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Oligomeric liquid crystals: From monomers to trimers

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Oligomeric liquid crystals: From monomers to trimers

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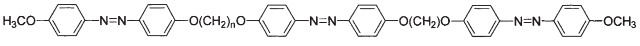
A homologous series of linear liquid crystal trimers, the 4,4′-bis[ω-(4-methoxyazobenzene-4′-yloxy)alkoxy]azobenzenes, has been synthesized and characterized. The transitional properties of the trimers are compared with those of the corresponding series of dimers, the α,ω-bis(4-methoxyazobenzene-4′-oxy)alkanes, and monomers, the 4-methoxy-4′-alkoxyazobenzenes. Characteristically pronounced odd–even effects were seen for the transitional properties of both dimers and trimers on varying the spacer lengths. The clearing temperatures of the trimers were higher than those of the corresponding dimers, but as the length of the flexible spacers was increased this difference became rather small. The ratios of T_{NI}, and $\Delta S_{NI}/R$ for monomer:dimer and dimer:trimer are discussed. These are very similar to reported values for similar materials, suggesting that there may be a rather general relationship between the transitional properties of liquid crystal oligomers as the number of mesogenic units is increased.

1. Introduction

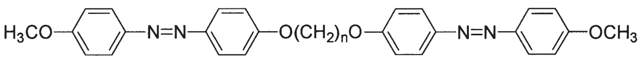
Liquid crystal trimers consist of molecules containing three mesogenic units joined by two flexible spacers [1–3]. A number of differing molecular architectures is possible for liquid crystal trimers; for example, linear [4–18], terminally/laterally connected [19–21], cyclic [22, 23], tribranched/star-shaped [24–30] and mixed calamitic/discotic trimers [19, 31, 32].

The interest in linear trimers arises not only from their potential to serve as model compounds for semi-flexible main chain polymers [1–3], but also because, like dimers, they may exhibit properties quite different from those of conventional low molar mass mesogens. Of particular interest is to establish how transitional properties evolve from conventional low molar mass mesogens through oligomers such as dimers and trimers to polymers. There are relatively few examples of linear liquid crystal trimers in the literature [4–12] and even fewer complete homologous series [9–11].

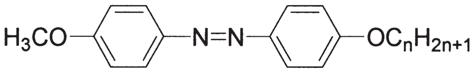
Thus, this paper describes the synthesis and transitional behaviour of a homologous series of linear liquid crystal trimers, the 4,4′-bis[ω-(4-methoxyazobenzene-4′-yloxy)alkoxy]azobenzenes,



These are referred to using the acronym 3Azo-*n*, where *n* refers to the number of methylene units in the flexible alkyl spacers. We also report the synthesis and properties of the corresponding dimers, the α,ω-bis (4-methoxyazobenzene-4′-oxy)alkanes,



These series were chosen because the properties of the corresponding monomers, the 4-methoxy-4′-alkoxyazobenzenes [33], have already been reported,



The acronyms used to describe the monomers and dimers are Azo-*n* and 2Azo-*n*, respectively, where *n* refers to the number of carbon atoms in the terminal chain of the Azo-*n* series and to the number of methylene units in the flexible spacer of the 2Azo-*n* series.

2. Experimental

The synthetic route for the dimers and trimers is shown in the scheme. 4-Methoxy-4′-hydroxyazobenzene, **1**, was synthesized according to the method described by Stewart and Imrie [34], and the α-bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes, **2**, were synthesized using the method described by Attard *et al.* [35].

