

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Synthesis and thermal behaviour of salicylaldimine-based liquid crystalline symmetrical dimers

C. V. Yelamaggad^a; Manoj Mathews^a; Uma Hiremath^a; Geetha Nair^a; D. S. Shankar Rao^a; S. Krishna Prasad^a

^a Centre for Liquid Crystal Research P.B. No.1329, Jalahalli Bangalore 560 013 India,

Online publication date: 11 November 2010

To cite this Article Yelamaggad, C. V. , Mathews, Manoj , Hiremath, Uma , Nair, Geetha , Rao, D. S. Shankar and Prasad, S. Krishna(2003) 'Synthesis and thermal behaviour of salicylaldimine-based liquid crystalline symmetrical dimers', *Liquid Crystals*, 30: 8, 899 – 908

To link to this Article: DOI: 10.1080/0267829031000138587

URL: <http://dx.doi.org/10.1080/0267829031000138587>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and thermal behaviour of salicylaldimine-based liquid crystalline symmetrical dimers

C. V. YELAMAGGAD*, MANOJ MATHEWS, UMA S. HIREMATH,
GEETHA G. NAIR, D. S. SHANKAR RAO and S. KRISHNA PRASAD
Centre for Liquid Crystal Research, P.B. No.1329, Jalahalli, Bangalore 560 013, India

(Received 6 January 2003; in final form 13 March 2003; accepted 25 March 2003)

A series of symmetrical dimers consisting of salicylaldimine moieties connected by flexible alkylene central spacer *via* ether linkages has been synthesized. In order to validate the empirical rule suggested by Date *et al.* to account for the smectic behaviour of such dimers, the chain length of the terminal alkoxy chain has been kept constant (C_8) while the number of methylene units in the central spacer was varied from C_3 to C_{11} . Another aim of the present investigation was to understand structure–property relationship in these dimers in which the salicylaldimine mesogenic segment has been used for the first time in dimers. The mesomorphic behaviour of these dimers was evaluated using optical microscopy and differential scanning calorimetry and the structure of some of the mesophases has been further investigated with the help of X-ray diffraction. Our studies reveal that the dimers consisting of 3 to 8 methylene units in the flexible spacer show only smectic (smectic C and smectic A) phases. For the dimers containing 4, 6 and 8 methylene units in the central spacer, a unique filament growth pattern has been observed in the smectic A phase while cooling from the isotropic phase. The dimers containing of C_9 to C_{11} methylene groups exhibit the nematic phase in addition to smectic modifications. This observation indicates that when the terminal chains are shorter than the spacer, the tendency to form smectic phases is not fully extinguished but is perhaps reduced.

1. Introduction

Conventional thermotropic liquid crystals consist of anisometric molecules (mesogens) that are either rod-shaped (calamitic) or disc-shaped (discotic). The thermal behaviour of these two types of liquid crystals is generally well understood and therefore they have been recognized as materials for many practical applications, especially in liquid crystal display devices. During the past two decades it has been shown that compounds with non-classical molecular structures such as oligomers also show liquid crystalline properties [1]. Among these, linear oligomeric liquid crystals (LOLCs) formed by joining 2 to 8 mesogenic cores in an end to end (axial) fashion by means of alkylene spacers have attracted particular attention [1, 2]. The first member of the LOLCs, namely the dimers (also referred to as dimesogens) are composed of either identical (symmetrical) or non-identical (non-symmetrical) mesogenic segments connected by a central spacer and have been extensively studied [2]. In this article we restrict ourselves to symmetrical dimers.

Symmetrical dimers, also referred to as twins, were first reported by Vorlander in 1927 [3]. It appears that

the importance of this discovery was overlooked until a report by Rault *et al.* in 1975 [4]. This paper also had little impact and the field only really became active when Griffin and Britt described the thermal behaviour of a series of diesters [5]. They showed that these dimers could be regarded as model compounds for the technologically important semi-flexible main chain liquid crystalline polymers. Since then several studies of symmetrical dimers have been reported, revealing that the liquid crystalline properties of these materials depend not only on both the parity (odd/even) and the length of the flexible central spacer, but also on the length of the terminal chains [1]. The compounds with an even-parity spacer show higher melting and clearing transition temperatures than the odd-members, a feature generally attributed to the dependence of the molecular shape on the parity of the spacer, when considered in the all-*trans* conformation. In such dimers the two mesogenic segments connected through an even-membered flexible spacer are almost antiparallel with respect to each other, imparting an almost rod-like shape to the dimer. In the case of the odd-members, the mesogenic segments are inclined with respect to each other and thus the molecular shape is bent. Owing to the reduced shape anisotropy in bent molecules, the

*Author for correspondence; e-mail: yelamaggad@yahoo.com

transition temperatures are obviously much lower when compared with dimers having a more linear conformation.

The most extensively studied series of dimers are the α,ω -bis(4'-cyanobiphenyl-4-yloxy) alkanes (abbreviated as BCBO n), and these show only the nematic phase [1, 6]. These compounds show a pronounced odd–even effect in which even members of the series show higher values of the nematic–isotropic transition temperatures, although the magnitude of the alternation diminishes on increasing the length of the spacer [6 *a*]. The entropy changes associated with this transition also show a pronounced alternation as the length and parity of the spacer is varied. Needless to say that even members show a higher magnitude of the entropy change. It is quite surprising that these series of compounds show only the nematic phase, even though the analogous conventional monomers show smectic behaviour. This observation has been attributed to the increased molecular flexibility of the dimer.

