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INFLUENCE OF FLUORINE SUBSTITUTION FOR HYDROGEN ON THE APPEARANCE OF SmC* PHASE BETWEEN SmA* AND SmC_A* PHASES

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Recently several fluorinated molecules have been investigated by many means [1]. We investigated in details physical properties of two antiferroelectric liquid crystals [2]: MHPB(H)PBC and MHPB(F)PBC.

In MHPB(H)PBC paraelectric SmA phase neighbours antiferroelectric SmC_A* phase, while in MHPB(F)PBC the substitution of fluorine for hydrogen leads to formation of additional narrow ferroelectric phase SmC* phase, placed between the mentioned above phases.*

We also found several other phenomena, namely: increasing of the phase transition temperatures for fluorinated compound in comparison with hydrogenated one, decreasing of the smectic layer thickness, and increasing of spontaneous polarisation.

In our work we focused on the explanation of these phenomena from the molecular point of view using computer molecular modelling.

Keywords: antiferroelectric and ferroelectric liquid crystals; fluorinated molecules; rotational potential

INTRODUCTION

We investigated two antiferroelectric liquid crystals: MHPB(H)PBC and MHPB(F)PBC with phase sequence shown in Table 1.

Substitution of fluorine for hydrogen causes many interesting phenomena. These phenomena should be connected with some kind of intermolecular interactions between fluorine and hydrogen. To explain it,

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TABLE 1 Phase Sequences for MHPB(H)PBC and MHPB(F)PBC

Phase	Cr	SmI_A^*	SmC_A^*			SmA^*	Iso
MHPB(H)PBC	67.0°C	(43.0°C)	92.8°C			116.2°C	
Phase	Cr	SmI_A^*	SmC_A^*		SmC^*	SmA^*	Iso
MHPB(F)PBC	83.5°C	(54.0°C)	121.0°C		123.6°C	128.8°C	

we have made several computer simulations using Hyper Chem 5.0 software.

In many previous publications [3,4] was shown that very important part of molecule for the phase formation as well as the magnitude of spontaneous polarisation, is the rigid central core as well as terminal tail with chiral atom. It seems that terminal tail without chiral centre is very important as well.

EXPERIMENTAL RESULTS

From the experimental data [5] it is seen that when fluorine is substituted for hydrogen the layer thickness decreases although the length of molecule increases (see Table 2).

In our investigations we focused attention on two substances only: MHPB(H)PBC and MHPB(F)PBC. It is worth to underline, that the very similar properties are observed for another fluorinated liquid crystals [5] (Tables 3 and 4). Even if the length of a molecule is similar for both: fluorinated and hydrogenated molecules, layer thickness is much smaller for fluorinated compound.

When we take into account the value of the spontaneous polarization P_S, we [2] and other authors [1,6] could find that substitution of fluorine for hydrogen causes an increasing of the spontaneous polarization magnitude. It is worth to notice that even substitution of just three fluorine atoms for three hydrogen atoms into terminal chain causes more than twofold increase of P_S. P_S as a function of reduced temperature is shown in Figure 2.

TABLE 2 Length of the Molecule and Smectic Layer Thickness

	MHPB(H)PBC	MHPB(F)PBC
Molecule length (Hyper Chem 5.0)	3,779 nm	3,811 nm
SmA^* layer thickness	3,49 nm	3,29 nm
SmC_A^* layer thickness (T_C-T = 20°C)	3,33 nm	3,01 nm
SmC_A^* layer thickness (T_C-T = 30°C)	3,33 nm	3,03 nm

TABLE 3 Length of the Molecule and Smectic Layer Thickness for LC Having CH_3- and CF_3- Terminal Groups Instead of C_3H_7- and C_3F_7- Groups Respectively.

	CH_3-	CF_3-
Molecule length (Hyper Chem)	3,584 nm	3,663 nm
SmA* layer thickness	3,43 nm	3,27 nm
SmC_A* layer thickness [minimum]	—	3,04 nm

The next phenomenon, easy to notice, is that smectic phases are stabilised by fluorine atoms. Phase transition temperatures are shifted into higher temperatures region.

From our previous study we found that perpendicular components of dipole moments are almost the same [2]. We can conclude that the source of the spontaneous polarisation might be rather connected with the intermolecular interactions, which can modify rotational potential, than with dipole moments values.

