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Salicylaldimine-based symmetric dimers: synthesis and thermal behaviour

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Several symmetrical dimers comprised of salicylaldimine-moieties connected through ester linkages to the termini of odd-parity alkanediols have been synthesized and investigated for their thermal behaviour. In order to understand the structure-property relations, the lengths of the central alkylene spacers (C_3 and C_5) as well as those of the terminal alkoxy chains (C_6 to C_{22}) have been varied. The dimers with a C_3 -alkylene spacer are non-liquid crystalline, while some of the compounds having a C_5 -alkylene spacer exhibit liquid crystalline properties. The dimer, with a C_5 -alkylene spacer and C_6 -alkoxy tails, shows an intercalated smectic C (SmC_c) phase, whereas the C_8 , C_{10} , C_{11} , and C_{12} homologues are non-mesomorphic. The higher homologues of this series with C_{16} , C_{18} , C_{20} and C_{22} alkoxy tails show a mesophase that has the signatures of a two-dimensional banana (B_1) phase. This mesophase is enantiotropic in the C_{16} and C_{18} homologues while it is monotropic in the other homologues. In these dimers, the spacer length has a remarkable influence on the thermal behaviour.

1. Introduction

Liquid crystalline symmetrical dimers [1] (also referred to as twins or bimesogens), formed by joining two identical mesogenic segments through a central spacer such as a polymethylene unit, are now attracting attention, not only because they are considered as model compounds for polymeric liquid crystals [2] but also due to their unique thermal behaviour [3]. Many studies of symmetrical dimers have been reported which reveal that the liquid crystalline properties depend not only on the parity and length of the flexible central spacer, but also on the length of the terminal chains. Among these symmetrical dimers, the compounds consisting of two mesogenic moieties connected through ester linkages to the termini of odd-alkylene spacers derived from n -alkanediols [4–6] are of current interest owing to their close resemblance to bent-core molecules.

Such compounds have been reported to show a significant odd–even effect [4–6] on the mesomorphic behaviour. It has been reported that dimeric compounds with an even-numbered spacer stabilize the SmA phase and those with an odd-numbered spacer show the smectic C (SmC) phase [4(a)]. Further, if the length of the terminal chains is smaller than or comparable to the length of the spacer, then an intercalated SmC structure

is observed [4(a, c)]. If the terminal chains are significantly longer than the spacer, a smectic structure in which the bent molecules are packed in the smectic layers with a uniform bend direction has been reported [5(a)]. Electro-optical measurements on such a smectic phase have shown that it has an antiferroelectric type of structure in which the spontaneous polarization points along the bend direction of the molecules [5(a)]. If the lengths of the spacer and the terminal chains lie between the cases mentioned above, then two-dimensionally ordered frustrated smectic phases are observed [5(a)]. However, until now it has not been clear whether the switchable phase exhibited by these compounds is similar to that observed for banana-shaped mesogens with a nucleus based on benzene [7].

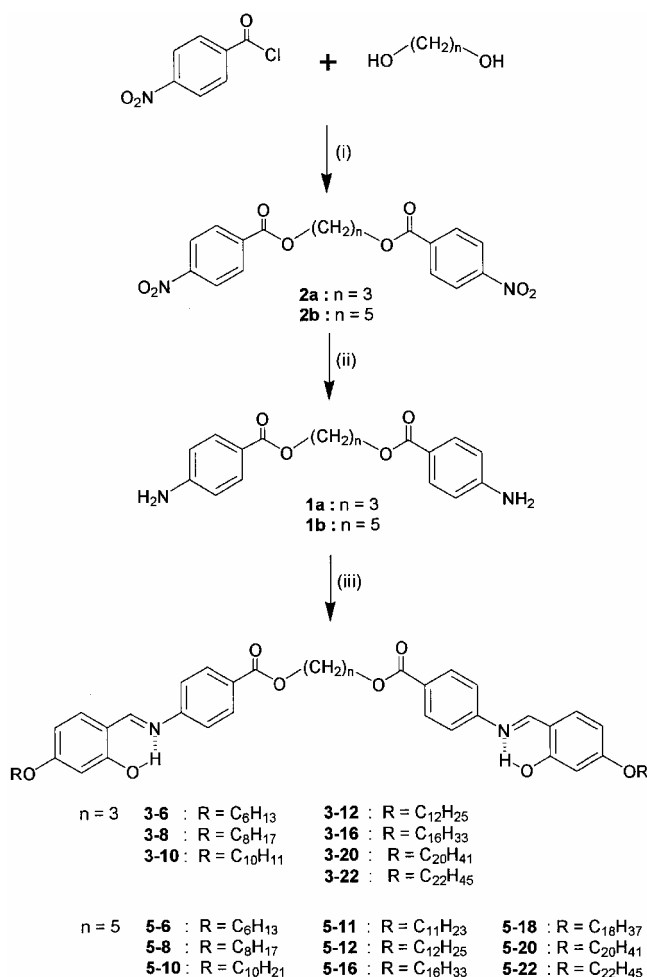
So far, either a biphenyl [4], a Schiff's base [5], an azobenzene [6] or a Schiff's base-benzoate mixed [4(d)] moiety has been attached to the two ends of diols to prepare diesters (dimer). In order clearly to understand underlying structure–property relations different cores have to be incorporated. To the best of our knowledge the salicylaldimine [N -(2-hydroxy-4-alkoxybenzylidene)-aniline] moiety has not been employed to realize such dimers. In continuation of our investigations on banana-shaped liquid crystals [8] here we report the synthesis and characterization of bent-shaped mesogenic dimers comprising odd-numbered (C_3 and C_5) methylene spacers connected to rigid salicylaldimine moieties.

