JOURNAL OF
Materials
CHEMISTRY

Liquid crystal trimers. The synthesis and characterisation of the 4,4′-bis[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]biphenyls

Corrie T. Imrie[*a]† **and Geoffrey R. Luckhurst**[b]

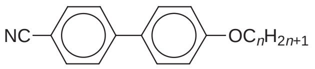
[a] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Scotland, UK AB24 3UE*

[b] *Department of Chemistry, University of Southampton, Southampton, England, UK SO17 1BJ*

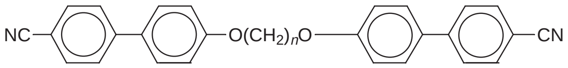
The synthesis and characterisation of a homologous series of liquid crystal trimers, the 4,4′-bis[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]biphenyls, is reported in which the length of the flexible spacers is varied from 3 to 12 methylene units. All the members of the series exhibit enantiotropic nematic behaviour and, in addition, monotropic smectic A behaviour is observed for compounds with spacers containing from 4 to 11 methylene units. The formation of a smectic phase in these compounds is attributed to a specific interaction between the unlike mesogenic groups, namely, the central biphenyl and the terminal cyanobiphenyl units. The nematic–isotropic transition temperatures and the associated entropy changes exhibit a dramatic odd–even effect as the length and parity of the spacers is varied, in which the even members exhibit the higher values. This behaviour is interpreted in terms of the geometry as well as the flexibility of the spacers and how these control the average molecular shape. A comparison of the magnitudes of these odd–even effects with those for the analogous dimeric series suggests that in the nematic phase the mesogenic units in the trimers are correlated to the same extent as in the dimers but that their orientational ordering is significantly higher.

Semi-flexible main-chain liquid-crystalline polymers are composed of mesogenic units linked *via* flexible alkyl spacers.[1,2] The transitional properties, in particular, the clearing temperature and the associated entropy change, exhibited by such a polymer are strongly dependent on the length and parity of the alkyl spacers.[3] In contrast, the transitional properties of conventional low molar mass mesogens, which are composed of molecules possessing a single semi-rigid core, attached to which are one or two alkyl chains, are modified to a much smaller extent by changes in the length and parity of the alkyl chain.[4] If just two mesogenic units, however, are linked through a flexible spacer, yielding the so-called liquid crystal dimers,[5,6] then the transitional properties are found to be critically dependent on the length and parity of the alkyl spacer in a manner reminiscent of the behaviour observed for polymeric systems.[7,8] In order to investigate how these properties evolve from the dimers to the polymers a small number of higher oligomers have been prepared and characterised. The majority of these are described as liquid crystal trimers as they contain molecules comprising three mesogenic groups and two flexible spacers[9–15] although liquid crystal tetramers containing four mesogenic groups and three spacers have also been reported.[16,17] In these examples the mesogenic units are linked in terminal positions but a range of other molecular architectures are also possible.[18–20]

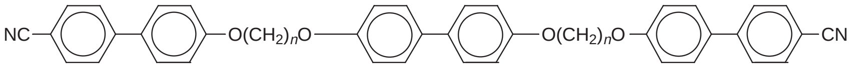
To extend such studies we have prepared and studied the transitional behaviour of a homologous series of trimeric mesogens, the 4,4′-bis[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]biphenyls, and use the acronym TCBO*n* to describe them; *n* refers to the number of methylene units in the flexible alkyl spacers. This particular series was selected because both the analogous monomers, the 4-cyano-4′-alkoxybiphenyls, and the corresponding dimers, the α,ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes, have been extensively investigated.[8,21–23] The acronym used to refer to the monomers is *n*OCB where *n* denotes the number of methylene units in the terminal chain while the dimers are described by BCBO*n* in which *n* now refers to the number of methylene units in the flexible spacer. The liquid crystalline behaviour of several members of the TCBO*n*[9,15] series has been reported in the literature but to the best of our knowledge this is the first report describing a homologous series of trimers in which as many as ten homologues have been characterised.