COMPUTER SIMULATIONS RESULTS

To find differences in behaviour of hydrogenated as well as fluorinated molecules we used Hyper Chem 5.0 molecular modelling software.

First shape of molecules was optimised. Results are presented in Figures 3 and 4.

After this we put 6 molecules together to establish virtual SmA* phase. After optimisation we put these molecules into virtual 200 K bath for several ps. Starting point and final order are presented in Figures 5 and 6, respectively.

One can see that the order is nearly unchanged. After this the 500 K bath was used. The final result is shown in Figure 7. It is worth to notice that virtual SmA* phase still exists. Of course the terminal chains are not

TABLE 4 Length of the Molecule and Smectic Layer Thickness for LC Having C_2H_5- and C_2F_5- Terminal Groups Instead of C_3H_7- and C_3F_7- Groups Respectively

	C_2H_5-	C_2F_5-
Molecule length (Hyper Chem)	3,714 nm	3,712 nm
SmA* layer thickness	3,40 nm	3,16 nm
SmC_A* layer thickness [minimum]	3,37 nm	2,94 nm

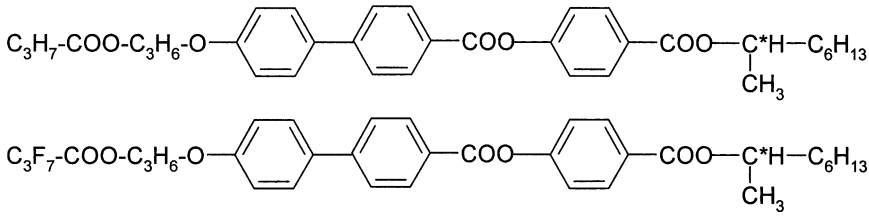

FIGURE 1 Molecular structure of MHPB(H)PBC and MHPB(F)PBC.

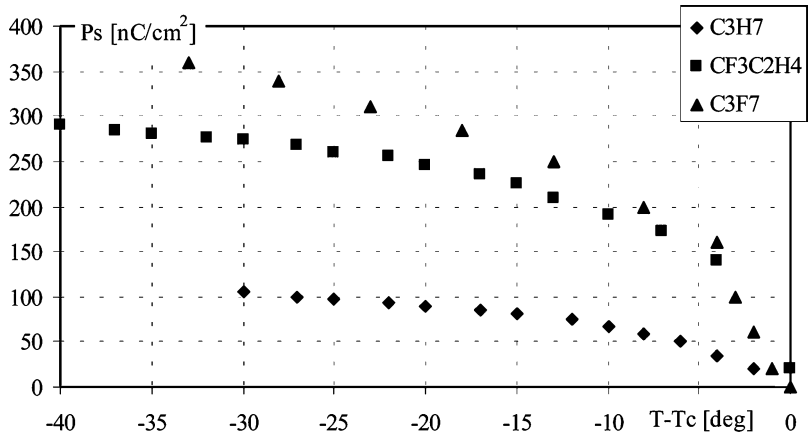

FIGURE 2 Results of the spontaneous polarization P_S for MHPB(H)PBC (C3H7) and MHPB(F)PBC (C3F7) compared with P_S for LC with a little modified terminal chain: $CF_3C_2H_4$ instead of C_3H_7 (CF3C2H4).

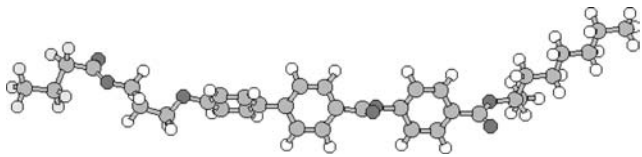

FIGURE 3 Optimised shape of MHPB(F)PBC molecule (Hyper Chem 5.0 MNDO-method).

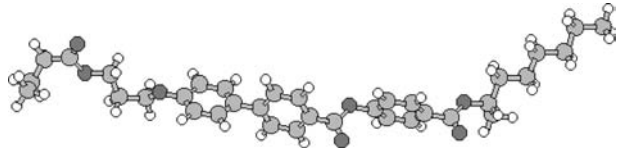

FIGURE 4 Optimised shape of MHPB(H)PBC molecule (Hyper Chem 5.0 MNDO-method).

