Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Smectic F Phases Exhibited by the -N-(4-N-Alkoxybenzylidene)-4′-n-Alkylanilines

JW Goodby [a] & GW Gray [a]
[a] Department of Chemistry, The University of Hull, HULL, HU6 7RX, England

Version of record first published: 19 Apr 2011.

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 43-49
0140-6566/79/5602-0043$04.50/0

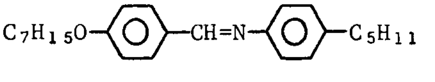
SMECTIC F PHASES EXHIBITED BY THE N-(4-n-ALKOXYBENZYLIDENE)-4'-n-ALKYLANILINES

JW GOODBY and GW GRAY
Department of Chemistry, The University of Hull, HULL, HU6 7RX, England

(Submitted for publication 19 July 1979)

Abstract: Studies of the *N*-(4-n-alkoxybenzylidene)-4'-n-alkylanilines have been made by numerous workers, and a large variety of phases has been shown to be exhibited by these materials. However, no authentic reports of smectic F properties have been cited. In the present study we have closely examined the compound *N*-(4-n-nonyloxybenzylidene)-4'-n-butylaniline, and we now believe that this is the first material for which a direct smectic A to smectic F transition has been observed.

Introduction: Since their mesomorphic properties were first examined by Smith, Gardlund, and Curtis[1,2] the *N*-(4-n-alkoxybenzylidene)-4'-n-alkylanilines (nO.ms) have been extensively studied by numerous respected research workers. As a consequence, major controversies[1,2,3,4,5] arose over the identities of the smectic phases exhibited by certain members, notably *N*-(4-n-heptyloxybenzylidene)-4'-n-pentylaniline (70.5) and *N*-(4-n-butyloxybenzylidene)-4'-n-ethylaniline (40.2) etc. However Doucet and Levelut[6] have recently shown quite clearly that the general pattern of phase behaviour for the pentapolymorphic members is nematic, S_A, S_C, S_B, and tilted S_B. For example, for 70.5 we have with falling temperature:

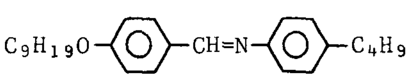


$$I \rightarrow N \rightarrow S_A \rightarrow S_C \rightarrow S_B \rightarrow S_H{}^{\dagger}$$

From these X-ray studies Doucet and Levelut were therefore able to show for the first time that orthogonal S_B to tilted S_B (S_H) transitions could occur in pure materials. This simple observation had complex repercussions on the interpretation of experiments based on miscibility techniques, and made a number of such studies invalid because of their assumption that the two S_B phases are miscible.

In our current work,[8] we have confirmed the observations of Doucet and Levelut by optical microscopy and miscibility studies. In the course of this work, we prepared *N*-(4-n-nonyloxybenzylidene)-4'-n-butylaniline (90.4). This compound was shown to exhibit S_A, S_F, and S_H phases, and the S_A to S_F phase transition is believed to be the first of this nature to be observed. All previously reported S_F phases have been formed from S_C phases on cooling.[9,10,11,12,13]

Results and Discussion: We have studied a number of *N*-(4-n-alkoxybenzylidene)-4'-n-butylanilines and the overall results are very interesting for the series as a whole. However, we will concentrate here on the specific properties of *N*-(4-n-nonyloxybenzylidene)-4'-n-butylaniline. Initial studies by optical microscopy confirmed that the material exhibited three liquid crystal phases and had the transition temperatures shown below.



(90.4)

$$I \underset{82^{\circ}}{\rightleftharpoons} S_1 \underset{69.5^{\circ}}{\rightleftharpoons} S_2 \underset{67^{\circ}}{\rightleftharpoons} S_3 \qquad (C\text{-}S_3,\ 50^{\circ})$$

Preliminary observations by optical microscopy showed that one phase (S_1) was orthogonal and the other two were

---

† Note: the nomenclature system used is that proposed by Goodby and Gray.[7]

tilted. On cooling the isotropic liquid, the first phase (S_1) separated in the form of bâtonnets. These coalesced on further cooling to give a phase exhibiting the focal-conic fan texture. The phase also exhibited the homeotropic or pseudoisotropic texture, thus indicating that it was orthogonal in nature. These observations were indicative that the phase was of the S_A type. Subsequent cooling produced the second phase (S_2) which exhibited the mosaic and chequerboard broken-fan textures. The mosaic texture was not typical of either a S_B or S_H phase, but was similar to that of the S_F phase of TBPA; the chequerboard fan texture was also very similar to that exhibited by most smectic F phases. On further cooling, the final phase (S_3) was obtained; this exhibited mosaic and broken fan textures which were typical of the smectic H (tilted S_B) phase.

