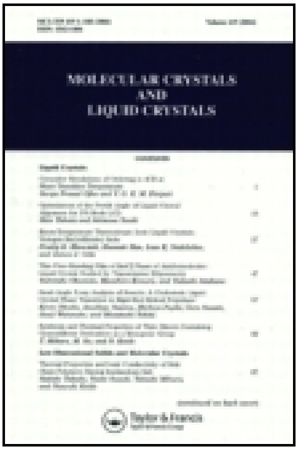

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Classification of the Smectic Phases of n-Pentyl 4-[4'-n-dodecyloxybenzylideneamino] cinnamate. The System of Smectic I Phases

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Classification of the Smectic Phases of *n*-Pentyl 4-[4′-*n*-dodecyloxybenzylideneamino] cinnamate. The System of Smectic I Phases.†

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The liquid crystal polymorphism of *n*-pentyl 4-[4′-*n*-dodecyloxybenzylideneamino] cinnamate, AABC (12.5), has been reconsidered. The revised variant of smectic polymorphism GICA has been found. All earlier investigations on miscibility with AABC (12.5) were critically examined. Incorporating the latest results, a summary of the spread of the occurrence of the phase type I is given. Smectic I phases are always the high temperature modifications in systems having ordered and tilted layer structures in a general temperature sequence HGFI.

1 INTRODUCTION

The first substances with smectic I phases were found in the homologous series of terephthalylidene-bis-[4-*n*-alkylanilines] (TBAA). In the members with $n = 9$ and $n = 10$ carbon atoms in the side chains, these phases appeared on the temperature scale between the F and C phases in a variant of polymorphism GFICA. First communications have already been made in summarizing congress reports.[1-3] The original and detailed results have been published in Refs. 4, 5.

Later, the Halle Liquid Crystal Group reported on the appearance of I phases in the homologous series of 4,4′-bis-[*n*-alkylamino]biphenyls[6] and

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†Paper no. 26: Relations of Isomorphism in Liquid Crystalline Phases; no. 25. see Ref. 5.

4-*n*-nonyl-4′-*n*-alkyloxyazobenzenes.[7] In these reports, the *n*-pentylester of 4-[4′-*n*-dodecyloxybenzylideneamino]cinnamic acid, AABC (12.5), served as a standard substance for I phases.

In earlier reports this I phase of AABC (12.5) was denominated as a B phase. The investigations which led to this change in the denomination will be discussed here. The consequences of this change for all the earlier investigations on miscibility in which AABC (12.5) was used will be examined.

On the basis of this check a summary of all I phases which are known so far will be given.

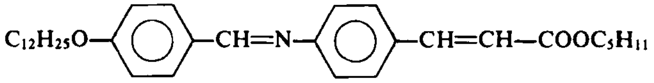
2 METHODS AND MATERIALS

The binary diagrams were investigated by hot stage microscopy. Separate preparations with unique concentrations of the components were used, and complementary investigations with contact preparations were made.

A phase symbol in parenthesis means the existence of a liquid crystal phase in a metastable region with respect to the crystalline solid phase.

Materials

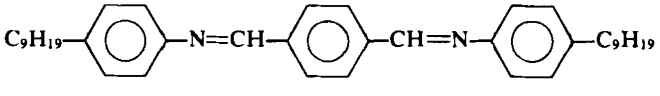
1) *n*-Pentyl 4-[4′-*n*-dodecyloxybenzylideneamino]cinnamate AABC (12.5)



Cr 73.9 (G ~ 71) I 95.0 C 106.7 A134.2 Is; newly synthesized material; new classification according to the results in section 3. The classification according to the earlier results[8] was Cr 73.9 B 95.0 C 106.7 A 134.3 Is.

2) Ethyl 4-[4′-ethoxybenzylideneamino]cinnamate AABC (2.2)
Cr 80.3 B 119.7 A 158.3 N 164.9 Is; standard substance for B phases; classification in Refs. 9, 10.

3) Terephthalylidene-bis-[4-*n*-nonylaniline] TBAA (9)



Cr 57.3 G 132.5 F 155.5 I 157.5 C 192.7 A 199.0 Is; classification see Refs. 4, 5.

3 THE POLYMORPHISM OF *n*-PENTYL 4-[4′-*n*-DODECYLOXYBENZYLIDENEAMINO]CINNAMATE

In 1968 the polymorphism of AABC (12.5) was tested by miscibility with the standard substance for B phases.[8] According to Figure 1, the miscibility relations yielded the polymorphism BCA.

