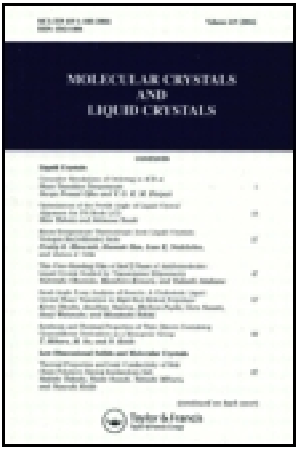

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Comparison of Helical Pitch of Four Homologous Series of Antiferroelectric Compounds

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The changes of the helical pitch in antiferroelectric phase versus temperature were calculated based on measurements of selective reflection of the light in four homologous series $C_nF_{2n+1}COO(CH_2)_6O{-}A{-}COOC^{*}H(CH_3)C_6H_{13}$ (A-the rigid core-PhCOOPhPh, PhPhCOOPh, PhPhCOO(F)Ph or PhPhCOOPh(F), Ph – phenyl ring, n is changed from 1 to 7). The values of helical pitch do not change in monotonous way with increase of the chain length. The even members have shorter pitches.

Keywords: antiferroelectric phase; helical pitch; light selective reflection

INTRODUCTION

Longer pitch of antiferroelectric phase is necessary to obtain better conditions for unwinding of the helix and monodomain orientation.

Recently we have published data concerning unwinding of helical pitch of antiferroelectric compounds by adding racemates and achiral compounds [1]. There we have presented four members (n = 3–6) of homologous series $C_nF_{2n+1}COO(CH_2)_6OPhCOOPhPhCOOC^{*}H(CH_3)C_6H_{13}$. We have noticed the non-monotonous change of values of helical pitch versus the length of fluorinated part of terminal chain. We have decided to check whether it is the only occasional example or that there is the rule in such kind of materials. We have completed the measurements for other members of previously presented homologous series, and we have performed measurements for three other series.

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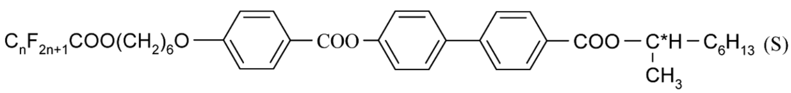
The results are described in this paper. The knowledge about relation between pitch and structure of compounds in smectic phase is still very pure.

EXPERIMENT

The recently prepared [2] four homologous series (I–IV) have been studied: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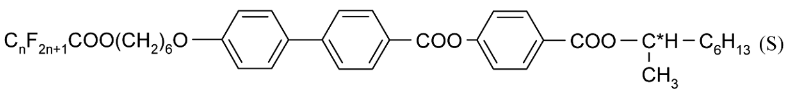
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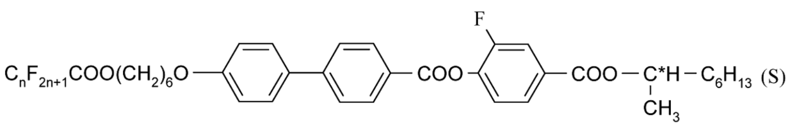
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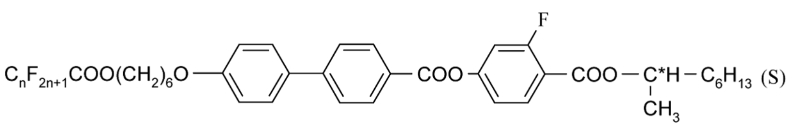
IV

Their phase transition temperatures taken from [2] are presented in Table 1.

For setting the helical pitch in an antiferroelectric phase of all compounds Ultraviolet-visible Spectroscopy was used. The measurements of light transmission were made on Varian Cary 3 UV-vis spectrometer in the range of 400–900 nm. The tested compounds were placed on glass plate with homeotropic aligning layer without covering with another glass plate. Peltier elements were used for changing the temperature; the temperature range of measurement is 0–100°C. The temperature accuracy was 0.1°C. Presented results were obtained during cooling cycle.

The well known dependence $\lambda_{\max} = n \cdot p$ connect the length of the selectively reflected light $\lambda_{\max}$ with the helical pitch p of compounds, where n is average refractive index.

For tested chiral compounds the average refractive index is about 1.51 [3], thus the helical pitch can be calculated using the following relation $p \approx \lambda_{\max}/1.5$.

