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## Liquid Crystals

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### Asymmetric dimeric liquid crystals with charge transfer groups

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## Asymmetric dimeric liquid crystals with charge transfer groups

by G. S. ATTARD, S. GARNETT, C. G. HICKMAN, C. T. IMRIE†  
and L. TAYLOR

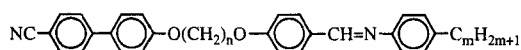
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Two series of asymmetric dimers, the  $\alpha$ -(4-*n*-butylanilinebenzylidene-4'-oxy)- $\omega$ -(4-nitroazobenzene-4'-oxy)alkanes and the  $\alpha$ -(4-dimethylaminoanilinebenzylidene-4'-oxy)- $\omega$ -(4-nitroazobenzene-4'-oxy)alkanes have been synthesized. Their thermal properties are compared with those of the symmetric dimers, the  $\alpha,\omega$ -bis(4-nitroazobenzene-4'-oxy)alkanes and the  $\alpha,\omega$ -bis(4-*n*-butylanilinebenzylidene-4'-oxy)alkanes. The asymmetric dimers exhibit a smectic A phase for which the ratio of the layer spacing to the molecular length is approximately 0.5; this is thought to imply an intercalated structure in which different parts of the molecule interleave. We propose that this structure is stabilized by a charge transfer interaction.

### 1. Introduction

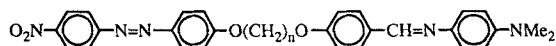
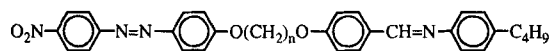
Dimeric liquid crystals are comprised of molecules possessing two semi-rigid anisometric units linked through a flexible spacer. The recent interest in dimers has been prompted by both their ability to act as model compounds for semi-flexible main chain polymers as well as their quite different properties to conventional low molar mass mesogens (see, for example, [1, 2]). The great majority of reported dimers may be termed symmetric in that the semi-rigid units linked are identical. In a recent paper, however, dimers in which the mesogenic groups differed were described and these were termed asymmetric dimers [3];



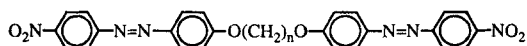
the mnemonic used for this series is CB.O $n$ O. $m$  where  $n$  refers to the number of methylene groups in the flexible spacer and  $m$  the length of the terminal alkyl chain. The behaviour of these compounds differed dramatically from that of conventional mesogens in that the stability of the smectic phase initially increased with increasing terminal chain length passed through a maximum and then fell dramatically. The smectic phase then reappeared at longer alkyl chain lengths. This behaviour was rationalized by proposing a novel intercalated smectic structure for short chain lengths. This structure was thought to be driven by a specific interaction, possibly charge transfer, between the cyanobiphenyl and Schiff's base moieties. In order to investigate this further we have synthesized two series of asymmetric dimers in which we vary one of the mesogenic moieties so that the dependence of the smectic phase stability on the strength of this interaction may be probed. In both the series one

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of the groups is nitroazobenzene an electron acceptor and the second is a benzylidene-aniline moiety with either a terminal butyl chain or a terminal dimethylamino group, both being electron donors,

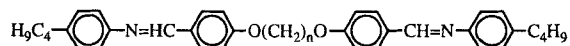


The mnemonics used for these series are NABO $n$ O.4 and NABO $n$ O.NMe $_2$  respectively;  $n$  in each case denotes the number of methylene units in the flexible spacer. The symmetric nitroazobenzene dimers, BNABO $n$ ,



have also been synthesized.

The symmetric Schiff's bases, 4.O $n$ O.4,

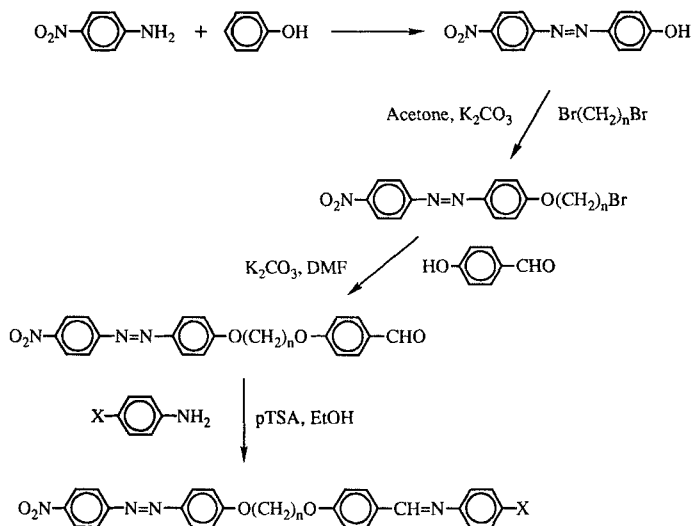


have been reported elsewhere [4, 5].

## 2. Experimental

### 2.1. Synthesis

The two series of asymmetric dimers were prepared using the same reaction scheme consisting of four steps.