In order to determine the influence of the flexible core on smectic behaviour in dimers, Date *et al.* reported eleven series of Schiff's base dimers, namely, the α,ω -bis[4-(alkylphenyliminomethyl)phenoxy]alkanes (abbreviated as the *m.OnO.m* series; *m* and *n* indicate the length of the terminal chain and spacer, respectively) [7]. It was found that the members of these series exhibit a rich smectic polymorphism, namely smectic A (SmA), smectic B (SmB), smectic C (smectic) and smectic F (SmF) phases and the crystal B, E, G and H phases. Even rare phase transitions like the SmF–SmA and crystal G–isotropic transitions were observed. The characteristic pronounced odd–even effect on varying the length of the spacer was observed in all the series. In addition these series made it possible to understand, at least to some extent, the factors governing structure–property relationships in symmetrical dimers. For example, a series of dimers having C₆ terminal alkyl chains, and spacers varying from C₂ to C₁₂, showed a pronounced odd–even effect. The early members of the series having C₂–C₆ and C₈ spacer length show exclusively the smectic behaviour, whereas higher members exhibit only nematic phase, this observation is not in accordance with the general behaviour found in low molar mass mesogens, that increasing the length of alkyl chains promotes smectic phases. Based on these results a simple empirical rule has emerged to relate the molecular structure to the occurrence of smectic behaviour: thus, if a symmetrical dimer is to exhibit smectic behaviour then the terminal chain length has to be greater than half the spacer length.

Recently Blatch and Luckhurst reported similar observations for the azobenzene-based symmetric

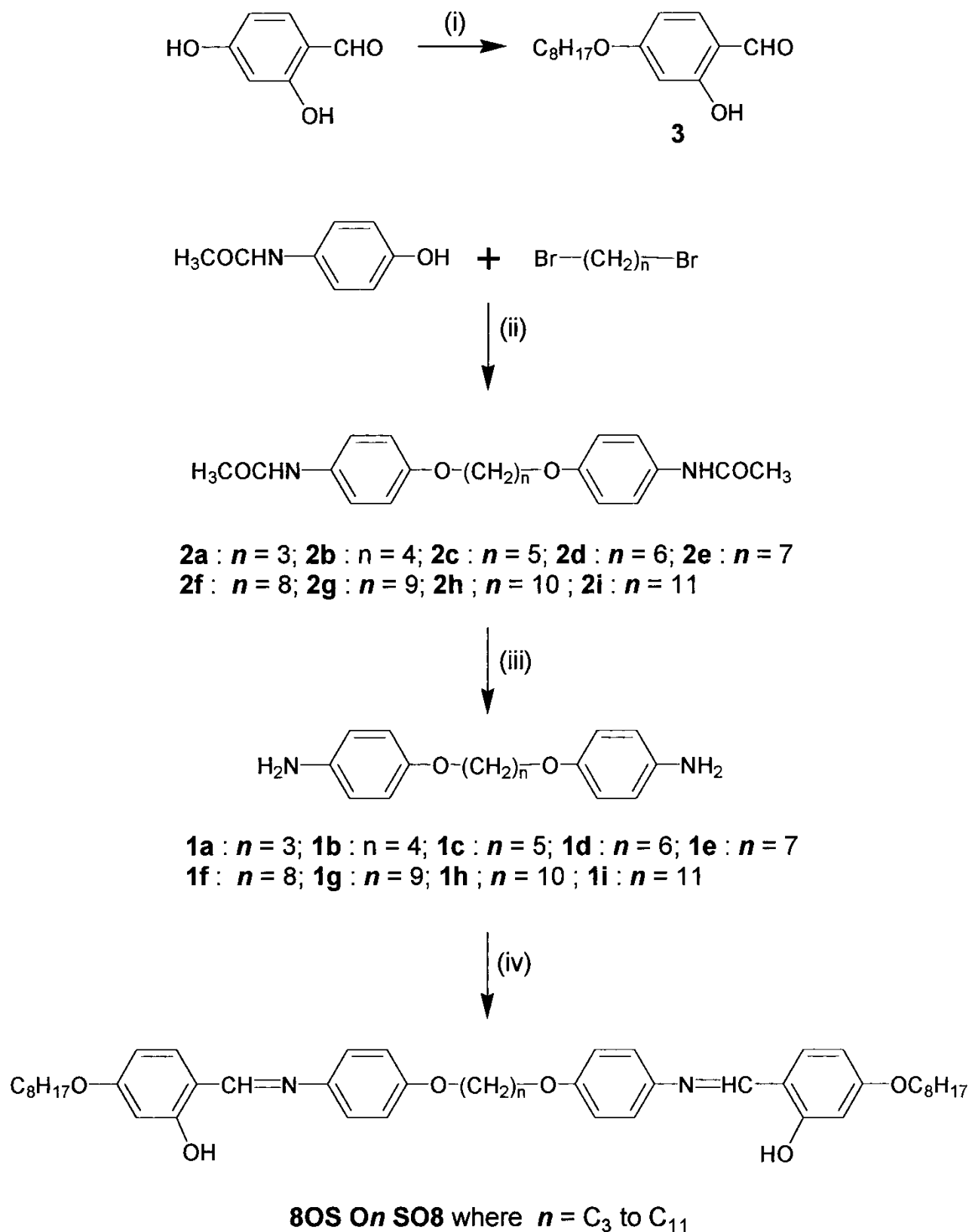
dimers (abbreviated as 5A n OA5 series; *n* indicates the spacer length, varying from 1 to 12) for which smectic behaviour was observed when the terminal chain was longer than half the spacer length [8]. To test this rule, three more dimers having C₁₀, C₁₂ and C₁₄ chain spacers and C₄, C₅ and C₆ in which alkyl chains, respectively, were synthesized. Surprisingly, all three compounds exhibit a SmA phase below the long range nematic phase. This observation is in contrast to the empirical rule suggesting that when the terminal chains are shorter than the spacer length, the tendency to form smectic phases is not extinguished but is greatly reduced. More recently Henderson *et al.* have reported a range of symmetrical dimers which differ in the nature of the link, which is either an ether or methylene link, between the spacer and mesogenic cores [9]. The change from an ether link to a methylene link results in a decrease in the nematic–isotropic transition temperature, and this effect is reported to be greater for odd-membered spacers. In contrast, the entropy change associated with the nematic–isotropic transition is higher for an even-membered methylene-linked dimer than for the corresponding ether-linked dimer. These differences in transitional properties of ether- and methylene-linked dimers can be attributed to geometrical factors [1]. Thus the thermal behaviour of symmetrical dimers consisting of Schiff's bases and azobenzene mesogenic segments appear to be comparable, to some extent, whereas the cyanobiphenyl-based dimers behave quite differently.

