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## Liquid Crystals

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### **Bent-core mesogens based on semi-flexible dicyclohexylmethane spacers**

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# Bent-core mesogens based on semi-flexible dicyclohexylmethane spacers

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New, bent-core mesogens are described in which the core of the molecule is a semiflexible, di(4-aminocyclohexyl)methane spacer. The compounds show nematic, columnar nematic and columnar phases as shown by a combination of X-ray diffraction and optical microscopy. The potential of these new mesogens as biaxial nematic candidates is considered.

## 1. Introduction

For many years, it was held to be true that mesophases resulted only from highly anisotropic molecules that, in the case of calamitic systems, possessed cores which were linear, or very close to linear. However, as exemplified at the time in an overview article by Demus [1], the late 1980s and subsequent years saw such ideas being challenged by synthetic chemists, and many new mesogenic motifs were identified. Among these were materials which were distinctly bent at their core and, for example, in 1993 Matsunaga and co-workers reported some 1,2-disubstituted benzenes that showed N and SmA phases [2], and some 2,5-bis(alkoxybenzylidene)cyclopentanones which were reported to have N, SmA and SmC phases (figure 1) [3]. Perhaps inspired by these reports, Niori *et al.* studied some 1,3-disubstituted benzene derivatives and were able to show ferroelectric response of these bent-core mesogens despite the fact that the molecules from which the phases were composed were not chiral [4]. This work generated considerable interest and led to something of an explosion of interest in bent-core mesogens [5]. The phenomenon of chirality in these systems was the major driver for this interest and, in 1997, Link *et al.* [6] proposed the now accepted model in which the chirality originates through a combination of the bent nature of the molecules and a lateral, in-plane tilt.

In general, candidate molecules for this behaviour have shown that they can be most sensitive to their chemical composition [7] (for example, simply reversing

an imine link can suppress mesomorphism) and, in particular, to the angle formed at the centre of the molecules between the two extended 'arms'. Angles that are too acute do not support mesomorphism, while if the angle opens up too far past 120°, more 'classical' mesomorphism results and smectic phases are observed [8]. Recently, certain substituted oxadiazoles [9, 10] which, despite their large internal angle of 140°, might be regarded as bent-core, have been reported to have a biaxial nematic phase, although the biaxial order parameter obtained by <sup>2</sup>H NMR studies is rather small at 0.1.

Dimeric mesogens linked by flexible chains have attracted considerable attention because strong variations in physical properties are observed as a function of chain parity, the most evident of which is the effect on clearing point and associated entropy change in, for example, dimers of cyanobiphenyls [11]. Additionally, flexible dimers have been shown [12, 13] to form ferro- and antiferro-electric phases and switching properties have been demonstrated.

We recently became interested in the use of new central linkers for the realization of bent-core mesogens and began to investigate the use of the dicyclohexylmethane unit in this regard. We therefore undertook the synthesis of compounds such as **6–10** as shown in scheme 1.

## 2. Synthesis and mesomorphism

Esterification of 4-alkoxybenzoic acids to give the aldehydes **1**, **2** and **3** used a straightforward methodology employing dicyclohexylcarbodiimide and 4-(N,N-dimethylamino)pyridine in dichloromethane; yields were up to 90%. However, as esterification of

