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ON THE RELATIONS BETWEEN THE SMECTIC PHASE TYPES B, E AND G (*)

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Abstract. — The miscibility relations between the liquid crystalline (l. c.) phases of Terephthylidene-*bis*-[4-n-butylaniline] (TBBA) and N-[4-n-Butyloxy-benzylidene]-4-ethyl-aniline (BBEA) with the l. c. phases of other substances have been investigated and yielded the following variants of liquid crystalline polymorphism :

TBBA : smectic 5, G, B, C, A, N ; BBEA : G, N.

The newest stand of the system of the l. c. phase types is discussed together with the relations to the l. c. structure types.

1. Introduction. — In 1971, 1972 and 1973 first communications concerning the existence of the new smectic phase types F, G and E appeared [1, 2, 3]. Meanwhile new substances of different classes showing these phase types have been found especially in the homologous series of the 2-[4-n-alkylphenyl]-5-[4-n-alkyloxy-phenyl]-pyrimidines (G phases) [4], the 4-n-alkyl-N-[4-n-alkyloxy-benzylidene]-anilines (G phases) [5, 6] and the N, N'-bis-[4-n-alkyloxy-benzylidene]-phenylenediamines (G phases) [7], some 4,4'-disubstituted biphenyls (E phases) [8, 9] and some other homologous series (E phases) [8, 10, 22, 23].

In 1972 de Vries and Fishel [11] have found a new structure type at the smectic modification of N-[4-nbutyloxy-benzylidene]-4-ethylaniline (BBEA). They marked this modification by the symbol H, without investigating the relations of miscibility with other smectic phases especially of the types F or G, which had been known at this time.

In 1974 Doucet, Levelut and Lambert [12] have investigated the structures of two smectic phases (VI and VII) of Terephthylidene-*bis*-[4-n-butylaniline] (TBBA), which exist as instable phases at lower temperatures besides the A, C and B phases. It seems that the

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structure of the phase VI of TBBA is the same as or very similar to the structure of the smectic phase of BBEA.

Further in 1973 Urbach [13] obtained results showing an uninterrupted miscibility between the smectic phase of BBEA and the B phase of the n-pentyl-4-[4-n-decyloxy-benzylidene-amino]-cinnamate.

Considering all these facts a confused situation exists. On the one hand the H phase of BBEA should be a B phase by the miscibility criterion, on the other hand a similarity of structures between the « H phase » of BBEA and the phase VI of TBBA exists, but not with the B phase of TBBA, as one could expect. Furthermore no miscibility relations of this phase with the modifications of the types E, F and G are known.

In order to clearify this situation we have undertaken investigations in the centre of which stand miscibility relations of the smectic phases of TBBA and BBEA with already classified modifications of other substances.

2. Materials. — The classification of the smectic modifications of the substances listed below is a result of earlier investigations or on anticipation of the results of the miscibility investigations described in the following sections of this paper.

Substances :

Nº 1 2-[4-n-pentyl-phenyl]-5-[4-n-pentyloxy-phenyl]-pyrimidine (PPP)

$$H_{11}C_5 - O - OC_5H_{11}$$

K 79.5, S_G 102.4, S_F 113.1, S_C 144.8, S_A 210, I

The synthesis and classification of this compound has been described in reference [1].

Nº 2 2-[4-n-butyl-phenyl]-5-[4-n-butyloxy-phenyl]-pyrimidine (BBP)



Synthesis analogous to substance Nº 1

K 90.5, S_G 113.7, S_C 120.8, S_A 214, I

Nº 3 Terephthylidene-bis-[4-n-butyl-aniline] (TBBA) [12, 14, 15]

$$H_9C_4$$
 \bigcirc $N=HC$ \bigcirc $CH=N$ \bigcirc C_4H_9

K 133.0 (S₅ 73-74, S_G 89.2) S_B 144.5, S_C 172.0, S_A 199.0, N 235, I

Synthesis by condensation of terephthalaldehyde with 4-n-butylaniline. The phases S_G resp. S_5 have been designated by Doucet *et al.* [12] as phase VI resp. phase VII.