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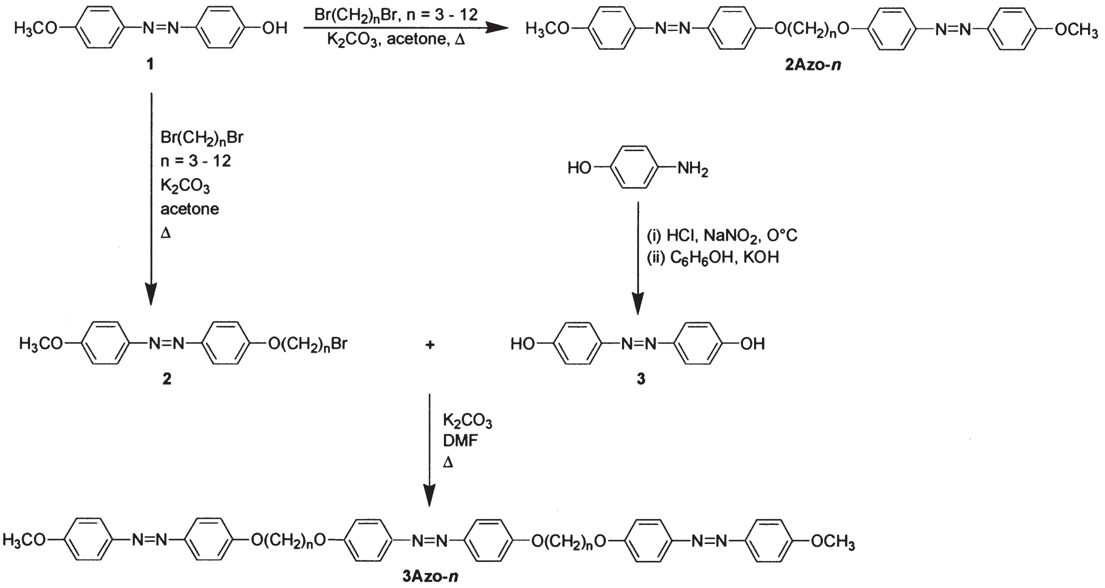

Scheme. Synthesis of the 2Azo-*n* and 3Azo-*n* series.

Several of the α-bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes were liquid crystalline and their properties are discussed in the results section. 4,4′-Dihydroxyazobenzene, **3**, was synthesized according to the method of Vanoppen *et al.* [36]. A representative method is given for the dimer, 1,8-bis(4-methoxyazobenzene-4′-oxy)octane, 2Azo-8, and for the trimer 4,4′-bis[3-(4-methoxyazobenzene-4′-yloxy)propoxy]azobenzene, 3Azo-3.

2.1. *Synthesis of 2Azo-8*

A mixture of 4-methoxy-4′-hydroxyazobenzene, **2**, (1.14 g, 5.0 mmol), 1-bromo-8-(4-methoxyazobenzene-4′-oxy)octane, **2**, (0.68 g, 2.5 mmol), and potassium carbonate (2.64 g, 20.0 mmol) in DMF (20 ml) was heated at reflux overnight. The reaction mixture was cooled and added to water (100 ml). The resulting precipitate was collected and dried prior to recrystallization twice from toluene to yield the product as a yellow powder (40%). Due to the insolubility of this in appropriate organic solvents NMR data were not obtained. IR (KBr) ν (cm^{-1}): 2936, 2856, (CH_2); 1601, 1581, 1496 (Ar–H); 1243 (OCH_3); 842 (*p*-substituted aromatic). Elemental analysis: calc, C 72.06, H 6.76, N 9.88%; found, C 71.88, H 6.77, N 9.70%.

2.2. *Synthesis of 3Azo-3*

A mixture of 1-bromo-3-(4-methoxyazobenzene-4′-oxy)propane, **2**, (0.821 g, 2.45 mmol), 4,4′-dihydroxyazobenzene, **3**, (0.250 g, 1.17 mmol) and potassium carbonate (0.807 g, 5.84 mmol) in DMF (50 ml) was heated at reflux overnight. The reaction mixture was cooled and added to water (200 ml). The resulting precipitate was collected and dried prior to recrystallization twice with hot filtration from toluene to yield the product as a yellow powder; yield 0.823 g, 93.7%. Due to the insolubility of this in appropriate organic solvents NMR data were not obtained. IR (KBr) ν (cm^{-1}): 2946, 2872, (CH_2); 1602, 1582, 1498 (Ar–H); 1246 (OCH_3); 843 (*p*-substituted aromatic). Elemental analysis: calc, C 70.38, H 5.64, N 11.19%; found, C 70.21, H 5.58, N 10.34%.

