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INVITED ARTICLE

Liquid crystal oligomers: going beyond dimers

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This review focuses on structure-property relationships in liquid crystal oligomers, which consist of molecules containing two or more mesogenic units linked via flexible spacers essentially in a linear fashion and so does not consider, for example, liquid crystal dendrimers and tetrapodes. Previous reviews have tended to focus mainly on liquid crystal dimers in which just two mesogenic units are interconnected by a single spacer. By contrast, this review is largely devoted to higher oligomers such as liquid crystal trimers and tetramers containing three or four mesogenic units connected by two or three spacers, respectively.

Keywords: liquid crystal oligomers; dimers; trimers; intercalated smectic phases

1. Introduction

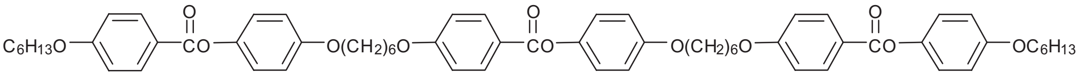
Liquid crystal oligomers consist of molecules containing two or more mesogenic units interconnected via flexible spacers, most commonly alkyl chains (*1–4*). Previous reviews of this class of materials have focused primarily on liquid crystal dimers in which two liquid crystal units are linked via a single flexible spacer and these continue to attract considerable research attention with recent studies including: the role of the spacer in determining liquid crystal behaviour (*5–7*); laterally connected dimers (*8*); dimers containing bent-core mesogenic units (*9*,*10*); cholesteryl-containing dimers (*11–18*); dimers containing rod- and disc-shaped mesogenic units and their potential to exhibit the biaxial nematic phase (*19–21*); hydrogen-bonded dimers (*22–24*); phase behaviour in bent odd-membered dimers (*25*); the flexoelectric properties of dimers (*26–28*); and light-emitting dimers (*29*). By contrast, our focus in this review is structure-property relationships in higher oligomers, specifically, molecules containing three or more mesogenic units interconnected via flexible spacers and essentially in a linear sense. Excluded from this review, therefore, are: molecular assemblages such as dendrimers (*30*); tetrapodes (*31*); non-linear discotic (*32*) and rod-disc oligomers (*33*, *34*); U-shaped (*35*, *36*), Y-shaped (*37*), λ-shaped (*38*), S-shaped (*39*) and other non-linear oligomers (*40*, *41*); some of these molecular architectures are shown schematically in Figure 1. Linear liquid crystal oligomers were of interest initially as model compounds for semi-flexible main chain liquid crystal polymers but, and as this review will reveal, interest in them now is strongly focused on their own transitional behaviour, which is quite different to that observed for conventional low molar mass liquid crystals.

2. Liquid crystal trimers

2.1 Background

A liquid crystal trimer consists of molecules containing three mesogenic units interconnected via two flexible spacers. These structural components may be assembled in a number of differing ways to give, for example: linear trimers (*42–54*); trimers in which one or more mesogenic units are connected in a lateral position (*55–58*); cyclic trimers (*59–64*); star-shaped trimers (*65–71*); trimers containing rod-like and disc-like mesogenic moieties (*55*, *72*, *73*). As noted earlier, the focus of this review is linear trimers and these may be classed as being either symmetric or non-symmetric. The non-symmetry may be introduced in a number of ways including by having differing mesogenic units (see, for example, (*52*, *72*)), by using alkyl chains of differing lengths (see, for example, (*74*, *75*)), by using differing terminal groups or indeed some combination of all these differences (see, for example, (*53*, *76*)).

The first reported linear trimer, **1**, was prepared by step-wise polymerisation as part of a series of



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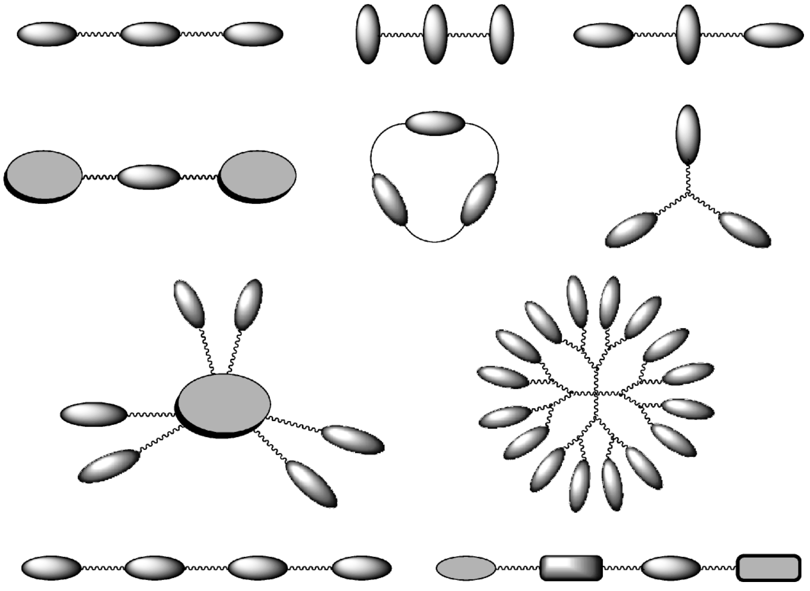


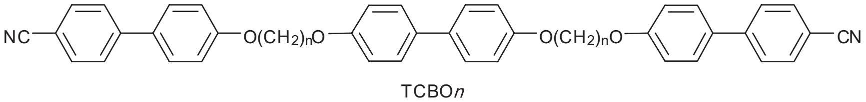
Figure 1. Schematic representations of the molecular architectures of a selection of liquid crystal oligomers.

oligomers in order to better understand the properties of liquid crystal polyesters (*77*).

The trimer did not exhibit liquid crystallinity even though the corresponding dimer showed enantiotropic smectic C and nematic phases, leading Keller to speculate that as many as six liquid crystal groups were required in a linear oligomer in order to observe mesogenic behaviour as suggested previously by Blumstein and Stickles (*78*). As we will see, however, this is not general behaviour.

2.2 *The odd–even effect*

The first homologous series of liquid crystal trimers, the 4,4'-bis[ω-(4-cyanobiphenyl-4'-yloxy)alkoxy)alkoxy]biphenyls, **2**, were reported by Imrie and Luckhurst (*47*) and contained two cyanobiphenyl groups and a central biphenyl core connected by two flexible spacers, although individual members of the series had previously been described (*42*, *46*).



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This series is referred to using the acronym TCBO*n* in which *n* refers to the number of methylene units in the flexible spacers. All 10 members of the series reported, *n* = 3–12, exhibit an enantiotropic nematic phase and also, with the exception of TCBO3 and TCBO12, show a monotropic smectic A phase. Figure 2 shows the dependence of the transition temperatures on the number of methylene units in the flexible alkyl spacers, *n*, and it is immediately apparent that the crystal–nematic, nematic–isotropic and smectic A–nematic transition temperatures all depend critically on the length and parity of the flexible spacers. Specifically, each set of transition temperatures exhibits a pronounced alternation in which the even members show the higher values on increasing *n* although for T_{NI} and T_{SmAN} this attenuates as the spacer length increases. We will return to discuss the smectic behaviour of trimers later.

The strong alternation in the crystal–nematic transition temperatures seen in Figure 2 is quite unlike the behaviour seen in conventional low molar mass liquid crystals but similar to that observed for the melting points of some, but not all, liquid crystal dimers (*1–4*). This pronounced alternation may indicate that the change in the conformation statistical weights of the spacers on melting is small for even-membered spacers but large for odd-membered. Alternatively, this strong alternation may be rationalised in terms of enthalpic effects, and reflects the difficulty that odd-membered trimers with their bent conformation experience in packing efficiently into a crystal arrangement as compared with the more elongated even-membered trimers.

In order to discuss the dependence of the nematic–isotropic transition temperatures on the length of the

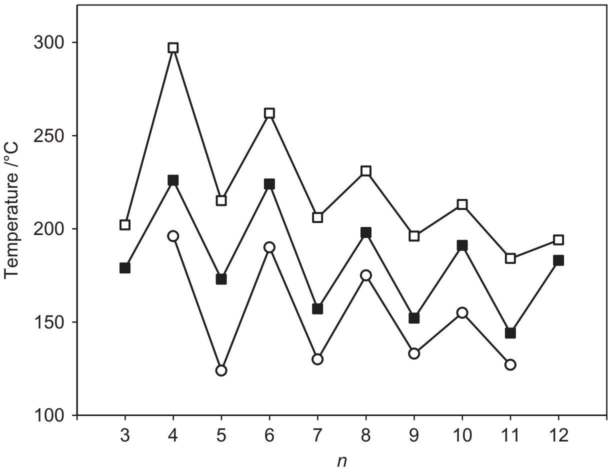


Figure 2. The dependence of the transition temperatures on the number of methylene units (*n*) in the alkyl spacers for the TCBO*n* series. Crystal–nematic transitions are denoted by ■, nematic–isotropic transitions by □ and monotropic smectic A–nematic transitions by ○.

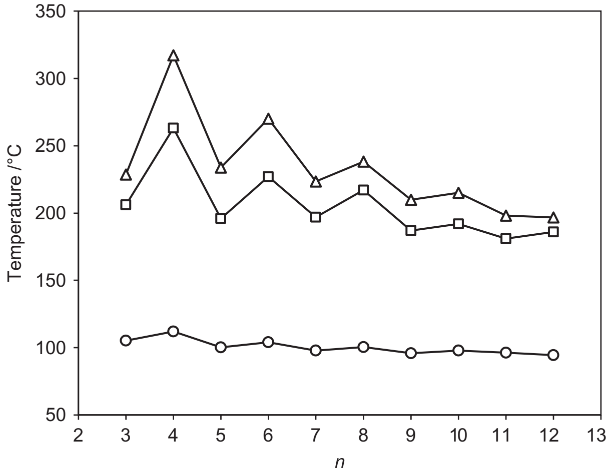
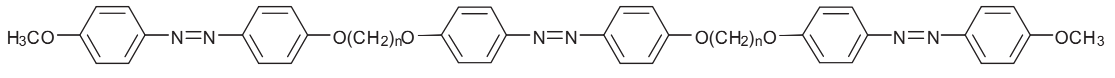


Figure 3. The dependence of the nematic–isotropic transition temperatures of the 3Azo-*n* (Δ), 2Azo-*n* (□) and Azo-*n* (○) series on the number of methylene units, *n*, in the alkyl chains in each series.

spacers, Figure 3 compares the nematic–isotropic transition temperatures of a series of trimers containing azobenzene mesogenic units (*79*), **3**, to those of the corresponding dimers (*79*), **4**, and conventional monomers (*80*), **5**.



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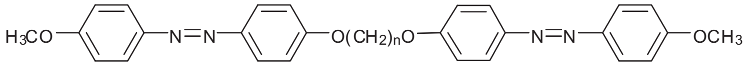
3Azo-*n*



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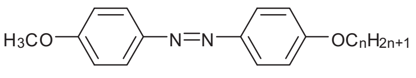
2Azo-*n*



5

Azo-*n*

The acronyms used to refer to these series are 3Azo-*n* for the trimers, 2Azo-*n* for the dimers and Azo-*n* for the monomers, where *n* indicates the number of methylene units in the alkyl chains in each structure. It is clear from Figure 3 that the trimers show the highest nematic–isotropic transition temperatures followed by the dimers and then the monomers. This trend is to be expected given the increase in shape anisotropy on passing from the monomeric to the dimeric and trimeric structures. The nematic–isotropic transition temperatures of the trimers and dimers show a pronounced alternation, which attenuates on increasing *n* whereas a much weaker alternation in T_{NI} is observed for the monomers as the length of the terminal alkyl chain is varied. It is interesting to note that as *n* is increased the nematic–isotropic transition temperatures of the dimers and trimers become more similar. Whether this trend continues as *n* is increased such that dimers having longer spacers would show values of T_{NI} greater than those of the corresponding trimers has yet to be established.