TABLE 1 Phase Transition Temperatures [°C] of Compounds of Homologous Series I–IV

No	n	Cr		SmC_A^*		SmC^*		SmA		Iso
I-1	1	*	40.1	*	71.3	*	107.2	*	112.5	*
I-2	2	*	30.8	*	91.2	*	112.9	*	113.4	*
I-3	3	*	18.5	*	98.0	*	113.2	*	119.6	*
I-4	4	*	31.0	*	102.3	*	121.9	*	124.4	*
I-5	5	*	39.3	*	102.3	*	125.8	*	131.2	*
I-6	6	*	40.9	*	112.2	*	119.9	*	135.5	*
I-7	7	*	33.8	*	115.0	*	131.6	*	119.6	*
II-1	1	*	39.8	*	104.3	*	119.7	*	125.6	*
II-2	2	*	40.4	*	111.2	*	111.9	*	124.9	*
II-3	3	*	29.4	*	111.4	*	122.5	*	129.3	*
II-4	4	*	39.7	*	121.4	*	124.7	*	134.3	*
II-5	5	*	46.2	*	120.9	*	127.4	*	140.4	*
II-6	6	*	58.3	*	129.7	*	131.7	*	147.7	*
II-7	7	*	51.1	*	127.4	*	134.0	*	152.6	*
III-1	1	*	41.3	*	70.6	*	90.6	*	100.4	*
III-2	2	*	28.3	*	82.2	*	92.8	*	95.9	*
III-3	3	*	39.6	*	86.5	*	98.4	*	98.5	*
III-4	4	*	43.2	*	98.9	*	102.7	*	102.8	*
III-5	5	*	39.5	*	99.1	*	107.3	*	108.7	*
III-6	6	*	43.8	*	110.4	*	112.9	*	116.1	*
III-7	7	*	40.4	*	108.6	*	116.0	*	121.0	*
IV-1	1	*	45.6	*	86.9	*	107.8	*	113.6	*
IV-2	2	*	40.1	*	69.2	*	107.8	*	115.3	*
IV-3	3	*	30.1	*	94.5	*	110.3	*	121.0	*
IV-4	4	*	35.2	*	106.8	*	112.0	*	126.6	*
IV-5	5	*	39.2	*	107.8	*	114.6	*	133.2	*
IV-6	6	*	55.6	*	114.7	*	119.0	*	141.0	*
IV-7	7	*	43.9	*	112.8	*	121.2	*	145.9	*

*indicated phase exists.

RESULTS

The maxima of light selective reflection versus temperature for compounds belonging to four homologous series I, II, III and IV are presented in Figures 1a, 2a, 3a and 4a, respectively. It was not possible to measure compounds IV-1 and IV-7 because they give the selective reflection out of the spectrophotometer range (in infrared region). Comparing all homologues it is seen that their helical pitches have similar temperature dependence, with only few exceptions for example III-6 or III-7 which curve slope is steeper. For homologues I-1 and III-1 the selective reflection was measured also in ferroelectric state.