To continue our investigations of oligomeric liquid crystals, we have prepared symmetrical dimers consisting of salicylalimine [*N*-(2-hydroxy-4-alkoxybenzylidene)aniline] cores to evaluate the structure–property relationships. Our main aim was to see whether the empirical rule proposed by Date *et al.* is applicable or not to this new series of dimers. Therefore the length of the terminal tail (C₈-chain) was kept constant while the spacer length was varied from C₃ to C₁₁. Here we report the synthesis and characterization of the α,ω -bis{4-[(2-hydroxy-4-*n*-octyloxyphenyl)iminomethyl]phenoxy}alkanes (or 8OSO n SO8 where 8, O, S, O and *n* denote the length of the terminal alkyl chains, an ether linkage between the alkyl chain and hydroxyphenyl ring, the salicylalimine moiety, the ether linkage between the salicylalimine moiety and the spacer, and the number of methylene units present in the central spacer, respectively).

2. Results and discussion

2.1. Synthesis

The symmetrical dimers 8OSO n SO8 and their intermediates (**1a–i**, **2a–i** and **3**) were synthesized as outlined in the scheme. 2-Hydroxy-4-*n*-octyloxybenzaldehyde (**3**)



Scheme. The general route employed for the synthesis of the symmetrical dimers. Reagents and Conditions: (i) Anhy·K₂CO₃, 1-bromooctane, acetone, reflux, 12 h (ii) Anhyd·K₂CO₃, acetone, reflux, 24 h (iii) Abs. EtOH, con·HCL, reflux 12 h (iv) 3; abs·EtOH, AcOH (catalytic amount), reflux, 4 h.

was prepared by heating under reflux 2,4-dihydroxybenzaldehyde with 1-*n*-bromooctane under mildly basic conditions in a solvent medium. α,ω -Bis(4-acetamidophenyl-1-oxy)alkanes (**2a–i**) were prepared by heating under reflux dibromoalkanes with 4-hydroxyacetanilide in dry acetone in the presence of anhydrous K_2CO_3 . The acetanilides were then subject to acid hydrolysis to obtain in the α,ω -bis(4-aminophenyl-1-oxy)alkanes (**1a–i**). The hydroxyaldehyde **3** was condensed with various aminophenylalkanes **1a–i** under mildly acidic conditions in absolute EtOH to obtain the target dimers 8OSO n SO8 in reasonably good yields. The molecular structures of all the compounds were confirmed by spectroscopic analysis (see experimental section).

2.2. Thermal behaviour

As mentioned earlier, to establish whether the empirical rule proposed by Date *et al.* is obeyed, or not, by these dimers the length of the terminal alkoxy chains was kept constant while the number of methylene units in the central spacer was varied from 3 to 11. Thus, the terminal chain was kept constant such that it is always greater than half the spacer length. The study of these dimers was also undertaken in order to enhance our understanding of structure–property relationships in liquid crystal dimers. The transition temperatures and the phase sequences of the symmetrical dimers 8OSO n SO8 are listed in the table. All the members of the series exhibit smectic behaviour which agrees with the suggestion of Date *et al.* that smectic behaviour in such dimers is driven principally by the tendency of the different regions of the molecules (the terminal chains, spacer and mesogenic moieties) to microphase separate. The members 8OSO3SO8 to 8OSO8SO8 exhibit enantiotropic SmC and SmA phases with the exception of 8OSO5SO8 to 8OSO7SO8 for which the SmC phase is monotropic. The presence of the SmA phase was confirmed, based on the microscopic observation of the characteristic focal-conic texture for slides treated for planar orientation, and a dark field of view for slides treated for homeotropic orientation. When untreated slides were employed, both the focal-conic and psuedoisotropic textures were observed.

Surprisingly, for the dimers with $n=4, 6$ and 8 while cooling slowly from isotropic phase, the SmA phase grows as filaments which coalesce to form a focal-conic texture on further cooling. Figure 1 shows the filament growth pattern appearing just below the isotropic phase for the dimer 8OSO4SO8. The filaments grow in length but not in diameter. During this growth process, the filaments buckle quasi-continuously, leading to a snake-like appearance. Of course these filaments are metastable, and eventually coalesce to focal-conic

domains. Naito *et al.* [10*a*] have developed a theory in which the filamentary structure is regarded as a smectic A tube, consisting of concentric cylindrical smectic layers. This theory explains our observations, namely that the growth has a strong temperature dependence during the cooling process, and that once the filaments have grown straight to a certain length (called the threshold length in the theory) buckling occurs. The filamentary growth is generally seen for binary/ternary mixtures [10*b, c*], although, as here, Arora *et al.* have reported it in a single component system. It is possible that this type of growth is observed when the system has a ‘structural degree of freedom’ (as in mixtures) or ‘configurational degree of freedom’ as in dimeric systems. The existence of a SmC phase was confirmed by the observation of a broken focal-conic in slides treated for planar orientation and schlieren texture (when the compounds were cooled from the homeotropic SmA phase) was observed for slides treated for homeotropic geometry. When untreated slides were used, both focal-conic and schlieren textures were seen.