4-Hydroxy-4'-nitroazobenzene was prepared by coupling diazotized 4-nitroaniline with phenol (see, for example, [6]) and purified by recrystallization from methanol. The  $\alpha$ -bromo- $\omega$ -(4-nitroazobenzene-4'-oxy)alkanes were prepared using the method described by Crivello *et al.* [7]; 4-hydroxy-4'-nitroazobenzene was reacted with a

ten-fold molar excess of the  $\alpha,\omega$ -dibromoalkane using potassium carbonate as base in dry acetone. The final products were recrystallized from ethanol. These were subsequently reacted with 4-hydroxybenzaldehyde using potassium carbonate as base in dimethylformamide to yield the  $\alpha$ -(4-formylphenyl-4'-oxy)- $\omega$ -(4-nitroazobenzene-4'-oxy)alkanes; these were recrystallized from ethanol. Finally, the asymmetric dimers were obtained by the condensation reaction of the aldehyde with a 4-substituted aniline in absolute ethanol using *p*-toluene sulphonic acid as catalyst. The final products were recrystallized from absolute ethanol, ethyl acetate or toluene.

The preparation of the symmetric dimers, the BNABOn series, followed the method described by Emsely *et al.* [1].

## 2.2. Characterization

The high purity of the products was checked using thin layer chromatography. Their structures were confirmed using both IR and  $^1\text{H-NMR}$  spectroscopy. The thermal properties of the dimers were determined using a Perkin-Elmer DSC-2C differential scanning calorimeter interfaced to an Opus PCII computer. The textures of the liquid crystal phases were examined using an Olympus BH2 polarizing microscope equipped with a Linkam hot stage. Selected examples of the smectic phases were studied further by X-ray diffraction with a bent quartz monochromator (R. Huber, F.R. Germany) using  $\text{CuK}_{\alpha 1}$  radiation ( $\lambda = 0.15405 \text{ nm}$ ).

## 3. Results and discussion

### 3.1. 4.OnO.4 series

Figure 1 shows the dependence of the transition temperatures on the length of the flexible spacer for the 4OnO.4 series. The behaviour of this series is very typical of symmetric dimeric mesogens; first, the clearing temperatures exhibit a dramatic alternation for small values of  $n$  which attenuates as  $n$  increases (see, for example, [1]) and second, increasing the length of the spacer decreases the smectic phase stability (see, for example, [8]). A detailed discussion of the properties of the 4.OnO.4 series together with a description of the phase assignments can be found elsewhere [4, 5].

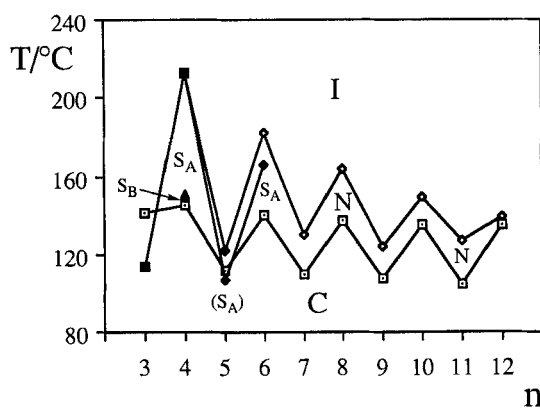
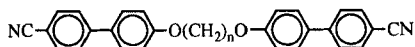


Figure 1. The dependence of the transition temperatures on the number of methylene units,  $n$ , in the flexible spacer in the 4.OnO.4 homologous series. The melting point is denoted by  $\square$ ,  $\blacksquare$  indicates the smectic A-isotropic transition,  $\blacktriangle$  the smectic A-smectic B transition,  $\blacklozenge$  the smectic A-nematic transition and  $\diamond$  the nematic-isotropic transition. Monotropic phases are marked in parentheses.

3.2. BNABO*n* series

The transitional properties of this series are given in table 1. All ten members of this series exhibit nematic behaviour although the third and fifth homologues are monotropic nematogens. The nematic phase was assigned on the basis of the schlieren optical texture observed when viewed through the polarizing microscope; this is shown in plate 1 for NABO11O.4. The dependence of the transition temperatures on the length of the flexible spacer is shown in figure 2. Again, the most striking feature is the pronounced alternation in the clearing temperatures. In contrast, there appears to be no regular dependence of the melting points on  $n$ . Figure 3 shows the dependence of the entropy change at the nematic–isotropic transition on  $n$  for the BNABO*n* and 4.O*n*O.4 series; also shown for comparison are the values for the BCBO*n* series [1].



The nematic–isotropic transition entropies of all three series exhibit an alternation on increasing  $n$  but it is very clear that this is a far more dramatic effect for the 4.O*n*O.4 and BCBO*n* series. Also, the values of  $\Delta S_{NI}/R$  for the BNABO*n* compounds and

Table 1. The transition temperatures and entropies of transition for the BNABO*n* homologous series; ( ) denotes a monotropic transition.