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2. Results and discussion

2.1. Synthesis

The proposed dimers having an odd-parity alkylene central spacer with C₃ (**3-6**, **3-8**, **3-10**, **3-12**, **3-16**, **3-20**, **3-22**) and C₅ (**5-6**, **5-8**, **5-10**, **5-11**, **5-12**, **5-16**, **5-18**, **5-20**, **5-22**) lengths have been synthesized as depicted in the scheme. The target molecules were realized by condensing 2-hydroxy-4-*n*-alkoxybenzaldehydes with 1,3-propanediol bis(4-aminobenzoate) (**2a**) and 1,5-pentane-1,5-diol bis(4-aminobenzoate) (**2b**). The requisite alkoxybenzaldehydes were prepared by heating 2,4-dihydroxybenzaldehyde with 1-*n*-bromoalkanes at reflux under mild basic reaction conditions in a solvent medium. The key intermediates, the diamines **1a** and **1b** were obtained by catalytic hydrogenation (H₂/Pd-C) of 1,3-propanediol bis(4-nitrobenzoate) (**2a**) and 1,5-pentane-1,5-diol bis(4-nitrobenzoate) (**2b**), respectively. These dinitro compounds



Scheme. General route employed for the synthesis of the symmetrical dimers. Reagents and conditions: (i) pyridine, rt, 24 h (quantitative); (ii) H₂/Pd-C (10%), 15 psi, EtOAc, 2.5 h (quantitative); (iii) 2-hydroxy-4-*n*-decyloxybenzaldehyde, abs. EtOH, AcOH (trace), 15 min. 22%.

2a and **2b** were prepared by treating 4-nitrobenzoyl chloride with 1,3-propanediol or 1,5-pentane-1,5-diol in the presence of pyridine as a mild base. Finally the amines and aldehydes were condensed under mild acidic reaction conditions to furnish the 1,3- or 1,5-bis{4-[(2-hydroxy-4-*n*-alkoxyphenyl)iminomethyl]benzoyloxy}propanes/pentanes (**3-6**, **3-8**, **3-10**, **3-12**, **3-16**, **3-20**, **3-22**)/(**5-6**, **5-8**, **5-10**, **5-11**, **5-12**, **5-16**, **5-18**, **5-20**, **5-22**) in reasonably good yield. Details of the synthetic procedures are given in § 4.

2.2. Thermal behaviour

In an effort to understand the structure–property relations the chain lengths of both the paraffinic spacer (within limits) as well as of the terminal alkoxy tails have been varied. The thermal behaviour and phase transition temperatures of all the new dimeric compounds are summarized in the table. As can be seen from the table, the dimers with a C₃-chain length spacer are non-mesomorphic. The lower homologues **3-6**, **3-8**, **3-10**, **3-12**, and **3-16** undergo a direct transition from the room temperature crystalline phase to the isotropic state while the higher homologues **3-20** and **3-22** show crystal to crystal transitions. This behaviour is reminiscent of the result obtained for another chiral dimer [4(*a*)] and may be attributed to the fact that in the dimers **3-6**, **3-8**, **3-10**, **3-12**, **3-16**, **3-20** and **3-22**, the salicylaldehyde moieties (which themselves are stiff due to the presence of intramolecular hydrogen bonding) do not have much mobility around the spacer, thus reducing the fluidity of the molecule as a whole. This argument is supported by molecular modelling (Chem3D, CambridgeSoft) studies which show that in the all-*trans*-conformation the two salicylaldehyde moieties are quite close to each other and hence sterically hindered. On increasing the chain length of the terminal alkoxy tails one might have expected to observe mesomorphic behaviour, but even the compounds with quite long chain lengths (C₂₂) are unable to stabilize any mesomorphic phase in this series.

On the other hand, with the exception of the **5-8**, **5-10**, **5-11** and **5-12** homologues, the other dimers having a C₅-length spacer (**5-6**, **5-16**, **5-18**, **5-20**, and **5-22**) are mesomorphic. All these dimers also exhibit transitions corresponding to crystal to crystal changes. The first compound of the series **5-6** with a C₆-tail, on cooling from isotropic phase, shows a mesophase having a focal-conic texture in the regions where the molecules have aligned homogeneously and a schlieren texture in regions with a tilted alignment (figure 1). These textures are characteristic of the SmC phase which, as we shall see later, was confirmed by X-ray studies. Surprisingly, the higher homologues **5-8**, **5-10**, **5-11** and **5-12** are non-mesomorphic samples, but show different crystalline states.

Table. Phase transition temperatures^a (°C) and enthalpies^b (J/gm) (in brackets) of the 1,3/1,5-bis{4-[(2-hydroxy-4-*n*-alkoxyphenyl)iminomethyl]benzoyl}propanes/pentanes. Cr = crystal; SmC_c = intercalated smectic C phase; B₁ = a two-dimensional smectic phase; I = isotropic phase.