2.3. *Characterization and thermal analysis*

All the trimers and their intermediates were characterized using a combination of ^{1}H NMR spectroscopy, using a Bruker AC-F 250 MHz spectrometer, FTIR spectroscopy using an ATI Mattson Genesis Series FTIR spectrometer, and elemental analysis carried out by Butterworth Laboratories. The thermal behaviour of the materials was investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 820 differential scanning calorimeter equipped with a TS0801RO sample robot and calibrated using indium and zinc standards. The heating profile in all cases was heat, cool and reheat at 10° min^{-1} with a 3-minute isotherm between heating and cooling. All samples were heated from 0°C to 20–40° above their clearing temperatures. Thermal data were normally extracted from the second heating trace. Phase characterization was performed using polarizing optical microscopy using an Olympus BH2 polarising microscope equipped with a Linkam TMS 92 hot stage.

3. Results and discussion

3.1. *α-Bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes*

The transition temperatures and associated entropy changes, $\Delta S/R$, for this series are shown in table 1. Several members of this series, namely the pentyloxy, heptyloxy, nonyloxy and undecyloxy homologues, exhibit an enantiotropic nematic phase, while the propoxy, butoxy and hexyloxy members show a monotropic nematic phase. The nematic phases were assigned on the basis of the characteristic schlieren texture observed when viewed through the polarizing microscope. The values of $\Delta S_{NI}/R$ are consistent with this assignment. It is interesting to note that it is only odd members of the series that exhibit enantiotropic phase behaviour.

The dependence of the transition temperatures on the number of methylene units in the terminal chain is shown in figure 1. The melting points exhibit a clear odd–even effect, as the length and parity of the terminal chain are varied, in which the even members have the higher values. This alternation is somewhat larger than normally observed for conventional low molar mass mesogens but is in the same sense. This suggests that the terminal bromine atom is not acting as a methylene group. This view is supported by the nematic–isotropic transition temperatures, which again exhibit an odd–even effect with the same sense to that normally seen, i.e. the even members show the higher values. Presumably the higher melting points of the even members preclude the observation of liquid crystal behaviour across the whole series.

Table 1. Transition temperatures and associated entropy changes for the α-bromo-ω-(4-methoxyazobenzene-4′-oxy) alkanes.

n	$T_{Cr-I}/°C$	$T_{NI}/°C$	$\Delta S_{Cr-I}/R$	$\Delta S_{NI}/R$
3	98	(88)	5.47	(0.15)
4	109	(96)	10.4	(0.15)
5	88	96	9.84	0.14
6	106	(101)	8.66	(0.22)
7	94	95	13.8	0.29
8	111	—	16.4	—
9	92	93	16.0	0.34
10	110	—	19.1	—
11	78	91	14.2	0.41
12	108	—	22.6	—

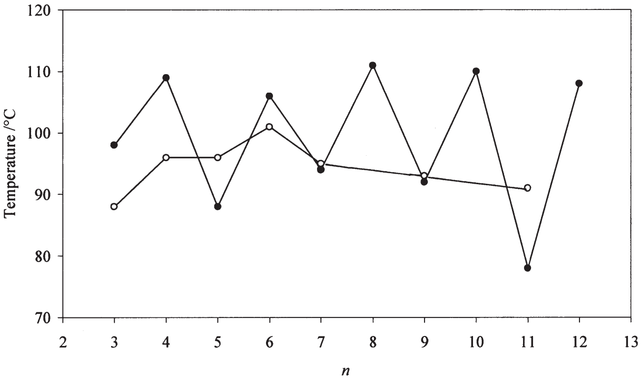

Figure 1. Dependence of the transition temperatures on the number of methylene units in the terminal chain for the α-bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes. (●) Melting point, (○) nematic–isotropic transition temperature.

3.2. *2Azo-n series*

The transition temperatures and associated entropy changes for the α,ω-bis(4-methoxyazobenzene-4′-oxy) alkanes are shown in table 2. All members of the 2Azo-*n* series exhibit a nematic phase. The nematic phase, for both the dimers and trimers, was identified on the basis of the observation of the characteristic schlieren texture observed when viewed through the polarizing microscope.