$n$	$T_C/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$\Delta S_C/R$	$\Delta S_{NI}/R$
3	233	(164)	15.8	–
4	251	253	11.7	0.66
5	200	(191)	5.35	0.22
6	203	227	11.8	0.71
7	176	191	18.4	0.29
8	189	204	14.2	0.82
9	151	184	12.7	0.40
10	189	193	15.0	0.95
11	148	177	18.4	0.65
12	160	181	18.7	1.06

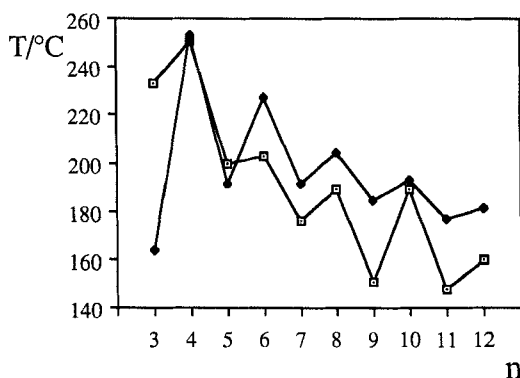


Figure 2. The dependence of the transition temperatures on the number of methylene units,  $n$ , in the flexible spacer in the BNABO*n* homologous series. The melting point is denoted by □ and ◆ indicates the nematic–isotropic transition.

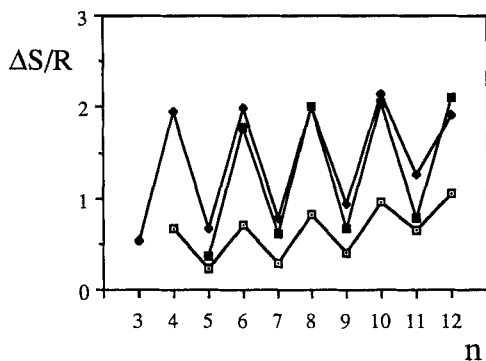


Figure 3. The dependence of the nematic-isotropic entropy on the number of methylene groups,  $n$  for the BNABOn (□), the 4.OnO.4 (■) and the BCBOOn (◆) homologous series of dimers.

particularly those with even membered spacers are considerably lower than those of the analogous 4.OnO.4 or BCBOOn homologue. It should be noted, however, that although these entropies for the even members are small when compared to other dimeric mesogens they are actually significantly larger than those typically quoted for monomeric liquid crystals; for example, the value of  $\Delta S_{NI}/R$  for 6O.1 is 0.36 [9].

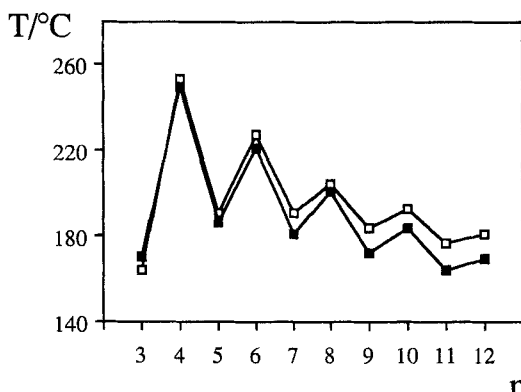
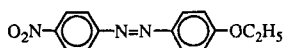


Figure 4. The dependence of the nematic-isotropic transition temperatures on the length of the flexible spacer for the BNABOn (□) and the BCBOOn (■) homologous series of dimers.

Figure 4 compares the nematic-isotropic transition temperatures of the BCBOOn and BNABOn series and reveals that on average, the  $T_{NI}$  of a BNABOn compound is just 6°C higher than that of the analogous BCBOOn homologue. In contrast the  $T_{NI}$  of



is 110°C as compared with 90.5°C for 2OCB. On this basis the transition temperatures of the BNABOn series should be significantly higher than those of the BCBOOn series. It is difficult to interpret this result unambiguously although a possible explanation is that the equilibrium ratio of the cis to trans-isomer is temperature dependent and as the temperature is increased this ratio tends to unity. At elevated temperatures, therefore, there is a significantly higher concentration of the cis-isomer. This

obviously reduces the length to breadth ratio of the molecule so diluting the anisotropic interactions resulting in a decreased  $T_{NI}$ . Also, the reduction of the interaction strength parameter of the aromatic units with the molecular field implies that the ends of the flexible core are not so strongly anchored and hence, the conformational entropy change at the nematic–isotropic transition is reduced. These results are in accord with the recent observation by Imrie [11] that laterally substituting a dimeric liquid crystal reduces both  $T_{NI}$  and  $\Delta S_{NI}/R$ ; this was rationalized in terms of the increase in molecular biaxiality or the reduction in electronic conjugation.