Compound	R	n	Mode	Phase sequence
3-6	C ₆ H ₁₃	3	Heating	Cr 184.5 I
3-8	C ₈ H ₁₇	3	Heating	Cr 180.1 I
3-10	C ₁₀ H ₂₁	3	Heating	Cr 175.4 I
3-12	C ₁₂ H ₂₅	3	Heating	Cr 175.3 I
3-16	C ₁₆ H ₃₃	3	Heating	Cr ₁ 168.5 I
3-20	C ₂₀ H ₄₁	3	Heating	Cr ₁ 67.7 Cr ₂ 153 Cr ₃ 165.6 I
3-22	C ₂₂ H ₄₅	3	Heating	Cr ₁ 148.8 (8.5) Cr ₂ 162.7 (16.3) I
5-6	C ₆ H ₁₃	5	Heating	Cr ₁ 112.4 Cr ₂ 144.6 (54.3) SmC _c 148.5 (15.5) I
			Cooling	I 146 (15.4) SmC _c 131.3 (52) Cr
5-8	C ₈ H ₁₇	5	Heating	Cr ₁ 104.3 Cr ₂ 110.7 Cr ₃ 141.8 I
5-10	C ₁₀ H ₂₁	5	Heating	Cr ₁ 91.1 Cr ₂ 139.2 I
5-11	C ₁₁ H ₂₃	5	Heating	Cr ₁ 92.2 Cr ₂ 138.9 I
5-12	C ₁₂ H ₂₅	5	Heating	Cr ₁ 95 Cr ₂ 98.9 Cr ₃ 137.8 I
5-16	C ₁₆ H ₃₃	5	Heating	Cr ₁ 121.1 Cr ₂ 132.3 (44.6) B ₁ 136.6 (14.4) I
			Cooling	I 134.6 (14.1) B ₁ 126 (7.9) Cr
5-18	C ₁₈ H ₃₇	5	Heating	Cr ₁ 102.2 Cr ₂ 119.8 Cr ₃ 125.7
				Cr ₄ 130.9 (39.3) B ₁ 135.2 (10.9) I
			Cooling	I 133.5 (14.8) B ₁ 120 (60.3) Cr
5-20	C ₂₀ H ₄₁	5	Heating	Cr ₁ 66.7 Cr ₂ 104.2 Cr ₃ 128.6 I
			Cooling	I 126.8 (3.5) B ₁ 122.7 (58.2) Cr
5-22	C ₂₂ H ₄₅	5	Heating	Cr ₁ 72.9 Cr ₂ 108.1 Cr ₃ 128.4 I
			Cooling	I 126.4 (3.2) B ₁ 124.4 (60.4) Cr

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

^b The enthalpies have been mentioned only for Cr–SmC_c/B₁, SmC_c/B₁–I and their reverse transitions.

^c Monotropic B₁ phase.

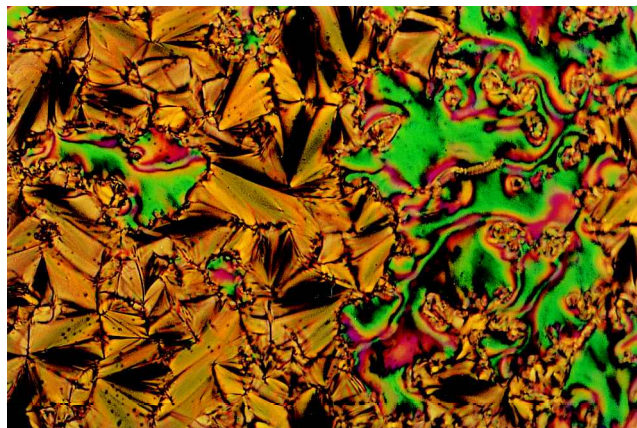


Figure 1. Photomicrograph of the texture observed at 145.1°C for the SmC_c phase on developing from the isotropic phase of dimer **5-6**.

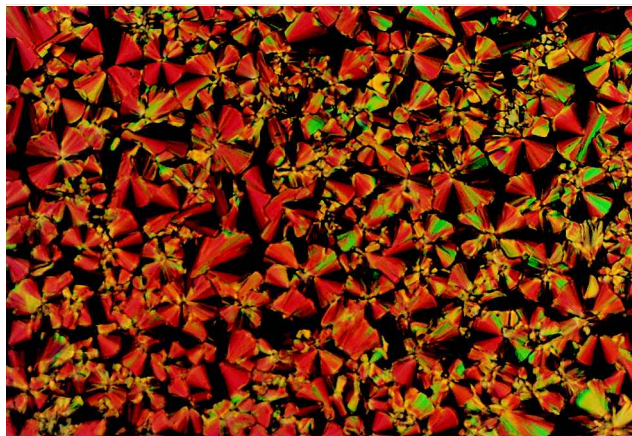


Figure 2. Photomicrograph of the texture observed for dimer **5-18** at 132.5°C in the enantiotropic B₁ phase obtained from the isotropic phase.

The **5-16** and **5-18** homologues exhibit only one enantiotropic mesophase. The dimers **5-20** and **5-22** also exhibit the same mesophase but these are now monotropic. On cooling from the isotropic phase the mesophase seen for compound **5-18** appears with a dendritic growth pattern (figure 2), which coalesces to form a mosaic texture with spherulitic domains. This textural pattern suggests the presence of a B₁ phase and this was confirmed by X-ray

diffraction (XRD) studies (see the following section for details). The DSC traces obtained both on heating and cooling cycles for sample **5-18** are shown in figure 3.

2.3. X-ray studies

In order to confirm the presence of the SmC and B₁ phases, XRD experiments were carried out on sample **5-6** and samples **5-16/5-18**, respectively. The powder

