spacer within the terminal substituent.

Figure 2 presents the phase transitions temperatures and phase sequences for compounds abbreviated (CH$_2$)nFphH with a single fluorosubstituted benzene ring within the rigid molecular core. The odd-even effect can be noticed here as well, but in the opposition to the previous Figure 1, compounds with even number of carbons in methylene spacer have melting points at higher temperature than those with odd number. One can see also that the orthogonal SmA* phase was induced for the compound (CH$_2$)**5**FphH with shorter spacer than that for the structural analogue with fully protonated molecular rigid core. The orthogonal SmA* is present for compounds with the longest spacer as well. The compound with n = 6 carbons in the spacer exhibits the largest temperature range of the synclinic SmC* ferroelectric phase.

In Figure 3 one can observe similar dependence as for (CH$_2$)nFphH series. The Fluorosubstitution within the molecular core lowered the melting temperatures. Compounds with 5 and 7 carbons in the methylene spacer have wider temperature ranges of antiferroelectric phase. For the compounds with bigger number of –(CH$_2$)– groups the SmA* phase temperature range decreased. (CH$_2$)**3**HphF compound exhibits antiferroelectric mesophase only what is not a case for other compounds with same number of –(CH$_2$)– groups in their spacers.

Figure 4 presents the mesogenic behaviour of difluorosubstituted series abbreviated here (CH$_2$)nFphF. One can observe that double fluorosubstitution leads to deacrease of antiferroelectric phase temperature range, because melting points increases.

HELICAL PITCH MEASUREMENTS

Esters with n = 2 of –(CH_2)– groups in the spacer exhibit maximum value of the pitch length which is about 1000 nm at high (~80°C) temperatures (see Fig. 5). This pitch length p is measured in antiferroelectric phase and its value typically decreases upon cooling. The higest pitch values are obtained for double fluorosubstituted (CH_2)**2**FphF compounds and the lowest for single fluorosubstituted (CH_2)**2**FphH compounds. The first one exhibits the strongest temperature dependence of the helical pitch value. The compound (CH_2)**2**HphH with fully protonated molecular rigid core exhibits the highest temperature stability of the helical pitch. For mono fluorosubstituted compounds (CH_2)**2**FphH and (CH_2)**2**HphF the alteration in temperature dependence is observed. At higher temperature at the synclinic SmC* phase the pitch is short and temperature independent and the rapidly increases upom phase transition to the antyclinic SmC$^*_A$ phase. For both single fluorosubstituted compounds (CH_2)**2**HphF and (CH_2)**2**FphH the pitch decreases similarly as for two other members of series n = 2.

In Figure 6 the same dependence for compounds (CH_2)**3**XphX with three –(CH_2)– groups is shown. These compounds exhibit short helical pitch and for all members of this series the regular decrease of helical pitch upon cooling is observed. The longest pitch at chosen temperature

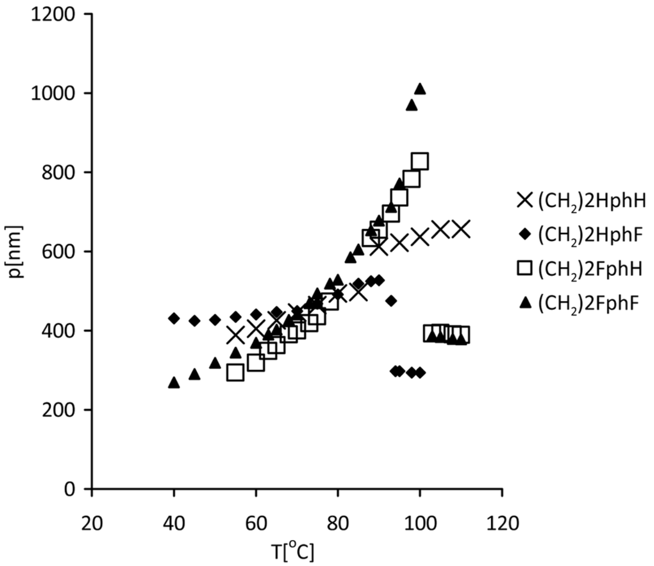


FIGURE 5 Helical pitch length p vs. temperature for (CH_2)2XphX series.

