Antiphase Behavior in the 4-n-alkoxybiphenylyl-4′-cyanobenzoates (nOBCB's)

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Antiphase Behavior in the 4-*n*-alkoxybiphenylyl-4'-cyanobenzoates (*n*OBCB's)

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A number of members of the 4-*n*-alkoxybiphenylyl-4'-cyanobenzoate (*n*OBCB) homologous series were prepared and found to exhibit smectic antiphase behavior. The early homologues (*n*-pentyloxy to *n*-heptyloxy) possess A_1 phases while the higher members (*n*-octyloxy to *n*-dodecyloxy) show Ad phases. At the *n*-octyl homologue a tilted C̃ antiphase is introduced. The Ad to C̃ phase change was shown to be strongly first order from differential scanning calorimetry. Later members of the series also exhibit smectic C phases on cooling the C̃ phase, for example, the decyloxy compound exhibits an Ad, C̃, C phase sequence on cooling. Miscibility studies between the early and later members show reentrant nematic phase behavior which occurs at the junction of the N–A_1 and N–Ad transition temperature curves. The analogous materials, the 4-cyanophenyl 4'-*n*-alkoxybiphenyl-4-carboxylates do not exhibit antiphases and simply show N and A phases.

1. INTRODUCTION

The ways in which polar molecules can overlap to form bilayer structures have recently been the subject of many investigations.[1-3] Consequently, a number of new smectic modifications have been defined which involve different forms of layering structure. For example, the smectic A phase has been divided into four basic groups by the different overlapping structures of the molecules; e.g., A_1 (monolayer), A_2 (bilayer), Ad (interdigitated bilayer), and Ã (antiphase, in-plane modulated structuring).[3] Similarly, the smectic C

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phase is being divided into subgroups along the same lines, e.g. C_1 (monolayer), C_2 (bilayer), and $\tilde{C}$ (ribbon or antiphase, in-plane modulation).[4]

This present study investigates the properties of 4-n-alkoxybiphenylyl-4'-cyanobenzoates (nOBCB's) in relation to these new developments in phase structure and classification. These substances were found to exhibit either A_1 or Ad phases, the C phase, and also the $\tilde{C}$ antiphase.

The title materials are a development of two phenyl ring structures, the 4-n-alkoxyphenyl 4-cyanobenzoates (nOPCB's) which had been studied previously.[5,6] These substances were found to possess a strongly bound overlapping bilayer structuring of the molecules resulting in the formation of Ad and C phases.

2. RESULTS

2.1. Homologous series

The transition temperatures obtained by differential scanning calorimetry for the 4-n-alkoxybiphenylyl-4'-cyanobenzoates (nOBCB's) are listed in Table I, and plotted as a function of increasing terminal alkoxy chain length in Fig. 1.

TABLE I

$C_nH_{2n+1}O-C_6H_5-C_6H_5-O.CO-C_6H_5-CN$

n	m.p.	Rec	B–A$_1$	$\tilde{C}$–A$_1$	C–Ad	C–$\tilde{C}$	$\tilde{C}$–Ad	A–N	N–I	A–I
5	136	112	(122)	—	—	—	—	187	261	—
ΔH	12.6	8.7	1.3	—	—	—	—	0.6	—	—
6	130	114	(119)	—	—	—	—	181	254	—
ΔH	9.7	6.7	1.3	—	—	—	—	0.6	0.5	—
7	132	113	—	—	—	—	—	164	238	—
8	130	121	—	(124)	—	—	—	161	238	—
ΔH	10.0	11.6	—	0.11	—	—	—	0.3	0.5	—
9	126	118	—	—	—	—	144	204	230	—
ΔH	7.3	6.4	—	—	—	—	0.3	•	0.4	—
10	127	122	—	—	—	118†	135	219	227	—
ΔH	11.0	10.3	—	—	—	—	0.4	0.1	0.7	—
11	119	117	—	—	—	121	123	217	218	—
ΔH	11.2	9.8	—	—	—	0.4	0.6	0.3	0.4	—
12	124	116	—	—	(123)	—	—	—	—	218
ΔH	7.7	5.2	—	—	1.27	—	—	—	—	1.8

*too small to be measured
ΔH   values in cal/g
†virtual transition temperature obtained from thermal optical microscopy
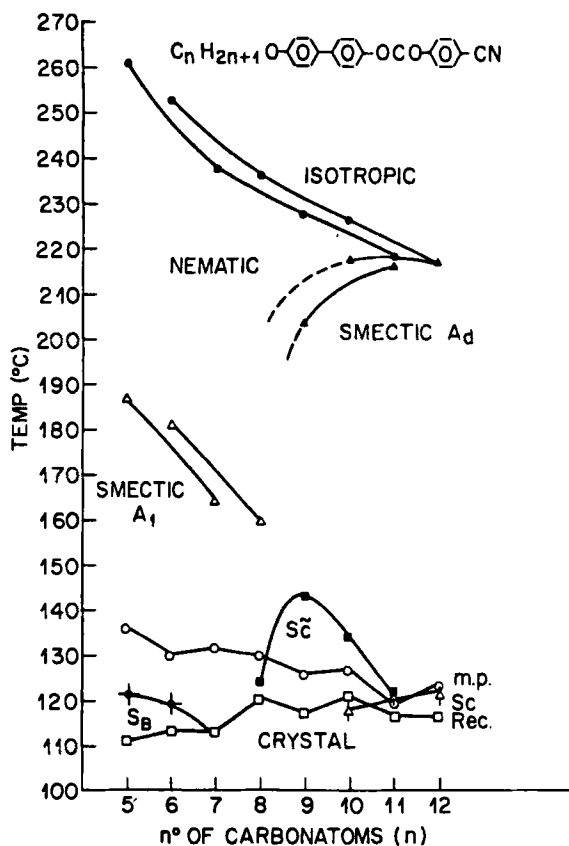( )   monotropic transition temperature

FIGURE 1   Plot of transition temperatures against the number of carbon atoms (*n*) in the *n*-alkoxy chain of the 4-*n*-alkoxybiphenylyl-4'-cyanobenzoates (*n*OBCB's). Key: ●, N–I; Δ, A_1–N; ▲, Ad–N or I; ■, C–A; ✦, B–A_1; ⟁, C–C or Ad; O, crystal-mesophase; □, mesophase-crystal on cooling.

