# Symmetric and non-symmetric liquid crystal dimers with branched terminal alkyl chains: racemic and chiral

**Andrew E. Blatch, Ian D. Fletcher and Geoffrey R. Luckhurst***

*Department of Chemistry, University of Southampton, Highfield, Southampton S017 1BJ, UK*

Two new series of racemic dimeric liquid crystals containing terminal alkyl chains with methyl branches are presented; in one the dimers are symmetric and in the other they are non-symmetric. Comparisons are made with the structurally isomeric series with no methyl branches in their terminal alkyl chains. The stability and clearing temperatures of the liquid crystal phases are markedly reduced for the dimers with methyl branches, particularly for the symmetric dimers. Chiral analogues of both series were also examined. The liquid crystal behaviour of the non-symmetric dimers is of particular interest. Four homologues were studied with the number of methylene units in the spacer ranging from six to nine. An odd–even effect was observed for the chiral properties of these materials. Blue phase I behaviour was exhibited by the heptane and nonane homologues but not by the even membered hexane and octane members of the series.

The chiral properties of low molar mass liquid crystals have continued to fascinate researchers ever since the discovery of the liquid crystalline state in 1888.[1] Today a plethora of chiral liquid crystal phases are known to exist.[2] Such interest stems not only from the applications of chiral liquid crystal materials in, for example, thermochromic devices and the use of the ferroelectric smectic C phase in electro-optics[3] but also results from their considerable fundamental importance as illustrated by the discoveries of the blue phases and the twist grain boundary (TGB) phase. Examples in the literature of chiral liquid crystal compounds are dominated to a large degree by low molar mass monomeric materials and to a lesser extent by chiral polymer liquid crystals. However, examples of chiral liquid crystal dimers, *i.e.* compounds composed of two mesogenic groups linked together by a flexible spacer, are scarce. The studies which do exist have either considered the influence of a chiral, flexible alkyl spacer on the phase behaviour of liquid crystal dimers[4,5] or have examined the induction of chiral nematic phases in nematic hosts by the addition of non-mesogenic dimers with chiral spacers.[6] Barberá *et al.*[4] have prepared a series of alkyloxy-substituted Schiff's base dimers with a spacer derived from (S)-2-chlorosuccinic acid. By increasing the dipole moment with a chlorine atom at the chiral centre it was hoped that low molar mass compounds with enhanced ferroelectric properties could be obtained. However, although a ferroelectric smectic C phase was formed by all of the homologues, the compounds proved unstable and decomposed on heating. One of the few published reports on liquid crystal dimers with branched terminal alkyl chains is by Shiraishi and co-workers.[7] They synthesized the dimer α,ω-bis{4-[(S)-2-methylbutylcinnamoate]-aminobenzylidene-4'-carbonyloxy}icosane† which exhibits a ferroelectric smectic C phase.

Liquid crystal dimers serve as useful models for semi-flexible, main chain liquid crystal polymers. Like polymers, it is well-known that the order within the liquid crystal phases exhibited by dimers depends greatly on the number of methylene units in the spacer.[8] Thus, as a result of their greater molecular anisotropy, the liquid crystal phases of even-membered dimers frequently possess higher clearing temperatures and entropies of transition than those of neighbouring odd-membered dimers. The observed odd–even effect results principally from the difference in the distribution of conformers available to odd-

or even-membered flexible alkyl spacers. Even-membered spacers possess more conformers which allow an essentially parallel arrangement of the mesogenic cores whereas odd-membered spacers tend to have more conformers which cause the mesogens to adopt an unfavourable bent configuration. Given such a marked dependence on the parity of the spacer we might expect the form chirality of the chiral phases exhibited by dimers with an odd- or even-membered spacer also to vary. In order to further our understanding of the structure–property relationships of racemic dimeric liquid crystals with branched terminal alkyl chains, and to examine the effect of the flexible alkyl spacer on the chiral properties of their optically pure analogues, we have synthesized two new homologous series of dimeric liquid crystals containing the 2-methylbutyl group in the terminal position: first the symmetric α,ω-bis{4-[4-(2-methylbutyl)phenyliminomethyl]phenoxy}alkanes and secondly the non-symmetric α-(4'-cyanobiphenyl-4-yloxy)-ω-{4-[4-(2-methylbutyl)phenyliminomethyl]phenoxy}alkanes. As well as the racemic compounds we have also prepared a selection of their chiral analogues. The symmetric dimers were chosen as their monomeric counterparts are known and typically have a nematic character for short terminal alkyl chains with increased smectic polymorphism as the terminal alkyl chain is lengthened.[9,10] The structurally isomeric, unbranched analogues of these dimers, the α,ω-bis[4-(4-pentylphenyliminomethyl)phenoxy)alkanes, have also been studied in detail and exhibit a rich smectic polymorphism.[11] The corresponding non-symmetric dimers, the α-(4'-cyanobiphenyl-4-yloxy)-ω-[4-(4-alkylphenyliminomethyl)phenoxy]alkanes are well characterised[12,13] and are of particular interest as they form intercalated smectic phases (see the Results and Discussion section for a description of the structure of this phase). To gauge the effect of branching in the terminal alkyl chain more fully for the non-symmetric dimers, the remaining homologues of the structurally isomeric α-(4'-cyanobiphenyl-4-yloxy)-ω-[4-(4-pentylphenyliminomethyl)phenoxy]alkanes were synthesized as only the homologues with propane to hexane spacers have been described.[12,13]

For convenience, we shall denote the α,ω-bis{4-[4-(2-methylbutyl)phenyliminomethyl]phenoxy}alkanes and the α-(4'-cyanobiphenyl-4-yloxy)-ω-{4-[4-(2-methylbutyl)phenylimino-methyl]phenoxy}alkanes by the mnemonics 2MB.O*n*O.2MB and CBO*n*O.2MB, respectively. Here, CB denotes the cyanobi-phenyl group, 2MB the 2-methylbutyl group, and *n* is the number of methylene units in the flexible alkyl spacer. The symmetric straight chain dimers are denoted by 5.O*n*O.5,

---

†The structure of the icosane is $(CH_2)_{20}[COOC_6H_4CH=NC_6H_4CH=CHCOOCH_2CH(CH_3)C_2H_5]_2$.

where 5 indicates the pentyl chain. The straight chain analogues of CBO$n$O.2MB, the α-(4′-cyanobiphenyl-4-yloxy)-ω-[4-(4-pentylphenyliminomethyl)phenoxy]alkanes, are denoted by CBO$n$O.5. The chiral analogues of the 2MB.O$n$O.2MB and CBO$n$O.2MB series are referred to as ($S$)2MB.O$n$O.($S$)2MB and CBO$n$O.($S$)2MB, respectively, where $S$ is the absolute configuration of the 2-methylbutyl substituent.

