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Liquid Crystals

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Liquid crystal tetramers: influence of molecular shape on liquid crystal behaviour

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The synthesis and characterization of two homologous series of tetramers in which four mesogenic units are linked via three alkyl spacers are reported. Both series contain a hexamethylene central spacer while the length of the two outer spacers, *n*, is varied from three to 12 methylene units. The two series differ only in the substitution pattern around the inner two mesogenic units. The series in which one mesogenic unit is attached to the central spacer in the 4-position while the other is connected at the 3-position is referred to as the *n*-*p*6*m*-*n* series, while in the *n*-*m*6*m*-*n* series both inner units are attached in the 3-position. All the members of the *n*-*p*6*m*-*n* series exhibited a nematic phase while no liquid crystallinity was observed for the *n*-*m*6*m*-*n* series. The thermal behaviour of this series is compared with that of the *n*-*p*6*p*-*n* series and also with that of the corresponding series containing a pentamethylene central spacer. The trends observed are interpreted in terms of the average molecular shapes of these tetramers.

1. Introduction

Liquid crystal oligomers consist of semi-rigid mesogenic units linked via flexible spacers [1–3]. The simplest class of oligomers are liquid crystal dimers in which two mesogenic groups are connected using a single flexible spacer and these have attracted considerable research interest. Initially this interest arose from the similarity in behaviour between dimers and semi-flexible main chain liquid crystal polymers; in particular, the transition temperatures and associated entropy changes exhibited by dimers are strongly dependent on the length and parity of the flexible spacer, in a manner strongly reminiscent of that seen for the polymers. Thus, dimers were recognized to have the potential to serve as model compounds for the more complex polymeric systems [4]. It soon became apparent, however, that the dimers exhibited quite different behaviour from conventional low molar mass liquid crystals consisting of molecules containing a single semi-rigid core attached to which are normally one or two alkyl chains, and hence dimers were seen to be of significant fundamental interest in their own right [1–3]. Of particular interest has been the discovery of a number of new smectic modifications in dimeric materials [1–3].

A great many liquid crystal dimers have now been reported in the literature and these can be divided into two groups: symmetric dimers in which the two mesogenic units are identical (see, for recent examples, [5, 6]); and non-symmetric dimers consisting of molecules containing two different mesogenic units (see, for recent examples, [7–11]). Recent studies on dimers have focussed on, for example, changing the chemical nature of the spacer [12–15] and the type of link between the spacer and mesogenic groups [6, 16–19].

We have noted already that the transitional properties of dimers in many respects are strongly reminiscent of those of semi-flexible main chain polymers. There are, however, a number of very significant differences between the dimers and polymers and perhaps most notably their relative tendencies to exhibit smectic phases. Specifically, the very general observation is that the tendency of a symmetric dimer to exhibit smectic behaviour decreases with increasing spacer length while quite the opposite is true for polymers [20]. This begged the question as to how the properties of the dimers evolve into those of the polymers and to address this issue a relatively small number of linear liquid crystal trimers have been reported [3, 6, 21–36]. These consist of molecules containing three mesogenic groups connected via two flexible spacers. The transitional behaviour of the trimers, like that of the dimers, strongly resembles that of the polymers although it is

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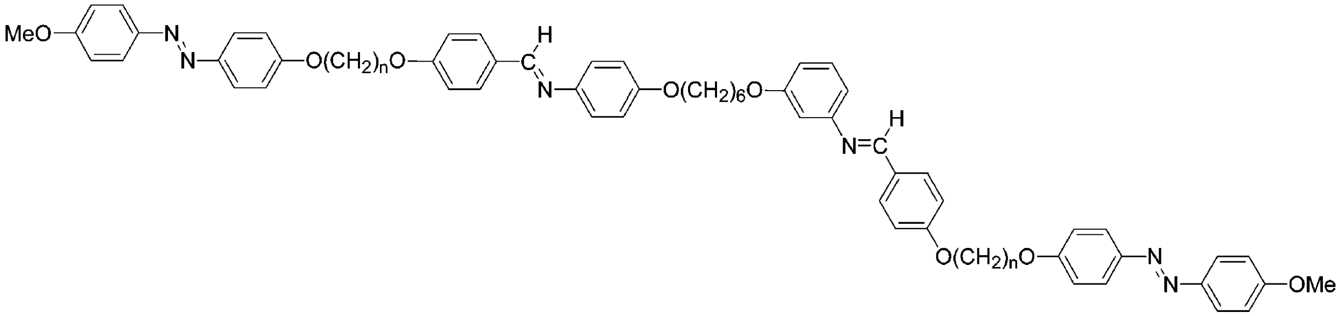
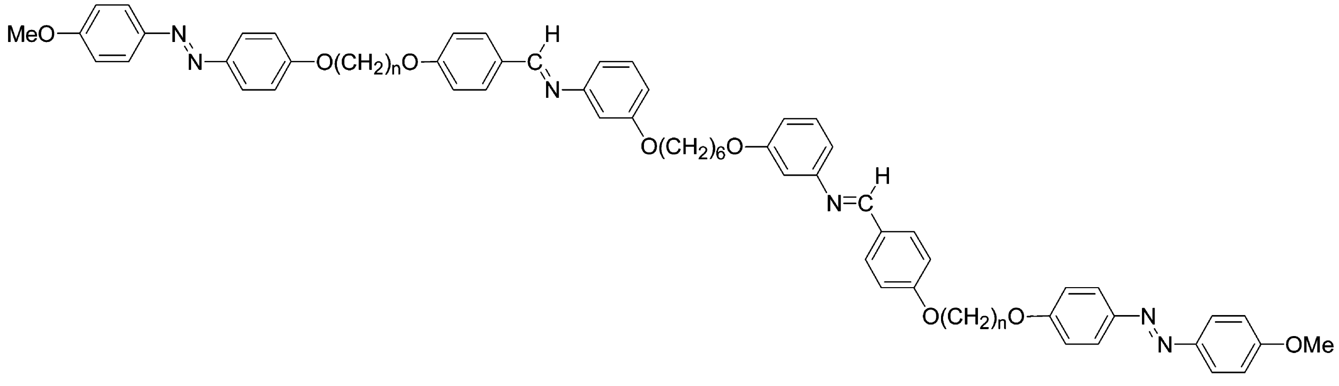
not yet clear how the smectic tendencies of the trimers depend on molecular structure. It is interesting to note, however, that like the dimers, trimers exhibit new intercalated smectic phases [35].

