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CLASSIFICATION OF SMECTIC POLYMORPHIC PHASES

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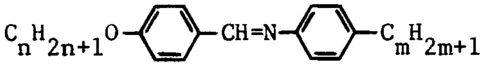
Abstract: Problems concerning the polymorphic smectic phases of the N-4-n-alkoxybenzylidene-4'-n-alkylanilines are reviewed. Literature data and our own experimental results now lead to conclusions concerning the classification of the smectic types involved and to a recommended nomenclature scheme for polymorphic smectic phases in general.

The N-(4-n-alkoxybenzylidene)-4'-n-alkylanilines are Schiff's bases which, despite their simple structure (I), may exhibit complex polymorphism of their smectic liquid crystal phases. The occurrence of sequences of four smectic phases is in fact common for many of the homologues.



(I)

Smith and Gardlund and their associates[1] studied a range of these materials (m = 4 to 8 for n = 1 to 7) and proposed the simple designation nO.m to describe particular members of the many series which may occur. The number of carbons (n) in the alkyl chain attached to oxygen (O) is followed by the number of carbons (m) in the other alkyl chain. Based on studies of the microscopic textures of the phases, they verified the occurrence of nematic phases in many members, and positively identified two of the smectic types as S_A and S_C. They also considered that S_F phases occurred with some members, and that S_B phases were also formed; in the latter case, they did not distinguish whether these were orthogonal

(S_{B_A}) or tilted (S_{B_C}) B phases.

For example, the compounds 70.4, 70.5, and 70.7 each form a nematic phase when the isotropic liquid is cooled, and this is then followed by a sequence of three (70.4) or four (70.5 and 70.7) smectic phases which they numbered S_1, S_2, S_3, S_4 with falling temperature. Their assignments were: $S_1 = S_A$; $S_2 = S_C$; $S_3 = S_B$; $S_4 = S_F$.

Later studies by Billard[2] employing miscibility techniques cast doubt on these assignments however, and it was proposed that S_3 was in fact S_F, and that S_4 was S_G for the compounds 70.4, 70.5, and 70.7.

However, in a paper by Doucet and Levelut,[3] reference is made to a private communication from Demus stating that the S_3 and S_4 phases of 70.7 and 50.6 were S_B and S_G phases, respectively. de Jeu and de Poorter[4] had also studied several of these compounds, and, in the case of 70.5, for example, they concluded that the phase sequence was

$$S_H, S_B, S_C, S_A, N, I$$

Since they used S_H to designate a tilted smectic B phase, and S_B to designate an orthogonal smectic B phase, this sequence (involving a tilted to orthogonal S_B phase transition) in fact agreed with that subsequently reported by Doucet and Levelut[3]

$$S_{B_C}, S_{B_A}, S_C, S_A, N, I$$

who used a different nomenclature.

Further doubts and uncertainties about the smectic phase classification in the nO.m series have also arisen in connection with the simpler compound 40.2. This was first studied in detail by de Vries[5] who concluded that its single smectic phase was different from any other smectic phase known *at that time*; he designated it as S_H, and the sequence for 40.2 was therefore S_H, N, I. However, Richter, Demus, and Sackmann[6] later disagreed with this assignment and proposed that the sequence was S_G, N, I, the single smectic phase being in fact the S_4 phase.

The confusing situation exists therefore that the S_3 phases of these nO.m compounds have variously been reported as S_B and S_F, and the S_4 phases as S_F, S_G, and S_{B_C} (S_H). In an attempt to clarify the position in the nO.m series, we prepared some twenty of the Schiff's bases and examined them in detail. The materials prepared and the results of certain physical studies made on them and on their smectic phases will be described in detail in a later publication. Here however, we concentrate simply on the conclusions we have reached about the smectic phase assignments and the reasons for the conflicting literature reports which have arisen on this subject.

To reassess the situation we have to realise that until recently the tilted B (S_{B_C} or S_H) phase was believed to be miscible with the orthogonal B phase (S_B or S_{B_A}). Based on this belief, a S_B to S_H transition in a pure material was impossible. However, Doucet and Levelut's[3] recent X-ray results clearly show that this is not so, and that the S_3 phase of say 70.5 is S_B and the S_4 phase is of the tilted B type. Moreover, our own miscibility studies fully agree with their assignment of phase types, and we have produced independent evidence that orthogonal and tilted S_B phases are immiscible.[7]

Working independently of these considerations, Richter, Demus, and Sackmann had studied nO.m's such as 40.2, and had shown that the S_4 phase was the same as the S_G phase of their pyrimidine derivative. They therefore named the S_4 phase S_G.[6]

As the realisation grew among other workers that the two B phases are not of the same type, a new letter for the tilted B phase had to be found. The majority of workers, not realising that Demus had already given the 'new' S_4 phase the code letter G, tended instead to use de Vries' S_H nomenclature first reported in his study of 40.2.