The dependence of the transition temperatures on the length of the flexible alkyl spacer for the 2Azo-*n* series is shown in figure 2. Both the melting and clearing temperatures show a large odd–even effect in which the even members have the higher values. The alternation with increasing n is attenuated for the clearing temperatures but not for the melting temperatures. This is archetypal behaviour for nematic dimers. The clearing entropies also show an odd–even effect in which even members show the higher values and which is not attenuated with increasing n, see figure 3. Again this is archetypal behaviour for liquid crystal dimers and will be discussed later.

3.3. *3Azo-n series*

Table 3 lists the transition temperatures and associated entropy changes for the 3Azo-*n* series. All members of the series exhibit an enantiotropic nematic phase except for 3Azo-12 which is a monotropic nematogen.

Table 2. Transition temperatures and associated entropy changes for the 2Azo-*n* series.

n	$T_{CrN}/°C$	$T_{NI}/°C$	$\Delta S_{CrN}/R$	$\Delta S_{NI}/R$
3	206	206	11.8	0.51
4	223	263	15.7	1.72
5	190	196	11.7	0.57
6	206	227	14.5	1.52
7	150	197	16.2	0.89
8	199	217	19.7	1.86
9	162	187	16.8	0.92
10	192	192	19.9	1.95
11	156	181	17.6	1.11
12	186	186	22.1	1.72

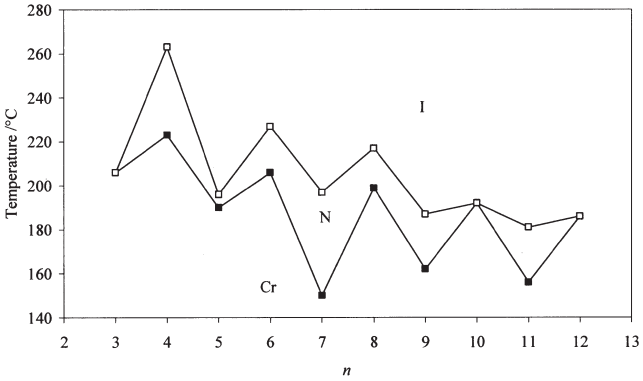

Figure 2. Dependence of the transition temperatures on the length of the flexible spacer, *n*, for the dimer series 2Azo-*n*. (■) Melting temperature, (□) nematic–isotropic temperature.

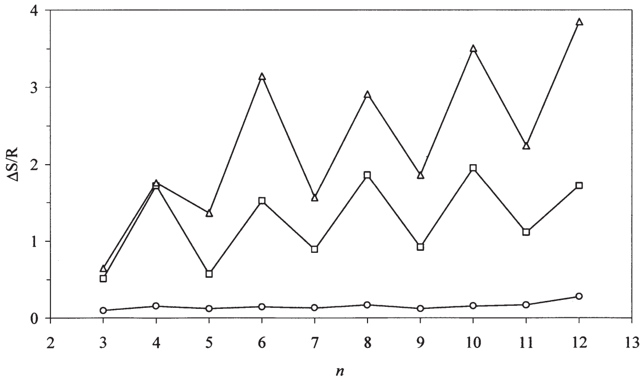

Figure 3. The dependence of the nematic–isotropic entropy change on the length of the flexible spacers for the 2Azo-*n* (□) and 3Azo-*n* (△) series. Also shown are the nematic–isotropic entropy changes for the Azo-*n* (○) series.