*n*OCB



BCBO*n*



TCBO*n*

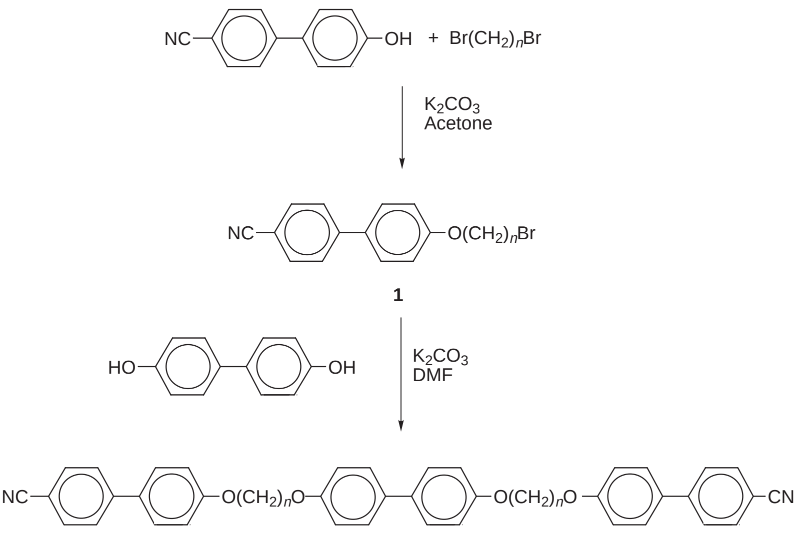
Experimental

Synthesis

The trimers were prepared using the synthetic route shown in Scheme 1. The synthesis of the α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkanes, **1**, has been described in detail elsewhere.[24] The coupling of **1** with 4,4′-dihydroxybiphenyl was performed using potassium carbonate as base in dimethylformamide. The reaction mixture was refluxed for 12 h, allowed to cool and then poured into water. The resulting precipitate was filtered

---

†E-mail: c.t.imrie@abdn.ac.uk



Scheme 1

off and dried. The crude trimer was recrystallized at least twice with hot filtration from large volumes of either toluene or ethyl acetate. The trimers were too insoluble to allow for structural characterisation using NMR spectroscopy, but their IR spectra were consistent with the proposed structures. Specifically, the IR spectra in all cases contained a band corresponding to the cyano stretch while there was no evidence to suggest the presence of unreacted hydroxy groups. In addition mass spectroscopy identified the molecular ion. The high level of purity of the trimers is also reflected in the narrow temperature ranges observed for the melting transitions and also in the good agreement with the data reported for members of this series in the literature.[9,15]

Thermal characterisation. The thermal properties of the trimers were investigated by differential scanning calorimetry using a Perkin-Elmer DSC-2C differential scanning calorimeter interfaced to an Opus PC II microcomputer. The optical textures of the mesophases were examined by polarised light microscopy using a Nikon polarising microscope equipped with a Linkam hot stage. The transition temperatures quoted for the trimers were extracted from the calorimetric data with the exception of the smectic A–nematic transition temperatures which were measured using the optical microscope because the samples crystallised during the calorimetric analysis.

Results and Discussion

The transitional properties of the trimers are listed in Table 1. All ten members exhibit an enantiotropic nematic phase and also, with the exception of the propyl and dodecyl members, a monotropic smectic A phase. The nematic phases have a schlieren optical texture containing both two and four brush point singularities when viewed through the polarising microscope, while for the smectic A phase coexisting regions of focal conic fan and homeotropic textures were observed. The monotropic nature of the smectic phase precluded the possibility of X-ray diffraction studies in order to determine the layer spacings. The nematic–isotropic temperatures listed in Table 1 are in good agreement with those given in the literature.[9,15] The smectic A phase exhibited by the TCBO*n* series has been overlooked in the previous studies[9,15] and a plausible explanation for this is the monotropic nature of the phase. It is noteworthy, however, that the interpretation of the electro-optical properties of TCBO10 invoked smectic fluctuations within the nematic phase.[15]