Most recently, we have extended this approach and reported the first complete homologous series of liquid crystal tetramers consisting of molecules containing four mesogenic units interconnected via three flexible spacers [37–39]. A small number of tetramers have also been reported by other workers [40–42], and a particularly attractive feature of this molecular architecture is the ability to combine four units of differing functionality giving a truly multifunctional material. A feature of the tetramers reported to date is that they tend to exhibit rather high transition temperatures, making their detailed physical study difficult as well as greatly reducing their application potential. One approach widely adopted to reduce the transition temperatures of semi-flexible main chain liquid crystal polymers involves the incorporation into the main chain of molecular kinks, which serve to inhibit efficient chain packing. To determine the value of this approach in the design of liquid crystal tetramers, we reported the transitional properties of three tetrameric series containing an odd-membered pentamethylene central spacer and non-linear rigid units [38].

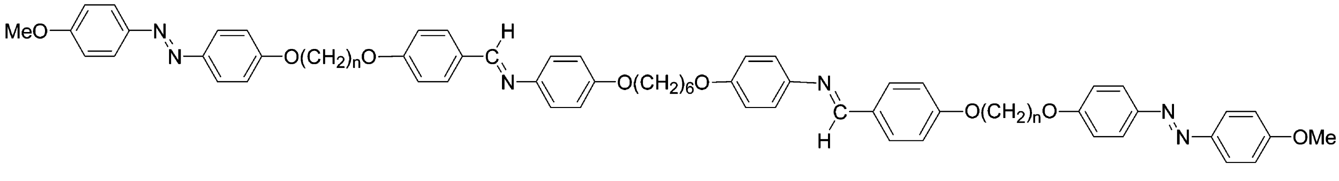
To extend this study, here we describe the corresponding materials containing an even-membered hexamethylene central spacer. These two homologous tetramer series contain either one non-linear semi-rigid unit, and are referred to using the acronym *n-p*6*m-n* (structure 1), or two non-linear units, described using the acronym *n-m*6*m-n* (structure 2). In both acronyms *n* refers to the number of methylene units in the outer flexible spacers. To establish the effects of introducing these non-linear segments, we compare the properties of the *n-p*6*m-n* and *n-m*6*m-n* series with those of the *n-p*6*p-n* series containing four linear units [39] (structure 3).



Structure 1.



Structure 2.

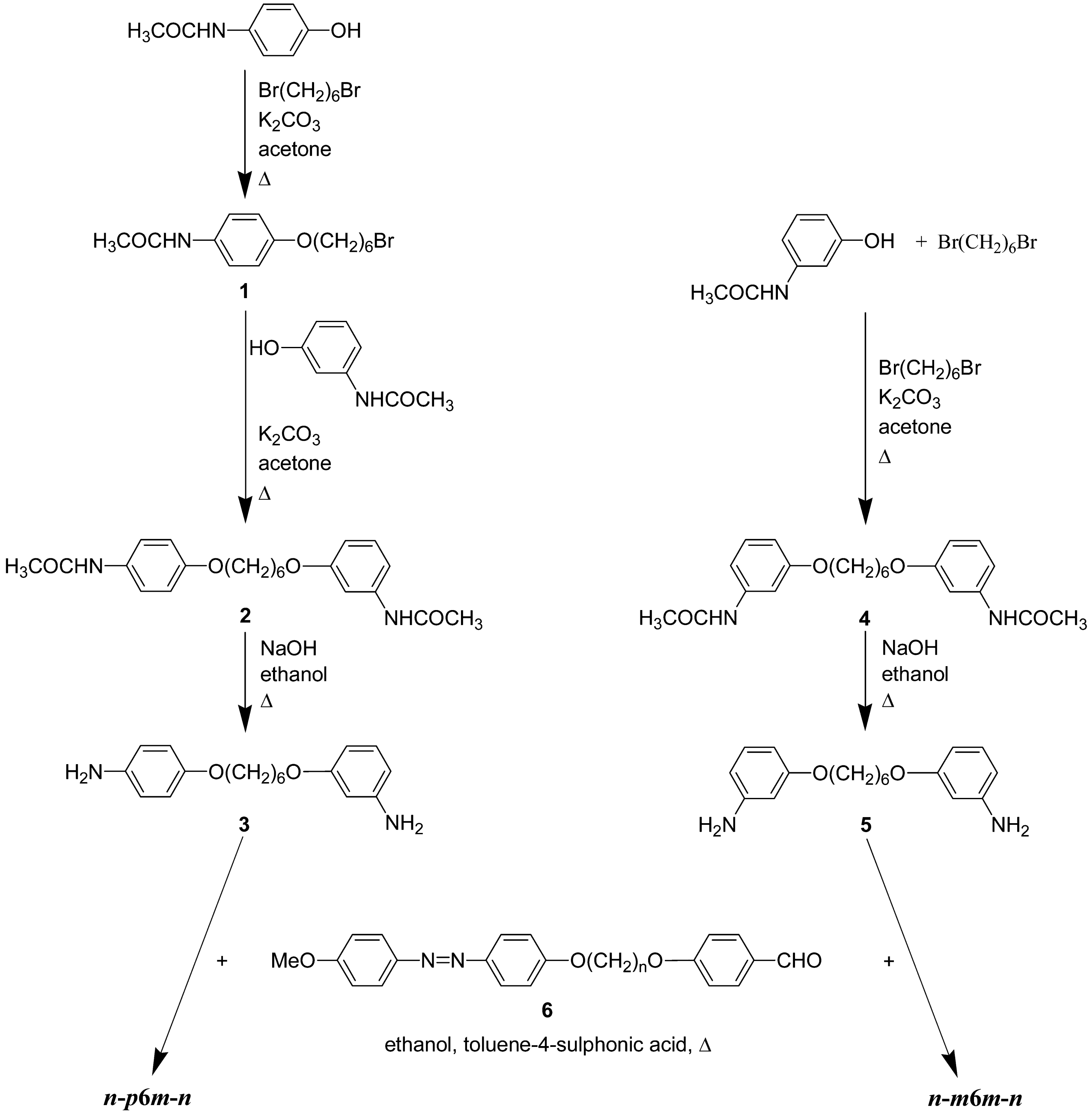


Structure 3.

The choice of a central flexible spacer containing six methylene units rather than four was made in the expectation of obtaining lower transition temperatures; the lengths of the two outer spacers are identical, as dictated by the synthetic route used, and varied from three to twelve methylene units. We also compare the transitional properties of these three tetramer series containing an even length central spacer with those of the corresponding materials containing five methylene units in the central spacer, *i.e.*, the *n-p*5*p-n*, *n-p*5*m-n* and *n-m*5*m-n* series [38].