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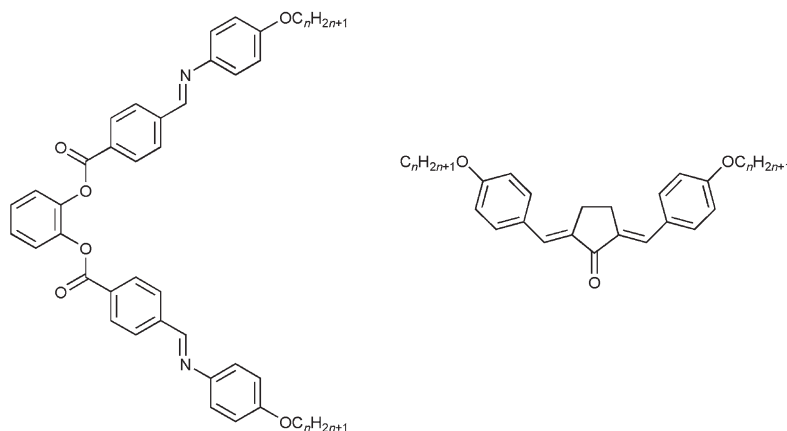
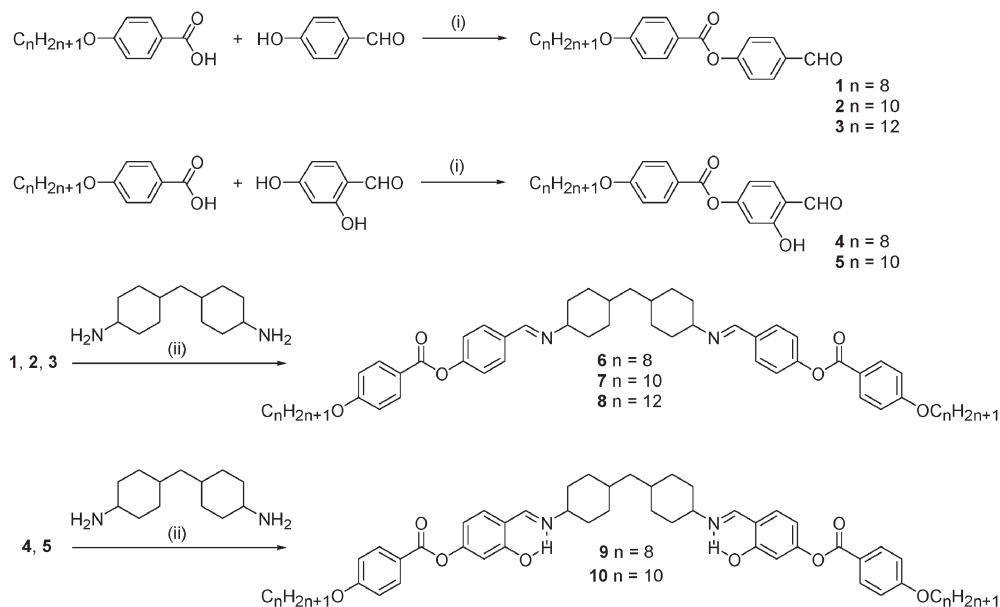


Figure 1. Bent-core materials reported by Matsunaga and co-workers [2, 3].

4-hydroxysalicylaldehyde can occur at both hydroxy groups, **4** and **5** were additionally purified by forming their Cu(II) complexes and then, after separation, hydrolysing them [14], lowering the overall yields to 42% and 46%, respectively. Formation of the corresponding imines (**6** to **10**) was achieved by reacting *trans*, *trans*-4,4'-diaminocyclohexyl-1,1'-methane with the aldehydes in toluene under reflux and under an inert atmosphere, using a catalytic amount of *p*-toluenesulphonic acid. The products **6** to **8** were obtained as colourless powders in moderate yields of 30 to 50%, while **9** and **10** were obtained as yellow needles. The mesomorphism of these new compounds was investigated by polarizing optical microscopy and differential scanning calorimetry (DSC); the results are collected in table 1.

On heating, compound **6** first showed a transition into another crystal phase at 132°C, before melting at 196°C to give a fluid phase whose texture on heating was poorly defined. At 201°C, this phase gave way to a nematic phase, figure 2(a) which then cleared at 218°C. On cooling, the nematic phase re-appeared from which the lower temperature phase formed either as a fan-like texture, figure 2(b) if from a schlieren nematic, or as strongly homeotropic if from a homeotropic texture. Applying mechanical stress by pressing on the upper slide caused the fan-like texture to change and oily streaks became visible as shown in figure 2(c).

Compound **7** behaved similarly, melting into the same lower temperature mesophase as **6** at 182°C before giving way to a nematic phase at 189°C and clearing at 205°C. The cooling behaviour was directly



Scheme 1. Synthesis of the new bent-core mesogens. (i) DCC/DMAP/CH<sub>2</sub>Cl<sub>2</sub>; (ii) TsOH/toluene/Δ.