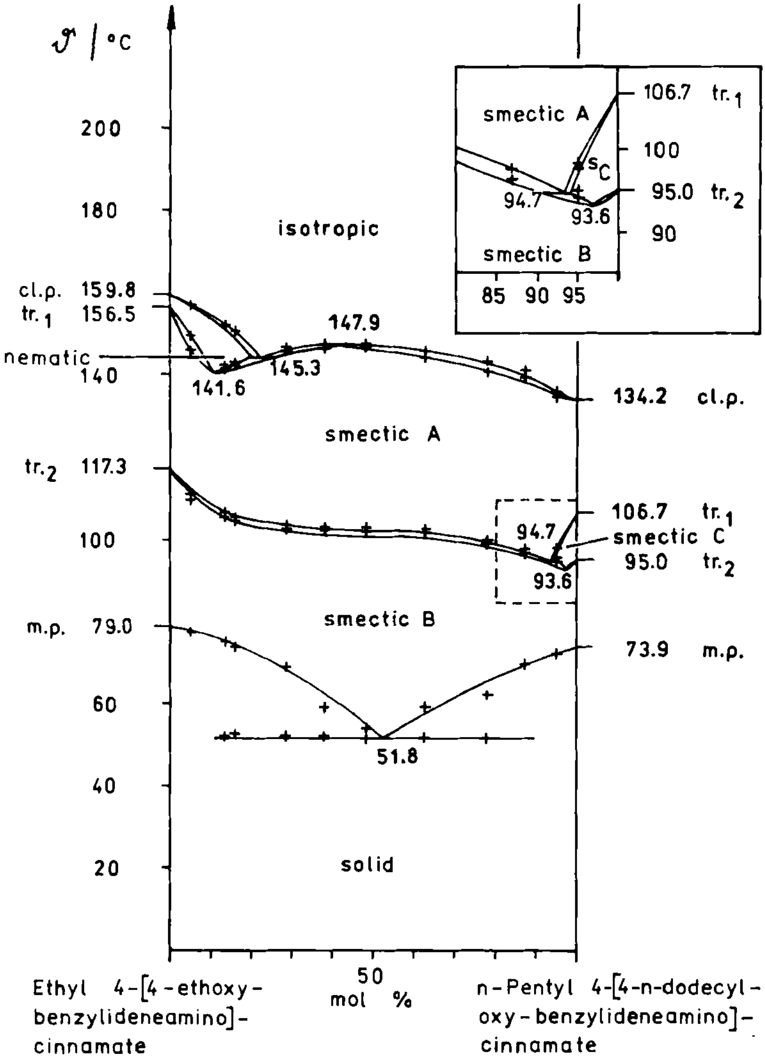


FIGURE 1 Binary phase diagrams for AABC (2.2) and AABC (12.5) earlier results.[8]

In order to test the relations between I and B phases, the miscibility between AABC (12.5) and the nonyl compound of the TBAA series was investigated. The results of this test are shown in Figure 2. There is an uninterrupted miscibility between the three high temperature modifications of the two compounds. The mixed phases F, starting from TBAA (9), have only a limited existence with concentration and temperature. The existence of the mixed phases G could also be observed in the supercooled region, and indicated the

