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Liquid crystal tetramers

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The first homologous series of liquid crystal tetramers in which four mesogenic groups are linked *via* three alkyl spacers has been synthesised and characterised. The length of the outer two spacers is varied from 3 to 12 methylene units while the central spacer is held at 8 methylene units. All the members of the series exhibit enantiotropic nematic behaviour except for the decyl and dodecyl homologues which exhibit exclusively smectic A behaviour. In addition, smectic A behavior is observed for the hexyl to dodecyl homologues. The transitional properties, namely the clearing temperatures and associated entropy changes, exhibit a dramatic odd–even effect as the length and parity of the outer spacers are varied. This behaviour is interpreted in terms of how the spacers control the average molecular shape. The ratio of the smectic periodicity to the estimated all *trans* molecular length for the nonyl homologue is just 0.27. Three differing local packing arrangements are suggested to account for this surprising result.

Introduction

Semi-flexible main chain liquid crystal polymers consist of alternating mesogenic groups and flexible spacers, most commonly alkyl chains.[1,2] These materials have attracted much interest and not only as a result of their considerable application potential in a range of advanced technologies but also because they provide a demanding challenge to our understanding of self-assembly in polymeric systems. A particular feature of the transitional behaviour of this class of materials is the dramatic odd–even effect exhibited by the clearing temperatures and the associated entropy changes of a homologous series of polymers on varying the length and parity of the spacer.[3] Specifically, if an odd number of atoms link the mesogenic groups then a considerably lower clearing temperature is observed compared to that seen for the corresponding polymer containing either one fewer or one greater number of atoms in the spacer. Such behaviour is mimicked by liquid crystal dimers in which just two mesogenic units are connected *via* a single flexible spacer[4,5] although the alternation in the transitional properties is not quite so large. In consequence liquid crystal dimers have been used widely as model compounds for the polymeric systems.[6] In order to investigate how the transitional behaviour evolves from the dimers to the polymers a small number of trimers have been characterised containing three mesogenic groups and two flexible spacers.[7–14] We have now extended this approach to include linear liquid crystal tetramers in which four mesogenic units are connected *via* three flexible alkyl spacers, see Fig. 1. The acronym used to refer to the tetrameric series is CBO*n*O.O8O.O*n*OCB where *n* denotes the number of methylene groups in the outer two flexible spacers. There are very few examples of liquid crystal tetramers described in the literature[15] and this is the first report in which the transitional behaviour of a complete homologous series is discussed.

Experimental

Synthesis

The tetrameric CBO*n*O.O8O.O*n*OCB series was prepared using the synthetic route shown in Scheme 1. The syntheses of the α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkanes, **2**, and the α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-formylphenyl-4′-oxy)alkanes **3**, have been described in detail elsewhere.[16]

1,8-Bis(4-nitrophenyloxy)octane, 4. A mixture containing 4-nitrophenol (10.0 g, 71.9 mmol), 1,8-dibromooctane (9.3 g, 34.3 mmol) and potassium carbonate (16.5 g, 120 mmol) in DMF (100 mL) was refluxed with stirring overnight. The reaction mixture was allowed to cool and poured into ice-cold water (1.5 L). The resulting yellow precipitate was collected by filtration, recrystallised with hot filtration from ethanol and dried under vacuum.

Yield 71%. δ_H ($CDCl_3$) 8.2 (d, aromatic *ortho* to NO_2, 2H, *J* 9.2); 6.9 (d, aromatic *meta* to NO_2, 2H, *J* 9.2); 4.0 (t, OCH_2, 2H, *J* 6.4); 1.8 (m, OCH_2CH_2, 2H); 1.4 (m, CH_2, 4H). IR (KBr) ν_{max}: 1336 cm^{-1} (N–O).

1,8-Bis(4-aminophenyloxy)octane, 5. 4 (2.86 g, 7.4 mmol) was dissolved in boiling ethanol (100 mL) and a solution of sodium sulfide nonahydrate (14.7 g, 61.3 mmol) in water (50 mL) was added. The resulting mixture was refluxed with stirring overnight. The reaction mixture was allowed to cool and the precipitate collected by filtration. The crude product was recrystallised from ethanol and dried under vacuum.

Yield 35%. δ_H 6.7, 6.6 (m, aromatic, 4H); 3.9 (t, OCH_2, 2H, *J* 6.6); 3.3 (bs, NH_2, 2H); 1.7 (m, OCH_2CH_2, 2H); 1.4 (m, CH_2, 4H). IR (KBr) ν_{max}: 3400, 3315 (N–H stretch); 1633 (N–H bend).