Table 1. Transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ ) in italics of compounds **6** to **10**. [] represents the  $\Delta S/R$  value. Cr=crystalline phase; Col<sub>L</sub>=lamello-columnar phase; N<sub>Col</sub>=nematic-columnar phase; N=nematic phase; I=isotropic phase, () indicates monotropic mesophase.

| Compound  | Cr | Col <sub>L</sub> | N <sub>Col</sub> | N | I |
|-----------|----|------------------|------------------|---|---|
| <b>6</b>  | •  |                  | •                | • | • |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |
| <b>7</b>  | •  | (•               | •                | • | • |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |
| <b>8</b>  | •  | (•               | •                | • | • |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |
| <b>9</b>  | •  | •                | •                | • | • |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |
| <b>10</b> | •  | •                |                  | • | • |
|           |    |                  |                  |   |   |
|           |    |                  |                  |   |   |

<sup>a</sup>Compound has crystal-crystal transition at  $132^{\circ}\text{C}$ ,  $\Delta H=32.03 \text{ kJ mol}^{-1}$ . <sup>b</sup>Compound has crystal-crystal transition at  $171^{\circ}\text{C}$ ,  $\Delta H=6.97 \text{ kJ mol}^{-1}$ . <sup>c</sup>Isotropization was accompanied by decomposition.

analogous to that of **6** except that below the lower temperature phase, a transition occurred to a monotropic phase whose texture (as obtained from the homeotropic variant) is shown in figure 3 and is distinctive for a columnar phase. The texture of this phase bears some resemblance to one some of us found in tetracatenar complexes of palladium(II), where the lines of optical interference do not meet to give the

distinctive Maltese cross [15]. This phase was found to be lamellar in nature and the probable presence of a columnar structure led to classification as lamello-columnar.

The mesomorphism of compound **8** was rather similar to that of **7**, and showed once more a nematic phase, a phase with a fan-like texture and a monotropic columnar phase (figure 4). Compounds **9** and **10** differ

