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Mesomorphic Properties of n-Alkyl-4′-n-Pentanoyloxy-Biphenyl-4-Carboxylates

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Esters in the homologous series n-alkyl-4′-n-pentanoyloxy-biphenyl-4-carboxylates (n4COOBC,n = 1-12) have been synthesized. Mesomorphic properties and phase transitions have been determined using polarizing hot-stage microscopy, DSC and x-ray. Phase transitions from S_A-S_B crystal and hexatic (tentatively) have been observed. The relationship between the incidence of hexatic phase and molecular structure has been discussed.

INTRODUCTION

Smectic B phase has been the subject of many structural investigations in recent years.[1,2] Only recently, however, it has been shown by high resolution x-ray investigation[3] that the smectic B phase exists in several distinct phase modifications—HEXATIC-B and several CRYSTAL-B phases.[4] In the hexatic phase the molecules have short range in-plane positional ordering and long range bond orientational ordering. The crystal-B phases have three dimensional lattices. Compounds exhibiting the stacked hexatic-B phase are of interest because of their scarcity and because of their importance in the study of

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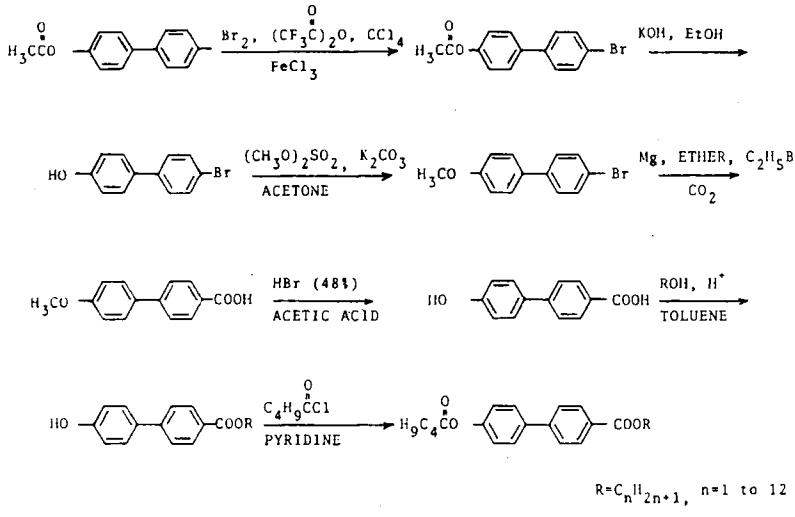
melting.[5] Relatively few homologous series exhibiting this phase have been found. The first stacked hexatic phase found was in n-hexyl-4'-pentyloxybiphenyl-4-carboxylate (65OBC).[3] Several hexatic B phases have since been found in the n-alkyl-4'-alkoxy-biphenyl-4-carboxylate homologous series (nmOBC). High resolution AC calorimetric studies[6] on the smectic A to smectic B hexatic transition of 65OBC indicate a strongly divergent heat capacity and little or no latent heat contrary to the weak pretransitional anomalies and relatively large latent heats at the smectic A-smectic B crystal transition. Our own high resolution calorimetry studies have revealed a strong heat capacity divergence and little or no latent heat for 45OBC and 125OBC as well.[7] In the absence of high resolution freely standing film x-ray studies, high resolution calorimetry should provide the best evidence for the characterization of the hexatic phase where it occurs below smectic A. With a view to studying the effect of relatively small structural modifications on the incidence of the hexatic phase, the new series of esters n-alkyl-4'-pentanoyloxy-biphenyl-4-carboxylates were synthesized and their mesmorphic properties investigated by thermal microscopy, DSC and x-ray photographic techniques.

SYNTHESIS

The compounds were synthesized according to the following scheme:



SCHEME 1

PHYSICAL MEASUREMENTS

The transition temperatures were determined using PERKIN ELMER DSC 4 and the phases were identified using a Leitz polarizing microscope in conjunction with Mettler FP82 hot stage and FP80 control unit. The purity of the compounds were checked by TLC and PERKIN ELMER HPLC. The purity of the compounds as estimated by HPLC was >99.5%. The compounds were characterized by IR PERKIN ELMER 283, NMR EM 360 60MHz. The smectic A and smectic B phases were further characterized by x-ray diffraction.