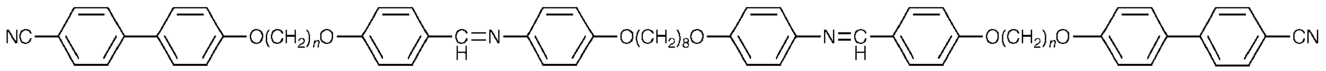
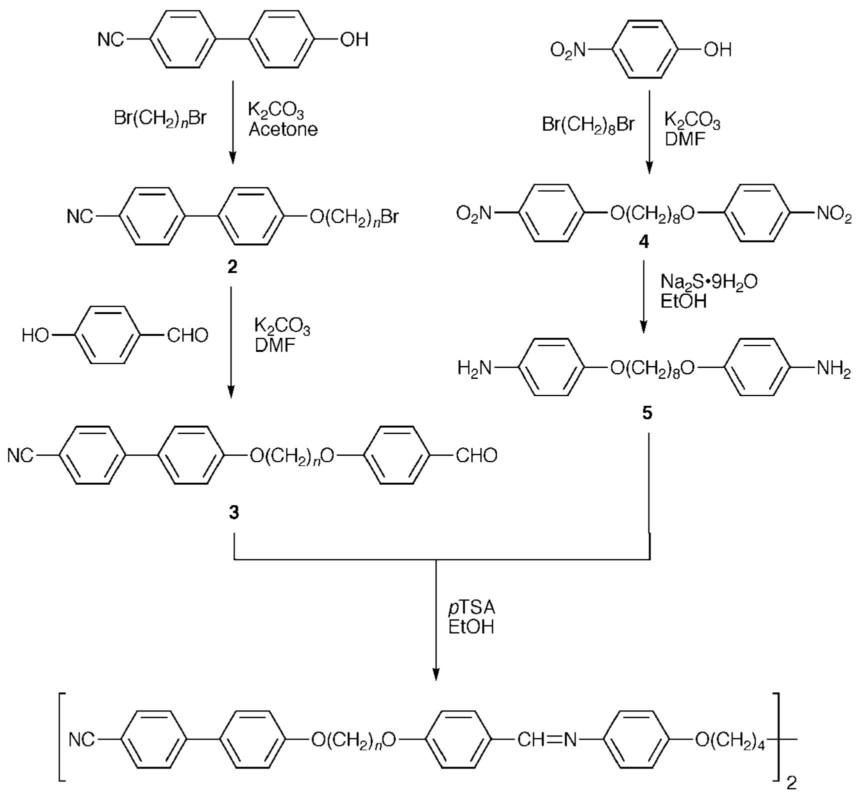


Fig. 1 The molecular structure of the tetrameric CBO*n*O.O8O.O*n*OCB series.



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Scheme 1

Tetramers, 1. A solution containing **3** (2.8 mmol), **5** (0.4 g, 1.3 mmol) and a trace of toluene-*p*-sulfonic acid in ethanol (50 mL) was refluxed with stirring overnight. The reaction mixture was allowed to cool and the precipitate obtained was purified by recrystallisation from DMF. The yields in all cases were in excess of 60%. The tetramers were too insoluble in any appropriate solvent to allow for structural characterisation using 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 **5** and that associated with the carbonyl bond in **3** are absent in the spectra of the tetramers. The products' spectra do contain, however, a band corresponding to the cyano stretch at *ca.* 2235 cm^{-1} and one at *ca.* 1620 cm^{-1} corresponding to the imine stretch.

Characterisation

The proposed structures of all the intermediates were verified using ^{1}H NMR and IR spectroscopy. ^{1}H NMR spectra were measured in $CDCl_3$ on a Bruker AC-F 250 MHz NMR spectrometer. IR spectra were recorded using an ATI Mattson Genesis Series FTIR spectrometer. The purities of all the intermediates were verified using thin layer chromatography.

Thermal properties were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 820 system equipped with an intracooler accessory and calibrated using an indium standard. The heating and cooling rates in all cases were 10 °C min^{-1}. Phase identification was performed by polarised light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and a TMS 91 control unit.