Table 3. Transition temperatures and associated entropy changes for the 3Azo-*n* series.

n	T_{CrN}/°C	T_{NI}/°C	$\Delta S_{CrN}/R$	$\Delta S_{NI}/R$
3	214	228	19.7	0.65
4	255	317	40.1	1.76
5	193	233	20.1	1.37
6	227	270	24.2	3.14
7	190	223	26.5	1.57
8	213	238	26.1	2.91
9	175	209	27.4	1.86
10	203	215	26.0	3.50
11	160	198	29.0	2.24
12	199	(196)	41.3	(3.85)

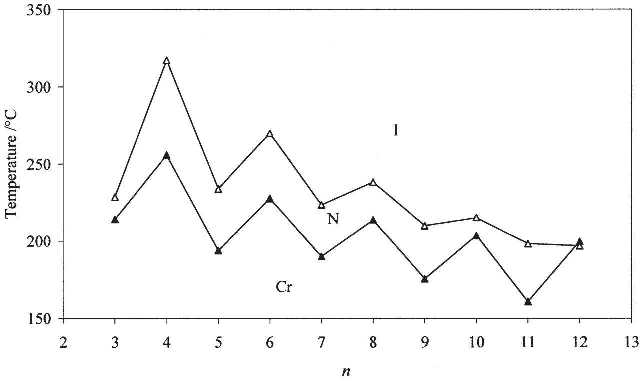

Figure 4. Dependence of the transition temperatures on the length of the flexible spacers, *n*, for the trimer series 3Azo-*n*. (▲) Melting temperature, (△) nematic–isotropic temperature.

The dependence of the transition temperatures on *n*, the number of methylene units in the two flexible spacers, for the 3Azo-*n* series is shown in figure 4. It can be seen that both the melting and clearing temperatures depend strongly on the length and parity of the flexible spacers. The melting temperatures exhibit a strong odd–even effect with increasing *n*, in which even members show the higher values and which does not appear to attenuate on increasing *n*. The nematic–isotropic transition temperatures also exhibit a pronounced odd–even effect, but which attenuates quickly with increasing *n*; again the even members show the higher values. For even members T_{NI} decreases more rapidly than the melting point with increasing *n*, and the dodecyl homologue is a monotropic nematogen. For odd members the decrease in T_{NI} is much less pronounced with increasing *n* and indeed passes through a shallow maximum at $n=5$. This behaviour is similar to that observed for another trimer series [10] as well for dimers and semi-flexible main chain polymers [37].

The dependence of the entropy changes associated with the nematic–isotropic transition on the length of the flexible spacers for the 3Azo-*n* series is shown in figure 3. A strong odd–even effect, in which the even members have the higher values, is observed and which is not attenuated on increasing *n*. The value of $\Delta S_{NI}/R$ for the butoxy derivative is somewhat lower than expected and may be linked to partial decomposition of the sample at the clearing temperature. The value of $\Delta S_{NI}/R$ for 3Azo-3 appears rather low although the physical significance of this is not immediately apparent. In general the values of $\Delta S_{NI}/R$ for the even members are approximately twice that of the adjacent odd members. Again, these results are similar to those observed in other trimeric series [10].

The observation of pronounced odd–even effects in both the transition temperatures and entropy changes as the length of the spacers are varied for the trimers (see figures 3 and 4) may be rationalized in the same manner as for the behaviour of dimers (see figures 2 and 3) and semi-flexible main chain polymers [1, 10, 11, 37]. Thus, if a trimer is considered in its most extended all-*trans*-conformation two quite different molecular shapes are possible depending on the parity of the spacers. For odd-membered trimers the two outer mesogenic units are inclined with respect to the central unit giving a stretched 'S' shape, see figure 5 (*a*). For even-membered trimers all three mesogenic units are co-parallel, resulting in an extended rod-like molecular structure, figure 5 (*b*). The enhanced shape anisotropy of the even-membered trimers allows the molecules to pack more efficiently in the liquid crystal phase, resulting in higher transition temperatures and entropy changes.

This argument does not take into account the flexibility of the alkyl spacers and a more realistic interpretation includes a wider range of conformations [1, 3]. For an even-membered dimer, for example, approximately half of the molecules assume an elongated conformation in the isotropic state, whereas for odd-membered dimers only about 10% of the molecules are in rod-like conformations. At the transition to the nematic phase many of the even-membered dimers having bent conformations are converted into the linear form, enhancing the orientational order of the nematic phase and resulting in a large entropy change. For odd-membered dimers, however, due to the larger energy difference between bent and linear conformations this conversion does not take place. In consequence the orientational order of the nematic phase is not increased and the entropy change is smaller. This approach, developed by Luckhurst and co-workers [1, 11], has also been used to model the behaviour of trimers successfully [38].

