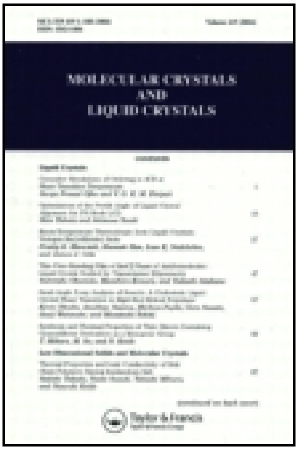

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Esters that Exhibit Smectic F to Isotropic Liquid Phase Transitions

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ESTERS THAT EXHIBIT SMECTIC F TO ISOTROPIC LIQUID PHASE TRANSITIONS

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ABSTRACT:

A number of esters of the type, 4-n-alkanoyloxy 4'-n-octyloxybiphenyl have been synthesized, and shown to exhibit direct isotropic liquid to hexatic smectic F phase transitions on cooling. The natural texture of the smectic F phase characterized by this transition separates from the isotropic liquid in the form of spherulites which have a hexagonal cross of optical discontinuity centered in them. Previously synthesized materials in which the direction of the ester function is reversed exhibit orthogonal hexatic B rather than tilted hexatic phases. This behavior can be linked directly to the extent of the polorization of the delocalized π electrons in the central aromatic core.

INTRODUCTION:

The smectic F phase has been shown by detailed x-ray diffraction studies to possess a three dimensional, stacked hexatic structure.[1,2,3] The hexagonally close packed molecules are tilted towards one edge of this matrix, and the in-plane positional correlation of the molecules is only short range. However, the phase possesses long range bond-orientational ordering. Unlike its tilted analogue S_I[4] the smectic F phase has not been observed on direct cooling from the isotropic liquid, and as a consequence its natural microscopic texture has not been seen. In this study a number of esters have been prepared and were shown to exhibit direct isotropic liquid to smectic F phase transitions.

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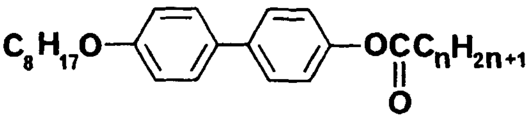
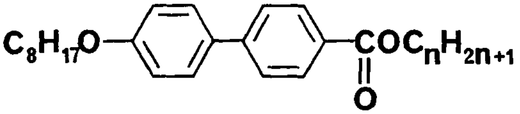
RESULTS AND DISCUSSION:

A number of the n-alkanoyloxy esters of 4-n-octyloxybiphenol were prepared and their liquid crystal phases classified by miscibility methods. The n-alkanoyloxy 4'-n-alkoxybiphenyls (I) were found to exhibit a rich variety of liquid crystal phases, with many of the phases being relatively well-ordered smectic phases, unlike those exhibited by the analogous n-alkyl 4'-n-alkoxybiphenyl-4-carboxylates (II)[5] which exhibit more fluid-like phases. For example, the n-alkanoyl 4'-n-octyloxybiphenyls exhibited direct S_B to isotropic transitions for the earlier members of the series, but the later members exhibited smectic F to isotropic liquid phase transitions. In the analogous n-alkyl 4'-n-octyloxybiphenyl-4-carboxylates, the early members exhibited S_A, $S_B$hex, S_C and S_E phases, but the later members were predominantly S_A in nature. The only real difference in molecular structure of these two types of ester lies in the direction of the ester function. In the latter case the ketone function is conjugated with the delocalized π electrons of the aromatic core, while in the materials (I) under investigation it is not. It is interesting therefore, to compare the transition temperatures of some of the members of these two series.[6]



(I)

n	cryst		S_G		S_F		Iso
9	·	67	·	107	·	108.5	·
11	·	78	·	105	·	108.5	·
13	·	82	·	104	·	108.0	·



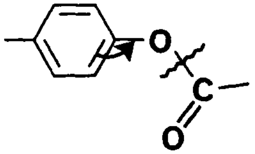
(II)

n	cryst		S_A		Iso
9	·	79	·	80	·
11	·	74	·	79	·
13	·	77	(·	76)	·

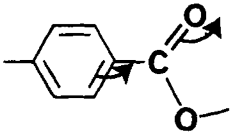
( ) monotropic transition temperature

The steric properties of these two homologous series are very similar, the only real differences arise with the coplanarity of the ester ketone function with the aromatic core. The ketone group is expected, because of its conjugation, to lie in the same plane as the biphenyl core in series (II), but to be allowed to rotate freely and independently of the core in series (I). However, this is only a relatively small perturbation of the overall steric shape of the molecules, and the major differences arise in the extent of the conjugation of the ketone with the delocalized π electrons. In case (II) the ester function interacts strongly with these mobile polarizable electrons while in the other (I) no real interaction is possible.

(I)



(II)



Thus in keeping with previous results,[7] these materials show that small changes in the electronic distribution within the central core have dramatic effects on the phases formed.