Results and discussion

The transition temperatures and associated entropy changes exhibited by the tetrameric series CBO*n*O.O8O.O*n*OCB are listed in Table 1. All ten members of the series exhibit liquid crystalline behaviour. The propyl, butyl and pentyl homologues show only nematic behaviour. The hexyl, heptyl, octyl, nonyl and undecyl homologues exhibit both smectic A and nematic phases while the decyl and dodecyl members show exclusively smectic A behaviour. Nematic phases were assigned on the basis of the schlieren optical texture containing both two

Table 1 The transition temperatures and associated entropy changes for the tetrameric CBO*n*O.O8O.O*n*OCB series

n	T_m/°C	T_{SmAN}/°C	T_{NI}/°C T_{SmAI}/°C^a	$(\Delta S_m/R)$	$(\Delta S_{SmAN}/R)$	$(\Delta S_{NI}/R)$ $(\Delta S_{SmAI}/R)^b$
3	192	—	246	22.4	—	2.16
4	221	—	307	17.5	—	5.08
5	161	—	250	23.5	—	2.47
6	202	220	279	14.8	0	5.39
7	179	174	241	11.6	0	2.85
8	192	243	258	28.2	0.41	5.34
9	152	217	235	22.3	0.63	3.30
10	176	—	238^a	26.0	—	5.06^b
11	150	190	210	19.0	—	3.05
12	174	—	220^a	18.0	—	5.18^b

and four brush point singularities when viewed through a polarised light microscope. For the smectic A phases focal conic fan textures were observed in co-existence with regions of homeotropic alignment.

The dependence of the transition temperatures on the number of methylene units, *n*, in the outer flexible alkyl spacers for the tetrameric CBO*n*O.O8O.O*n*OCB series is shown in Fig. 2. The melting points exhibit a pronounced alternation which is only weakly attenuated on increasing *n*. Similar behaviour has been observed for liquid crystal trimers[14] and for nematic dimers[17] but not for smectic dimers.[18] This may indicate that the change in the conformation statistical weights of the spacer on melting into a nematic phase is small for even-membered spacers but large for odd-membered spacers. Alternatively, this pronounced alternation in the melting points reflects the difficulty that the bent conformations of the odd-membered compounds experience in packing efficiently into a crystal lattice compared with the more elongated all even-membered tetramers, see Fig. 3. We will return to a more detailed discussion of molecular shape later.

The clearing temperatures also show a dramatic odd–even effect as the length and parity of the outer spacers are varied although this attenuates on increasing *n*, see Fig. 2. For even members the clearing temperature decreases on increasing *n* whereas for odd members it is less sensitive to changes in spacer length and indeed passes through a weak maximum on increasing *n*. The dependence of the smectic A–nematic and smectic A–isotropic transition temperatures on *n* is, however, quite different. The thermal stability of the SmA phase is critically dependent on the parity of the outer spacers. Specifically for the even members the thermal stability increases on passing from the hexyl to the octyl and decyl homologues but subsequently decreases for the dodecyl member. By comparison there is a much larger increase in T_{SmAN} on passing from the heptyl to the nonyl homologue but also a larger subsequent decrease to the undecyl homologue. Thus, the stability of the phase is more susceptible to changes in the length of odd- rather than even-membered spacers. This is highlighted by the observation of smectic A–isotropic transitions for even- but not for odd-membered homologues. Thus the smectic tendencies of the tetramers do not simply increase on increasing spacer length as is observed for semi-flexible main chain liquid crystal polymers[1,2] nor do they simply decrease as for symmetric liquid crystal dimers[18] or for liquid crystal trimers.[14]

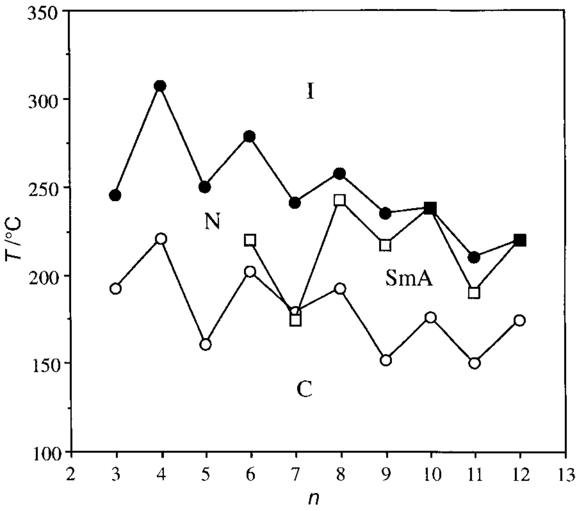

Fig. 2 The dependence of the transition temperatures on the number of methylene units (*n*) in the outer flexible alkyl spacers for the tetrameric CBO.*n*O.O8O.O*n*OCB series: (○) melting points, (●) nematic–isotropic transitions, (□) smectic A–nematic transitions and (■) smectic A–isotropic transitions.