As a representative case, an X-ray diffraction study was carried out on 8OSO7SO8 to prove the presence of a SmA phase beyond doubt. The sample contained in a Lindemann capillary tube was aligned by slow cooling from the isotropic phase in the presence of a magnetic field of strength 2 T (Bruker electromagnet). After cooling well into the mesophase the sample was transferred to the goniometer for X-ray diffraction experiments. Figure 2 shows the 2-dimensional diffraction pattern and the one-dimensional intensity vs 2θ profile obtained at 155°C. In the low angle region two sharp peaks, corresponding to spacings of 51 and 25 Å are seen. The calculated length l of the molecule in the most extended form is 50.7 Å. Thus the low angle peak corresponding to a 51.2 Å spacing must be associated with the length of the molecule. The ratio, $d/l \sim 1$, d being the layer spacing, confirms that the mesophase under observation is indeed a smectic A phase. In the wide angle region there is a diffuse reflection corresponding to a spacing of 4.6 Å and arising from liquid-like ordering within the layer. The second reflection, whose spacing is half that for the first, is enhanced by the dimeric nature of the molecule. Attempts to obtain a diffraction pattern of the sample in the SmC phase at about 130°C were unseccessful, as it rapidly crystallizes.

On further increasing the number of methylene units in the spacer, with $n=9, 10$ and 11 , the resulting dimers 8OSO9SO8, 8OSO10SO8 and 8OSO11SO8 show smectic phases below the nematic phase (N). The N phases showed the characteristic schlieren texture, with two- and four-brush patterns. The dimer (8OSO9SO8) exhibits enantiotropic N and SmA phases

Table. Transition temperatures^a (°C) and associated enthalpies (kJ mol⁻¹, in brackets) of the symmetrical dimers 8OSO_nSO8. I=isotropic liquid; N=nematic phase; SmA=smectic A phase; SmC=smectic C phase; SmX₁=a highly ordered unknown smectic phase; SmX₂=a highly ordered unknown smectic phases which exhibits the characteristics of aG phase; Cr=Crystal.

Dimers	Cr ₁	Heating Cooling	Cr ₂	Heating Cooling	SmX ₁	Heating Cooling	SmX ₂	Heating Cooling	SmC	Heating Cooling	SmA	Heating Cooling	N	Heating Cooling	I
8OSO3SO8	•	153.9(36.3) 149.4(35.1)	—	—	—	—	—	—	•	158.7 ^b 157.1 ^b	•	183.6(9.8 182.5(8.5))	—	—	•
8OSO4SO8	•	64(14.3)	•	169.9(64.4) 155.6(59.9)	—	—	—	—	•	216.1 ^b 214.3 ^b	•	241.4(21.9) 238.4(15.8)	—	—	•
8OSO5SO8	•	154.5(73.8) 127.9(51.9)	—	—	—	—	—	—	•	— 140.1 ^b	•	181.6(11.1) 180.1(12.8)	—	—	•
8OSO6SO8	•	69.6(14.4)	•	163.7(76.4) 148.3(71.5)	—	—	—	—	•	183.7 ^b 182.5 ^b	•	213.1(21.0) 211.3(21.2)	—	—	•
8OSO7SO8	•	79.9(12.0)	•	144(79.3) 113.3(55.9)	—	—	—	—	•	— 131.9 ^b	•	167.3(10.1) 166.5(10.4)	—	—	•
8OSO8SO8	•	69.2(10.6)	•	161.2(79.8) 145.9(77.0)	—	—	—	—	•	166.3 ^b 165.6 ^b	•	189.1(18.5) 187.8(18.1)	—	—	•
8OSO9SO8	•	138.4(78.6) 110.1(52.3)	—	—	•	121.5(6.5)	—	—	•	— 125(4.0)	•	154.2(1.8) 153.6(1.8)	•	159.2(2.8) 158.6(2.9)	•
8OSO10SO8	•	160.4(88.6) 147.6(81.1)	—	—	•	151.6 ^b	—	—	•	— 155(1.1)	•	169.8(2.6) 169.1(2.0)	•	171.8(7.7) 171.1(7.0)	•
8OSO11SO8	•	132.4(82.0) 102.8(48.9)	—	—	—	—	•	—	—	—	•	136.9 ^b 136.4 ^b	•	155.6(3.2) 155.0(3.2)	•

^aPeak temperatures in the DSC thermograms obtained during heating cycle at 5° min⁻¹.

^bThe phase transition was observed under polarizing microscope but was too weak to detect by in DSC.