## Experimental

The synthetic steps taken to the racemic and chiral 2MB.O$n$O.2MB and CBO$n$O.2MB series are shown in Schemes 1 and 2, respectively, and in this section we give the experimental details for the syntheses of ($S$)2MB.O6O.($S$)2MB and CBO6O.($S$)2MB as examples. The syntheses of ($S$)-(+)-2-methylbutylbenzene[9] and the α-(4′-cyanobiphenyl-4-yloxy)-ω-(4-formylphenoxy)alkanes[12,13] where carried out using literature procedures. ($S$)-(+)-4-(2-Methylbutyl)aniline ([α]$^{23}$ −5.8, neat) was synthesized using the methods outlined in ref. 14. All intermediates were structurally characterized by IR (Perkin Elmer 1600 series FTIR spectrometer) and $^{1}$H NMR spectroscopy (JEOL FX90Q NMR spectrometer). The purity of the final products was controlled by high field $^{1}$H NMR spectroscopy (Bruker AM 360MHz NMR spectrometer) and mass spectroscopy (VG 70-250). Specific rotations were measured with an AA-100 polarimeter (Optical Activity Ltd.). The liquid crystal properties were investigated using an Olympus BH-2 polarizing microscope together with a TMS90 Linkam hot stage. The thermal characteristics of the liquid crystal transitions were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 differential scanning calorimeter. The layer spacings of the smectic phases were determined by X-ray diffraction: a Guinier diffraction camera was used with nickel-filtered Cu-K$\alpha$ radiation ($\lambda = 0.154$ nm) and a magnetic field (1.1 T) was used to align the samples. The wavelength of selective reflection, which is proportional to the helical pitch of pure chiral nematics, was measured as
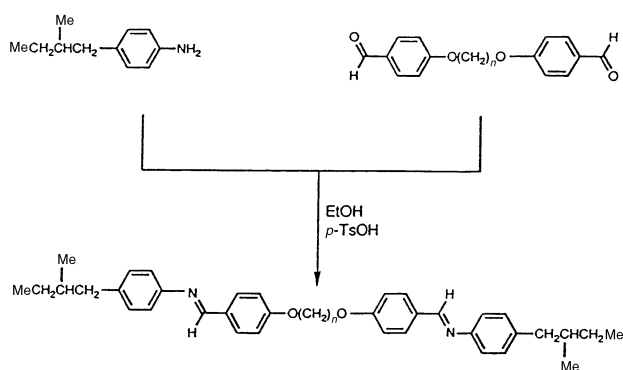


**Scheme 1** The synthetic route to the 2MB.O$n$O.2MB series of compounds
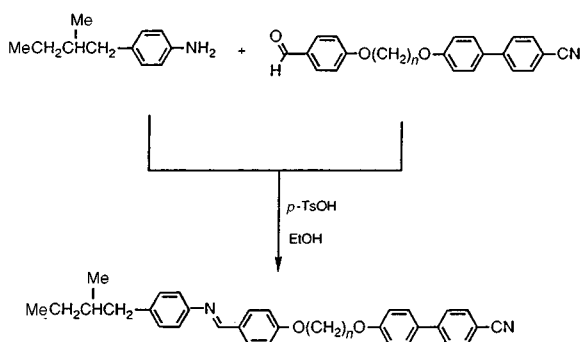


**Scheme 2** The synthetic route to the CBO$n$O.2MB series of compounds

a function of temperature using a TMS90 Linkam hot stage to heat the sample. The hot stage was placed on a purpose-built housing which allowed the heated sample to be positioned in the beam of a Philips PU8730 UV–VIS spectrometer interfaced to an Opus PC II computer. The Grandjean planar texture used in the measurement was obtained by shearing the sample between two glass slides. The helical twisting power was also determined for several chiral materials by dissolving the chiral compound in a room temperature nematic host (Merck E7, $T_{CN} = -10$ °C and $T_{NI} = 61$ °C) and measuring the pitch of the induced chiral nematic phase using the Cano-wedge method.[16] Two solute concentrations, approximately 5 and 11 mass%, were used and the inverse of the pitch was then extrapolated to give the helical twisting power.

### ($S$,$S$)-(+)-α,ω-Bis{4-[4-(2-methylbutyl)phenyliminomethyl]phenoxy}hexane

($S$)-(+)-4-(2-Methylbutyl)aniline (0.5 g, 3.07 mmol) was added to a hot solution of α,ω-bis(4-formylphenoxy)hexane (0.5 g, 1.46 mmol) with a few crystals of toluene-$p$-sulfonic acid in absolute ethanol (30 ml) in a 50 ml conical flask fitted with a calcium chloride guard tube. While cooling to room temperature, the reaction mixture was stirred for 5 h. A creamy yellow precipitate formed which was filtered off and recrystallized twice from ethyl acetate to give white crystals which were dried *in vacuo* at 30 °C (0.61 g, 68%). The yields of the other homologues were all in excess of 65%; $\nu_{max}$(film)/cm$^{-1}$ 1624 (C=N); $^{1}$H NMR (CDCl$_3$): δ 0.8–1.0 (t, 4H), 1.1–1.9 (m, 22H), 2.1–2.8 (2q, 4H), 3.9–4.1 (t, 4H), 6.7 (d, 4H), 6.9 (s, 8H), 7.6 (d, 4H), 8.1 (s, 2H); $m/z$ (EI) 469 (M$^+$ − C$_5$H$_{11}$Ph), 616 (M$^+$); [α]$^{20}$ +17.5 ($c$ 1.04, CHCl$_3$).

### ($S$)-α-(4′-Cyanobiphenyl-4-yloxy)-ω-{4-[4-(2-methylbutyl)phenyliminomethyl]phenoxy}hexane

($S$)-(+)-4-(2-Methylbutyl)aniline (0.5 g, 3.1 mmol) was added to a stirred solution of α-(4′-cyanobiphenyl-4-yloxy)-ω-(4-formylphenoxy)hexane (1.3 g, 3.2 mmol) with a few crystals of toluene-$p$-sulfonic acid in hot absolute ethanol in a 50 ml conical flask fitted with a calcium chloride guard tube. The reaction mixture was stirred for 5 h while cooling. A creamy yellow precipitate formed which was filtered off and recrystallized twice from ethyl acetate to give white crystals which were dried *in vacuo* at 30 °C (1.1 g, 66%). The yields of the other homologues were all in excess of 65%; $\nu_{max}$(film)/cm$^{-1}$ 1602 (C=N), 2248 (C≡N); $^{1}$H NMR (CDCl$_3$): δ 0.8–1.2 (t, 2H), 1.2–2.0 (m, 15H), 2.3–2.7 (2q, 2H), 3.9–4.2 (m, 4H), 6.8–7.4 (m, 8H), 7.5–8.0 (m, 8H), 8.4 (s, 1H); $m/z$ (EI) 487 (M$^+$ − C$_4$H$_9$), 544 (M$^+$); [α]$^{20}$ +8.5 ($c$ 0.9, CHCl$_3$).

## Results and Discussion

### The racemic dimers

**The 2MB.O$n$O.2MB series: the symmetric dimers.** The transition temperatures, enthalpies and entropies of transition for the 2MB.O$n$O.2MB series are listed in Table 1. From these results we see that this series exhibits both smectic A and nematic phases. The smectic A phase was characterised by its optical texture which showed the coexistence of focal-conic fan and homeotropic textures. The nematic phase was recognised by its schlieren texture which had both two and four point singularities and flashed when subjected to mechanical stress. As expected for this series, linking two mesogenic groups together by a flexible spacer led to a reduction in the smectic polymorphism compared to the analogous monomers. Fig. 1($a$) shows the effect of varying the number of methylene units $n$ in the flexible spacer on the liquid crystal behaviour for this series. We see that there is a strong odd–even effect for the liquid crystal-to-isotropic transition temperature which is

