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Dimeric Salicylaldimine-Based Mesogens with Flexible Spacers: Parity-Dependent Mesomorphism

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New series of dimeric molecules with flexible spacers are described in which the mesogenic salicylaldimine group is linked to the alkylene spacer via an imino group. To study the structure−property relations, the lengths of the alkylene spacers ($m = 5-8$) as well as those of the terminal alkoxy chains ($n = 4-14$) have been varied. The compounds with even-numbered spacers behave as classic rodlike mesogens displaying nematic and/or smectic C phases, while those with odd-numbered spacers show nematic, columnar nematic, and columnar rectangular phases, behaving as bent-core mesogens. The effect on the liquid-crystalline behavior of the effective geometric change arising from the spacer parity and the imino linkage is discussed.

Introduction

For many years, symmetric, dimeric, liquid-crystalline compounds, formed by two identical mesogenic units linked via a flexible spacer, have been investigated as model compounds for liquid-crystalline polymers,[1,2] while the study of unsymmetric dimers[3] has yielded materials with a rich mesomorphism. Recently, the dimers themselves have attracted attention as they display an unusual mesomorphism, different to that of the corresponding monomers. One of the main characteristics of this class of materials is that their mesomorphic properties depend on the parity of the flexible spacer and the nature of the link between the spacer and the mesomorphic units (Figure 1).[4] Thus, in dimers with an even-numbered spacer (Figure 1a), the mesogenic groups are disposed to give an overall rodlike shape, whereas with an odd-numbered spacer (Figure 1b), the mesogenic groups are inclined with respect to each other giving a bent-shaped motif.

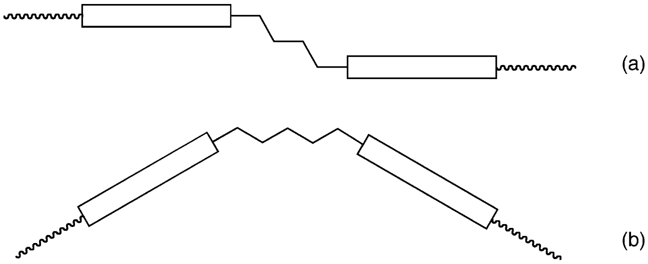

Figure 1. Schematic representation of the molecular shape of symmetric dimers containing (a) an even-numbered spacer and (b) an odd-numberd spacer.

Niori et al.[5] and Watanabe et al.[6] showed that symmetric dimeric compounds with an even-numbered spacer form a SmA phase and/or a nematic phase and that those with an odd-numbered spacer display a SmC phase. Furthermore, changing the ratio between the length of the spacer and the length of the terminal chain can modify the structure of the smectic phase. Thus, if the length of the terminal chains is smaller than, or comparable to, the length of the spacer, an intercalated structure is observed characterized by single-layer structures obtained by random mixing of the terminal chains and the spacer.[4,5] On the other hand, if the terminal chains are significantly longer than the spacer chain then the tails and the spacer can segregate, forming double-layer structures that can, in the case of dimers with an odd-numbered spacer, display ferroelectric or antiferroelectric properties.[7] Although many series of symmetric dimers reported in the literature employ a Schiff base link[8−10] only a limited number of salicylaldimine-based dimers[11,12] have

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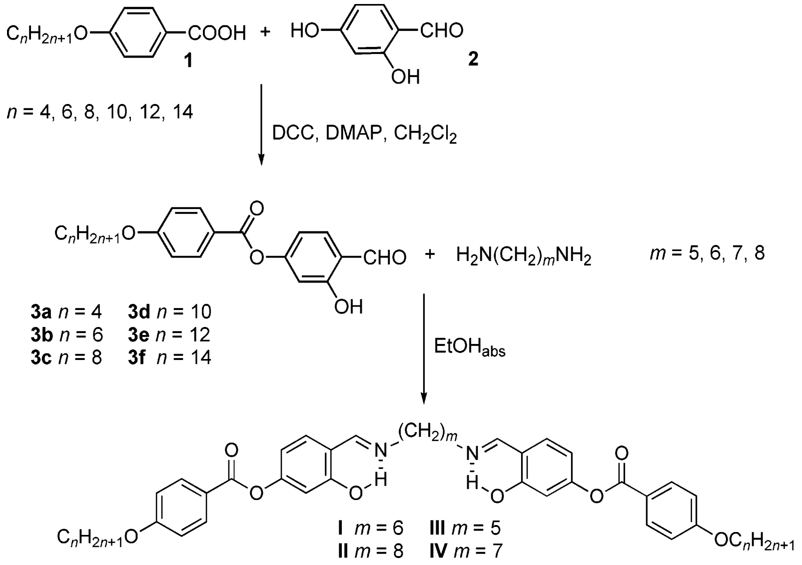
Scheme 1. Synthetic Route for Series I−IV[a]



[a] Compounds are abbreviated as ***m-n***.

been studied, and in all cases the more rigid salicylaldimine moiety has been incorporated into the mesogenic unit connected to the alkylene spacer via an ester link.

Here we report on the synthesis and mesomorphic properties of four homologous series of dimeric molecules in which the salicylaldimine core is linked to the alkylene spacer via an imino group. These molecules also possess hydroxy functions that enable intramolecular hydrogen bonding to the imine nitrogen of the spacer constraining the conformational freedom of the molecules. The effect on the mesomorphic properties of both terminal and spacer chain length is investigated.