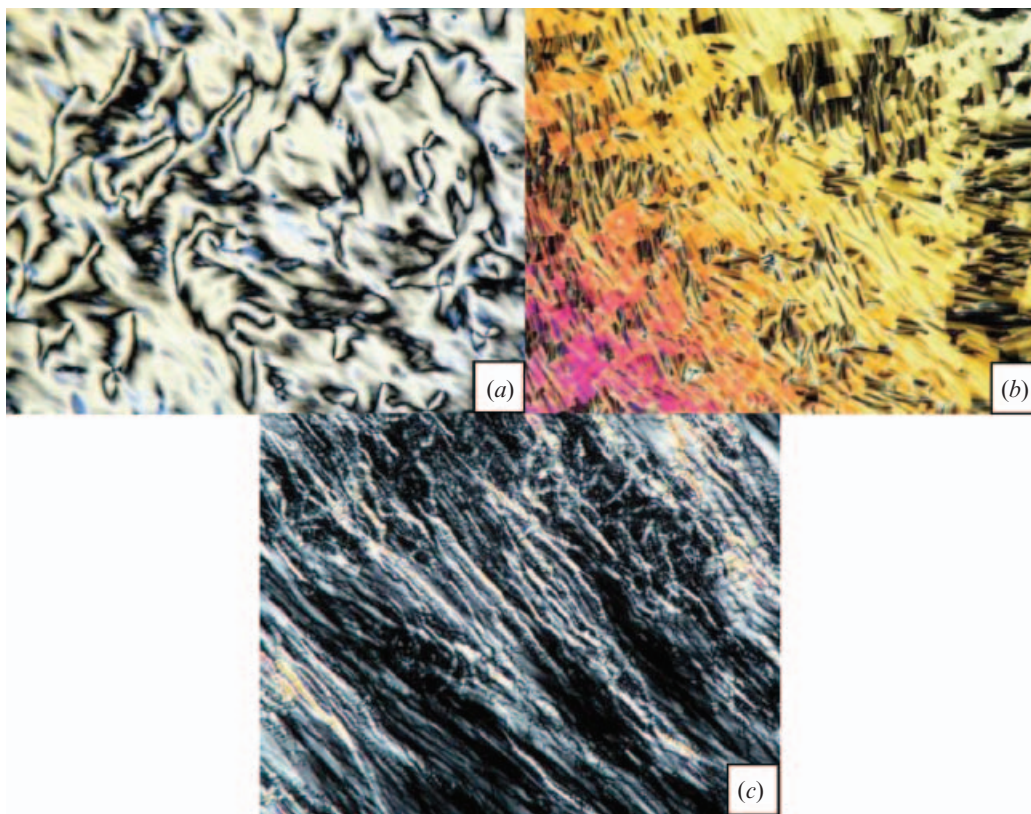


Figure 2. Photomicrographs of compound **6**; (a) schlieren texture of the N phase observed at  $198^{\circ}\text{C}$ ; (b) fan-like texture of the N<sub>Col</sub> phase observed at  $194^{\circ}\text{C}$ ; (c) texture of the N<sub>Col</sub> phase obtained at  $190^{\circ}\text{C}$  after mechanical stress of the fan-like texture.



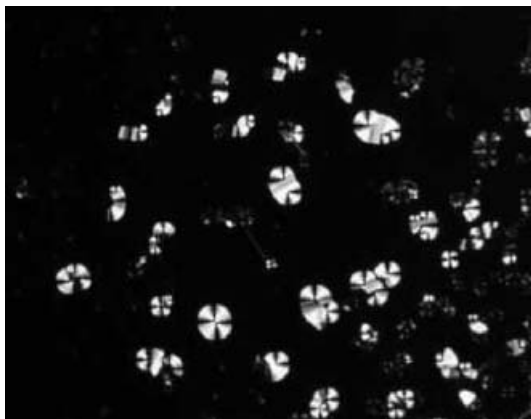


Figure 3. Optical texture of the columnar phase of **7** obtained at 170°C on cooling.

from **6** to **8** in being derived from 4-hydroxysalicylaldehyde and as such possess a hydroxy function that hydrogen bonds into the imine nitrogen to give a six-membered ring structure (evidenced by the chemical shift of the hydroxy proton at  $\delta$  13.99) which rigidifies the molecule to some degree. A major effect of this structural change is an increase in the transition temperatures, in particular of the melting point, so that **9** melted at 197°C to give way to a columnar phase which then led to a phase with a highly homeotropic texture at 236°C, followed by a nematic at 242°C. Clearing was accompanied by decomposition at 259°C. To obtain any texture at all from the homeotropic phase was difficult and shearing produced no visible change, but by the use of non-oriented nylon-covered slides we were able to obtain a fan-like texture similar to that found for compound **7** (figure 5).

Compound **10** melted at 189°C to give the mesophase that we have identified as columnar, and further heating led to a nematic phase that was strongly homeotropic and showed characteristic flashing; once more it is

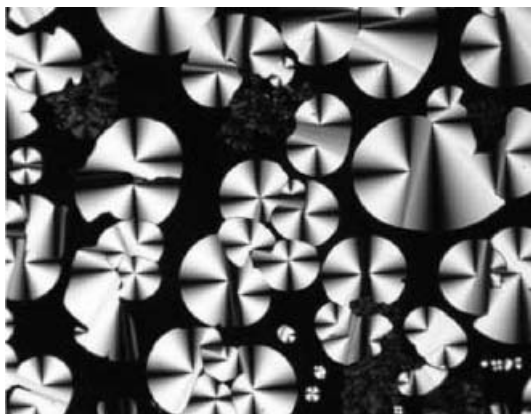


Figure 4. Monotropic columnar phase of **8** at 162°C.