Smectic behaviour was not observed for the 3Azo-*n* series. Of the few trimer series that have been reported, smectic behaviour has only been observed for those compounds which contained either a combination of electron-rich and electron-deficient mesogenic units [8, 10, 13] or terminal alkyl chains [7]. For example, we recently reported the observation of a novel intercalated alternating SmC phase in a trimer containing three different mesogenic units. The formation of the smectic phase was attributed to a specific interaction between the two different mesogenic groups [39]. For the dimers the general rule is that smectic phases are only observed when the terminal chain length is greater than half the central spacer length [1–3]. We now need to establish whether a similar relationship holds for trimers.

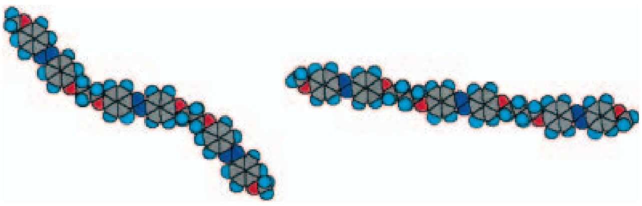

Figure 5. Molecular shapes of the all-*trans*-conformation of trimers containing (*a*) odd ($n=3$) and (*b*) even ($n=4$) membered flexible spacers.

3.4. *Comparison of monomers, dimers and trimers*

The melting points of the trimers are compared with those of the corresponding dimers and monomers [33] in figure 6. The trimers have the highest melting temperatures, followed by the dimers, with the monomers having the lowest melting points. The melting points of both the trimers and dimers exhibit an odd–even effect which attenuates slightly with increasing *n*, while those of the monomer series show only a weak dependence on *n*.

The dependence of the clearing temperatures on *n* for the three series is shown in figure 7. Again, the trimers have the highest clearing temperatures, followed by the dimers and then the monomers. This is expected, as adding mesogenic units increases the shape anisotropy of the molecule. A pronounced odd–even effect is seen for the clearing temperatures of the dimers and trimers which attenuates with increasing *n*. For the monomers, a much weaker alternation in T_{NI} is observed as the length of the terminal alkyl chain is varied. For each series increasing *n* reduces the clearing temperature more rapidly than the melting point, and thus the temperature width of the nematic phase is reduced on

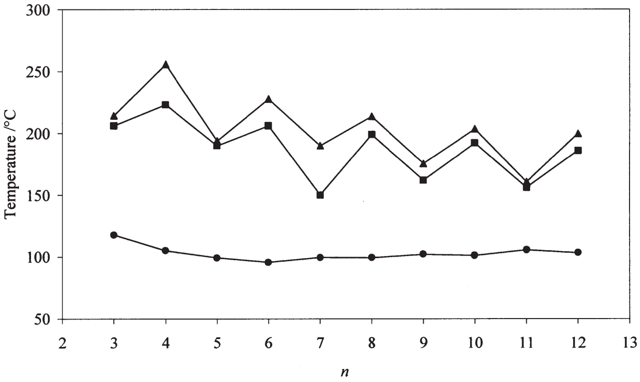

Figure 6. Dependence of the melting temperatures of the 3Azo-*n* (▲), 2Azo-*n* (■) and Azo-*n* (●) series on the length of the alkyl chains in each series.

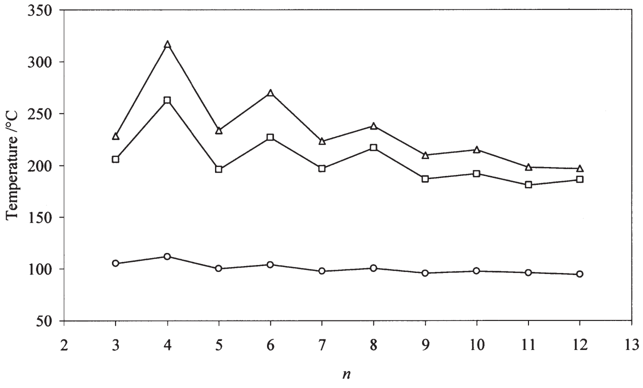

Figure 7. Dependence of the nematic–isotropic transition temperatures of the 3Azo-*n* (△), 2Azo-*n* (□) and Azo-*n* (○) series on the length of the alkyl chains in each series.