The transition temperatures obtained from optical microscopy were confirmed by differential thermal analysis. The melting point of 90.4 was determined by DTA, and the value of 50^o confirmed that the three smectic phases were enantiotropic.

The smectic phases of *N*-(4-n-nonyloxybenzylidene)-4'-n-butylaniline were next firmly classified by miscibility studies using various standard materials exhibiting smectic F phases. For example, the test Schiff's base (90.4) was shown to exhibit S_A, S_F, and S_H phases by their separate co-miscibility with the relevant known smectic phases of terephthalylidene-bis-4-n-pentylaniline (TBPA): N, S_A, S_C, S_F, S_H, and S_G phases.

Interesting results were obtained in one case, with the standard material 4-(2'-methylbutyl)phenyl 4'-n-nonyloxy-biphenyl-4-carboxylate (90SF).[10] When this material was used to confirm the identification of the three smectic phases of 90.4, an unusual injection of S_B properties was obtained with certain binary compositions. The miscibility diagram of state for binary mixtures of 90SF (N, S_A, S_C, S_F, S_H, and S_G phases) and 90.4 (S_A, S_F, and S_H phases) is shown in Figure 1.

The two smectic F phases appeared to be miscible until mixtures containing from 60 to 90% by weight of 90.4 were investigated. In this range, mixtures gave the phase sequence S_A, S_B, S_H. This is suprising, as neither of the components exhibits S_B phases. Moreover, the S_A to S_B

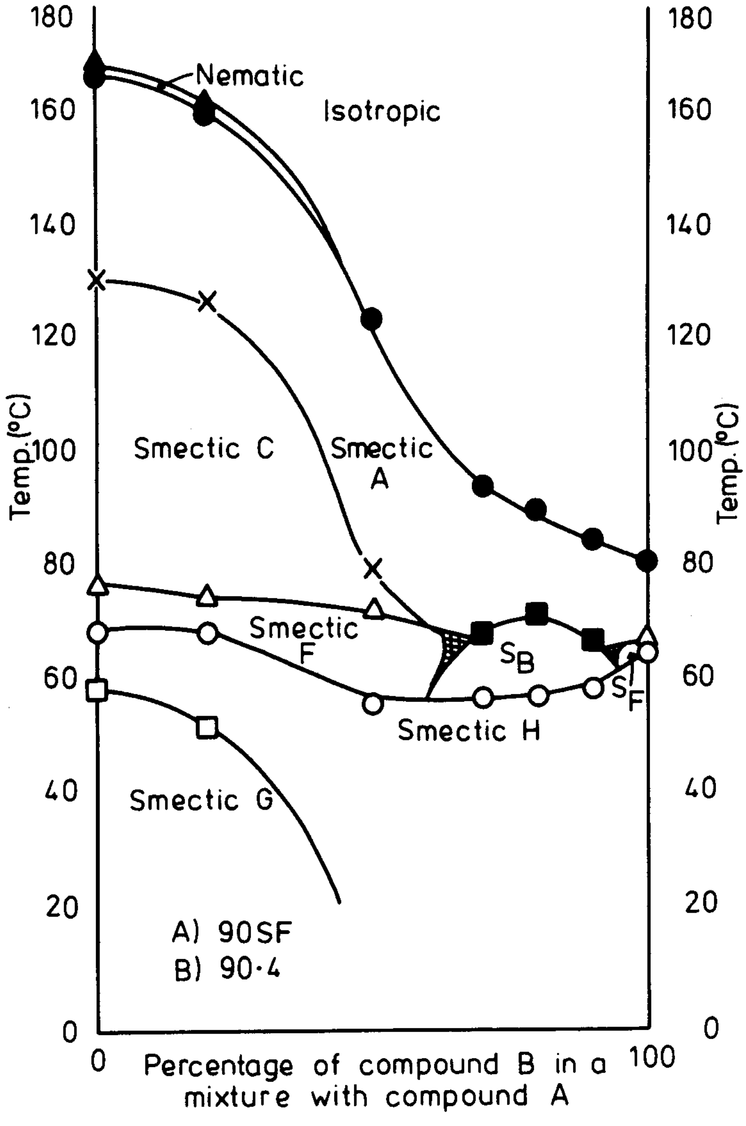


FIGURE 1 Miscibility diagram of state for 4-(2'-methylbutyl)phenyl 4'-n-nonyloxybiphenyl-4-carboxylate (90SF) - compound A - with N-(4-n-nonyloxybenzylidene)-4'-n-butylaniline - compound B.

transition temperatures for the binary mixtures in this percentage composition range lie *above* the S_A or S_C to S_F transition temperatures for mixtures on either side of the region in which the S_B phase is injected. Thus, the injected S_B phase would appear to be more thermally stable in this part of the composition range than the tilted S_F phase.

