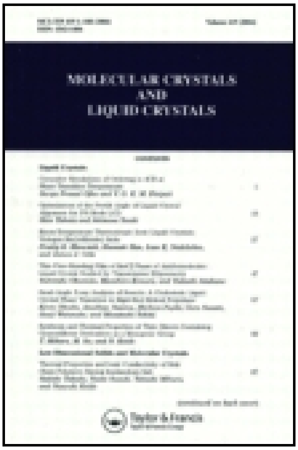

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The Effect of the Reversal of the Central Schiff's Base Linkage on Liquid Crystal Properties: the 4-Phenylbenzylidene-4'-n-alkoxyanilines and 4-(4'-n-Alkoxy-benzylideneamino)-biphenyls

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The Effect of the Reversal of the Central Schiff's Base Linkage on Liquid Crystal Properties: the 4-Phenylbenzylidene-4′-*n*-alkoxyanilines and 4-(4′-*n*-Alkoxybenzylideneamino)-biphenyls

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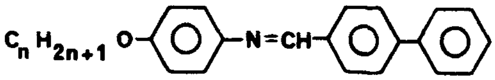
Twelve 4-phenylbenzylidene-4′-*n*-alkoxyanilines have been prepared and their liquid crystal phases have been categorised. The properties of these compounds are compared with those of the analogous Schiff's bases, the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls, in which the central imino-linkage is reversed. A structural factor that may be responsible for an unusual fan texture of the S_B phase of Schiff's bases is suggested.

INTRODUCTION

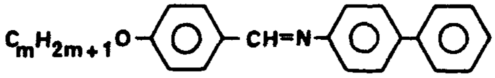
Numerous studies have been made in recent years of the effects of changes in molecular framework on the incidence and stability of various liquid crystal phases.[1, 2, 3]

Many of these studies have involved investigations of the effects of changes in terminal alkyl chain length on the incidence of particular types of liquid crystal phase.

We have prepared twelve members (methoxy to *n*-decyloxy, *n*-dodecyloxy and *n*-tetradecyloxy) of the homologous series of 4-phenylbenzylidene-4′-*n*-alkoxyanilines (I) in order to establish both the variations in liquid crystal properties with increase in the terminal alkyl chain length and to provide a direct comparison of the results obtained with those reported by Gray, Hartley, Ibbotson, and Jones[4] for the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls (II).



(I)



(II)

The methoxy and ethoxy compounds of series (I) have been reported previously, both compounds being nematogens.[5]

In earlier work, results [1,6] for materials of the common structure

R-core-R′

have shown that when the terminal alkyl chains are reversed (R for R′), the resultant effect on the liquid crystal polymorphism of the system is strongly dependent on the overall core shape, and on the lengths of the terminal alkyl chains. In the present study, we have examined the effect of reversal of one small part of the core (i.e., the imino-linkage) on the thermal stability and incidence of the various phases, in particular the smectic phases, in a system with only one terminal alkyl chain.

RESULTS AND DISCUSSION

a The 4-phenylbenzylidene-4′-*n*-alkoxyanilines

The transition temperatures for the 4-phenylbenzylidene-4′-*n*-alkoxyanilines are plotted against terminal carbon chain length (*n*) in Figure 1, which also indicates the phase types shown. Examination of Figure 1 indicates the following:

i) All the members exhibit nematic phases except the *n*-dodecyloxy and *n*-tetradecyloxy compounds which form S_A phases directly on cooling the isotropic liquid. The points for the nematic to isotropic liquid transition