Figure 4 shows the dependence of the entropy changes associated with the nematic–isotropic transition, $\Delta S_{NI}/R$, on the length of the alkyl chains in each series. All three series showed an odd–even effect, which is not attenuated on increasing the chain length. This odd–even effect is weakest for the monomers and most pronounced for the trimers. Indeed, for the dimers and trimers the values of $\Delta S_{NI}/R$ are strongly dependent on

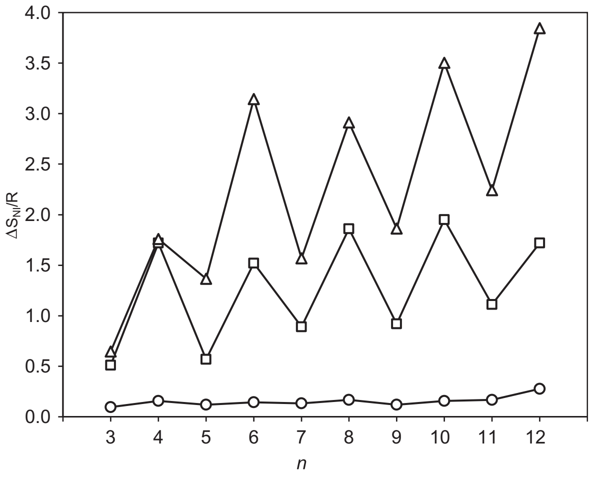


Figure 4. The dependence of the nematic–isotropic entropy change, $\Delta S_{\mathrm{NI}}/R$, on the number of methylene units, *n*, the alkyl chains for the 3Azo-*n* (Δ), 2Azo-*n* (□) and Azo-*n* (○) series.

the length and parity of the spacers. It is worth noting that $\Delta S_{\mathrm{NI}}/R$ for 3Azo-4 appears to be rather low, but this is simply a consequence of sample decomposition at high temperatures. By contrast, the physical significance of the low value of $\Delta S_{\mathrm{NI}}/R$ shown by 3Azo-3 is not clear, although we will discuss this later. It should be noted that the values of $\Delta S_{\mathrm{NI}}/R$ are highest for the trimers and these are typically twice those of the corresponding dimers. The values of $\Delta S_{\mathrm{NI}}/R$ shown by the monomers are considerably lower than those of either the dimers or trimers. The observation of pronounced odd–even effects in both the transition temperatures and entropy changes as the length of the spacers are varied for the trimers is most often attributed to the dependence of the molecular shape on the parity of the spacers considered in the all-*trans* conformation. Thus, if a trimer is considered in its most extended all-*trans* conformation, two quite distinct molecular shapes are obtained which depend on the parity of the spacer. Specifically, for odd-membered trimers the two outer mesogenic groups are inclined with respect to the central moiety giving a stretched S-shape (see Figure 5(a)), whereas in an even-membered trimer all three mesogenic units are co-parallel resulting in an extended rod-like structure (see Figure 5(b)). We note, however, that the extent to which the mesogenic groups are co-parallel will depend on the geometry of the specific links between the spacer and the mesogenic groups as well as the geometry of the spacer itself. The enhanced shape anisotropy of the even-membered trimers allows the molecules to pack more efficiently in the liquid crystal phase giving higher transition temperatures and entropy changes. This rationalisation, however, fails to take into account the flexibility of the alkyl spacers and a more realistic interpretation must include a wider range of conformations. Luckhurst and co-workers (*1*, *74*) developed such an approach to account for the behaviour of dimers, which has also been used to model the behaviour of trimers successfully (*81*). Thus, for an even-membered dimer approximately half of the molecules assume an elongated conformation in the isotropic phase whereas for odd-membered dimers this value is only about 10%. At the isotropic–nematic phase transition, many of the even-membered dimers having bent conformations are converted into the linear form so enhancing the orientational order of the nematic phase giving a large entropy change. By contrast, the larger energy difference between the bent and linear conformations for an odd-membered dimer prevents this conversion taking place. In consequence, the orientational order of the nematic phase is not enhanced and the entropy change is smaller.

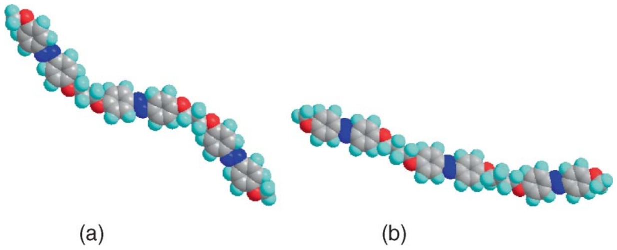


Figure 5. Molecular shapes in the all-*trans* conformations of (a) 3Azo-3 and (b) 3Azo-4.

We return now to the observation that both the nematic–isotropic transition temperatures and $\Delta S_{\mathrm{NI}}/R$ are highest for the trimers and lowest for the monomers. The question arises, however, whether in making such comparisons we should in fact allow in some way for the different number of mesogenic units in each structure. In an attempt to address this issue, Figure 6 shows the dependence of the ratio of the nematic–isotropic transition temperatures of the dimers to the monomers and those of the trimers to the dimers on increasing the length of the alkyl chains, while Figure 7 shows the same comparison for the values of $\Delta S_{\mathrm{NI}}/R$. In each case, the ratio of the respective quantity of the dimer to the monomer shows a strong odd-effect whereas the same ratio from the trimer to dimer shows a much weaker dependence on *n*. The weaker dependence of the latter ratios is a result of the strong odd–even effect exhibited by the dimers and trimers in both quantities cancelling each other out. The rather low value of this ratio for 2Azo-12/Azo-12 reflects the relatively high value of $\Delta S_{\mathrm{NI}}/R$ measured for Azo-12 when compared with the other members of the Azo-*n* series. This is still considerably smaller, however, than $\Delta S_{\mathrm{NI}}/R$ seen for 2Azo-12. It is clear that a more dramatic increase in T_{NI} is seen on passing from the monomer to dimer than going from the dimer to trimer as

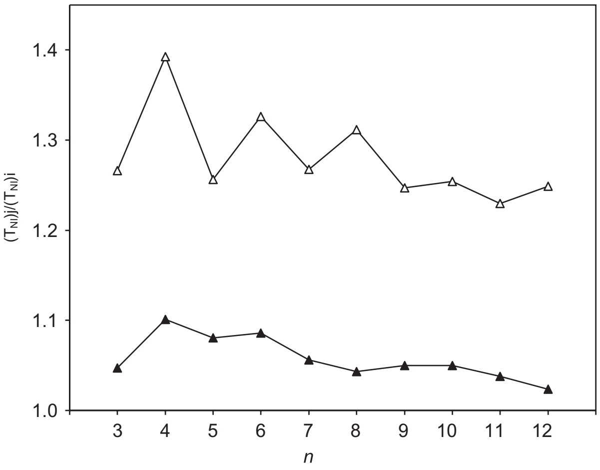


Figure 6. Ratio of the nematic–isotropic transition temperatures of 2Azo-*n*: Azo-*n* (Δ) and 3Azo-*n*: 2Azo-*n* (▲).

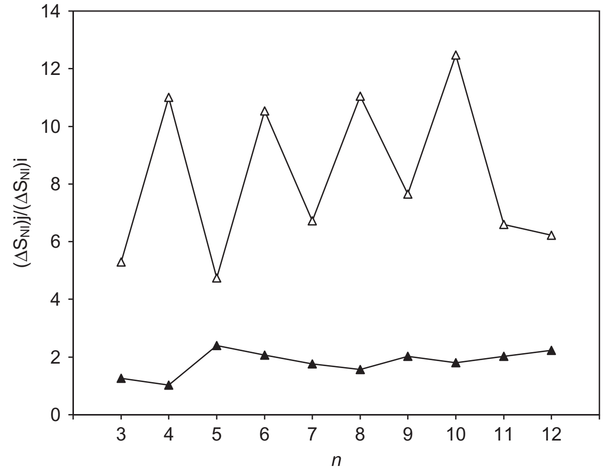


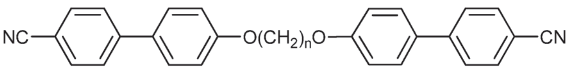
Figure 7. Ratio of $\Delta S_{NI}/R$ of the 2Azo-*n:* Azo-*n* (Δ) and 3Azo-*n*: 2Azo-*n* (▲).

evidenced by the values of the ratios of T_{NI} (see Figure 6). A similar trend is also seen for $\Delta S_{NI}/R$ (see Figure 7), but the relative increase in $\Delta S_{NI}/R$ on going from the dimer to trimer is larger than that seen for T_{NI}. Very similar behaviour has also been seen for cyanobiphenyl-based trimers, dimers and monomers (*47*). The smaller relative increase in T_{NI} suggests that the orientations of the mesogenic units in the trimers are correlated to the same extent as in the dimers, whereas the larger relative increase in $\Delta S_{NI}/R$ suggests a significant increase in the orientational order of the mesogenic groups on passing from the dimer to the trimer. It has been suggested that a value of 3/2 would be expected for the ratio of the nematic–isotropic transition temperatures of the trimers to dimers (*47*). This was based on the predictions of a model developed to calculate the transition temperatures of oligomers composed of rigid mesogenic units in which T_{NI} for an oligomer containing *n* repeat units is simply *n* times that of the monomer (*82*), although this was only true for very long monomers. For the 3Azo-*n* and 2Azo-*n* materials the trimer:dimer T_{NI} ratio is in the region 1.02–1.10, which is less than the predicted value of 3/2, while for the TCBO*n* and BCBO*n* materials the same ratio lies in the range 1.05–1.09. These lower than predicted ratios are presumably due to the presence of flexible spacers in the molecule which destroy the linearity of the structure. A rather general relationship appears to exist, however, between the transitional properties of structurally corresponding dimers and trimers but this must now be tested for a much wider set of materials.

2.3 Smectic Behaviour of Liquid Crystal Trimers

We saw earlier that the TCBO*n* series, **2**, showed a monotropic smectic A phase (see Figure 2), and that increasing the spacer length does not strongly promote smectic behaviour. This is similar to the general behaviour seen for symmetric liquid crystal dimers (*83*), but very different to that of semi-flexible main chain liquid crystal polymers for which increasing spacer length enhances smectic behaviour (*84*). This implies that the driving force for smectic phase formation must differ between the oligomers and polymers, for which presumably the driving force is an entropic one in order to disentangle the polymer chains.