### 3.3. *NABOnO.NMe<sub>2</sub> series*

The transitional properties of this series are given in table 2. The third and sixth homologues decomposed before melting while the fourth member decomposed in the nematic phase. The remaining homologues all exhibited nematic behaviour; the nematic phase was again assigned on the basis of the schlieren optical texture when viewed through the polarizing microscope. On cooling the nematic phase of the eleventh and twelfth member, the schlieren texture changed to give regions of focal conic fans and homeotropic areas; an example of the focal conic fan texture is given as plate 2 for the  $S_A$  phase of NABO11O.4. In consequence this lower phase is assigned as a smectic A. Figure 5 shows the dependence of the transition temperatures on  $n$  for the *NABOnO.NMe<sub>2</sub>* series; the most surprising feature is the increase in smectic stability as  $n$  is increased. The transitional properties of this series will be discussed in detail alongside those of the *NABOnO.4* series.

Table 2. The transition temperatures and entropies of transition for the *NABOnO.NMe<sub>2</sub>* homologous series; ( ) denotes a monotropic transition while (dec.) indicates decomposition of the sample.

$n$	$T_c/^\circ\text{C}$	$T_{S_A N}/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$\Delta S_C/R$	$\Delta S_{NI}/R$
3	220(dec.)	–	–	–	–
4	260	–	270(dec.)	–	–
5	205	–	(198)	12.9	0.31
6	250(dec.)	–	–	–	–
7	193	–	195	12.9	0.44
8	222	–	(220)	18.1	1.47
9	185	–	192	15.2	0.68
10	210	–	(203)	14.8	1.72
11	177	(158)	186	11.8	0.85
12	202	(186)	(195)	20.9	1.89

### 3.4. *NABOnO.4 series*

The transitional properties of this series are given in table 3; the assignments of the smectic A and nematic phases were made using the arguments described for the *NABOnO.NMe<sub>2</sub>* series; plates 1 and 2 show the textures of the nematic and smectic A phases respectively. On cooling the smectic A phases of the seventh, ninth and eleventh members, schlieren textures of low birefringence developed in the homeotropic areas and bright threads developed across the fans; this texture is shown in plate 3. The schlieren texture appears to contain both types of point singularity as can be seen in plate 4. The presence of both types of point singularity in a schlieren texture is normally thought to imply a nematic phase. In this case, however, such an assignment would be inconsistent with the accompanying focalconic fan

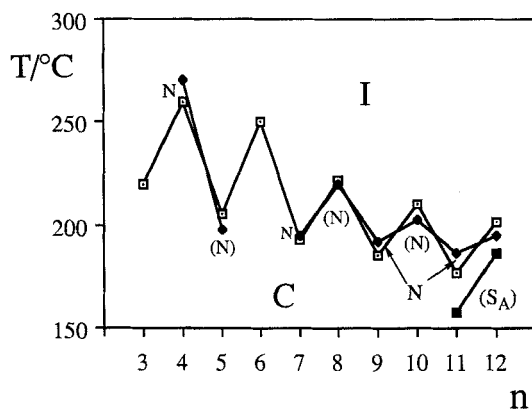


Figure 5. The dependence of the transition temperatures on the number of methylene units,  $n$ , in the flexible spacer in the  $\text{NABOnO.NMe}_2$  homologous series of asymmetric dimers. The melting point is denoted by  $\square$ ,  $\blacksquare$  indicates the smectic A-nematic transition and  $\blacklozenge$  the nematic-isotropic transition.

Table 3. The transition temperatures and entropies of transition of the  $\text{NABOnO.0.4}$  homologous series; ( ) denotes a monotropic transition.

$n$	$T_C/^\circ\text{C}$	$T_{S_X S_A}/^\circ\text{C}$	$T_{S_A N}/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$\Delta S_C/R$	$\Delta S_{S_X S_A}/R$	$\Delta S_{S_A N}/R$	$\Delta S_{NI}/R$	$\Delta S_{S_A I}/R^\dagger$
3	148	—	—	(124)	12.8	—	—	—	—
4	152	—	—	228	10.8	—	—	1.20	—
5	130	—	(88)	156	9.07	—	—	0.26	—
6	141	—	(137)	202	12.1	—	—	1.21	—
7	132	(109)	(113)	170	10.7	—	1.20 $\ddagger$	0.44	—
8	140	—	169	189	15.8	—	0.50	1.49	—
9	125	132	139	161	13.4	0.15	0.69	0.63	—
10	130	—	169	174	15.4	—	—	3.63 $\ddagger$	—
11	109	128	151	159	14.5	0.09	1.00	0.71	—
12	131	—	—	169	16.3	—	—	3.40 $\ddagger$	—

$\ddagger$  The peaks could not be resolved.