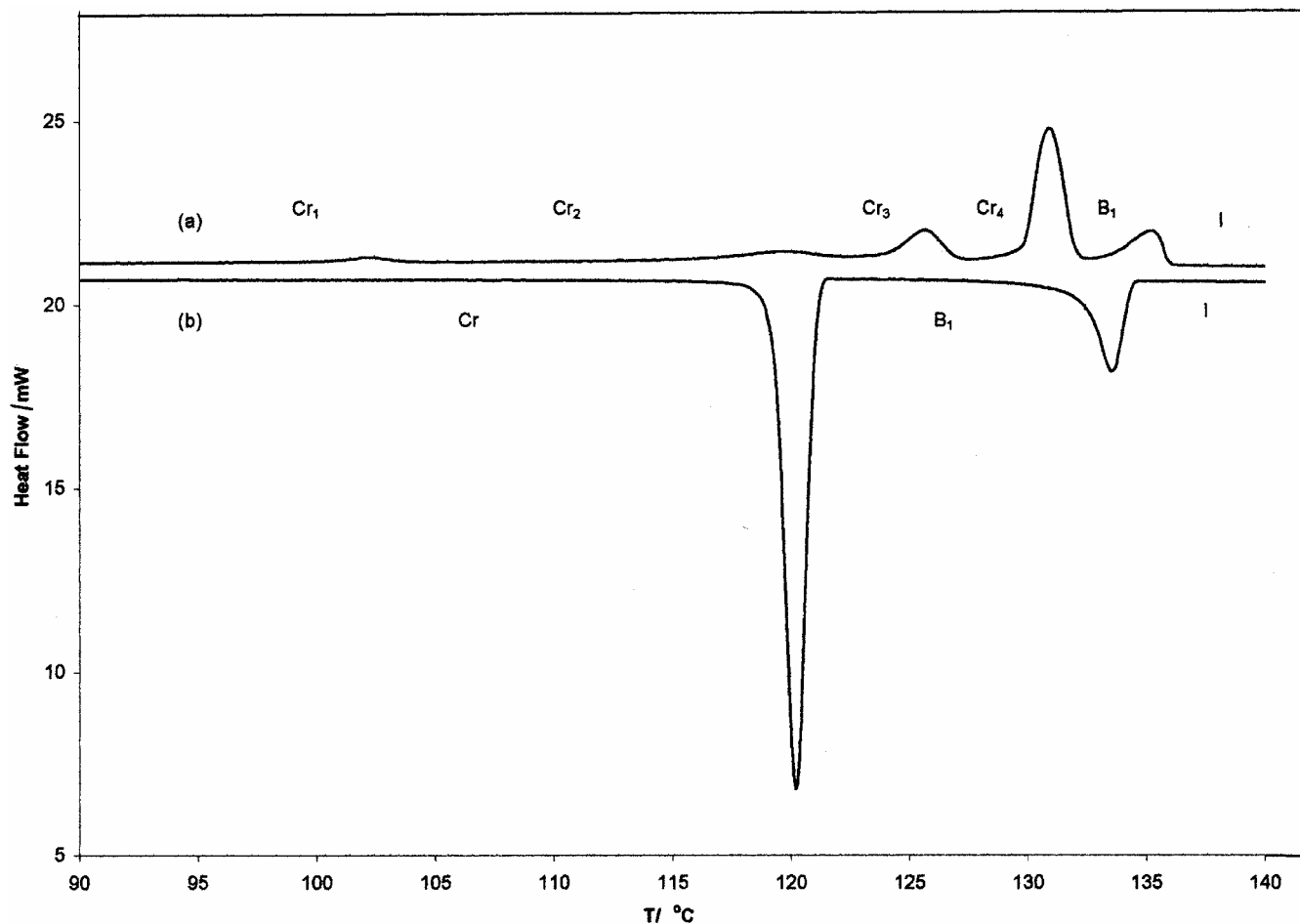


Figure 3. DSC thermograms obtained at a rate of $5^{\circ}\text{C min}^{-1}$ for the compound **5-18**: (a) heating mode, (b) cooling mode.

diffraction pattern and the derived one-dimensional intensity versus 2θ profiles obtained for the mesophase of **5-6** are shown in figure 4. We see two sharp reflections

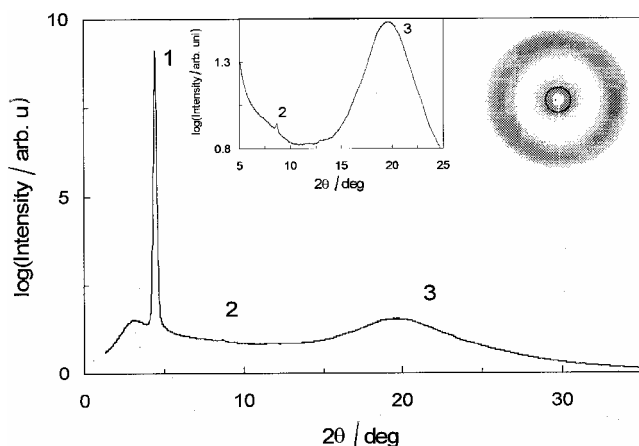


Figure 4. The XRD pattern and the derived one-dimensional intensity versus 2θ profiles obtained for the SmC mesophase of compound **5-6**. The inset shows the intensity versus 2θ profile in more detail.

at low angles $2\theta = 4.46^{\circ}$, 8.68° and one broad diffuse peak at high angle, $2\theta = 19.8^{\circ}$; the corresponding d -spacings being 2.08, 1.04 and 0.46 nm, respectively. It should be noticed here that the measured d -spacing (2.08 nm) is about half the length of the molecule. The peak $2\theta = 8.68^{\circ}$ is due to the second harmonic reflection. The diffuse nature of the peak in the wide angle region corresponds to short range correlation in the direction perpendicular to molecules within the layer plane. Based on the textural observation (focal-conic and also schlieren texture) and the X ray data we concluded that this phase is SmC_c phase.

