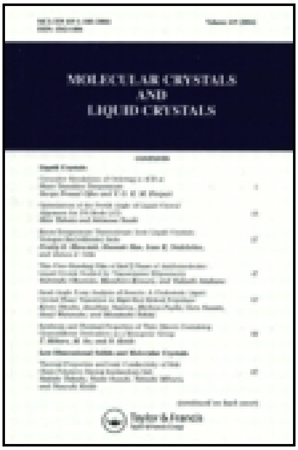


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Induced Smectic Mesomorphism by Incompatible Nematogens

Chan S. Oh [a]

[a] Beckman Instruments, Inc., Helipot Division, Fullerton, California, 92634

Version of record first published: 28 Mar 2007.

To cite this article: Chan S. Oh (1977): Induced Smectic Mesomorphism by Incompatible Nematogens, Molecular Crystals and Liquid Crystals, 42:1, 1-14

To link to this article: http://dx.doi.org/10.1080/15421407708084491

Mol. Cryst. Liq. Cryst., 1977, Vol. 42, pp. 1–14
© Gordon and Breach Science Publishers, Ltd., 1977
Printed in Holland

Induced Smectic Mesomorphism by Incompatible Nematogens

CHAN S. OH

Beckman Instruments, Inc., Helipot Division, Fullerton, California 92634

(*Received September 1, 1976; in final form December 27, 1976*)

Non-linear behaviors of nematic–isotropic transition temperatures and the appearance of the "solid-like" phase found in the mixtures between MBBA and 4-cyano-4′-*n*-pentylbiphenyl (CPB)[1] are now found to be quite general among many other nematogens. The cyano-group containing nematogens do not have to be biphenyl derivatives, nor do the "donner" type molecules need to be limited to Schiff Bases and azo-type compounds. This type of phase diagram has also been obtained in mixtures of CPB with phenyl benzoates, azoxy and tolan nematogens. Other cyano-group containing nematogens, such as substituted 4′-cyanophenyl benzoates and 4′-alkoxybenzylidene-4-aminobenzonitriles gave rise to behavior identical with the above nematogens. A detailed study on the phase diagram of mixtures containing 4-cyano-4′-*n*-octyloxybiphenyl and 4′-*n*-hexyloxy-phenyl-4-*n*-butyl benzoate has yielded further insight into the nature of the "solid-like" phase. The smectic thermal stability of the alkoxycyano-biphenyl decreased sharply as the concentration of the phenyl benzoate nematogen increased, while the thermal stability of the "solid-like" phase increased, drawing the typical conical shape, to such an extent that the mixtures of certain concentration ranges failed to exhibit any nematic phase. Careful observation of the "solid-like" phase, as it appeared from its isotropic phase, under a polarizing microscope, revealed many characteristics of the classical smectic mesophase, e.g. bâtonnets, focal conic fan textures, and Grandjean terraces. The mixtures outside of this range exhibited a series of phase transitions; isotropic to nematic, isotropic and nematic to solid-like phase, and nematic to true solid. All these phase transitions, except for the last one, were reversible without super-cooling. These results cast doubts over the nature of this solid-like phase which has been claimed to be due to formation of a charge transfer type compound in the literature.[1] A substructure between the two incompatible nematogens, such as a dipole induced lamellar structure, is proposed as an alternative model to account for the results.

INTRODUCTION

It has been common experience among chemists to obtain a uniform nematic liquid crystal by mixing two thermotropic, enantiotropic or monotropic nematic liquid crystalline materials. The melting points of the mixtures are usually lower than those of the single components. Furthermore, the nematic–isotropic transition temperatures of the mixtures usually fall between those of the single components and a smooth line can be drawn connecting the nematic–isotropic points of these mixtures when they are plotted against their composition.

Nematogens containing a cyano group attached directly to an aromatic ring are becoming more important in industrial applications due to their use in display devices of the twisted nematic or related field effect types. Thus, attempts have been made to blend the cyano-containing nematogen with some of the readily available nematic compounds to obtain mixtures with low melting points and wide nematic temperature ranges, which would be more acceptable in liquid crystal display applications. It has been found, however, that not all nematogens will freely intermix to yield a uniform nematic phase. Some, instead, form an unusual non-nematic material. For example, 4-cyano-4′-*n*-pentylbiphenyl forms a "solid-like" non-nematic phase with MBBA[1], EBBA, nematogens derived from phenyl benzoates, azoxy compounds and even tolans. A detailed study of the phase diagram and some microscopic observations of this "solid-like" phase have revealed that this phase is some type of solution induced smectic mesophase. A recent report[1] on the unusual phase diagram of mixture liquid crystals between CPB and MBBA suggests that the two compounds form a charge-transfer type complex. This postulation was based on the presence of an increased ΔT_{NI}, two eutectic compositions, a shift in the UV absorption bands and a non-linear ΔH solid–nematic composition curve. This, however, does not explain satisfactorily the textures and the thermal behaviors, such as the reversible transitions between the nematic and the "solid-like" phase, and the scope of incompatibilities among the various chemical species examined during the course of the present study. In order to explain these phenomena, a new substructure between the two incompatible nematogens, such as a dipole induced lamellar structure is proposed.