In order to understand the unusual dependence of smectic phase stability on spacer length seen in Fig. 2, the smectic periodicity, *d*, was measured using X-ray diffraction for CBO9O.O8O.O9OCB and found to be 19.5 Å. The estimated all-*trans* molecular length, *l*, for this homologue is 71 Å and thus, the layer thickness is considerably smaller than the molecular length. It should be noted that the observation of regions of homeotropic alignment excludes the possibility that this is a highly tilted phase.

In considering possible driving forces for smectic phase formation by these tetramers we note that they contain two electron deficient moieties, the cyanobiphenyl groups, and two electron rich benzylideneaniline units. Smectic phase formation both in binary mixtures of low molar mass mesogens containing similar groups[19–26] and in non-symmetric liquid crystal dimers[27–29] in which similar units are linked *via* an alkyl spacer, is attributed to a specific interaction between the unlike mesogenic groups. The precise nature of this interaction is somewhat ambiguous but is most commonly thought to be a charge transfer interaction. More recently, however, it has been suggested that the liquid crystalline behaviour is controlled by electrostatic quadrupoles between groups with quadrupole moments which are opposite in sign.[30] It seems reasonable to suggest that this specific interaction between the unlike mesogenic groups is also, at least in part, the driving force for smectic phase formation by the tetramers. Fig. 4(a) shows a schematic representation of the local molecular arrangement within a smectic phase composed of tetramers in which the interactions between the unlike mesogenic groups are maximised. At first sight this packing arrangement is analogous to

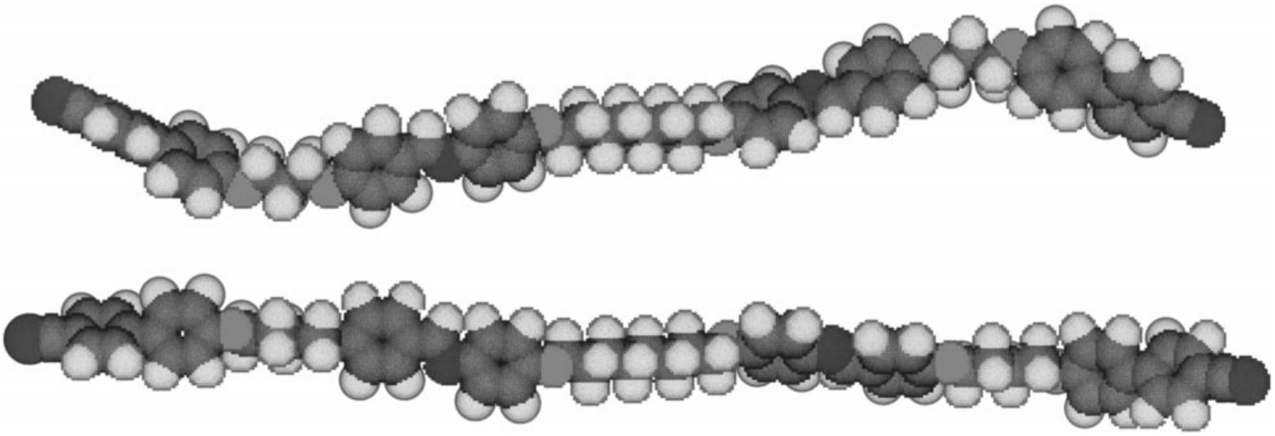

Fig. 3 The molecular shapes of CBO3O.O8O.O3OCB (upper structure) and CBO4O.O8O.O4OCB (lower structure) with the spacers in the all-*trans* conformation.