Experimental Section

General Methods. All the solvents were either *puriss p.a.* quality or distilled over appropriate drying reagents.[13] All the other reagents were used as purchased from Aldrich. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker AV 300 instrument in $CDCl_3$ with $SiMe_4$ as the internal standard unless stated otherwise. Infrared spectra were recorded on a Bomem MB 102 spectrophotometer; absorption maxima are given in cm^{-1}. Phase transition temperatures and textures were determined using an Olympus BX51 polarizing microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. Enthalpies of transition were determined from thermograms recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter operated at scanning rates of 5−10 K min^{-1}. Powder X-ray patterns were obtained with a Guinier film camera (HUBER Diffraktionstechnik, Germany) using quartz-monochromated Cu Kα radiation. The samples in glass capillaries (diameter 1 mm) were mounted in a temperature-controlled heating stage. Patterns of aligned samples on a glass plate on a temperature-controlled heating stage (alignment at the sample−glass or at the sample−air interface, sample fiberlike disordered around an ∞-fold axis perpendicular to this interface) were obtained with a two-dimensional detector (HI-STAR, Siemens).

General Procedure for the Preparation of Imines. To a hot solution of the appropriate aldehyde (**3a**−**f**; 2 mmol) in ethanol (absolute, 15 mL) was added dropwise a solution of the appropriate α,ω-diamino alkane (1 mmol) in ethanol (absolute, 2 mL). The reaction mixture was heated under reflux in an inert atmosphere for 1 h. After cooling, the crystalline product was separated by filtration and purified several times by crystallization. Compounds with an odd-numbered spacer were crystallized from the solvent mixture hexane/tetrahydrofuran (THF)/acetone (10:1:1), while the compounds with even-numbered spacers were crystallized from acetone/THF (10:1). Pure, dimeric salicylaldimines were obtained as yellow crystalline or powder solids in yields of 70−93%.

Analytical data for the new dimeric compounds are collected in Table 1S shown in Supporting Information. Spectroscopic data are given for one salicylaldimine homologue, because the only significant difference in the NMR spectra relates to the number of carbons in the alkoxy chains and alkylene spacer.

*N,N′-Bis[4′-(4″-butyloxybenzoyloxy)-2′-hydroxybenzylidene]-pentane-1,5-diamine (**5-4**).* ^1H NMR ($CDCl_3$) 1.0 (t, $J = 7.35$ Hz, 6H, $-CH_3$); 1.47−1.53 (m, 6H, $-CH_2-$); 1.74−1.83 (m, 8H, $-CH_2-$); 3.61 (t, $J = 6.51$ Hz, 4H, $-CH{=}N-\mathit{CH_2}-$); 4.05 (t, $J = 6.42$ Hz, 4H, $-CH_2O-$); 6.72 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 2H Ar); 6.80 (d, $J = 1.5$ Hz, 2H Ar); 6.96 (AA′XX′, $J = 8.6$ Hz: 4H Ar); 7.26 (d, $J = 8.5$ Hz, 2H Ar); 8.12 (AA′XX′, $J = 8.6$ Hz, 4H Ar); 8.32 (s, 2H, $-CH{=}N-$); 14.02 (s, 2H, $-OH$) ppm; ^{13}C NMR ($CDCl_3$) 14.0; 19.4; 24.8; 30.6; 31.3; 59.0; 68.2; 110.8; 112.5; 114.5; 116.7; 121.6; 132.2; 132.5; 154.4; 163.5; 163.8; 164.3; 164.6 ppm.

Results and Discussion

Synthesis and Characterization. The salicylaldimine dimers were prepared following the synthetic route described in Scheme 1. 4-Alkoxybenzoic acids were prepared by *O*-alkylation of methyl 4-hydroxybenzoate followed by hydrolysis under basic conditions. 4-(4′-Alkoxybenzoyloxy)-2-hydroxybenzaldehydes **3a**−**f** were prepared according to the procedure reported by Ghedini et al.[14] in yields of 60%. Addition of α,ω-diamino alkane to the corresponding

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Table 1. Transition Temperatures (°C), Enthalpies (kJ mol^{-1}) in Italics, and the Dimensionless Value of Δ*S*/*R* in Brackets of Homologues Series I and II

dimer	Cr$_1$		Cr$_2$		SmC		N		I
6-4	•	118 *1.15* [0.35]	•	150 *31.17* [8.86]			•	202 *9.03* [2.29]	•
6-6	•	115 *0.62* [0.19]	•	147 *38.18* [10.92]			•	188 *9.43* [2.46]	•
6-8	•	114 *0.70* [0.22]	•	131 *30.10* [8.98]	•	155 *0.37* [0.10]	•	178 *9.51* [2.54]	•
6-10	•	151 *41.26* [11.71]			•	177 *16.31* [4.35]			•
6-12	•	142 *43.62* [12.63]			•	179 *21.15* [5.63]			•
6-14	•	133 *42.33* [12.54]			•	176 *21.96* [5.88]			•
8-4	•	126 *4.82* [1.45]	•	140 *42.47* [12.37]			•	176 *8.84* [2.37]	•
8-6	•	107 *64.00* [20.25]					•	164 *9.03* [2.48]	•
8-8	•	91 *16.99* [5.61]	•	108 *38.89* [12.28]			•	159 *9.77* [2.72]	•
8-10	•	67 *16.23* [5.74]	•	115 *41.47* [12.85]	•	149 *1.58* [0.45]	•	154 *12.27* [3.43]	•
8-12	•	118 *47.24* [14.53]			•	155 *21.29* [5.98]			•
8-14	•	78 *51.15* [17.53]	•	108 *45.78* [14.45]	•	157 *24.55* [6.87]			•