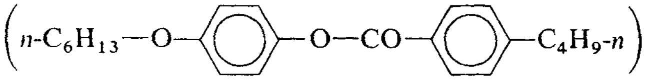
EXPERIMENTAL

Materials: All the single component nematogens were prepared and purified by the published methods[2,3] and the correct transition temperatures were obtained. Mixtures were prepared by weighing materials into a clean vial and mixing thoroughly by agitating the mixture solution in its isotropic state. Tolans and Azoxy nematogens were purchased from Gallard Schlesinger Chemicals and E. Merck, respectively, and materials from the fresh vials were used without purifications.

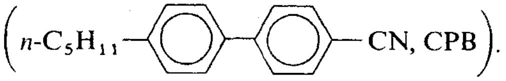
Determination of Transition Temperatures: Samples were sealed in capillary tubes in the isotropic phase and kept in an ice chest (−10°C) until used. The transition temperatures were measured in a Thomas–Hoover melting point apparatus. The transitions between the "solid-like" and nematic phases could readily be observed by the abrupt changes in the light scattering characteristics of the sample bulk. The temperatures were reproducible within 1°C between the heating and cooling cycles. Solid to "solid-like" phase transitions were obtained in the same manner. Most of the transition temperatures were also measured using a differential scanning calorimeter (DuPont Model 990). The sample sizes were 2–10 mg, and the heating and cooling rates were 10°C per minute unless otherwise noted. The textures of the mesophases were examined with a Wild microscope equipped with Polarizers and a hot stage at magnifications of 120X.

RESULTS AND DISCUSSION

A series of mixtures was prepared from 4′-*n*-hexyloxyphenyl-4*n*-butylbenzoate[2]



and 4-cyano-4′-*n*-pentylbiphenyl[3]



Except for the mixtures containing major proportions of either compound, all the mixtures appeared viscous and adhered to the wall of the capillary tube, which is a typical behavior of smectic mesophases. On heating, this viscous material was converted into a nematic phase at a finite temperature in a reversible transition. Further heating gave the clear isotropic liquid.

The nematic–isotropic and the "solid-like" to nematic phase transition temperatures as determined in capillary tubes are plotted versus the composition of the mixtures in Figure 1. Notice the non-linear behavior of the N–I transition temperatures versus composition curve with a maximum at approximately equimolar composition, and the steep rise in the thermal stability of the "solid-like" phase. This equimolar mixture was examined under a polarizing microscope at room temperature, and the photomicrograph is reproduced in Figure 2. It exhibits the typical focal conic texture of a smectic mesophase, and the cover glass could easily be displaced resulting in disrupting the texture. A typical "Grandjean" stepped layer structure was observed, using a polarizing microscope, when a drop of the sample was placed on a clean slide which had been treated with the homeotropic aligning