TEXTURES OF THE SMECTIC F PHASE:

On separation from the isotropic liquid two distinct types of texture were formed. One was analogous to the focal-conic texture in which spherulites and lancets were produced. The other texture was characterized by the formation of droplets, typically in uncovered supported films of the material. These droplets expanded to form a normal mosaic pattern commonly associated with smectic F phases. In doing so, however, the spherulites or discs went through a stage where they exhibited a hexagonal cross of optical discontinuity (Plate 1). The opposed portions of this hexagonal texture appeared to show a similar birefringence, and therefore they probably possess similar topologies. A possible explanation is that parallel molecular layers are formed into six different orientations which meet at a point singularity, or that the molecules in these segments tilt toward, or away from the singularity, see Fig. 1.

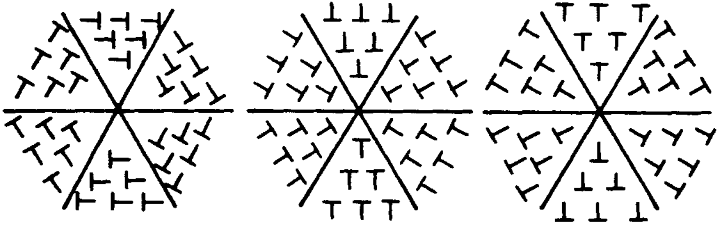
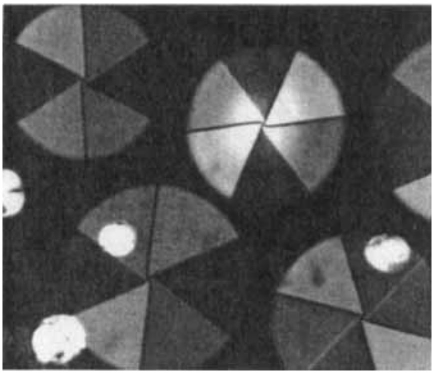


Figure 1

The F phase separating from the isotropic liquid for 4-n-tetradecanoyloxy 4'-n-octyloxybiphenyl (x100)



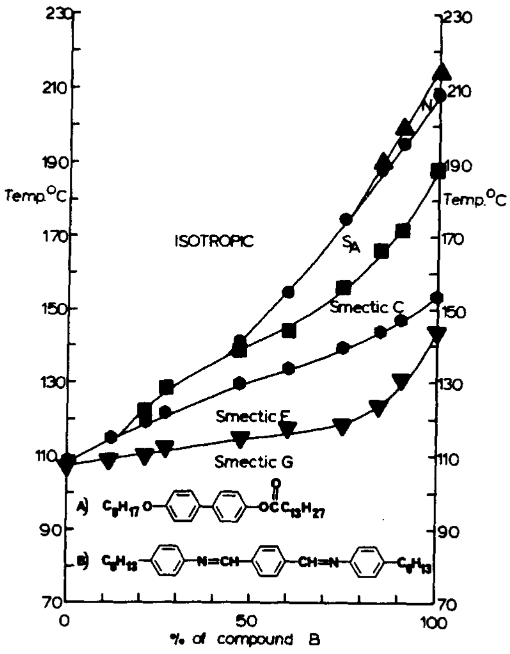
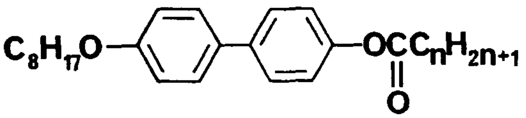


Figure 2

MISCIBILITY STUDIES:

4-n-tetradecanoyloxy 4′-n-octyloxybiphenyl (F and G phases) was shown to be separately comiscible with the F and G phases of the standard material terephthalylidene-bis-4-n-hexylaniline (N,A,C,F, G, and H phases)[8] as shown in Fig. 2. The nematic, A and C phases of the standard material fall away rapidly on the addition of the test material. As approximately 90% by wt. of the test ester in the binary mixture is reached a direct isotropic liquid to S_F transition is observed. The F to G transition temperature curve almost meets the Iso-S_F curve at 100% by wt of the test compound, almost producing a Iso-S_F/S_G phase transition.

DIFFERENTIAL SCANNING CALORIMETRY:



n	ΔHS_F-Iso	ΔHS_F-S_G	ΔH cryst$-S_G$
9	9.25	-+	12.31
11	8.0	-	12.27
13	9.5	-	13.59

+ too small to be detected
values in cal/g

Differential scanning calorimetry of the phase transitions of these esters shows that the isotropic liquid-hexatic F phase transition is first order, but that the S_F-S_G phase change is either weakly first order or second order in nature.

CONCLUSION:

The 4-n-alkanoyloxy 4′-n-alkoxybiphenyls exhibit direct isotropic liquid to smectic F phase transitions. The way in which the mobile electrons of the delocalized aromatic core structure are polarized has a very pronounced effect on phase formation.

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