**Table 1** Transition temperatures, enthalpies and entropies of transition for the racemic 2MB.O$n$O.2MB series. Parentheses indicate a monotropic transition

| $n$ | $T$/°C | | | $\Delta H$/kJ mol$^{-1}$ | | $\Delta S/R$ | |
|---|---|---|---|---|---|---|---|
| | C– | S$_A$–N | N–I | C– | N–I | C– | N–I |
| 3 | 136 | | | 39.7 | | 11.7 | |
| 4 | 156 | | 183[a] | 32.2 | 9.9[a] | 9.1 | 2.6[a] |
| 5 | 124 | | (91)[b] | 35.3 | | 10.7 | |
| 6 | 154 | (138)[c] | (151) | 42.6 | 4.5 | 12.2 | 1.3 |
| 7 | 147 | | (96)[b] | 37.0 | | 11.4 | |
| 8 | 132 | | 133 | 38.6 | 4.0 | 11.7 | 1.2 |
| 9 | 108 | | (94)[b] | 38.5 | | 12.2 | |
| 10 | 121 | | 120 | 52.3 | 4.6 | 16.2 | 1.4 |
| 11 | 110 | | (95)[b] | 42.0 | | 13.2 | |
| 12 | 119 | | (114) | 65.3 | | 20.2 | |

[a]S$_A$–I transition. [b]Observed only with polarising microscopy by supercooling isotropic droplets. [c]The phase transition could only be observed by polarising microscopy.
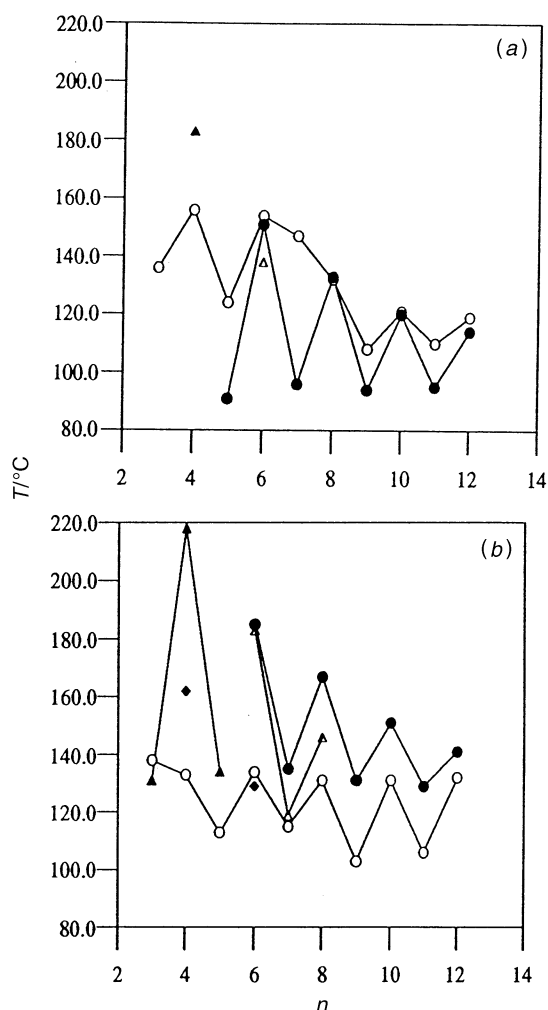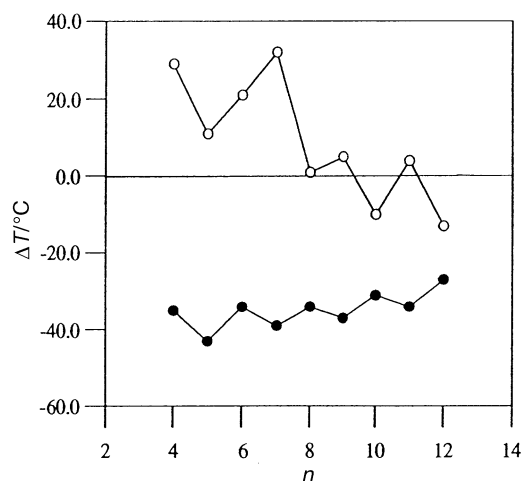


**Fig. 1** The influence of the number of methylene groups $n$ in the flexible alkyl spacer on the transition temperatures for (a) the 2MB.O$n$O.2MB and (b) the 5.O$n$O.5 series. C–(○), S$_A$–I (▲), S$_A$–N (△), N–I (●), S$_B$–S$_A$ (◆).

attenuated on ascending the series. It is also evident that the liquid crystal phases occur predominantly below the melting point; indeed only the $n=4$ and 8 homologues exhibit enantiotropic phases. The nematic-to-isotropic transition temperatures of homologues with an odd numbered spacer could only be observed with polarizing microscopy by supercooling isolated, isotropic droplets. The $n=4$ and 6 homologues form smectic A phases which show strong homeotropic alignment

for thin samples. The remaining homologues are all nematogenic. An X-ray investigation of the smectic A phase of the $n=4$ homologue gave a small angle reflection which corresponds to a smectic periodicity of 33.7 Å which is relatively close to the all-*trans* molecular length of 38 Å as measured from a CPK molecular model. This result indicates that the molecules are arranged in monolayers and that, as expected, there is no significant interpenetration of the molecules between the layers.

The effect of the branched terminal alkyl chains on the liquid crystalline behaviour is clearly highlighted by a comparison of the phase behaviour for the structurally isomeric 5.O$n$O.5 series with no methyl branches in their terminal pentyl chains [see Fig. 1(b)].[11] We see that the 5.O$n$O.5 series has higher clearing temperatures and exhibits a greater smectic polymorphism than their branched analogues. The smaller values for the branched compounds may be due to the methyl branch in the alkyl chain, which tends to reduce the structural anisotropy and, in addition, the lateral interactions responsible for smectic phase stabilisation.[17] Furthermore, the effect is known to be greatest for methyl branches close to the mesogenic core.[17] Normally the insertion of a methyl branch also leads to a reduction in the melting point of the material and yet strangely for this series the reverse is the case. This result is hard to explain and presumably reflects a greater packing ability in the crystal phase for the branched dimers compared to their unbranched analogues. From a comparison of Figs. 1(a) and (b) we also notice that the magnitude of the odd–even effect for the clearing temperatures is slightly greater for the branched dimers. The contrasting liquid crystalline behaviour for the two series is further highlighted in Fig. 2, which shows the difference in the transition temperatures [$T$(2MB.O$n$O.2MB) − $T$(5.O$n$O.5)] *versus* the number of methylene units $n$ in the flexible alkyl spacer. The results show an odd–even effect for the differences in the clearing temperatures which diminishes across the series and also emphasises the considerably higher melting points for the branched dimers. The attenuation of the differences in the clearing temperatures across the series appears to reflect the diminishing effect of the methyl branch on the length-to-breadth ratio, that is the shape anisotropy, as the spacer is lengthened. The entropy changes at the clearing point could only be measured for the $n=4,6,8$ and 10 homologues of the 2MB.O$n$O.2MB series and they are all lower than their unbranched analogues[11] (see Fig. 3). This is strange but not unknown, as lateral substitution has also been shown to have an effect on the clearing entropy change. For example, the α,ω-bis[4-(2,4-dimethylphenyliminomethyl)-phenoxy]alkanes have been found to exhibit a reduced