Table 1 The transitional properties of the TCBO*n* homologous series

n	T_{CN}/°C	T_{SmAN}/°C	T_{NI}/°C	$\Delta S_{CN}/R$	$\Delta S_{NI}/R$
3	179		202	10.5	0.81
4	226	(196)	297	18.4	3.51
5	173	(124)	215	18.7	1.15
6	224	(190)	262	23.9	3.93
7	157	(130)	206	19.9	1.40
8	198	(175)	231	20.2	4.08
9	152	(133)	196	21.9	1.86
10	191	(155)	213	23.9	4.57
11	144	(127)	184	20.2	2.25
12	183		194	26.0	4.64

The dependence of the transition temperatures on the number of methylene units, *n*, in the flexible alkyl spacers for the TCBO*n* series is shown in Fig. 1. It is immediately apparent that the melting points, the nematic–isotropic temperatures and the smectic A–nematic temperatures all depend critically on the length and parity of the flexible spacers. Specifically, the melting points exhibit a pronounced alternation which does not attenuate on increasing *n*. The nematic–isotropic and smectic A–nematic transition temperatures also show a dramatic odd–even effect although in both cases it is attenuated on increasing *n*. For even members the stability of the smectic A phase decreases with increasing *n* while for odd members the thermal stability of the phase passes through a weak maximum. Thus, increasing the spacer length does not strongly

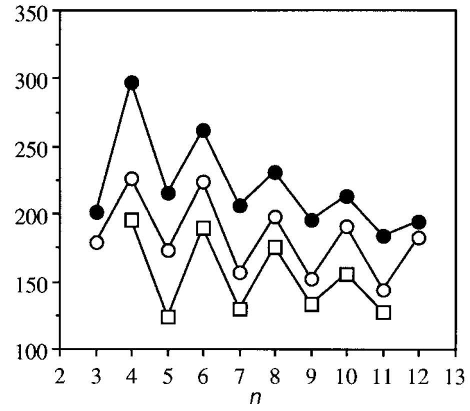
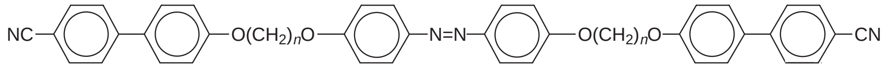


Fig. 1 The dependence of the transition temperatures on the number of methylene units (*n*) in the flexible alkyl spacers for the TCBO*n* series: (○) melting points, (●) nematic–isotropic transitions and (□) monotropic smectic A–nematic transitions

promote smectic behaviour. This is similar to the behaviour observed for symmetric liquid crystal dimers[25] but quite unlike that of semi-flexible main chain liquid crystal polymers for which increasing spacer length enhances smectic behaviour.[1,2] Thus the driving force for smectic phase formation must differ between the dimers and trimers, and the polymers. Presumably for the polymers this driving force must be an entropic one in order to disentangle the polymer chains.

In considering possible molecular factors for the observation of smectic behaviour for the TCBO*n* series, it is interesting to note that the analogous dimers, the BCBO*n* series, are exclusively nematics.[8] Indeed, the smectic A–nematic temperatures exhibited by the trimers are generally higher than the temperatures to which the nematic phases of the dimers can be supercooled. This implies that smectic phase formation is more favourable for the trimers. The trimers contain two electron deficient moieties, the cyanobiphenyl groups, and a central electron rich biphenyl unit. Smectic phase formation in non-symmetric liquid crystal dimers containing electron rich and electron poor moieties is attributed to the specific interaction between the unlike mesogenic units.[26,27] The precise nature of this interaction is unclear and most recently it has been suggested that it is electrostatic quadrupolar interactions between groups with quadrupole moments which are opposite in sign.[28] A similar explanation would serve to rationalise the observation of smectic behaviour for the trimers and not for the dimers. For the trimers, therefore, the driving force responsible for smectic behaviour may be the specific interaction between the electron rich biphenyl unit and the cyanobiphenyl moieties of high electron affinity. This view is supported by the transitional properties of four homologues of a closely related trimeric series to the TCBO*n* series,[12] which exhibit exclusively smectic behaviour. The central azobenzene unit is more electron rich than the biphenyl unit in the TCBO*n* series and it is reasonable to assume that the specific interaction between the quadrupole moments of the unlike groups will be more favourable. Thus it would be expected, and indeed observed, that smectic behaviour would be enhanced for these trimers relative to the corresponding members of the TCBO*n* series. By analogy to non-symmetric dimers, this driving force for smectic phase formation should result in the formation of intercalated phases[26] but unfortunately, and as we noted earlier, it was not possible to investigate the structure of the smectic A phase using X-ray diffraction. Hence, it would be unwise to speculate further on the local structure within the phase.