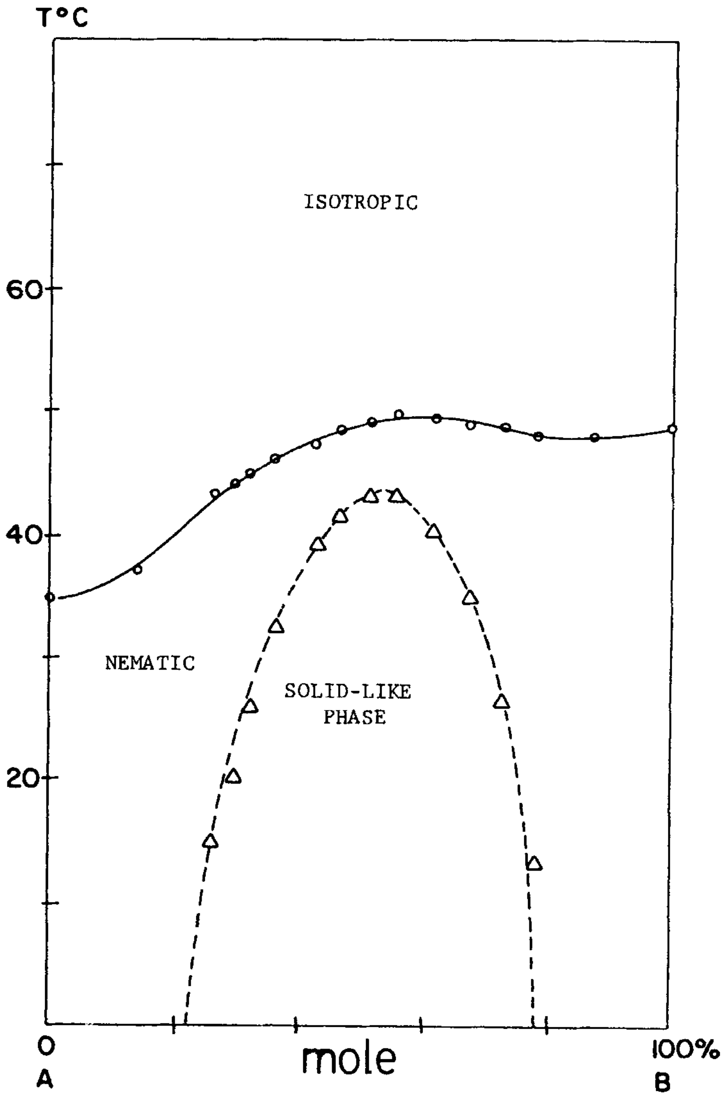


FIGURE 1 Phase diagram of mixture of CPB (A) and 4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate (B).

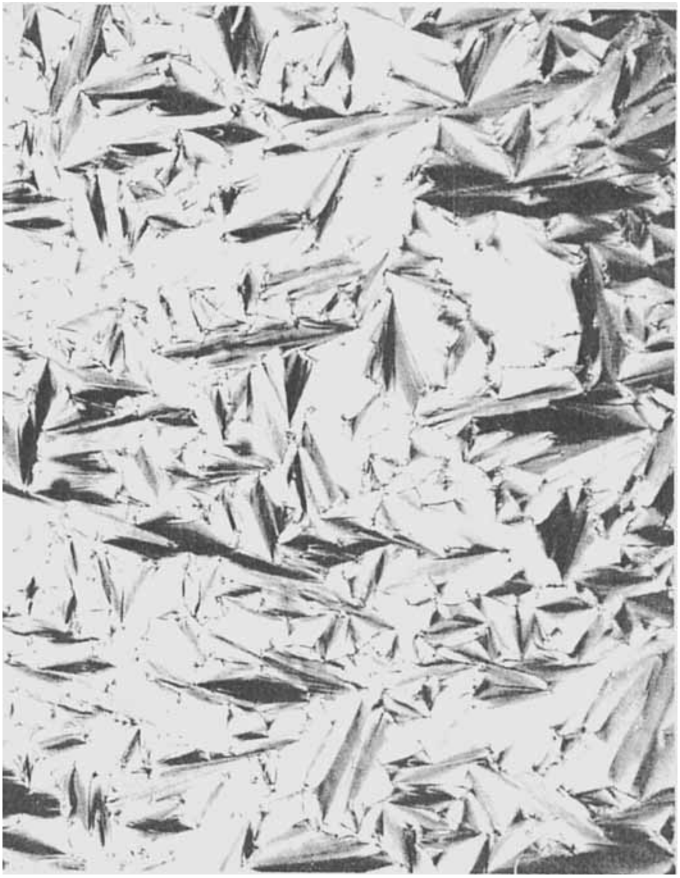


FIGURE 2 Focal conic texture of the "solid-like" phase.

silane derivative[4] and without a cover slip. A differential scanning calorimetric curve for this mixture[5] showed two distinct transitions representing the "solid-like" to nematic and nematic to isotropic phase transitions (Figure 3). No attempt was made to obtain the thermogram of the solid to "solid-like" phase transition which probably exists at a very low temperature. The two peaks appeared at essentially the same temperatures during both the heating and cooling cycles, indicating that the transitions are most likely mesophase–mesophase and mesophase–isotropic types.

The smectic nature of the "solid-like" phase was further studied using another series of mixtures consisting of a cyanobiphenyl derivative which has its own enantiotropic smectic mesophase[3] and the phenyl benzoate nematogen. A more complex phase diagram was obtained for mixtures of