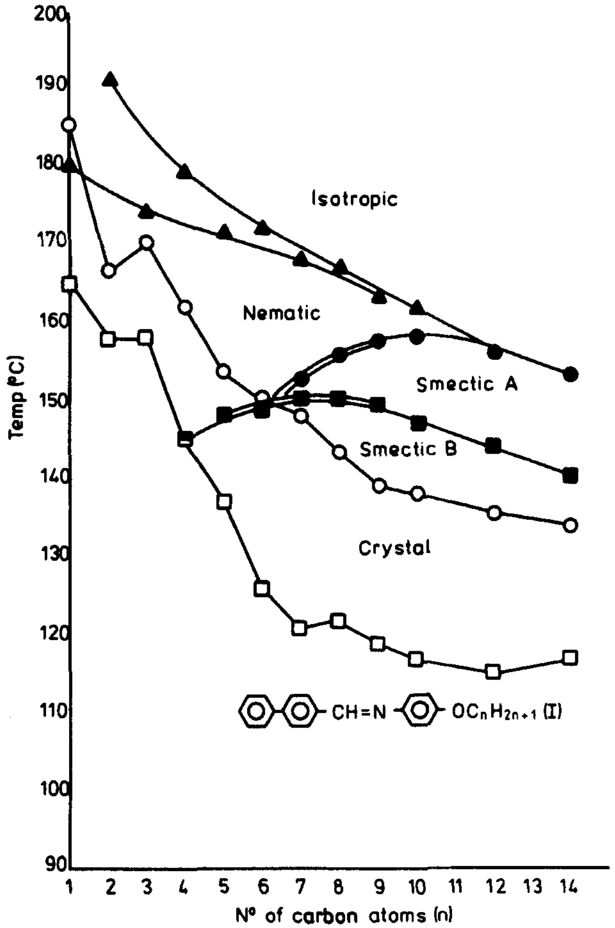


FIGURE 1 Plot of the transition temperatures against the number of carbon atoms (n) in the n-alkyl chain of the 4-phenylbenzylidene-4′-n-alkoxyanilines (I). Key: ▲, N-I; ●, S_A-N or I; ■, S_B-N or S_A; ○, crystal-N, S_B or I; □, mesophase-crystal on cooling.

temperatures lie on two falling curves which converge as n increases, the uppermost curve relating to members for which n is even.

ii) Orthogonal smectic B properties appear at the n-butyloxy compound. These B phases are then observed in each member up to and including the n-tetradecyloxy compound. The plot of the S_B-N or S_A transition temperatures reveals two "parabolic" curves which reach maxima at $n = 7$ and 8. These two curves show an opposite alternation of the transition temperatures to that exhibited by the N-I values, i.e., members for which n is odd now give rise to the uppermost curve.[2,7]

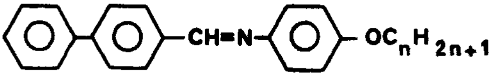
iii) Further smectic properties occur at $n = 7$ with the appearance of a smectic *A* phase which persists throughout the remainder of the series. The points for the S_A-N or I transition temperatures again lie on two curves, and the sense of alternation is now the same as that for the N-I transition temperatures; both the curves rise at first. Since after $n = 10$, only even members of the series were examined, the curve for even members alone shows a maximum (at $n = 10$) before it subsequently falls with increasing chain length.

iv) The melting points and recrystallisation temperatures (obtained using a cooling rate of 10°/min) generally decrease with increasing terminal alkyl chain length.

The transition temperatures for the 4-phenylbenzylidene-4′-*n*-alkoxyanilines were determined by optical microscopy and confirmed by differential scanning calorimetry. The results are listed in Table I.

TABLE I

Transition temperatures in °C for compounds of general structure:



n	mp	Rec temp[b]	I-N or S_A	N-S_A	S_A-S_B	N-S_B
1	185	165	180[a]	—	—	—
2	166.5	158	191	—	—	—
3	170	158	174	—	—	—
4	162	145	179	—	—	145[a]
5	154	137	171.4	—	—	148[a]
6	150	126	172	—	—	149[a]
7	148	121	168	152.5	150.3	—
8	143.5	122	167	156	150	—
9	139	119	163	157.5	149	—
10	138	117	162	158	147	—
12	135.5	115	156	—	144	—
14	134	117	153	—	140	

[a] Monotropic transition temperatures.
[b] Temperature of recrystallisation.

b The identification and classification of the various phases

The phases, particularly the smectic modifications, were identified by observation of their microscopic textures and unambiguously classified by miscibility techniques.