**Fig. 2** The difference [$T$(2MB.O$n$O.2MB) − $T$(5.O$n$O.5)] between the melting (○) and clearing (●) temperatures for the 2MB.O$n$O.2MB and 5.O$n$O.5 series as a function of the number of methylene groups $n$ in the spacer
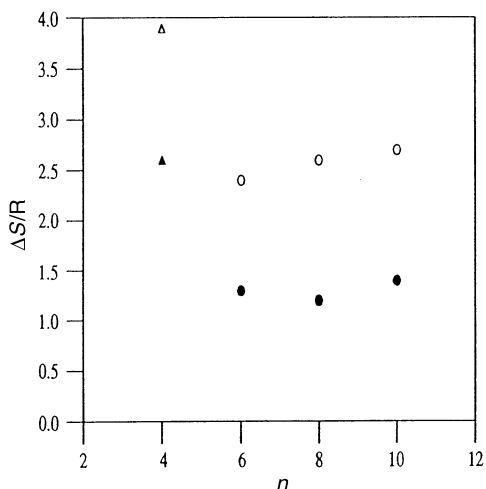
Fig. 3 The influence of the number of methylene groups $n$ in the flexible alkyl spacer on the clearing entropies of transition for the $n=$ 4,6,8 and 10 members of the 2MB.OnO.2MB series [$S_A$–I (▲), N–I (●)] and the 5.OnO.5 series [$S_A$–I (△), N–I (○)]

nematic-to-isotropic entropy change, which was attributed to either an increase in the molecular biaxiality or a reduction in the conjugation of the mesogenic core.[18] From Fig. 3 we see that the differences between the entropy changes for the unbranched and branched compounds are constant for both the nematic-to-isotropic and smectic A-to-isotropic transitions. It would appear that the difference in the average conformation of both odd- and even-membered dimers in the isotropic and nematic phases is somewhat less pronounced for the branched dimers compared to their unbranched counterparts. The lower clearing entropy changes for the branched dimers might also be a consequence of the increased molecular biaxiality, resulting from a decreased length-to-breadth ratio relative to their unbranched analogues.

**The CBOnO.2MB series: the non-symmetric dimers.** Table 2 gives the transition temperatures, enthalpies and entropies of transition for the CBOnO.2MB series. Smectic A and nematic phases are exhibited by the members of the series and were characterised, as before, by polarizing microscopy. All but one of the homologues are enantiotropic mesogens; the $n=3$ member exhibits a nematic phase just 12 °C below the melting point. Fig. 4(a) shows the effect of changing the number of methylene groups in the spacer on the liquid crystalline properties of this series. Both the smectic A-to-nematic and nematic-to-isotropic transitions show the anticipated odd–even effect across the series. The $n=6$–12 homologues all form a smectic A phase, the stability of which increases as the series is ascended such that it clears directly into the isotropic phase
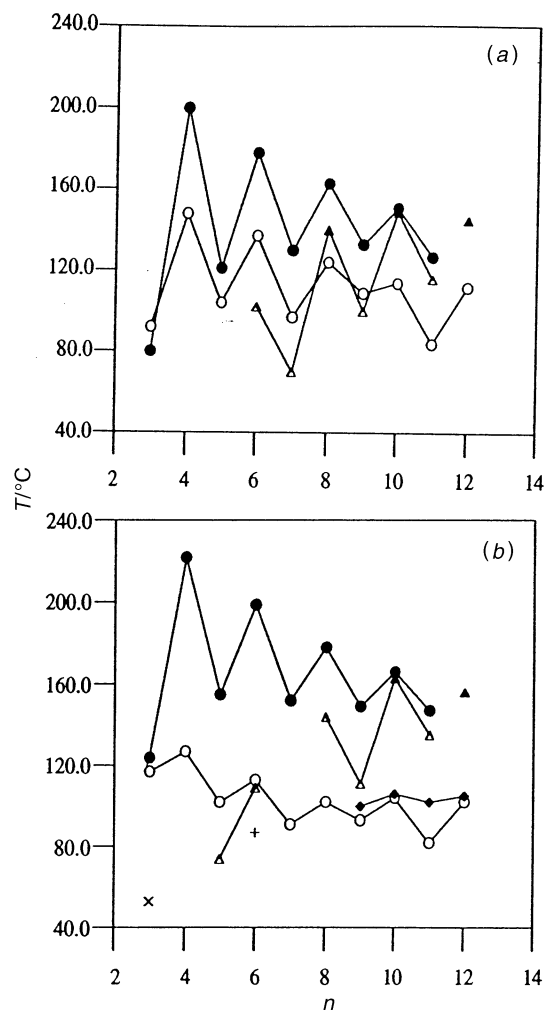


Fig. 4 The influence of the number of methylene groups $n$ in the flexible alkyl spacer on the transition temperatures for (a) the CBOnO.2MB and (b) the CBOnO.5 series. C–(○), $S_A$–I (▲), $S_A$–N (△), N–I (●), $S_I$–$S_A$ (+), $S_B$–$S_A$ (◆), $S_I$–N (x).

for the $n=12$ homologue. The improved stability of the smectic A phase as the spacer is lengthened, which is not observed for symmetric dimers, is well-known for non-symmetric dimers of this type.[12,13] X-Ray diffraction studies of aligned smectic A phases of the $n=8$ and 11 homologues and a powder sample of the $n=12$ homologue all gave smectic periodicities equal to approximately half their all-*trans* molecular lengths as measured from CPK molecular models (see Table 3). These results indicate that the smectic A phases have an intercalated structure (see Fig. 5) and are comparable to

Table 2 Transition temperatures, enthalpies and entropies of transition for the racemic CBOnO.2MB series. Parentheses indicate a monotropic transition
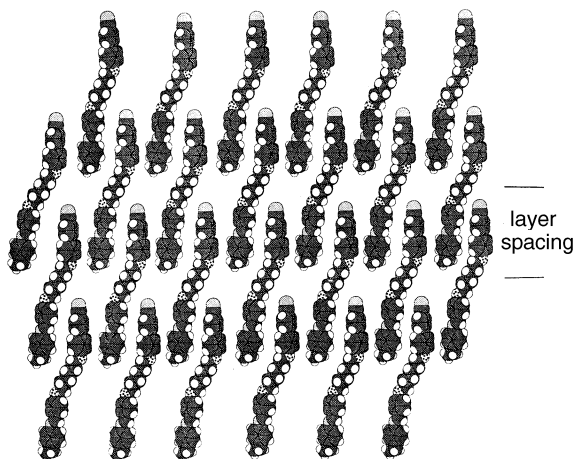
| $n$ | T/°C | | | $\Delta H$/kJ mol$^{-1}$ | | | $\Delta S/R$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | C– | $S_A$–N | N–I | C– | $S_A$–N | N–I | C– | $S_A$–N | N–I |
| 3 | 92 | | (80) | 25.0 | | (0.3) | 8.3 | | (0.1) |
| 4 | 148 | | 200 | 32.0 | | 4.0 | 9.2 | | 1.0 |
| 5 | 104 | | 121 | 31.2 | | 0.5 | 10.0 | | 0.1 |
| 6 | 137 | (102) | 178 | 29.3 | (0.4) | 4.2 | 8.6 | (0.1) | 1.1 |
| 7 | 97 | (70) | 130 | 48.0 | (3.9) | 0.6 | 16.0 | (1.4) | 0.2 |
| 8 | 124 | 140 | 163 | 32.4 | 2.2 | 5.0 | 9.8 | 0.6 | 1.4 |
| 9 | 109 | (100) | 133 | 40.0 | (3.7) | 1.3 | 13.0 | (1.2) | 0.4 |
| 10 | 114 | 149 | 151 | 41.4 | 3.5 | 2.9 | 13.0 | 1.0 | 0.8 |
| 11 | 84 | 116 | 127 | 28.4 | 2.8 | 2.4 | 9.6 | 0.9 | 0.7 |
| 12 | 112 | | 145$^a$ | 48.4 | | 14.0$^a$ | 15.0 | | 4.0$^a$ |

$^a$$S_A$–I transition.