2. Experimental

The two new tetrameric series were prepared using the synthetic route shown in scheme 1 which is identical to that used to prepare the *n-p*5*m-n* and *n-m*5*m-n* series.



Scheme 1. Synthesis of the liquid crystal tetramers.

2.1. *Synthesis of 1-(4-aminophenyloxy)-6-(3-aminophenyloxy)hexane, 3*

The synthesis of compound **3** was analogous to that described for 1-(4-aminophenyloxy)-5-(3-aminophenyloxy)pentane [38], thus only characterization data for **3** and its intermediates are provided.

2.1.1. 1-(4-Acetamidophenyloxy)-6-bromohexane, 1. Yield 68%, m.p. 119–121°C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.3 (d, 2H, Ar–H, J=8.75 Hz), 6.8 (d, 2H, Ar–H, J=9.0 Hz), 3.9 (t, 2H, $OC\underline{H}_2CH_2$, J=6.5 Hz), 3.4 (t, 2H, $BrC\underline{H}_2CH_2$, J=6.75 Hz), 2.1 (s, 3H, $C\underline{H}_3CO$), 1.9 (qn, 2H, $CH_2C\underline{H}_2CH_2$, J=6.75 Hz), 1.8 (qn, 2H, $CH_2C\underline{H}_2CH_2$, J=7.0 Hz), 1.5 (m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$). IR (KBr) ν (cm^{-1}): 3298, 3258, 1657 (CONH); 830 (*p*-substituted aromatic).

2.1.2. 1-(4-Acetamidophenyloxy)-6-(3-acetamidophenyloxy) hexane, 2. Yield, 50%, m.p. 144–145°C. IR (KBr) ν (cm^{-1}): 3308, 1654 (CONH); 1595, 1511, (Ar–H); 830 (*p*-substituted aromatic), 768 (*m*-substituted aromatic). Compound **2** was insoluble in common organic solvents so no ^{1}H NMR spectrum was obtained.

2.1.3. 1-(4-Aminophenyloxy)-6-(3-aminophenyloxy)hexane, 3. Yield 68%, m.p. 101–102°C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.0 (t, 1H, Ar–H *ortho* to NH_2 and OCH_2, J=7.5 Hz), 6.7–6.6 (dd, 4H, Ar–H on *para* ring, J=8.5 Hz), 6.3–6.2 (m, 3H, Ar–H on *meta* ring) 3.9 (dt, 4H, $OC\underline{H}_2CH_2$,), 3.5 (s, broad, 4H, $ArN\underline{H}_2$), 1.8 (m, 4H, $CH_2C\underline{H}_2CH_2CH_2C\underline{H}_2CH_2$), 1.6 (m, 4H, $CH_2CH_2C\underline{H}_2C\underline{H}_2CH_2CH_2$,). IR (KBr) ν (cm^{-1}): 3458, 3365, (*ortho* and *para* aromatic NH_2), 823 (*p*-substituted aromatic), 757 (*m*-substituted aromatic).

2.2. *Synthesis of 1,6-bis(3-aminophenyl)hexane, 5*

The synthesis of compound **5** was analogous to that described for 1,5-bis(3-aminophenyl)pentane [38], thus only characterization data for **5** and its intermediate, **4**, are provided.

2.2.1. 1,6-Bis(3-acetamidophenyl)hexane, 4. Yield, 66%, m.p. 201–202°C. IR (KBr): ν (cm^{-1}): 3269 (CONH), 1662 (CO), 790 (*m*-substituted aromatic). Compound **4** was insoluble in common organic solvents, so no ^{1}H NMR spectrum was obtained. Elemental analysis: calc. C 68.73, H 7.34, N 7.29; found. C 68.08, H 7.25, N 6.93%.

2.2.2. 1,6-Bis(3-aminophenyl)hexane, 5. Yield, 67%, m.p. 102–103°C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.0 (t, 2H, Ar–H *ortho* to NH_2 and OCH_2, J=7.75 Hz), 6.3–6.2 (m, 6H, Ar–H), 3.9 (t, 4H, $OC\underline{H}_2CH_2$, J=6.5), 3.4 (s, 4H, $ArN\underline{H}_2$), 1.8 (m, 4H, $CH_2C\underline{H}_2CH_2CH_2C\underline{H}_2CH_2$), 1.6 (m, 4H, $CH_2CH_2C\underline{H}_2C\underline{H}_2CH_2CH_2$,). IR (KBr) ν (cm^{-1}): 3269, 3216 (aromatic NH_2), 2942, 2903, 2868 (CH_2), 791 (*m*-substituted aromatic).

2.3. *Synthesis of the tetramer series*

The synthesis of the α-(4-methoxyazobenzene-4′-oxy)-ω-(4-formylphenyloxy)alkanes, **6**, is described in detail elsewhere [38]. The syntheses of the *n*-*p*6*m*-*n* and *n*-*m*6*m*-*n* series were analogous to those of the corresponding materials containing a pentamethylene central spacer [38]. The tetramers were recrystallized from toluene and the products obtained in yields of 50–80%. The members of both series were insufficiently soluble in any appropriate solvent to allow for structural characterization using ^{1}H NMR spectroscopy. Their IR spectra, however, were consistent with the proposed structures. Specifically the bands associated with the stretch and bend deformations of the N–H bond in the amines (**3** and **5**) and that associated with the carbonyl band in the aldehydes (**6**) are absent in the spectra of the products. In addition elemental analysis data are consistent with the proposed structures and representative data are provided. 3-*p*6*m*-3: calc. C 73.54, H 6.17, N 8.04; found C 73.78, H 6.20, N 7.85%; 3-*m*6*m*-3: calc. C 73.54, H 6.17, N 8.04; found C 73.59, H 6.10, N 7.70%.

3. Results and discussion

3.1. *n-p6m-n Series*

The transition temperatures and associated entropy changes for the *n*-*p*6*m*-*n* series are given in table 1. All the members of this series exhibit an enantiotropic nematic mesophase except for the propyl homologue, 3-*p*6*m*-3, which is a monotropic nematogen. The nematic phase was assigned on the basis of the observation of characteristic schlieren optical textures containing both 2- and 4-point disclinations and which flashed when subjected to mechanical stress.