(i) *Optical microscopy:* The most interesting microscopic observations fall into two categories, namely those relating to S_B-N transitions (for

n = 4, 5, and 6) and those relating to S_B-S_A and S_A-N transitions (n = 7, 8, 9, 10, 12, and 14).

The results obtained for a typical example of the former category, e.g., 4-phenylbenzylidene-4′-*n*-pentyloxyaniline were as follows:

On cooling the isotropic liquid, a nematic phase separated and this was characterised by its typical schlieren texture and shimmering motion. On cooling to T_{N-S_B}, mosaic areas, characteristically oblong in shape, separated from the nematic phase (Plate 1). On further slight cooling, these mosaic areas coalesced to give the typical mosaic texture shown in Plate 2. Within this texture small areas that exhibited the homeotropic or pseudoisotropic texture existed, thus indicating that the phase type must be orthogonal. The phase was therefore classified as of the S_B type (see also Plate 3).

For the compounds exhibiting nematic, S_A, *and* S_B phases (e.g., the *n*-octyloxy compound), cooling the isotropic liquid again gave a nematic phase with a schlieren texture, but on further cooling bâtonnets were formed which coalesced to give a focal-conic fan texture. These observations are consistent with the formation of a S_A phase. On decreasing the temperature to $T_{S_A-S_B}$ the backs of the fans became crossed with arcs (transition bars). These fairly wide arcs existed over a range of temperature of as much as 2–3°, after which they disappeared and the fans "healed" to give a texture with slightly more "stunted" fans than those observed for the preceding S_A phase (Plate 4, for n = 8). These observations are compatible with the phase being S_B in type. The focal-conic fan texture of the *B* phase was readily obtained in this truncated form; the fans appeared almost broken, but showed no fracturing across their backs. We have previously observed fans of this nature only for the 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines (the nO.m series),[3] and this texture may be typical of the *B* phases of certain Schiff's bases.

(ii) *Miscibility studies:* Taking 4-phenylbenzylidene-4′-*n*-heptyloxyaniline as a typical example, this compound was shown to exhibit smectic *A* and smectic *B* phases by their separate co-miscibility with the smectic *A* and smectic *B* phases of the standard material, *n*-decyl 4-(4′-phenylbenzylideneamino)cinnamate (S_A, S_B, and S_E phases).

c Comparison of the 4-phenylbenzylidene-4′-*n*-alkoxyanilines (I) with the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls (II)

The 4-(4′-*n*-alkoxybenzylideneamino)biphenyls (II), in which the imino-linkage is reversed relative to the 4-phenylbenzylidene-4′-*n*-alkoxyanilines (I), have been known for many years.[4] A more recent reinvestigation[8] established the occurrence of both S_A and S_B modifications for the *n*-decyloxy compound of series (II). As no other members of the series were examined

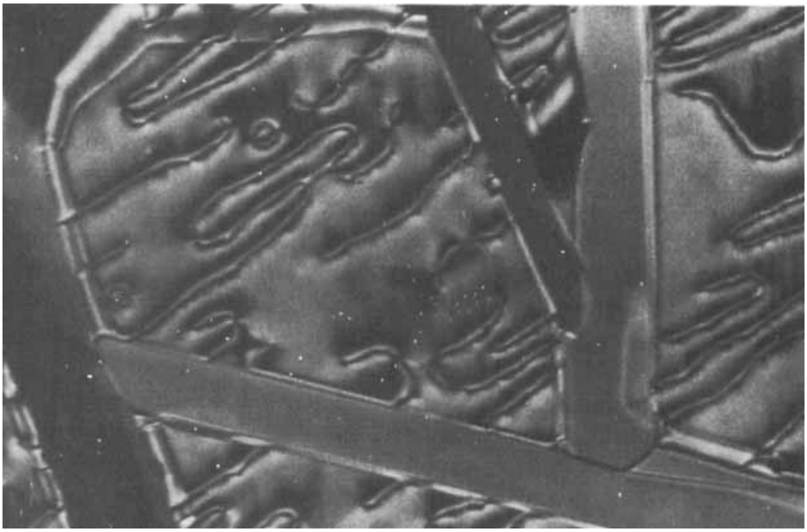


PLATE 1 The mosaic texture of the smectic *B* phase separating from the nematic schlieren texture at the N-S_B transition for 4-phenylbenzylidene-4-*n*-pentyloxyaniline (×200).

