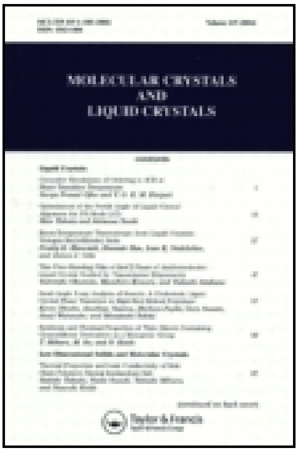

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Synthesis and Physical Properties of Novel Terphenyl Type Ferroelectric Liquid Crystals

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SYNTHESIS AND PHYSICAL PROPERTIES OF NOVEL TERPHENYL TYPE FERROELECTRIC LIQUID CRYSTALS

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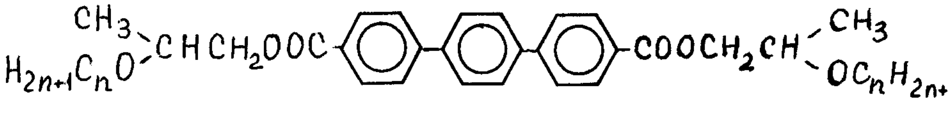
Abstract A new series of optically active compounds have been prepared using 4,4"-terphenyldicarboxylic acid and S-2-alcoxypropanols-1. These are Sm*C, SmA and N* chemically stable - especially with regard to racemization and UV-light compounds with a small P_S value, high twisting power and left handedness of helix.

INTRODUCTION

Initial studies of nonmesomorphic esters formed from 4,4"-terphenyldicarboxylic acid and 2-alkanols[1] indicated that considerable broadening of matrix SmC-temperature range could be obtained using such systems as chiral dopants. Introduction of $-CH_2$-unit between the ester link and chiral centre on both sides of the molecule essentially increased the susceptibility of the compound to form a mesophase as it was in the case of 2-methylbutyl derivative (Cr → SmA → N*-sequence). Some lengthening of the alkyl tail and additional attachment of chlorine atom to the chiral centre led to injection of chiral SmC properties.[2] In order to check the validity of these structure peculiarities in developing SmC* properties in this type of compounds we have prepared and investigated a new series of compounds of the following general formula

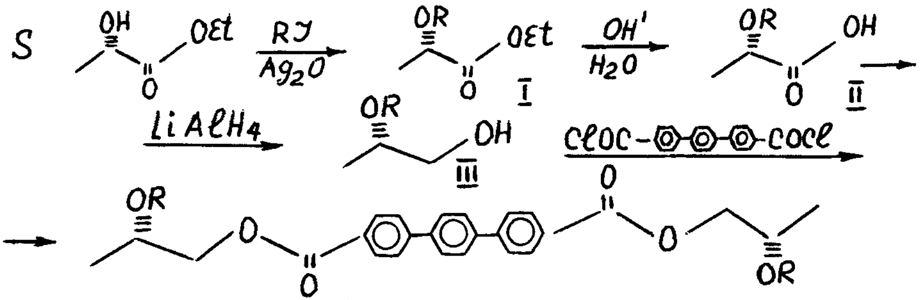


where n = 2-8.

Another point of interest was to clear up the effect of the hetero-atom adjacent to the chiral centre on the handedness of the induced and own helixes.

EXPERIMENTAL PART

The chiral starting material for the above series is (S)-ethyl lactate readily available in high enantiomeric purity. The synthesis was carried out as outlined in the scheme below



The absolute configurations of the final compounds were predetermined by the known absolute configuration of the starting S-ethyl lactate. S-2--Alkoxypropanols-1 were synthesized in three steps by alkylation of S-ethyl lactate with an appropriate hydrocarbon iodide in the presence of Ag_2O; hydrolysis of the obtained ester and reduction of 2-alkoxypropanoic acids with $LiAlH_4$. The optical rotation data for 2-alkoxypropanols-1 were as follows: R and $[a}_D^{20}$ are given: C_2H_5, +28.0 (neat); C_3H_7, +26.1 (neat); C_4H_9, +24.3 (neat); C_5H_{11}, +22.4 (neat); C_6H_{13}, +19.9 (neat); C_7H_{15}, +17.4 (neat); C_8H_{17}, +16.7 (neat). The final compounds were prepared by esterification of the appropriate S-2-alkoxypropanols-1 with 4,4"-terphenyldicarboxylic acid dichloride in the medium of absolute pyridine.

The molecular structure of the synthesized compounds was confirmed by IR, NMR and mass spectrometry. The results were in agreement with the predicted structures. Phase transition temperatures for the products were determined by thermal analysis and microscopic examination of the textures of their phases using a polarizing microscope. The enthalpies of the transitions and independent confirmations of the transition temperatures were determined by differential scanning calorimetry. *The nematic twisting power and helix handedness* were estimated by the modified Kano-Grandjean method[3] for 2% (mol) solutions of each chiral substance in the nematic phase of 2-(4-hexyloxyphenyl)-5-octyl-pyrimidine (HOPOP) (Cr $^{\underline{27.5}}$ SmC $^{\underline{44.5}}$ SmA $^{\underline{57.5}}$ N $^{\underline{65.0}}$ I) at 64°C, i.e. 2° below I ⟶ N* phase transition. The induced helix handedness for all compounds was found to be left. The results are summarized in Table 1.