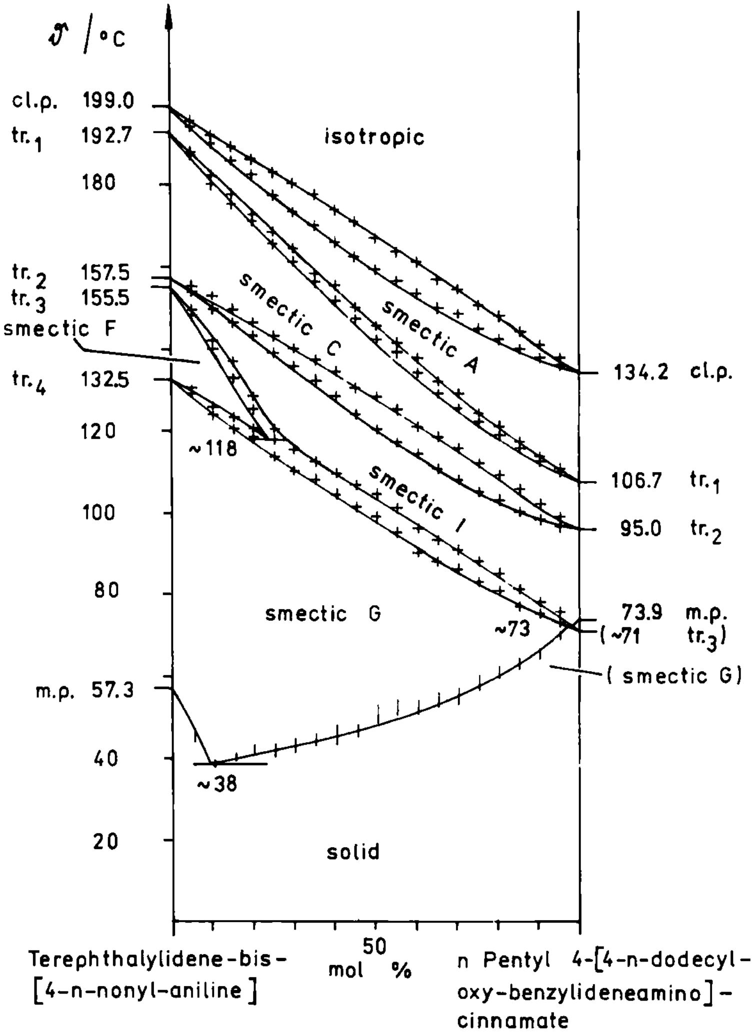


FIGURE 2 Binary phase diagram for TBAA (9) and AABC (12.5).

existence of a metastable G phase in AABC (12.5); this could also be observed in the pure substance.

The uninterrupted miscibility between the phases named I in Figure 2 contradicted either the denomination B of the third phase in AABC (12.5) (Figure 1), or the denomination I for the third phase in TBAA (9). Because of the existence of tilted layer structures in the phases of both TBAA (9)[11] and AABC (12.5),[12] and of a layer structure with perpendicular orientation of the molecular long axes in AABC (2.2),[13] a reinvestigation of the binary system (Figure 1) was essential.

The result of this reinvestigation is shown in Figure 3. Especially the regions of existence of the three mixed phases A, B, and C were observed. Now the existence of a miscibility gap which falls strongly with decreasing temperature in a small concentration interval has been found.

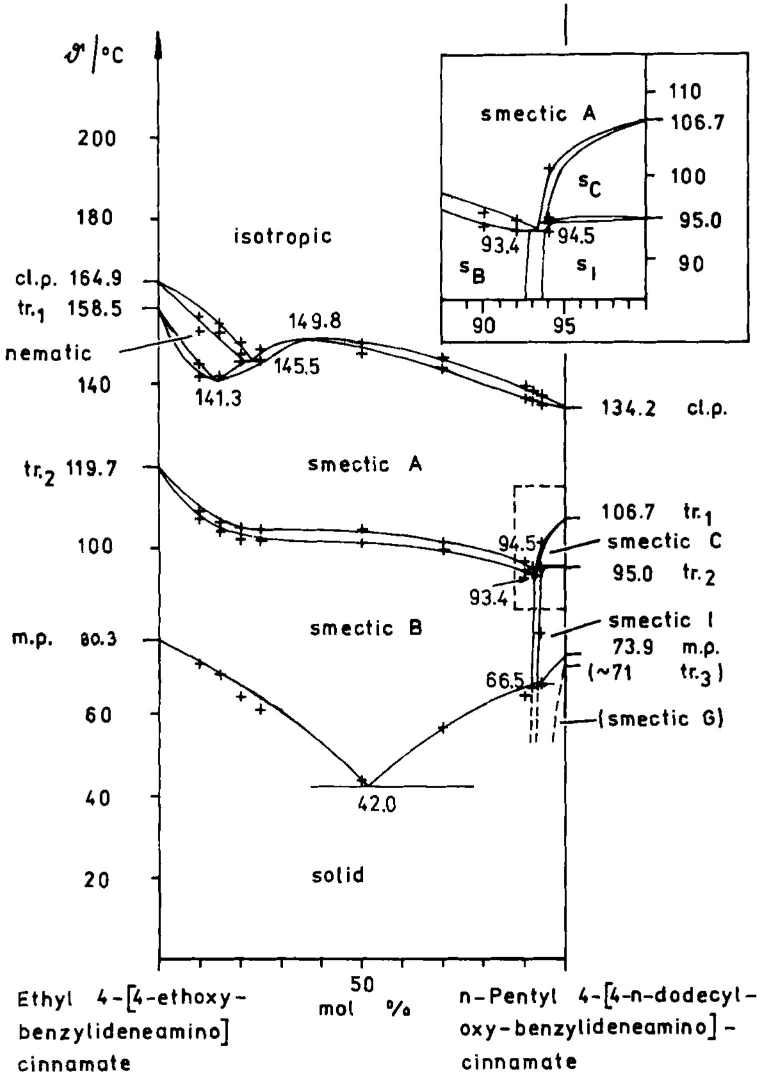


FIGURE 3 Binary phase diagram for AABC (2.2) and AABC (12.5).