**Table 3** Smectic periodicity $d$ of some members of the CBO$n$O.2MB and CBO$n$O.5 series measured by X-ray diffraction. The values are compared to their all-*trans* molecular lengths $l$ as estimated from CPK molecular models

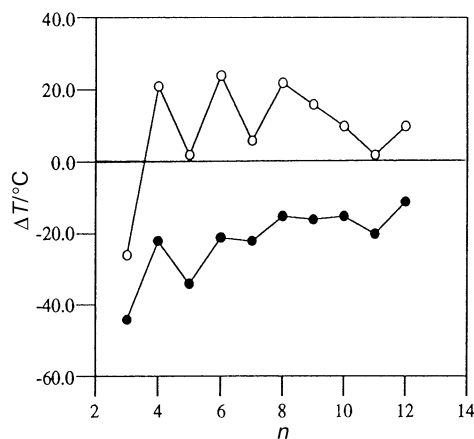| Compound | $l/\text{Å}$ | $d/\text{Å}$ | $d/l$ |
| --- | --- | --- | --- |
| CBO8O.2MB | 39.1 | 18.9 | 0.48 |
| CBO11O.2MB | 41.4 | 21.4 | 0.52 |
| CBO12O.2MB | 44.0 | 21.6 | 0.49 |
| CBO6O.5[a] | 38.0 | 19.5 | 0.51 |
| CBO9O.5 | 40.2 | 20.1 | 0.50 |
| CBO12O.5 | 45.0 | 21.9 | 0.49 |
| CBO12O.5[b] | 45.0 | 24.8 | 0.55 |

[a]Taken from ref. 12. [b]Smectic B phase.



**Fig. 5** A schematic representation of the proposed molecular organisation in the intercalated smectic A phase (ref. 13)



**Fig. 6** The difference $[T(\text{CBO}n\text{O.2MB}) - T(\text{CBO}n\text{O.5})]$ between the melting ($\bigcirc$) and clearing ($\bullet$) temperatures for the CBO$n$O.2MB and CBO$n$O.5 series as a function of the number of methylene groups $n$ in the spacer
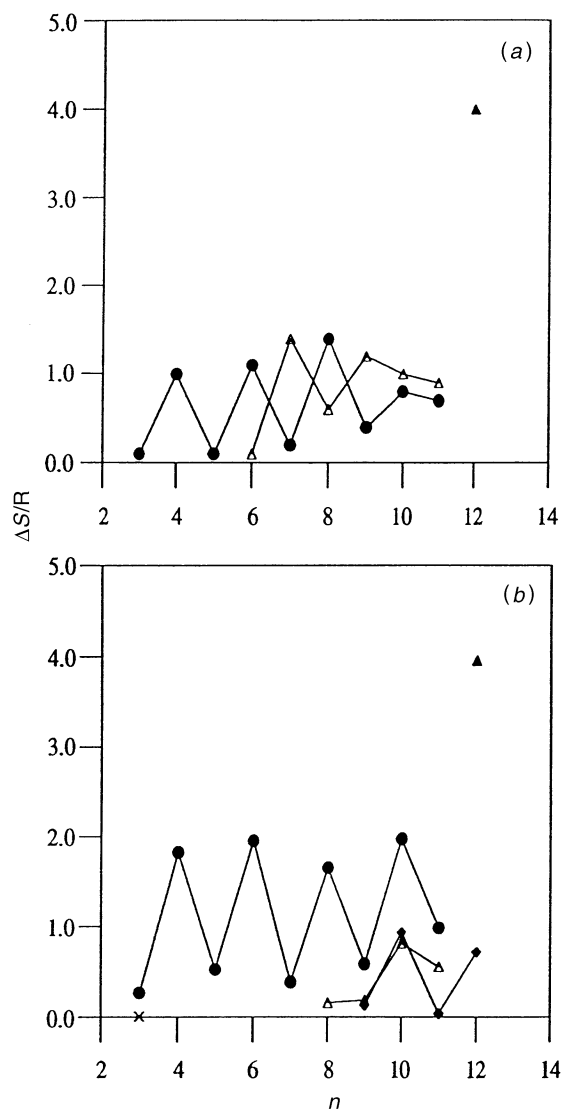
the measured smectic periodicities of similar compounds previously reported.[12,13] The proposed structure of the intercalated smectic phase shown in Fig. 5 is thought to result from a specific interaction between the unlike mesogenic cores[19] enhanced by an entropy gain resulting from the uniform mixing of such groups.[20] In addition, the stability of these phases is expected to be influenced by the amount of space between the mesogenic groups available to accommodate the terminal alkyl chain; an intercalated smectic phase is likely if the terminal alkyl chain can be accommodated in this space. Thus the increase in thermal stability of the intercalated smectic A phase for the CBO$n$O.2MB series as the spacer length grows can be attributed to the increasing amount of space available to the 2-methylbutyl chain. However, a smectic A phase is not observed for the $n = 3–5$ homologues as the space available to the 2-methylbutyl group is presumably insufficient. We should note that another somewhat more exotic model has recently been proposed for the rationalisation of the properties of the smectic A phase of non-symmetric mesogens; in this the molecules are depicted as adopting a hairpin or horseshoe conformation.[20] Thus a thorough and definitive understanding of the structure of the intercalated smectic A phase remains unavailable.

The effect of the methyl branch on the transition temperatures of the CBO$n$O.2MB series is clearly seen if we compare them with those of their structural analogues, the CBO$n$O.5 series. Fig. 4(*b*) shows the dependence of the transition temperatures of the CBO$n$O.5 compounds on the number of methylene units in the spacer. We see that not only do the CBO$n$O.5 species have higher clearing temperatures but, in addition to smectic A and nematic phases, they also exhibit smectic B phases, as indicated by the smoothness of the focal-conic fans in their optical textures. As mentioned previously the greater smectic polymorphism is consistent with the stronger lateral

interactions of the CBO$n$O.5 series compared to their branched analogues. The monotropic smectic phases exhibited by the $n = 3,5$ and 6 homologues could not be identified as they were only observed fleetingly on rapidly cooling the isotropic liquid prior to crystallization. The periodicities of the smectic A phases for the $n = 6$ and 9 homologues of the CBO$n$O.5 series were determined by X-ray diffraction and these phases were found to be intercalated as was the smectic B phase of the $n = 12$ homologue. Fig. 6 shows the difference between the melting and clearing temperatures for the two series $[T(\text{CBO}n\text{O.2MB}) - T(\text{CBO}n\text{O.5})]$ as a function of the number of methylene units $n$ in the spacer. Apart from the $n = 3$ homologue, we see that the melting points of the CBO$n$O.5 series are lower than those of the CBO$n$O.2MB series; a similar difference was observed for the 2MB.O$n$O.2MB and 5.O$n$O.5 series. Again the higher melting points for the branched dimers are hard to explain and we can only speculate that perhaps the methyl branch helps fill space more efficiently in the crystal phase than for dimers without branches in their terminal alkyl chains. The difference in the clearing temperatures exhibits an odd–even effect which is attenuated across the series and again reflects the diminishing effect of the methyl branch on the length-to-breadth ratio as the spacer length grows. The magnitude of the odd–even effect for the clearing temperatures is again slightly greater for the branched dimers. Fig. 7 shows the transitional entropies as the number of methylene units $n$ in the spacer is varied for the CBO$n$O.2MB and CBO$n$O.5 series. We see that for both series the smectic A-to-nematic and the nematic-to-isotropic transitional entropies exhibit an odd–even effect. The nematic-to-isotropic entropy changes are all smaller for the CBO$n$O.2MB series, with some of the odd-membered homologues possessing particularly small entropies of transition, which suggest incipient biaxial nematic behaviour.[21] Interestingly, the odd–even effect for the smectic A-to-nematic transitional entropies of the CBO$n$O.2MB series has an opposite sense to that of the CBO$n$O.5 series. Indeed, the entropy changes for the smectic A-to-nematic transitions do not agree with those expected from the ratio of the smectic A-to-nematic and nematic-to-isotropic transition temperatures.[22] Thus, when the difference between the smectic A-to-nematic and nematic-to-isotropic transition temperatures is large it does not always follow that the entropy change for the smectic A-to-nematic transition is small, as the heptane homologue shows (see Table 4). Such behaviour is hard to rationalise and might be a consequence of the restricted conformational freedom of the 2-methylbutyl group.