Nº 4 N-[4-n-butyloxy-benzylidene]-4-ethyl-aniline (BBEA) [11]

$$H_9C_4O$$
 \bigcirc $-CH = N$ \bigcirc $-C_2H_5$
K 38.7, S_G 50.5, N 64.8, I

Synthesis by condensation of 4-n-butyloxybenzaldehyde with 4-ethylaniline.

Nº 5 n-pentyl-4-[4-n-decyloxy-benzylidene-amino]-cinnamate (PDBC) [16]

$$H_{21}C_{10}O$$
 CH=N O CH=CH-COOC₅ H_{11}
K 73.8, S_B 97.0, S_C 105.6, S_A 136.8, I

The synthesis and the classification have been described in reference [16].

Nº 6 ethyl-4-[4-ethoxy-benzylidene-amino]-cinnamate (EEBC)

$$C_2H_5O$$
 O $CH=N$ O $CH=CH$ $COOC_2H_5$

K 81.4, S_B 119.3, S_A 157.3, N 160.2, I

The classification of this substance has been described in references [17, 18].

Nº 7 4-n-propyloxy-4'-ethanoyl-biphenyl (PEB) [9]



K 107.0, S_E 156.5, I

Synthesis and classification have been described in reference [9].

3. Relations of miscibility. — 3.1 DIAGRAMS OF STATE. — The diagrams of state (isobaric temperature-concentration diagrams) have been obtained by microscopical observation in polarized light. The experimental technique has been given more detailed in references [19, 20].

We use the following abbreviations :

cl. p. = clearing point ; tr. = transition temperature ; m. p. = melting point .

The numbers within the diagrams denote the temperatures of maxima, minima and three phase equilibria.

System 1 (PPP/BBP). — As to be seen in figure 1 the smectic low temperature modifications of both of



FIG. 1. -- Diagram of state of system 1.

the compounds show a region of uninterrupted miscibility. According to the rule of selective miscibility with respect to the smectic G modification of PPP the smectic low temperature modification of BBP must be attached to the type smectic G. The diagram further proves the existence of smectic A and C at BBP, whereas smectic F is lacking.

System 2 (BBEA/BBP). — In figure 2*a* the stable phase diagram of the system is to be seen. The transition curves between the solid states and the liquid crystalline states are observed by heating of the solid crystalline samples. Miscibility regions of nematic, smectic A-, C- and G- phases are observable all of



FIG. 2a. — Diagram of state of system 2 (observed at increasing temperature).



FIG. 2b. — Diagram of state of system 2 (observed at decreasing temperature).

which start from the pure substances. In the middle part of the diagram a region of smectic B exists. We have characterized this phase region by X-ray investigation. A non oriented sample with 48 mole percent BBP shows the sharp narrow and the sharp wide ring typical for smectic B. The X-ray-pattern is strongly altered at 45-47 °C pointing to a mixture of smectic G and solid crystalline phases. As to be seen no uninterrupted miscibility between the modifications of the pure compounds exists.

Cooling the preparations the crystallisation can be avoided and further smectic-smectic transitions in the supercooled region are to be observed. The diagram as it is observed at decreasing temperature including the supercooled state has been drawn in figure 2b. There an uninterrupted region of miscibility between the smectic low-temperature-modifications of BBEA and BBP exists. Therefore the smectic phase of BBEA must be marked as smectic G.

System 3 (TBBA/EEBC). — In system 3 (Fig. 3) the classification of two of the smectic modifications of



FIG. 3. - Diagram of state of system 3.

TBBA is to be seen. The uninterrupted miscibility between the smectic A and B phases of EEBC, the substance at which the first S_B modification has been defined [17] and the high and low temperature smectic phases of TBBA yields the classification of these phases. System 3 has been investigated already by a contact preparation [13] in good accordance to our results.