It can be seen from Fig. 1 that the smectic A modification is divided into two branches; one at shorter terminal alkoxy chain lengths (*n*-pentyloxy to *n*-octyloxy) which conforms to the A_1 modification, and the other at longer chain lengths (*n*-nonyloxy to *n*-dodecyloxy) which is of the Ad type. There is an abrupt discontinuity between the transition temperature curves for the A_1 and the Ad modifications. Thus, the series is divided into two separate formats, the shorter members (*n* = 5 to 8) exhibiting nematic, A_1, and B phases, and the longer members (*n* = 9 to 12) nematic, Ad, $\tilde{C}$, and C phases.

The B phase falls sharply away with increasing alkoxy chain length and is replaced with the sudden injection of a $\tilde{C}$ phase at the

n-octyloxy homologue. The A–C̃ transition temperatures rise rapidly and falls again just as quickly with increasing terminal chain length. Thus, only the *n*-octyloxy to *n*-undecyloxy members exhibit this phase. A smectic C phase is injected at the *n*-decyl member and the C̃ to C or A–C transition temperatures continue to rise with increasing chain length.

2.2. Differential scanning calorimetry

The enthalpy values (cal/g) are given below the analogous phase transition in Table I for each homologue. From this tabulation it can be seen that the enthalpy for the nematic to A_1 phase transition is relatively large, but conversely it is very small for the nematic to Ad phase change. For the *n*-nonyloxy member, the enthalpy for this transition was so small it could not be measured accurately. This can be seen clearly by comparing Figs. 2 and 3 for 6OBCB and 9OBCB, almost no peak of transition is seen for the Ad–N transition in 9OBCB, but a large enthalpy of transition appears for the N–A_1 transition in 6OBCB.

Some other observations can be made from these figures. Firstly in Fig. 2 for the cooling cycle of 6OBCB, a large enthalpy is detected for the monotropic A_1–B transition which appears to be first order in nature. Optical microscopic investigations of this transition seem to indicate that the B phase is of the crystal B type. Secondly, Fig. 3
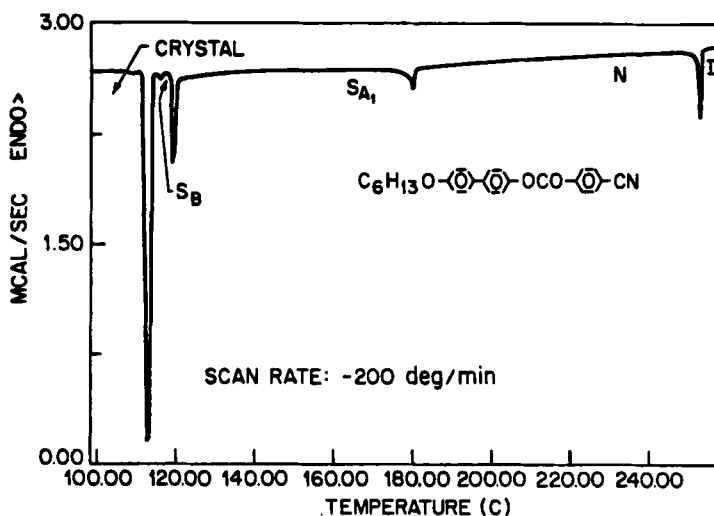

FIGURE 2 DSC cooling cycle for 4-*n*-hexyloxybiphenylyl-4′-cyanobenzoate (6OBCB). Scan rate 2°/min.
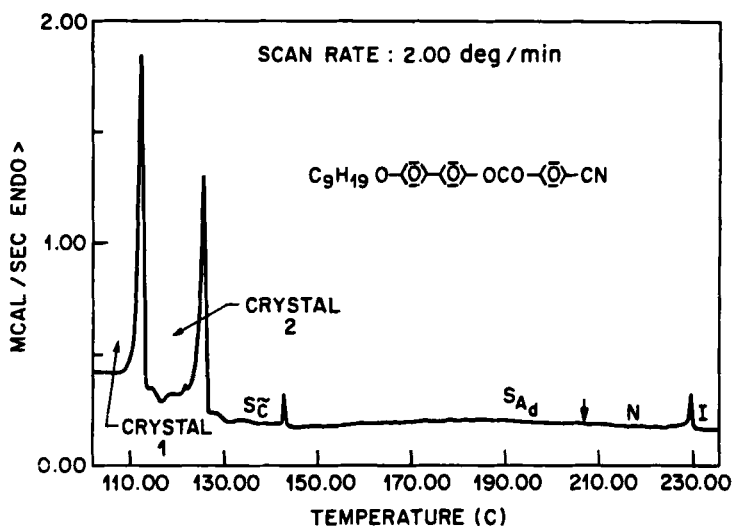
FIGURE 3   DSC heating cycle for 4-*n*-nonyloxybiphenylyl-4'-cyanobenzoate (9OBCB). Scan rate 2°/min.
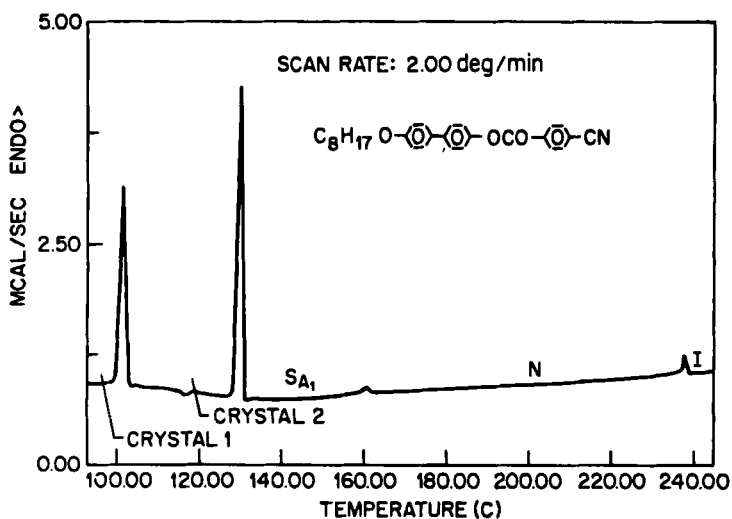
FIGURE 4   DSC heating cycle for 4-*n*-octyloxybiphenylyl-4'-cyanobenzoate (8OBCB). Scan rate 2°/min.
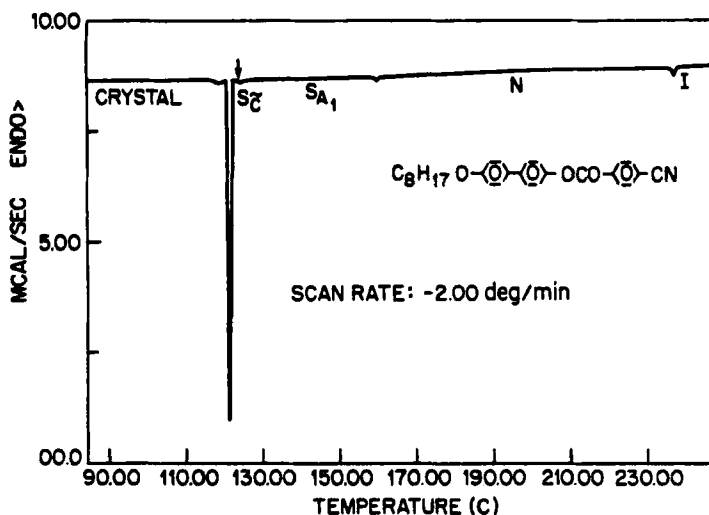
FIGURE 5   DSC cooling cycle for 4-n-octyloxybiphenylyl-4′-cyanobenzoate (8OBCB). Scan rate 2°/min.