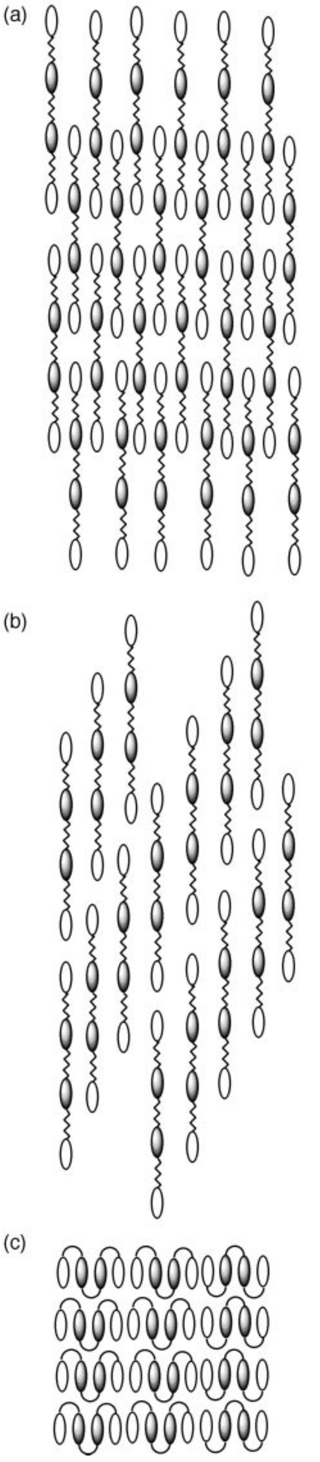

Fig. 4 Sketches of possible molecular arrangements of the tetramers in the smectic A phase.

that seen in the intercalated smectic phases exhibited by nonsymmetric liquid crystal dimers.[4,5] The term 'intercalated', however, was used to indicate that differing parts of the molecules overlapped. In the arrangement shown in Fig. 4(a) differing mesogenic groups interact but it is similar spacers which overlap giving a phase consisting of three regions: one domain composed of mesogenic groups, one containing the outer flexible spacers and the other the inner spacers. Thus this should not be termed an intercalated arrangement. The periodicity of this arrangement does not in fact correspond to the observed $d{:}l$ ratio of 0.27 but instead is approximately two thirds. If we assume, however, that the scattering powers of the two differing alkyl regions are similar then the apparent periodicity would indeed approximate to the experimentally observed value.

Two alternative smectic phase structures exist which are consistent with the observation $d{:}l \approx 0.27$. In the first of these the spacers as well as the mesogenic cores are mixed giving a smectic phase composed of two domains, one containing mesogenic units and the other alkyl spacers, see Fig. 4(b). The driving force here may not only be entropic but also arises from the formation of anti-parallel cyanobiphenyl dimers which in turn interact with the Schiff bases. The other possible smectic phase structure is composed of concertinaed tetramers, see Fig. 4(c). This arrangement while consistent with the X-ray data is the least plausible on energetic grounds of the three suggested. In addition, it is unclear how such an arrangement is consistent with the dramatic dependence of the transition temperatures on spacer length. In order to remove the ambiguity in the structure of the phase a greater range of tetramers must now be studied and in addition further X-ray studies are necessary in order to determine whether these smectic phases have modulated structures. Unfortunately, miscibility studies cannot be used as an aid to phase characterisation because there are no appropriate standard materials.

The molecular arrangements shown in Fig. 4(a) and (b) do, however, allow us to rationalise the unusual dependence of smectic tendency on spacer length. The more linear all-even-membered tetramers will pack more efficiently into either structure than the bent tetramers containing odd-membered spacers and hence the higher transition temperatures are observed for the former. In order to maximise the interactions between mesogenic groups, the arrangement shown in Fig. 4(b) requires the inner and outer spacers to be of comparable length and is presumably most stable when the spacers are of equal length. This is consistent with the dependence of the smectic transition temperatures on n, see Fig. 2. The stability of the arrangement shown in Fig. 4(a), however, should be relatively insensitive to differences in the outer spacer lengths if the principal driving force for smectic phase formation is the mixed interaction and thus, quite unlike the behaviour seen in Fig. 2. This suggests instead that the phase may form as a result of entropically driven microphase separation.

Fig. 5 shows the dependence of the entropy change associated with the clearing transition, expressed as the dimensionless quantity $\Delta S/R$, on the number of methylene units in the outer flexible spacers. A pronounced odd–even