It is interesting to note that the corresponding liquid crystal dimers, the BCBO*n* series, are exclusively nematics for spacers up to 24 methylene units in length (*85*, *86*). Furthermore, the smectic A–nematic transition temperatures exhibited by the trimers are generally higher than the temperatures to which the nematic phases of the BCBO*n* series may be supercooled. Thus, for this series at least, smectic phase formation is more favourable for trimers than dimers. It is also interesting to note that non-symmetric analogues of the TCBO*n* series containing spacers of differing lengths,



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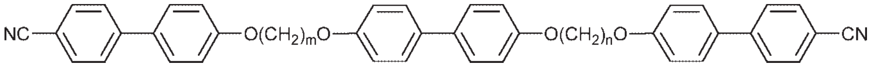

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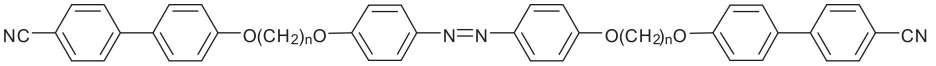
also exhibited smectic A behaviour (*74*, *75*). It was suggested that the enhanced smectic behaviour of the TCBO*n* series may be attributed to a favourable specific interaction between the electron-rich biphenyl unit and the cyanobiphenyl moieities of high electron affinity. It is well known that non-symmetric liquid crystal dimers containing electron-rich and electron-deficient moieties have a tendency to exhibit intercalated smectic phases often attributed to a specific interaction between the unlike mesogenic units (*87–90*). The precise nature of this interaction has yet to be established but it has been suggested that it is an electrostatic quadrupolar interaction between groups with quadrupole moments which are opposite in sign (*91*). For the TCBO*n* series the strongly monotropic nature of the smectic A phase precluded the possibility of establishing its structure using X-ray diffraction, although it would now be of interest to use X-ray scattering to study smectic correlations in the nematic phase, which may provide some indication of the potential smectic structure. This view that the specific interaction between the biphenyl and cyanobiphenyl units is the driving force responsible for smectic behaviour is supported by the behaviour of the trimer series in which the biphenyl unit has been replaced by an azobenzene group (*45*), **8**.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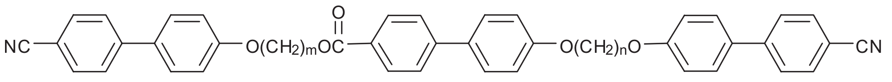
The four homologues prepared exhibited exclusively smectic behaviour. The azobenzene group is more electron-rich than the biphenyl unit and so it is reasonable to assume that the specific interaction between the unlike mesogenic units is enhanced in the azobenzene-based trimers. Further support for this suggestion that the driving force for smectic phase formation is a specific interaction between the unlike mesogenic groups can be found in the transitional properties of another closely related trimer series: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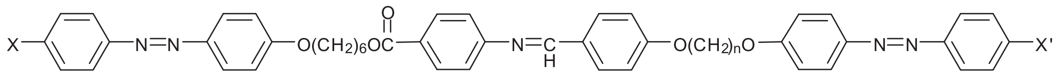
m = 3-11 ; n = m+1

in which non-symmetry has been introduced by the introduction of an ester linkage in place of an ether linkage to the central mesogenic unit (*92*). This change will increase the electron affinity of the central moiety and so presumably reduce the interaction between the unlike mesogenic groups. It would be expected, therefore, that these trimers would exhibit reduced smectic tendencies and indeed this is the case. The nine homologues prepared exhibit exclusively nematogenic behaviour. It is also noteworthy that the 3Azo-*n* series, **3**, discussed earlier are exclusively nematics. In this series all three mesogenic groups are essentially identical so removing the possibility of a specific interaction between unlike groups. In this case, however, it must also be noted that there is a significant mismatch between the lengths of the terminal group and the flexible spacers which for dimers is known to inhibit smectic phase formation (*83*).

In order to better understand smectic phase formation in trimers Imrie *et al.* (93) and Henderson and Imrie (*94*) studied the properties of four related series of nonsymmetric trimers, **10**.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X = X' = OCH_3, MeO6E.nOMe; X = OCH_3, X' = CN, MeO6E.nCN;
X = CN, X' = OCH_3, CN6E.nOMe; X = X' = CN, CN6E.nCN
n = 3-12

In each of these series one spacer length has been held constant at six methylene units while the second is varied from 3 to 12 methylene units. The two outer mesogenic units are azobenzene-based while the inner one is a Schiff's base unit. The terminal units have been varied in such a way to allow an investigation of how the inclusion of electron-rich and electron-deficient units affect smectic phase formation. Figure 8 shows the dependence of the transition temperatures on the number of methylene units, *n*, in the variable flexible spacer for each series. All 40 homologues exhibited an enantrotropic nematic phase while just two showed smectic behaviour, specifically, MeO6E.11CN and CN6E.11OMe. The smectic phase of CN6E.110Me exhibits a texture consisting of well-defined focal-conic fans, which shear to give a schlieren texture. A thin film of the smectic phase showed a schlieren texture indicating a tilted phase. On cooling regions of homeotropically aligned nematic phase, a schlieren texture developed containing both two- and four-point disclinations implying the presence of an alternating tilted phase in which the global tilt angle is zero. The X-ray diffraction pattern obtained for the phase contained a low angle peak with a *d*-spacing of 19.0 Å compared with an estimated molecular length of 60.4 Å, and a diffuse band in the wide angle region. These data were interpreted in terms of a triply intercalated alternating smectic C phase; see Figure 9 in which the tilt direction of the local director is indicated. Within this structure, the bent odd-membered trimers pack efficiently and a microphase separation occurs to give two types of domains, one consisting of mesogenic groups and the other of alkyl chains. Each sub-layer of mesogenic groups consists of equal numbers of the three different moieties, which is both entropically favourable and also maximises the favourable specific interactions between the unlike units, i.e. the electron-deficient cyano-substituted units and electron-rich central and methoxy substituted groups. The alternation in the sense of the tilt angle on passing through the phase requires a correlation of the mesogenic groups, which is thought to be provided by a combination of the specific interaction between the unlike groups, and the flexible spacers providing the oligomeric nature of the system. To understand the distinction between a conventional smectic C phase and an alternating smectic C phase it is instructive to consider that in the ground state of the smectic C phase the major principal axis of some second rank tensor is tilted with respect to the layer normal. By contrast, for the alternating smectic C phase, the major principal axis of the tensor is parallel to the layer normal as for a smectic A phase. In both cases, however, the principal components of the tensors are biaxial, consistent with the symmetry of the phase. It is interesting to note that a binary equimolar mixture of MeO6E.11OMe and CN6E.11CN exhibited a monotropic smectic phase even though the two trimers are exclusively nematogenic and similar behaviour has been observed for binary mixtures of symmetric dimers (*89*). This strongly suggests that the specific interaction between the unlike mesogenic groups does drive the formation of the smectic phase, but unfortunately the strongly monotropic nature of the smectic phase shown by the mixture precluded its study using X-ray diffraction.

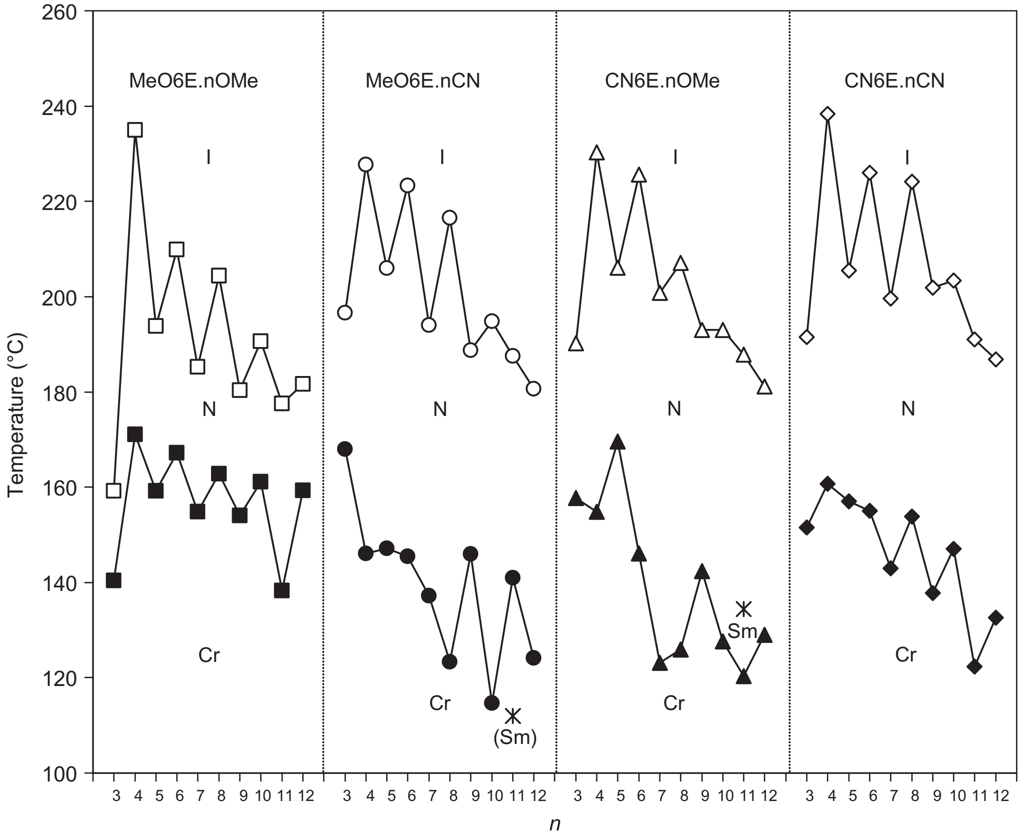


Figure 8. The dependence of the transition temperatures on the number of methylene units, *n*, in the variable flexible spacer for the four non-symmetric trimer series, **10**.

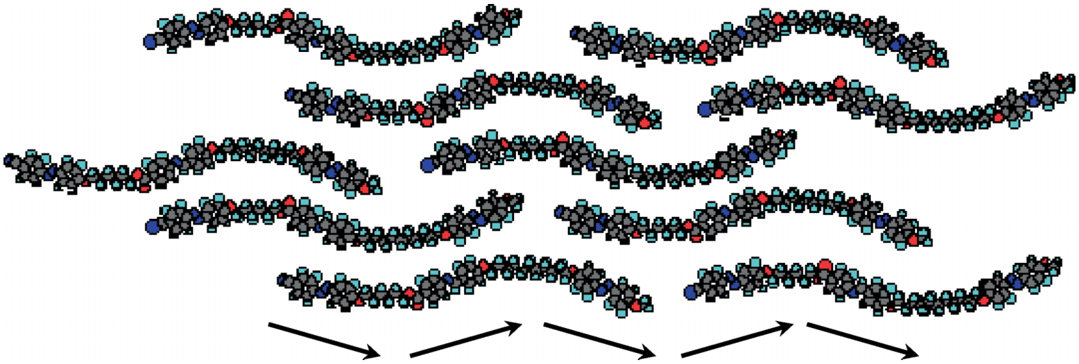
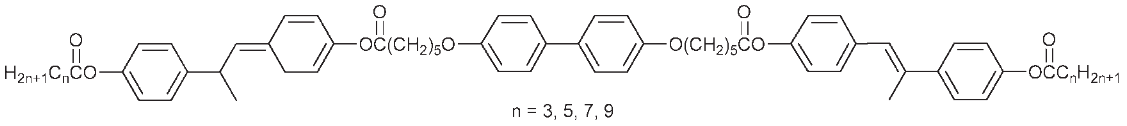


Figure 9. Schematic representation of the triply intercalated alternating smectic C phase exhibited by CN6E.11OMe.

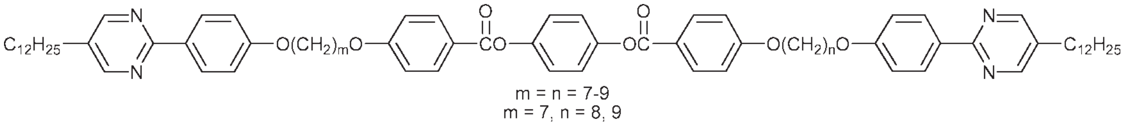
Although our discussion of the formation of smectic phases has focused on the possible role of a specific interaction between unlike mesogenic groups in providing the driving force, we should note that the formation of smectic phases does seem to depend in a subtle way on the nature and geometry of the link between the spacer and mesogenic groups. For example, we have seen that the BCBO*n* series are exclusively nematogenic, whereas the analogous methylene-linked dimers with odd spacers exhibit smectic behaviour (*95*).