shows the heating cycle of 9OBCB exhibiting two crystalline phases accompanied by large transition heats, and a $\tilde{C}$ to Ad transition which has a relatively large enthalpy value indicating that it is probably a first order phase transition.

Figures 4 and 5 show typical heating and cooling cycles for 8OBCB. Again the heating cycle exhibits two crystal forms before melting directly to the A$_1$ phase. Cooling shows an A$_1$ to $\tilde{C}$ phase transition occurring just before crystallization. It can be seen from Table I that most of these materials do not readily supercool, and differential scanning calorimetry also shows that they all have many crystalline phases.

Finally it should be noted from Table I that the enthalpy value for the Ad–C transition is relatively large for a phase change of this type which is usually second order in nature.

2.3. Optical microscopy

The most interesting phase sequence observed in these materials was the Ad–$\tilde{C}$–C progression observed in 10OBCB. The textural changes that occur in this sequence are shown in Figures 6–8. Figure 6 shows the $\tilde{C}$ phase separating from the homeotropic Ad phase on cooling, and Figure 7 shows the final texture after the transition was complete. The resulting texture is very similar to that of some columnar phases,
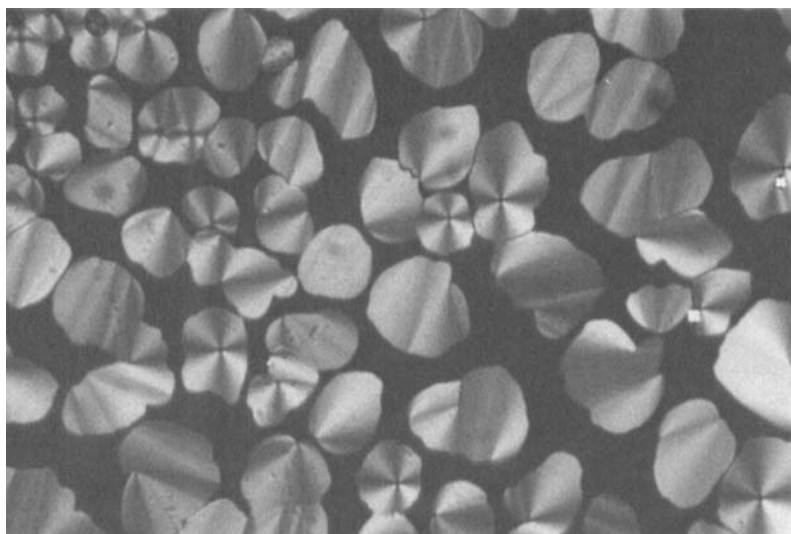
FIGURE 6   The C̃ phase separating from the homeotropic texture of the Ad phase of 4-n-decyloxybiphenylyl-4'-cyanobenzoate (10OBCB).

FIGURE 7   The fully developed texture of C̃ phase 4-n-decyloxybiphenylyl-4'-cyanobenzoate (10OBCB).