Table 2. Transition Temperatures (°C), Enthalpies (kJ mol^{-1}) in Italics, and the Dimensionless Value of Δ*S*/*R* in Brackets of Homologues Series III and IV[a]

dimer	Cr		M$_X$		Col$_{rec}$		N$_{Col}$		N		I
5-4	•	106 *29.38* [9.31]							(•	102) *−0.22* [0.07]	•
5-6	•	113 *48.53* [15.12]					(•	87) *−0.80* [0.26]	(•	97) -0.18 [0.06]	•
5-8	•	103 *45.95* [14.68]			(•	99) *−8.59* [2.77]			(•	102) *−0.45* [0.14]	•
5-10	•	105 *37.21* [11.82]			•	111 *13.48* [4.22]					•
5-12	•	107 *42.15* [13.35]			•	116 *14.80* [4.57]					•
5-14[b]	•	105 *43.39* [13.82]	•	114 *1.24* [0.38]	•	120 *14.29* [4.27]					•
7-4	•	119 *49.04* [15.05]							•	121 *0.37* [0.11]	•
7-6	•	98 *50.80* [16.47]					(•	93) *−0.24* [0.08]	•	113 *0.31* [0.10]	•
7-8	•	103 *42.00* [13.43]							•	110 *0.51* [0.16]	•
7-10	•	97 *35.31* [11.48]			•	106 *10.98* [3.48]			•	108 *0.49* [0.15]	•
7-12[c]	•	100 *42.70* [13.77]			•	112 *16.77* [5.24]					•
7-14[d]	•	99 *42.80* [13.84]			•	117 *17.27* [5.32]					•

[a] Col$_{rec}$, columnar rectangular phase; M$_X$, unidentified mesophase; N$_{col}$, columnar nematic phase. [b] Compound has crystal−crystal transition at 74 °C, Δ*H* = 33.76 kJ mol^{-1}. [c] Compound has crystal−crystal transition at 90 °C, Δ*H* = 1.54 kJ mol^{-1}. [d] Compound has crystal−crystal transition at 71 °C, Δ*H* = 37.82 kJ mol^{-1}.

aldehyde gave salicylaldimine dimers in good yields. The dimers were identified by ^{1}H and ^{13}C NMR spectroscopy, while purity was established by elemental analysis. The mesophase behavior of the prepared compounds has been studied by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction measurements.

Mesomorphic Properties. The thermal behavior of the homologue series I−IV is given in Tables 1 (series I and II) and 2 (series III and IV), respectively, and reveals that all the dimers are mesomorphic.

The compounds with an even number of methylene units in the spacer (series I and II) showed mesomorphism characteristic of calamitic materials, in agreement with their overall rod shape, and comparison of the mesomorphic behavior of the homologues within these series showed certain regularities. Thus, in both series the lower homologues ($n \leq m$) displayed only the nematic phase, identified by its characteristic schlieren and marbled textures. Increasing the chain length by two methylene units resulted in the additional appearance of a SmC phase, and during the cooling cycle, the characteristic fingerprint texture of the N−SmC transition was observed. On further elongation of the chains, the nematic phase disappeared and only the smectic C phase remained. The nature of the SmC phase was deduced from optical textures characterized by both the broken-fan and the schlieren textures, the latter showing only four-brush defects.

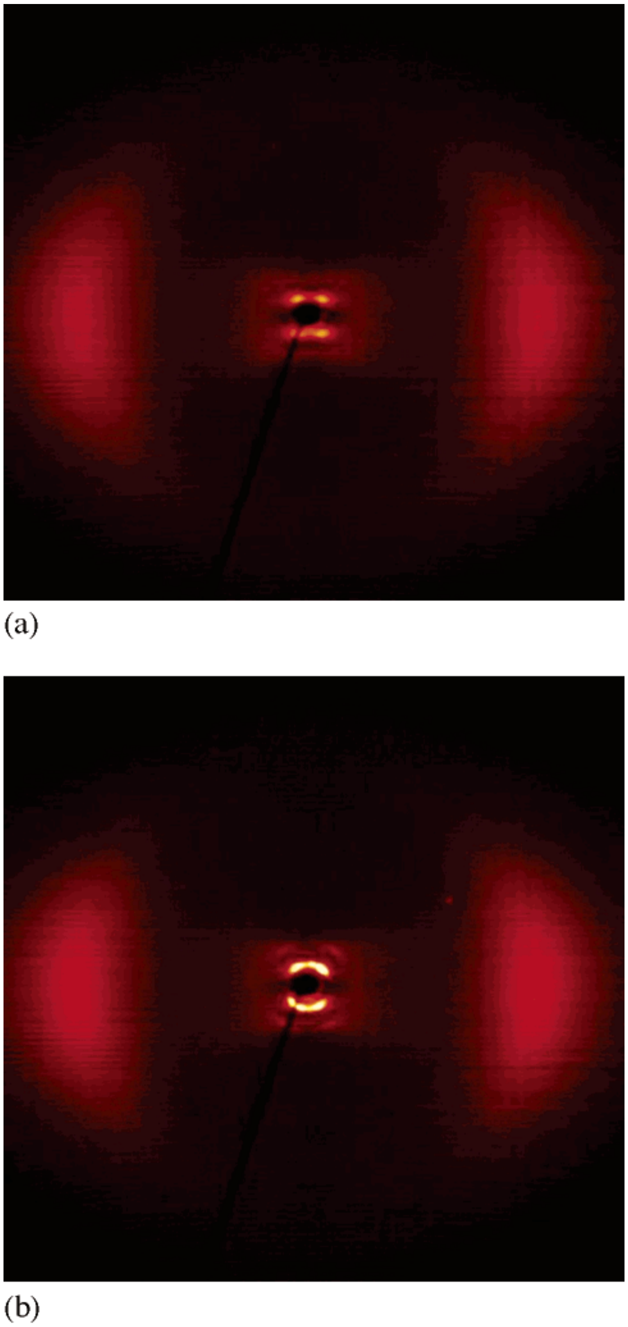

Figure 2. X-ray patterns obtained for a sample of **8-10** aligned in the magnetic field: (a) nematic phase at 145 °C and (b) SmC phase at 130 °C on cooling.