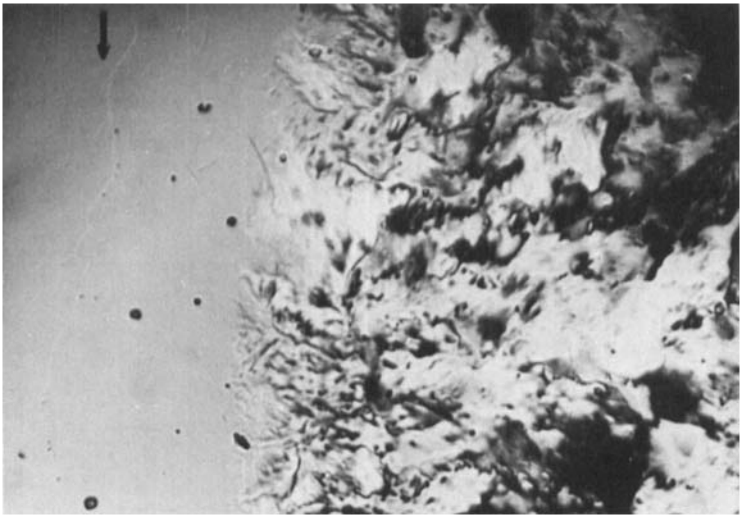


FIGURE 4 Contact preparation for AABC (2.2)-AABC (12.5) × 160, 95.3°C.

The existence of the phases in the region of the transitions between the phases A, C, B, and I can be seen in the textures of the isothermal contact preparations (Figures 4–7).

In Figure 4, a small clear line (see arrow) separates the homeotropic phases B and A. The phase A is separated from a schlieren texture of the C phase. In Figure 5, parts of the schlieren texture of the phase C pass over to a schlieren

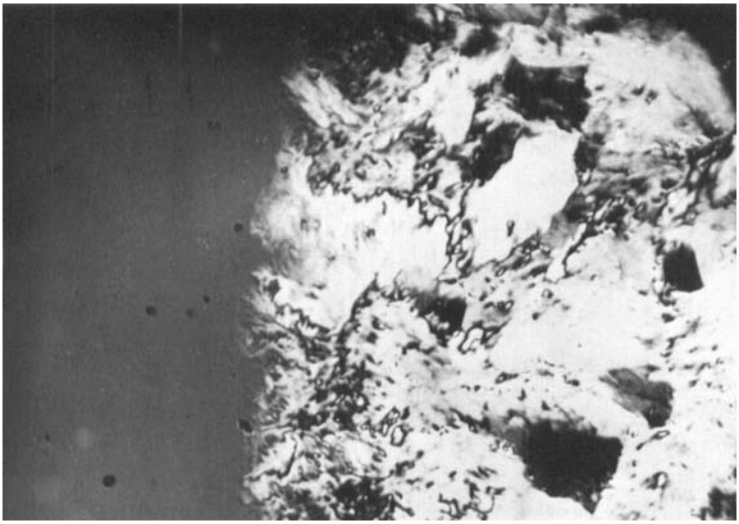


FIGURE 5 Contact preparation for AABC (2.2)-AABC (12.5) × 160, 95°C.

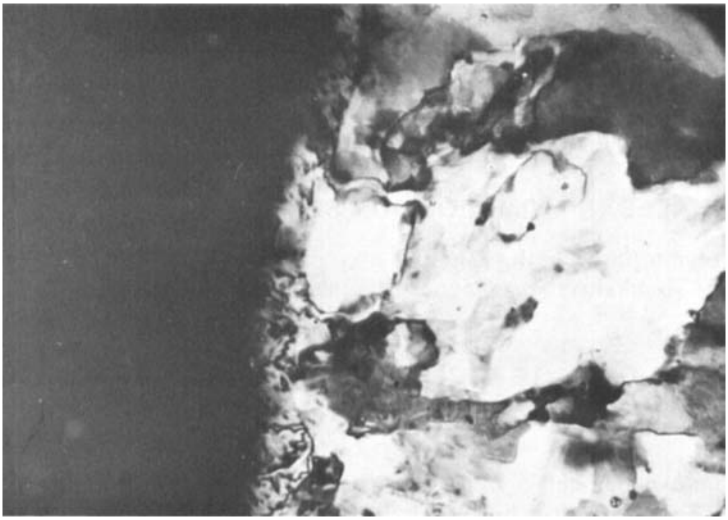


FIGURE 6 Contact preparation for AABC (2.2)-AABC (12.5) × 160, 94.8°C.