Trimeric series

The entropy change associated with the nematic–isotropic transition for the TCBO*n* series also exhibits a dramatic alternation as *n* is increased (Fig. 2). The values for the even members are typically 2–3 times larger than those of the odd members. This odd–even effect does not attenuate on increasing *n,* although it may be argued that it is attenuated in a relative sense since the values of $\Delta S_{\mathrm{NI}}/R$ increase with increasing *n* but the difference between the *n* and $(n+1)$ homologues appears to be approximately constant.

Thus we have seen that the transitional properties of the trimers depend critically on the length and parity of the spacer in a manner reminiscent of both dimers and the semi-flexible main chain polymers. For the dimers this behaviour is most often attributed to the dependence of the molecular shape on the parity of the spacer considered in the all-*trans* conformation. Specifically, in an even-membered dimer the mesogenic groups are antiparallel whereas in an odd-membered dimer they are inclined. This structure for even-membered dimers is then considered to be more compatible with the molecular organisation found in the nematic phase than for the odd-membered dimers and it is this greater compatibility which results in, for example, the higher nematic–isotropic entropies found for the even-membered dimers. Such an argument neglects the flexibility of the spacer and a more realistic interpretation of the dependence of the transitional properties on the parity of the spacer certainly includes a wide range of conformations and not solely the all-*trans* conformation.[5] In the isotropic phase approximately half the conformers of an even-membered dimer are essentially linear whereas for an odd membered dimer just 10% are linear. There exists a synergy between conformational and orientational order and hence at the transition to the nematic phase for even-membered dimers many of the bent conformers are converted to a linear form. This enhances the orientational order of the nematic phase resulting in a larger nematic–isotropic entropy than would be expected for a monomer. For odd-membered dimers, however, the difference in free energy between the bent and linear conformers is such that the orientational order of the nematic phase is insufficient to convert bent into linear conformers. Hence, the orientational order is not enhanced and a smaller nematic–isotropic entropy would be expected. Models have been developed based on a molecular field to describe this synergy between conformational and orientational order which are able to predict most of the properties of nematic liquid crystal dimers.[5] It is reasonable to assume that a similar treatment of liquid crystal trimers would also successfully predict their transitional behaviour and such calculations will be reported elsewhere.

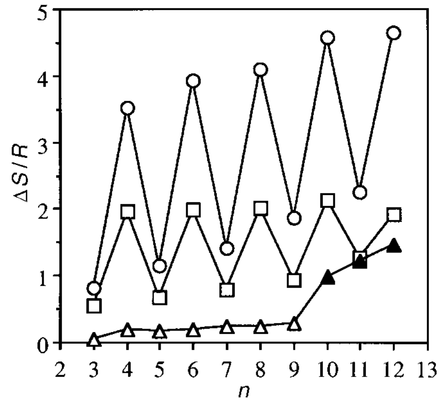


Fig. 2 (○) The dependence of the entropy change associated with the nematic–isotropic transition on the number of methylene units (*n*) in the flexible alkyl spacers for the TCBO*n* series. Also shown are the nematic–isotropic entropies for (□) the BCBO*n* series[8] and (△) the *n*OCB series.[29] Filled symbols denote smectic A–isotropic transitions for the monomers.