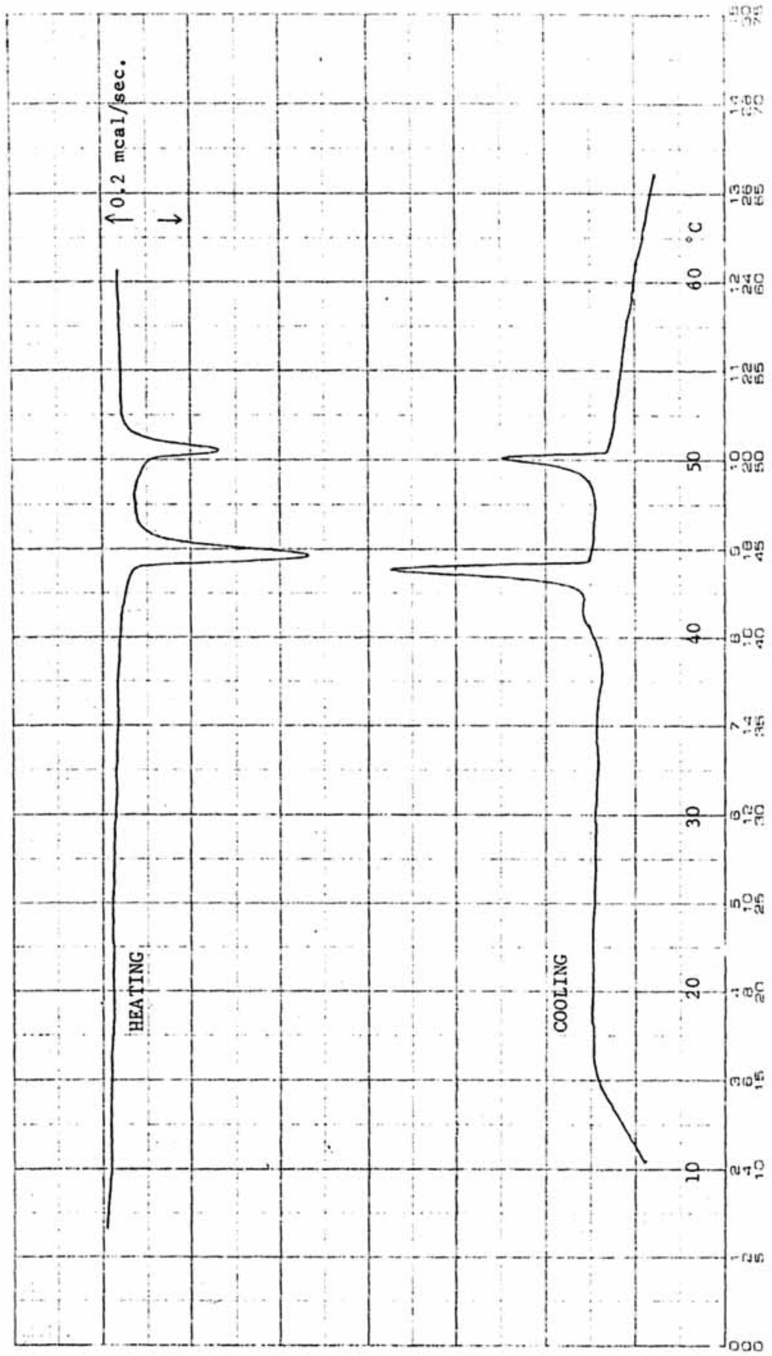
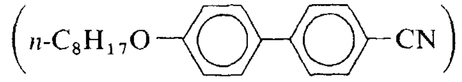


FIGURE 3 DSC Curve of Mixture of 50 Mole % CPB in 4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate.

4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate and 4-cyano-4′-*n*-octyloxybiphenyl



as shown in Figure 4. These mixtures solidified readily near or above ambient temperatures. For example, a mixture containing 26.9 mole % phenylbenzoate in the biphenyl derivative melted into a "solid-like" phase at 64°C, which then underwent "solid-like" to nematic and nematic–isotropic phase transitions at 59°C and 76.5°C, respectively. A DSC curve of the same mixture is shown in Figure 5[6].

Upon examination of Figure 4, several unusual features are noticed in addition to the melting point depression and the appearance of the "solid-like" phase as expected. Several of these mixtures were readily super-cooled below the melting temperature, thus, monotropic "solid-like" phases were observed. The thermal stability of the smectic phase of 4-cyano-4′-*n*-octyloxybiphenyl decreased sharply as the concentration of the phenyl benzoate was increased. On the other hand, the thermal stability of the "solid-like" phase increased to such an extent as to overtake the nematic thermal stability of the mixtures. Indeed, the points "d," "e," "f," and "g" (in Figure 4) developed the characteristic bâtonnets instead of nematic spherulites when their isotropic liquids were slowly cooled below the transition temperatures The bâtonnets could be observed, as shown in Figure 6, when the mixture "d" was cooled from its isotropic phase.

This phase diagram also indicates that the smectic mesophase of 4-cyano-4′-*n*-octyloxybiphenyl, which is believed to be a bilayered smectic A phase,[7] is immiscible with the induced "solid-like" phase of the mixture. Thus, according to the known miscibility tests for smectic mesophases,[8] the smectic phase of the biphenyl material and the induced "solid-like" phase are of a different kind and probably not a smectic A phase. The transition temperatures for the lowest temperature phase transition which could be supercooled are indicated by "X" (crystal to mesophase) in Figure 4. A line drawn through these points represents the typical melting point depression curve between two solids, having an eutectic composition at about 52 mole % of the phenyl benzoate nematogen in 4-cyano-4′-*n*-octyloxybiphenyl. While the literature report[1] indicated the existence of two eutectic points in their MBBA–CPB mixtures, the present experimental data directly contradicts these results. If formation of a charge transfer type molecular complex gave rise to the observed "solid-like" phase between incompatible nematogens, then the molecular interactions would have to occur through the highly polarizable aromatic nuclei and in conjunction with the permanent dipoles of the nematic molecules. However, compounds in which either the pentyl