X-ray measurements performed on compound **8-10** showed the scattering typical of a nematic phase with cybotactic groups of the SmC type at 145 °C (Figure 2a), and a SmC phase at 130 °C on cooling (Figure 2b). The tilt angle of the molecules is about 35 to 40° as measured from the two-dimensional patterns of a sample aligned in the magnetic field. This value agrees very well with an estimate of the tilt amounting to 41° that was calculated from the layer distance of 4.7 nm (from the X-ray measurements) and the length of 6.2 nm for the fully stretched molecule (from CPK models), assuming no interdigitation of molecules in adjacent layers.

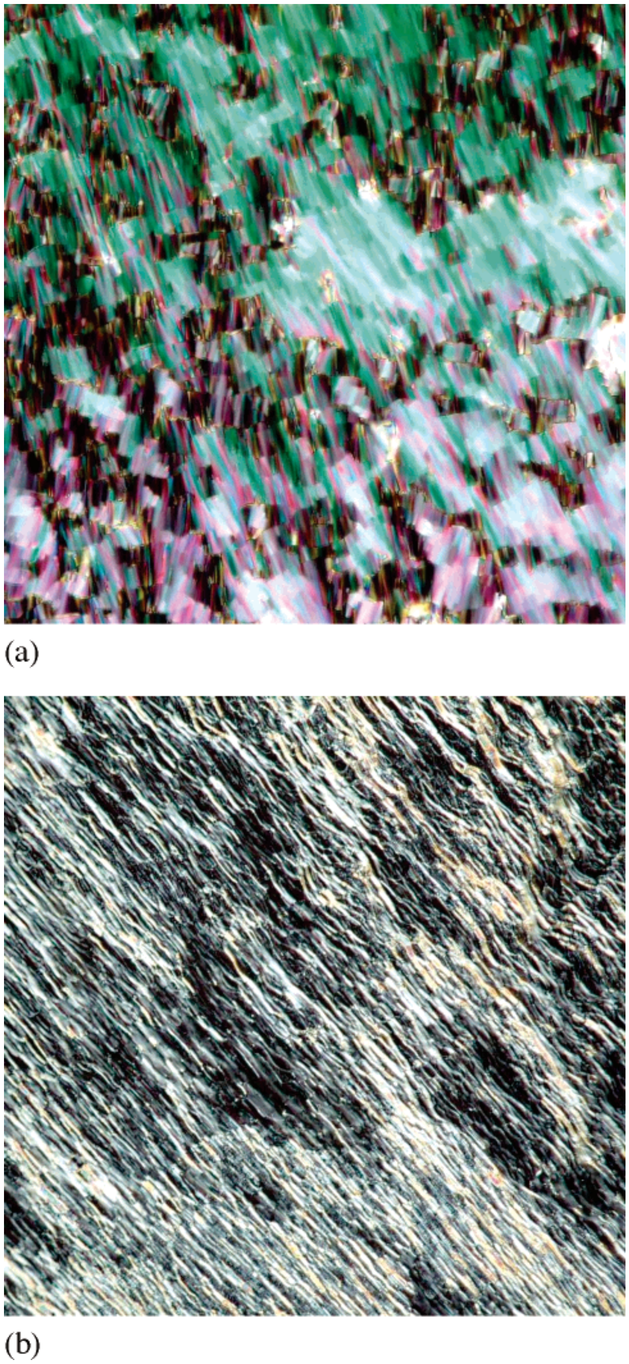

Figure 3. Photomicrographs of compound **5-6**: (a) fanlike texture of the N_{Col} phase and (b) oily streaks texture obtained after shearing the fanlike texture.

Similar to the series with even-numbered spacers, the lower homologues with odd-numbered spacers also showed only the nematic phase. The compounds with five methylene units in the spacer displayed a monotropic nematic phase that became enantiotropic with the C_7 spacer. In addition to the classical nematic phase, characterized by a very fluid schlieren texture, a monotropic N_{Col} phase was observed in compounds **5-6** and **7-6**. The phase was identified by direct analogy with the behavior displayed by the short-chain homologues of unsymmetrically disubstituted piperazines[15] and dimeric imines with dicyclohexylmethane spacers.[16] On cooling from the schlieren nematic texture, the N_{Col} phase

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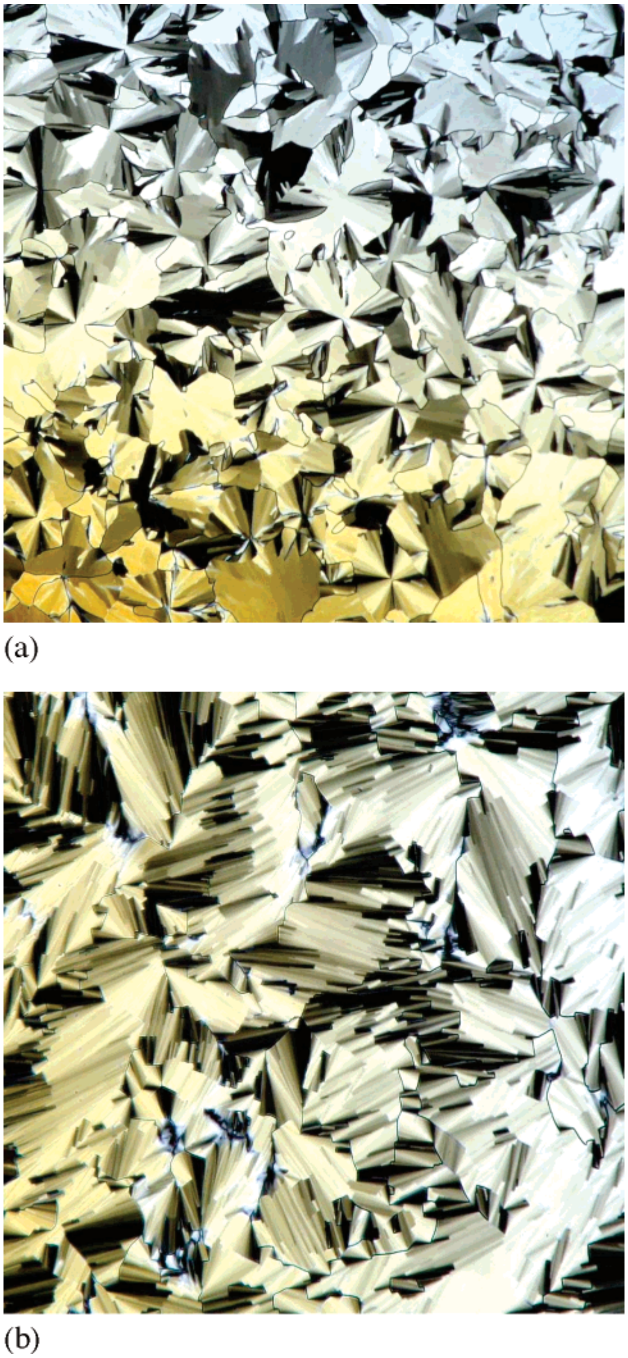
(a)