Conventional monolayer smectic phases have also been observed for trimers. For example, Centore *et al.* (*44*) reported a series of trimers in which they varied the terminal alkyl chain length, **11**.



11

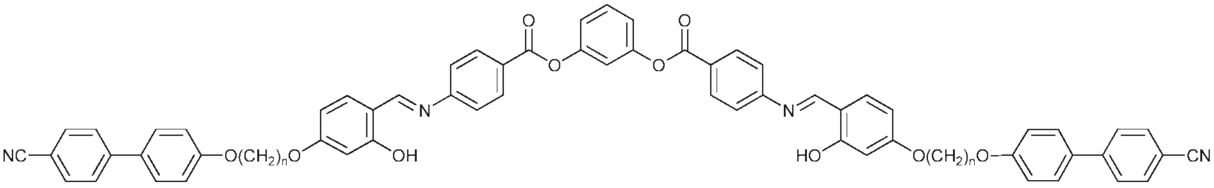
These trimers exhibited smectic A and C phases and the layer spacing in the smectic C phase measured using X-ray diffraction was indicative of a conventional monolayer smectic C phase. Yoshizawa *et al.* (*96*) reported the transitional behaviour of the trimers, **12**.



12

All these trimers exhibited enantiotropic smectic C and N phases, and with the exception of the homologue for which both spacers consisted of seven methylene units, a smectic I phase. X-ray diffraction studies suggested that the smectic C phase had a conventional monolayer structure. For both these sets of compounds, **11** and **12**, the length of the terminal alkyl chain prevents the formation of an intercalated smectic phase and their behaviour is obeying the general rule developed for dimers that for smectic behaviour to be observed the length of the terminal chain must exceed half that of the spacers (*83*). The generality of this behaviour for the trimers has yet to be established.

Yelamaggad and Shashikala (*97*) reported the first examples of trimers containing rod-like and bent-core mesogenic groups, **13**.

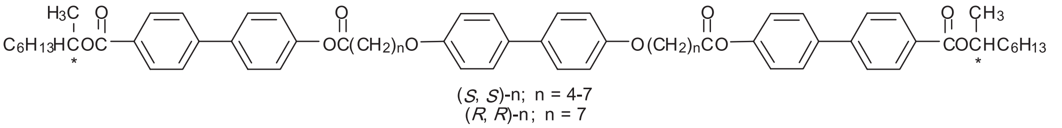


13

All four homologues exhibited an enantiotropic nematic phase and in addition, the heptyl homologue showed a monotropic smectic phase. It was not possible to study this phase using X-ray diffraction because of its monotropic nature. It is interesting to note, however, that these materials did not exhibit stable smectic phases as might have been expected given the combination of electron-deficient and electron-rich mesogenic groups, although the differing geometries of the central and terminal mesogenic units may also be important in determining smectic behaviour.

2.4 *Chiral liquid crystal trimers*

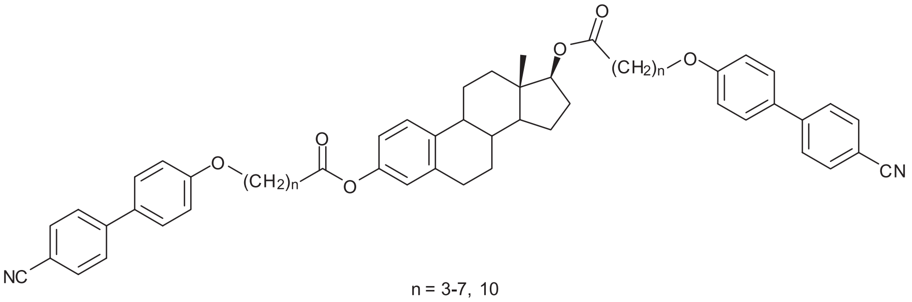
Nishiyama *et al.* (*98*) have reported the transitional properties of a set of chiral liquid crystal trimers, **14**.



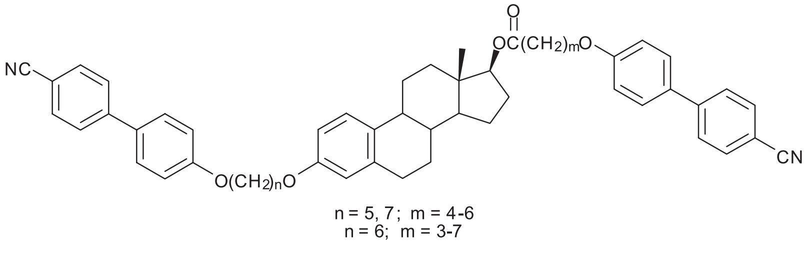
14

Three homologues (*S,S-5*), (*S,S-7*) and (*R,R-7*) showed two smectic phases in which the global tilt angle was zero but for which microscopic observations indicated a locally non-zero tilt angle. The global tilt angle was assessed on the basis of the observation that for homogeneous optical textures of these phases, the extinction direction was always parallel or normal to the polarisers indicating the average molecular tilt is zero. Taken together with electro-optic measurements and X-ray diffraction studies, these phases were assigned as antiferroelectric smectic C and I phases; a subscript A was used by the authors to denote the antiferroelectric structure. The X-ray diffraction patterns of the smectic phases contained three-layer reflections in the small angle region indicating a well-defined layer structure. The authors suggested that this may arise from the microsegregation of the chemically distinct parts of the trimer while their covalent interconnectivity stabilises the anticlinic structure. A racemic mixture of (*S,S*-7) and (*R,R-7*) also showed antiferroelectric smectic C and I phases indicating that the chirality dependent properties do not drive the formation of the anticlinic phases.

Marcelis *et al.* (*50*, *99*) have studied the properties of two sets of trimers based on optically active estradiol and containing two cyanobiphenyl moieties.



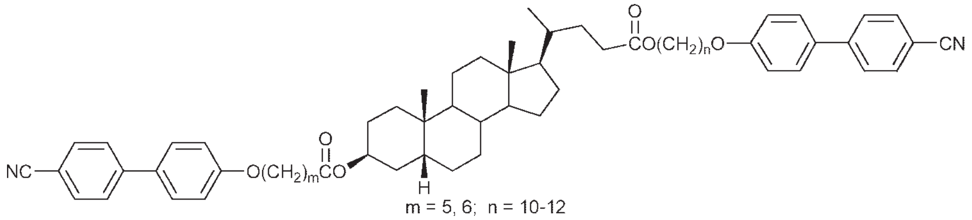
15



16

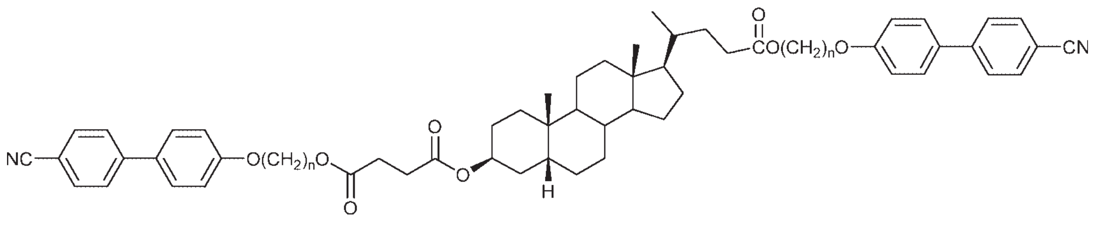
All these trimers exhibited a chiral nematic phase. For the former compounds, **15**, the nematic–isotropic transition temperatures and associated entropy changes only exhibit a weak dependence on the parity of the spacers. This is thought to be a consequence of the fact that the bonds connecting the spacers to the steroid nucleus are not co-parallel and so changing the parity of the spacers has a much reduced effect on the average molecular shape. For the latter materials, **16**, a more pronounced odd–even effect is seen in the nematic–isotropic transition temperatures and associated entropy changes when comparing compounds having the same value of *m* and varying *n*. This is thought to indicate that changing the parity of the spacer on the 3-ether side of the molecule has a more pronounced effect on shape than changing the spacer length on the 17-ester side. It should not be overlooked, however, that it has been shown for liquid crystal dimers that changing the nature of the linkage to the mesogenic units changes the magnitude of the alternations seen for the transitional properties (*100–102*). One of these trimers exhibited a smectic A phase, **16,** *n* = 7 and *m* = 5, but the local molecular organisation within the phase was not reported.

Marcelis *et al.* (*103*) have also reported the transitional behaviour of two sets of trimers based on isolithocholic acid.



17

m = 5, 6; n = 10-12

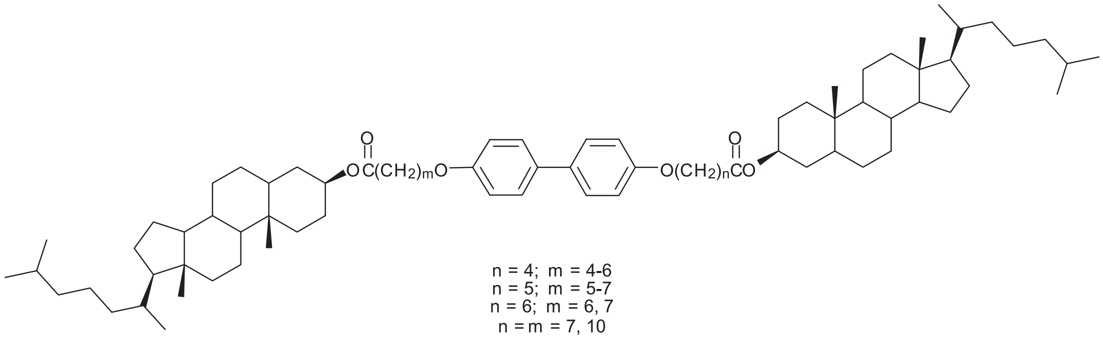


18

n = 10-12

All these trimers exhibit a monotropic chiral nematic phase. As with trimers **15**, the transitional properties of **17** and **18** showed only a weak dependence on the parity of the spacers. This was attributed to the fact that the bonds connecting the spacers to the steroid nucleus are not co-parallel with the major axis of the steroid and thus, changing the parity of the spacers does not significantly change the average molecular shape.

The majority of chiral liquid crystal trimers contain cholesteryl-based groups and as with cholesterol-based liquid crystal dimers (*104*), these are a rich source of frustrated smectic phases. Marcelis *et al.* (*49*) reported the first trimers containing dihydrocholesteryl groups, **19**.

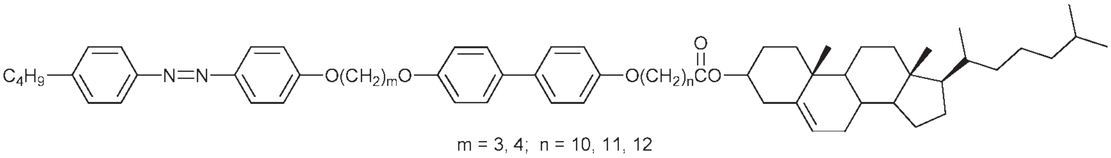


19

n = 4; m = 4-6
n = 5; m = 5-7
n = 6; m = 6, 7
n = m = 7, 10

All these trimers exhibited an enantiotropic nematic phase and in addition, for those homologues containing two even-membered spacers, a smectic A phase was also observed. The authors subsequently extended this study to include the corresponding trimers containing two cholesteryl-groups, and also the non-symmetric variants containing one dihydrocholesteryl and one cholesteryl unit (*105*). For each set of trimers twist grain boundary C* (TGBC*) phases were observed for the shorter even-membered spacers. In the TGBC* phase, the ratio of the periodicity to the estimated all-trans molecular length was approximately 1. By contrast, in the SmA phase seen for longer even-membered spacers, the ratio of the smectic periodicity to the molecular length was approximately 0.33. This implies a triply intercalated arrangement, although the driving force for phase formation is not clear. A Schiff's base analogue containing two cholesteryl groups and five methylene units in both spacers exhibits a chiral nematic phase and an unidentified mesophase (*106*).