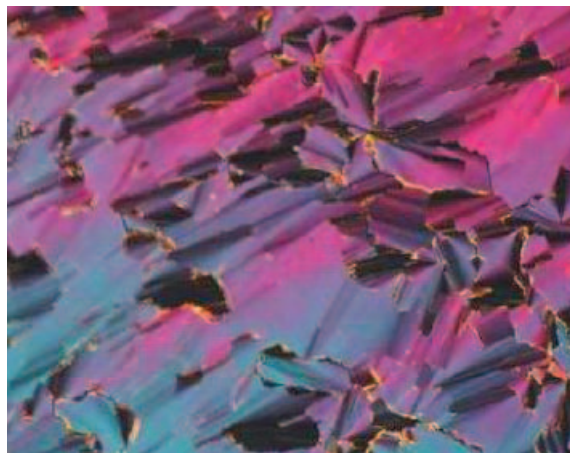


Figure 5. Texture of the mesophase of **9** obtained at 237°C on heating in a nylon-coated cell.

suspected that decomposition sets in within the nematic phase. Cooling the nematic phase then allowed the lower temperature phase to be properly identified as the texture is characteristic of that for a columnar phase, as shown in figure 6 for textures obtained on slides treated with nylon 6/6.

### 3. Discussion

These compounds clearly present an interesting range of mesomorphism. Using AM1 calculations [16], the angle at the central methylene group in these systems is found to be 116°, opened out by some 7° from the perfect tetrahedral angle, while when the flexibility of the ester groups is taken into account (using the AM1-optimized core along with MM2 methods), the structure opens out to give an overall bend angle in the range 123° to 139°.

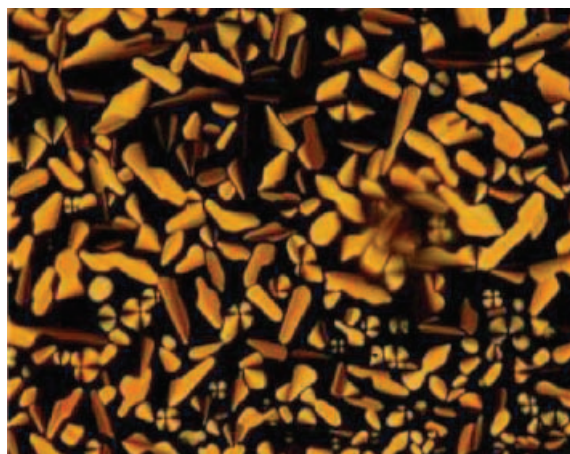


Figure 6. Texture of the Col phase of **10** obtained on cooling from the nematic phase on nylon 6/6-treated slides at 173°C.

This would tend to suggest that the materials ought to be regarded initially as bent-core in nature.

One of the aspects of the mesomorphism that deserves discussion relates to the thermodynamic data for the  $T_{NI}$  transition, where it can be seen that the transition appears to be almost second order with very small enthalpy changes for **6** and **7** and, consequently, very small entropy changes. The N–I transition of calamitic mesogens is weakly first order with values of  $\Delta S/R$  of around 0.3–0.4, although lower values are often found in discotic materials. However, second order N–I transitions are expected only at the so-called Landau point when there is a direct transition from the isotropic to the biaxial nematic phase,  $N_B$  [17]. Theoretical studies of the biaxial nematic phase by Teixeira *et al.* [18] and by Luckhurst [19] showed that for a jointed rigid rod, the Landau point was observed at  $109^\circ 28'$  — the perfect tetrahedral angle. The calculated angle at the central methylene of the compounds under study is  $116^\circ$ , which is somewhat greater than the theoretical ideal, and of course calculations for the entire molecule did show an overall molecular bend angle in the range  $123^\circ$  to  $139^\circ$ . However, while such theoretical models do inform a programme of synthesis, they cannot, by their nature, take into account all the subtleties of intermolecular interactions arising from factors such as local dipoles and particular conformations [20]. Thus, the conclusion that must be drawn is that, in principle, bent-core mesogens can show a  $N_B$  phase, although as figure 7 shows, in the theoretical model there is a small range of bend angles within which observation of the  $N_B$  phase might be possible.