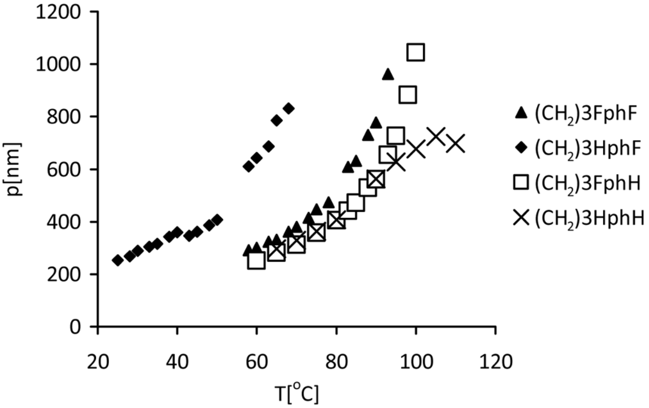


FIGURE 6 Helical pitch length p versus temperature for $(CH_2)3XphX$ compounds.

of about 70°C was measured for (CH_2)**3**HphF and the lowest for the (CH_2)**3**FphH compound. The helical pitch p is less then 200 nm at 20°C for all those compounds.

The results for the series of single fluorosubstituted compounds with five $-(CH_2)-$ groups within spacer of the ester abbreviated as (CH_2)**5**HphF shows quite different properties than the others (Fig. 7). The important finding of presented study is an observation that this compound exhibits an inverse pitch length temperature dependence.

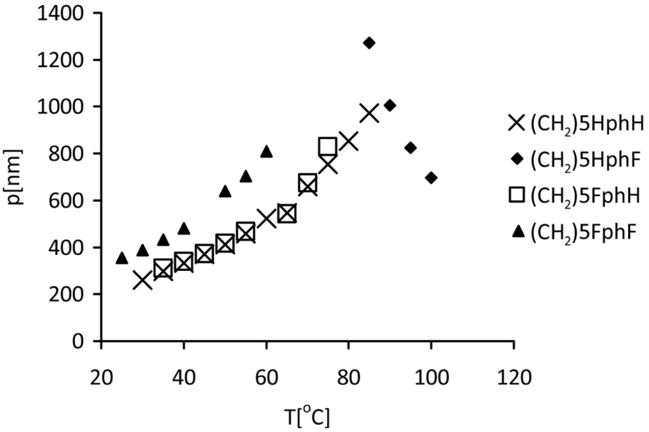


FIGURE 7 Helical pitch length p versus temperature for $(CH_2)5XphX$ compounds.

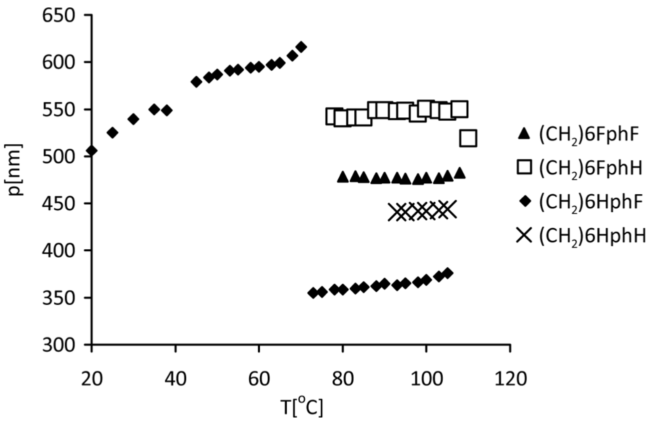


FIGURE 8 Helical pitch length p vs. temperature for (CH$_2$)**6**XphX compounds.

Its helical pitch length increases upon cooling. It's approximated pitch at 20°C is much more than 2000 nm so it can be considered as a good component of long pitch (O)AFLC mixtures. The rest of the compounds from this group exhibits regular temperature dependence of the helical pitch length and measured values do not exceed 1000 nm at high temperatures.

The other interesting finding is for compounds with 6 methylene –(CH$_2$)– groups within the spacer where the helical pitch p in antiferroelectric phase was measurable for the (CH$_2$)**6**HphF compound only by using of our measuring set-up.