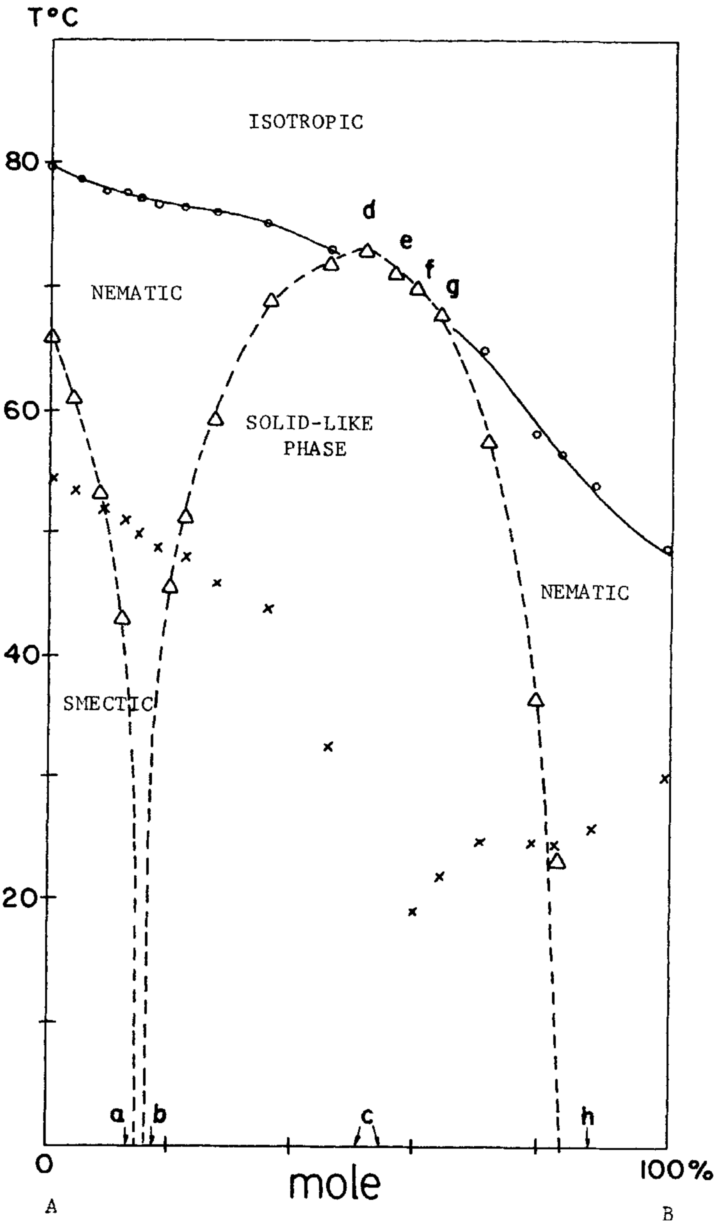


FIGURE 4 Phase Diagram of Mixture of 4-cyano-4′-*n*-octyloxybiphenyl (A) and 4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate (B).