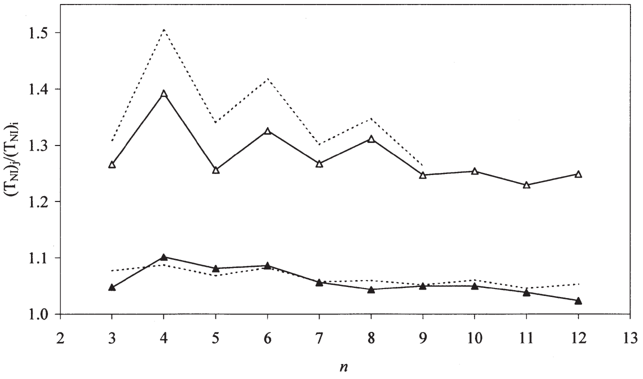

Figure 8. Ratio of the clearing temperatures of the 2Azo-*n*:Azo-*n* (△) and 3Azo-*n*:2Azo-*n* (▲). Dotted lines show the corresponding values for cyanobiphenyl-based trimers, dimers and monomers [10].

ascending each series. This effect is seen more strongly in the even-membered homologues. Indeed, 3Azo-12 is monotropic, 2Azo-10 and 2Azo-12 exhibit only fleeting enantiotropic phases on melting, and several of the Azo-*n* members are monotropic. It is interesting to note that as *n* is increased the transition temperatures of the dimers and trimers become more similar. This begs the question as to whether the clearing temperatures of the dimers would actually be greater than those of the trimers for much longer spacers. To our knowledge such materials have not been prepared.

The nematic–isotropic transition entropies for the monomers, dimers and trimers are shown in figure 4. All three series show an odd–even effect which is not attenuated with increasing *n*. The odd–even effect is weakest for the monomers and most pronounced for the trimers. The rather low values of $\Delta S_{NI}/R$ seen for 3Azo-3 and 3Azo-4 have been discussed already. The values of $\Delta S_{NI}/R$ are highest for the trimers, and in general twice those of the corresponding dimers. The values of $\Delta S_{NI}/R$ for the monomers are appreciably lower than either those of the dimers or trimers. The $\Delta S_{NI}/R$ values of the odd-membered trimers are similar to those observed for the even-membered dimers. There is a greater increase in $\Delta S_{NI}/R$ on going from an even-membered dimer to an even-membered trimer than is seen for the odd-members, and hence the magnitude of the odd–even effect for the trimers is greater than that seen for the dimers.

Figure 8 shows the dependence of the ratio of the clearing temperatures of the dimers to the monomers and of those of the trimers to the dimers on increasing *n*. The ratio of the clearing temperatures of the dimers to the monomers shows a strong odd–even effect. This reflects the large difference in transition temperatures between dimers and monomers and the strong odd–even effect observed in the clearing temperatures of the dimers. The effect attenuates with increasing *n* because of the attenuation in the odd–even effect of the clearing temperatures of the dimers. The ratio of the clearing temperatures of the trimers to dimers is far smaller and does not exhibit an odd–even effect as *n* is varied. This reflects the greater similarity in the behaviour of the transition temperatures of the dimers and trimers. The ratio appears to decrease with increasing *n* and suggests that as *n* is increased to very long chains the clearing temperatures of the trimers and dimers may crossover, as discussed previously. Similar trends were observed for cyanobiphenyl-based monomers, dimers and trimers [10], see figure 8.

