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A S_A-S_{CH} TRANSITION - THE PROBLEMS OF PHASE ASSIGNMENT

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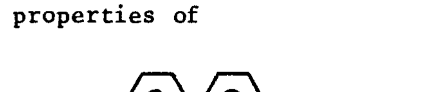
Abstract: Re-examination of the smectic polymorphism of certain n-alkyl esters of some 4'-n-alkoxybiphenyl-4-carboxylic acids, by X-ray and miscibility techniques has shown a further phase to be present. This extra phase is proved to be a tilted smectic B (S_H) phase. One of the esters, n-butyl 4'-n-octyloxybiphenyl-4-carboxylate, is shown to exhibit S_A, S_C and SB_C (S_H) phases, but the S_C phase is so extremely short-lived that the impression is that the ester exhibits a S_A-S_{CH} transition.

Introduction: Previously,[1,2] we reported the smectic polymorphic behaviour of a number of the n-alkyl 4'-n-alkoxy-biphenyl-4-carboxylates. Particular importance was attached to the smectic properties of



n-butyl 4'-n-octyloxybiphenyl-4-carboxylate. This ester was shown by miscibility studies to exhibit S_A and S_C phases and to have latent S_B characteristics.

Results: Firstly, we will consider the properties of n-butyl 4'-n-octyloxybiphenyl-4-carboxylate, because a large number of results for other materials are directly linked to this ester. The S_C phase of this material was confirmed by its co-miscibility with the S_C phase of the standard[3] 4-n-octyloxybenzoic acid (N and S_C phases). Secondly, the ester was shown to exhibit a S_A phase and to have latent S_B characteristics by a miscibility study with the standard[4] n-nonyl 4-(4'-phenylbenzylideneamino)cinnamate. At the time of this study it was believed that the orthogonal B and tilted B phases were miscible; therefore the fact that the material exhibited latent S_B properties led us to exclude the possibility of its exhibiting a tilted B phase.

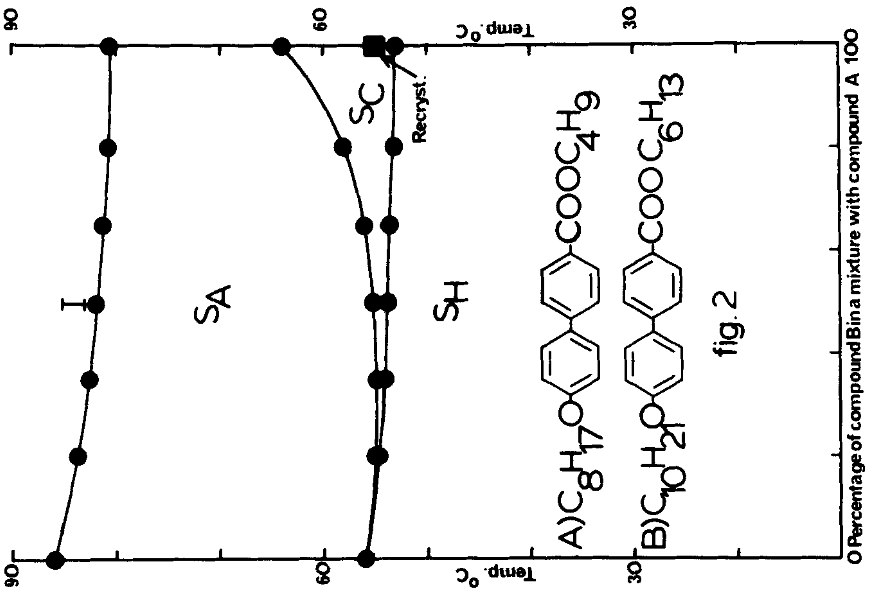
However, X-ray studies and further more elaborate miscibility studies have shown that the ester does exhibit a tilted B phase. Firstly a study was carried out with the standard cyclohexyl 4'-n-octyloxybiphenyl-4-carboxylate (S_A and S_C phases). The miscibility diagram of state for binary mixtures of these two materials is shown in Figure 1. This diagram of state shows that the ester does exhibit a S_A phase and that the S_A to S_C and S_C to S_H transition temperature lines approach each other tangentially as the percentage of the test ester is increased. A surprising injection of S_F properties also occurred in mixtures of approximately 50% by weight of each component.