FIGURE 8   The schlieren texture of the smectic C phase formed on cooling the $\tilde{C}$ phase of 4-*n*-decyloxybiphenylyl-4'-cyanobenzoate (10OBCB).
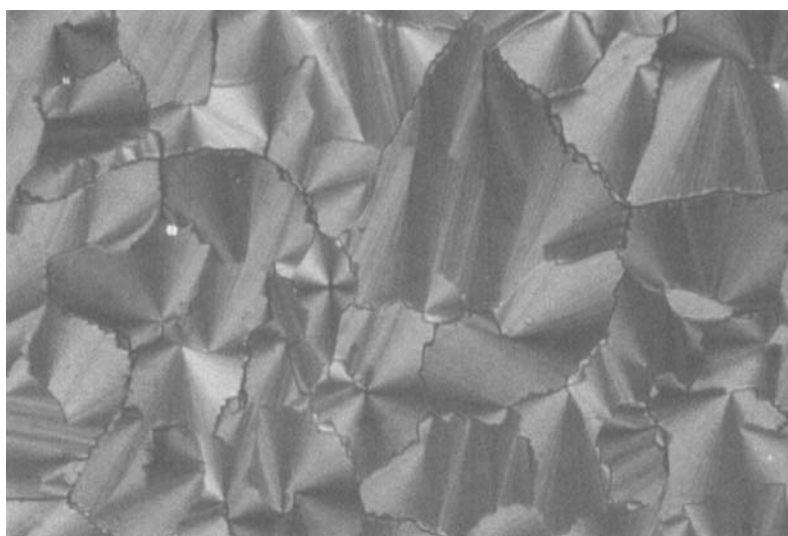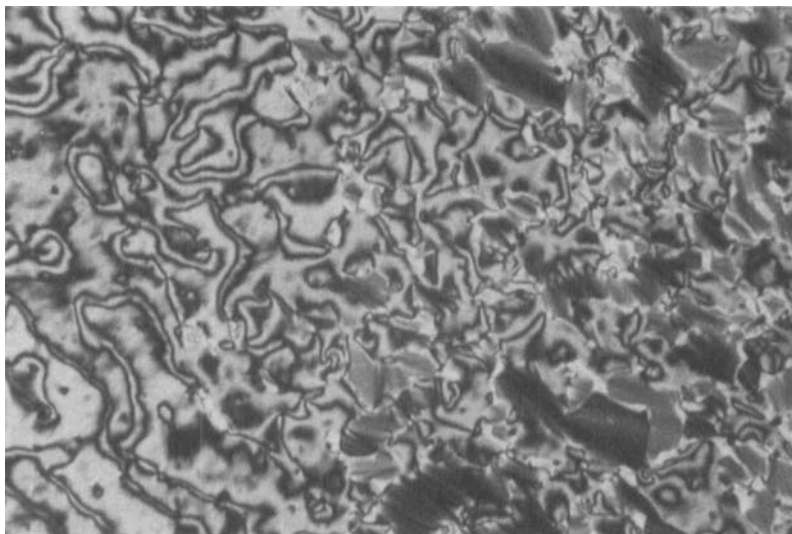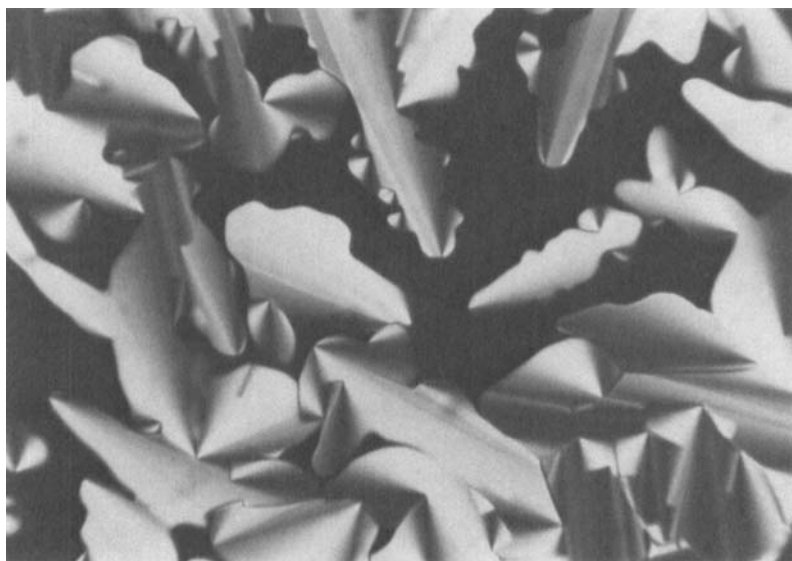

FIGURE 9   The $\tilde{C}$ phase forming in the homeotropic free-standing film of the Ad phase of 4-*n*-decyloxybiphenylyl-4'-cyanobenzoate (10OBCB).

i.e., discotic. Cooling of the focal-conic texture of the Ad phase resulted in the formation of a pseudo broken focal-conic texture for the $\tilde{C}$ phase. Cooling of the discotic-like texture of the $\tilde{C}$ phase produced a *schlieren* texture of the C phase (Figure 8).

Free-standing films of 10OBCB produced a homeotropic texture of the Ad phase, cooling of this phase to the $\tilde{C}$ modification again resulted in the formation of a discotic-type of texture (Figure 9). There was a considerable rise in the Ad–$\tilde{C}$ transition temperature ($\sim 10°$) due to the film thickness (~ 200 layers), and no $\tilde{C}$ to C phase transition was observed because of an accompanying rise in the recrystallization temperature.

As the $\tilde{C}$ phase segregated from the Ad phase on cooling the free-standing film of 10OBCB, thermal gradients gave rise to fluctuations in the texture. The Ad phase remained fluid, but the $\tilde{C}$ phase was very stiff (almost solid-like) to movements in the film due to these fluctuations.

The transitions in 5OBCB showed typical textures for an N–A_1–B phase sequence. As discussed previously the A_1–B phase change appeared to be accompanied by transition bars and stepping edges in the focal-conic domains indicating that the B phase is possibly of the crystal type and not hexatic.

2.4. Miscibility studies

A number of miscibility studies were made in order to investigate the properties of the phases of the nOBCB's, and these are best listed by their figure numbers.

Figure 10: A miscibility study between 12OBCB and 4-n-decyloxyphenyl 4'-cyanobenzoate (10OPCB)[5] was undertaken in order to examine the miscibility between the two A and C phases of these compounds. The A phases were found to be completely compatible, and as the A phase of 10OPCB had earlier been shown to be of the Ad type,[6] this study classifies the A phase of 12OBCB as Ad. The C phases of the two compounds appear to be miscible except for a region were the A to C transition temperature curve drops below the recrystallization line. The dotted line shows the 'virtual' transition temperatures obtained from quenching droplets of the individual mixtures in order to observe the A to C transition. The C phase of 10OBCB was previously shown to be of an interdigitated type,[6] and therefore this classes the C phase of 12OBCB as an interdigitated C phase, provided that the technique of quenching droplets does not involve segregation of the materials. Definitive classification therefore must await X-ray diffraction studies of the pure materials.
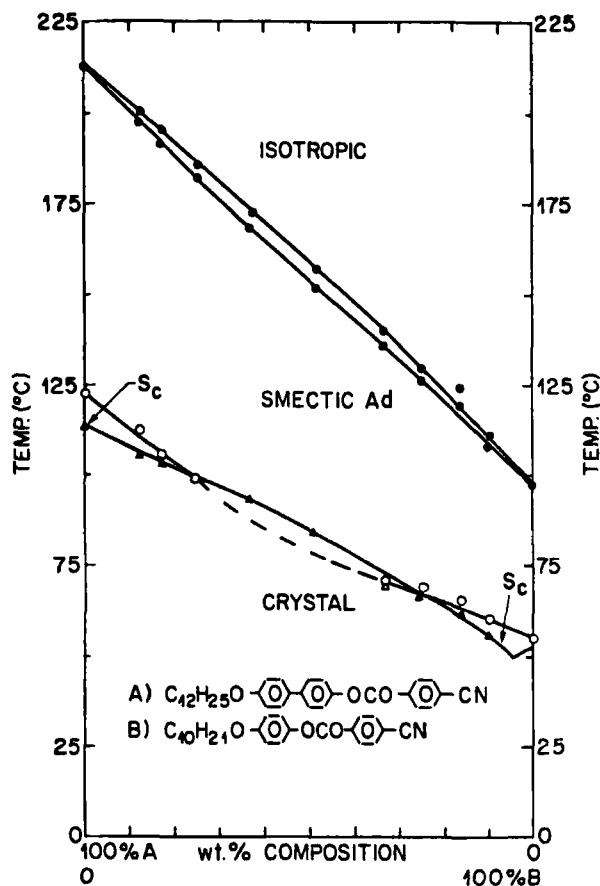
FIGURE 10   Miscibility phase diagram for mixtures (wt.%) between 4-*n*-dodecyloxybiphenylyl-4'-cyanobenzoate (12OBCB) A, and 4-*n*-decyloxyphenyl-4' cyanobenzoate (10OPCB) B. Dotted line indicates virtual transitions.