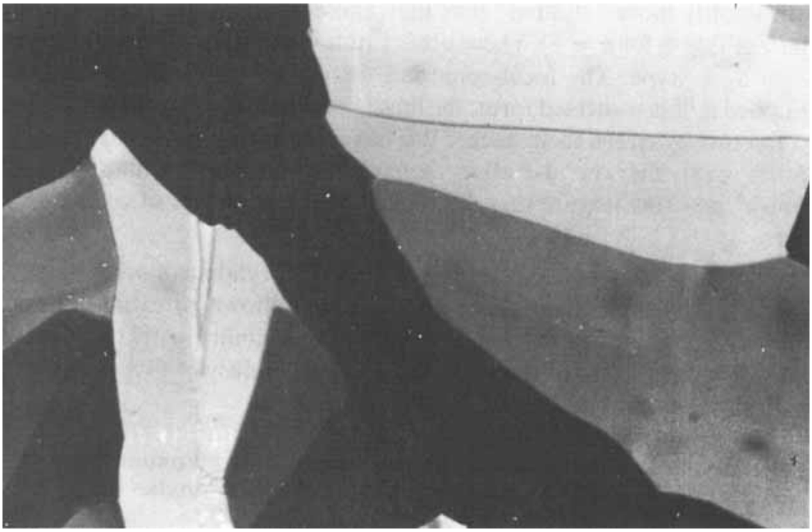


PLATE 2 The mosaic texture of the smectic *B* phase of 4-phenylbenzylidene-4′-*n*-pentyloxyaniline (×200).

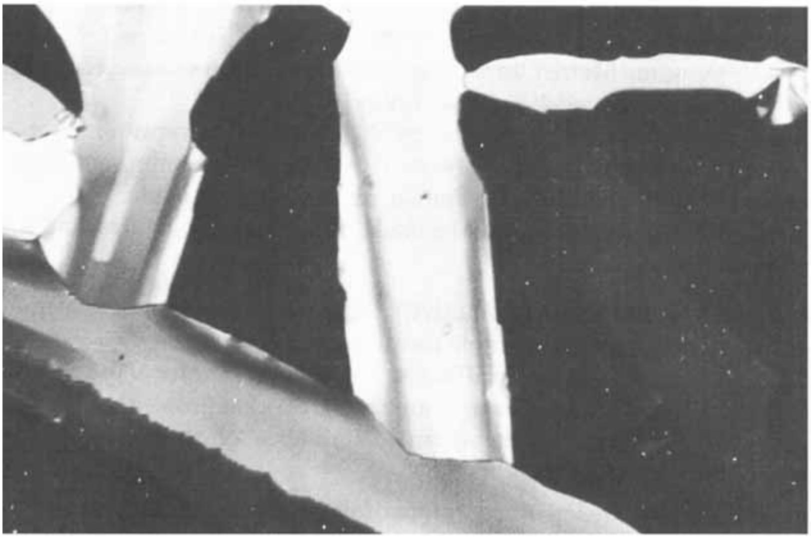


PLATE 3 The mosaic and homeotropic (black areas) textures of the smectic *B* phase of 4-phenylbenzylidene-4′-*n*-pentyloxyaniline (× 200).