Given this possibility, we examined the N–I transition in **6** more closely and attempted to measure the enthalpy of transition as a function of scan rate in order to obtain a pseudo adiabatic value, following the method described by Ratna and Chandrasekhar [21]. With decreasing scan rate, very quickly the enthalpy change became almost immeasurably small. At the present time we simply note this observation and, in due course, will undertake a true adiabatic determination of  $\Delta H$ . Thus, at present, we do not claim that the

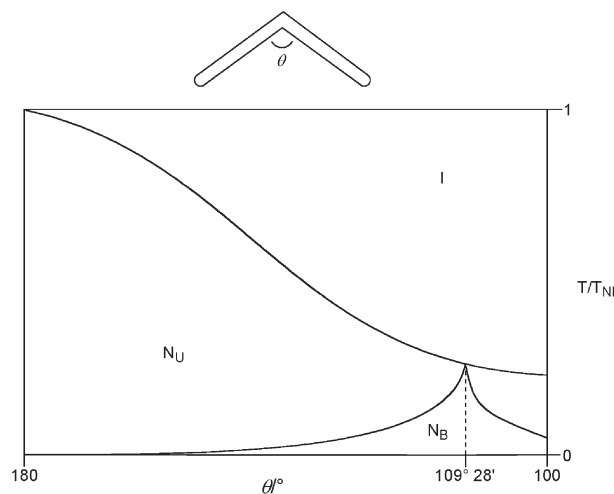


Figure 7. Phase diagram relating the bend angle  $\theta$  to phase stability for the molecular figure shown at the top of the diagram; adapted from [19].

compounds described in this work do show a biaxial nematic phase as we have insufficient evidence on which to base such a conclusion, but we do draw attention to the fact that the clearing entropies are very small and that the molecular shape is not entirely inconsistent with that predicted to give rise to the  $N_B$  phase.

Another issue to be addressed in these compounds is the nature of the phase below the nematic phase in **6** to **9**. As described above, the phase can appear as strongly homeotropic or can show a form of fan texture, and X-ray diffraction (XRD) investigations of this phase in **7** and **8** showed the absence of any layer structure. However, this behaviour and the observed texture shown in figures 2(b) and 5, suggest strongly that the phase is columnar nematic ( $N_{Col}$ ) by direct analogy with the behaviour found in unsymmetrically disubstituted piperazines **11** (figure 8) [22].

In compounds **11**, the  $N_{Col}$  phase is found in short chain homologues ( $n=4, 5, 6$ ) and for  $n=4$  and  $5$ , it is below the nematic phase and above the crystal state, but for  $n=6$  it is below the N phase but above a rectangular columnar phase ( $Col_r$  phase) and as such was regarded

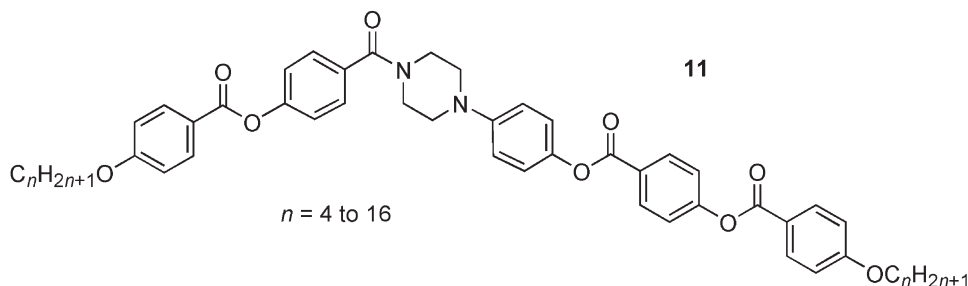


Figure 8. Chemical structure of unsymmetrically disubstituted piperazines **11**.

as a precursor to the formation of the organized columnar structure. A similar phase sequence is observed here. However, the difference in these compounds is that, from the optical textures observed, it would appear that the columnar phase we have is of a lamello-columnar type. Indeed, XRD measurements carried out on compound **10** showed first and second order layer reflections with a  $d$  value of 5.2 nm and a diffuse outer scattering with a maximum at about  $8.8^\circ$  in  $\theta$  corresponding to  $d=0.50$  nm at  $190^\circ\text{C}$  on heating — see the 2D pattern of a partially aligned sample in figure 9(a). These findings would support the existence of a layer structure. However, an additional weak reflection (detected during the heating as well as the cooling run and which can be seen also in the Guinier powder pattern) with a  $d$  value of about 4.3 nm, points to a more complex structure, Figure 9(b). Its origin could be an undulation of the layers with an undulation wavelength of about 7.7 nm perpendicular to the layer normal, which would support the model of the lamello-columnar phase. Some uncertainty remains, however, since due to the high transition temperatures and the decomposition tendency we could not get patterns of sufficiently well aligned samples.