texture which indicates the structure is layered. Also, the lines that develop across the backs of the fans suggest a change in the correlation length normal to the layer planes. The phase has been studied using X-ray diffraction and this reveals that there is no perceptible change in the wide angle although a second order reflection in the small angle region appears on cooling into the lower temperature phase. In addition, the X-ray diffraction patterns from aligned samples suggest that within the resolution of our experiment ( $\beta \leq 8^\circ$ ) the phase is not tilted. This is consistent with the texture shown in plate 3 in which the relatively unblemished fans imply that if there is a tilt then it is very small. The layer spacing in both the smectic phases is 22.5 Å for  $\text{NABO11O.4}$  and this is approximately half the molecular length. An equimolar mixture of  $\text{BNABO11}$  and  $\text{4.O11O.4}$  shows the same phase sequence as  $\text{NABO11O.4}$ . It was not possible to construct the entire phase diagram of the symmetric dimers due to the very large differences in transition temperatures. In addition, we have synthesized  $\text{CB.O11O.4}$  and this also shows this unusual smectic phase. The phase has been designated  $S_X$  and we plan to investigate it further using



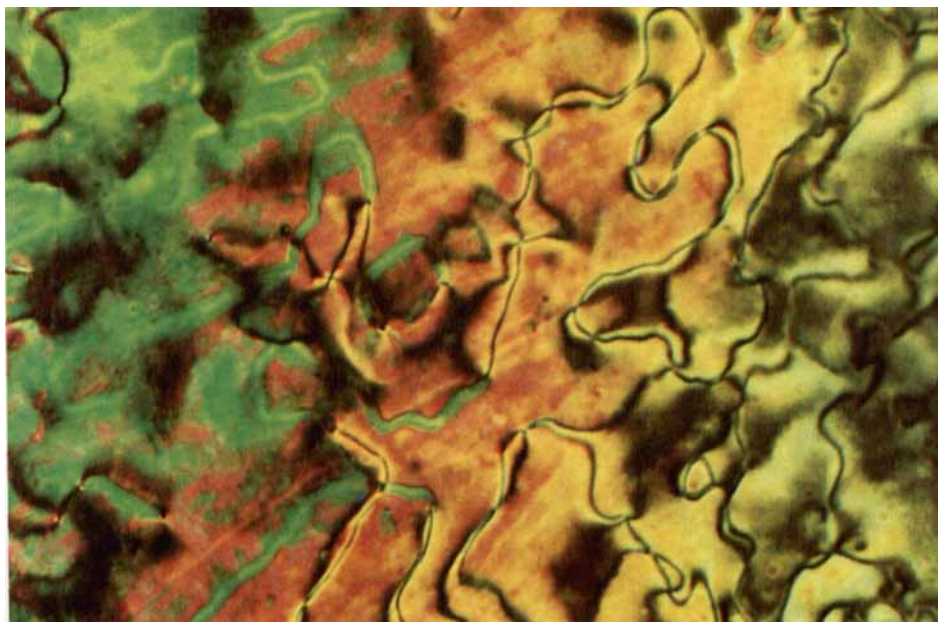


Plate 1. Schlieren texture of the nematic phase of NABO110.4 ( $\times 166$ ).

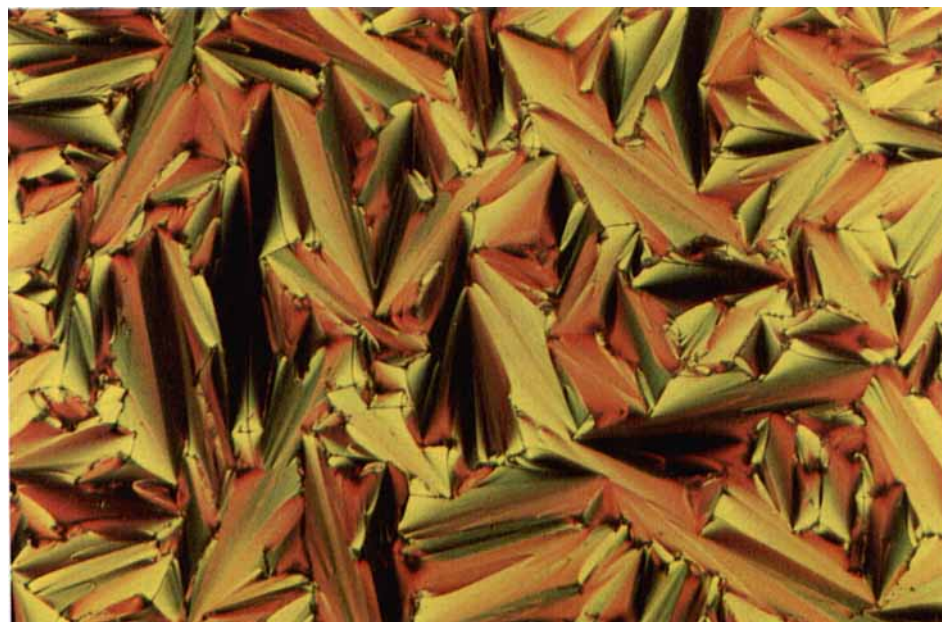


Plate 2. Focal conic texture of the smectic A phase of NABO110.4 ( $\times 83$ ).