A number of other studies were carried out to confirm that the lower temperature phase of the n-butyl ester was of the tilted B or H type and these will be presented in a subsequent more detailed account.

A second miscibility diagram of state for mixtures of n-butyl 4'-n-octyloxybiphenyl-4-carboxylate with n-hexyl 4'-n-decyloxybiphenyl-4-carboxylate (S_A and SC phases) is however, shown in Figure 2. This miscibility study again shows that the n-butyl ester exhibits a well-defined S_A phase along with an extremely short-lived S_C phase, which quickly changes to S_H. The n-hexyl ester is therefore confirmed as a S_A, S_C material, but it also has latent, tilted B (S_H) characteristics.

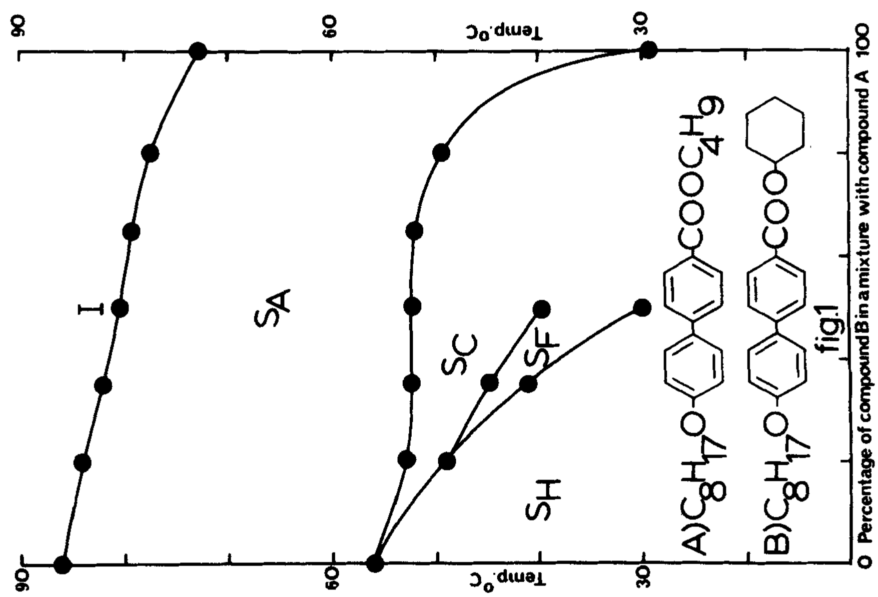
The lowest temperature phase of the n-butyl ester was also studied by X-ray techniques, and the results were fundamental to our present re-examination of this ester. The X-ray diffraction pattern for the tilted B phase (S_H) is shown in Plate 1.

The sample was contained in a Lindemann glass tube and was at a temperature of 45°. Filtered Cu K_α radiation was used. The sharp inner reflections and the single sharp outer reflection of this photograph are characteristic of B type smectic structures.[5,6] The inner reflections correspond to



90
60
30
Temp. °C
I
S_A
S_C
S_H
Recryst.
A) $C_8H_{17}O$-⟨⟩-⟨⟩-$COOC_4H_9$
B) $C_{10}H_{21}O$-⟨⟩-⟨⟩-$COOC_6H_{13}$
O Percentage of compound B in a mixture with compound A 100

fig. 2



90
60
30
Temp. °C
I
S_A
S_C
S_F
S_H
A) $C_8H_{17}O$-⟨⟩-⟨⟩-$COOC_4H_9$
B) $C_8H_{17}O$-⟨⟩-⟨⟩-COO-⟨⟩
O Percentage of compound B in a mixture with compound A 100