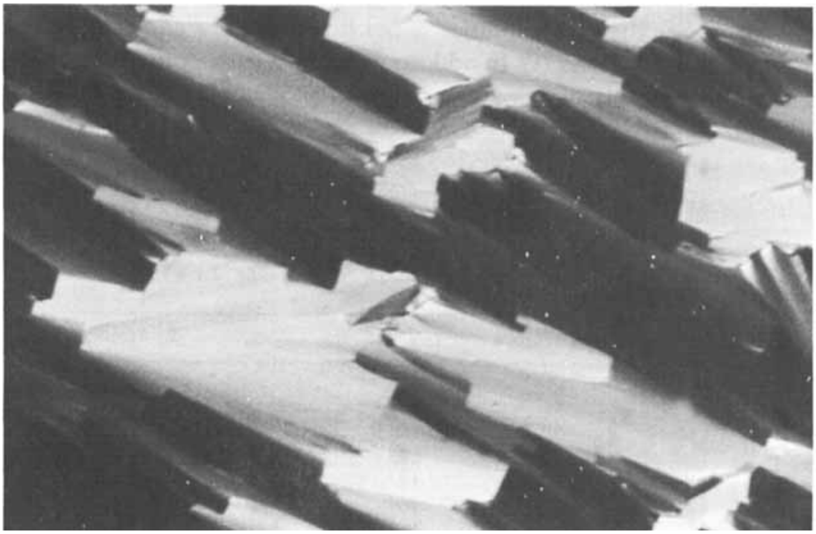


PLATE 4 The "stunted" focal-conic fan texture of the smectic *B* phase of 4-phenylbenzylidene-4′-*n*-octyloxyaniline (× 200).

for smectic polymorphism, we have now reinvestigated those members of the originally reported series that are still available[4] (i.e., $m = 1–8$, 10 and 16) using the same Mettler apparatus as that used for the measurements on the 4-phenylbenzylidene-4′-*n*-alkoxyanilines.

A graphical presentation (similar to Figure 1) of the transition temperatures and phase types for the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls is given in Figure 2, and Table II summarises the numerical data.

A number of comparisons can be made using these two figures, and these may be listed as follows:

i) The trends shown are qualitatively similar and corresponding members of the two series have comparable transition temperatures.

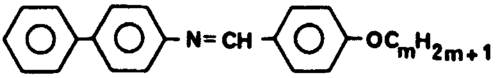
Thus, the inversion of the Schiff's base linkage in the centre of the biphenyl-alkoxyphenyl core does not bring about any great change in either the liquid crystal polymorphism or the thermal stabilities of the various phases exhibited by the two series.

ii) The *N-I* transition temperatures follow much the same pattern of alternation; the values for the 4-phenylbenzylidene-4′-*n*-alkoxyanilines (I) are slightly higher than those for the analogous series (II), particularly in the cases for which *n*/*m* has an odd value.

iii) The S_B phase appears at the *n*-butyloxy member in both series, despite the fact that the thermal stabilities of the *B* phases are significantly greater (by about 10%) in series (I). In addition, the S_B–S_A transition temperatures increase more steeply over a greater number of members of series (II), and

TABLE II

Transition temperatures in °C for compounds of general structure:



m	mp	Rec temp[b]	I-N or S_A	N-S_A	S_A-S_B	N-S_B
1	161	152	169	—	—	—
2	147.5	140	187.5	—	—	—
3	156	145	168.5	—	—	—
4	147	131	175	—	—	132[a]
5	137	107	167	—	—	136[a]
6	132	120	169	144	137	—
7	134	107	165	150	141	—
8	127	110	164.5	154	141	—
10	126	98	159	157	140	—
16	122	111	145	—	129	—

[a] Monotropic transition temperatures.
[b] Temperature of recrystallisation.