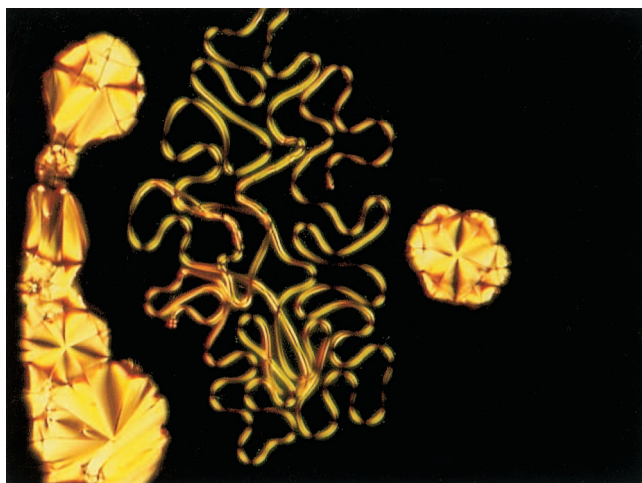


Figure 1. Photomicrograph of the texture observed at 185°C at a cooling rate of $0.1^{\circ}\text{Cmin}^{-1}$ of the SmA phase developing from the isotropic phase, for the dimer 8OSO8SO8. Note the filament growth pattern (middle portion) which coalesces to a focal-conic texture (left and right portion of the photograph).

in addition to two monotropic smectic phases that can be seen in the DSC thermograms shown in figure 3. Based on the observation of a characteristic broken focal conic texture (figure 4) the smectic phase appearing just below the SmA phase was confirmed to be SmC. Cooling, from the SmC phase, a smeared focal-conic texture (figure 5) appears at about 121.5°C. When examined with homeotropic surface conditions, the SmC phase exhibits the expected schlieren texture, which on further cooling changes to another mesophase (at about 121.5°C) with a significant change in the texture which subsequently remains unchanged until crystallization (at about 110°C). We suggest that the mesophase appearing below the SmC phase is a highly ordered smectic phase (SmX_1).

Similar observations were made for the dimer 8OSO10SO8, except that the temperature range of the N phase is decreased, 2°C against 5°C for 8OSO9SO8. Attempts to characterize the SmX_1 phase with the help of X-ray diffraction were unsuccessful as both 8OSO9SO8 and 8OSO10SO8 crystallize rapidly on keeping the sample in the SmX_1 phase. The final member of the series, 8OSO11SO8, shows enantiotropic SmA and N phases. As can be seen in the table, the temperature range of the SmA phase decreases while that of the N phase increases with the loss of the SmC phase. In addition, it exhibits a monotropic phase that appears to be a highly ordered smectic phase which we denote as SmX_2 . With planar boundary conditions the mesophase SmX_2 shows a non-specific texture in which bands running over the focal-conics can be

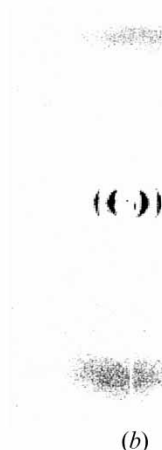
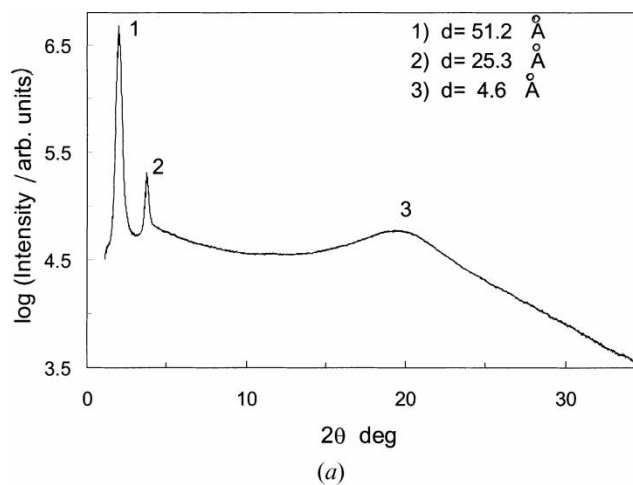


Figure 2. (a) X-ray intensity profile of the dimer 8OSO7SO8 obtained for the SmA phase at 155°C on cooling from the isotropic phase. Note a diffuse peak in the wide angle region indicating liquid-like order, and two sharp reflections in the low angle region; (b) The two-dimensional diffraction pattern.

seen (figure 6). With homeotropic surface conditions the SmX_2 phase exhibits a mosaic texture (figure 7). These textural patterns are reported to be observed for the crystal G or crystal J phase [11].

The transitional behaviour of these dimers exhibits a dramatic dependence on the length and parity of the central alkylene spacer. Figure 8 shows the dependence of the melting, SmC–SmA, SmA–N, SmA–I and N–I transition temperatures on the number of methylene units n in the flexible spacer, and reveals large odd–even effects. The even members of the series show higher values of mesophase–isotropic transition temperatures, although the magnitude of the alternation diminishes on increasing the length of the spacer, a feature commonly observed for symmetrical dimers as already mentioned. The entropy changes associated with SmA–I and N–I transitions of the series also show a

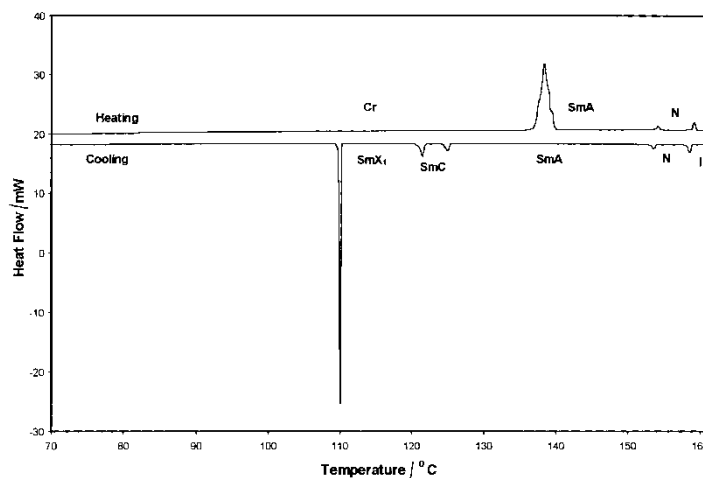


Figure 3. DSC traces obtained for the heating and cooling cycles of the dimer 8OSO9SO8 at a rate of $5^{\circ}\text{C min}^{-1}$.