Figure 11: Mixtures between 8OBCB and 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB) show reentrant nematic and two forms of A phase behavior in the region of 10–30% by weight of 8OBCB. The A phase of 8OCB has been shown to be of the Ad type,[7] and this is not miscible with the A phase of the test material. The A phase of 8OBCB was in fact shown to be miscible with that of 5OBCB (see later) which in turn was shown to be of the A$_1$ type by X-ray diffraction studies.[8] Thus, this would class the A phase of 8OBCB as A$_1$. Therefore, an unusual phase sequence of N, A$_1$, N, Ad is apparently obtained in this miscibility study on cooling mixtures in the region of 10–30% by weight of 8OBCB. Alternatively, 8OBCB can appear to act as both as
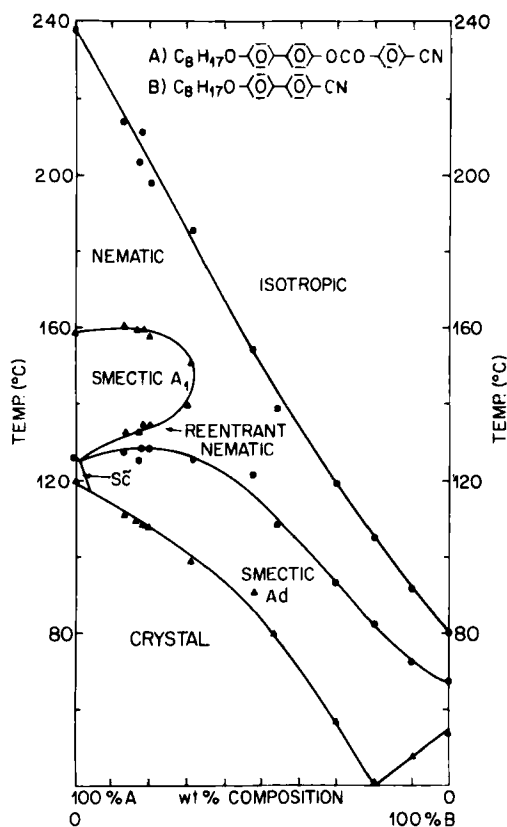
FIGURE 11   Miscibility phase diagram for mixtures (wt.%) between 4-n-octyloxybiphenylyl-4'-cyanobenzoate (8OBCB) A, and 4-n-octyloxy-4'-cyanobiphenyl (8OCB) B.

A_1 or an Ad material (see Fig. 14), therefore an N, Ad, N, Ad sequence cannot be ruled out for mixtures in this region.

Figure 12: The study between 5OBCB and 8OBCB was performed in order to investigate which branch of the A phase 8OBCB belonged to (A_1 or Ad). This study shows that the A phases of these two compounds are miscible, thus the A phase of 8OBCB is A_1 in type. The B phase of the parent compound 5OBCB fell alway on the addition of 8OBCB indicating that the n-octyl homologue does not exhibit this phase.

Similarly, the A_1 phase of 5OBCB was found to be immiscible with the Ad phase of 8OCB, except unlike in the 8OBCB case, no re-eentrant nematic behavior was observed.
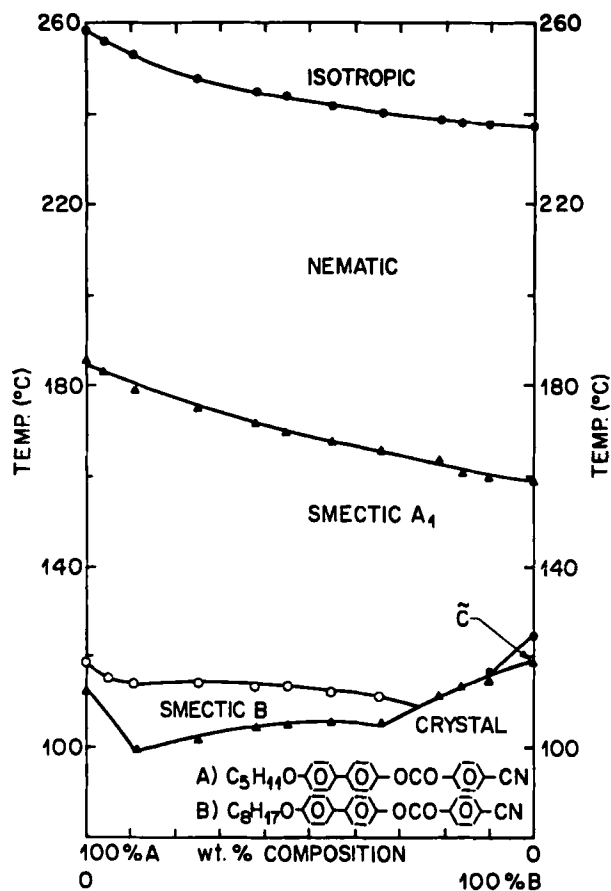
Figure 13: A study between 4-n-nonyloxyphenyl 4-nitro-

FIGURE 12 Miscibility phase diagram for mixtures (wt.%) between 4-*n*-pentyloxybiphenylyl-4'-cyanobenzoate (5OBCB) A, and 4-*n*-octyloxybiphenylyl-4'-cyanobenzoate (8OBCB) B.