RESULTS AND DISCUSSION

The transition temperatures for the series n-alkyl-4'-pentanoyloxy-biphenyl-4-carboxylates are given in Table I. The plot of the transition temperatures against the number of carbon atoms (n) in the ester chain is given in Figure 1. All the members of the series exhibit smectic mesomorphism except 12. The compounds 3-9 exhibit enantiotropic smectic A phases while the compounds 1 and 2 exhibit enantiotropic smectic B phases. Compounds 3-9 exhibit both the smectic B and the smectic A phase. On cooling from the isotropic liquid they go over

TABLE I

Transition temperature (°C) for n-alkyl-4'-n-pentanoyloxy-biphenyl-4-carboxylates

n	K	SB_1	SB_2	SB_3	S_A	I
1	.	86.5 .	112 .			116 .
2	.		96 .			100 .
3	.			59.6	63.3	81 .
4	.	60.3 .	63.4 .		64.9 .	74.4 .
5	.	49.7 .	52.8 .		55.4 .	70.2 .
6	.		49.1 .		56.7 .	68.4 .
7	.		47.3 .		52.6 .	66.6 .
8	.		[52.3 .]		61.4 .	64.9 .
9	.			[48.4 .]	49.6 .	61.8 .
10	.				[60.2 .]	68.4 .
11	.				59.5 .	62.8 .
12	.					75 .

. Phase Exists
[] Monotropic
SB_1 Unidentified Smectic
SB_2 Crystal B
SB_3 Hexatic B (Tentatively)

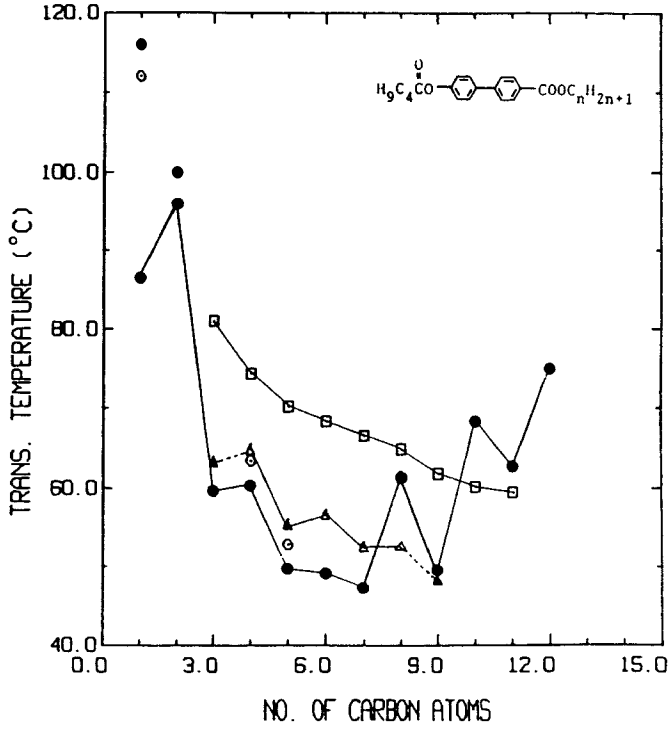


FIGURE 1 Plot of the transition temperature against the number of carbon atoms (n) in the n-alkyl chain of n-alkyl-4'-pentanoyloxybiphenyl-4-carboxylates. Key: K - Mesophase or K—I

□—I - S_A
△—S_A-S_{B2}
▲—S_A-S_{B3}
⊙—S_{B2}-S_{B1}
⊕—I-S_{B2}
●—Melting

to the smectic A focal conic fan texture via the formation of batonnet's. On further cooling, fan texture remains the same but for n = 4 to 8 one sees weak transition bars appearing at the phase transition from smectic A to smectic B, while n = 3 and 9 do not. X-ray investigations on compound 6 suggest that the phase transition is from S_A to S_B crystal. The x-ray photograph of 6 showed graininess in the inner ring and spots in the outer ring. On cooling compounds 3 and 9 into the smectic B phase we observed no transition bars, but on warming back to the smectic A we observed parabolic focal conic defects, suggesting the stacked hexatic B phase. These "wishbones" were suggestive of a smectic A to hexatic B transition[8] and the x-ray

photographs of these compounds supported this in that they showed no graininess in the inner ring and no spots in the outer ring. The comparison of the x-ray photographs with that of 65OBC showed great similarities in that both rings were structureless and comparably diffuse. Nevertheless, only high resolution x-ray studies on freely suspended films can give a definitive result.[3]

Compound 1 on cooling from the isotropic phase gives rise to mosaic platelets with the mosaic texture of the smectic B phase. This on further cooling goes over to another phase which still has the mosaic texture but now much more colorful. In view of the fact that this mosaic phase is obtained from the uniaxial smectic B phase, and by comparison with known textures it is tentatively assigned as the S_G-phase.

The transition enthalpies for the series n-alkyl-4′-pentanoyloxy-biphenyl-4-carboxylates is given in Table II. The plot of the transition enthalpies against the number of carbon atoms (n) in the ester chain is given in Figure 2. The transition enthalpies associated with the S_A to S_B crystal and S_A-S_B hexatic are not significantly different.