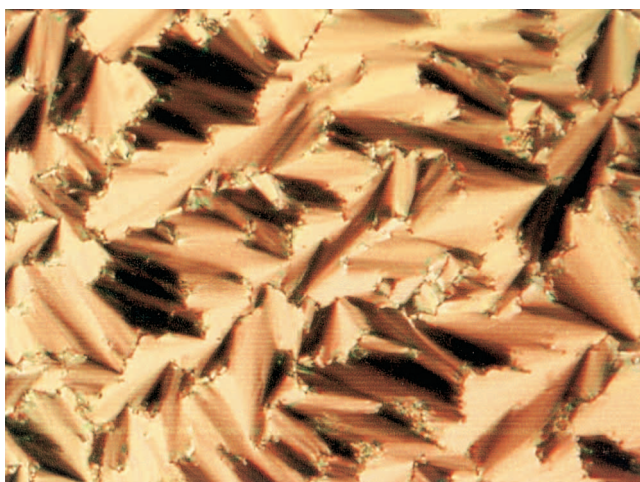


Figure 4. Photomicrograph of the broken focal-conic texture observed for the SmC phase of the dimer 8OSO9SO8 at 124.6°C during a cooling cycle.

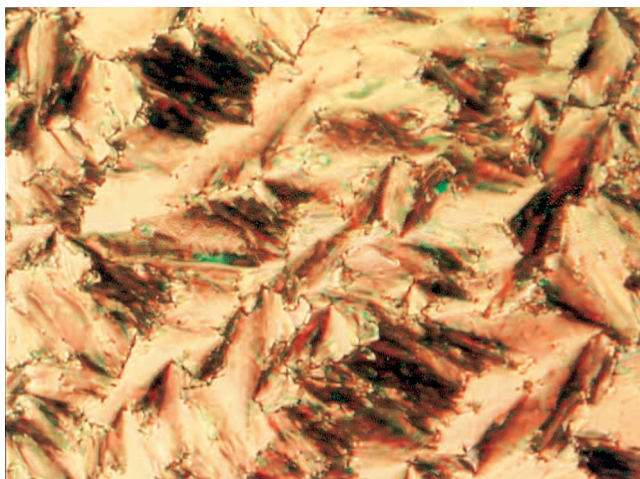


Figure 5. Photomicrograph of the SmX₁ texture seen at 121.1°C , for the dimer 8OSO9SO8.

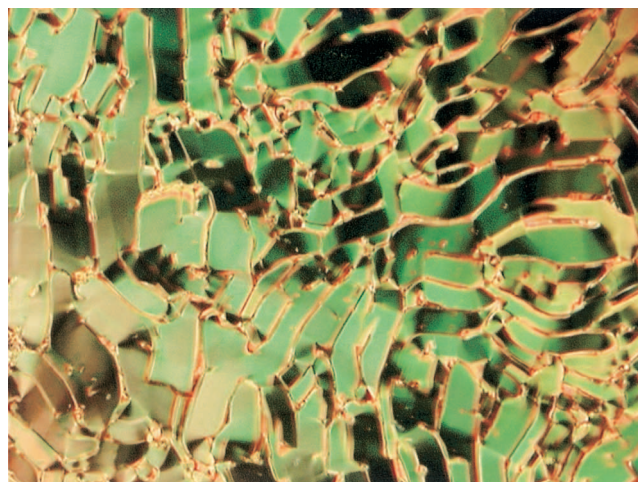


Figure 6. A non-characteristic texture observed at 125.2°C in the SmX₂ phase while cooling from the SmA phase for 8OSO11SO8; the slides were treated for planar orientation.



Figure 7. Mosaic texture observed for the SmX₂ phase at 121.6°C , for 8OSO11SO8 cooled from the SmA phase using slides treated for homeotropic alignment.

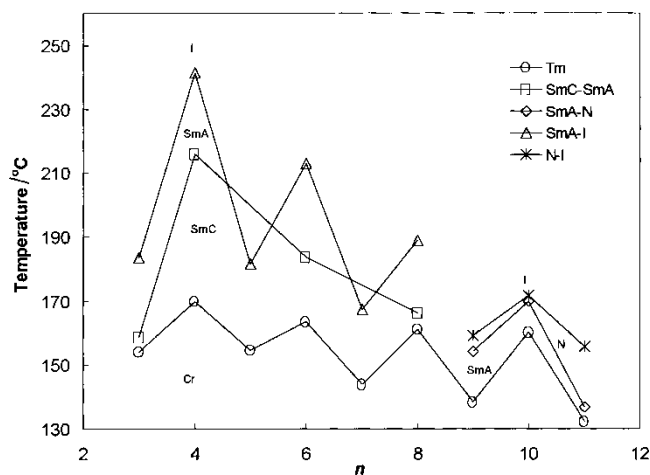


Figure 8. The dependence of the transition temperatures on the number of methylene units n in the flexible spacer.