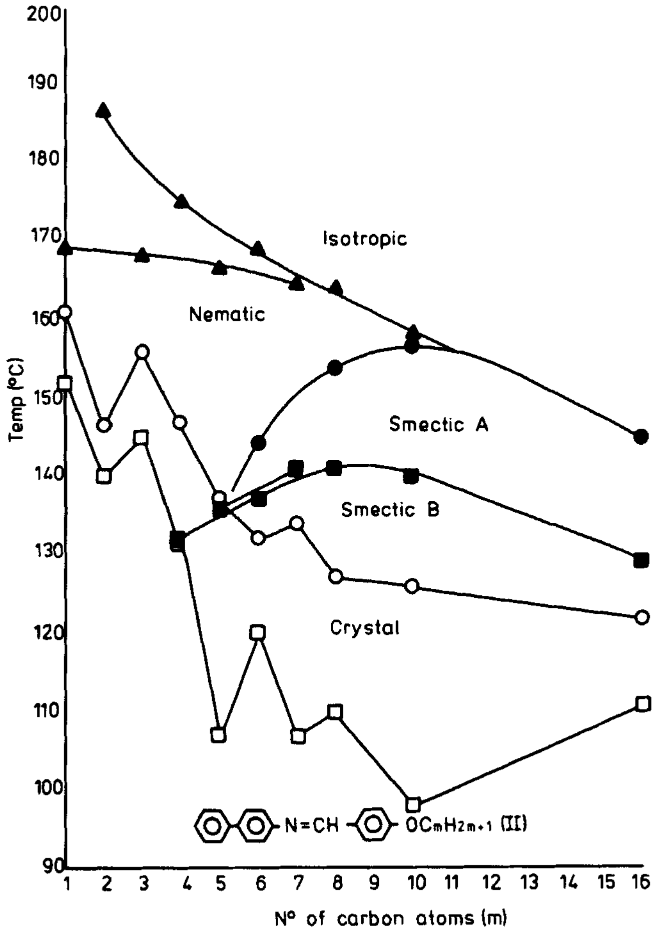


FIGURE 2 Plot of the transition temperatures against the number of carbon atoms (*m*) in the *n*-alkyl chain of the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls (II). Key: ▲, *N-I*; ●, S_A-*N* or *I*; ■, S_B-*N* or S_A; ○, crystal-*N* or S_B; □, mesophase-crystal on cooling.

the S_B–S_A transition temperatures reach a maximum earlier in series (I) than in series (II). Thus, in respect of the similarly shaped S_B–S_A transition temperature curves, there is a displacement of the maximum towards longer alkyl chain lengths in series (II) compared with series (I).

iv) The S_A–N or I transition temperatures for the two series are almost identical, within experimental error, for analogous members. The S_A phase occurs in the two series at $n = 7$ (I) and at $m = 6$ (II). The earlier occurrence of the S_A phase in the 4-(4′-*n*-alkoxybenzylideneamino)biphenyls (II) is because the S_B phases in this series have a lower thermal stability.

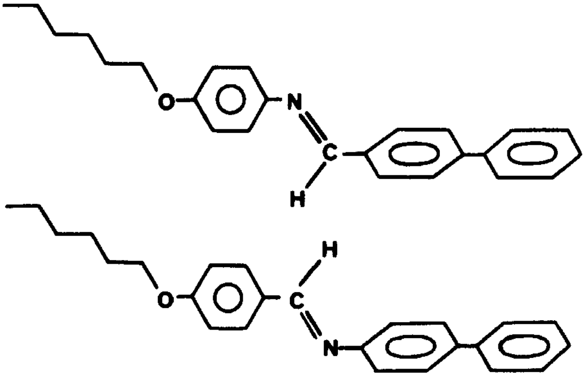
Both series of Schiff's bases have only one terminal alkyl chain, and by analogy with other similar compounds which show S_A, S_B, and S_E phases, they would be expected to exhibit only orthogonal phases.[1,2,3] The thermal stabilities of the nematic and smectic *A* phases of the two series are not affected greatly by the small change in molecular structure represented by reversal of the central linkage. This is to be expected, as in both these phases of relatively low order, specific contacts or associations between the molecules are not as important as those in the more ordered smectic phases. Hence, the effect of the reversal of the imino-linkage is minimal for these two phases.

In the smectic *B* phase, there is a much closer packing of the molecules, and therefore the orientation of the central linkage with respect to the remainder of the molecule could well have a significant effect on the thermal stability of the packing arrangement.

Levelut and Lambert[9] have shown that the molecules are packed in an hexagonally close-packed array within the layers of the *B* phase, and that the dimension of the hexagonal net is of the order of 5 Å for materials similar to those now under discussion, e.g., ethyl 4-(4′-ethoxybenzylideneamino)cinnamate.