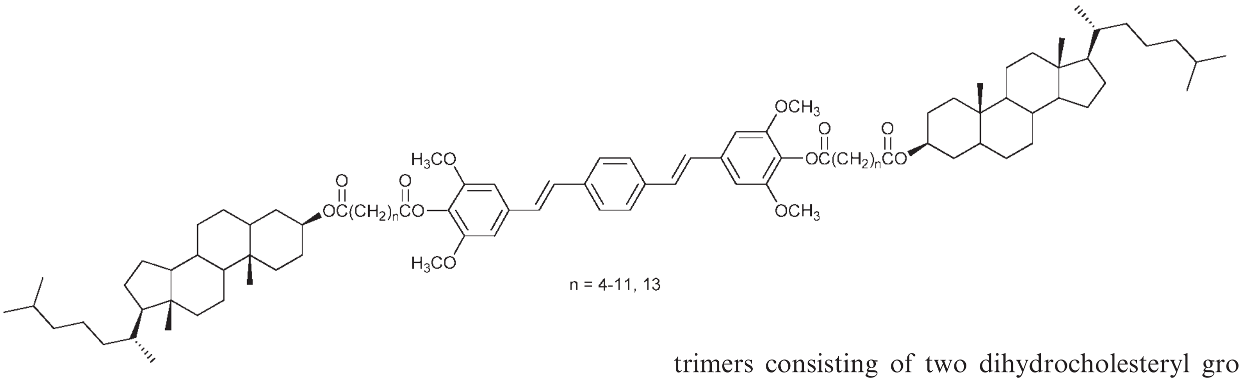
Yelamaggad *et al.* (*52*, *53*, *76*) have reported trimers containing three different mesogenic units, including cholesteryl and two differing spacer lengths, **20**.



20

The homologues containing spacers of matched parity showed the undulating twist grain boundary (TGB) phase over a wide temperature range. By contrast, for compounds containing spacers of differing parities there is a fleeting TGB phase observed between the chiral nematic and smectic A phases.

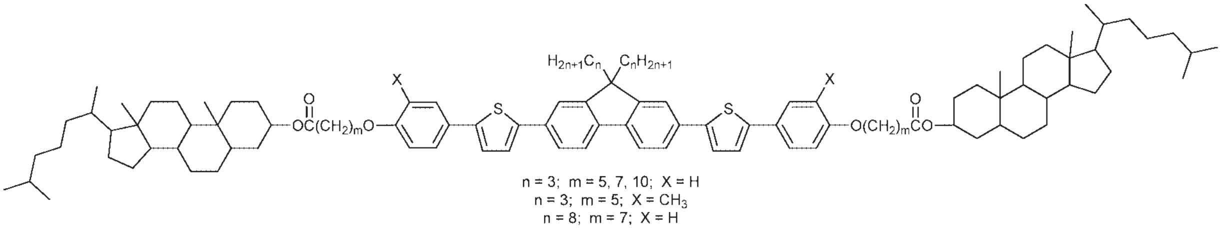
Liquid crystal trimers consisting of mesogenic units having light emitting properties have been reported by Sentman and Gin (*54*), **21**.



21

The trimers with even-membered spacers tend to exhibit a strongly monotropic smectic A phase. It was possible, however, to measure the layer spacing for the decyl homologue and this was 83 Å as compared with the estimated molecular length of 84 Å. It appears, therefore, that this is a conventional monolayer smectic A phase. For the odd members, a monotropic smectic phase is also observed for which the layer spacer spacing is typically somewhat less than the estimated molecular length. For example, for the nonyl homologue the layer spacing is 74 Å as compared with the molecular length of 80 Å. The authors suggested that this implies either an interdigitation of the layers and/or a tilting of the director with respect to the layer normal. On cooling the smectic phases seen for the odd-membered trimers, anisotropic glasses are obtained. Similar behaviour has been observed for liquid crystal dimers (*107*).

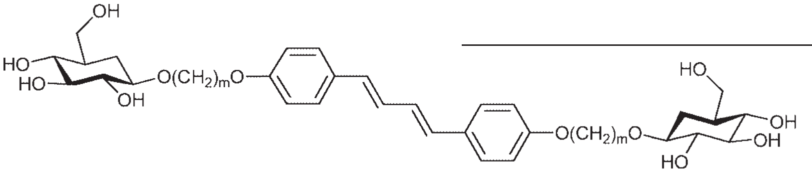
More recently, Kelly and co-workers (*108*) reported the behaviour of light emitting liquid crystal trimers consisting of two dihydrocholesteryl groups and an extended aromatic core, **22**.



22

These trimers exhibit chiral nematic phases and in addition, for m = 10, n = 3, a smectic C* phase is observed for which the layer spacing is 29 Å. This is considerably less than the molecular length of around 71 Å implying either a highly intercalated structure and/or a high tilt angle.

Das *et al.* (*109*) have recently reported a liquid crystal trimer series consisting of two glucopyranoside groups and a central diphenylbutadiene central unit.



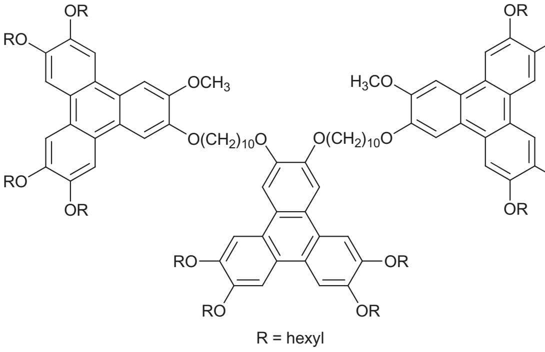
m = 2-5, 7, 8, 10, 12

23

The trimers with the three shortest spacers exhibited smectic A and C* phases while the remaining exhibited exclusively smectic C* behaviour. X-ray diffraction studies indicated an interdigitated arrangement of the molecules within the smectic phases, presumably driven by hydrogen bonding between the glucopyranosides. However, the observation of a chiral smectic phase for sugar-based mesogens is highly unusual, instead smectic A phases are almost invariably observed. The authors attribute the formation of a SmC* phase to the microphase segregation being more pronounced due to the presence of the diphenylbutadiene central group. The generality of this observation has still to be established.

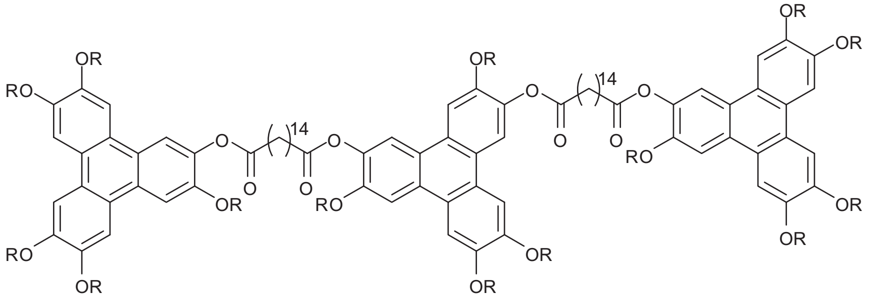
2.5 *Liquid crystal trimers containing discotic moieties*

A discotic liquid crystal trimer containing three triphenylene units attached via two flexible spacers has been reported (*110*).



24

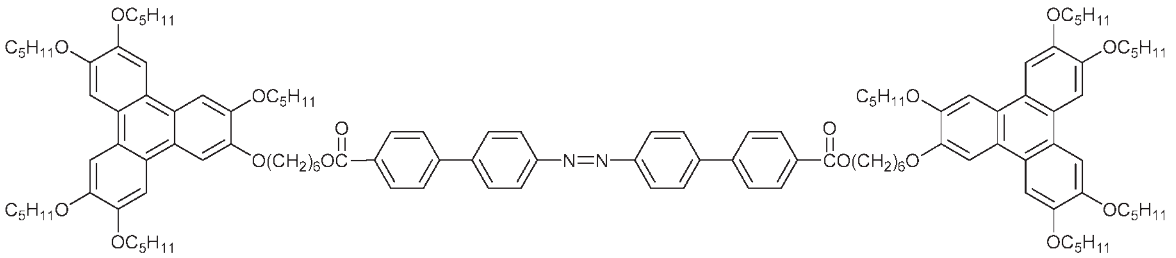
This trimer showed a hexagonal columnar phase similar in structure to that seen for the corresponding monomer, dimer and polymer. Indeed, the clearing temperatures were also very similar suggesting that the stability of the liquid crystal is governed principally by the packing of the triphenylene cores. The role of the alkyl chains is then to fill the space between the aromatic columns. Ringsdorf and co-workers (*111*) have also prepared a liquid crystal trimer containing three triphenylene units.



R = C_7H_{15}

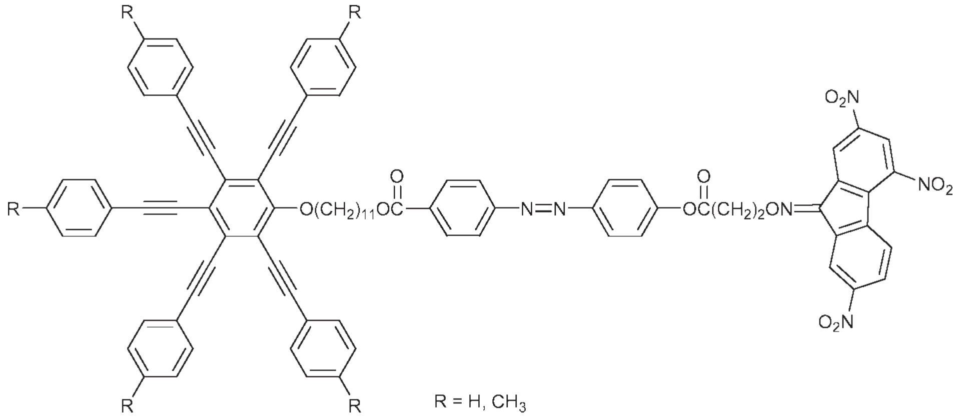
25

This trimer showed a hexagonal columnar phase which remained in the liquid crystal phase on cooling to room temperature. Liquid crystal trimers have been reported which consist of molecules containing both discotic and calamatic mesogenic units; for example, Ringsdorf and co-workers (*112*) reported the transitional behaviour of a trimer containing two triphenylene moieties attached to a central azobenzene-based unit, **26**.



26

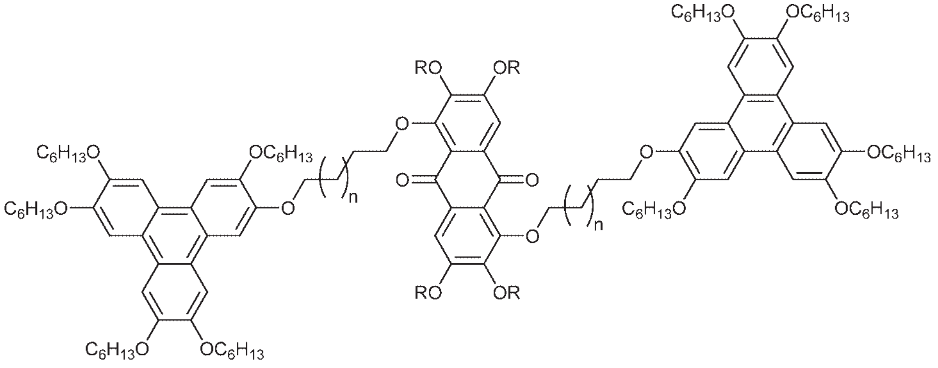
The liquid crystal phase exhibited by this trimer showed an optical texture similar to that of a smectic B phase while X-ray diffraction studies revealed a layered structure in which the triphenylene groups were regularly stacked as observed in a columnar phase. It is interesting to note that rod-disc trimers such as these are, by analogy with rod-disc dimers, potential candidates to exhibit the biaxial nematic phase (*4*). A trimeric molecule in which one of the mesogenic units is strictly an anisometric, but not inherently mesogenic, nitrofluorenone-based unit has been described by Mahlstedt *et al.* (*113*).