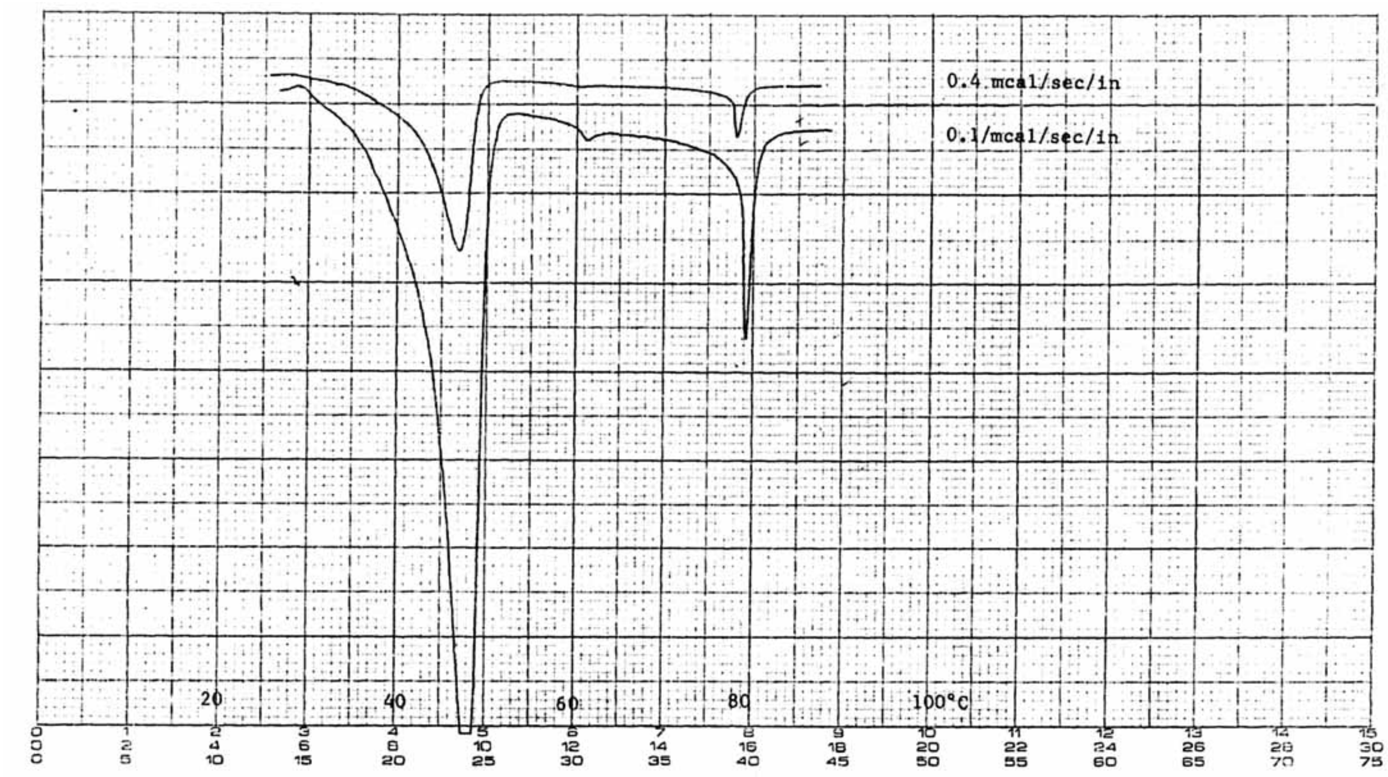


FIGURE 5 DSC curve of mixture of 4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate (A, 26.9 mole %) in 4-cyano-4′-*n*-octylaxybiphenyl.

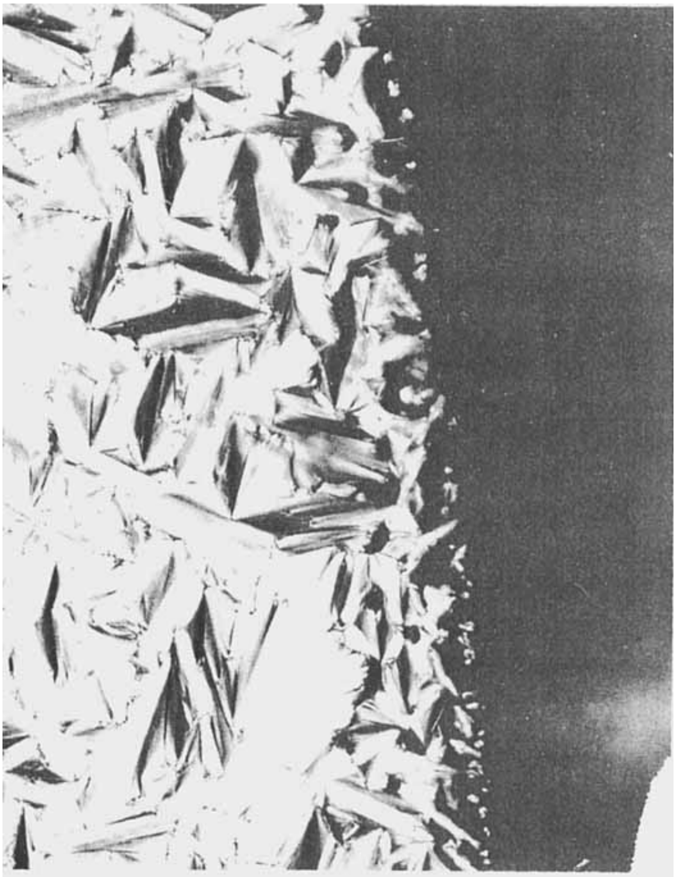


FIGURE 6 Bâtonnets of mixture "d" as it appeared from isotropic phase.

or the cyano group has been removed from CPB did not give this "solid-like" phase when these compounds were tested for their compatibilities with the same phenyl benzoate nematogen. Instead, the nematic thermal stability of the ester nematogen dropped sharply. Even the so-called "latent" nematic properties of these compounds did not yield the "solid-like" phase with the phenyl benzoate nematogen, indicating that the cyano-containing material must have fairly high nematic thermal stability in order to form this incompatible mixture with other nematogens.