**Fig. 7** The influence of the number of methylene groups $n$ in the flexible alkyl spacer on the entropies of transition for (a) the CBO$n$O.2MB and (b) the CBO$n$O.5 series. $S_A$–N ($\triangle$), N–I ($\bullet$), $S_A$–I ($\blacktriangle$), $S_B$–$S_A$ ($\blacklozenge$), $S_I$–N (x).

**Table 4** Comparison of the ratio of the smectic A-to-nematic to nematic-to-isotropic transition temperatures *versus* the smectic A-to-nematic entropy of transition for the CBO$n$O.2MB series

| $n$ | $T_{S_A-N}/T_{N-I}$ | $\Delta S_{S_A-N}/R$ |
|---|---|---|
| 6 | 0.831 | 0.1 |
| 7 | 0.851 | 1.4 |
| 8 | 0.947 | 0.6 |
| 9 | 0.915 | 1.2 |
| 10 | 0.995 | 1.0 |
| 11 | 0.973 | 0.9 |

**The chiral dimers**

**The ($S$)2MB.O$n$O.($S$)2MB series: the symmetric dimers.** The transition temperatures, enthalpies and entropies for the $n=6$ and 8 homologues of the ($S$)2MB.O$n$O.($S$)2MB series are given in Table 5. We see that, as expected, the data are similar to those for the racemic analogues. On cooling the $n=6$ and 8 homologues, a focal-conic fan texture is obtained which, when sheared, gave the Grandjean texture which is indicative of a chiral nematic phase. On cooling the chiral nematic phase of the $n=6$ homologue a change to a focal-conic fan coexistent with a homeotropic texture occurred which was characterized as that of a smectic A phase. On slow heating (0.2 °C min$^{-1}$)

bright threads appear in the homeotropic regions of the smectic A phase which thicken as the temperature is increased. The resulting web-like structure then coalesces into the Grandjean texture. Similar effects have been observed for the chiral, monomeric analogues.[9] The sense of the chiral helix was determined to be dextrorotatory by contact preparations with the laevorotatory compound cholesteryl benzoate (C 150 °C N* 178 °C I, Eastman Kodak Co., Rochester, USA) which showed a nematic phase at the junction of the two components.[23] This result agrees with the Gray and McDonnell rules,[24] which state that for an $S$ absolute configuration the sense of the chirality should be dextrorotatory when the chiral centre is an even number of atoms away from the mesogenic group, and laevorotatory when it is an odd number of atoms away. As these rules were devised principally for monomeric liquid crystals, we have overcome the problem of counting the number of atoms between the chiral centre and the mesogenic group in dimers by simply splitting the dimer into its constituent monomeric parts. Since the chiral nematic phase of 2MB.O6O.2MB is monotropic and that of 2MB.O8O.2MB has a very short range, we have not determined the wavelength of selective reflection for the pure materials. However, we have obtained an indication of the form chirality of these two chiral symmetric dimers by measuring their helical twisting powers $\beta_M$.[25] This is achieved by plotting the inverse of the pitch $p$ of the induced chiral nematic phase as a function of the solute concentration. According to theory,[26] $p^{-1}$ should be linear in the solute concentration which is best expressed as the mole fraction $x$,[27] although claims to have found a better linearity with the weight fraction have been made.[28] However, for the low concentrations used in most measurements, both methods of expressing the solute concentration give linear plots and so we shall use the mole fraction [eqn. (1)].

$$\beta_M = p^{-1}/x \qquad (1)$$

The mole fractions for the solutions were calculated using an average molar mass for the nematic solvent E7 of 271 g since this is a mixture of cyanobiphenyls.

The helical twisting powers obtained in this way for the hexane and octane dimers are given in Table 5. We see that they are the same (12.5 μm$^{-1}$) which is not so surprising because theory suggests[29] that the helical twisting power is proportional to the scalar product of the ordering shape tensor of the chiral solute and the chiral shape tensor. Since the two dimers have a similar structure and their nematic-to-isotropic transitional entropies are the same (see Table 1), it might be expected that their orientational order in a common solvent would be similar. What is surprising is that the helical twisting powers of monomers with the same chiral 2-methylbutyl group in the same nematic solvent is essentially half that for the two dimers.[30] This is unexpected because the orientational order of the monomer is much less than that of an even-membered dimer in the same nematic solvent.[31] As a consequence, after allowing for the presence of two chiral centres in the dimers, their $\beta_M$ values should be greater than twice that for a monomer. We shall return to this point when we consider the helical twisting powers for the chiral non-symmetric dimers in the following section.

**The CBO$n$O.($S$)2MB series: the non-symmetric dimers.** Table 6 presents the transition temperatures, enthalpies and entropies of transition for the phase behaviour of the $n=6$ to 9 homologues of the CBO$n$O.($S$)2MB series. The transition temperatures as well as the clearing entropy changes agree closely with those of the analogous racemic compounds, as expected. On slow cooling of the isotropic liquid for the $n=6$ and 8 homologues the focal-conic fan texture of the chiral nematic phase forms which, when sheared, showed the oily streaks characteristic of the Grandjean plane texture. In contrast, the $n=7$ and 9 homologues show different behaviour.

**Table 5** Transition temperatures, enthalpies and entropies of transition for the chiral $(S)$2MB.O$n$O.$(S)$2MB series. Parentheses indicate a monotropic transition

| $n$ | $T/°C$ | | | $\Delta H$/kJ mol$^{-1}$ | | | $\Delta S/R$ | | | $\beta_M/\mu m^{-1}$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | C– | S$_A$–N* | N*–I | C– | S$_A$–N* | N*–I | C– | S$_A$–N* | N*–I | |
| 6 | 149 | (138) | (148) | 49.3 | 0.8 | 4.6 | 14.1 | 0.2 | 1.3 | 12.5 |
| 8 | 127 | | 131 | 42.0 | | 4.3 | 12.6 | | 1.3 | 12.5 |