Figures 5 and 6 show the XRD pattern and one-dimensional intensity versus 2θ profile obtained for **5-16** and **5-18**, respectively. For the C₁₆ homologue (**5-16**), four sharp peaks are seen in the low angle region at angles $2\theta = 1.87^{\circ}$, 3.37° , 4.95° and 6.53° , the corresponding d -spacings being 5.38, 2.81, 1.86 and 1.39 nm, respectively. Further, a diffuse reflection is seen at wide angles centred around $2\theta = 19.36^{\circ}$ with a 0.46 nm spacing associated with a liquid-like ordering. Thus the low angle reflections can be indexed as $\{2\ 0\}$, $\{1\ 1\}$, $\{4\ 1\}$ and $\{2\ 2\}$ arising

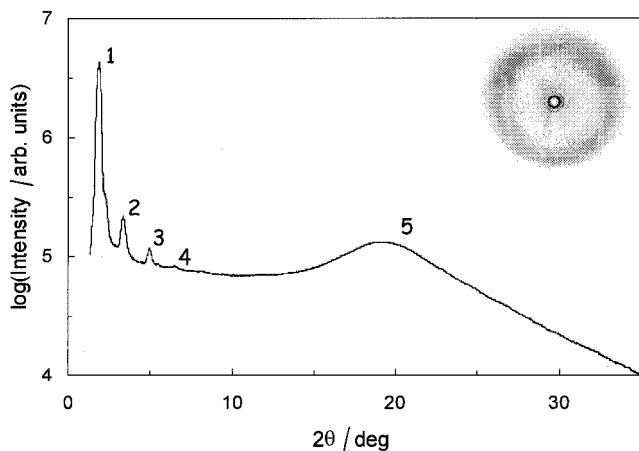


Figure 5. X-ray intensity profile of an unoriented sample of **5-16** obtained for the B_1 phase. Notice the diffuse peak in the wide angle region indicating a liquid-like order, and four sharp reflections at low angles indicating a two-dimensional structure (a similar pattern is also seen in figure 6).

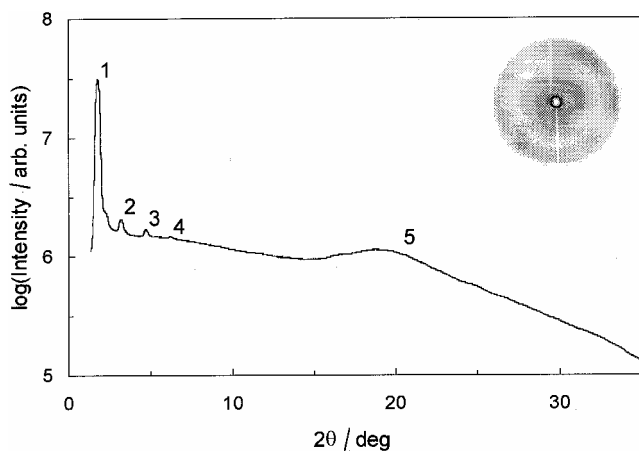


Figure 6. X-ray intensity profile of an unoriented sample of **5-18** in the B_1 phase.

from a rectangular lattice. Similarly, for the C_{18} homologue (**5-18**), four sharp peaks were seen at $2\theta = 1.8^\circ$, 3.2° , 4.72° and 6.24° with $d = 5.62$, 2.97 , 1.96 and 1.46 nm, respectively. Again these spacings can be indexed as $\{20\}$, $\{11\}$, $\{41\}$ and $\{22\}$ of a 2D rectangular lattice. The diffuse peak at wide angles, $2\theta = 19.36^\circ$, corresponds to liquid-like ordering within the layer. The X-ray data in conjunction with the textural pattern suggest that the mesophase is a B_1 phase.

3. Summary

In conclusion, we have reported the first examples of symmetric dimers consisting of a salicylaldimine rigid core attached to the termini of odd (C_3 and C_5)-parity alkanediols through ester linkages. Currently such compounds are of interest because such materials, especially

dimers having a C_5 -length central spacer, are known to acquire a bent-conformation and therefore are able to form an antiferroelectric structure in which the spontaneous polarization is directed in the bend direction of the molecules. Our studies indicate that in these dimers, the length of the spacer has a remarkable influence on the thermal behaviour. The dimers with a C_3 -parity alkylene spacer are non-mesomorphic, whereas some of the compounds having a C_5 -alkylene spacer exhibit an intercalated SmC or a B_1 phase. These molecular assemblies may help towards a better understanding of the underlying relations between molecular structure and mesomorphic behaviour. Currently we are working on similar symmetrical dimers in which the central alkylene spacer is connected to the salicylaldimine moieties through ether linkages.

4. Experimental

2,4-Dihydroxybenzaldehyde and Pd-C (10%) were obtained from Aldrich; 1,3-propanediol and 1,5-pentane-diol were purchased from Lancaster Company. These chemicals were used as received, while the solvents obtained from local sources were dried following standard procedures. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 10, F254). Column chromatographic separations were performed using silica gel (60–120 mesh). IR spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer. ^1H NMR spectra were recorded using a Bruker AMX-400 (400 MHz) spectrometer and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. Mass spectra were recorded using a Jeol JMS-600H spectrometer in the FAB positive mode using 3-nitrobenzyl alcohol as a liquid matrix.

The dimers were investigated for liquid crystalline behaviour by polarizing optical microscopy (Leitz DMRXP) with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). The preliminary optical observations were made with untreated slides. For confirmation of textures, two different surface-coated slides, one treated for homogeneous alignment and another for homeotropic alignment were used. The optical observations were also made using untreated slides. XRD studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics and the sample was contained in a Lindemann capillary tube.

4.1. 1,3-Propanediol/1,5-pentane-diol bis(4-nitrobenzoate) (**2a**, **2b**)

Into a 100 ml two-necked round-bottomed flask equipped with an argon inlet and a septum were placed dry pyridine (AR Grade, 20 ml) and 1,3-propanediol

or 1,5-pentanediol (41.1 mmol, 1 equiv). The resulting solution was cooled (5–10°C) and then a solution of 4-nitrobenzoyl chloride (30.5 g, 164.4 mmol, 4 equiv) in dry THF (60 ml) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temperature and vigorous stirring was continued for 24 h. The reaction mixture was concentrated and the thick pale yellow mass obtained was poured into ice-cold 3M HCl; the yellow solid that separated was collected by filtration. This solid was dissolved in CH₂Cl₂ (80 ml), washed with 5% aqueous NaOH (20 ml × 2) followed by water and dried over anhydrous Na₂SO₄. Evaporation of the solvent furnished a crude product that was purified by column chromatography using silica gel (60–120 mesh). Eluting with a mixture of 10% ethyl acetate–hexanes furnished a yellow solid, which was further purified by repeated recrystallization from a mixture of absolute ethanol–CH₂Cl₂ (9:1).