benzoyloxybenzoate[9] (N, Ad, N, Ad, N, A_1, $S_?$, C_2) and 9OBCB was undertaken to investigate the miscibility of the $\tilde{C}$ phase of the test material with that of the $S_?$ phase of the standard compound. The phase diagram shows that the higher temperature nematic and Ad phases are completely miscible, as are the $C_?$ and $\tilde{C}$ phases. The lower temperature nematic, Ad and A_1 phases of the standard compound disappear rapidly with the addition of 9OBCB. The $C_?$ phase of the test material had previously been shown to be miscible with the $\tilde{C}$ phase of a standard material indicating that this phase of 9OBCB should be classed accordingly as $\tilde{C}$.
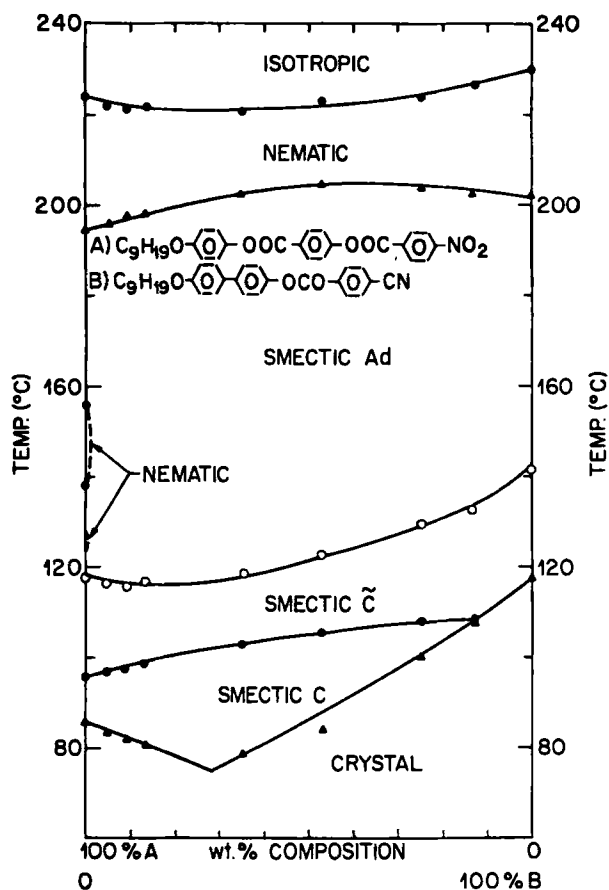
FIGURE 13   Miscibility phase diagram for mixtures (wt.%) between 4-n-nonyloxyphenylyl 4-nitrobenzoyloxybenzoate (DB$_9$ONO$_2$) A, and 4-n-nonyloxybiphenylyl-4'-cyanobenzoate (9OBCB) B. Dotted line indicates schematically how the N and Ad (reentrant) curves would appear. These transitions were not observed in any of the weighed mixtures.

Figure 14: The miscibility of 8OBCB and 12OBCB was investigated in this study. The A phase of 8OBCB although classed as A$_1$ also appeared to be miscible with the Ad phase of 12OBCB. However, A–A transitions (presumably Ad to A$_1$) were detected in the region of 5 to 15% by weight of 12OBCB suggesting that the Ad–N transition temperature line falls short of the A–N transition in pure 8OBCB. Further details concerning this part of the phase diagram will have to await detailed X-ray and DSC studies. In this region of the phase diagram, however, the A$_1$–$\tilde{C}$ transition temperatures rise rapidly to
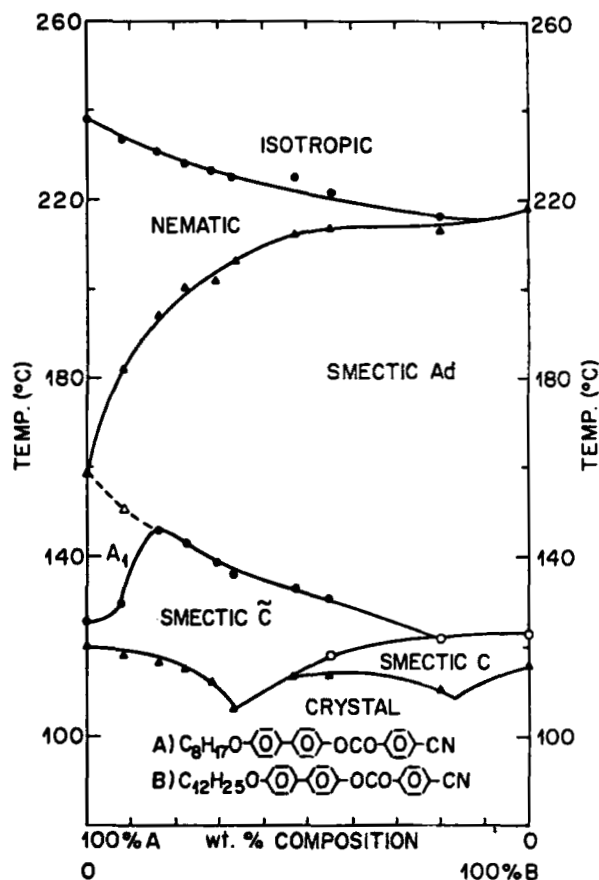
FIGURE 14   Miscibility phase diagram for mixtures (wt.%) between 4-*n*-octyloxybiphenylyl-4'-cyanobenzoate (8OBCB) A, and 4-*n*-dodecyloxybiphenylyl-4'-cyanobenzoate (12OBCB) B.

approximately 15% by weight of 12OBCB where the $\tilde{C}$ phase becomes more stable than the A_1 phase which then disappears.