texture of phase I. In Figure 6, a small phase region C (in the middle) separates the I phase on the right from the homeotropic A and B phase regions. In Figure 7, the C phase has disappeared. Only homeotropic regions of the phase B and a phase region I, which has a partly mosaic-like texture, can be seen.

In this way, the small miscibility gap between the two mixed phases B and I

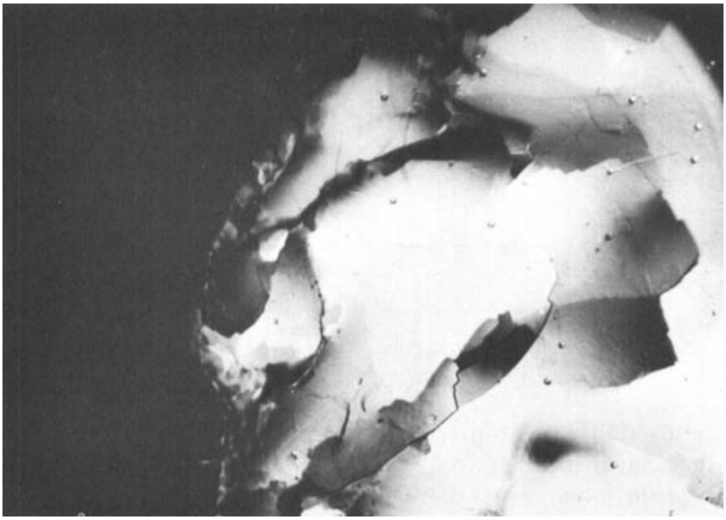
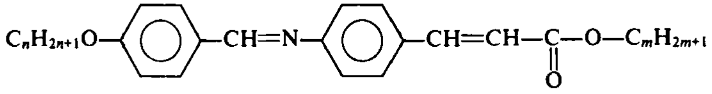


FIGURE 7 Contact preparation for AABC (2.2)-AABC (12.5) × 160, 85°C.

was proved. This region, being placed at higher concentrations of AABC (12.5), could not be found in the earlier investigation (Figure 1). According to the results for the system TBAA (9)-AABC (12.5) (Figure 2), AABC (12.5) possesses the polymorphism (G) ICA.

4 I PHASES IN HOMOLOGOUS SERIES

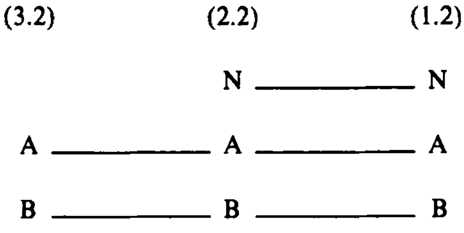
4.1 Polymorphism in the series of Alkyl 4-[4'-*n*-alkyloxybenzylideneamino]cinnamates (AABC)



In the known members of these series (derived by variation of *n* and *m*) a smectic trimorphism was the highest smectic polymorphism found.[14] The variants of all known members seemed to be derivable from a general variant BCAN. As standards in miscibility experiments, the esters AABC (2.2) and AABC (12.5) have been used. Besides investigations of miscibility, the trends of the transition temperatures in the series and texture observations were used for phase classification.

The new classification of AABC (12.5) described in section 3 now demands a re-examination of these earlier results.

Smectic BA dimorphism was proved according to the complete miscibility found in the binary systems with the members of the series AABC (3.2)-(2.2)[15] and (2.2)-(1.2).[9] The results are cited in the following scheme



(The lines represent complete miscibility between two phases with the same symbol).

The trends of the transition temperatures[15] between the two smectic phases in the other known members (4.2), (5.2), (6.2), and (9.2) allow us to assume the presence of the polymorphism BA in the series (*n*.2).

In the members (12.5), (10.5), (9.5), smectic trimorphism was found.[8] The texture observations and the trends of the transition temperatures for these neighboring members allowed a transfer of the phase code from (12.5) to (10.5) and (9.5). Therefore (10.5) and (9.5) should now have the variant of polymorphism ICA according to the results in section 3.