2a: $R_f = 0.22$ (20% EtOAc–hexanes), pale yellow solid, yield quantitative, m.p. = 117–118°C. IR (KBr pellet): ν_{\max} 2962, 2899, 1727, 1607 and 1530 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, $J = 8.9$ Hz, 4H, Ar), 8.2 (d, $J = 8.9$, 4H, Ar), 4.56 (t, $J = 6.26$, 4H, 2 × COOCH₂) and 2.35–2.29 (m, 2H, CH₂). FAB Mass: m/z 374.3 [M⁺ + 1]⁺. Calc. for C₁₇H₁₄N₂O₈.

2b: $R_f = 0.22$ (20% EtOAc–hexanes), pale yellow solid, yield quantitative, m.p. = 102–103°C. IR (KBr pellet): ν_{\max} 2962, 2899, 1727, 1607, 1530 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, $J = 8.76$ Hz, 4H, Ar), 8.13 (d, $J = 8.8$, 4H, Ar), 4.41 (t, $J = 6.58$, 4H, 2 × COOCH₂), 1.93–1.58 (m, 6H, 3 × CH₂). FAB Mass: m/z 403.2 [M⁺ + 1]⁺. Calc. for C₁₉H₁₈N₂O₈.

4.2. 1,3-Propanediol/1,5-pentanediol bis(4-aminobenzoate) (**1a**, **1b**)

A mixture 1,3-propanediol or 1,5-pentanediol bis(4-nitrobenzoate) (**2a** or **2b**) (7.46 mmol), dry EtOAc (40 ml) and activated Pd-C (10%) (0.3 g) was hydrogenated at 15 psi pressure over a period of 2.5 h. The reaction mixture was filtered on a Celite bed and the filtrate was evaporated to dryness *in vacuo* furnishing the pure product.

1a: $R_f = 0.35$ (40% EtOAc–hexanes), white solid, yield quantitative, m.p. = 126–127°C. IR (KBr pellet): ν_{\max} 3390, 3240, 2977, 2946, 1704, 1694, 1633, 1561 and 1504 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 8.6$ Hz, 4H, Ar), 6.62 (d, $J = 8.6$, 4H, Ar), 4.4 (t, $J = 6.26$, 4H, 2 × COOCH₂), 4.05 (s, 4H, 2 × -NH₂⁺) and 2.22–2.15 (m, 2H, CH₂). FAB Mass: m/z 314.5 [M⁺] calc. for C₁₇H₁₈N₂O₄.

1b: $R_f = 0.35$ (40% EtOAc–hexanes), white solid, yield quantitative, m.p. = 133–136°C. IR (KBr pellet): ν_{\max} 3390, 3240, 2977, 2946, 1704, 1694, 1633, 1561 and 1504 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.84

(d, $J = 8.76$ Hz, 4H, Ar), 6.62 (d, $J = 8.68$, 4H, Ar), 4.41 (t, $J = 6.58$, 2 × COOCH₂, 4H) and 1.93–1.58 (m, 6H, 3 × CH₂). FAB Mass: m/z 342.9 [M⁺] calc. for C₁₉H₂₂N₂O₄.

4.3. 1,3/1,5-Bis{4-[(2-hydroxy-4-*n*-alkoxyphenyl)-iminomethyl]benzoyloxy}propanes/pentanes (**3-6**, **3-8**, **3-10**, **3-12**, **3-16**, **3-20**, **3-22**)/(**5-6**, **5-8**, **5-10**, **5-11**, **5-12**, **5-16**, **5-18**, **5-20**, **5-22**)

General Procedure: A mixture of 1,3-propanediol or 1,5-pentanediol bis(4-aminobenzoate) (**1a** or **1b**) (2.9 mmol, 1 equiv), the 2-hydroxy-4-*n*-alkoxybenzaldehyde (6.09 mmol, 2.1 equiv), absolute ethanol (50 ml) and a few drops of acetic acid were heated under reflux until a yellow solid compound was precipitated (15 min). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was further purified by repeated recrystallization from absolute ethanol–CH₂Cl₂ (9:1); yield 65–88%.

4.3.1. 1,3-Bis{4-[(2-hydroxy-4-*n*-hexyloxyphenyl)-iminomethyl]benzoyloxy}propane (**3-6**)

IR (KBr pellet): ν_{\max} 2919, 2848, 1706, 1628, 1608, 1568 and 1521 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 13.39 (s, 2H, 2 × -OH), 8.52 (s, 2H, 2 × CH=N), 8.06 (d, $J = 8.36$ Hz, 4H, Ar), 7.26 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.52 (t, $J = 6.1$, 4H, 2 × OCOCH₂), 4.00 (t, $J = 6.54$, 4H, 2 × OCH₂), 2.29 (t, $J = 6.14$, 2H, CH₂), 1.8–1.34 (m, 16H, 8 × CH₂) and 0.91 (t, $J = 6.84$, 6H, 2 × CH₃).