The dependence of the melting points on *n* for the monomeric, dimeric and trimeric series is shown in Fig. 3. The trimers exhibit the highest melting points with the single exception of the propane homologues for which the melting point of BCBO3 is just higher than that of TCBO3. The strong alternation in the melting points of the dimers and trimers is not evident in those of the monomers; it is interesting to note that this pronounced alternation in the melting points is only found for nematic dimers and is not observed for smectic dimers.[25] It was suggested that for nematic dimers this may indicate that the change in the conformation statistical weights of the spacer on melting is small for even-membered spacers

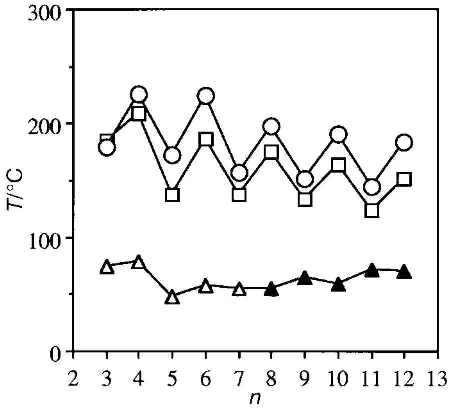


Fig. 3 The dependence of the melting points on the number of methylene units (n) in the alkyl chains for (○) the TCBOn series, (□) the BCBOn series[8] and (△) the nOCB[29] series. Filled symbols denote crystal–smectic A transitions.

but large for odd-membered compounds.[8] This would also be a reasonable assumption to make for the trimeric compounds. An alternative explanation, however, considers enthalpic effects. Thus at the root of this odd–even effect is possibly the difficulty that the odd membered compounds, with their bent conformations, experience in packing efficiently into a crystalline structure as compared with the more elongated even-membered trimers, see Fig. 4.

Fig. 5 compares the clearing temperatures of the monomeric, dimeric and trimeric series. For any given value of n, the trimer has the highest clearing point, then the dimer, while the monomer invariably exhibits the lowest clearing temperature. This trend is to be expected given the enhanced shape anisotropy on passing from the monomeric to the dimeric and trimeric structures.

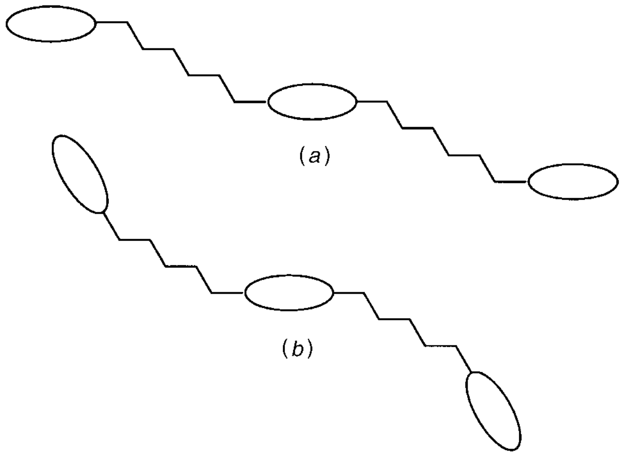


Fig. 4 Schematic representation of the all-*trans* conformation of (*a*) an even and (*b*) an odd membered trimer

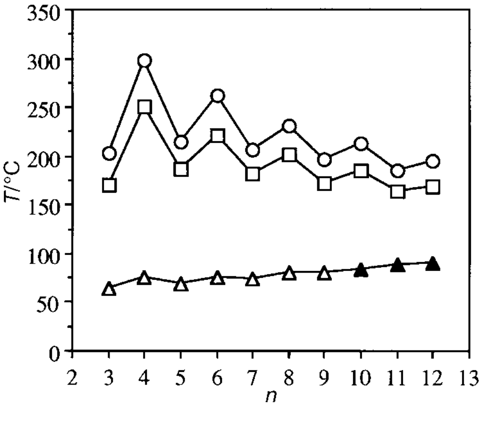


Fig. 5 The dependence of the clearing points on the number of methylene units (n) in the alkyl chains for (○) the TCBOn series, (□) the BCBOn series[8] and (△) the nOCB[29] series. Open symbols denote nematic–isotropic transitions and filled symbols smectic A–isotropic transitions for the monomers.