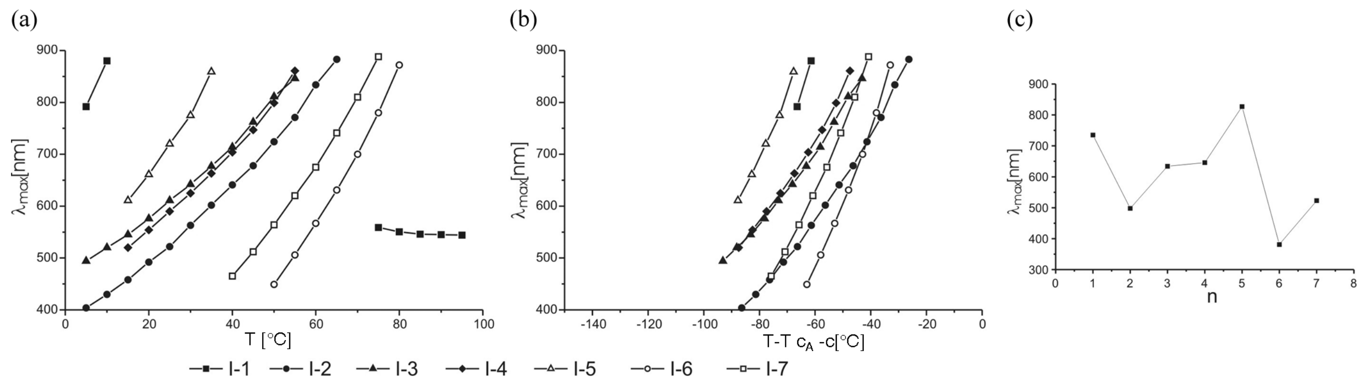

FIGURE 1 Maxima of selectively reflected light, for series I, versus temperature (a), reduced temperature $T - T_{SmC^*A\text{-}SmC^*}$ (b), and versus n for reduced temperature $T - T_{SmC^*A\text{-}SmC^*} = -70^{\circ}C$ (c).

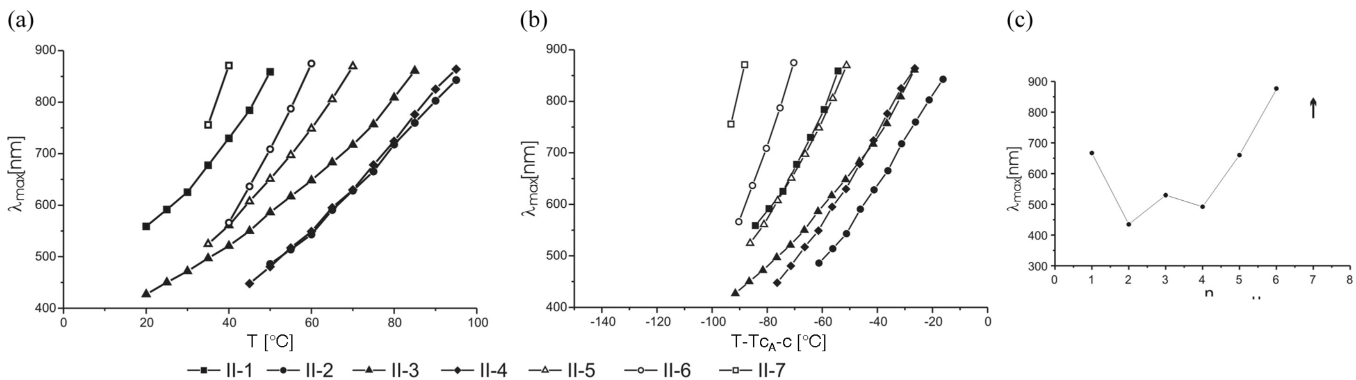

FIGURE 2 Maxima of selectively reflected light, for series II, versus temperature (a), reduced temperature $T - T_{SmC^*A\text{-}SmC^*}$ (b), and versus n for reduced temperature $T - T_{SmC^*A\text{-}SmC^*} = -70°C$ (c).

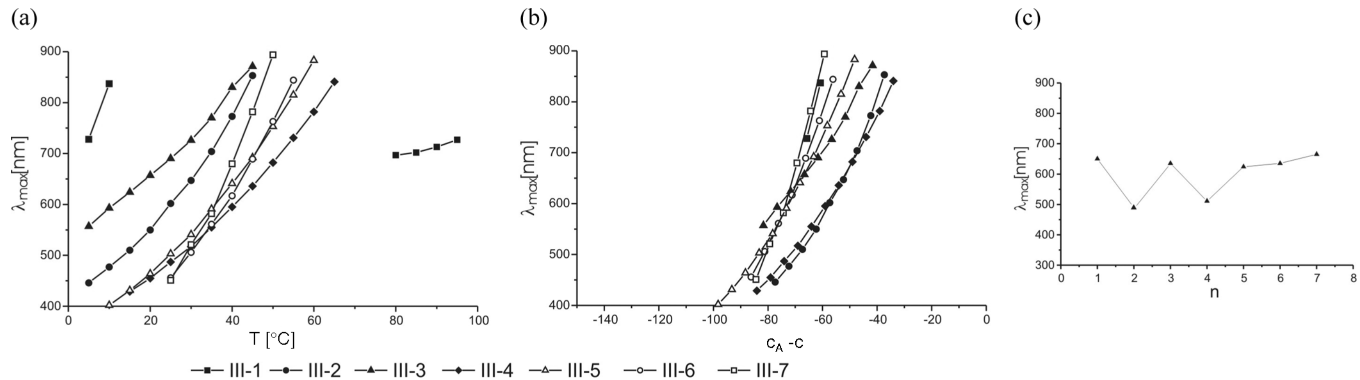

FIGURE 3 Maxima of selectively reflected light, for series III, versus temperature (a), reduced temperature $T - T_{SmC^*A\text{-}SmC^*}$ (b), and versus n for reduced temperature $T - T_{SmC^*A\text{-}SmC^*} = -70°C$ (c).