(b)

Figure 4. Photomicrographs of compound **5-10**: (a) mosaic texture and (b) fanlike texture obtained after shearing the mosaic texture.

appeared as a fanlike texture (Figure 3a) that changed into oily streaks on shearing the sample (Figure 3b).

On increasing the terminal chain length, one might have expected to observe a SmC phase as shown for many other symmetric dimers with odd-numbered spacers,[8] but surprisingly, all higher homologues in series III and IV displayed a texture characteristic of a columnar phase. For example, on cooling compound **5-10**, the mesophase appeared as dendritic growths that coalesced to form a mosaic texture (Figure 4a); on shearing the mosaic texture was transformed into either a fanlike (Figure 4b) or a pseudohomeotropic texture (see below).

To establish the nature of the proposed columnar phase, X-ray experiments were carried out on samples **5-10**, **5-14**, **7-10**, and **7-14**. The Guinier powder patterns of the four compounds within the columnar phase were very similar. They showed two stronger, sharp reflections along with a couple of very weak reflections in the small-angle region at *d* values that were not multiples of one another, thus excluding a simple layer structure; the diffuse outer scattering proved the liquid-crystalline nature of the phase. Further insights into the geometry of the phase were provided by the patterns of aligned samples of compounds **5-14**, **7-10**, and **7-14** recorded with the area detector, and the results obtained for compound **7-10** derived from the patterns at 102 °C (Figure 5) are now discussed as an example.

The interpretation of the small-angle Bragg reflections as resulting from a two-dimensional rectangular lattice is illustrated in Figure 5b. It shows the reciprocal lattice for the two domains contributing mainly to the scattering diagram along with the indices of the observed reflections (observed only for indices *hk* with $h + k = 2n$). The fiber axis of the sample is perpendicular to the (11) line of the two-dimensional lattice in this rectangular interpretation.

The outer diffuse scattering at $d \approx 4.6$ Å forms a comparatively broad halo centered at the equator of the pattern. The most probable locations of the maxima of this scattering are at a line perpendicular to the *b* axis of the unit cell, indicating a nontilted arrangement of the molecular cores with respect to the unit cell axes. The halo should show four intensity maxima twisted out of the equator of the pattern by about 18°. Intensity scans along the halo allow a fit by four Gaussian functions with their maxima near the expected positions for such a conclusion (see Supporting Information, Figure 1S). Similar two-dimensional X-ray patterns have been recorded for aligned samples of compound **5-14** and **7-14** (see Supporting Information, Figures 2S and 3S).

The corresponding lattice parameters calculated from calibrated Guinier powder patterns are summarized in Table 3 along with those for compound **5-10**, where the indexation of the reflections for **5-10** was carried out by analogy with the other compounds (see Supporting Information, Table 2S for details). The results of this interpretation of the experimental values reveal the plane group *c2mm* for the two-dimensional lattice of the columnar phase. Considerations based on MM2-optimized molecules support this assumption, as the molecular lengths derived for the bent-shaped models (Figure 6) are in excellent agreement with the *b* axis of the unit cell of all four compounds. The columns arranged in the centered, two-dimensional lattice have the dimensions *b* (corresponding to the length of the long molecular axis) in the *y* direction and *a*/2 in *z* direction, that is, the number of molecules in the cross section of a column obviously varies from compound to compound.

Thus, the phase is columnar, with a centered, two-dimensional, rectangular lattice as found already for other bent-shaped molecules.[18−20] The centering of the unit cell

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(17) Molecular modeling was performed using ChemBats3D (Cambridge software corporation).