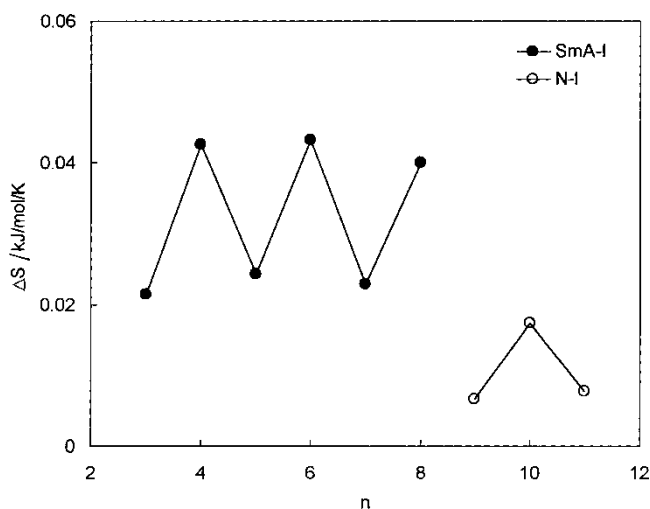


Figure 9. The dependence of the entropy change associated with the SmA-I and N-I transition on the number of methylene units n in the flexible spacer.

pronounced alternation (figure 9) as the length and parity of the spacer is varied (even members exhibit higher values). Our studies reveal that the dimers 8OSO3SO8 to 8OSO8SO8, in which the length of the terminal chains is greater than or equal to the spacer length, show only smectic phases, indicating that the empirical rule is being obeyed by this set of dimers. The dimers 8OSO9SO8 to 8OSO11SO8 show a nematic phase in addition to smectic modifications, indicating that when the terminal chains are shorter than the spacer length, the tendency to form smectic phases is not extinguished but is reduced.

3. Summary

In conclusion, we present the synthesis and characterization of symmetrical dimers consisting of salicylaldehyde

moieties connected through a flexible alkylene central spacer via ether linkages. In order to check the empirical rule suggested by Date *et al.* for the observation of smectic behaviour in such dimers, the chain length of the terminal alkoxy tail was kept constant (C_8) while the number of methylene units in the central spacer was varied from 3 to 11. Our studies show that these dimers, in which the terminal chain was longer than half the spacer length, show several smectic modifications indicating that these dimers obey the empirical rule.

4. Experimental

4.1. General information

Dibromoalkanes were obtained from Aldrich while 2,4-dihydroxybenzaldehyde was obtained from Lancaster and used without further purification. Solvents were obtained from local sources and dried following standard procedures. IR spectra were recorded using a Perkin-Elmer Spectrum 1000 FTIR spectrometer. 1H NMR spectra were recorded using a Bruker DRX-500 (500 MHz), Bruker AMX-400 (400 MHz) or Bruker Avance series DPX-200 (200 MHz) spectrometers. For 1H NMR spectra, the chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Mass spectra were recorded on a Jeol JMS-600H spectrometer in FAB⁺ mode using 3-nitrobenzylalcohol as a liquid matrix. The compounds were investigated for liquid crystalline behaviour using a polarizing optical microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90), and by differential scanning calorimetry (Perkin Elmer DSC7). Optical observations were made with two different surface-coated slides, one treated for homogeneous alignment and another with homeotropic alignment. X-ray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with double-mirror focusing optics, with the sample contained in a Lindemann capillary tube.

4.2. α,ω -Bis(4-acetamidophenyl-1-oxy)alkanes 2a-i

In a general procedure, a flask equipped with a magnetic stirring bar, reflux condenser and argon inlet was charged with acetone (50 ml), anhyd. K_2CO_3 (10.3 g, 74.5 mmol, 5 equiv), 4-hydroxyacetanilide (5 g, 33.1 mmol, 2.2 equiv) and dibromoalkane (15 mmol, 1 equiv). The reaction mixture was heated at reflux for 24 h and was evaporated *in vacuo* to obtain a solid residue that was mixed with water (50 ml). The off-white solid separated was collected by filtration. It was purified by repeated recrystallization (three times) from methanol to obtain products in reasonably good yield. Typical characterization results are as follows:

1,5-Bis(4-acetamidophenyl-1-oxy)pentane **2c**: white solid, m.p. 199–200°C, yield 3.9 g (71%). IR (KBr pellet): ν_{\max} 3338, 3080, 1631 and 1510 cm^{-1} . ^1H NMR (DMSO, 200 MHz): δ 9.7 (s, 2H, $-2\times\text{-NH-}$), 7.5 (d, $J=9.02$ Hz, 4H, Ar), 6.9 (d, $J=9.02$ Hz, 4H, Ar), 3.9 (t, $J=6.32$ Hz, 4H, $2\times\text{-OCH}_2\text{-}$), 2.0 (s, 6H, $2\times\text{-CH}_3$) and 1.5–1.7 (m, 6H, $3\times\text{-CH}_2\text{-}$).

4.3. α,ω -Bis(4-aminophenyl-1-oxy)alkanes **1a-i**

In a general procedure, a mixture of α,ω -bis(4-acetamidophenyl-1-oxy)alkane (**3a-i**) (8.8 mmol), ethanol (50 ml), and conc. HCl was heated at reflux for 12 h (TLC monitored). The reaction mixture was cooled, poured onto crushed ice and neutralized with 50% aqueous NaOH. The off-white solid obtained was collected by filtration and purified by repeated recrystallization (three times) from a mixture of hexanes/ CH_2Cl_2 (90/10). Typical characterization results are as follows.

1,5-Bis(4-aminophenyl-1-oxy)pentane **1c**: light brown solid, m.p. 76–77°C, yield 1.6 g (70%). IR (KBr pellet): ν_{\max} 3432, 3338, 3040, 2949, 1588 and 1511 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz): δ 6.7 (m, 4H, Ar), 6.6 (m, 4H, Ar), 3.9 (t, $J=6.3$ Hz, 4H, $2\times\text{-OCH}_2\text{-}$), 3.4 (s, 4H, $2\times\text{-NH}_2$) and 1.6–1.82 (m, 6H, $3\times\text{-CH}_2\text{-}$).