4.3.2. 1,3-Bis{4-[(2-hydroxy-4-*n*-octyloxyphenyl)-iminomethyl]benzoyloxy}propane (**3-8**)

IR (KBr pellet): ν_{\max} 2921, 2849, 1704, 1625, 1600, 1567 and 1519 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 13.39 (s, 2H, 2 × -OH), 8.52 (s, 2H, 2 × CH=N), 8.06 (d, $J = 8.5$ Hz, 4H, Ar), 7.26 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.52 (t, $J = 6.12$, 4H, 2 × OCOCH₂), 4.00 (t, $J = 6.58$, 4H, 2 × OCH₂), 2.28 (t, $J = 6.14$, 2H, CH₂), 1.83–1.29 (m, 24H, 12 × CH₂) and 0.89 (t, $J = 6.7$, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃, Spin Echo FT): δ 166.2 (C), 164.2 (C), 164.12 (C), 162.85 (CH), 152.77 (C), 133.95 (CH), 131.1 (CH), 127.76 (C), 120.99 (CH), 112.86 (C), 108.04 (CH), 101.65 (CH), 68.40 (OCH₂), 61.98 (OCH₂), 31.83 (CH₂), 29.3 (CH₂), 29.22 (CH₂), 29.1 (CH₂), 28.39 (CH₂), 26.02 (CH₂), 22.65 (CH₂), and 14.06 (CH₃).

4.3.3. 1,3-Bis{4-[(2-hydroxy-4-*n*-decyloxyphenyl)-iminomethyl]benzoyloxy}propane (**3-10**)

IR (KBr pellet): ν_{\max} 2921, 2848, 1705, 1626, 1600, 1567 and 1519 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 13.38 (s, 2H, 2 × -OH), 8.51 (s, 2H, 2 × CH=N), 8.06 (d, $J = 8.28$ Hz, 4H, Ar), 7.25 (m, 6H, Ar), 6.48 (m, 4H, Ar), 4.52 (t, $J = 5.96$, 4H, 2 × OCOCH₂), 4.00 (t, $J = 6.46$,

4H, $2 \times \text{OCH}_2$), 2.29 (t, $J = 6.2$, 2H, CH_2), 1.8–1.2 (m, 32H, $16 \times \text{CH}_2$) and 0.87 (t, $J = 6.96$, 6H, $2 \times \text{CH}_3$).

4.3.4. *1,3-Bis{4-[(2-hydroxy-4-n-dodecyloxyphenyl)-iminomethyl]benzoyloxy}propane (3-12)*

IR (KBr pellet): ν_{max} 2920, 2848, 1704, 1626, 1600, 1567 and 1519 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.39 (s, 2H, $2 \times \text{-OH}$), 8.52 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.4 \text{ Hz}$, 4H, Ar), 7.26 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.53 (t, $J = 5.98$, 4H, $2 \times \text{OCOCH}_2$), 4.00 (t, $J = 6.52$, 4H, $2 \times \text{OCH}_2$), 2.29 (m, 2H, CH_2), 1.81–1.26 (m, 40H, $20 \times \text{CH}_2$) and 0.88 (t, $J = 6.48$, 6H, $2 \times \text{CH}_3$).

4.3.5. *1,3-Bis{4-[(2-hydroxy-4-n-hexadecyloxyphenyl)-iminomethyl]benzoyloxy}propane (3-16)*

IR (KBr pellet): ν_{max} 2918, 2848, 1704, 1628, 1600, 1567 and 1519 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.38 (s, 2H, $2 \times \text{-OH}$), 8.52 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.48 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.48 (m, 4H, Ar), 4.53 (t, $J = 5.6$, 4H, $2 \times \text{OCOCH}_2$), 4.00 (t, $J = 6.48$, 4H, $2 \times \text{OCH}_2$), 2.28 (m, 2H, CH_2), 1.79–1.26 (m, 56H, $28 \times \text{CH}_2$) and 0.88 (t, $J = 6.6$, 6H, $2 \times \text{CH}_3$).

4.3.6. *1,3-Bis{4-[(2-hydroxy-4-n-eicosyloxyphenyl)-iminomethyl]benzoyloxy}propane (3-20)*

IR (KBr pellet) ν_{max} 2919, 2848, 1704, 1626, 1600, 1567 and 1519 cm^{-1} . Owing to the insolubility of the sample in organic solvents, it was not possible to record NMR spectra.

4.3.7. *1,3-Bis{4-[(2-hydroxy-4-n-docosyloxyphenyl)-iminomethyl]benzoyloxy}propane (3-22)*

IR (KBr pellet): ν_{max} 2921, 2848, 1706, 1626, 1600, 1561 and 1521 cm^{-1} . Owing to the insolubility of the sample in common organic solvents, it was not possible to record NMR spectra.

4.3.8. *1,5-Bis{4-[(2-hydroxy-4-n-hexyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-6)*

IR (KBr pellet): ν_{max} 2937, 2857, 1713, 1627, 1599 and 1518 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.4 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.50 (m, 4H, Ar), 4.37 (t, $J = 6.44$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.58$, 4H, $2 \times \text{OCH}_2$), 1.95–1.25 (m, 22H, $11 \times \text{CH}_2$) and 0.91 (t, $J = 6.94$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 749.6 [M^+] calc. for $\text{C}_{45}\text{H}_{54}\text{N}_2\text{O}_8$.

4.3.9. *1,5-Bis{4-[(2-hydroxy-4-n-octyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-8)*

IR (KBr pellet): ν_{max} 2920, 2848, 1716, 1624, 1599 and 1567 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.48 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.50 (m, 4H, Ar), 4.37

(t, $J = 6.4$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.56$, 4H, $2 \times \text{OCH}_2$), 1.95–1.25 (m, 30H, $15 \times \text{CH}_2$) and 0.89 (t, $J = 6.66$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 807.5 [M^+] calc. for $\text{C}_{49}\text{H}_{62}\text{N}_2\text{O}_8$.