This dimension would seem too small to permit the aromatic rings of neighbouring molecules to lie next to one another and still allow the molecules to rotate freely about their long axes. Only a co-operative rotation seems to be possible, giving a situation such that aromatic rings are arranged with the plane of one ring presented to the side of a neighbouring ring. Descamps and Coulon[10] have in fact shown that the molecules do rotate co-operatively about their long axes in the close packed arrangement of the *B* phase.

In certain Schiff's bases it is known[11] that the molecules are twisted out of coplanarity on either side of the central Schiff's base linkage. If this is true of the Schiff's bases discussed in this paper, their structures would be as shown below:



Apart from the flexible alkyl chains, the molecules consist of a fairly rigid core structure which can be thought of as two non-coplanar parts. Provided that the molecules pack together in the smectic layers with the core structures juxtaposed, we can envisage a particularly favourable, close packed situation of the kind shown in Figure 3 having a dimension for the hexagonal net of the S_B phase which is small, so that with a co-operative rotational arrangement, the molecules conveniently share the space which they occupy.

When the transition from the S_B to the S_A phase occurs, the molecules can rotate freely in the unstructured S_A layers. It is possible therefore that at $T_{S_A-S_B}$ a considerable change in volume may occur, and that this may be greater than the volume changes involved at similar transitions for mesogens such as esters which consist of near planar molecules. In these terms, we may offer a possible explanation of the truncation of the fans of the S_B phase and the occurrence of rather pronounced and broad transition bars when the S_B phases of these and related Schiff's bases are formed from the S_A phases on cooling. By analogy, much less marked changes in the fans of the S_A phases of esters are observed at $T_{S_A-S_B}$, and the transition bars are merely transitory in nature.

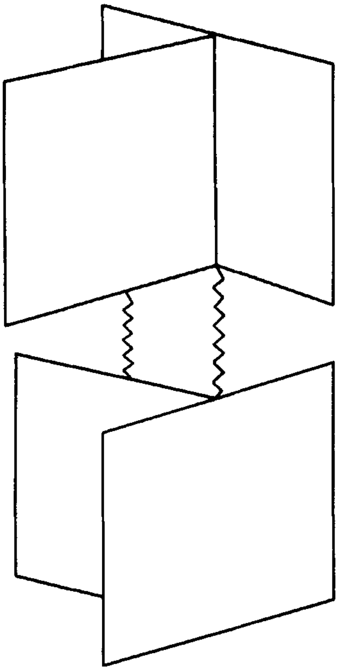


FIGURE 3 The proposed twisted structure of the cores of two molecules in the hexagonally close packed smectic *B* phase. The core structures are juxtaposed, thus showing the edge of one part of the core of one molecule presented to the side of the other molecule.

However, to establish whether these ideas are correct it will be necessary to have detailed X-ray diffraction data to establish the exact relative locations of the atoms of neighbouring molecules and also neutron scattering data to ascertain the dynamics of the molecular motion in the S_B phases of the two series of Schiff's bases (I and II).

EXPERIMENTAL

a Preparation of materials

4-n-Alkoxynitrobenzenes These were prepared from 4-nitrophenol (0.2 mol), anhydrous potassium carbonate (0.8 mol), and the appropriate *n*-alkyl bromide (0.3 mol) in hot cyclohexanone (250 ml) by the method of Gray and Jones.[12] After distillation under reduced pressure and (where appropriate) recrystallisation from light petrol (bp 40–60°), the yields of the nitroethers varied between 70 and 80%. The bps and/or mps were in good agreement with values recorded in the literature.

4-n-Alkoxyanilines These were obtained by the dropwise addition of a solution of the 4-*n*-alkoxynitrobenzene (0.1 mol) in methylated spirit (320 ml) to a warm solution of tin II chloride (0.32 mol) in concentrated hydrochloric acid (60 ml). The reaction mixture was heated under reflux for 5 h, after which roughly half of the solvent was distilled off. The residue was cooled and poured into sufficient aqueous sodium hydroxide containing ice to release the free base which was then extracted into ether. The amines were purified either:

i) by distillation under reduced pressure followed (where appropriate) by recrystallisation from light petrol (bp 40–60°), or

ii) by isolation and crystallisation of their hydrochlorides followed (where appropriate) by crystallisation of the regenerated free bases.