System 4 (TBBA/BBP). — System 4 elucidates the miscibility relations between the two substances TBBA and BBP (Fig. 4). The two smectic high temperature



modifications of both compounds exhibit regions of complete miscibility. Regarding BBP as reference substance the two smectic high temperature modifications of TBBA have to be designed $S_{\rm A}$ resp. $S_{\rm C}$ in accordance to reference [12]. Between the smectic B phase region starting from the low temperature modification of TBBA and the smectic G phase region starting from the low temperature modification of BBP a transition (miscibility gap) is to be seen, as it is to be expected between different phase types. The existence of the small intermediate S_F region has been proved by the occurrence of the typical S_F texture (broken focal conic texture with concentric arcs [1]). Observing the preparations with decreasing temperature the crystallisation can be avoided and supercooling occurs. Cooling preparations with 80 and 70 mole % TBBA in the supercooled state a texture change is observable, corresponding to the transition S_B/S_G . Therefore in the supercooled state an uninterrupted region of mixed liquid crystals can be observed starting from the S_G modification of BBP. Considering this fact the fourth smectic modification of TBBA has to be attached to the type S_G.



FIG. 5a. — Diagram of state of system 5 (observed at increasing temperature).



FIG. 5b. — Diagram of state of system 5 (observed at decreasing temperature).

The preparation with 80 mole % TBBA shows an additional texture change near 70 °C, corresponding to the transition S_G/S_5 . Cooling the preparation with 70 mole % TBBA down to 25 °C this transition is not observable, indicating a strong slope of the respective transition curve. The three low temperature modifications of TBBA, B, G and VII (smectic 5) appear in mosaic textures. At the phase transitions only slight texture changes occur. Therefore the observation of the phase transitions is difficult.

System 5 (BBEA/TBBA). — Because of the complicated shape of the diagram of state the stable part obtained by heating of the crystalline solid samples and the diagram with the partly instable part obtained by cooling of the liquid crystalline samples are displayed seperately (Fig. 5a and 5b).

In figure 5a the nematic modifications show complete miscibility. At middle concentrations no smectic phase regions occur. The solid crystals melt immediately yielding the nematic state. Without great difficulties the preparations may be supercooled remarkably. Observed at decreasing temperature the diagram displays the shape of figure 5b. Starting from the B-modification of TBBA the B phase region is extended to the instable part of the diagram. Additionally an intermediate B phase region exists. At temperatures below the B phase regions an uninterrupted series of mixed liquid crystals occurs between the smectic modification of BBEA and the fourth smectic phase of TBBA, indicating the same phase type smectic G at these two substances.

System 6 (BBEA/PDBC). — System 6 already has been investigated in reference [13]. In the proposed



FIG. 6. — Diagram of state of system 6.

phase diagram the two smectic low temperature modifications are connected by a region of complete miscibility. Since according to the diagram described above these smectics have been classified as S_G resp. S_B , this behaviour would be in contradiction to the rule of selective miscibility. Therefore we have reinvestigated this system carefully. The results are demonstrated in figure 6. The main difference between the transition curves given in reference [13] and in figure 6 concerns the shape of the transition curves between the N and B phase regions at high concentrations of BBEA. In reference [13] the transition curves nematic-smectic are joined by a minimum, therefore pretending an uninterrupted field of mixed liquid crystals between the two smectic phases. In the concentration region of the minimum observations on only two preparations of different concentrations had been done. Because of the similarity of the textures of G and B phases the heterogeneous region between smectic B and G only difficultly is visible. The transition temperatures of the substance PDBC used by us are not identical with those of the substance PDBC of reference [13]. This points to differences in the purity which may cause some other differences in the diagram of state.