The dependence of the transition temperatures on the number of methylene units in the outer flexible spacers for the *n*-*p*6*m*-*n* series is shown in figure 1. The melting points show no regular dependence on the length of the outer spacers. This is partly due to the lower than expected melting point of 6-*p*6*m*-6. By contrast, the nematic–isotropic transition temperatures do show an odd–even effect which is attenuated on increasing *n* and in which the even members exhibit the higher values. The decrease in T_{NI} with increasing *n* is more apparent for the members with an even value of *n*, although T_{NI} appears to pass through a minimum around 10-*p*6*m*-10. The decrease in the clearing temperature when *n* is odd is less regular with increasing *n*; these temperatures

Table 1. Transition temperatures and associated entropy changes for the *n-p*6*m-n* series. Monotropic transitions are given in brackets.

n	T_{CrN}/°C	T_{NI}/°C	$\Delta S_{\mathrm{CrN}}/R$	$\Delta S_{\mathrm{NI}}/R$
3	182	(149)	18.0	(0.52)
4	212	229	30.9	2.34
5	165	181	13.5	0.83
6	146	184	14.1	2.94
7	125	152	18.8	1.13
8	157	174	19.7	1.58
9	127	154	10.9	1.32
10	145	156	23.7	2.49
11	143	153	20.7	1.42
12	143	164	26.7	2.47

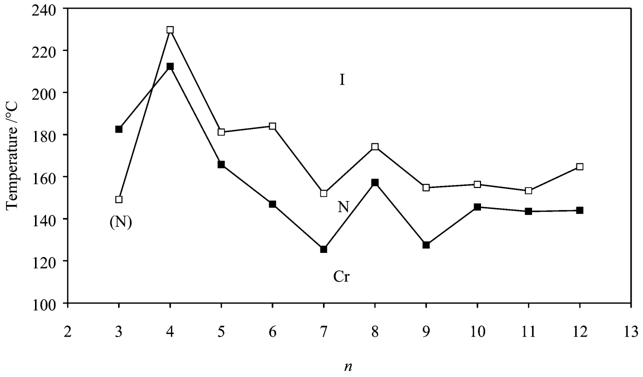


Figure 1. Dependence of transition temperature on the number of methylene units, *n*, in the outer flexible spacer for the *n-p*6*m-n* series. (■) Cr–N, (□) N–I.

appear to pass through a maximum at 5-*p*6*m*-5, and a weak minimum at 7-*p*6*m*-7.

The dependence of the nematic–isotropic entropy change, $\Delta S_{\mathrm{NI}}/R$, on *n* is shown in figure 2. An odd–even effect is observed which attenuates quickly with increasing *n*, with the entropy changes for n=8, 10 and 12 being lower than those seen for n=2 and 4. This rather surprising result may be attributed, at least in part, to overlapping peaks in the DSC traces resulting in an underestimation of the nematic–isotropic enthalpy changes for the higher homologues. For the odd members $\Delta S_{\mathrm{NI}}/R$ increases almost linearly with increasing *n*, which is expected behaviour for a homologous series.

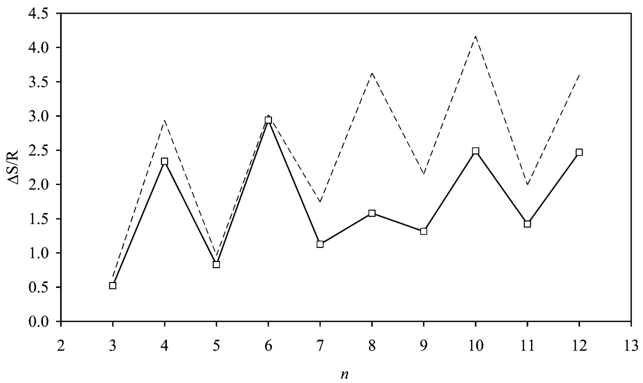


Figure 2. Dependence of the nematic–isotropic entropy change, $\Delta S_{\mathrm{NI}}/R$, on *n* for the *n-p*6*m-n* series. Also shown are the values of $\Delta S_{\mathrm{NI}}/R$ for the *n-p*6*p-n* series (dotted line).

3.2. *n-m6m-n* Series

The melting points and associated entropy changes for the *n-m*6*m-n* series are listed in table 2. Liquid crystalline behaviour was not observed for any member of this series. On initial heating, complex melting and crystallisation behaviour was exhibited by several of the homologues but on the subsequent reheats just a single melting transition was observed. Figure 3 shows the dependence of the melting point on the length of the outer spacers for this series, and an odd–even effect is evident in which the even members exhibit the higher values. This alternation attenuates quickly with increasing *n* and the melting points of the octyl and decyl homologues are somewhat lower than expected.

Table 2. Melting points and associated entropy changes for the *n-m*6*m-n* series.

n	T_{CrI}/°C	$\Delta S_{\mathrm{CrI}}/R$
3	164	26.9
4	199	30.5
5	163	28.4
6	173	32.3
7	152	26.7
8	151	28.8
9	148	37.4
10	149	24.3
11	136	31.8
12	143	39.1

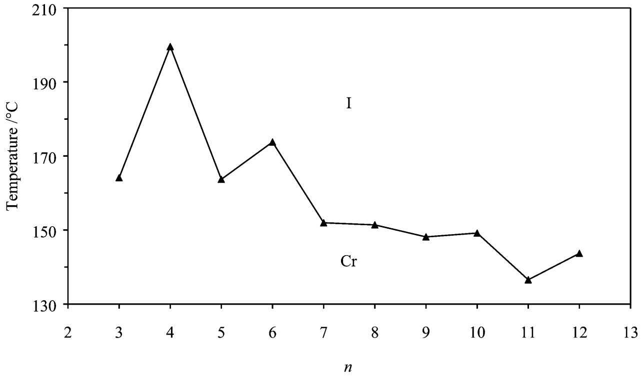


Figure 3. Dependence of the melting point on the number of methylene units, *n*, in the outer flexible spacer for the *n-m*6*m-n* series.

3.3. *n-p6p-n Series*

The thermal behaviour of the *n-p*6*p-n* series has been described in detail elsewhere [39]. All the members of the series exhibited an enantiotropic nematic phase. Pronounced alternations were observed in both the melting and clearing temperatures as the outer spacer lengths were increased, in which the even spacers exhibited the higher values. A strong odd–even effect was also observed for the nematic–isotropic entropy change with increasing *n*, in which the values for the even members were typically 1.5–2 times larger than those of the odd members, see figure 2.