On the basis of the experimental data the phase sequence  $\text{N-N}_{\text{Col}}\text{-Col}_\text{L}$ , observed in almost all the compounds, can be rationalized in the following way. In the nematic phase the molecules exhibit only an orientational order. Now, bearing in mind that the molecules contain three structurally incompatible segments (dicyclohexylmethane spacer, aromatic mesogenic group and aliphatic chains) and bent-shape, we have assumed that in the  $\text{N}_{\text{Col}}$  phase they segregate in a bent direction forming bundles of molecules. On further cooling the bundles organize themselves into undulated layers forming the lamello-columnar phase.

The  $\text{N}_{\text{Col}}\text{-Col}$  phase transition does, of course, have a direct parallel in the phase behaviour of lyotropic

columnar materials [23] where the nematic phase forms at higher water concentration and, as the water concentration drops, the columns that make up the nematic phase approach one another more closely and pack together into what is normally a hexagonal arrangement, directly analogous to its thermotropic equivalent.

#### 4. Conclusion

Here we have reported the first examples of symmetric dimers containing the semiflexible, di(4-aminocyclohexyl)methane spacer. Taking into account the flexibility of the molecule, molecular modelling showed overall bend angles in the range  $123^\circ$  to  $139^\circ$ , implying bent-core materials. The nature of the central part has a remarkable influence on mesogenic properties, and the compounds display two types of nematic phase. The higher temperature nematic phase is intriguing because the clearing entropies are minutely small and the molecular shape is not entirely inconsistent with that predicted to give rise to the  $\text{N}_\text{B}$  phase. The lower temperature nematic phase, assigned as columnar nematic, is regarded as a precursor to the following, rather rare, lamello-columnar phase.

#### 5. Experimental

##### 5.1. Characterization

All the solvents were either ‘puriss p.a.’ quality or distilled over appropriate drying reagents. All the other reagents were used as purchase from Aldrich.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  NMR (75.5 MHz) Spectra: Varian XL-Gemini 300 instrument with  $\text{SiMe}_4$  as internal standard, in  $\text{CDCl}_3$  unless otherwise stated,  $J$  in Hz. IR Spectra: Bomem MB 102 spectrophotometer; absorption bands in  $\text{cm}^{-1}$ . TLC: DC-Alufolien Kieselgel 60 F<sub>254</sub>, Merck plates; substances detected with UV lamp ( $\lambda=254$  nm). Phase transition

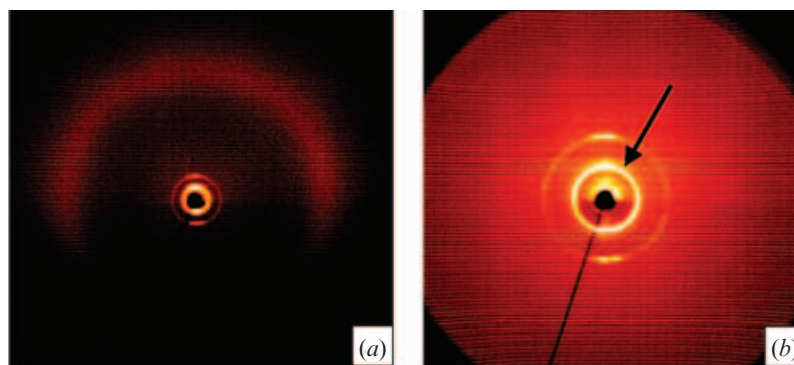


Figure 9. X-ray patterns of a partially aligned sample of **10** at  $190^\circ\text{C}$ : (a) full scattering range, (b) small angle region, the arrow indicating the weak reflection.



temperatures and textures were determined using a Zeiss Labpol polarizing microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. The enthalpies of transitions were determined from thermograms recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter operated at scanning rates of 5–10 K min<sup>-1</sup>.