The yields of the 4-*n*-alkoxyanilines were in the range 52–64% and the bps and/or mps were in accord with those quoted in the literature. The *hydrochloride* of *4-n-nonyloxyaniline* had mp 107–109° (Found: C, 66.5; H, 9.7; N, 5.3. $C_{15}H_{26}ClNO$ requires C, 66.3; H, 9.6; N, 5.2%).

4-Phenylbenzylidene-4′-n-alkoxyanilines Biphenyl-4-carboxaldehyde (0.5 g) and a slight molar excess of the appropriate 4-*n*-alkoxyaniline were each dissolved in ethanol (20–25 ml). The solutions were combined and the mixture was heated on a steam bath. Glacial acetic acid (5 drops) was added, and after 15 min the solution was allowed to cool. The crystalline Schiff's bases were

TABLE III

Elemental analyses for 4-phenylbenzylidene-4′-*n*-alkoxyanilines (I)

Substituent C_nH_{2n+1}	Found % C	Found % H	Found % N	Molecular formula	Required % C	Required % H	Required % N
$^aCH_3$	83.5	6.1	4.7	$C_{20}H_{17}NO$	83.6	6.0	4.9
$^aC_2H_5$	83.5	6.6	4.7	$C_{21}H_{19}NO$	83.7	6.4	4.6
n-C_3H_7	83.8	6.9	4.5	$C_{22}H_{21}NO$	83.8	6.7	4.6
n-C_4H_9	84.2	7.0	4.4	$C_{23}H_{23}NO$	83.9	7.0	4.2
n-C_5H_{11}	83.7	7.6	4.0	$C_{24}H_{25}NO$	84.0	7.4	4.1
n-C_6H_{13}	83.7	7.3	3.8	$C_{25}H_{27}NO$	84.0	7.6	3.9
n-C_7H_{15}	84.4	8.0	3.9	$C_{26}H_{29}NO$	84.1	7.9	3.8
n-C_8H_{17}	84.1	8.0	3.4	$C_{27}H_{31}NO$	84.2	8.1	3.6
n-C_9H_{19}	84.4	8.5	3.5	$C_{28}H_{33}NO$	84.2	8.3	3.5
n-$C_{10}H_{21}$	84.0	8.7	3.4	$C_{29}H_{35}NO$	84.3	8.5	3.4
n-$C_{12}H_{25}$	84.3	8.8	3.1	$C_{31}H_{39}NO$	84.3	8.9	3.2
n-$C_{14}H_{29}$	84.7	9.2	3.0	$C_{33}H_{43}NO$	84.4	9.2	2.9

[a] Not new.

purified by recrystallisation several times from petrol (bp 100–120°), ethanol, or cyclohexane.

The transition temperatures for the *4-phenylbenzylidene-4′-n-alkoxyanilines* are listed in Table I and their elemental analyses are given in Table III.

4-(4′-n-Alkoxybenzylideneamino)biphenyls The Schiff's bases listed in Table II were available from a previous study.[4] Prior to their examination, the compounds were given a further crystallisation.

b Physical measurements

The measurements of transition temperatures and observations of the microscopic textures were made using a Nikon L-KE polarising microscope in conjunction with a Mettler FP52 hot-stage and control unit. Confirmation of the various transitions was given by differential scanning calorimetry using a Perkin–Elmer DSC2 instrument.

CONCLUSIONS

i) The thermal stabilities of the S_B phases of the 4-phenylbenzylidene-4′-*n*-alkoxyanilines were significantly higher than those of the corresponding 4-(4′-*n*-alkoxybenzylideneamino)biphenyls.

ii) There was little effect on the incidence of the different phases as the series were ascended or on the thermal stabilities of the nematic and smectic *A* phases which could be attributed to the simple reversal of the Schiff's base linkage.

iii) Quite pronounced textural changes accompanied the transitions from the S_A to the S_B phases of both series of compounds.

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