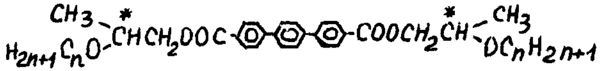
RESULTS AND DISCUSSION

Comparison of the data given in Table 1 reveals the fact of increasing the length of the hydrocarbon chain attached to the chiral centre by means of O-atom consequtively by a methylene unit. The first member of the series possesses enantiotropic N*, SmA and SmC* phases and a reasonably low melting point. Bearing in mind the phase transition temperatures for 2-methylbutyl diester of 4,4"-terphenyldicarboxylic acid (Cr $^{\underline{132.4}}$ SmA $^{\underline{143.1}}$ N* $^{\underline{145.0}}$ I), these data show that introduction of O-atom between the chiral centre and hydrocarbon chain results in an abundant SmC* phase and a considerable lowering of the melting point. *Quite surprisingly, the melting points of the homologous* series are remarkably similar. The thermal stability of the SmC* phase decreases gradually with increasing chain length and the higher homologues of the series (n = 7,8) demonstrate only SmA properties.

As can be seen from Table 1, the enthalpies of fusion are rather low for almost all compounds synthesized and, moreover, there is an unusual pattern of alternation: ΔH values for the substances with odd numbers of carbon atoms in the alkyl chain are much lower than those for even numbered compounds.

As one could expect, owing to the structure of the chiral tail and especially because of the remote position of the chiral centres with respect to the molecular rigid core, the P_S values of the compounds in their own SmC* phase are rather

TABLE 1 Physical properties of compounds with general formula



n	Phase transition temperatures, °C									ΔH Kcal/m	P_n μm at 64°C	Sm*C→SmA transition temperature for 2% solution
	Cr		Sm*C		SmA		N*		I			
2	.	61.5	.	104.2	-		.	120.4	.	3.31	7.7	45.0
3	.	64.8	.	84.3	.	87.2	.	102.8	.	2.35	7.5	44.5
4	.	65.8	.	77.5	.	87.8	.	94.7	.	5.9	6.6	44.0
5	.	60.3	.	65.2	.	85.7	.	86.3	.	2.42	7.8	41.0
6	.	58.3	.	63.6	.	84.1	-		.	5.9	8.1	39.5
7	.	57.8	-		.	80.1	-		.	2.58	8.6	38.0
8	.	63.0	-		.	84.1	-		.	7.64	9.9	36.0

small and do not exceed 5 nC/cm^2. It means that the O-atom adjacent to the chiral centre does not affect essentially the polarization magnitude.

As mentioned earlier, the twisting power of the materials was estimated in the nematic phase. The results for the homologous series are plotted against increasing alkoxy chain length in Fig. 1. This figure shows that the compounds demonstrate an extremely high twisting power. The pitch value does not increase monotonically as a function of alkoxy tail length but the minimum pitch is obtained for the butyloxy homologue.This relationship resembles to some extent the one established before for individual ferroelectric liquid crystals in their SmC* phases.[4] It was also found that in the SmC* phases many of the compounds (n = 2, 3, 5) have helical pitches in the visible region.

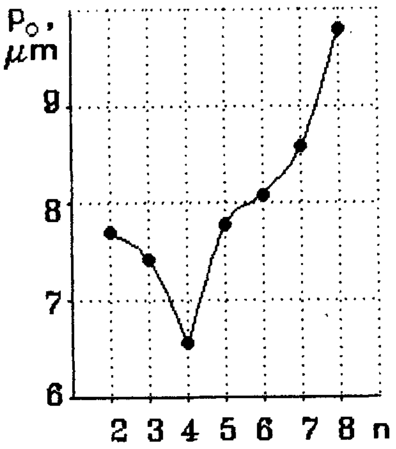


FIGURE 1 P$_0$ versus n

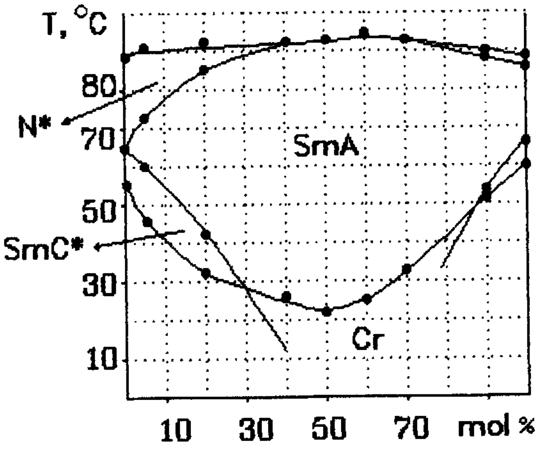


FIGURE 2 Phase diagram of HOPOOB and compound n=5

The investigation of the helix ordering of the molecules (n = 2-6) in their SmC* phases by the contact method[5] showed in their own SmC* and induced N* phases the helix handednesses coincide, their sense being left. So, the materials described by Goodby et al. According to these rules, the compounds would demonstrate right helix handednesses as one would infer from the positions of the chiral centres relative to the rigid core of the molecule and their absolute spatial configuration.

Examination of the data collated in Table 1 reveals that introduction of even a very small amount of optically active compounds (2%) results in a considerable lowering of the SmC* - - SmA phase transition temperatures of the pyrimidine type SmC matrix. This fact prompted us to investigate a binary phase diagram of the compound with n = 5 and SmC matrix with a larger tilt angle (*4-hexyloxyphenyl 4-octyloxybenzoate*, HOPOOB). As can be seen from Figure 2, these materials do not mix over the whole concentration range and thermodynamically stable solutions could be obtained only in the region of boundary concentations. Further investigation of the synthesized compounds' miscibility in other SmC matrices is in progress.

CONCLUSION

The correlation between the molecular structure and smectic polymorphism in one of the main problems in designing ferroelectric liquid crystals. It is to be noted that predicting liquid crystalline properties for new materials still remains extremely difficult. This work shows that for the type of molecules investigated the replacement of the alkyl group at the chiral centre by the more polar alkoxy substituents leads to the injection of the chiral SmC properties and inversion of the helix handedness.

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