**Table 6** Transition temperatures, enthalpies and entropies of transition for the chiral CBO$n$O.$(S)$2MB series. Parentheses indicate a monotropic transition
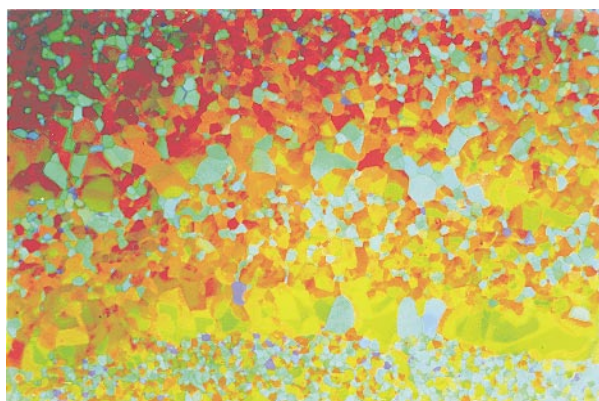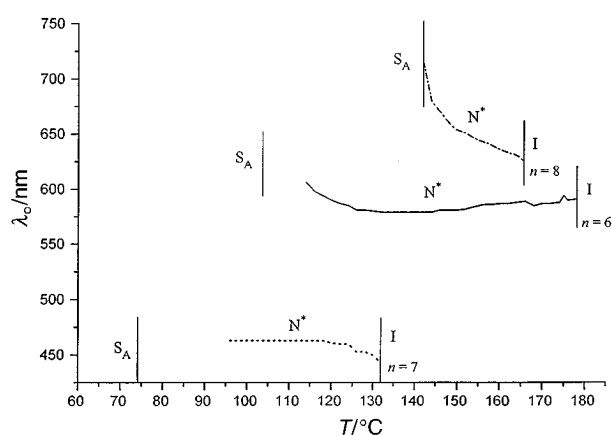
| $n$ | $T/°C$ | | | | $\Delta H$/kJ mol$^{-1}$ | | | $\Delta S/R$ | | | $\beta_M/\mu m^{-1}$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | C– | S$_A$–N* | N*–BPI | BPI–I | C– | S$_A$–N* | N*–I | C– | S$_A$–N* | N*–I | |
| 6 | 137 | (104) | | 176$^a$ | 32.0 | 0.7 | 4.5 | 9.4 | 0.2 | 1.2 | 5.6 |
| 7 | 97 | (74) | 131.5$^b$ | 131.9$^b$ | 45.8 | 4.3 | 0.7 | 15.0 | 1.5 | 0.2 | 5.9 |
| 8 | 128 | 143 | | 165$^a$ | 36.3 | 1.9 | 5.1 | 11.0 | 0.6 | 1.5 | 6.7 |
| 9 | 110 | (102) | 132.2$^b$ | 132.8$^b$ | 45.2 | 3.8 | 1.3 | 14.0 | 1.2 | 0.4 | $^c$ |

$^a$N*–I transition. $^b$Transition could only be observed by polarising microscopy. $^c$Value was not measured.

On slow cooling (0.2 °C min$^{-1}$) the isotropic liquid is seen to exhibit a homeotropic blue colour of low birefringence before a platelet texture composed of blue and red plates quickly grows; crinkled lines between the plates are clearly observed and this is indicative of blue phase I (Plate 1). The transition to the blue phase could not be detected by DSC. If the blue phase is submitted to mechanical stress the Grandjean plane texture forms. The thermal range of blue phase I is 0.4 and 0.6 °C for the $n=7$ and 9 homologues, respectively. At the smectic A-to-chiral nematic transition bâtonnets form which coalesce into the smectic A focal-conic fan texture. There was no indication from the optical texture that the smectic A phase was of the twist grain boundary (TGB) type.[32] Indeed, the intercalated nature of the smectic A phase might well inhibit the layers from twisting into a helix. The sense of the helix in the chiral nematic phase was determined to be dextrorotatory for all four compounds by contact preparations with cholesteryl benzoate and again this agrees with the Gray and McDonnell rules. The helical pitch $p$ can be determined from the central wavelength $\lambda_o$ of the peak in the UV–VIS spectrum obtained for normal incidence, but to do this it is necessary to know the mean refractive index of the material $n$ since $p=\lambda_o/n$.[33] As we do not have accurate values for the refractive indices of the dimers which we have studied we shall discuss instead the wavelength of the maximum reflection. This has been measured for the chiral non-symmetric dimers CBO$n$O.2MB with both odd and even spacers ($n=6$, 7 and 8) and the results are plotted as a function of temperature in Fig. 8. Since the mean refractive index is not expected to change significantly with



**Fig. 8** The temperature dependence of the wavelength $\lambda_o$ of maximum reflection for the chiral non-symmetric dimers CBO$n$O.2MB with $n=$ 6,7 and 8. The nature of the phases and the transitions between them are also shown.



**Plate 1** The blue phase I platelet texture of CBO7O.2MB on cooling from the isotropic phase (0.2 °C min$^{-1}$); $T=131.7$ °C, magnification $\times 200$

the spacer the results for the wavelengths show that the helical pitch for the odd dimer is significantly smaller than for the two even dimers, even allowing for the pretransitional growth in $p$ for these compounds. Analogous results have been found for the non-symmetric dimers formed by linking a cyanobiphenyl group to either a cholesteryl[34] or a dihydrocholesteryl group.[35] Such a difference in the pitch for odd and even chiral dimers can be understood in terms of their elastic properties. It is to be expected that just as the pitch of an induced chiral nematic phase is proportional to the twist elastic constant of the nematic solvent,[29] so the pitch of the pure chiral nematic would be proportional to its twist elastic constant. Although the elastic constants have not been determined for the dimers which we have studied, results are available for analogous systems.[36] These show that the twist elastic constant for a dimer with an odd spacer is about half as large as that for a neighbouring dimer with an even spacer. This difference is in accord with the higher orientational order found for even dimers in comparison with their odd counterparts.[8] We see, therefore, that the smaller pitch found for the odd dimer can be understood in terms of the lower twist elastic constant and orientational order found for the odd dimers relative to the even. This relationship would then suggest that the increase in the helical pitch with the length of the even spacer shown by our results is caused by a corresponding increase in the twist elastic constant. However, we should note that this trend is reversed for the cyanobiphenyl-cholesteryl dimers, where the

pitch appears to decrease with increasing length of the even spacer.[34] This would, then, imply a decrease in the twist elastic constant.

The small value of the pitch found for the chiral non-symmetric dimer with an odd spacer is consistent with the observation of a blue phase for the two odd dimers, but not for those with even spacers. Experimentally, the temperature range over which the blue phase exists is found to decrease with an increase in the helical pitch.[37] The critical value of the pitch at which the blue phase vanishes depends on the molecular structure; for cholesteryl alkanoates it is about 300 nm, whereas for mixtures of chiral and achiral materials it is approximately 400 nm. If the mean refractive index is taken to be approximately 1.5 then the pitch for the odd dimer is about 300 nm, whereas for the even dimers $p$ is about 430 nm. The critical pitch for the chiral non-symmetric dimers is between these two values, in reasonable agreement with results found for chiral monomers.[37] In concluding our discussion of the helical pitch, we should comment on its temperature dependence. For the odd dimer (CBO7O.2MB) the pitch increases slightly from the chiral nematic-to-isotropic transition, but then is essentially independent of temperature. It was not possible to make measurements near the monotropic $S_A$–N* transition because the sample crystallised. However, the relatively high transitional entropy (see Table 6) suggests that the pretransitional growth in the pitch would be weak. In contrast, the entropy change at the smectic A-to-chiral nematic transition is relatively small for the even dimers (see Table 6) and so the pretransitional growth in the pitch is expected to be strong. This is certainly the case for CBO8O.2MB, where it was possible to make measurements very close to the transition to the smectic A phase (see Fig. 8). For the other even dimer, CBO6O.2MB, the pitch is essentially constant over most of the wide chiral nematic range. However, it then starts to grow as the monotropic transition to the smectic A phase is approached, but the sample crystallises before the pitch can become very large. Such pretransitional growth in the pitch, which is observed for the even dimers, is typical of that found for monomers when the smectic A-to-chiral nematic transition is weak.