3.4. *Comparison of the n-p6p-n, n-p6m-n and n-m6m-n series*

The dependence of the melting points on the number of methylene units, *n*, in the outer flexible alkyl spacers is shown for all three tetramer series containing a hexamthylene central spacer in figure 4. As we have noted already the melting points of the *n-p*6*p-n* series exhibit a pronounced alternation as *n* is increased, which does not attenuate on moving through the series. The behaviour may be interpreted in two ways. It may indicate that the change in the conformational statistical weights of the spacer on melting into a nematic phase is small for an even membered spacer but large for an odd membered spacer. Alternatively, this behaviour may reflect that the all-even-membered tetramers, which can adopt more elongated conformations, pack more efficiently into a crystal lattice than their odd membered counterparts which adopt, on average, bent molecular shapes. This difference in molecular shape between even and odd members in the *n-p*6*p-n* series is shown schematically in figure 5 (*a*).

By comparison, the melting points of the *n-p*6*m-n* and *n-m*6*m-n* series depend in a less regular manner on *n*. This suggests that the average molecular shape is now

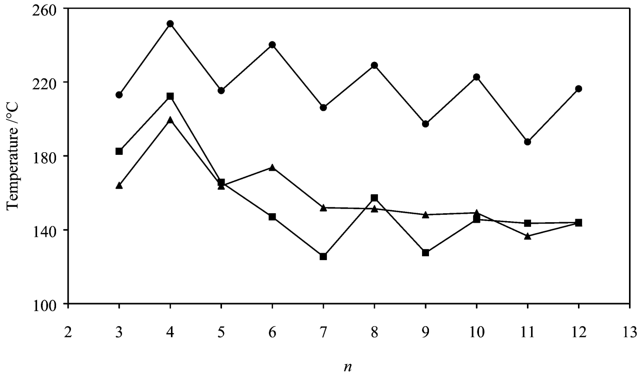


Figure 4. Dependence of the melting point on *n* for the *n-p*6*p-n* (●), *n-p*6*m-n* (■) and *n-m*6*m-n* (▲) series.

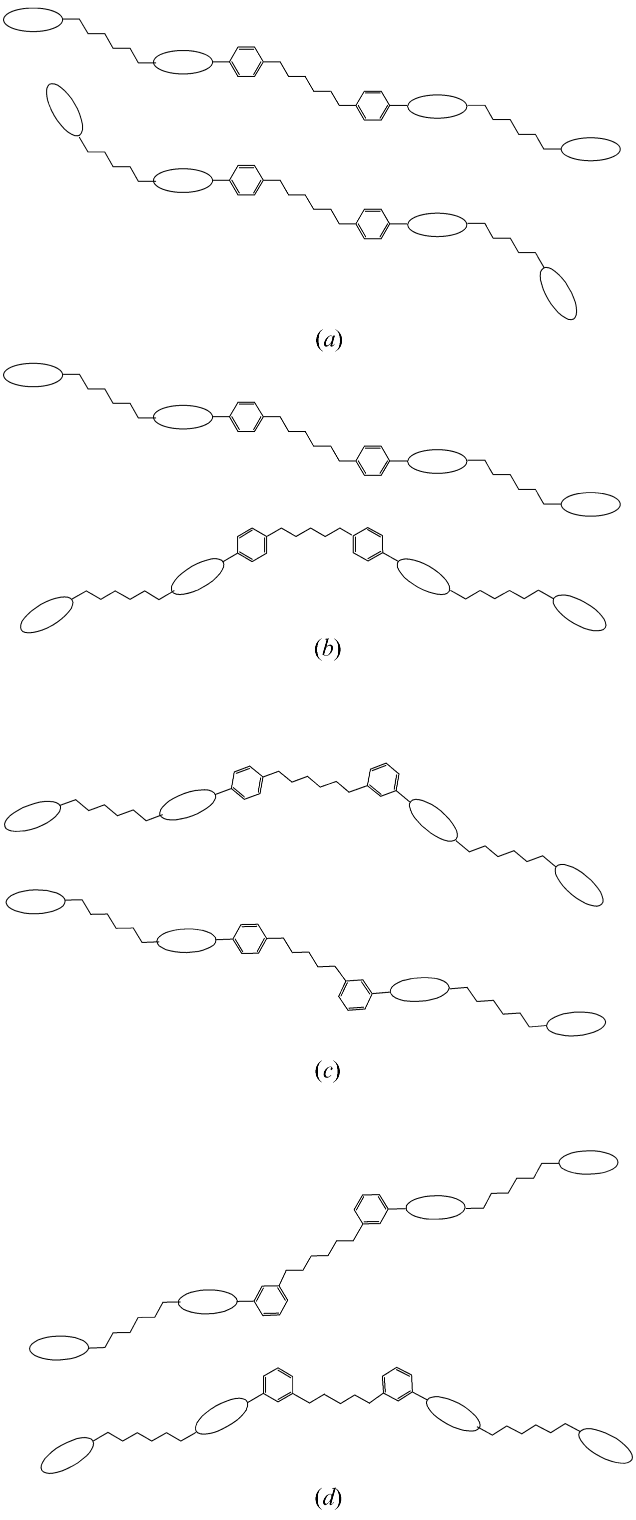


Figure 5. Schematic representations of the molecular shapes of (*a*) 6-*p*6*p*-6 and 5-*p*6*p*-5; (*b*) 6-*p*6*p*-6 and 6-*p*5*p*-6; (*c*) 6-*p*6*m*-6 and 6-*p*5*m*-6; (*d*) 6-*m*6*m*-6 and 6-*m*5*m*-6; the ellipses represent the mesogenic groups and the three flexible spacers are in the all-*trans* conformation.

less dependent on the length and parity of the outer flexible spacers and thus, *n* is less critical in determining the efficiency of packing in the crystal lattice. This view is supported by the trends in melting points on changing the substitution pattern of the two inner mesogenic groups. Thus, for all values of *n*, *n-p*6*p-n*, (*i.e.* the most linear molecular structure) shows the highest melting point while the relative ordering of the melting points for the other two series depends on *n*, see figure 4. This indicates that for the more bent *n-p*6*m-n* and *n-m*6*m-n* series, the average shape and hence, the ability of the molecules to pack efficiently, is not solely a function of *n*. It is also noticeable that the difference in melting temperature between *n-p*6*p-n* and the next highest melting point for a compound with the same value of *n* is larger than that between those of the corresponding *n-p*6*m-n* and *n-m*6*m-n* members. Again, this suggest a larger difference in shape between *n-p*6*p-n* and either *n-p*6*m-n* or *n-m*6*m-n* than there is between *n-p*6*m-n* and *n-m*6*m-n*.