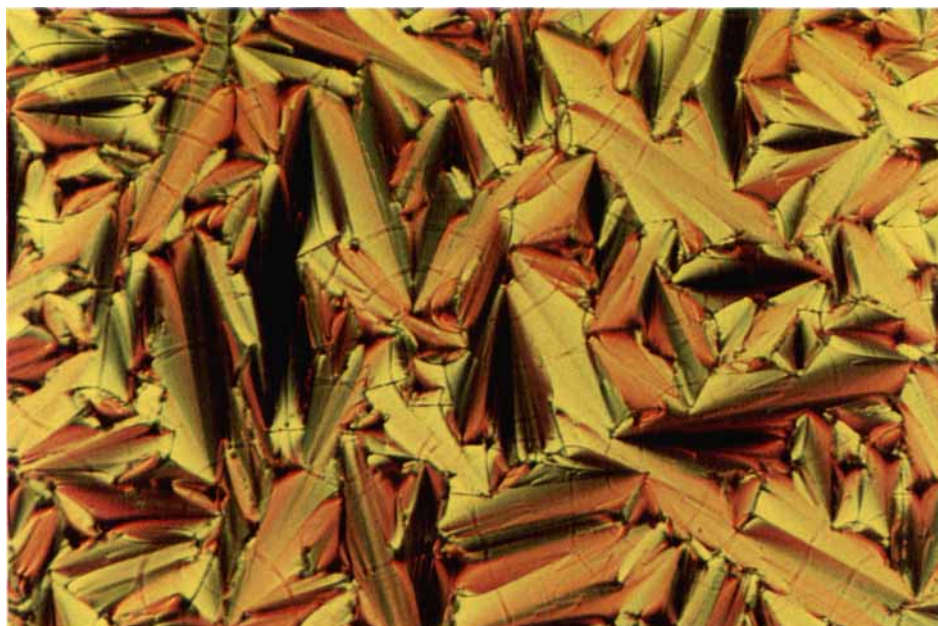


Plate 3. Photomicrograph showing the threads that develop across the focal conic fans on entering the  $S_x$  phase of NABO11O.4 ( $\times 83$ ).

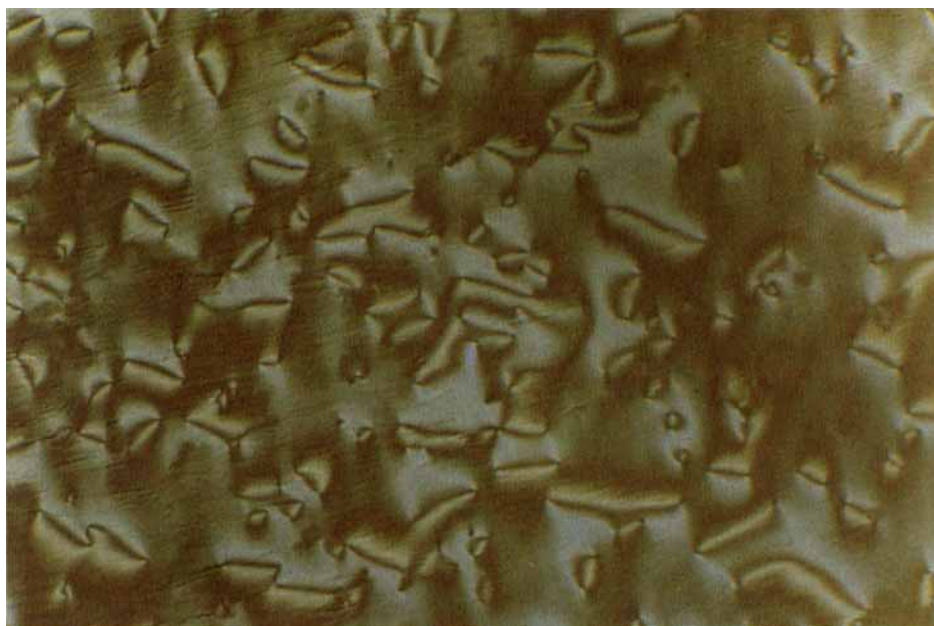


Plate 4. Schlieren texture of the  $S_x$  phase of NABO11O.4 showing both four- and two-brush point singularities ( $\times 415$ ).

conoscopy to establish whether it is a biaxial phase. It should be noted that the texture shown in plate 4 serves as a warning against assigning a phase as a reentrant nematic solely upon the observation of both types of point singularity in a schlieren optical texture.

All twelve members of this series show liquid crystal phases although the third homologue forms a monotropic nematic. Smectic properties emerge at the fifth member and the twelfth homologue exhibits a smectic A–isotropic transition. Figure 6 shows the dependence of the transition temperatures on the length of the flexible spacer for the  $\text{NABOnO.4}$  series. The nematic–isotropic temperatures show the normal dependence on  $n$  for dimers, namely a dramatic alternation for small values of  $n$  which tends to attenuate as  $n$  is increased. In contrast, the smectic phase stability is unusual. The smectic A–nematic transition temperatures show a pronounced alternation on increasing  $n$  and the underlying trend is undoubtedly an increasing one.