System 7 (PEB/BBEA). — In system 7 (Fig. 7) miscibility gaps between the nematic and G phase regions starting from BBEA and the E phase region starting



from PEB have been found, according to the rule of selective miscibility.

3.2 REMARKS ON THE TEXTURE OBSERVATIONS OF THE PHASES B, E AND G. — As especially discussed in

reference [21] the smectic B, E and G modifications usually occur as stable mosaic textures. Therefore the transitions between these phases are accompanied by only little changes in textures. As an example in figures 8 and 9 a transition between B and G in system 5 is to be seen. The smectic B texture shows in general sharp boarders of the single mosaics. At the transition to G these boarders become broader and partly change to bright areas with characteristic interference colours. Furthermore should be reminded of the appearance of paramorphic textures if these smectic modifications originate from A phases by cooling the latter.

Therefore for the investigation of the miscibility relations the only use of the contact method in polymorphic systems with these low temperature phases is not commendable. Investigations using preparations of single concentration should be done absolutely, if neccessary completed by investigations with other methods as calorimetric and X-ray investigations.

3.3 INTERMEDIATE LIQUID-CRYSTALLINE PHASES. -In the systems 2, 4 and 5 the existence of intermediate phases of the types B and F are to be seen. As we have shown already in a former publication [24] such phases often can be explained as stabilized phase regions starting from instable or hypothetical phases of one or two of the compounds. The intermediate B phases in figures 2, 4 and 5 can be considered as a stabilized field, which starts from a hypothetical instable B-phase of BBEA. The higher members in the homologous series of the alkoxybenzylidene-alkylanilines possess the stable polymorphism with the sequence GBA resp. GBAN, whereas the series of the second compound in system 2 does not exhibit B-phases. The field of the intermediate phase F in figure 5 may start from an hypothetical F modification of BBP. In this series the polymorphism GFCA at higher members is known [1], whereas the series of the second compound does not exhibit F phases. We may mention here that Billard [25] with success used the concept of instable or hypothetical liquid crystalline modifications for the calculation of the phase behaviour in binary systems.

4. Discussion. - 4.1 SUMMARY OF THE RESULTS. -The experimental results of the section 3 schematically are summarized in table I. The full lines indicate the existence of uninterrupted miscibility between two phases. The lines \rightarrow show the observed existence of transitions between neighboured mixed phase regions of different types (gaps of miscibility). In system 1 the existence of a G-phase of BBP has been established starting from the substance PPP on which the existence of the first smectic F and G modification has been stated. The BBP lacks a F phase. The use of substances with a degree of polymorphism as low as possible is very suitable for the classification of other modifications by miscibility relations because the binary diagrams generally become more simple.





In the systems 2 and 4 the characterization of the smectic phase of BBEA and the instable smectic phase S_4 of TBBA — both are G modifications — is shown. These both phases show uninterrupted miscibility with the G phase of BBP. Further the systems 3 and 4 contain the proof of the existence of the smectic A, C and B phases of TBBA in accordance to results from the literature [12, 14, 15].

In the system 5 uninterrupted miscibility between the two G-phases of BBEA and TBBA is realized. This is a confirmation of the results of the miscibility investigation of the systems 2 and 4.

The system 6 contains a revision of earlier investigations. Between the G resp. B modifications of BBEA resp. PDBC no uninterrupted miscibility occurs.

The system 7 contains the first result on relations between E and G phases. As to be expected by the rule of selective miscibility the two neighboured mixed phase-regions of type E and G are divided by miscibility gaps.

It is to be emphasized that all results of system 1-7 are in full accordance with the rule of selective miscibility.

4.2 THE SYSTEM OF THE LIQUID CRYSTALLINE PHASE TYPES. — 4.2.1 The variants of polymorphism. — The last summarizing article on the system of the liquid crystal phases types in 1973 [21] was published. The newer results of references [5, 26] and of this article produce the following new variants of polymorphism

GN; GAN; GBA; GBAN; GCA; GBCAN.