Fig. 2 shows the dependence of the entropy change associated with the liquid crystal–isotropic transition for the trimers, dimers[8] and monomers.[29] Both odd and even members of the trimeric TCBOn series exhibit higher, typically twice as large, values of $\Delta S_{NI}/R$ than observed for the analogous dimer. The size of the alternation exhibited by $\Delta S_{NI}/R$ on increasing n for the trimers is also greater than for the dimers. The values of $\Delta S_{NI}/R$ exhibited by the monomers are considerably smaller than either the dimers or the trimers and in addition, do not exhibit the dramatic alternation seen for the BCBOn and TCBOn series.

The question arises, however, when we compare the entropies and nematic–isotropic temperatures for the monomers, dimers and trimers how or indeed whether we should normalise the results to allow for the different number of mesogenic units. In order to address this issue, Fig. 6 shows the dependence of the ratios of the T_{NI}s for the dimers to those of the monomers and the trimers to those of the dimers on the number of carbon atoms in the terminal chain or the flexible spacers. The dimer/monomer ratio exhibits a pronounced odd–even effect which reflects the much larger alternation exhibited by the dimers when compared with the monomers. In contrast, the ratios for the trimer/dimer transition temperatures exhibit a weak odd–even effect and this is a result of the strong alternations exhibited by both sets of compounds cancelling each other out. A far more dramatic increase in T_{NI} is evident on passing from the monomer to the dimer as compared with going from dimer to trimer, as is clear from the higher values of the ratios of the transition temperatures, see Fig. 6. Fig. 7 compares the ratios of the entropies associated with the nematic–isotropic transition and again a dramatic odd–even effect is observed for the dimer/monomer ratios whereas the trimer/dimer values exhibit a very weak dependence on the length of the flexible spacers. It should be noted that the dimer/monomer ratio for $n=3$ is probably too large, resulting from an underestimation of $\Delta S_{NI}/R$ for 3OCB.[29] We note, however, that the clearing temperatures and entropies of the monomers do not show any significant dependence on n on the scale of that seen for the dimers and trimers and hence, the dimer/monomer ratios essentially reflect the behaviour of the dimers. A comparison of Fig. 6 and 7 reveals that the change in $\Delta S_{NI}/R$ on going from the dimer to the trimer is larger than that seen in T_{NI}. The ratios of T_{NI} all lie in the range 1.05–1.09 whereas for the entropies the corresponding

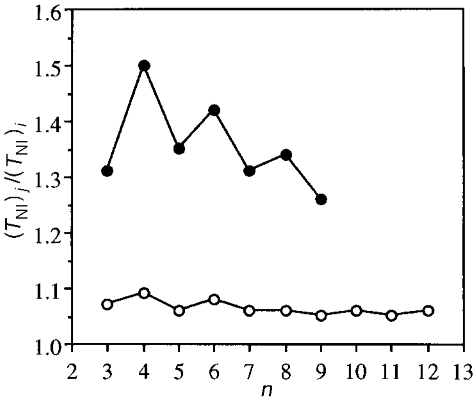


Fig. 6 The dependence of the ratio of the nematic–isotropic transition temperatures for (●) the BCBOn series to those of the nOCB series,[29] and for (○) the TCBOn series to those of the BCBOn series,[8] on the number of carbon atoms (n) in the alkyl chains

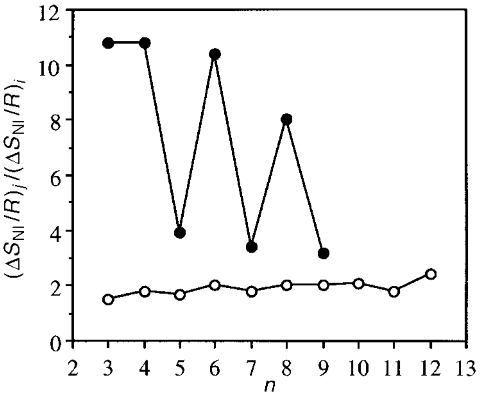


Fig. 7 The dependence of the ratio of the nematic–isotropic entropies for (●) the BCBO*n* series to those of the *n*OCB series, and for (○) the TCBO*n* series to those of the BCBO*n* series, on the number of carbon atoms (*n*) in the alkyl chains

range is 1.5–2.4. This small increase in T_{NI} suggests that the mesogenic units in the trimers are correlated to the same extent as in the dimers whereas the larger increase in $\Delta S_{NI}/R$ suggests a significant increase in the orientational order of the mesogenic groups on passing from the dimer to trimer. Alternatively, if the results were scaled according to the number of mesogenic units, the value 3/2 might be expected. These observations, however, are based on just a single set of materials and much research is now required to establish the generality or otherwise of their behaviour.