These incompatibilities were also experienced among many other commonly known nematogens. Mixtures of MBBA and CPB, 4′-*n*-hexyloxyphenyl-4-*n*-butylbenzoate and 4′-cyanophenyl-4-*n*-alkylbenzoates, 4′-*n*-hexyloxybenzylidene-4-aminobenzonitrile and EBBA, tolanes and CPB, and E. Merck's Nematic Phase IV and CPB, yielded similar "solid-like" phase and their phase diagrams exhibited the non-linear nematic–isotropic phase transition lines. In all of these examples, at least one of the components is a cyano-group containing nematogen and is not necessarily derived from biphenyl. A more striking example is the second pair in which both of the nematogens were phenyl benzoate derivatives, yet yielded the incompatible mixtures. In general, higher homologs of the alkyl group attached to a given nematogen had a tendency to yield "solid-like" phases of higher thermal stability. If both components were cyano-group containing nematogens, as in

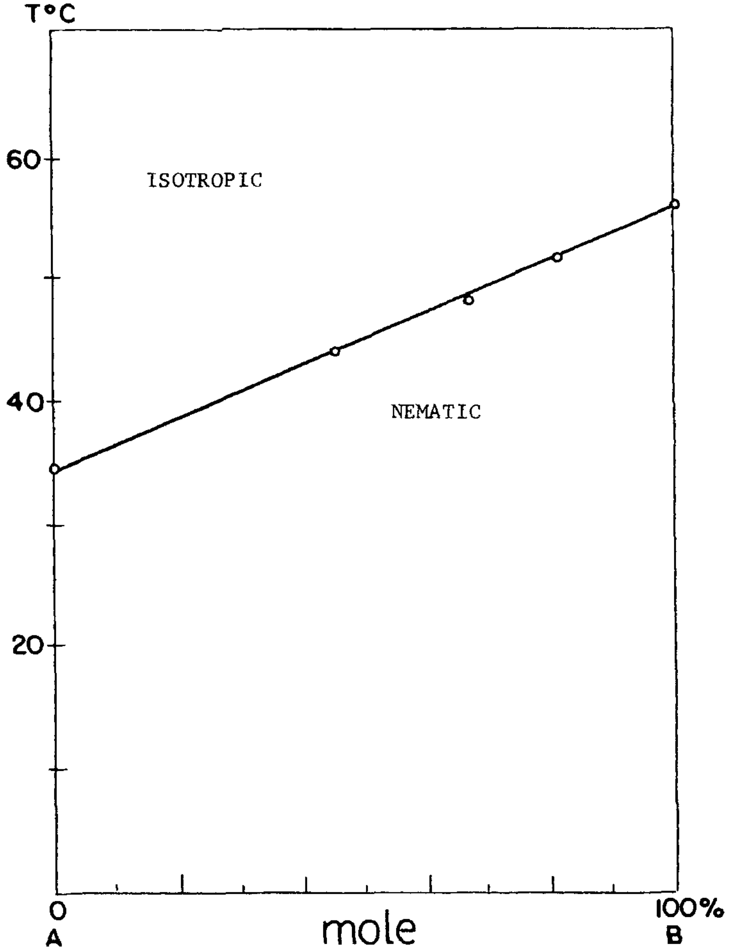


FIGURE 7 Phase diagram of mixture of CPB (A) and 4′-cyanophenyl-4-*n*-heptylbenzoate (B).