In table II the newest state of the system of liquidcrystalline modifications is to be seen.

In accordance with reference [26] all variants with the symbol CH (cholesteric) have been omitted. As it is known in the presence of chiralic molecules nematic and smectic C-phases are always replaced by twisted structures (cholesteric resp. twisted smectic C). These phases are always miscible with the normal phases N and C respectively. Therefore in the sence of the rule of selective miscibility the phases with twisted and not twisted structures belong to the same phase type and consequently table II does not contain the variants with twisted modifications as special cases.

TABLE II

Variants of Polymorphism

monomorphism	Ν	trimorphism	BAN
-	Α		CAN
	С		GAN
	E		BCN
			EBA
dimorphism	AN		BCA
	BN		CDA
	CN		GBA
	GN		GCA
	CA		
	BA		
	EA	tetramorphism	BCAN
	CD		EBAN
	BC		GBAN
	EB		GFCA
		pentamorphism	GBCAN

4.2.2 The rule of the sequence of the modifications. — In all new variants of polymorphism the smectic G modifications are low temperature phases, compared with smectic B, F, C, A.

The position of the F-modifications in this sequence, with respect of the B and E phases is not finally fixed because substances with F as well as B or E phases are not known. But the first X-ray characteristics and the characteristic schlieren texture [1] refer to a phase type similar to smectic C. For this reason the F phases can be considered as a high temperature type with respect also to the B, E and not only to G phases.

The relative position of E and G in the temperature sequence is unknown owing to the absence of a substance possessing E as well as G phases.

According to this rule of the sequence of the modifications the variants of table II are derivable from a hypothetical variant of polymorphism

The investigations of the smectic phase of BBEA in this article demands the cancellation of the symbol H for this phase. It is pointed out, that this phase belongs to the phase type G, first described in 1971 [1].

Smectic G modifications are no exotic forms. Similar to B and E modifications they can be observed in several classes of substances. The appearance of these phase types in a smaller number of cases compared with the phases N, A or C partly is due to their existence as low temperature forms according to the sequence rule. If it is possible to avoid the crystallisation sometimes additional modifications of this type can be observed (as for example in TBBA).

4.5 PHASES TYPES AND STRUCTURES TYPES. — The system of smectic phase types is based on the rule of selective miscibility, which has been established as a result of miscibility investigations [20, 21]. The advantage of this method consists in comprehending a great number of substances with comparatively small expense. The consistency of the system is shown in all investigations. As to be seen in this work, also some apparent contradictions existing in the literature have been clearified.

It would be desirable to reduce this system to a counterpart on the structural level. The structures of some smectic phases of the types B, E and G have been investigated in the last years. The most complete investigations of B phases have been done by Levelut and Lambert [27, 30] showing in the first B structure type the existence of a hexagonal layer structure with an orthogonal orientation of the long molecular axes.

The second **B** structure type is a monoclinic (pseudohexagonal) layer structure with tilted molecular long axes [1].

A G-phase type first by De Vries and Fishel [31] has been investigated. They found a monoclinic lattice with tilted long axes of the molecules in a herring bone arrangement. The investigations of Doucet, Levelut and Lambert [30] on the G phase of TBBA yielded the same result.

Diele [36] and at the same time Doucet, Levelut and Lambert [37] established structures of E phases. They found as the most probable structure type an orthorhombic cell with a herring bone arrangement of the long molecular axes in the layers.

As can be seen the phase types, B, E and G are represented by different structure types. So far two structure types are known at the B phases and one at each of the E resp. G phases.