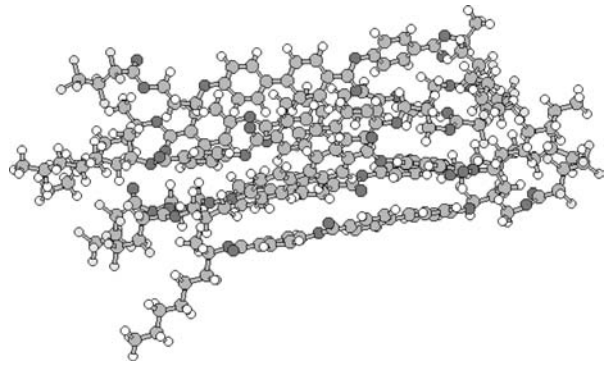

FIGURE 5 Starting point for parallel orientation of six MHPB(F)PBC molecules.

parallel to the rigid cores of molecules as it was after 200 K bath, due to thermal motions.

Exactly the same simulation was prepared for six MHPB(H)PBC molecules. It is seen that for 200 K the order is like in SmA* phase (Fig. 9)

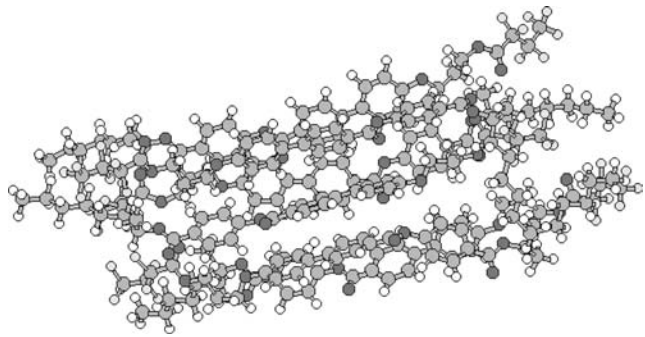

FIGURE 6 The final order after 5 ps virtual bath (200 K) for six MHPB(F)PBC molecules.

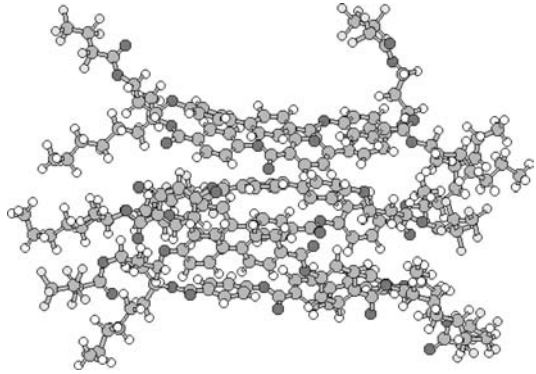

FIGURE 7 The final order after 5 ps virtual bath (500 K) for six MHPB(F)PBC molecules.

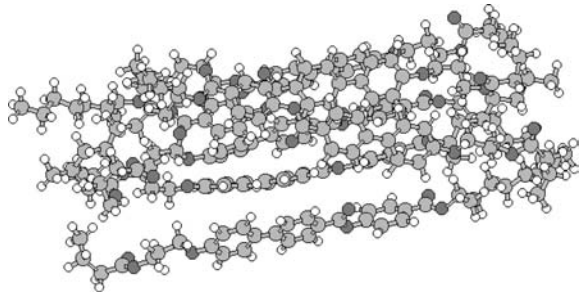

FIGURE 8 Starting point for parallel orientation of six MHPB(H)PBC molecules.

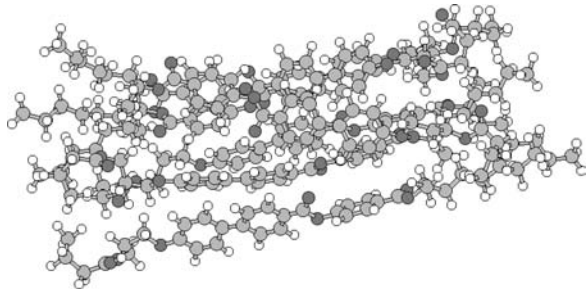

FIGURE 9 The final order after 5 ps virtual bath (200 K) for MHPB(H)PBC molecules.