4.4. α,ω -Bis{4-[(2-hydroxy-4-octyloxyphenyl)iminomethyl]phenoxy}alkanes **8OSO_nSO₈**

In a general procedure, a mixture of α,ω -bis(4-aminophenyl-1-oxy)alkane **2a-i** (0.97 mmol, 1 equiv), 2-hydroxy-4-*n*-octyloxybenzaldehyde (0.51 g, 2.04 mmol, 2.1 equiv), absolute ethanol (10 ml) and a few traces of acetic acid was heated to reflux until a yellow solid compound precipitated out (4 h). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol, then purified by repeated recrystallization from DMF. Typical characterization results are as follows.

1,5-Bis{4-[(2-hydroxy-4-octyloxyphenyl)iminomethyl]phenoxy}pentane **8OSO₅SO₈**: intense yellow solid, yield 361 mg (50%). IR (KBr pellet): ν_{\max} 2918, 1620, 1568 and 1516 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz): δ 13.8 (b s, 2H, $2\times\text{-OH}$), 8.5 (s, 2H, $2\times\text{-CH=N}$), 7.2 (m, 6H, Ar), 6.9 (d, $J=8.9$ Hz, 4H, Ar), 6.5 (m, 4H, Ar), 4.1 (m, 8H, $4\times\text{-OCH}_2\text{-}$), 1.3–1.9 (m, 30H, $15\times\text{-CH}_2\text{-}$) and 0.9 (m, 6H, $2\times\text{-CH}_3$); δ : 163.8, 163.4, 159.6, 158.0, 141.7, 133.1, 122.0, 115.4, 113.3, 107.4, 101.8, 68.3, 68.3, 31.8, 29.3, 29.2, 29.1, 26.0, 22.8, 22.6

and 14.0. FAB Mass: 751.6 $[\text{MH}]^+$ (calculated for $\text{C}_{47}\text{H}_{62}\text{N}_2\text{O}_6$).

We wish to thank Prof. S. Chandrasekhar for encouragement and helpful discussions.

References

- [1] For a recent review on dimers see: (a) IMRIE, C. T. 1999, *Liquid Crystals*, Vol. II, edited by D. M. P. Mingos (Berlin, Heidelberg: Springer-Verlag) p. 149; (b) IMRIE, C. T., and LUCKHURST, G. R., 1998, *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim Wiley-VCH), p. 801.
- [2] (a) YELAMAGGAD, C. V., ANITHA NAGAMANI, S., HIREMATH, U. S., SHANKAR RAO, D. S., and KRISHNA PRASAD, S., 2002, *Liq. Cryst.*, **29**, 231; (b) HARDOUIN, F., ACHARD, M. F., JIN, J.-I. SHIN, J.-W., and YUN, Y.-K. 1994, *J. Phys. II Fr.*, **4**, 627; (c) ATTARD, G. S. and IMRIE, C. T., 1989, *Liq. Cryst.*, **6**, 387; (d) MARCELIS, A. T. M., KOUDIJS, A., and SUDHOLTER, E. J. R., 1995, *Liq. Cryst.*, **18**, 851; (e) MARCELIS, A. T. M., KOUDIJS, A. and SUDHOLTER, E. J. R., 1996, *Liq. Cryst.*, **21**, 87; (f) IMRIE, C. T., STEWART, D., REMY, C., CHRISTIE, D. W., HAMLEY, I. W., and HARDING, R., 1999, *J. mater. Chem.*, **9**, 2321.
- [3] VORLANDER, D., 1927, *Z. phys. Chem.*, **126**, 449.
- [4] RAULT, J., LIEBERT, L., and STRZELECKI, L., 1975, *Bull Soc. Chem. Fr.*, 1175.
- [5] GRIFFIN, A. C., and BRITT, T. R., 1981, *J. Am. chem. Soc.*, **103**, 4957.
- [6] (a) EMSLEY, J. W., LUCKHURST, G. R., SHILSTONE, G. N., and SAGE, I., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102**, 223; (b) MALPEZZI, L., BRUCKNER, S., GALBIATI, E., ZERBI, G., and LUCKHURST, G. R., 1991, *Mol. Cryst. liq. Cryst.*, **195**, 179; (c) HEEKS, S. K., and LUCKHURST, G. R., 1993, *J. chem. Soc., Faraday Trans.*, **89**, 3289; (d) ABE, A., and NAM, S. Y., 1995, *Macromolecules*, **28**, 90.
- [7] (a) DATE, R. W., IMRIE, C. T., LUCKHURST, G. R., and SEDDON, J. M., 1992, *Liq. Cryst.*, **12**, 203; (b) IMRIE, C. T., 1989, *Liq. Cryst.*, **6**, 391; (c) ATTARD, G. S., GARNETT, S., HICKMAN, C. G., IMRIE, C. T., and TAYLOR, L. 1990, *Liq. Cryst.*, **7**, 495.
- [8] BLATCH, A. E., and LUCKHURST, G. R., 2000, *Liq. Cryst.*, **27**, 775.
- [9] HENDERSON, P. A., NIEMEYER, O., and IMRIE, C. T., 2001, *Liq. Cryst.*, **28**, 463.
- [10] (a) NAITO, H., OKUDA, M., and ZHONG-CAN, 1997, *Phy. Rev. E*, **55**, 1655; (b) PRATIBHA, R., and MADHUSUDANA, N. V., 1992, *J. de Phys. II*, **2**, 383; (c) ADAMCZYK, A., 1995, *Mol. Cryst. liq. Cryst.*, **261**, 271; (d) ARORA, S. L., PALFFY-MUHORAY, P., VORA, R. A., DAVID, D. J., and DASGUPTA, 1989, *Liq. Cryst.*, **5**, 133.
- [11] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Glasgow and London: Leonard Hill).