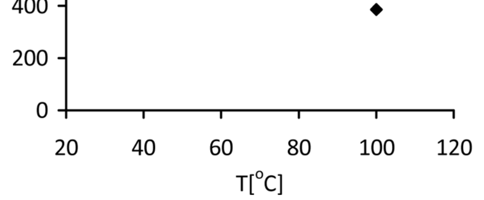


FIGURE 9 The helical pitch p vs. temperature for (CH$_2$)**7**XphX compounds.

Other compounds have higher pitch length which was beyond our measurement range. Interesting property of this group of compounds is that the pitch length measured in ferroelectric phase seems to be almost temperature independent (see the Figure 8). Two compounds with seven –(CH_2)– methylene spacer, (CH_2)**7**HphF and (CH_2)**7**FphH, in antiferroelectric SmC_A^* phase exhibit helical pitch which was measurable by using of our measuring set up (see Fig. 9). Their helical pitch increase upon cooling cycle. The pitch p of (CH_2)**7**HphF compound was only 800 nm only at 20 C deg., but pitch length for the (CH_2)**7**FphH reaches about 2000 nm at 20 C deg. The helical pitch of the other compounds is higher which was confirmed upon investigation of mixtures containing these compounds and (CH_2)**7**HphF compound.

DISCUSSION AND CONCLUSIONS

From the phase transition measurements we can observe that the length of the alkyl chain promotes the presence of SmA^* phase. We can also indicate a strong odd-even effect for the antiferroelectric SmC_A^* phase temperature range and stability. Compounds with odd number of –(CH_2)– groups in the alkyl chain exhibit wider temperature range of anticlinic SmC_A^* phase than those with the even number and moreover very narrow range of the synclinic SmC^* ferroelectric phase. Protonated (CH_2)**n**HphH exhibit an increase of the pitch value with the elongation of terminal chain. For the single fluorosubstituted (CH_2)**n**HphF homologous series a strong odd-even effect is observed for the pitch length with increase of the molecular weight. The odd members of the homologues series exhibit larger pitch values than even ones. One can also indicate that highest pitch values were measured for (CH_2)**5**HphF compound. Members of these series with longer alkyl chains have lower pitch values. It is worth to point out for (CH_2)**5**HphF and (CH_2)**7**HphF compounds where the inverse temperature dependence of the pitch value in the SmC_A^* phase is observed. This kind of behavior is not observed for any even members of any homologous series. Some anomalies from odd-even effect are present in (CH_2)**n**FphH homologous series. The (CH_2)**6**FphH compound seems to have larger pitch than odd members of this series with lower molecular weight. For (CH_2)**7**FphH compound one again can observe reverse temperature behavior of the pitch value. Compounds with double fluorosubstituted benzene ring show odd-even effects which is inverse to the one observed for other series. Compounds with even number of –(CH_2)– groups seem to have larger pitch values than compounds with odd number of –(CH_2)– groups, but to fully confirm that further research needs to be conducted.

Taking the above into considerations one can conclude that compounds abbreviated as (CH_2)**5**HphF and (CH_2)**7**HphF seem to be most useful for formulation of mixtures with long pitch because they exhibit the widest temperature ranges of antiferroelectric phases and approximated pitch values are above 2000 nm. Such a value is highly desirable from the application point of view. Research also show that two basic factors promote inverse temperature behavior of pitch length value in investigated compounds; one is the odd number of $–(CH_2)–$ groups in alkyl chain, the other is monofluorosubstitution. The research also shows that lateral monofluorosubstitution disturbs strong odd-even effects present in protonated or difluorosubstituted compounds. It is noticeable that difluorosubstituted compounds exhibit inverse odd-even effect. Interesting regular effects upon fulorosubstitution may be associated with change of dipole moment value and orientation as well as the intermolecular interactions caused by fluorosubstitution which was observed previously for other compounds [8]. As to clarify the influence of the structure of molecular elements for the mesogenic behavior and for the value of the helical pitch of compounds exhibiting anticlinic ordering the extensive research needs to be conducted.

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