The dependence on *n* of the nematic–isotropic transition temperatures for the *n-p*6*p-n* and *n-p*6*m-n* series are compared in figure 6. As we have noted already, for both series an odd–even effect is seen in T_{NI} on varying *n*, which attenuates with increasing *n*. This alternation is stronger for the *n-p*6*p-n* series. It is clear that for any given value of *n*, *n-p*6*p-n* has a considerably higher clearing temperature than *n-p*6*m-n*. As with the melting points, this trend presumably reflects the greater shape anisotropy of the *n-p*6*p-n* member, see figure 5. It is interesting to note that although the melting temperatures of the *n-p*6*m-n* and *n-m*6*m-n* series in several cases are rather similar, see figure 4, the clearing temperatures of the latter series must be much lower. Indeed, extensive supercooling of the isotropic melt for the *n-m*6*m-n* series did not reveal liquid crystallinity. This reflects the greater non-linearity of the average molecular shapes of the *n-m*6*m-n* compounds, see figure 5, and reveals that the melting temperatures are less sensitive than the clearing temperature to these shape differences.

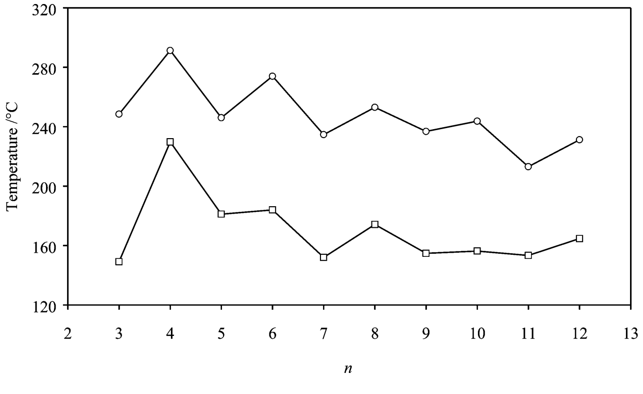


Figure 6. Nematic–isotropic transition temperatures for the *n-p*6*p-n* (○) and *n-p*6*m-n* (□) tetramer series.

The dependence of the nematic–isotropic entropy changes, $\Delta S_{\mathrm{NI}}/R$, for the *n-p*6*p-n* and *n-p*6*m-n* series on *n* are compared in figure 2. $\Delta S_{\mathrm{NI}}/R$ for both series shows a pronounced dependence on *n*, with the values of $\Delta S_{\mathrm{NI}}/R$ for homologues having even values of *n* being typically 1.5–2 times those of the odd members. The values of $\Delta S/R$ for the *n-p*6*p-n* series are approximately twice those of the *n-p*6*m-n* series although, as already noted, the values of n=8, 10 and 12 for the *n-p*6*m-n* series are lower than expected. This decrease on passing from the *n-p*6*p-n* to the *n-p*6*m-n* series presumably reflects the difference in average molecular shape between these series, see figure 5, and more specifically the increased molecular biaxiality of the *n-p*6*m-n* series.

3.5. *Comparison of the n-p(5|6)p-n, n-p(5|6)m-n and n-m(5|6)m-n series*

The thermal behaviour of the *n-p*5*p-n*, *n-p*5*m-n* and *n-m*5*m-n* series has been described in detail elsewhere [38]. All the members of the *n-p*5*p-n* series exhibit exclusively nematic behaviour although 12-*p*5*p*-12 is a monotropic nematogen. All the members of the *n-p*5*m-n* series also exhibit nematic behaviour with 10-*p*5*m*-10 monotropic in nature. In addition, 4-*p*5*m*-4 and 5-*p*5*m*-5 exhibit a strongly monotropic smectic phase. Five members of the *n-m*5*m-n* series exhibit liquid crystallinity; 4-*m*5*m*-4 shows an alternating smectic C phase and a nematic phase, while for the hexyl, octyl, nonyl and decyl homologues a highly disordered crystal phase and a nematic phase are seen.

The melting points of the six series of tetramers are compared in figure 7. The *n-p*5*p-n* and *n-p*6*p-n* series

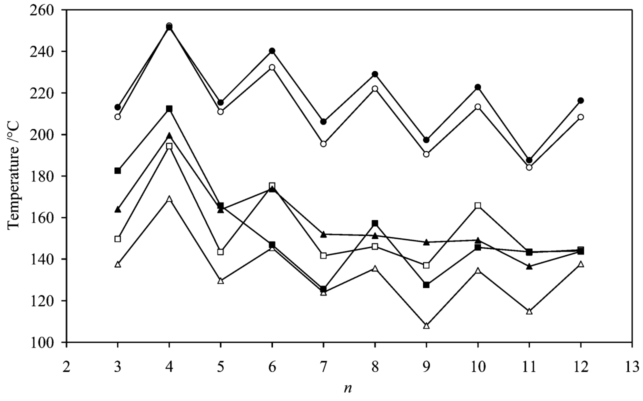


Figure 7. Dependence of the melting point on the length of the flexible outer spacers, *n*, for the *n-p*6*p-n* (●), *n-p*6*m-n* (■), *n-m*6*m-n* (▲), *n-p*5*p-n* (○), *n-p*5*m-n* (□) and *n-m*5*m-n* (△) series.

both exhibit a regular and pronounced alternation in melting point as the length and parity of the outer spacers are varied. The melting point of *n-p*6*p-n* is higher than that of the corresponding member of the *n-p*5*p-n* series, with the exception of the butyl homologues for which the melting points are essentially the same. It is interesting to note, however, that the difference in melting points between the corresponding members of the two series is rather small. The dependence of the melting point on *n* for the other four series is somewhat less regular. For short outer spacers the melting point increases in the sequence: *n-m*5*m-n*<*n-p*5*m-n*<*n-m*6*m-n*<*n-p*6*m-n*. As the outer spacer lengths are increased, *n-m*5*m-n* has the lowest melting points, while the ordering of those of the other three series varies.

The dependence of the nematic–isotropic transition temperatures on *n* for the five liquid crystal tetramer series is shown in figure 8. As seen for the melting points, the *n-p*6*p-n* series exhibits higher values than the corresponding members of the *n-p*5*p-n* series. Again the differences are rather small and we should note that T_{NI} for 4-*p*6*p*-4 is lower than expected because of the onset of decomposition at such elevated temperatures [39]. By contrast the clearing temperatures of the *n-p*5*m-n* series tend to be higher than those of the corresponding members of the *n-p*6*m-n* series. Figure 8 shows the clearing temperatures for the *n-m*5*m-n* series while, and as we saw earlier, extensive supercooling of the isotropic phases of the *n-m*6*m-n* series to temperatures lower than the clearing temperatures of the *n-m*5*m-n* series failed to reveal liquid crystallinity. Thus, for the four series containing bent semi-rigid units, an odd-membered spacer promotes liquid crystallinity to a greater extent than an even-membered spacer.