Figure 15: The miscibility between 5OBCB and 10OBCB was charted in this figure. Here nematic, A_1, Ad, $\tilde{C}$ and B phases were observed, and the composition region around 40% by weight of 5OBCB was found to be of primary interest. As 10OBCB is added to 5OBCB a point is reached where the two become incompatible and a reentrant nematic phase is obtained. The A_1 phase then changes sharply to the $\tilde{C}$ phase. The N–A_1 and the Ad–$\tilde{C}$ transition temperature lines appear to constitute a single curve which is almost a straight
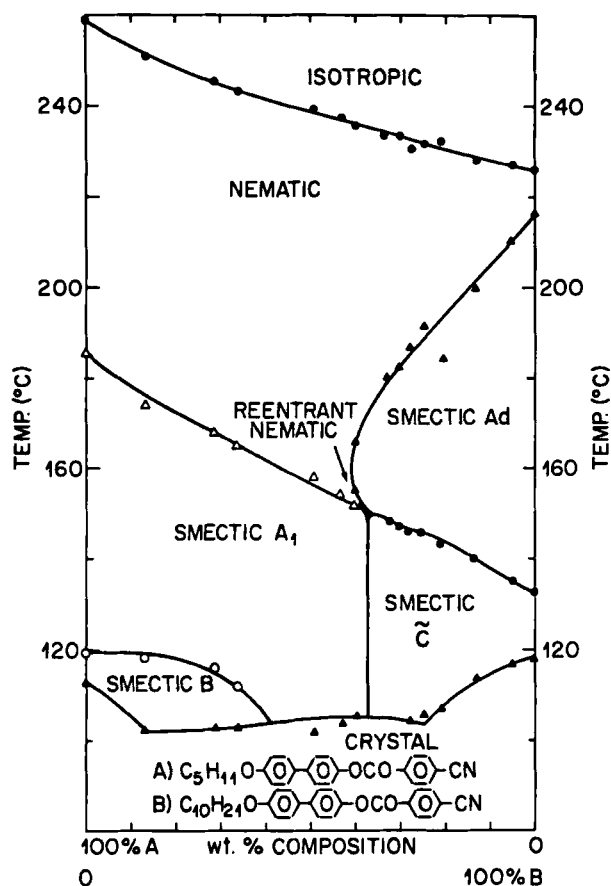
FIGURE 15 Miscibility phase diagram for mixtures (wt.%) between 4-*n*-pentyloxybiphenylyl-4′-cyanobenzoate (5OBCB) A, and 4-*n*-decyloxybiphenylyl-4′-cyanobenzoate (10OBCB) B.

line. There is an abrupt delineation between A_1 and $\tilde{C}$ which suggests that at this point (38% by weight of 5OBCB) there is a breakdown caused by the incommensurate lengths of the two molecules. This is caused by trying to fit molecules of differing lengths together in certain proportions which results in the formation of the $\tilde{C}$ phase.

Figure 16: This phase diagram, between 5OBCB and 12OBCB, is similar to that for 5OBCB and 10OBCB (Fig. 15) except that neither component in its pure form exhibits a $\tilde{C}$ phase, and yet this phase appears in the region of 60–85% by weight of 12OBCB. Again this phase is injected at the point where the A_1 and Ad phases meet to
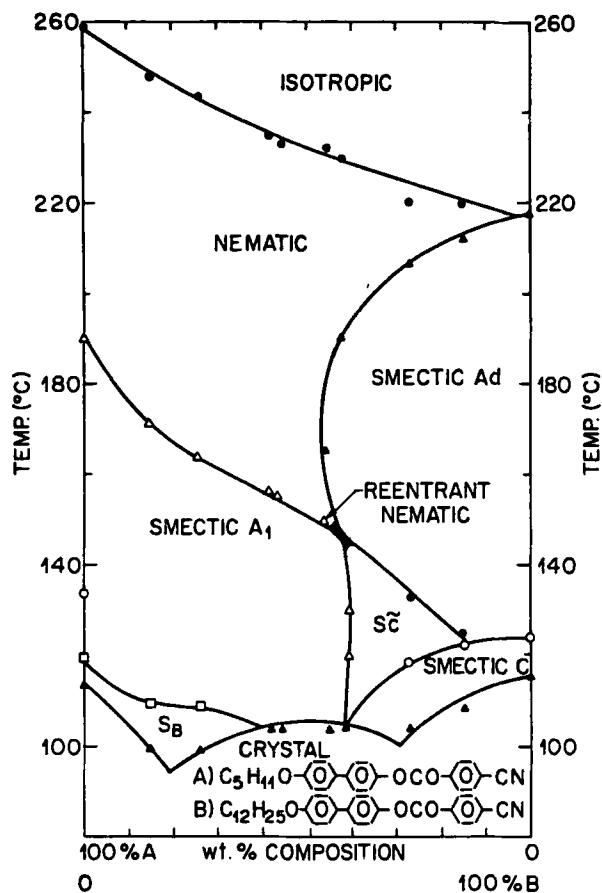
FIGURE 16 Miscibility phase diagram for mixtures (wt.%) between 4-n-pentyloxybiphenylyl-4'-cyanobenzoate (5OBCB) A, and 4-n-dodecyloxybiphenylyl-4'-cyanobenzoate (12OBCB) B.

produce a reentrant nematic phase. The A_1 to $\tilde{C}$ transition line this time is not quite vertical and the 60% by weight of 12OBCB mixture exhibits a tendency to form a homeotropic phase from 120 to 130°.

2.5. Ferroelectric switching studies

In order to examine the properties of the C and $\tilde{C}$ phases further an optically active analogue of this series was prepared so that it could be mixed with the parent system to produce ferroelectric properties. The compound S-4-(2'-methylbutyloxy)biphenylyl-4'-cyanobenzoate (2M4OBCB) was synthesized and found to have the following phases

and transition temperatures.

$$\text{Cryst.}1 \xrightarrow[89.7]{} \text{Cryst.}2 \xrightarrow[117.61]{} S_A \xrightarrow[162.5]{} \text{Ch} \xrightarrow[225]{} \text{Iso}$$
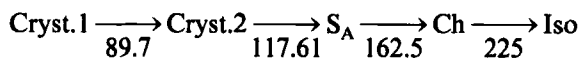
Switching studies in a contact preparation between 2M4OBCB and 12OBCB proved interesting. A Č phase was injected into the contact region so that an A, Č, C phase sequence could be observed across the mixture region with varying concentrations of the two components. The C phase appeared at the side richer in 12OBCB and the A phase at the edge richer in 2M4OBCB. On the application of 67.5 volts DC to the cell the C region switched to give a dark state; reversal of the polarity produced a light state. However, no effect was observed for the Č phase. The concentration of 2M4OBCB in 12OBCB was sufficient to produce a C* phase that exhibited ferroelectric switching, but the region of Č phase which contained a higher proportion of 2M4OBCB failed to respond.

Similar results were obtained for a contact between 2M4OBCB and 9OBCB except in this case no C* phase was observed and no switching was obtained either for the Č phase.