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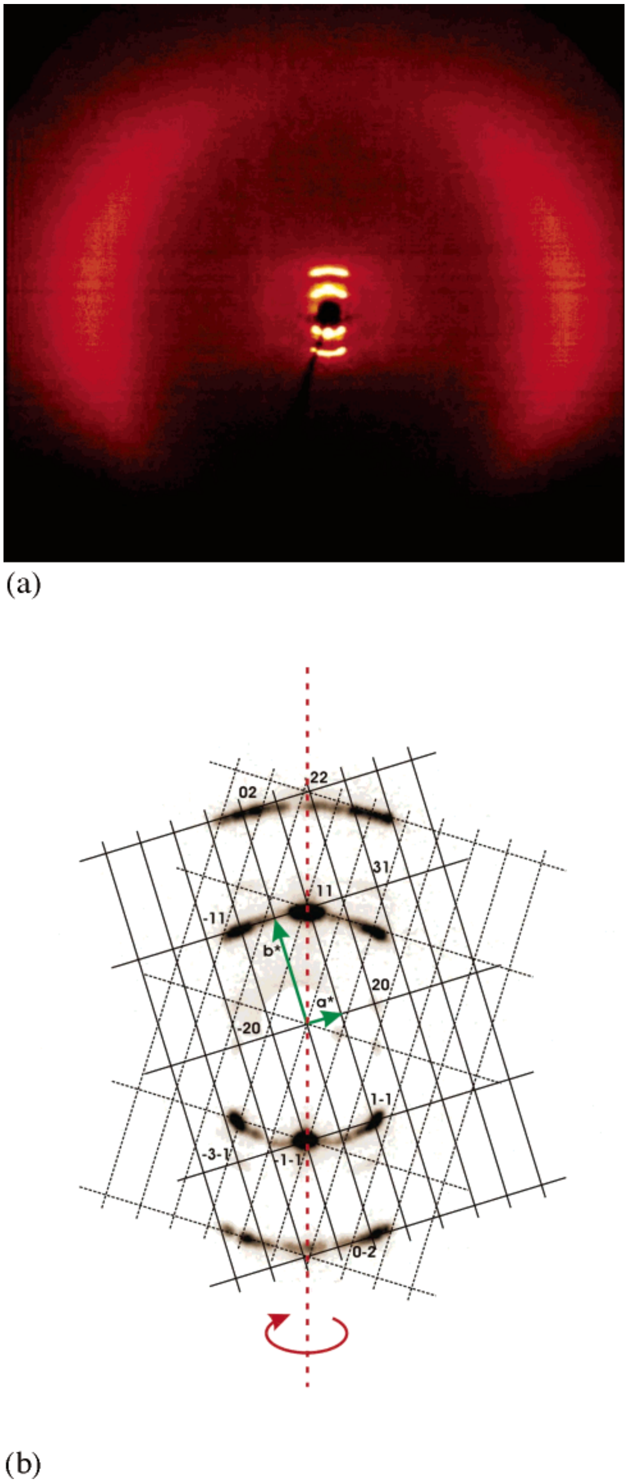

Figure 5. X-ray diffraction of an aligned sample of **7-10** at 102 °C on cooling: (a) two-dimensional pattern and (b) small-angle region showing the direction of the fiber axis (dashed red line), the reciprocal lattice for the two mainly scattering domains (full and dashed black lines, respectively), the unit cell axes (green arrows), and the indices for the observed reflections of one domain.

implies that the original model of the B_1 phase,[6,21,22] with the C_2 axes of the molecules parallel to the *b* axis, cannot be applied.[19] Instead, an arrangement of the molecules with their C_2 axes perpendicular to the *ab* plane of the lattice is likely.[18,19] Such phases were given several names in the literature, for instance, B_{1o},[19] B_{1rev},[20] Col_r,[23] Col_{rec},[24] or frustrated layer structure,[18] depending on the structural aspect the authors wished to emphasize (bent shape of the molecules, columnar nature of the building blocks, or there being fragments of smectic-like layers, respectively). We refer to the phase as Col_{rec} herein. However, the assignment of the two-dimensional space group *c2mm* neglects the polar character of the molecules, which has to be taken into account for the packing in real space. A model for the molecular packing with the highest symmetry possible for the bent-shaped molecules in this phase is that according to the layer group *pmmn*[25] where the directions of the polar axes of molecules in neighboring columns alternate along *a* (Figure 7). A systematic name based on the symmetry of the phase is, in that case, $\mathrm{Col}_{rec}^{pmmn}$. It must be emphasized that this strongly idealized pattern is derived mainly from X-ray investigations, which give insight into bulk properties and overemphasize the aspect of regularities within the structure.[26] The liquidlike behavior of the chains and the much less ordered arrangement of the molecules within the building blocks, as well as the real nature of the interfaces between these blocks (as discussed for instance by Clark et al.),[27] are not shown in Figure 7.

Table 3. Comparison of the of the Lattice Parameters in the Col_{rec} Phase with the Molecular Length[a]

dimer	*T*, °C	*a*	*b*	*L*	*d*
5-10	106	9.7	4.8	4.8	
5-14	114	13.8	5.4	5.4	0.46
7-10	102	16.0	5.1	5.2	0.46
7-14	95	14.0	5.8	5.8	0.46

[a] *a* and *b* represent lattice parameters (nm), *d* is the *d* value (Bragg) for the outer diffuse scattering, and *L* is the molecular length (nm) as measured from MM2-optimized models.[17]

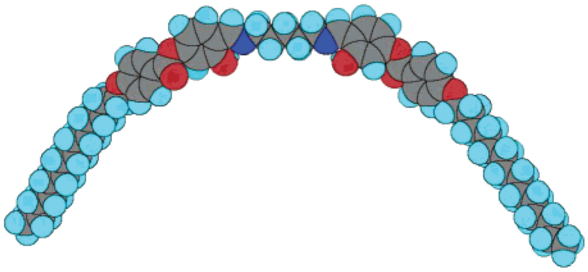

Figure 6. Space filling model of the bent conformer of **5-14** with molecular lengths of 54 Å.

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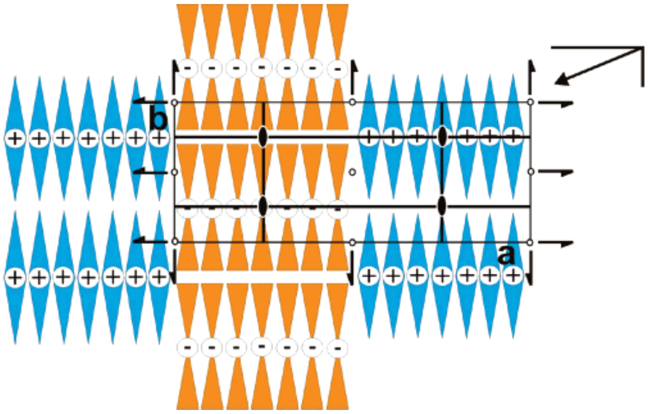

Figure 7. Model for the molecular packing with the highest possible symmetry in the $\mathrm{Col_{rec}}$ phase of compounds **5-10**, **5-14**, **7-10**, and **7-14** showing the symmetry elements for the appropriate layer group *pmmn*.[25]

Switching experiments on the $\mathrm{Col}_{\mathrm{rec}}^{pmmn}$ phase showed no polar electro-optical response on applying comparatively strong electric fields up to 35 V μm^{-1}.