Figure 9 shows the dependence of the entropy change, $\Delta S_{\mathrm{NI}}/R$, associated with the nematic–isotropic transition on *n* for the five liquid crystal series. The *n-p*6*p-n* series exhibits higher values of $\Delta S_{\mathrm{NI}}/R$ than the corresponding member of the *n-p*5*p-n* series, although both series exhibit considerably larger values than those exhibited by conventional low molar mass mesogens. Surprisingly, this trend is reversed for the *n-p*5*m-n* and *n-p*6*m-n* series, for which *n-p*5*m-n* shows higher values of $\Delta S_{\mathrm{NI}}/R$ than the corresponding member of the *n-p*6*m-n* series. It is not possible to comment on the relative values of the entropy changes shown by the *n-m*5*m-n* series, as these are associated with a combined mesophase–nematic–isotropic transition.

The transitional properties of liquid crystal oligomers are most often understood in terms of the dependence of the molecular shape on the parity of the spacers considered in the all-*trans* conformation. If we consider the simplest oligomer, a dimer, then in an even-membered dimer the mesogenic units are antiparallel whereas in an odd-membered dimer they are inclined at some angle with respect to each other. The more linear even-membered structure is more compatible with the molecular organization found in the nematic phase, and may result in, for example, the higher values of $\Delta S_{\mathrm{NI}}/R$ observed for even members. Such an explanation is unrealistic, however, and account must be taken of the flexible nature of these molecules. Luckhurst developed a model which includes a range of spacer conformations and showed that in the isotropic phase approximately half the conformers of an even-membered dimer are essentially linear while only 10% of the conformers of an odd-membered dimer are linear [4]. At the isotropic–nematic transition, the synergy that exists between conformational and orientational order ensures that many of the bent conformers are converted to a linear

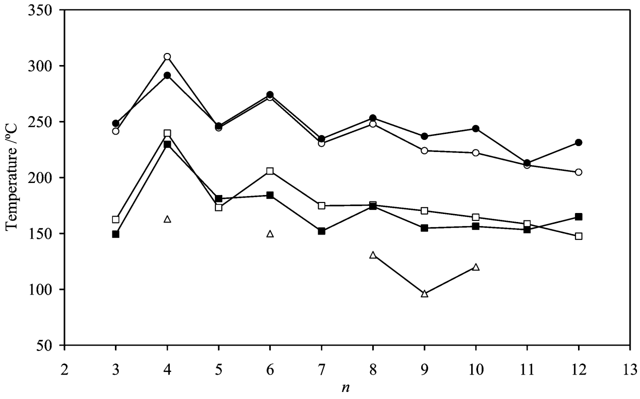


Figure 8. Dependence of the nematic–isotropic transition temperature on the length of the flexible outer spacers, *n*, for the *n-p*6*p-n* (●), *n-p*6*m-n* (■), *n-m*6*m-n* (▲), *n-p*5*p-n* (○), *n-p*5*m-n* (□) and *n-m*5*m-n* (△) series.

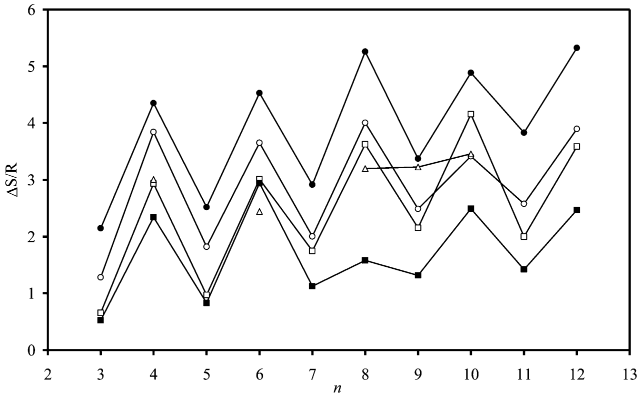


Figure 9. Dependence of the entropy change, $\Delta S_{\mathrm{NI}}/R$, associated with the nematic–isotropic transition on the length of the flexible outer spacers, *n*, for the *n-p*6*p-n* (●), *n-p*6*m-n* (■), *n-m*6*m-n* (▲), *n-p*5*p-n* (○), *n-p*5*m-n* (□) and *n-m*5*m-n* (△) series. For the *n-m*5*m-n* series the entropy changes are associated with a combined M–N–I transition.

form in the case of an even-membered dimer, which enhances the orientational order of the nematic phase. By comparison, for an odd-membered dimer the difference in free energy between the bent and linear conformers is too large for the orientational order of the nematic phase to convert bent into linear conformers. Thus, even-membered dimers exhibit higher values of $\Delta S_{NI}/R$ than odd-membered dimers. Although this model was developed for dimers, it should also be applicable to the tetramers in which we now have three flexible spacers.

If we first consider the melting points of the six series (see figure 7), then as expected the most linear series, *i.e.* the *n*-*p*6*p*-*n* series (see figure 5), exhibits the highest melting points. Surprisingly, however, and as we have seen, the melting points of the *n*-*p*5*p*-*n* series, the members of which have a bent molecular shape when considered in the all-*trans* conformation (see figure 5) are rather similar to those of the *n*-*p*6*p*-*n* series. Based on the behaviour of dimers and trimers, a greater reduction in melting point would be expected on replacing an even membered spacer by an odd one. This suggests that the parity of the central spacer now has a weaker effect on the average molecular shape. The rather irregular behaviour seen for the melting points of the other four series reinforces this view that the average molecular shape is controlled by a number of factors and not just by the parity of the central spacer.

Turning now to the nematic–isotropic transition temperatures, the surprising similarity between those of the *n*-*p*5*p*-*n* and *n*-*p*6*p*-*n* series supports the view that the average shapes of these molecules in the mesophase are similar. This suggests that orientationally the four mesogenic units are not strongly correlated via the central spacer but rather that the length and parity of the two outer spacers play a larger role in determining shape.