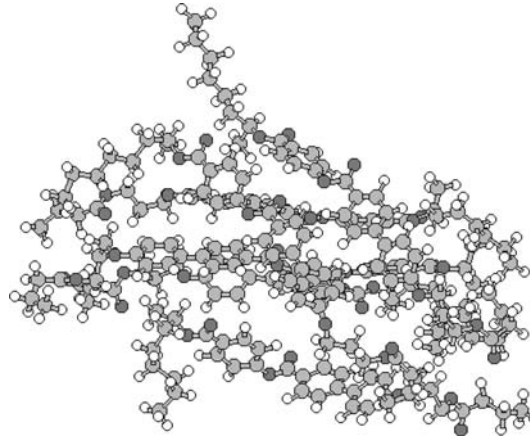

FIGURE 10 The final order after 5 ps virtual bath (500 K) for MHPB(H)PBC molecules.

but for 500 K bath hydrogenated molecules are more disordered (Fig. 10) than fluorinated ones (Fig. 7).

CONCLUSIONS

It seems that rigid parts of molecules are more ordered for fluorinated molecules than for hydrogenated in smectic phases. Of course for low temperature (200 K) there is no special difference but for higher temperature (500 K), forces are strong enough only for fluorinated compound to keep all molecules together.

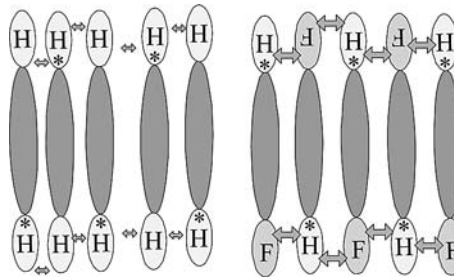

FIGURE 11 Forces between hydrogenated terminal chains are weaker than forces between hydrogenated and fluorinated chains, it is why smectic phases are more stable in case of fluorinated compound.

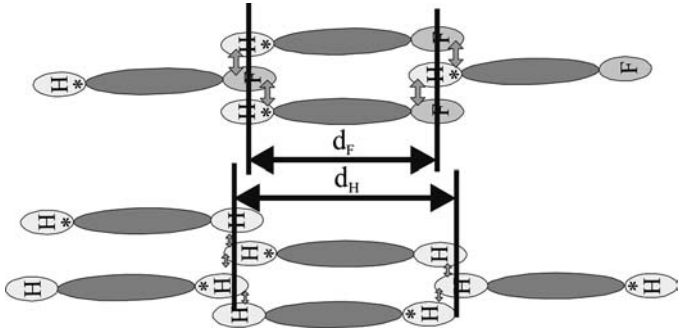

FIGURE 12 Intermolecular interactions H-F as a source of decreasing smectic layer thickness. d_H – layer thickness for MHPB(H)PBC, d_F – layer thickness for MHPB(F)PBC.

It is worth to underline that using the same forces we can explain smaller smectic layer thickness for fluorinated LC (Fig. 12).

Because both molecules have the same central rigid parts, it seems that the main reason of high value of P_S are the interlayer interactions - not dipole interactions between rigid parts.

When we compare distances between rigid parts and distances between terminal chains we can see that interactions between rigid parts are less important than interactions between terminal chains (Fig. 13).

The last problem is: why SmC* is created between SmA* and SmC_A* for fluorinated molecules?

The factor responsible for the phase creation is difficult to define at the moment. Experimental facts are as follows. For asymmetry between terminal chains, molecules for high temperatures prefer synclinic (SmC*) than anticlinic (SmC_A*) orientation. For hydrogenated molecules

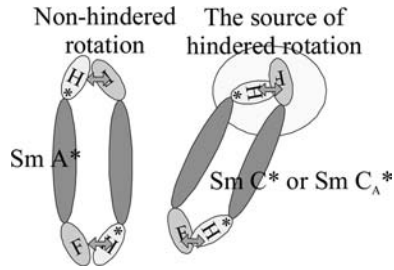

FIGURE 13 Interactions between terminal chains as an important source of spontaneous polarization.

interactions between molecular terminal chains are weaker and anticlinic structure is created at once. For fluorinated molecules interactions between terminal chains are stronger and synclinic structure is formed. As far as we can deduce that intermolecular interactions are important in this phase creation.

It will be the aim of our next investigations.

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