In the compound (8.5), only two smectic modifications were observed. The miscibility in a binary system with the trimorphic (9.5) compound (ICA) showed complete miscibility between the phases A and between the low temperature modifications.[16] Therefore the polymorphism of (8.5) now should be IA.

However, a first renewed check of the diagram by texture observations of contact preparations showed an inhomogeneity in the mixed phase region for the low temperature phases (Figure 8). From left to right with increasing concentration of (8.5), a striped mosaic texture changes to a pseudomorphic fan-shaped texture with a diminished number of discontinuities; this characterizes a B phase.

This represents the existence of an interrupted miscibility which was not found in the earlier investigations.[8] The existence of a BA polymorphism in (8.5) can be supposed, but a more detailed appraisal of the phase diagram of the system (9.5)–(8.5) is to be done.

The polymorphism BA was also supposed in the (8.3) compound by comparing texture observations.[16] Measurements of the birefringence for the low temperature smectic phases of (2.2), (3.2), (4.3), (8.3), and (8.5) proved the existence of optically uniaxial phases and confirmed the polymorphism BA in these substances.[17]

The complete miscibility in the binary system (12.5)–(8.*i*5) (*i* = iso) between

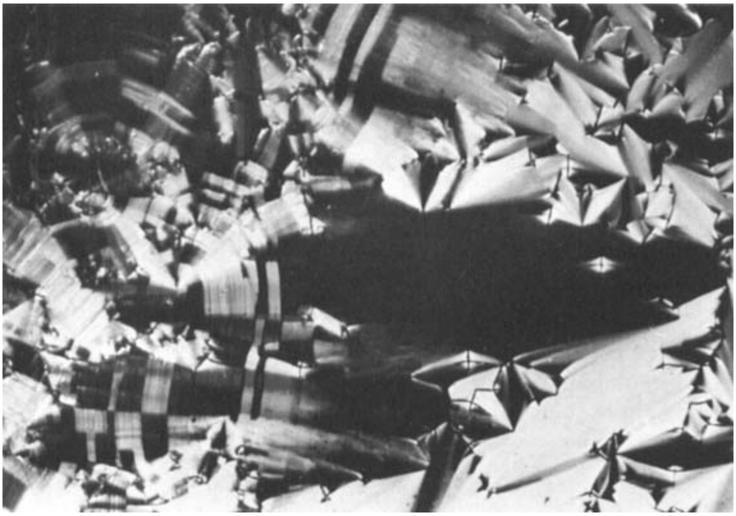
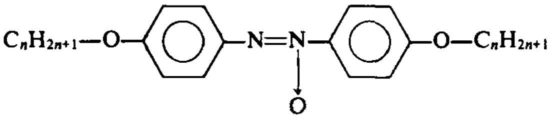


FIGURE 8 Contact preparation for the system AABC (9.5)–(8.5), × 50, 75°C.

all the three smectic modifications[8] signifies the polymorphism ICA with an I phase in the former place of a B phase. The polymorphism ICA can also be supposed in the smectic trimorphic substances (10.*i*5) and (12.*i*5).[8]

Summarizing these results, in the higher members of the series of pentyl esters and iso-pentyl esters (9.5), (10.5), (12.5), (8.*i*5), (10.*i*5), and (12.*i*5), the smectic trimorphism ICA has now to be introduced. In the other known substances with lower (*n*, *m*) combinations, the denomination BA can be retained.

4.2 I phases in the homologous series of the 4,4'-bis-[*n*-alkyloxy]azoxybenzenes (AAOB)



In earlier investigations of the members $n = 6$ to $n = 12$, smectic C phases were found.[9,18] Arnold *et al.*[19] observed in the members with $n = 16$ and $n = 18$ a second smectic phase at lower temperatures and supposed the presence of a B phase. In miscibility experiments[20] with AABC (12.5), this classification was checked.

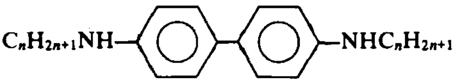
The miscibility in the two binary systems was found to be

AAOB (16)	AABC (12.5)	AAOB (18)
	A	
C ————	C ————	C
I ————	I ————	I

and now has to be formulated with I phases (instead of B phases).