fig.1

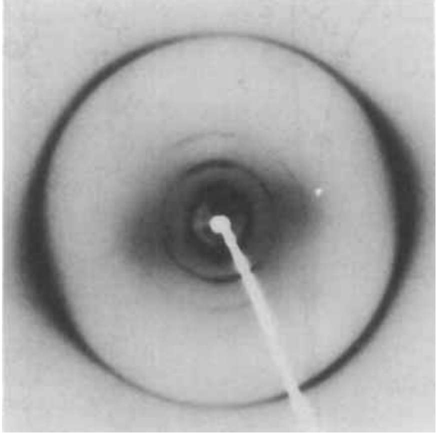


PLATE 1. *The X-ray diffraction pattern of n-butyl 4'-n-octyloxybiphenyl-4-carboxylate. The photograph was taken with a temperature-controlled camera specially designed for liquid crystal studies.**

three diffracted orders from the layer spacing. They indicate a layer thickness of 27.2 (+0.1) Å. This value is significantly less than the length of the fully extended molecule (29.0 Å, as estimated from molecular models) and it implies that there is some degree of interlayer penetration of molecules and/or that the molecules are tilted within the layer. The single outer reflection corresponds to a spacing of 4.41 Å and is very much in accordance with previous observations of the S_B phases of molecules with similar cross-section. It can be seen that the line joining the maxima of the outer ring is not exactly perpendicular to the line joining the maxima of the inner rings. The discrepancy is about 7^o, and this is a further indication that the molecules are tilted in the layers. Although we made no attempt to orientate the sample, the photograph shows that

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* Coakley and Lydon, *J Phys E, Sci Instr*, 1977, *10*, 296

a considerable degree of orientation has occurred spontaneously with both the outer and the inner rings showing arcs of maximum intensity.

Discussion: From this work it has been shown that n-butyl 4'-n-octyloxybiphenyl-4-carboxylate exhibits S_A, S_C and S_{B_C} (S_H) phases, but since the S_C phase is extremely short, the material appears to exhibit a S_A-S_{CH} transition. The consequences of this are extremely far-reaching. This material can in fact exhibit dual properties as far as miscibility techniques are concerned, ie, it can act as both a standard S_C and a standard S_H material. Bearing this fact in mind, it has been shown that the appropriate n-alkyl esters of 4'-n-heptyloxybiphenyl-4-carboxylic acid are S_H and *not* S_C in type, the esters of 4'-n-nonyloxybiphenyl-4-carboxylic acid exhibit S_C *and* S_H phases, and finally the esters of 4'-n-decyloxybiphenyl-4-carboxylic acid are S_C in type (as previously reported).

Therefore, the assignment of phase types by either miscibility or X-ray techniques *alone* is obviously inadequate. In the first report of the phase behaviour of n-butyl 4'-n-octyloxybiphenyl-4-carboxylate, the phases were identified using materials showing N, S_C phases and S_A, S_B, S_E phases. As the S_C phase is so short-lived, obviously these studies were inadequate. However, if studies are carried out using a S_A, S_C, S_H standard material, the identification of the S_H phase is made difficult by the injection of S_{B_A} properties which usually accompanies such studies. Moreover, any assignment of phase type based on the 'apparent' miscibility[7] of the S_H phase of the n-butyl ester and the S_{B_A} phase of a standard material, is also made difficult due to the lack of transition bars at the S_A to S_{B_A} transition for binary mixtures of these types of material. Therefore, clearly the choice of a *number* of miscibility standards is important.

Our miscibility studies were carried out by weighing out mixtures on a microscope slide and determining the transition temperatures by optical microscopy. If, however, the contact technique had been used, the S_A-S_{CH} transition would not have been detected and hence further problems would have occurred in later miscibility studies.

A similar situation would have occurred using identification by X-ray methods only; again the true nature of the S_A-S_{CH} transition would have been missed and the phase assignment would have been SA, S_{B_C} (SH). Since a number of these double transitional types are now being discovered,[8,9] eg, S_{AB}-I, S_A-S_{BE} etc, careful analysis is required by a number of techniques in order to identify correctly the phase types involved. For *absolute* identification of phase sequences and types, optical microscopy, miscibility studies and detailed X-ray analysis are *all required*.

Experimental: The transition temperatures of the pure materials and the binary mixtures used in the miscibility studies were determined by optical microscopy using a Mettler FP52 hot-stage and control unit.

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