Hexatic B phase is mostly exhibited by compounds containing —COO—linkage while compounds containing —CH=N and —COS-linkages usually exhibit crystal B phase. The importance of dipolar effects for the incidence of the hexatic phase has been recognized[9] and the same, as opposed to shape effects, has been invoked as

TABLE II

Transition enthalpies (Kcal/m) for n-alkyl-4′-n-pentanoyl-oxybiphenyl-4-carboxylates

n	K	SB_1	SB_2	SB_3	S_A	I
1	. 4.77	. 0.56	.			2.89 .
2	.	6.51				2.70 .
3	.		5.86	.	0.26 .	1.46 .
4	. 4.04	. 0.02	.		0.33 .	1.85 .
5	. 6.27	. 0.01	.		0.27 .	1.44 .
6	.	7.9	.		0.30 .	1.41 .
7	.	4.2	.		0.33 .	1.47 .
8	.	[0.32	.]		10.9 .	1.52 .
9	.		[0.32	.]	9.6 .	1.44 .
10	.				[1.5 .]	13.84 .
11	.				15.7 .	4.25 .
12	.					16.68 .

. Phase Exists
[] Monotropic
SB_1 Unidentified Smectic
SB_2 Crystal B
SB_3 Hexatic B (Tentatively)

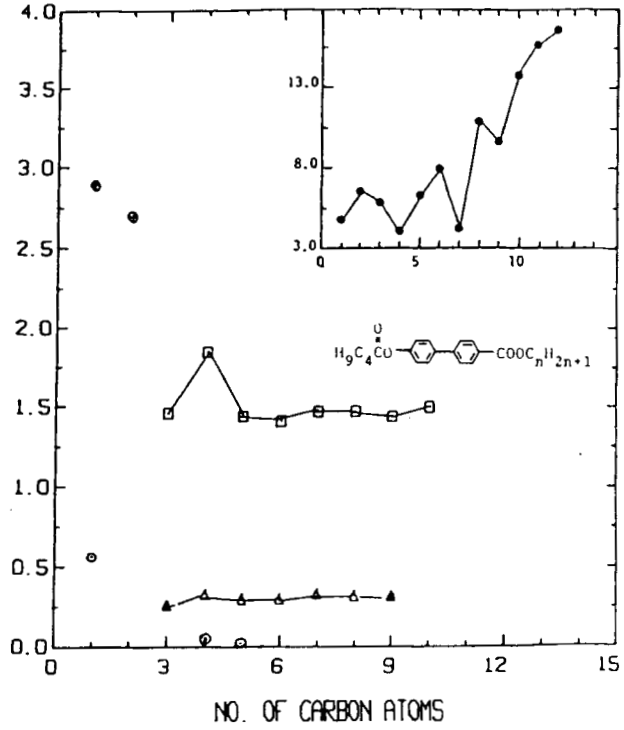
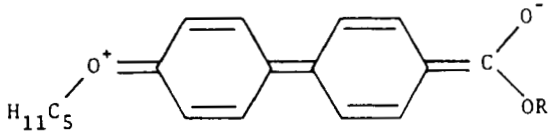


FIGURE 2 Plot of the transition enthalpy against the number of carbon atoms (n) in the n-alkyl chain of n-alkyl-4′-pentanoyloxybiphenyl-4-carboxylates. Key: K—Mesophase or K-I

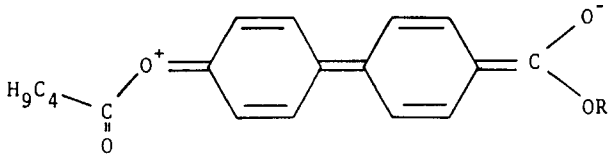
□—I-S_A
△—S_A-S_{B2}
▲—S_A-S_{B3}
⊙—S_B-S_{B1}
⊕—-I-S_{B2}
●- Melting

necessary to the hexatic phase exhibited by compounds in the series n-alkyl-4′-n-alkyloxybiphenyl-4-carboxylates (nmOBC). In these compounds, the presence of an alkoxy group and ester group in the 4 and 4′ positions of the central biphenyl moiety contributes to the reasonably stable canonical structure.



STRUCTURE-1

Thus, there is the polarization of electrons towards the ester function increasing its overall lateral dipole-moment. In the new series investigated (n4COOBC), the alkonoyloxy group and the ester group occupy the 4 and 4′ positions of the central biphenyl moiety. The mesomeric structure in these compounds



STRUCTURE-2

would be destabilized by the presence of the acyloxy group. Hence, the strength of the lateral dipole moment will be much less. The incidence of hexatic phase (only tentatively assigned here) in these compounds would be significant because the lateral dipole moment is very much reduced. We are currently investigating them by high resolution A.C. microcalorimetry. The results will be published elsewhere.

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