X-ray investigations done on oriented samples of AAOB (18)[21] proved a tilted monoclinic (pseudohexagonal) structure for the phase now designated I. This corresponds with the results of the X-ray investigation of the I phase of AABC (12.5).[12]

4.3 The homologous series of the 4,4'-Bis-[*n*-alkylamino]biphenyls (AABPh)



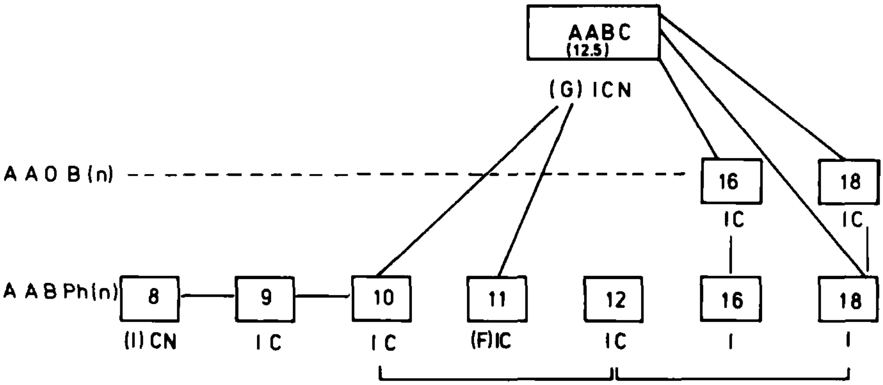


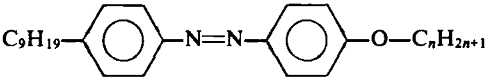
FIGURE 9 Relations of miscibility with AABPh members (Ref. 6 and section 4.2).

The polymorphism of this series was described extensively in Ref. 6. The classification of the phases was derived by miscibility measurements, which used AABC (12.5) as a standard. X-ray investigations and calorimetric measurements were also done.

In Figure 9, the miscibility relations in this series are schematically summarized.

All variants found are derivable from a sequence FICN. A tilted layer structure for the I phases was proved by X-ray investigations.

4.4 The homologous series of the 4-*n*-nonyl-4'-*n*-alkyloxyazobenzenes (NAAB)



Recent investigations on miscibility, X-ray diffraction, transition heats, and textures have been published.[7]

AABC (12.5) was used as a standard substance in the binary system AABC (12.5)–NAAB (14). Contact preparations for the binary systems of the series NAAB (14)–(10), (8)–(10), (8)–(16) proved uninterrupted miscibility between phases of the same type.[22] Together with the trends of the transition temperatures in the series (Figure 10) and the texture observations, the codes of phases listed in Figure 10 can be derived.

All variants of the single members are sequences of a more general variant GICAN.

First X-ray measurements of the compound (18)[23] proved a tilted layer structure for the phase now coded I. This result is transferable to all the I

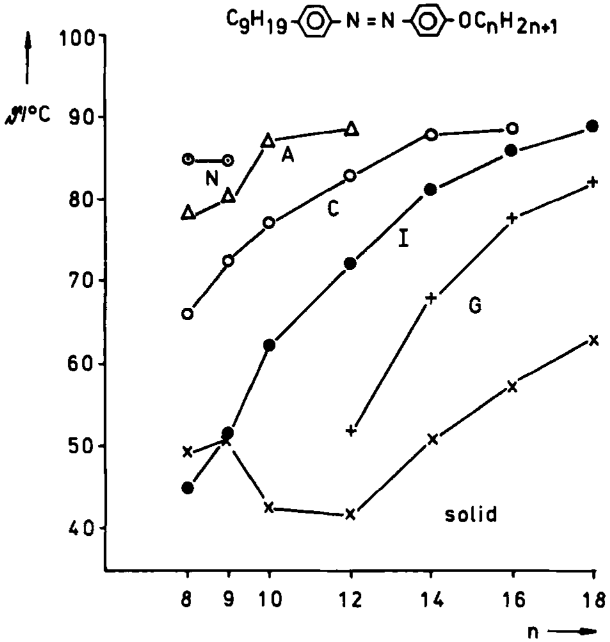
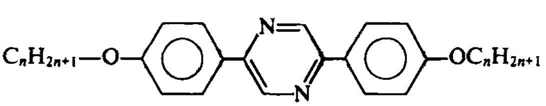


FIGURE 10 Transition temperatures in the series NAAB.

phases in this series in agreement with the X-ray investigations and the texture observations in Ref. 7.

4.5 The homologous series of 2,5-Bis-[4'-*n*-alkyloxyphenyl]pyrazines (BAPhP)



The members of the series (n = 6, 7, 8) have a low temperature smectic phase besides a phase C. In a binary system BAPhP(8)–AABC(12.5) uninterrupted miscibility between this low temperature phase and the phase I of AABC (12.5) was found.[24] Therefore the earlier code B for this phase should be changed to I. However, in a first renewed investigation of this system, complete miscibility could not be confirmed.[25] These smectic phases of the BAPhP seem to belong to the phase type H. Therefore they are neither B phases nor I phases, and further investigations have yet to be done.