3. DISCUSSION

The production of A phases of different layering structures lies in the ratio of the lengths of the aliphatic to aromatic portions of the individual molecules, and the forms of interaction between neighboring molecules. Most of the materials which exhibts this multiplicity of A phases contain a strongly electronegative terminal substituent which is conjugated to a central linkage in which the flow of delocalized electrons has been disrupted.

For example, consider the 4-cyanobenzoyloxy moiety (I) and compare it to the reversed situation (II).

(I)   (II)
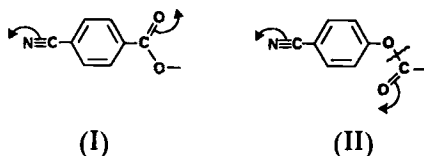
Both the ketone function of the ester group and the cyano terminal substituent of (I) require electrons. The aromatic core therefore becomes deficient of electrons, but both of the substituents never realise

their full requirement for them either. Thus, the terminal cyano group is also electron deficient, and therefore attempts to rectify the situation are made in interactions with neighboring molecules.
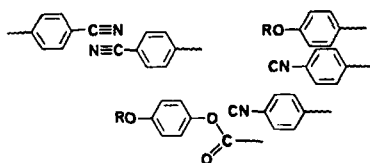
In situations where the constituent molecules contain a number of aromatic ring structures a variety of overlapping positions become possible leading to dimers of varying lengths. The incommensurability of these lengths in turn lead to the possibility of a number of phases being formed.[13]

This would appear to be the situation in the case of the 4-*n*-alkoxybiphenylyl-4'-cyanobenzoates. In comparison to the two-ring homologues, the 4-*n*-alkoxyphenyl 4-cyanobenzoates which only exhibit N, Ad, and C phases, the longer three-ring system of the *n*OBCB's can produce a variety of overlap positions resulting in the formation of a greater number of phases. Similarly the mixing of monolayer A_1 and bilayer Ad materials in miscibility studies results in the formation of the reentrant nematic phase (see Figs. 15 and 16). Furthermore, in the homologous series as the length of the *n*-alkoxy chain is increased in proportion to the aromatic core there is a change over from A_1 to Ad phases at the *n*-octyl to *n*-nonyl members emphasing the effect of the ratio of the aromatic to alkoxy lengths.

Studies of the properties of the $\tilde{C}$ phase, however, lead to quite different postulations. Firstly, the phase exhibits a discotic and pseudo focal-conic texture, neither of which are in keeping with a layered structure. Particularly in the focal-conic texture, the lines of optical discontinuity (ellipse and hyperbola) tend to disappear or become angular. Moreover these crosses return in both the Ad and C phases obtained respectively on heating or cooling the $\tilde{C}$ phase. The free-standing film texture of the $\tilde{C}$ phase also indicates that its structure is very solid-like.

Secondly, if the structure of the $\tilde{C}$ phase is composed of slabs or ribbons of tilted C domains as reported previously,[4] then the phase should undergo ferroelectric switching in the studies where it was doped with an optically active material. Even phases which possess

long range positional ordering of chiral molecules (e.g., J or G) show ferroelectric switching, whereas the proposed $\tilde{C}$ structure only possesses an in-plane density modulation, i.e., an orientational structural parameter. This lack of ferroelectric behavior, while the ensuing C phase formed on cooling possesses it, would seem to indicate that either the tilt angle in this phase is not large enough to produce strong ferroelectric properties, or the phase is *not* a subgroup of the C class.

The fact that the texture of the C phase closely resembles the texture of a discotic phase may indicate an analogy of the A, $\tilde{C}$, C phase sequence of these materials to that of the A, D, C sequence in the 3'-nitro-4'-*n*-alkoxybiphenyl-4-carboxylic acids.[10] In these substances the A to C transition is disrupted in the *n*-hexadecyloxy member producing a cubic D phase, i.e. the layer structuring is broken. D was also shown to be in equilibrium with another phase S_4[11] which was postulated to be of a discotic nature.[12] For these compounds an A to C transition, i.e., the production of a tilted phase becomes difficult at long chain lengths, and so the lamellar spacing breaks down to produce a columnar or micellar phase. The molecular interactions in this process involve strong lateral dipolar forces and hydrogen bonding between adjacent molecules. Although these interactions are much stronger than those involved in the *n*OBCB series, it is still possible that the layered structuring in this case also gives way to another ordering which is not lamellar at the A to $\tilde{C}$ transition. transition.

Further details of the structure of this phase and the nature of its phase transitions are being studied by P. E. Cladis *et al.*,[8] and will be published in due course.

4. EXPERIMENTAL

The materials were prepared by standard methods by alkylating 4,4'-biphenol and esterifying the monoalkylated derivatives with 4-cyanobenzoyl chloride. The final products were purifed by column chromatography over silica-gel (60–200 mesh, 30 × 3 cm) using dichloromethane/hexane, 1 : 1, as the eluant. Their purities were checked by reverse phase HPLC using a 5 μm pore size ODS column (25 × 0.46 cm) and acetonitrile as the eluant. All the products were found to be in excess of 99% purity.

The structures of the esters, checked by IR spectroscopy and NMR, were found to be in agreement with those postulated for the products.

Transition temperatures were determined by thermal optical microscopy using a Zeiss Universal microscope and a Mettler FP52 hot-stage in conjunction with a Mettler FP5 control unit, and by differential scanning calorimetry using a Perkin-Elmer DSC-4-TADS system. Miscibility studies were performed by microscopy using individually weighed mixtures to chart the phase diagram. Enthalpy data was obtained from DSC measurements.

Ferroelectric switching studies were carried out in aligned ITO glass cells using rubbed nylon as the surfactant. The glass plate separation in the cells was 25 μm, and a 67.5 volt battery was used as the power source.

5. CONCLUSION

The 4-n-alkoxybiphenylyl-4'-cyanobenzoates (nOBCB's) were shown to exhibit N, A_1, and B phases for the earlier homologoues (5OBCB to 8OBCB), while the later members exhibited N, Ad, $\tilde{C}$ and C phases. The $\tilde{C}$ phase did not possess ferroelectric properties in doping studies while the C phase formed below it on cooling did. This indicates that the $\tilde{C}$ phase may not be a subgroup of the smectic C class.

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