The fiberlike pattern observed in the X-ray patterns of these materials arises from the orientation of the columns parallel to the sample/air interface and a fiberlike disorder of the columns perpendicular to this interface. The pseudo-homeotropic texture of this phase referred to above arises when the preparation used in the microscopy experiments is disturbed mechanically, and we propose that the apparent contradiction between the rectangular nature of the phase and the observation of a homeotropic texture arises as the same fiberlike disorder is induced on mechanical disturbance.

Compound **5-14** showed an additional mesophase that appeared below the $\mathrm{Col_{rec}}$ phase. The transition is accompanied by a clear change in the mosaic texture developed previously (Figure 8). The X-ray data for this phase cannot be interpreted unambiguously. The Guinier powder patterns display inner reflections with *d* values in a ratio of 2:3:4:6 yielding a parameter $d = 9.5$ nm. The two-dimensional patterns show additionally the first order of this scattering (see Supporting Information, Figure 4S). Unfortunately, the sample could only be aligned partially and the alignment became even worse at the phase transition from the high-temperature columnar phase to the low-temperature phase, although the positions of the maxima of the outer diffuse scattering remained almost the same. The ring of the second-order reflection shows six maxima, two on the meridian of the pattern and four equidistant from it. (The intensity of the first- and higher-order reflections is too weak to find their assumed equivalents on the rings out of the meridian.) It is, therefore, not possible to determine if the scattering arises from multidomains of a layer structure with a kind of double layer and tilted molecules or from a two-dimensional-modulated (columnar) structure, with either a rectangular or oblique lattice.

The results presented above show clearly the influence of the chain length within each series. Generally, homologues with $n \leq m$ displayed a nematic phase, while homologues with $n > m$ displayed more highly ordered mesophases, so that SmC and $\mathrm{Col_{rec}}$ phases were observed for members with even- and odd-numbered spacers, respectively. Furthermore, the parity of the spacer has a remarkable effect on the mesogenic behavior. Thus, the isotropization temperatures for the homologues with even-numbered spacers are much higher than those of their odd-numbered counterparts, and comparison of the thermodynamic data for the lower homologues reveals a very large odd−even effect for the N-to-I transition. The values of $\Delta S_{\mathrm{NI}}/R$ exhibited by the odd dimers are significantly lower than those of the even dimers. The observed alternating behavior is typical of liquid-crystal dimers; however, the magnitude of the odd−even effect depends strongly on the nature of the link between mesogenic unit and the alkylene spacer. Ferranini et al.[4] showed that this dependence has been attributed to a change in the molecular geometry, which arose from the difference in the bond angle between the para axis of the mesogen and the

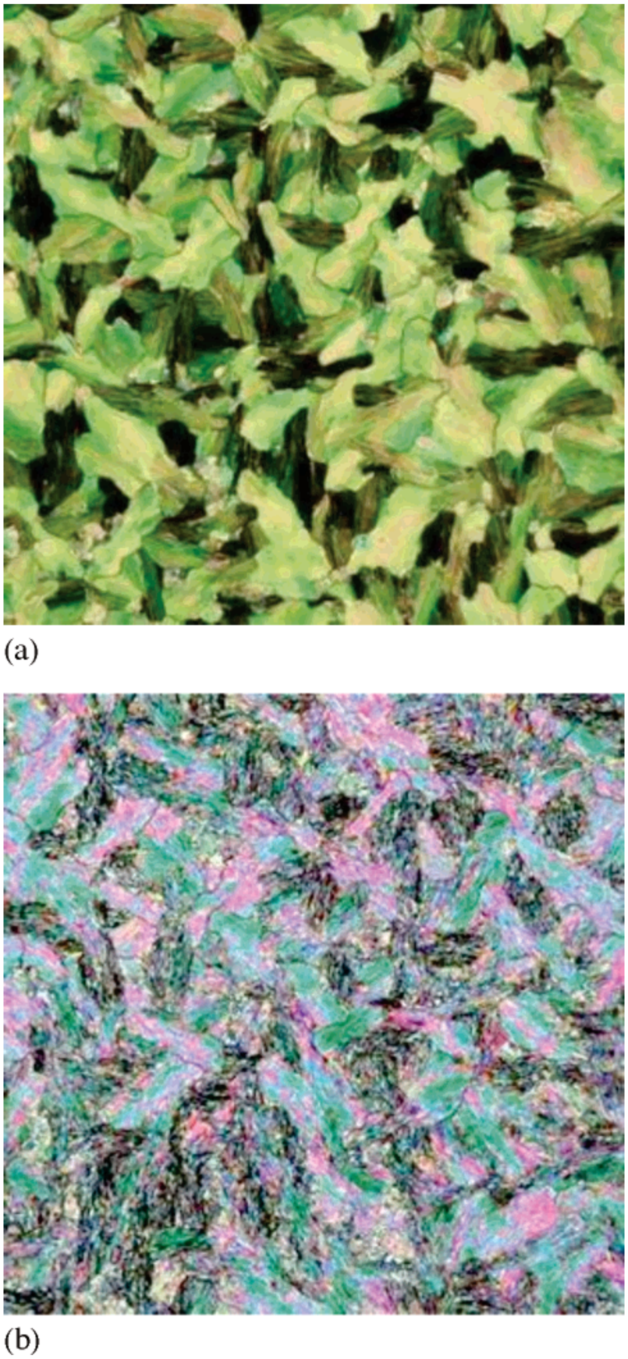

Figure 8. Photomicrographs of compound **5-14**: (a) mosaic texture of the $\mathrm{Col_{rec}}$ and (b) texture of $\mathrm{M_X}$ phase.