The major problem therefore becomes one of finding a generally acceptable nomenclature system for smectic polymorphic phases. A recommended nomenclature system (in thermodynamic order) can be defined as follows:

SMECTIC LAYER STRUCTURE		CODE LETTERS PREVIOUSLY USED	RECOMMENDED CODE LETTER
PACKING ARRANGEMENT	MOLECULAR DISPOSITION		
random	orthogonal	S_A	S_A
cubic	micelles or rods	S_D	S_D
random	tilted	S_C	S_C
pseudo-hexagonal	tilted	S_F	S_F
hexagonally close-packed	orthogonal	S_B, S_{B_A}	S_B
hexagonally close-packed	tilted	S_B,[6] S_{B_C}, S_G,[8] S_H[5]	S_H
orthorhombic	orthogonal	S_E, S_{E_A}	S_E
orthorhombic	tilted	S_{E_C}, S_G,[6] S_H[8]	S_G

Therefore on this recommended basis the phase sequences of some *standard* materials are given below:

(1) TBBA:[9] $I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_H \rightarrow S_G$
(2) TBPA:[9] $I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_F \rightarrow S_H \rightarrow S_G$
(3) 40.2:[3] $I \rightarrow N \rightarrow S_H$
(4) 70.5:[3] $I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_B \rightarrow S_H$
(5) Pyrimidine:[10] $I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_F \rightarrow S_H$
(6) 80SF:[11] $I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_F \rightarrow S_H \rightarrow S_G$

The major remaining problem is still centred on the S_B and S_H phases. De Vries,[5] in his study of the smectic phase of 40.2 suggests that it has a tilted, hexagonally close-packed arrangement of the molecules in the layers. Furthermore, he suggests that the layers are correlated to give a three-dimensional lattice. Earlier classical work by Levelut and Lambert[12] had also shown that the layers of the smectic B phases of *certain* compounds were correlated over several layers, and recently, Doucet[13] has shown that a ferro-electric material can exhibit a tilted, hexagonally close-packed, uncorrelated phase as well as a tilted, hexagonally close-packed correlated phase. Thus, it will be interesting to see if a similar duality of phase type, depending on the presence or absence of correlations, is observed in other materials and if this in turn will give rise to two types of B and H phases. At present we can be certain of the distinction *between* B and H phases by microscopic and conoscopic observations, but if both of these phases are sub-divided into two types (correlated and uncorrelated), then miscibility studies will probably not be able to separate one type from another. Moreover, the *extent* of the correlations between layers would also be important in deciding the sub-group involved or indeed whether the phase is really a solid.

However, despite the fact that miscibility may not be the ultimate technique for the identification of smectic phases, it will always remain the most useful tool in phase categorisation. Miscibility will always classify phases into the simple smectic polymorphic groups, whereas classification based on minute structural detail could itself give rise to ambiguities of assignment unless a complex nomenclature scheme - which may not be generally comprehended - is adopted.

Conclusion To those who work with smectic phases but are not deeply involved in the structural complexities of smectic polymorphism and the accompanying nomenclature problems, there is little doubt that a simple system of code letters would be welcome. However, the situation is not straightforward. Indeed, in view of the above mentioned uncertainties and the possibility that more ambiguities may arise in this complex area of smectic polymorphism, still further changes in nomenclature may in fact be necessary. Until a clear picture develops, it is however hoped that the comments in this letter on smectic phase nomenclature, with particular reference to the nO.m's, will be a useful guide through a confusing literature situation.

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References

1 GW Smith, ZG Gardlund, and RJ Curtis, *Mol Cryst Liq Cryst, 19*, 237 (1973); GW Smith and ZG Gardlund, *J Chem Phys, 59*, 3214 (1973).

2 J Billard, *Compt rend, 208B*, 573 (1975).

3 J Doucet and A-M Levelut, *J Physique, 38*, 1163 (1977).

4 WH de Jeu and JA de Poorter, *Phys Lett, 61A*, 114 (1977).

5 A de Vries and DL Fishel, *Mol Cryst Liq Cryst, 16*, 311 (1972).

6 L Richter, D Demus, and H Sackmann, *J Physique, 37*, 41 (1976).

7 JW Goodby and GW Gray, to be published in *J Physique*.

8 H Sackmann, to be published in *J Physique*.

9 JW Goodby, GW Gray, and A Mosley, *Mol Cryst Liq Cryst Lett, 41*, 183 (1978).

10 D Demus, S Diele, M Klapperstück, V Link, and H Zaschke, *Mol Cryst Liq Cryst, 15*, 161 (1971).

11 JW Goodby and GW Gray, to be published in *J Physique*.

12 A-M Levelut and M Lambert, *Compt rend*, *272*, 1018 (1971).

13 J Doucet, P Keller, A-M Levelut, and P Porquat, *J Physique*, *39*, 548 (1978).