4.3.10. *1,5-Bis{4-[(2-hydroxy-4-n-decyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-10)*

IR (KBr pellet): ν_{max} 2919, 2851, 1713, 1632, 1599, 1538 and 1519 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.36 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.28 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.50 (m, 4H, Ar), 4.37 (t, $J = 6.44$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.58$, 4H, $2 \times \text{OCH}_2$), 1.95–1.25 (m, 38H, $19 \times \text{CH}_2$) and 0.88 (t, $J = 6.7$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 863.7 [M^+] calc. for $\text{C}_{53}\text{H}_{70}\text{N}_2\text{O}_8$.

4.3.11. *1,5-Bis{4-[(2-hydroxy-4-n-undecyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-11)*

IR (KBr pellet): ν_{max} 2918, 2850, 1713, 1630, 1569, 1538 and 1517 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.44 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.37 (t, $J = 6.34$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.44$, 4H, $2 \times \text{OCH}_2$), 1.95–1.25 (m, 42H, $21 \times \text{CH}_2$) and 0.88 (t, $J = 6.6$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 891.7 [M^+] calc. for $\text{C}_{55}\text{H}_{74}\text{N}_2\text{O}_8$.

4.3.12. *1,5-Bis{4-[(2-hydroxy-4-n-dodecyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-12)*

IR (KBr pellet): ν_{max} 2922, 2847, 1716, 1624, 1599, 1567 and 1538 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.06 (d, $J = 8.56 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.5 (m, 4H, Ar), 4.37 (t, $J = 6.44$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.58$, 4H, $2 \times \text{OCH}_2$), 1.91–1.26 (m, 46H, $23 \times \text{CH}_2$) and 0.88 (t, $J = 6.82$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 891.7 [M^+] calc. for $\text{C}_{57}\text{H}_{78}\text{N}_2\text{O}_8$.

4.3.13. *1,5-Bis{4-[(2-hydroxy-4-n-hexadecyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-16)*

IR (KBr pellet): ν_{max} 2919, 2857, 1715, 1681, 1651, 1621 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times \text{-OH}$), 8.51 (s, 2H, $2 \times \text{CH=N}$), 8.05 (d, $J = 8.2 \text{ Hz}$, 4H, Ar), 7.25 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.37 (t, $J = 6.4$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.54$, 4H, $2 \times \text{OCH}_2$), 1.91–1.21 (m, 62H, $31 \times \text{CH}_2$), 0.87 (t, $J = 6.6$, 6H, $2 \times \text{CH}_3$). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , Spin Echo FT): δ 166.19 (C), 164.2 (C), 164.11 (C), 162.79 (CH), 152.63 (C), 133.93 (CH), 131.02 (CH), 128.06 (C), 120.98 (CH), 112.87 (C), 108.02 (CH), 101.65 (CH), 68.40 (OCH_2), 61.73 (OCH_2), 31.95 (CH_2), 29.7 (CH_2), 29.38 (CH_2), 29.11 (CH_2), 28.43 (CH_2), 26.02 (CH_2), 22.70 (CH_2), and 14.09 (CH_3). FAB mass: m/z 1031.5 [M^+] calc. for $\text{C}_{65}\text{H}_{94}\text{N}_2\text{O}_8$.

4.3.14. *1,5-Bis{4-[(2-hydroxy-4-n-octadecyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-18)*

IR (KBr pellet): ν_{\max} 2916, 2857, 1714, 1627, 1599, 1516 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.41 (s, 2H, $2 \times -\text{OH}$), 8.51 (s, 2H, $2 \times \text{CH}=\text{N}$), 8.06 (d, $J = 8.44$ Hz, 4H, Ar), 7.25 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.37 (t, $J = 6.36$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.54$, 4H, $2 \times \text{OCH}_2$), 1.90–1.25 (m, 70H, $35 \times \text{CH}_2$), 0.87 (t, $J = 6.76$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 1087 [M^+] calc. for $\text{C}_{69}\text{H}_{102}\text{N}_2\text{O}_8$.

4.3.15. *1,5-Bis{4-[(2-hydroxy-4-n-eicosyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-20)*

IR (KBr pellet): ν_{\max} 2917, 2850, 1712, 1629, 1598, 1515 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.38 (s, 2H, $2 \times -\text{OH}$), 8.51 (s, 2H, $2 \times \text{CH}=\text{N}$), 8.06 (d, $J = 8.48$ Hz, 4H, Ar), 7.25 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.37 (t, $J = 6.42$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.56$, 4H, $2 \times \text{OCH}_2$), 1.91–1.25 (m, 78H, $39 \times \text{CH}_2$), 0.87 (t, $J = 6.74$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 1142 [M^+] calc. for $\text{C}_{73}\text{H}_{110}\text{N}_2\text{O}_8$.

4.3.16. *1,5-Bis{4-[(2-hydroxy-4-n-docosyloxyphenyl)-iminomethyl]benzoyloxy}pentane (5-22)*

IR (KBr pellet): ν_{\max} 2917, 2857, 1714, 1633, 1598, 1515 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 13.37 (s, 2H, $2 \times -\text{OH}$), 8.51 (s, 2H, $2 \times \text{CH}=\text{N}$), 8.06 (d, $J = 8.44$ Hz, 4H, Ar), 7.24 (m, 6H, Ar), 6.47 (m, 4H, Ar), 4.37 (t, $J = 6.36$, 4H, $2 \times \text{OCOCH}_2$), 3.99 (t, $J = 6.526$, 4H, $2 \times \text{OCH}_2$), 1.90–1.25 (m, 86H, $43 \times \text{CH}_2$), 0.87 (t, $J = 6.7$, 6H, $2 \times \text{CH}_3$). FAB mass: m/z 1199.9 [$\text{M}^+ + 1$] calc. for $\text{C}_{77}\text{H}_{118}\text{N}_2\text{O}_8$.

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