References

1 H. Finkelmann, in *Thermotropic Liquid Crystals*, ed. G. W. Gray, Wiley, Chichester, 1987, ch. 6.
2 C. K. Ober, J.-I. Jin and R. W. Lenz, *Adv. Polym. Sci.*, 1984, **59**, 103.
3 A. Blumstein and O. Thomas, *Macromolecules*, 1982, **15**, 1264.
4 G. W. Gray, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray, Academic Press, London, 1979, ch. 1.
5 C. T. Imrie and G. R. Luckhurst, in *Handbook of Liquid Crystals, vol. 2B*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, ch. 10, pp. 801–834.
6 G. R. Luckhurst, *Macromol. Symp.*, 1995, **96**, 1.
7 A. C. Griffin and T. R. Britt, *J. Am. Chem. Soc.*, 1981, **103**, 4957.
8 J. W. Emsley, G. R. Luckhurst, G. N. Shilstone and I. Sage, *Mol. Cryst. Liq. Cryst. Lett.*, 1984, **102**, 223.
9 H. Furuya, K. Asahi and A. Abe, *Polym. J.*, 1986, **18**, 779.
10 G. S. Attard and C. T. Imrie, *Liq. Cryst.*, 1989, **6**, 387.
11 R. Centore, A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, 1990, **182B**, 233.
12 T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, 1990, **182B**, 357.
13 A. T. Marcelis, A. Koudijs and E. J. R. Sudhölterr, *Liq. Cryst.*, 1996, **21**, 87.
14 A. T. Marcelis, A. Koudijs and E. J. R. Sudhölterr, *Liq. Cryst.*, 1995, **18**, 851.
15 N. V. Tsvetkov, V. V. Zuev and V. N. Tsvetkov, *Liq. Cryst.*, 1997, **22**, 245.
16 A. C. Griffin, S. L. Sullivan and W. E. Hughes, *Liq. Cryst.*, 1989, **4**, 677.
17 C. T. Imrie, D. Stewart, C. Remy, D. W. Christie, I. W. Hamley, R. Harding and J. Pople, unpublished work.
18 D. Demus, *Liq. Crys.*, 1989, **5**, 75.
19 K. Zab, D. Joachimi, E. Novotna, S. Diele and C. Tschierske, *Liq. Cryst.*, 1995, **18**, 631.
20 V. Percec and M. Kawasumi, *J. Mater. Chem.*, 1993, **3**, 725.
21 J. W. Emsley, G. R. Luckhurst and G. N. Shilstone, *Mol. Phys.*, 1984, **53**, 1023.
22 J. W. Emsley, G. R. Luckhurst and B. A. Timimi, *Chem. Phys. Lett.*, 1985, **114**, 19.
23 D. A. Dunmur and M. R. Wilson, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 961.
24 G. S. Attard, C. T. Imrie and F. E. Karasz, *Chem. Mater.*, 1992, **4**, 1246.
25 R. W. Date, C. T. Imrie, G. R. Luckhurst and J. M. Seddon, *Liq. Cryst.*, 1992, **12**, 203.
26 J. L. Hogan, C. T. Imrie and G. R. Luckhurst, *Liq. Cryst.*, 1988, **3**, 645.
27 G. S. Attard, S. Garnett, C. G. Hickman, C. T. Imrie and L. Taylor, *Liq. Cryst.*, 1990, **7**, 495.
28 A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *Liq. Cryst.*, 1995, **18**, 801.
29 C. T. Imrie, F. E. Karasz and G. S. Attard, *Macromolecules*, 1993, **26**, 3803.

Paper 8/01128A; *Received* 9*th February*, 1998