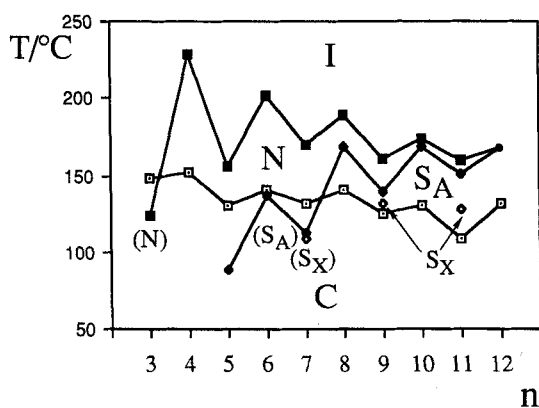


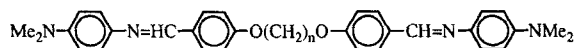
Figure 6. The dependence of the transition temperatures on the number of methylene units,  $n$ , in the flexible spacer in the  $\text{NABOnO.4}$  homologous series of asymmetric dimers. The melting point is denoted by  $\square$ ,  $\blacksquare$  indicates the nematic–isotropic transition,  $\blacklozenge$  the smectic A–nematic transition,  $\diamond$  the smectic X–smectic A transition and  $\bullet$  the smectic A–isotropic transition. Monotropic phases are marked in parentheses.

### 3.5. Comparisons of the series

Figure 7 compares the clearing temperatures of the two symmetric dimer series with those of the asymmetric series and it is evident that for any given spacer length the transition temperatures are in the order,

$$\text{NABOnO.NMe}_2 > \text{BNABOn} > \text{NABOnO.4} > \text{4.OnO.4.}$$

The asymmetric  $\text{NABOnO.4}$  dimers have clearing temperatures intermediate between those of the symmetric parent  $\text{BNABOn}$  and  $\text{4.OnO.4}$  dimers. A simplistic interpretation of this assumes that interactions between the mesogenic units are dominant in determining the clearing temperatures and that the nitroazobenzeneoxy–nitroazobenzeneoxy interaction is greater than the mixed core interaction which in turn is larger than Schiff's base–Schiff's base interaction. In contrast, the clearing temperatures of the  $\text{NABOnO.NMe}_2$  series lie above those of the  $\text{BNABOn}$  series. This prompts the question as to where the symmetric  $\text{Me}_2\text{N.OnO.NMe}_2$  series,



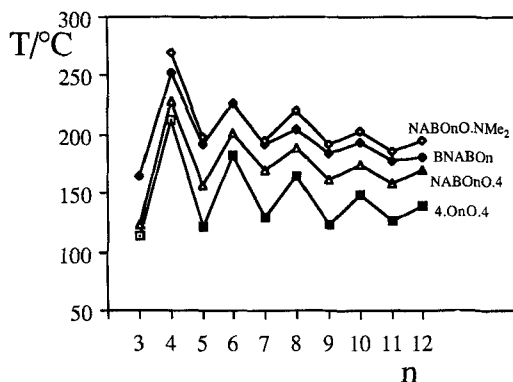


Figure 7. The dependence of the clearing points on the length of the flexible spacer for the 4.OnO.4 series ■ indicates the nematic–isotropic transition and □ the smectic A–isotropic transition, the BNABOn series ◆ indicates the nematic–isotropic transition, the NABOnO.4 series △ denotes the nematic–isotropic transition and ▲ the smectic A–isotropic transition, and the NABOnO.NMe<sub>2</sub> series for which ◇ indicates the nematic–isotropic transition.

would occur in this sequence. Attempts to synthesize these materials yielded very high melting strongly monotropic nematics which proved very difficult to purify. These results, however, suggest that their clearing temperature lie below those of the BNABOn series. This would also be anticipated on considering the molecular structures of the two series; first, the azo-linkage is planar whereas Schiff's bases are considerably twisted and secondly, the dimethylamino group is thought to lie out of the molecular plane so rendering it a poorer terminal substituent than the nitro group in promoting nematic behaviour in aromatic systems [12]. It appears, therefore, that within our simplistic model that the nitrobenzenoxy–dimethylaminobenzylideneoxy mixed core interaction is greater than either of the like–like core interactions. This is certainly not an unreasonable conclusion considering the strongly non-ideal behaviour observed for binary mixtures of dimethylamino-substituted and nitro-substituted compounds (see, for example [10, 13]).

Figure 8 compares the entropy change associated with the nematic–isotropic transition for the four series of dimers. It is clear that for a given spacer length, the 4.OnO.4 homologue has the highest value of  $\Delta S_{Ni}/R$  and the BNABOn compound the lowest. The two series of asymmetric dimers have very similar values of  $\Delta S_{Ni}/R$ , indeed it is difficult to separate them on the figure. Interpreting these results is difficult since there are many competing factors and further speculation must await the results from model calculations in which the interaction strength parameter of the mesogenic unit is systematically varied.