5 SUMMARY: THE SYSTEM OF I PHASES

The results on miscibility in the binary system with TBAA (9) described in section 3 demand a revised sequence of the phases in AABC (12.5):

(G)ICA.

The smectic phase formerly named B now has to be coded as an I phase, and a G phase was additionally found at lower temperatures, in a metastable region.

This result requires an inspection of all the binary systems in which AABC (12.5) incorrectly was considered to be a component with a B phase.

A renewed investigation of the binary system AABC (12.5)–AABC (2.2) (Figure 3) proved a small region of interrupted miscibility between the mixed phases B starting from AABC (2.2) and the mixed phases I starting from AABC (12.5). This heterogeneous region was not found in earlier investigations, and led to the incorrect denomination of the "B phase" of AABC (12.5).

In all earlier investigated binary systems showing complete miscibility between a liquid crystal phase and the I phase of AABC (12.5), a redesignation of the B phase as an I phase was needed. This was not done schematically. All the binary systems were critically checked by comparison with new texture observations, with sequences of transition temperatures for neighboring members of a series, or with results from X-ray investigations.

Therefore some earlier results on miscibility in the AABC series (section 4.1) and the BAPhP series (section 4.5) have been excluded and put aside for renewed investigations. Together with more recent investigations on miscibility (sections 4.3 and 4.4), a list of substances with I phases can now be given in Table I.

All the variants found can be derived from the sequence

GFICAN

allowing for the absence of one or several phases in single substances.

In all I phases investigated by X-ray diffraction a tilted layer structure was observed, and in some cases a pseudohexagonal packing of the molecular long axes has been proved.

Considering the general connection between smectic structure and texture, the I phases due to their tilted structure can occur in mosaic or schlieren textures and in pseudomorphic fan-shaped textures, but not in homeotropic textures. Therefore texture observations in many cases allow a distinction to be made between I phases and B phases, because the latter can be forced to adopt a homeotropic orientation.

The differences between the structures of F and I phases were proved by X-ray investigations of these two phases in TBAA (10).[26] Both phases have a

TABLE I

Series		Polymorphism
TBAA	*n, n*	
	9, 9	GFICA
	10, 10	GFICA
AABC	*n, m*	
	10, 5	ICA
	12, 5	(G)ICAN
	8. *i*5	ICA
	10. *i*5	ICA
	12. *i*5	ICA
NAAB		
	9, 8	(I)CAN
	9, 9	ICAN
	9, 10	ICA
	9, 12	GICA
	9, 14	GIC
	9, 16	GIC
	9, 18	GI
AABPh	*n, n*	
	8, 8	(I)CN
	9, 9	IC
	10, 10	IC
	11, 11	(F)IC
	12, 12	IC
	16, 16	I
	18, 18	I
AAOB	*n, n*	
	16, 16	IC
	18, 18	IC

C-centered monoclinic (pseudohexagonal) cell with the parameters $a > b$ in the F phase and $b > a$ in the I phase. This is caused by the direction of the tilt being either towards an edge (F phase) or an apex (I phase) of the hexagons.

The symmetry with $b > a$ was also found for the I phase of AABC (12.5).[12]

The transition from ordered smectic I phases to non-ordered smectic phases occurred in all cases by a transition between the tilted phases I and C (Table I). The appearance of a non-tilted ordered modification in sequences involving I phases was found only in mixed phases. In these cases the sequence . . . IB . . . was observed.[6]

Of the smectic phases with an ordered tilted layer structure (IFGH), the I phases are always the high temperature modification. With respect to the G and H phases, the I phases have a higher rotational motion, and this could be responsible for the observed sequence of the phases.

The alternative directions of the tilt in F and I phases were also found in the low temperature modifications that follow F and I phases, respectively. The structures G and H with parameters $a > b$ were distinguished from the structures G′ and H′ with parameters $b > a$.[26]

This point was noted by the authors only after this manuscript had been prepared. No differentiation between G and G′, and H and H′ phases has therefore been attempted in the preceding text. Moreover, a separation of four phase types G, H, G′, and H′ by miscibility has not been observed so far, although this separation would be expected. This requires new investigations of the phase transitions in binary systems which have low temperature modifications besides F and I phases.

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