For comparison with the results for the chiral symmetric dimers, we have also determined the helical twisting powers of the chiral non-symmetric dimers with hexane, heptane and octane spacers. The results are given in Table 6 and we see that $\beta_M$ is about 6 μm$^{-1}$ for these dimers, which is essentially half the value found for the analogous symmetric dimers with two 2-methylbutyl groups. It is also approximately the same as for monomers with the same chiral centre.[30] These results also support the view that it is the nature of the chiral centre which seems to control the helical twisting power and not the anisotropy of the group to which it is attached. Such an explanation is at variance with theory,[29] and an alternative interpretation might be that as the anisotropy of the group attached to the chiral centre grows, the increase in the orientational ordering tensor is compensated for by a decrease in the chiral ordering tensor. It remains to be seen whether such an explanation is correct. Although the $\beta_M$ values for the non-symmetric dimers are essentially constant, there is a slight increase with the length of the spacer. There is not, however, any indication of an odd–even effect for the helical twisting power. This is in marked contrast with the behaviour of the helical pitch, for which a strong dependence on the parity of the spacer is found. Such an observation emphasises the fact that the helical twisting power can be a poor indicator of the form chirality of the chiral nematic phase exhibited by the pure chiral solute.

## Conclusions

The structure–property relationships of two series of dimers, one symmetric, the other non-symmetric, with branched ter-minal alkyl chains have been presented. The branched chains have a marked effect on the liquid crystal properties of the 2MB.OnO.2MB series, as they exhibited lower clearing temperatures and a reduced smectic polymorphism with respect to their unbranched analogues, the 5.OnO.5 series. Indeed, the nematic-to-isotropic transition temperatures of some homologues of the 2MB.OnO.2MB series were so far below the melting point that they could only be measured by supercooling small, isolated isotropic droplets. In contrast, for the CBOnO.2MB series the inclusion of a branched terminal alkyl chain led to a less dramatic reduction in the clearing temperatures and smectic polymorphism (as compared to their straight chain analogues the CBOnO.5 series), presumably because only one branched terminal alkyl chain is involved. X-Ray diffraction studies of the $n = 8$, 11 and 12 homologues of the CBOnO.2MB series showed their smectic A phases to be intercalated as expected for non-symmetric dimers of this type. Of the chiral compounds studied, those of the CBOnO.(S)2MB series possessed the most interesting properties. Four homologues were synthesized with the number of methylene units in the flexible alkyl spacer ranging from 6 to 9. An interesting odd–even effect was observed for the chiral properties of these materials. Blue phase I behaviour was only observed for the odd non-symmetric dimers and not their even spacer counterparts. This marked difference is consistent with the smaller pitch found for the odd dimer relative to the even dimers. This can be related to the smaller twist elastic constant of the odd dimers, which is related to their lower orientational order. In contrast to this strong odd–even effect, the helical twisting powers of the dimers seem to depend solely on the nature of the 2-methylbutyl chiral centre and not on the details of the remaining molecular structure.

## References

1  F. Reinitzer, *Monatsh. Chem.*, 1888, **9**, 421.
2  See for example, J. W. Goodby, I. Nishiyama, A. J. Slaney, C. J. Booth and K. J. Toyne, *Liq. Cryst.*, 1993, **14**, 37 and references cited therein.
3  S. Chandrasekhar, *Liquid Crystals*, 2nd edn., Cambridge University Press, 1992, ch. 4 and 5.
4  J. Barberá, A. Omenat and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, 1989, **166**, 167.
5  J. Barberá, A. Omenat, J. L. Serrano and T. Sierra, *Liq. Cryst.*, 1989, **5**, 1775.
6  G. Heppke, D. Lötzsch and F. Oestreicher, *Z. Naturforsch., Teil A: Phys. Sci.*, 1987, **42**, 279.
7  K. Shiraishi, K. Kato and K. Sugiyama, *Chem. Lett.*, 1990, 971.
8  J. W. Emsley, G. R. Luckhurst and G. N. Shilstone, *Mol. Phys.*, 1984, **53**, 1023.
9  D. Dolphin, Z. Muljiani, J. Cheng and R. B. Meyer, *J. Chem. Phys.*, 1973, **58**, 413.
10  Y. Y. Hsu and D. Dolphin, *Mol. Cryst. Liq. Cryst.*, 1977, **42**, 327.
11  R. W. Date, C. T. Imrie, G. R. Luckhurst and J. M. Seddon, *Liq. Cryst.*, 1992, **12**, 203.
12  J. L. Hogan, C. T. Imrie and G. R. Luckhurst, *Liq. Cryst.*, 1988, **3**, 645.
13  G. S. Attard, R. W. Date, C. T. Imrie, G. R. Luckhurst, S. J. Roskilly, J. M. Seddon and L. Taylor, *Liq. Cryst.*, 1994, **16**, 529.
14  P. Keller and L. Liebert, *Solid State Phys.*, 1978, Suppl. 14, 19.
15  See for example, H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, 1980, ch. 7 and references cited therein.
16  R. Cano, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1968, **91**, 20.
17  See for example, G. W. Gray, *Liquid Crystals and Plastic Crystals*, eds. G. W. Gray and P. A. Winsor, Ellis Horwood, 1974, vol. 1, ch. 4.

18   C. T. Imrie, *Liq. Cryst.*, 1989, **6**, 391.
19   J. W. Park, C. S. Bak and M. M. Labes, *J. Am. Chem. Soc.*, 1975, **97**, 4398.
20   A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *Liq. Cryst.*, 1995, **18**, 801.
21   M. J. Freiser, *Phys. Rev. Lett.*, 1970, **24**, 1041.
22   W. J. McMillan, *Phys. Rev. A*, 1972, **6**, 936.
23   See for example, H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, 1980, ch. 1 and references cited therein.
24   G. W. Gray and D. G. McDonnell, *Electron. Lett.*, 1975, **11**, 556.
25   See for example, G. Solladie and R. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 328.
26   W. J. A. Goossens, *Mol. Cryst. Liq. Cryst.*, 1971, **12**, 237.
27   J. M. Ruxer, G. Solladie and S. Candau, *Mol. Cryst. Liq. Cryst. Lett. Sect.*, 1978, **41**, 109.
28   M. Tsukamoto, T. Ohtsuka, K. Morimoto and Y. Murakami, *Jpn. J. Appl. Phys.*, 1975, **14**, 1307.
29   A. Ferrarini, G. J. Moro and P. L. Nordio, *Liq. Cryst.*, 1995, **19**, 397.
30   M. J. Goulding, PhD Thesis, 1995, University of Southampton.
31   P. J. Le Masurier, G. R. Luckhurst, S. J. Roskilly and G. Saielli, unpublished data.
32   J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *J. Am. Chem. Soc.*, 1989, **111**, 8119.
33   See for example, N. H. Hartshorne, *Liquid Crystals and Plastic Crystals*, eds. G. W. Gray and P. A. Winsor, Ellis Horwood, 1974, vol. 2, ch. 2.
34   A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Rec. Trav. Chim. Pays-Bas*, 1994, **113**, 524.
35   A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Liq. Cryst.*, 1995, **18**, 843.
36   G. A. DiLisi, E. M. Terentjev, A. C. Griffin and C. Rosenblatt, *J. Phys. II*, 1993, **3**, 597.
37   H. Stegemeyer, T. Blumel, K. Hiltrop, H. Onusseit and F. Porsch, *Liq. Cryst.*, 1986, **1**, 1.