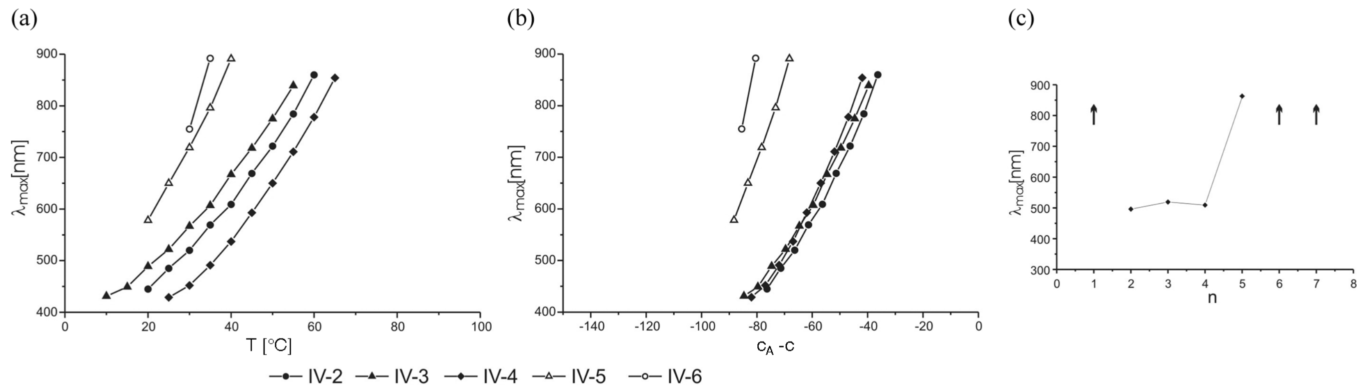

FIGURE 4 Maxima of selectively reflected light, for series IV, versus temperature (a), reduced temperature $T - T_{SmC^*A\text{-}SmC^*}$ (b), and versus n for reduced temperature $T - T_{SmC^*A\text{-}SmC^*} = -70°C$ (c).

We have presented the results versus reduced temperature $T - T_{SmC^*A\text{-}SmC^*}$; Figures 1b, 2b, 3b and 4b, respectively. Comparison of helical pitch values for reduced temperature $T - T_{SmC^*A\text{-}SmC^*} = -70°C$ enable better discussion, Figures 1c, 2c, 3c and 4c, respectively. Some values were obtained by extrapolation, and some of them were not extrapolated because of possibility of making too big error.

Odd-even effect for dependence of pitch upon chain length is well observed for most members of series I–IV. The even members have lower pitch. But generaly the increase of the fluorinated part of the terminal chain of homologous series causes the increase of the pitch.

The differences between results for homologs of series III are very small because of different steepnest of the curves, but comparison of results for another reduced temperature, e.g., $-60°C$ gives the same relation as for other series.

The presence of fluorine atom laterally substituted to benzene ring causes the formation of helix with little longer pitch than for unsubstituted ones. For most members substitution into position 2 gives stronger twisting compare to substitution 3. It can be seen from the fact that selective reflection of compounds IV-1 and IV-7 is out of the spectrophotometer range (>900 nm). Homologues IV-5 and IV-6 have also high helical pitch. This rule is not preserved for all members, because for example for member containing three carbon atoms in terminal alkyl chain, it was observed that the substitution into position 3 causes stronger twisting than into position 2.

CONCLUSIONS

The measurements of the helical pitch in antiferroelectric phase of four homologous series ($C_nF_{2n+1}COO(CH_2)_6O{-}A{-}COOC^*H(CH_3)C_6H_{13}$ with the rigid core A = PhCOOPhPh, PhPhCOOPh, PhPhCOO(F)Ph, PhPhCOOPh(F)) versus temperature show strong non-monotonous dependence of pitch with increasing of the chain length. The even members have in most cases longer pitch than odd members. Members containing fluorine atom attached to benzene ring in the position 3 have the highest helical pitch compare to other presented compounds.

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