27

These trimers exhibited a nematic columnar phase in which the columns consist of stacks of intercalated electron-rich donor penta-alkynylbenzene units and electron-deficient acceptor nitrofluoronone-groups. The rod-like azobenzene-based groups are oriented with their long axes perpendicular to the major column axis. This phase is driven by the specific interaction between the donor-acceptor groups, which is only possible to accommodate if the length of the spacer attaching the acceptor groups to the rod-like central unit exceeds that of the chains surrounding the donor unit. Thus, replacing the methyl groups in structure **27** by pentyl chains destroys the liquid crystallinity because the donor and acceptor groups can no longer intercalate.

More recently, Kumar and co-workers (*114*) reported the transitional behaviour of two sets of trimers containing a central anthraquinone-based group and two triphenylene units.



28

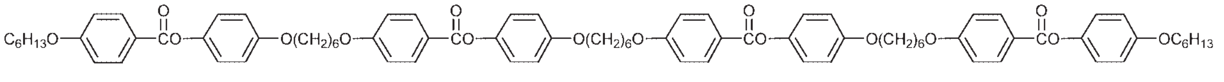
n = 7; R = n-C_6H_{13}, n-C_7H_{15}
n = 9; R = n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, n-$C_{10}H_{21}$, 3,7-dimethyloctyl

A number of these trimers exhibited a hexagonal columnar phase but as the chains attached to the anthraquinone group were increased in length this was extinguished. X-ray diffraction studies suggested that the triphenylene- and anthraquinone-based units were arranged statistically within the columns. A more extensive overview of oligomers containing molecules consisting of a combination of disk-like and rod-like moieties can be found elsewhere (*115*).

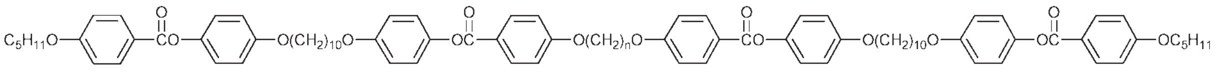
3. Liquid crystal tetramers

3.1 Background

Liquid crystal tetramers consist of molecules containing four interconnected mesogenic units linked via three flexible spacers and, as with trimers, our focus here are tetramers, which are assembled in a linear sense. Keller (*77*) reported the first linear tetramer intended to exhibit liquid crystallinity,

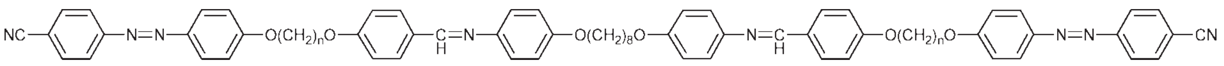

29

although it melted directly into the isotropic phase. With hindsight this is a rather surprising result given that the corresponding dimer exhibited enantiotropic smectic C and nematic phases. The first liquid crystal tetramers were reported by Griffin *et al.* (*116*), in which the central flexible spacer was varied,


30

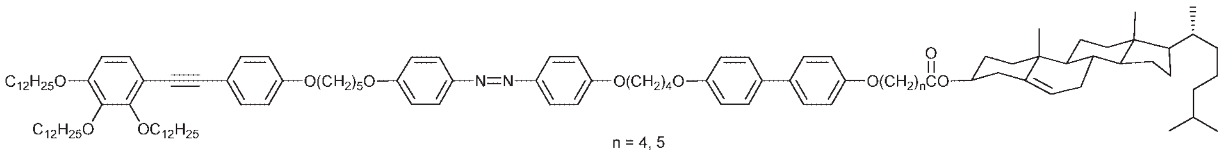
All four tetramers exhibited an enantiotropic nematic phase, with the transition temperatures closer to those of the corresponding polymers rather than to those of the analogous dimers, suggesting that liquid crystal properties evolve from the dimer through higher oligomers to the polymer. The similarity of structures **29** and **30** does make it surprising that liquid crystallinity was not observed for the former. The reversal of the ester linkages in these compounds would not normally be expected to significantly affect their transition temperatures.

The first complete homologous series of tetramers was reported by Imrie *et al.* (*117*). In this series the central spacer was held constant and the two outer spacers were varied from $n = 3$ to $n = 12$ methylene units in length.


31

This series exhibited nematic and smectic phases. All members of the series except $n = 10$ and 12 exhibited a nematic phase, with $n = 6$–12 also showing a smectic A phase, while $n = 10$ and 12 are solely smectic in nature. We will return to a discussion of the structure of the smectic phase later.

More recently, Yelamaggad *et al.* have reported two tetramers containing four differing mesogenic moieties (*118*, *119*).



32

Both tetramers exhibited a liquid crystal phase structurally thought to be similar to a rectangular columnar phase.

3.2 The odd–even effect

Imrie, Henderson and co-workers (*120–122*) have reported the transitional properties of six closely related homologous series of tetramers, which allow for the effects of varying the length and parity of the flexible spacers and of varying the molecular shape on

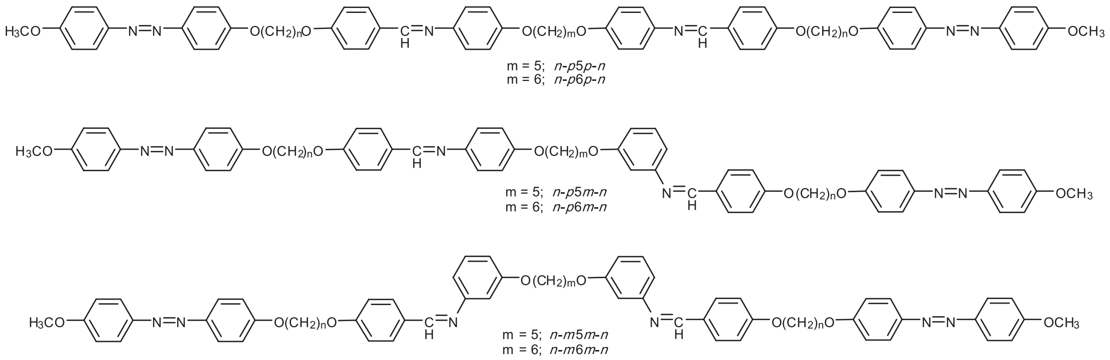


Figure 10. Structures of isomeric liquid crystal tetramers and the acronyms used to refer to them.

liquid crystal behaviour to be evaluated. Figure 10 shows the structures of these isomeric liquid crystal tetramers along with the acronyms used to refer to them, which describe the lengths of each of the spacers and molecular architecture. In each, *n* refers to the number of carbon atoms in the outer two flexible spacers, the central number, either five or six, refers to the number of methylene groups in the central spacer, while *p* and *m* refer to *para* and *meta* linkages, respectively. Thus, the most linear tetramer series would be considered to be the *n*-*p*6*p*-*n* series, consisting of an even-membered central spacer with *para* linkages between it and the two inner mesogenic units.

All members of the *n*-*p*6*p*-*n*, *n*-*p*5p-*n*, *n*-*p*6*m*-*n* and *n*-*p*5*m*-*n* series exhibit nematic behaviour. In addition, 4-*p*5*m*-4 and 5-*p*5*m*-5 show a monotropic smectic phase. In the *n*-*m*5*m*-*n* series, five members, n = 4, 6, 8, 9 and 10, exhibit smectic and nematic behaviour, while liquid crystalline behaviour is not observed for the *n*-*m*6*m*-*n* series. Figure 11 shows the nematic–isotropic transition temperatures for each series. Initially, each series exhibits a strong odd–even effect in the nematic–isotropic transition temperatures on varying the number of methylene units in the two outer flexible spacers, with the even-membered spacers exhibiting the higher values. The magnitude of the odd–even

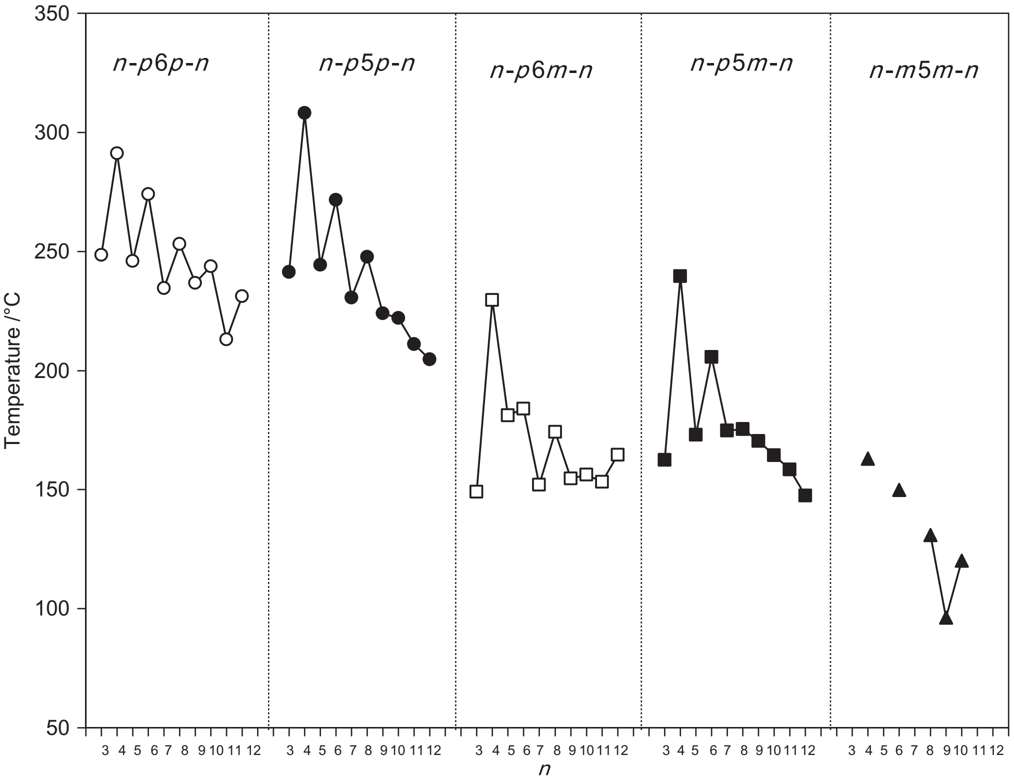


Figure 11. The nematic–isotropic transition temperatures for the tetramers shown in Figure 10.