In the more ordered smectic phases **B**, E and G according to the sequence rule the B phases are always high temperature phases (see Table II). The B phases possess rotational freedom of the molecules around their long axis, whereas the rotational disorder is lacking at the E and G phases. With respect to a successive breakdown of order with increasing temperature

TABLE III

Phase type	compound (Polymorphism)	Ref.
Ξ _B	ethyl-4-[4-ethoxybenzylidene-amino]- cinnamate (B, A, N) terephthylidene- <i>bis</i> -[4-n-butylaniline] TBBA (G, B, C, A, N)	[27] [29] [27] [29] [28] [30]
	4,4'- <i>bis</i> -n-octadecyloxy-azoxybenzene (B, C)	[28]
	N-[4-n-butyloxy-benzylidene]-4-n-octyl- aniline (B, A, N) BBOA	[28]
S _E	di-n-propyl-p-terphenyl-4,4"-di-carboxy- late (E, A)	[35] [36]
	n-pentyl-4-[4-phenylbenzylidene-amino]- cinnamate (E, B, A) 1-methyl-heptyl-4-[4-phenylbenzylidene- aminol-cinnamate (E, B, A)	[37] [37]
	4-n-alkyloxy-4'-n-alkanoyl-biphenyls (E) (8 members of the homologous series)	[38]
S _G	N-[4-n-butyloxybenzylidene]-4-ethylani- line (G, N) BBEA	[31] [33] [28]
N- nil N- nil N- an nil 2-[ny 2-[ny 2-[ny 2-[ny	N-[4-n-pentyloxybenzylidene]-4-ethyla- niline N-[4-n-hexyloxybenzylidene]-4-ethyla-	[32]
	niline N-[4-n-heptyloxy-benzylidene]-4-ethyla-	[32]
	niline N-[4-n-hexyloxybenzylidene]-4-n-propyl- aniline terephthylidene. <i>bis</i> .[4-n-butyla-	[32] [32]
	niline]	[30]
	nyl]-pyrimidine (G, F, C, A) 2-[4-n-hexylphenyl]-5-[4-n-hexyloxyphe-	[34]
	nyl]-pyrimidine (G, F, C, A) 2-[4-n-butylphenyl]-5-[4-n-butyloxyphe- nyl]-pyrimidine (G, C, A)	[34] [34]

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in polymorphic variants this sequence is understandable.

In consideration of the existing insecurities, the origin of which in the introduction is cited, the designation of some smectic phases in the literature is faulty. Therefore in table III we have listed all available substances exhibiting B, G and E phases, which have been investigated by X-ray measurements.

As to be seen, in the investigation of structures today only a small number of substances is included. This means that the basis of the judgement on the connection between the system of phase types and its structural background is small. The most simple behaviour, which could be expected in a strong parallelism between miscibility and structure would be : Each phase type characterized by miscibility represents one structure type. Indeed in A phases the principles of structures seem to be uniform. At G resp. E phases also one structure type is known so far. But on the B phases two structure types have been found. Further at nematic and smectic C phases besides the normal type a twisted type occurring at chiral molecules is known [21]. The interesting question arises why between two different structures (if they also possess strong similarities) an uninterrupted miscibility can occur. The existence of transitions of higher order not observable in miscibility experiments seems to be a possible explanation.

The investigations on structures show the existence of layer structures on nearly all smectic phases of nonamphiphilic compounds. The D phases which have been found at two substances only [35, 39] seem to possess a structure of a micellaric character perhaps

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similar to those of amphiphilic compounds. Therefore the appearance of these phases in the temperature sequence is a special case. It seems to be efficient to concentrate the attention on the sequence of smectic phase types with layer structures i. e.

The existence of smectic 5 at TBBA as well as the polymorphic behaviour of some other substances indicates the occurrence of additional new variants of polymorphism and possibly new phase types.

Note added in proof. - Mme Lambert has noticed in a private communication that in ref. [30] the results on the G-phase of BBEA are interpreted as a structure with pseudohexagonal symmetry (and with only local herring bone packing), as it is characteristic for the tilted B-phase (phase V) of TBBA. But to this problem see also de Vries ref. [33]. This underlines the remark above on the small base of the investigated structures of these phase types, strengthened by differences in the interpretation of the results of this small material.

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