However, it is difficult to decide whether the S_B phase arises from a mixture of the two F phases of the two components or if the injection is caused by the admixture of the two S_H phases. Certainly, mixtures of two S_H phases can produce an orthogonal S_B phase in binary mixtures.[14] However, in the cases reported, this has always given S_B to S_H transition temperatures lower than the neighbouring S to S_H transition temperatures, thus causing a depression in the transition temperature curve. In this case, the S_F or S_B to S_H transition curve is unaffected, and it is the S_F or S_A to S_B curve that shows a *maximum*; ie, the opposite situation now arises.

Earlier results obtained by Billard[6] on the classification of various phases in the nO.m series may shed light on this problem. In his studies of *N*-(4-n-heptyloxy-benzylidene)-4'-n-heptylaniline (70.7), Billard concluded that it exhibited S_A, S_C, S_F, and S_G* phases by their separate co-miscibility with the phases of the standard 2-(4'-n-pentylphenyl)-5-(4"-n-pentyloxyphenyl)pyrimidine (S_A, S_C, S_F, and S_G* phases). However, the correct assignment of phases for 70.7 is now known to be S_A, S_C, S_B, and S_H.[6] This would imply that Billard may have found some affinity between the S_B phase of 70.7 and the S_F phase of the pyrimidine, leading him to conclude that they were miscible. This might indicate that the natures of the two phases (S_F and S_B) are not totally incompatible, and hence, the S_F phases of 90.4 and 90SF may be able to produce a S_B phase under certain conditions of mixing.

---

* Note: the nomenclature used is that given by Sackmann and Demus (for S_G read S_H).[9,10]

Experimental: *N*-(4-n-Nonyloxybenzylidene)-4'-n-butylaniline (90.4) was prepared by standard procedures from 4-n-nonyloxybenzaldehyde and 4-n-butylaniline, each of known structure and purity. The Schiff's base was purified by crystallisation from light petrol (bp 40-60°). The structure of the product was confirmed by nmr and infra-red spectroscopy.

Optical microscopy and measurement of the transition temperatures were carried out using a Nikon L-KE polarising microscope in conjunction with a Mettler FP52 hot-stage and control unit. Differential thermal analysis was performed using a Stanton-Redcroft low-temperature differential thermal analyser (Model 671B).

Conclusions:

1. *N*-(4-n-nonyloxybenzylidene)-4'-n-butylaniline (90.4) exhibits a smectic F phase; it also gives a direct smectic A to smectic F transition, the first transition of its kind to be observed.

2. Smectic F phases have been shown to produce smectic B phases in certain two component binary mixtures.

Acknowledgment: The authors wish to thank the Science Research Council, London, for a research grant.

References

1. GW Smith, ZG Gardlund, and RJ Curtis, *Mol Cryst Liq Cryst*, *19*, 237,(1973).
2. GW Smith and ZG Gardlund, *J Chem Phys*, 59, 3214 (1973).
3. L Richter, D Demus, and H Sackmann, *J Physique*, 37, 41 (1976).
4. A de Vries and DL Fishel, *Mol Cryst Liq Cryst*, *16*, 311 (1972).
5. J Billard, *Compt rend*, *208B*, 573 (1975).
6. J Doucet and A-M Levelut, *J Physique*, *38*, 1163 (1977).

7 JW Goodby and GW Gray, *Mol Cryst Liq Cryst Lett*, *41*, 217 (1979).

8 JW Goodby and GW Gray, unpublished results.

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

10 JW Goodby and GW Gray, *J Physique*, *40*, 27 (1979).

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

12 J-C Dubois, *Ann Phys*, *3*, 131 (1978).

13 EM Barrall II, JW Goodby, and GW Gray, to be published in *Mol Cryst Liq Cryst Lett*.

14 JW Goodby and GW Gray, *J Physique*, *40*, 363 (1979).