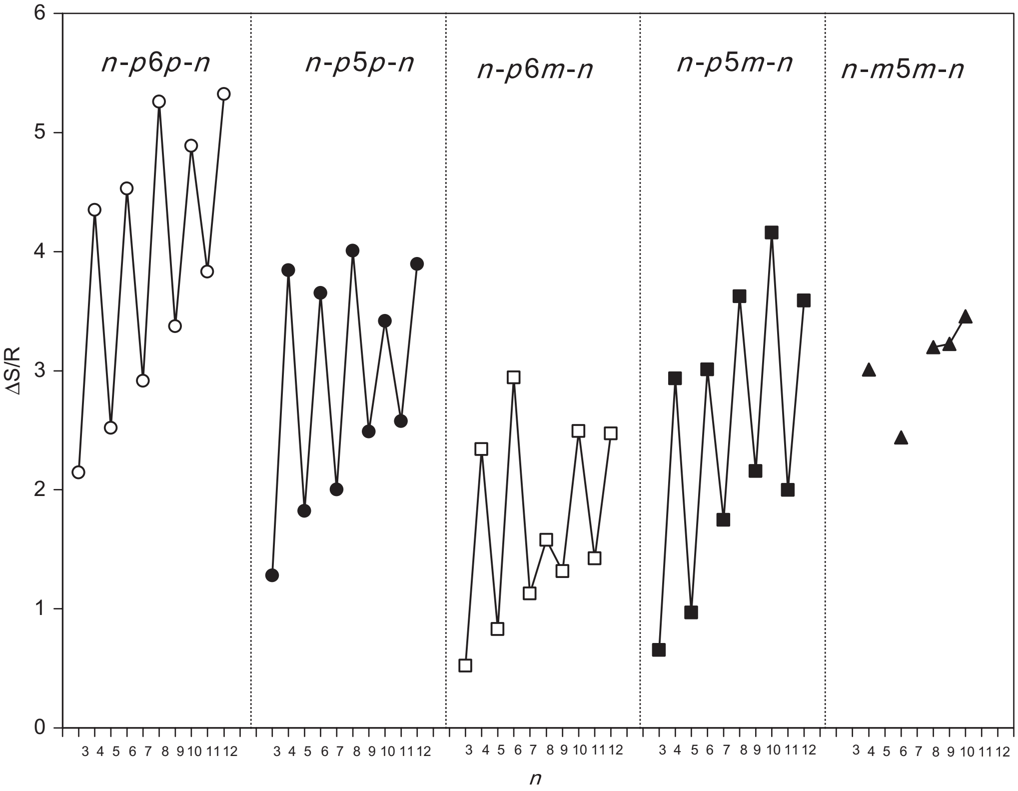


Figure 12. The nematic–isotropic entropies for the tetramers shown in Figure 10.

effect seen for the nematic–isotropic transition temperatures is attenuated on increasing *n*, with the temperatures for the even members falling more rapidly than those of the odd. The nematic–isotropic entropies also show an odd–even effect (see Figure 12). A pronounced odd–even effect is observed for each series except the *n-m*5*m-n* series, in which the values for the even members are typically 1.5–2 times larger than those of the odd members. The *n-p*6*p-n* series shows higher values than the corresponding *n-p*5p-*n* series, presumably reflecting the more linear nature of the even-membered tetramers. This trend is reversed however, for the nematic–isotropic entropies of the *n-p*5*m-n* series compared with those of the *n-p*6*m-n* series, and we will discuss this later.

The nematic–isotropic transition temperatures decrease on moving from the *n-p*(5,6)*p-n* series to the *n-p*(5,6)*m-n* series with the lowest temperatures seen for the *n-m*5*m-n* tetramers. This can be explained in terms of changes in molecular shape, with the most linear compounds having the highest transition temperatures (see Figure 13). It is rather surprising to note, however, the similarity in nematic–isotropic transition temperatures between tetramers with odd- and even-membered central spacers having the same substitution pattern. This suggests a very weak odd–even effect in the

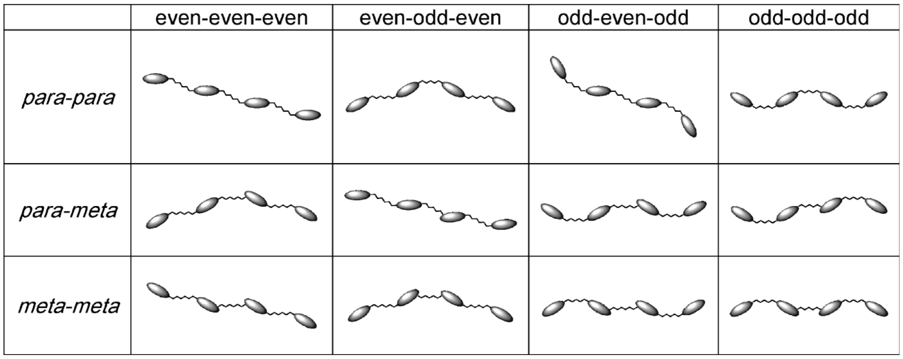


Figure 13. Schematic representations of the extended molecular shapes of the tetramers shown in Figure 10.

nematic–isotropic transition temperature on varying the parity of the central flexible spacer. This surprising result undermines the simple structural pictures often used to understand the transitional properties of oligomers and suggests that the four mesogenic units in the tetramer are not strongly correlated. The nematic–isotropic transition temperatures tend to be higher for the *n-p*5*m-n* than the *n-p*6*m-n* series suggesting that the bent odd-membered spacer tends to counteract the deviation in linearity arising from the 1,3-substitution of one of the phenyl rings. A similar effect has been seen for liquid crystal dimers (*123*).

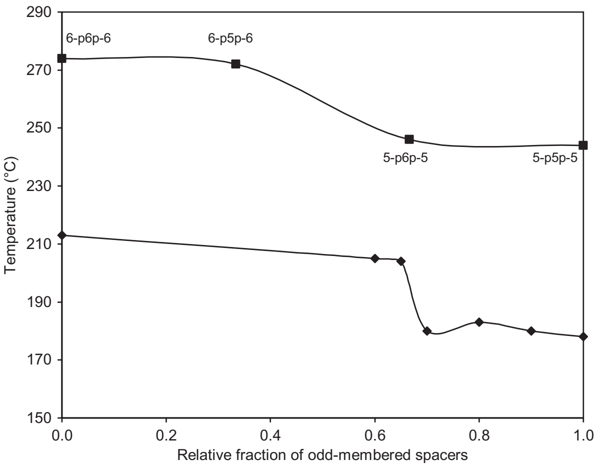
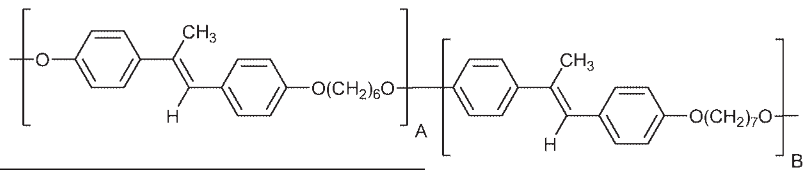


Figure 14. Dependence of clearing temperature on the relative fraction of odd-membered spacers in (◆) copolymers **34** and (■) tetramers.

3.3 Model compounds for liquid crystal copolymers

Percec *et al.* (*124*) had some time ago reported the transitional properties of a series of copolymers containing odd- and even-membered spacers differing by only one methylene unit,



33

and expressed their composition in terms of the relative fraction of odd-membered spacers, given by *B*/(*A*+*B*). The clearing temperatures of these copolymers do not show a linear dependence on the relative amount of the odd-membered spacers (see Figure 14). Instead, the clearing temperature is rather insensitive to increasing the amounts of the odd-membered spacer up to about 0.6 at which point the clearing temperature falls. Further increases in the amount of odd-membered spacers have essentially no effect on the clearing temperature. This behaviour has never been rationalised. Henderson and Imrie (*121*) used these data to see to what extent tetramers can be used as model compounds for the copolymers. Although the mesogenic units in the tetramers and copolymers are not identical, the authors assumed that the interaction strength parameters between the mesogenic units within each system will be similar while any similarity in transitional behaviour between the polymers and tetramers would serve to highlight the possible generality of the data. Four tetramers were used in the comparison; 5-*p*5*p*-5, 5-*p*6*p*-5, 6 *p*6*p*-6 and 6-*p*5*p*-6. The tetramers having three identical spacers can be considered as possible model compounds for homopolymers while those having differing spacers may act as model compounds for 2:1 copolymers (see Figure 15).

The dependence of the nematic–isotropic transition temperatures of the tetramers on the relative fraction of odd-membered spacers present is also shown in Figure 14. As seen for the polymers, the nematic–isotropic transition temperature does not show a linear dependence on the relative fraction of odd-membered spacers. Instead and as we have seen already, 5-*p*6*p*-5 and 5-*p*5*p*-5 exhibit rather similar nematic–isotropic transition temperatures as do 6-*p*6*p*-6 and 6-*p*5*p*-6, with the latter showing higher nematic–isotropic transition temperatures. The tetramers show very similar behaviour to that of the polymers. This suggests that the length and parity of the spacer having the major compositional fraction determines the transition

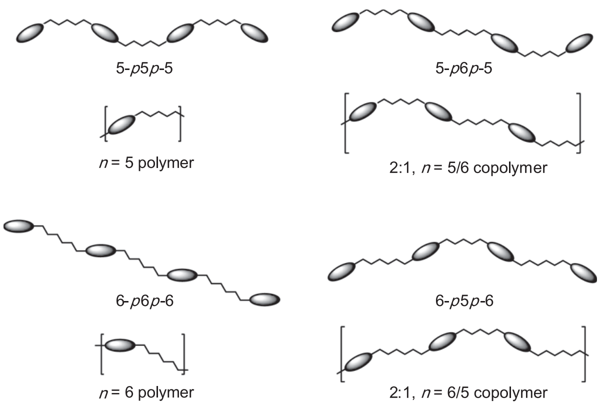


Figure 15. Schematic representations of odd- and even-membered tetramers and the polymers they resemble.

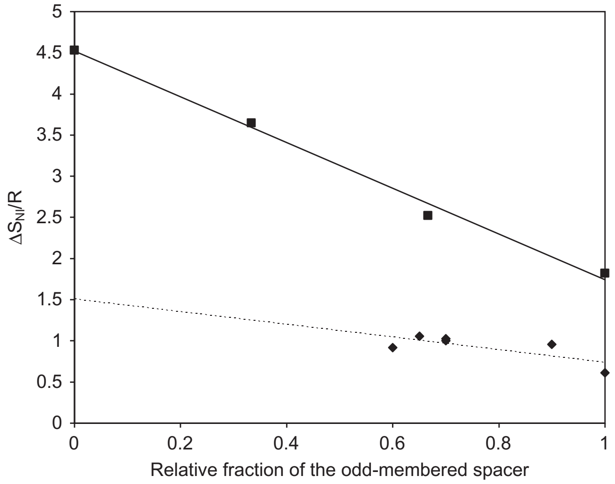


Figure 16. Dependence of the clearing entropy on the relative fraction of odd-membered spacers in the (◆) copolymers and (■) tetramers.

temperatures and that the orientations of the four mesogenic units are not strongly correlated along the length of the tetramer.

The dependence of the nematic–isotropic entropies for the tetramers on the relative fraction of odd-membered spacers is shown in Figure 16. We now have an apparent linear dependence of the nematic–isotropic entropy on the relative fraction of the odd-membered spacer. The corresponding data for the polymers are also shown in Figure 16, expressed as the entropy change per repeat unit. The copolymers also appear to show a linear dependence of clearing entropy on composition. The molecular significance of the dependence of the clearing entropy on spacer lengths for both the tetramer and polymer is unclear and a wider range of the *n-pxp-n* family of tetramers should now be investigated to test the generality of these observations.