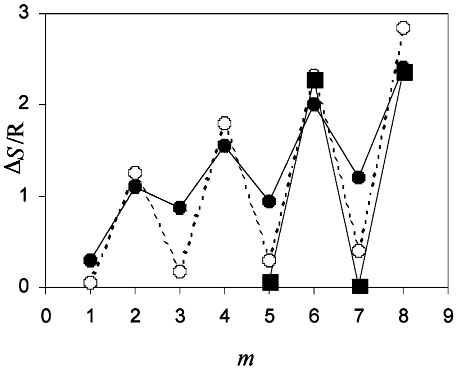

Figure 9. Dependence of the entropy of the N-to-I transition on the number of carbon atoms in the flexible spacer predicted for the cyanobiphenyl dimers with methylene (○) and ether (●) linkages adopted from ref 28 and experimentally obtained for salicylaldimine dimers with imino linkage and butyloxy chains (■).

first bond in the spacer. Thus, increasing the bond angle resulted in diminution of the odd−even effect. The magnitude of the odd−even effect observed for salicylaldimine dimers is similar to that calculated for the methylene-linked dimers (Figure 9).[28] Regarding the six-membered ring, formed by an intramolecular hydrogen bond as a part of the mesogenic unit, it leads to a structure in which the alkylene spacer is linked directly to the mesogenic units. The calculated angle between the spacer and the extended mesogenic unit is 112.7°, similar to the 113.5° in methylene-linked dimers, and results in the strong odd−even effect. The tiny N−I entropy changes for odd members, therefore, imply a high molar fraction of the bent conformer in the nematic phase.

It is predicted[29] that a direct transition from the isotropic to biaxial nematic phase (N_B) will be second order in nature, and so the entropy change at the transition will be zero. The very small entropy changes observed here, coupled with the recent proposal for identification of an N_B phase in nonlinear oxadiazole mesogens,[30,31] and in 2,6-disubstituted toluenes[32] suggested that these transitions might profitably be examined more closely. Thus, adiabatic scanning calorimetry was used to study compound **7-10** over the temperature range 94−112 °C and confirmed the first-order nature of the Cr−$\mathrm{Col}_{\mathrm{rec}}$ and $\mathrm{Col}_{\mathrm{rec}}$−N transitions. Unfortunately, sample decomposition meant that no accurate data were obtained for the N−I transition, but an estimate of a nonzero latent heat of the order of 0.2 J g^{-1} can be made, substantially lower than that observed in, for example, MBBA, which itself has quite a small value.[33]

The spacer parity has a strong influence not only on the thermodynamic data but also on the type of mesophase displayed by the higher homologues. Thus, smectic C and $\mathrm{Col}_{\mathrm{rec}}$ phases were observed for even and odd members, respectively. This confirmed that the geometry that arises from the spacer parity and the imine−spacer linkage has an important role in the determination of the liquid-crystalline behavior. The effect of spacer parity and imine−spacer linkage is especially pronounced in odd dimers leading to the bent conformers. High population of the bent conformer causes a tiny entropy of the N-to-I transition and the formation of the columnar rectangular phase in which the length of the *b* axis of the two-dimensional unit cell is approximately equal to the length of the molecule with the most bent conformation. For comparison, dimers reported by Yelamaggad et al.[11] and Achten et al.[12] in which the imines linkage has been altered (Figure 10) are less bent and have a higher degree of conformational freedom around the spacer, resulting in a different type of mesogenic behavior. The shorter homologues of the series V ($n = 5-7$) display a monotropic intercalated SmC phase while the higher ones ($n = 8-12$) form a monotropic B_1 ($\mathrm{Col}_{\mathrm{rec}}$) mesophase. Only the short- ($n = 4$) and the long-tailed ($n = 12-16$) compounds exhibit enantiotropic mesophases. These results imply that a broadening of the mesogenic unit as a result of intramolecular hydrogen bonding favors the columnar organization.

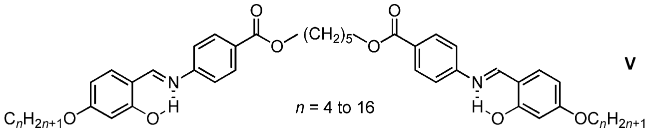

Figure 10. Molecular structure of the compounds reported by Yelamaggad et al.[11] and by Achten et al.[12]

Conclusion

Here we have reported on the synthesis and the mesogenic properties of four series of dimeric molecules with flexible spacers in which the salicylaldimine core is linked to the alkylene spacer via an imino group. To study the structure−property relations the lengths of the alkylene spacers ($m = 5-8$) as well as those of the terminal alkoxy chains ($n = 4-14$) have been varied. Our studies revealed a strong odd−even effect in entropy changes for the N-to-I transition implying a big difference in the geometry between the odd and the even members. As expected, the even members behave like rods displaying nematic and/or smectic C phase. On the other hand the odd dimers showed nematic, nematic-columnar, and columnar rectangular phases indicating a highly bent geometry of the molecules. The polar character of the molecules resulting from their bent shape led us to the conclusion that the symmetry of the columnar rectangular phase can be described by the layer group *pmmn* (the phase named as $\mathrm{Col}_{\mathrm{rec}}^{pmmn}$). The results presented in this work showed that the geometry, which arises from the spacer parity and the imine-spacer linkage, has an important role in the determination of the liquid-crystalline behavior.

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Supporting Information Available: Analytical data for the new dimeric compounds, X-ray data from Guinier powder patterns, and additional two-dimensional X-ray patterns of **7-10**, **5-14**, and **7-14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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