A comparison of the ratios of the clearing entropies for the dimers to those of the monomers and for the trimers and dimers is given in figure 9. The ratio of $\Delta S_{NI}/R$ for the dimers to monomers exhibits a large odd–even effect which reflects both the larger $\Delta S_{NI}/R$ values and the odd–even effect seen for the dimers. The ratios of $\Delta S_{NI}/R$ for the trimers to the dimers are considerably smaller, approximately 2, and do not exhibit a regular odd–even effect as *n* is increased. This reflects the similarity in the odd–even effects seen for the dimers and trimers, and shows that, on average, the clearing entropies for the trimers are twice those of the dimers for both odd and even members. It should again be noted that the ratio for $n=4$ is lower than expected due to the decomposition of 3Azo-4 at temperatures close to its clearing temperature.

Comparing the ratios of the clearing entropies and temperatures (see figures 8 and 9), shows that the increase in $\Delta S_{NI}/R$ on going from dimers to trimers is greater than that seen for the clearing temperatures. The ratios of T_{NI} lie in the range 1.02–1.10 and the entropies in the range 0.94–2.39. These values are

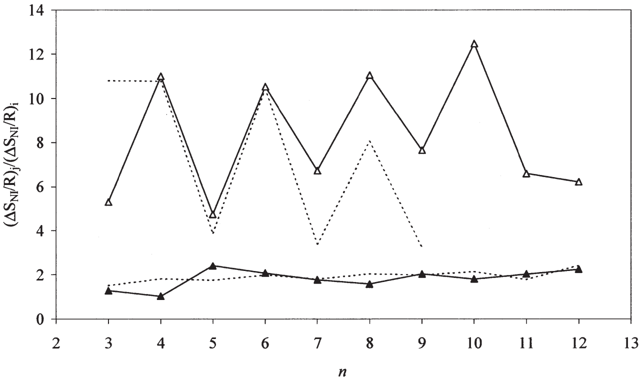

Figure 9. Ratio of clearing entropies of the 2Azo-*n*:Azo-*n* (△) and 3Azo-*n*:2Azo-*n* (▲). Dotted lines represent the corresponding values for cyanobiphenyl-based trimers, dimers and monomers [33].

similar to those obtained for cyanobiphenyl-based dimers and trimers, which are shown as dotted lines in figures 8 and 9. This small increase in T_{NI} suggests that the mesogenic units in the trimers are correlated to the same extent as in the dimers, whereas the larger increase in $\Delta S_{NI}/R$ suggests a significant increase in the orientational order of the mesogenic groups on passing from the dimer to trimer.

It has been suggested that a value of 3/2 would be expected for the ratio of the clearing temperatures of the trimers to dimers [10]. This was based on the predictions of a model developed to calculate the transition temperatures of oligomers composed of rigid mesogenic units in which T_{NI} for an oligomer containing *n* repeat units is just *n* times that of the monomer [40], although this was only true for very long monomers. Here the value of the trimer:dimer clearing temperature ratio is in the region 1.02–1.10 which is less than the predicted value of 3/2. This is presumably due to the presence of flexible spacers in the molecule which destroys the linearity of the structure.

We have seen that the ratios of the clearing temperatures and entropies for the 3Azo-*n* and 2Azo-*n* series are remarkably similar to those reported for the corresponding cyanobiphenyl-based materials suggesting this represents rather general behaviour, see figures 8 and 9. This observation, however, is based on just two data sets, and to speculate further on the physical significance of this would at present be unwise. This apparent generality must now be tested for a much wider range of materials.

4. Conclusions

A series of linear liquid crystal trimers, the 4,4′-bis[ω-(4-methoxyazobenzene-4′-yloxy)alkoxy]azobenzenes, has been synthesized and characterized. All the members of the series exhibit a nematic phase. Smectic behaviour was not observed for these trimers. On comparing these trimers to the corresponding dimers and monomers it is evident that on increasing the number of mesogenic units there is an increase in both the transition temperatures and entropies, which presumably arises from the increased molecular anisotropy. The odd–even effects seen in the transitional behaviour of the trimers are reminiscent of those seen for dimers and are accounted for using similar arguments. For long spacer lengths the clearing temperatures of the dimers and trimers appear to converge and may cross over for sufficiently long spacers. The ratios of the dimer:trimer clearing temperatures and associated entropy changes for these and other reported series are very similar, strongly suggesting a rather general relationship between the transitional properties of the structurally similar dimers and trimers.

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