3.4 Smectic behaviour

We have seen that two members of the *n-p5m-n* series exhibited smectic behaviour but the strongly monotropic nature of these phases precluded their investigation using X-ray diffraction. It was possible, however, to study the smectic phase seen for two of the *n-m5m-n* series using X-ray diffraction and optical microscopy. For example, for 4-*m*5*m*-4 an optical texture consisting of coexisting regions of focal-conic fan and schlieren texture was observed. The schlieren texture contained both types of point singularity suggesting an alternating smectic C phase. The layer spacing measured using X-ray diffraction was 33 Å, which is approximately half the estimated molecular length. Figure 17 shows a sketch of the proposed local molecular arrangement within the smectic phase exhibited by 4-*m*5*m*-4. The mesogenic units are tilted with respect to the layer normals and this local director is indicated on Figure 17, but the tilt direction alternates on passing from one layer to another such that the global tilt angle is zero. Presumably, the driving force for the formation of this phase is the ability of these highly bent molecules to pack efficiently into the structure. The smectic phase seen for 6-*m*5*m*-6 is quite different. The optical texture consists of coexisting regions of truncated focal conic fans and homeotropic textures. The X-ray diffraction pattern is very similar to that of the B_3 phase seen for bent-core mesogens (*125*), again implying that shape is playing a key role in phase formation.

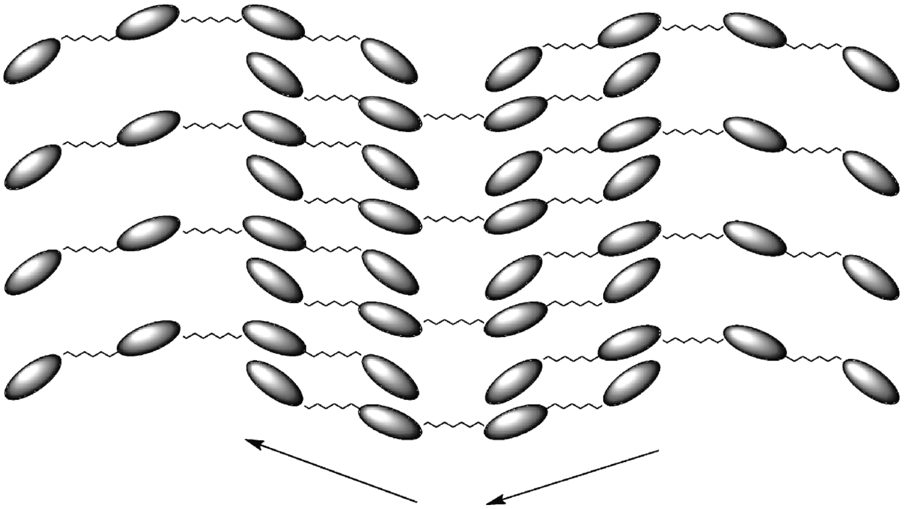


Figure 17. Sketch of the local molecular organisation within the smectic phase exhibited by 4-*m*5*m*-4.

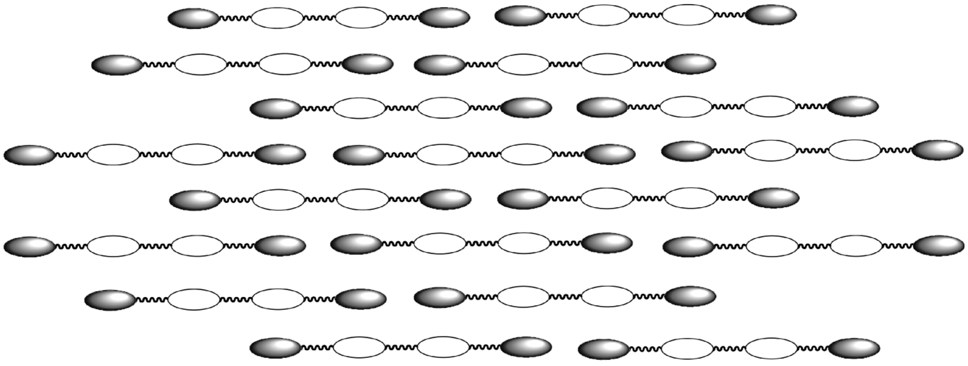
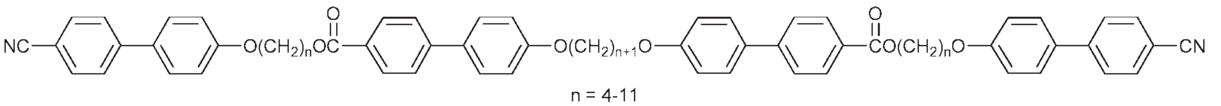


Figure 18. The intercalated smectic A phase exhibited by tetramers **31**.

If we return to the tetramers, **31**, described earlier (*117*), seven members exhibited smectic behaviour. For the tetramer containing nonyl outer spacers and a octyl inner space, the measured smectic periodicity was 19.5 Å compared with an estimated molecular length of 71 Å. The optical texture of the phase consisted of coexisting areas of focal conic fans and homeotropic regions. These data were rationalised in terms of an intercalated smectic A phase (see Figure 18). As with the non-symmetric trimers, the specific interaction between the unlike mesogenic groups is assumed to drive the formation of the phase.

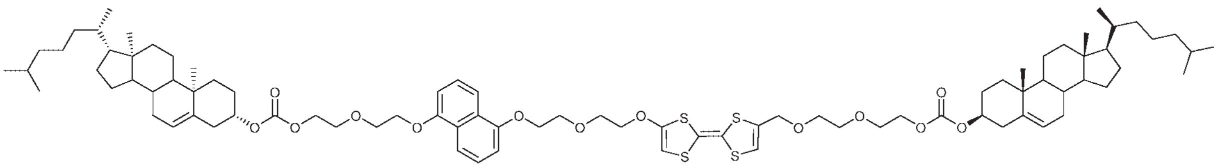
Itahara and Tamura (*126*) have reported the tetramer analogues of trimers **9**.



34

The members with n = 6–11 showed a smectic phase assigned as a smectic A phase except for that seen for n = 9, which was thought to be a smectic C phase. The authors do not report the structures of these smectic phases and hence, it would be unwise to speculate on the driving force responsible for the observation of smectic behaviour.

Most recently, Zhao *et al.* (*127*) reported the behaviour of a tetrameric molecule containing cholesteryl-based units, a tetrathiafuvalene (TTF) group and a 1,5-dioxynaphthalene (DNP) moiety.

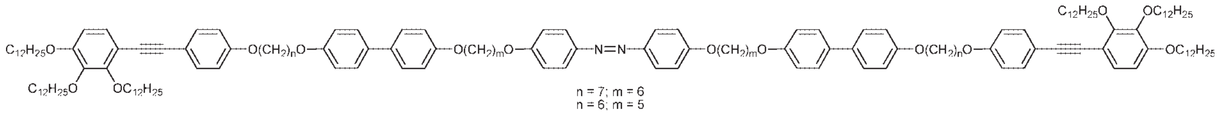


35

This tetramer showed a monolayer smectic A phase. It was suggested that the formation of this was driven by the packing of the cholesteryl-based groups and the π-π interactions involving the aromatic TTF and DNP groups.

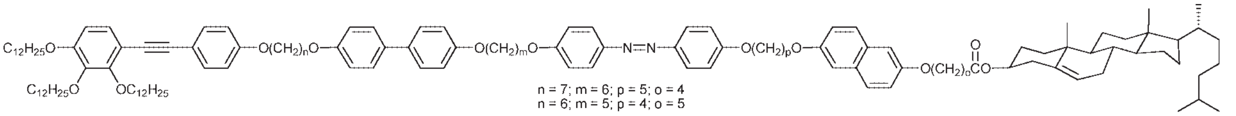
4. Liquid crystal pentamers

The first examples of a monodisperse liquid crystal pentamer was reported recently by Yelamaggad *et al.* (*128*), and consisted of five mesogenic units linked through four flexible spacers. The first examples were symmetrical about the central group.



36

Both pentamers exhibit an enantiotropic mesophase which, although differing slightly in their optical textures, were miscible. The X-ray diffraction patterns for the two phases were indistinguishable, consisting of two sharp reflections in the small angle region and a broad wide angle peak. The layer spacing, *d*, was considerably smaller than the estimated molecular length, *l*, with the ratio $d/l \approx 0.7$. The authors accounted for these observations by proposing an intercalated smectic phase driven by a combination of the specific electrostatic interaction between the unlike mesogenic groups and from issues of space filling. The second two materials contained five differing mesogenic groups.

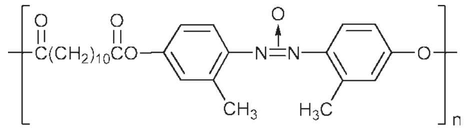


37

Both materials displayed an enantiotropic mesophase, which exhibited a mosaic texture that sheared to give a pseudoisotropic texture. The X-ray diffraction pattern of the mesophase consisted of two sharp reflections in the low angle region and a diffuse peak in the wide angle region. The layer periodicity was approximately equal to the molecular length indicating a monolayer arrangement. The authors suggested an anti-parallel packing of the molecules within the layers such that the cholesteryl-moieties were located close to the alkyl chains surrounding the tolane group in order to maximise packing efficiency.

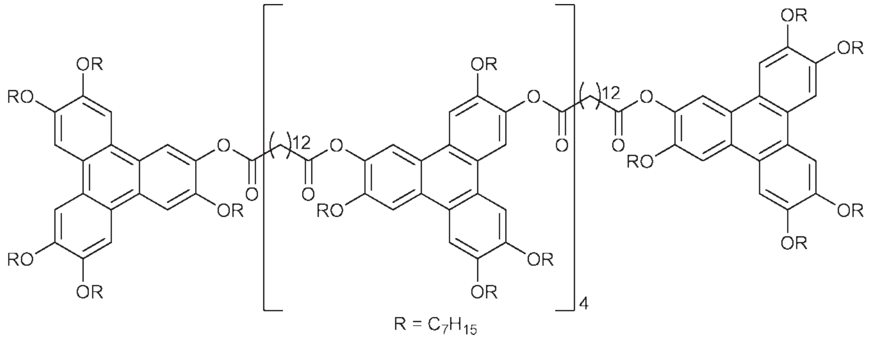
5. Liquid Crystal Hexamers

Blumstein and Stickles (*78*) studied a range of oligomeric fractions related to the polymer, **38**.



38

The lowest molar mass fraction to exhibit liquid crystallinity corresponded to approximately six repeat units per chain, i.e. the hexamer. This was not, however, a monodisperse sample and it is not a general result that the appearance of liquid crystal behaviour is associated with the development of a polymeric structure. To our knowledge a monodisperse calamitic hexamer has not yet been reported but a linear hexamer containing six triphenylene units has (*111*).



39

This hexamer showed a columnar phase.

6. What next for oligomers?

This review has sought to describe our present understanding of structure property relationships in liquid crystal oligomers, but has perhaps only succeeded in revealing how little we know about this fascinating class of materials. Fundamentally, we have only just begun to investigate the behaviour of oligomers containing incompatible mesogenic groups. By analogy with block copolymers, studies of such systems would be expected to lead to the discovery of rich new smectic polymorphism. Already the study of tetrameric systems is beginning to inform our understanding of liquid crystal polymers, but there is still a key difference between the smectic behaviour of oligomers and polymers which needs to be resolved. Technologically, the oligomer molecular architecture allows us to construct truly multifunctional materials, which unlike mixtures, do not have problems with phase separation. Areas rich for development include rod-disc oligomers as potential candidates to exhibit the biaxial nematic phase and new oligomeric materials, which by analogy to dimers may exhibit very wide temperature range blue phases and high flexoelectric coefficients (*129*). To exploit this potential and design materials in a rational manner, it is not sufficient simply to attach units together having the desired range of properties, but we must also understand how these units self-organise in liquid crystal phases. This brings us back to the importance of establishing the empirical rules relating structure to properties in these systems. Theory will also have an important role to play in understanding the transitional behaviour of these higher oligomers as it did for dimers (*1*), and such studies must go hand in hand with the experimental investigations. It is clear, therefore, that the field of liquid crystal oligomers is an extremely buoyant area and one that will remain highly active for the foreseeable future!

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