### 3.6. The smectic behaviour of the asymmetric dimers

A particularly surprising feature of figures 5 and 6 is that the smectic phase stability for the asymmetric dimers increases with increasing spacer length. In an attempt to rationalize this, the structure of the smectic phase was investigated using X-ray diffraction; the experiments were confined to the phases exhibited by the NABOnO.4 series because the smectic phases exhibited by the NABOnO.NMe<sub>2</sub> are monotropic and tend to crystallize within the time-scale of the experiment. The layer spacings measured for the smectic A phase are given in table 4 and it is apparent

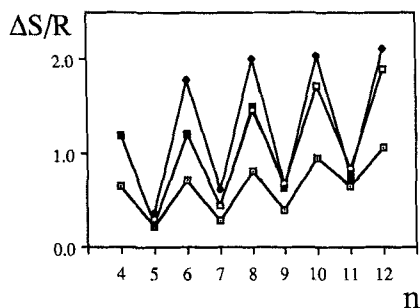


Figure 8. The dependence of the nematic-isotropic transition entropies on the length of the flexible spacer for the BNABOn series (□), the 4.OnO.4 series (◆), the NABOnO.NMe<sub>2</sub> series (□) and the NABOnO.4 series (■).

Table 4. The smectic A layer spacing,  $d$ , and the estimated all-trans molecular length,  $l$ , for the NABOnO.4 series.

$n$	$T/T_{S_A N}$	$d/\text{Å}$	$l/\text{Å}$	$d/l$
7	0.99	18.9	38.8	0.49
8	0.96	20.5	40.0	0.51
9	0.98	20.3	41.6	0.49
10	0.97	21.8	43.2	0.51
11	0.97	22.5	44.8	0.50

that these are actually smaller than the molecular length. In fact, the ratio of the layer spacing to the molecular length is just 0.5. This unusual result was also found for the smectic A phase of CB.O6O.2 and CB.O6O.5 [3] and is thought to imply that the molecules are forming an interleaved structure in which different parts of the molecules are overlapped; this structure is sketched in figure 9 and was termed an intercalated smectic A phase. The phase is termed intercalated in order to stress that different regions of the molecule overlap whereas in an interdigitated phase the same groups, either the mesogenic groups (see for example, [14]) or alkyl chains [15], of different molecules interleave. An analogous intercalated structure was proposed by Diele *et al.* [16] for the smectic A phase of a compound possessing a lateral chain terminating in a cyanophenyl group,

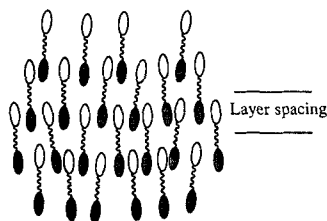
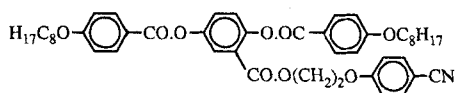


Figure 9. The intercalated smectic A phase.



The structure sketched in figure 9 should possess ferroelectric properties and these are presumably removed by the random arrangement of such units at the macroscopic level. It was suggested that the driving force for the formation of this phase by the CB.O6O.*m* compounds was the charge transfer interaction between the cyanobiphenyl group and the Schiff's base and that the stability of the phase is, in part, governed by the ease of which the terminal substituents can be accommodated into the space between the layers [3]. For the NABO<sub>*n*</sub>O.4 and NABO<sub>*n*</sub>.NMe<sub>2</sub> smectic phases the charge transfer interaction is presumably between the electron deficient azobenzene group and the electron rich benzylideneaniline group. It is interesting to note that the NABO<sub>*n*</sub>O.NMe<sub>2</sub> compounds are red-brown in colour and this is typical of mixtures containing these moieties [10, 13]. This colouration has been assigned to the charge transfer band and the persistence of this on melting has been thought to imply the presence of the interaction in the mesophase. The smectic A thermal stability of NABO11O.4 and NABO12O.4 is lower than that of the analogous NABO<sub>*n*</sub>.NMe<sub>2</sub> compounds and this is in accord with the general observation that the stability of an induced smectic phase increases with the strength of the charge transfer interaction [17]. Further evidence of molecular complexation are the higher melting points found for the NABO<sub>*n*</sub>O.NMe<sub>2</sub> series when compared to the BNABO<sub>*n*</sub> series. The thermal stability of the smectic phase exhibited by these asymmetric dimers increases with increasing spacer length. This presumably reflects the increasing size of the space between the intercalated layers and therefore, the ease at which the butyl chain or the bulky dimethylamino group can be accommodated within the structure.

#### 4. Conclusions

The thermal properties of these asymmetric dimers appear to be dominated by charge transfer interactions. In particular, the unusual smectic behaviour and phase structure is driven by this specific interaction. We plan to investigate this complexation using dielectric relaxation and UV-visible spectroscopy.

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