Effect of 3-fluoro-4-cyano substituted benzoates in the formation of induced smectic phases with N-[4-ethoxybenzylidene]-4'-n-butylaniline

N K Sharma*, Anila Charak & F Ostereichert
Liquid Crystal Group, Department of Chemistry, University of Jammu, Jammu 180 004

Received 6 September 1991; accepted 28 February 1992

Diagrams of state of the binary liquid crystalline systems, in which one component is a 4-cyano-3-fluoro substituted benzoate and the other component is N-[4-ethoxybenzylidene]-4'-n-butylaniline, have been investigated. The nematic phase shows uninterrupted miscibility in all the binary systems. Induced smectic A phase is observed in all but one diagram of state. The effect of 4-cyano-3-fluoro substitution on induced phases is discussed on the basis of dipole moments.

Isobaric diagrams of state of binary liquid crystalline systems with similar chemical structures of the components constituting the system show, in general, nearly linear phase boundaries. However, binary liquid crystalline systems, in which the components possess different molecular structures, often give unusual diagrams of state. Smectic phases are stabilised in middle concentrations in certain nematogenic mixtures consisting of components with a polar and a non-polar end groups. A model based upon non-polar (N) and polar (P) end groups was provided by Engelen et al., in which NP type mixtures were shown to exhibit induced smectic phases. Moreover, mixtures of nematic electron donors and acceptors form induced smectic phases, which exhibit typical charge transfer absorption bands. Furthermore, mixtures consisting of a bilayer (B) and a monolayer (M) liquid crystals also show induced smectic phases. de Jeu et al. provided a mathematical explanation for the formation of induced smectic phases.

This paper presents the results of investigations on the mesomorphism in the mixed phases in binary liquid crystalline systems consisting of N-(4-ethoxybenzylidene)-4'-n-butylaniline (EBBA) and 3-fluoro-4-cyano benzoates. The appearance of different modifications and the dependence of transition temperatures on the 3-fluoro-4-cyano end group is discussed.

Materials and Methods
The chemical names, the structural formulae, the different mesophases and transition temperatures of the liquid crystals used in this paper are as follows:

(a) (4-Cyano-3-fluorophenyl) -4- [4'-n-heptylcyclohexyl*-benzoate [CFPHCHB]
Cr 84.3 N* 182 Is

(b) (4-Cyano-3-fluorophenyl) - 4 - [4'- (2-methylbutyl)phenyl]-benzoate [CFPMBPB]
Cr 48 N* 145 Is

(c) (4-Cyano-3-fluorophenyl)-4-[4'-(2-n-pentylphenyl]-benzoate [CFPPPB]
Cr 90.5 N* 190 Is

(d) (4-Cyano-3-fluorophenyl) -4'-n-decylbenzoate [CFPDB]
Cr 55 SA 57 N* 63 Is

(e) (4-Cyano-3-fluorophenyl) - 4 - [4'- (n-dodecyloxyphenyl]-benzoate [CFPDOB]
Cr 66.5 (SA 66) Is
(f) 4-(4-Cyano-3-fluorophenyl)-phenyl-4-(4'-n-\text{-heptylphenyl})-benzoate [CFPPHPB]
Cr 85.5 N* 183.5 Is

(g) N-4-Ethoxybenzylidene-4'-n-butylniline [EBBA]
Cr 35.5 N 80.1 Is

The compounds (a)-(f) are benzoates with a 4-cyano-3-fluorophenyl substitution; these were first reported by Kelly and Schad. The synthesis of these compounds for the use of this work was carried out in the laboratories of the Berlin Liquid Crystal Group.

**Results and Discussion**

All the components used in this study possess nematic or cholesteric phase except CFPDDB which possesses additionally smectic A phase and CFPDOB, which shows only monotropic smectic A phase.

The diagrams of state of EBBA, which is a non-polar liquid crystal and a substance with polar 4-cyano-3-fluoro groups attached to the end phenyl ring, were studied. The details of only one representative diagram of state between EBBA and CFPHCHB are given Fig. 1. The nematic phases of both the liquid crystals were uninterrupted miscible with each other. The nematic phase also covers the largest area of this system. Neither EBBA nor CFPHCHB possesses smectic A phase, which appears at 64.8°C on the side of EBBA as shown in Fig. 1. Smectic A phase is restricted by the solidification fronts at 52.2°C and 29.0°C. The eutectic is found at 22.5°C.

Similar diagrams of state were observed in the binary liquid crystalline systems EBBA/CFPMBPB, EBBA/CFPPOB, EBBA/CFPDB and EBBA/CFPPHPB. All these systems showed uninterrupted miscibility of nematic modification and a small area of induced smectic A phase. The highest induction temperatures at which smectic A modification appears on cooling from nematic are listed in Table 1. However, no induced smectic A phase was observed in the system EBBA/CFPDOB.

The difference in clearing points of the two components in these binary liquid crystalline systems is very large; hence, a smooth nematic/isotropic heterogeneous region between the two clearing points is observed. On the contrary, a minimum is observed in nematic/isotropic heterogeneous region in the system EBBA/CFPDB as the difference in the clearing points of the two components is small.

Interestingly, the induced smectic A of the system EBBA/CFPDB is not miscible with the smectic A of the pure component CFPDB. The compounds with cyano end group are said to possess a double layer structure whereas induced smectic A phase is monolayer and the immiscibility may be due to two types of smectic A modifications.
EBBA is non-polar, whereas the compounds with 4-cyano-3-fluoro group should be highly polar. As the polar groups are at adjacent positions, the polarity of 4-cyano-3-fluoro group will be less than that of the compound with only $-\text{CN}$ or $-\text{F}$ substitution, which is evident from the investigations carried out by Schneider et al.\(^8\) on the binary systems with EBBA as one of the components and alkyl or alkoxy cyano biphenyls as the other component. Much higher enhancement in transition temperatures was observed in systems with cyano biphenyls than that in the systems with cyano fluoro phenyls. As against only induced smectic A in cyano fluoro systems, induced nematic, induced smectic A, induced smectic B and induced smectic E were observed in systems with cyano biphenyls.

Mixtures of non-polar-non-polar (N-N) or polar-polar (P-P) liquid crystals show no enhancement in the transition temperature but a binary system of polar-non polar (P-N) liquid crystals shows induced phases. All the systems investigated fall under the P-N category.

In compounds with cyano fluoro end group, electrons are withdrawn from the aromatic ring rendering it electron deficient. There is an increase in the electron affinity of the aromatic ring with the electron cloud protruding towards cyano fluoro substituents. The ethoxy and butyl substituents of EBBA are electron donating which release electrons to the aromatic ring rendering it electron rich. This results in the decrease in the ionisation potential of $\pi$-electrons on the side of ethoxy and $\sigma$-electrons on the side of butyl group. Two such moieties interact to form charge transfer complexes. This interaction tends to lead towards the formation and induction of smectic A phase in these systems. The effect of bridging group, $-\text{CH}=\text{N}-$, could not be ascertained, as also reported earlier\(^9,10\).

References