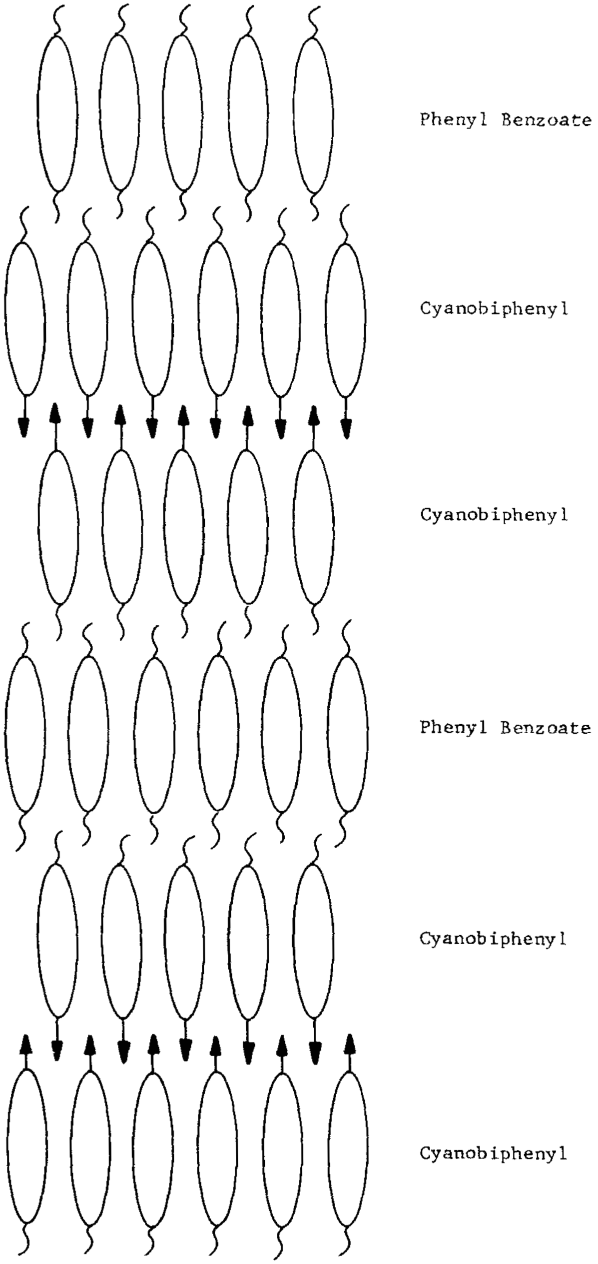


FIGURE 8 The proposed Lamellar model for the "solid-like" phase.

mixtures between CPB and 4′-cyanophenyl-4-*n*-heptylbenzoate, the phase diagram of a typical compatible system appeared, as illustrated in Figure 7; i.e., a linear relationship of the nematic–isotropic transition temperatures versus the composition of the mixture.

Based on the above results, it has been shown that the "solid-like" phase produced by mixing two incompatible nematic liquid crystals resembles a smectic mesophase more than a solid. While it is quite probable that a donor–acceptor type molecular complex formation is taking place in these "solid-like" phases, the nature of these phases is probably not a simple solid as postulated in the literature.[1] Factors which favor the formation of a nematic mesophase in the cyano-group containing nematogens may be due to the strong dipolar group interaction. On the other hand, those in the phenyl benzoates and other nematogens are probably due to the conventional lateral-to-terminal attractive force balances. Thus, when these two vastly different nematic materials are mixed, the forces which give rise to the respective nematic mesophase become weaker and another type of molecular interaction occurs, which favors a new molecular level association. The strongly dipolar solutes pair up through the permanent dipole, then simply disperse among the relatively less polar nematic solvent. This molecular pair would behave like rod-shaped molecules with long terminal hydrocarbon chains, which encourages formation of the smectic type mesophase.

Alternatively, in view of the recent comments on the smectic mesophase of cyanobiphenyl mesogens,[9] it is quite possible that these cyano-containing molecules tend to form aggregates through the alternating cyano-group dipoles. A lamellar structure IV, as shown in Figure 2 of Ref. 9, would have sandwiched layers with both surfaces being the hydrocarbon layers. The nematic host material which has two hydrocarbon chains at both ends of the rod-like molecules, can then form another layer on top of the lamellar structure, as shown in Figure 8. A similar model was used to explain the lyotropic phase G, which exhibits many of the microscopic textures of a thermotropic smectic mesophase.[10]

References

1. J. W. Park, C. S. Bak, and M. M. Labes, *J. Amer. Chem. Soc.*, **97(15)** 4398 (1975).
2. M. E. Neubert, L. T. Carlino, R. D'Sidocky, and D. L. Fishel, *Liquid Crystal and Ordered Fluids*, Vol. 2, Ed., Johnson, J. F., Porter, R. S., Plenum Press, New York, 1974, p. 293.
3. G. W. Gray, K. J. Harrison, and J. A. Nash, *Liquid Crystal and Ordered Fluids*, Vol. 2, Ed., Johnson, J. F., Porter, R. S., Plenum Press, New York, 1974, p. 617.
4. F. J. Kahn, *Appl. Phys. Lett.*, **22(8)**, 386, 1973.
5. 5 mg sample, 5°/min. heating and cooling rate on a differential scanning calorimeter, DuPont Model 990. DuPont Instrument.
6. 2.60 mg sample, 10°C/min. heating and cooling rate on the same instrument. The sample was cooled overnight at −10°C.

7. J. E. Lydon and C. J. Coakley, *J. de Phys.*, **36**, C1-45 (1975).
8. H. Sackman and D. Demus, *Liquid Crystals*, Ed., Brown, G. H., Dienes, G. J., and Labes, M. M., Gordon and Breach Science Publishers, New York, 1966, p. 341.
9. G. W. Gray and J. E. Lydon, *Nature*, **352**, 221 (1974).
10. *Liquid Crystals and Plastic Crystals*, Vol. 2, Ed., Gray, G. W., and Winsor, P. A., Ellis Horwood Ltd., Chichester, England, 1974, p. 52.