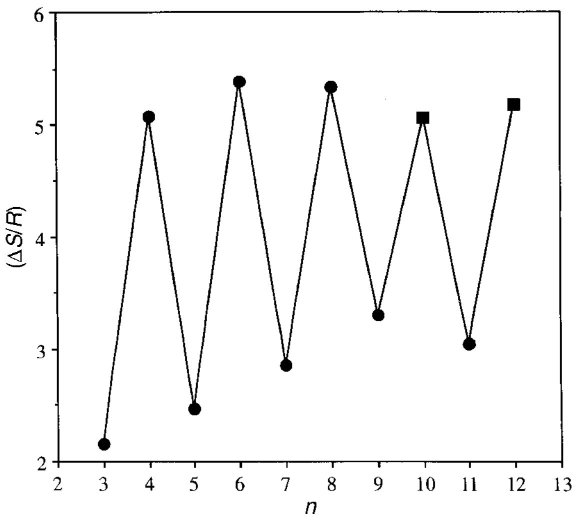

Fig. 5 The dependence of the entropy change associated with the clearing transition on the number of methylene units, n, in the outer flexible alkyl spacers for the tetrameric CBOnO.O8O.OnOCB series: (●) nematic–isotropic transitions and (■) smectic A–isotropic transitions.

effect can be clearly seen in which the values of $\Delta S/R$ for all-even members are typically more than twice those of the odd members. The values of $\Delta S_{NI}/R$ for the even members are greater than 5 and such high values are without precedent for low molar mass mesogens. These values do, however, fit the emerging trend that $\Delta S_{NI}/R$ increases on passing from monomer to dimer to trimer[14] and now, to tetramer. It is not possible to comment further on this because in these tetramers the inner spacer has a different length to that of the outer spacers. Similarly, it is not possible to compare the behaviour of the odd-membered dimers and trimers with that of the tetramers as these have an even-membered inner spacer. It may be argued that the exceptionally high values of $\Delta S_{NI}/R$ seen in Fig. 5 should be scaled according to the number of mesogenic units and such a scaling is, in essence, routinely and without question performed for semi-flexible main chain polymers. It is not possible to compare, however, the scaled values of $\Delta S_{NI}/R$ for the tetramers with those of analogous trimers and dimers because the inner spacer is different in length to the outer spacers. The only example for which a valid comparison can be made is CBO8O.O8O.O8O.O8OCB and for this the scaled $\Delta S_{NI}/R$ (*i.e.* $[\Delta S_{NI}/R]/4 = 1.34$) is equal to the scaled value for the analogous trimer (*i.e.* $[\Delta S_{NI}/R]/3 = 1.36$) but greater than that of the dimer (*i.e.* $[\Delta S_{NI}/R]/2 = 1.01$). The scaled $\Delta S_{NI}/R$ exhibited by the dimer is considerably larger than that of the analogous monomer (*i.e.* $[\Delta S_{NI}/R] = 0.25$). Thus it would appear that linking two mesogenic groups together *via* an even-membered spacer has a dramatic effect on the scaled $\Delta S_{NI}/R$ but adding a further mesogenic unit *via* an additional spacer leads to a much smaller increase in the scaled $\Delta S_{NI}/R$ which is subsequently insensitive to further additions. This observation has clear implications in the manner in which we interpret thermodynamic data for semi-flexible main chain liquid crystal polymers but further speculation must await the characterisation of a greater number of trimeric and tetrameric series in order to test the generality of these data.

A surprising feature of Fig. 5 is that the entropy changes associated with the smectic A–isotropic transitions are of comparable magnitudes to $\Delta S_{NI}/R$. This presumably implies that the translational ordering in the SmA phase is low. This is somewhat surprising given our assumption earlier that the mixed core interaction at least in part drives the formation of the smectic phase. This would imply a high degree of translational ordering.

We have seen, therefore, that the transitional properties of the tetramers show a pronounced dependence on the length and parity of the flexible spacers, see Fig. 2 and 5. For dimers such behaviour has been successfully interpreted using a model which allows specifically for the flexibility of the spacer and does not solely consider differences in the shapes of the all-*trans* conformations of even and odd members, see Fig. 3.[4] Thus, for an even-membered dimer in the isotropic phase, approximately half the conformers are essentially linear whereas for an odd-membered dimer this value falls to just 10% being linear. At the transition to the nematic phase the synergy that exists between conformational and orientational order ensures that for even-membered dimers many of the bent conformers are converted to a linear form as this enhances the orientational order of the nematic phase. Thus, $\Delta S_{NI}/R$ is larger than would be expected for a monomer. The situation for odd-membered dimers is quite different because the difference in free energy between the bent and linear conformers is such that the orientational order of the nematic phase is insufficient to convert bent into linear conformers. Hence, $\Delta S_{NI}/R$ exhibited by odd-membered dimers is small. It would seem reasonable that this approach would also successfully predict the properties of trimers and tetramers although this assumption must now be tested.

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