The surprising inversion of the nematic–isotropic transition temperatures for the *n*-*p*5*m*-*n* and *n*-*p*6*m*-*n* series, such that the odd-membered central spacer gives rise to the higher transition temperatures, reflects that

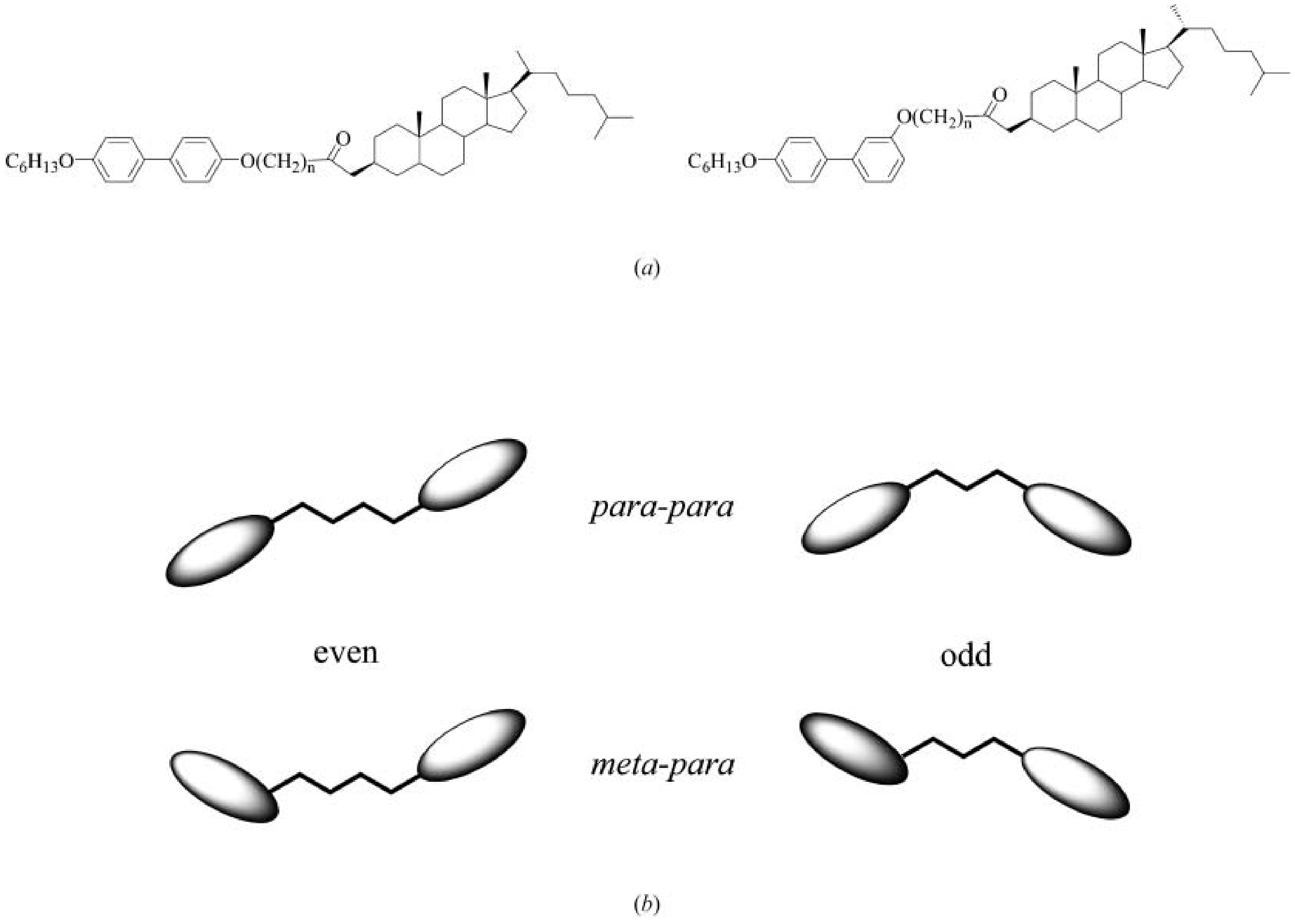


Figure 10. (*a*) Structures of liquid crystal dimers in which the linking point of the spacer to one mesogenic unit has been changed from *para* to *meta* and (*b*) sketches of the molecular shapes for such dimers.

the incorporation of the *meta* linkage introduces an aspect of non-linearity into the even membered structure, such that the two innermost mesogenic units are no longer coparallel. By contrast, for an odd-membered spacer the *meta* linkage means that the two innermost mesogenic units are now essentially coparallel, see figure 5. Analogous behaviour has been observed for liquid crystal dimers in which the point of attachment of the spacer to one of the mesogenic groups was varied from the *para* to the *meta* position, see figure 10 [43]. For these series, the *para*-*para* dimers exhibited a conventional odd–even effect in their transition temperatures, in which the even members exhibited the higher values. By contrast, for the *meta*-*para* dimers the odd–even effect was inverted, *i.e.* the odd members now exhibited the higher transition temperatures. The authors suggested that the combination of the *meta*-substituted mesogenic unit and an odd-membered spacer produced overall a more linear shape, see figure 10.

Finally, the difference in behaviour between the *n*-*m*5*m*-*n* and *n*-*m*6*m*-*n* series may also be rationalized in terms of the average molecular shapes. The overall length-to-breadth ratio of the *n*-*m*6*m*-*n* tetramers is very much higher than that of the *n*-*m*5*m*-*n* series, see figure 5; and indeed, the even-membered series may be considered as a pair of laterally linked dimers. This reduction in the shape anisotropy will significantly reduce their liquid crystal–isotropic transition temperatures when compared to those of the *n*-*m*5*m*-*n* series.

4. Conclusions

We have compared the transitional properties of six homologous series of liquid crystal tetramers and three rather surprising trends have emerged. Firstly, the nematic–isotropic transition temperatures of the *n*-*p*5*p*-*n* and *n*-*p*6*p*-*n* series are unexpectedly similar, suggesting that the average shapes of corresponding homologues in the two series are also similar. This implies that orientationally the four mesogenic units are not strongly correlated via the central spacer. Instead the average shape of these molecules appears to depend to a greater extent on the length and parity of the two outer spacers. This observation has important consequences in how we interpret thermodynamic behaviour for liquid crystal polymers, for which the scaling factor is by convention the repeat unit. Secondly, the nematic–isotropic transition temperatures of the *n*-*p*5*m*-*n* are higher than those of the corresponding members of the *n*-*p*6*m*-*n* series. This is attributed to the introduction of the kinked rigid unit which results in a more linear core for the odd membered tetramer. It is interesting to note that similar behaviour has been observed for liquid crystal dimers [43]. Finally, the *n*-*m*5*m*-*n* series exhibited significantly higher clearing temperatures than the *n*-*m*6*m*-*n* series, and again this was rationalized in terms of the average shapes of the tetramers.

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