Powder X-ray patterns were obtained with a Guinier film camera (HUBER Diffraktionstechnik, Germany) using quartz-monochromatized CuK<sub>α</sub> 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 disordered around an ∞-fold axis perpendicular to this interface) were obtained with a 2D detector (HI-STAR, Siemens).

## 5.2. Synthesis

4-Alkoxybenzoic acids were prepared by *O*-alkylation of methyl 4-hydroxybenzoate followed by hydrolysis under basic conditions. 4-(4'-Alkoxybenzoyloxy)benzaldehydes **1** and **2** were synthesized by esterification of the appropriate alkoxybenzoic acid with 4-hydroxybenzaldehyde using DCC and DMAP in dichloromethane in yields up to 90%. Aldehydes **3** and **4** were prepared according to the procedure reported by Ghedini *et al.* [14] in yields of 42% and 46%, respectively.

Yields and analytical data for the new compounds are collected in table 2. For each homologous pair of compounds, spectroscopic data are given for one, the only significant difference being in the NMR spectra where these relate to the number of carbons in the alkoxy chains.

In the general procedure for the preparation of imines **5–8**, a solution of 4,4'-diaminodicyclohexylmethane (1 mmol), the appropriate aldehyde (**1–4**; 2 mmol) and a catalytic amount of *p*-TsOH in toluene (20 cm<sup>3</sup>) was heated under reflux under argon for 24 h. Then, the volume of the solvent was reduced to 10 cm<sup>3</sup> by distillation. After cooling, the crystalline product was

separated by filtration. Pure product was obtained after several crystallizations from acetone or toluene.

*trans, trans-N,N'*-Bis[4''-(4'''-octyloxybenzoyloxy)-benzylidene]dicyclohexylmethane-4,4'-diamine (**5**). IR (KBr)  $\nu$  (cm<sup>-1</sup>): 2900, 2820, 1720, 1600, 1250, 1150. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.89 (t,  $J$ =6.3 Hz, 6 H); 1.20–1.90 (m, 46H); 4.05 (t,  $J$ =6.6 Hz, 4 H–OCH<sub>2</sub>); 6.99 (d,  $J$ =9.0 Hz, 4 H Ar); 7.41 (d,  $J$ =8.5 Hz, 4 H Ar); 7.98 (d,  $J$ =8.5 Hz, 4 H Ar); 8.15 (d,  $J$ =8.8 Hz, 4 H Ar); 8.34 (s, 2 H, CH=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.99, 22.54, 25.86, 28.96, 29.10, 29.20, 31.68, 31.76, 31.87, 33.51, 33.84, 68.22, 68.27, 114.20, 114.30, 121.99, 122.49, 131.12, 132.21, 132.31, 155.78, 163.52, 190.91.

*trans, trans-N,N'*-Bis[4''-(4'''-octyloxybenzoyloxy)-2-hydroxybenzylidene]dicyclohexylmethane-4,4'-diamine (**7**). IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3445, 2922, 1735, 1605, 1252. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.90 (t,  $J$ =6.6 Hz, 6H), 0.97–1.93 (m, 44H), 3.16–3.27 (m, 2H), 4.04 (t,  $J$ =6.6 Hz, 4H, –OCH<sub>2</sub>), 6.73 (d,  $J$ =8.4 Hz, 2H Ar), 6.81 (s, 2H Ar), 6.97 (d,  $J$ =9.0 Hz, 4H Ar), 7.32 (d,  $J$ =8.4 Hz, 2H Ar), 8.13 (d,  $J$ =9.0 Hz, 4H Ar), 8.39 (s, 2H, CH=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.99, 22.54, 25.85, 28.96, 29.09, 29.20, 31.51, 31.68, 33.36, 33.85, 44.15, 66.92, 68.21, 110.65, 112.28, 114.18, 116.10, 121.09, 132.06, 132.23, 154.25, 161.89, 163.51, 163.80, 164.26.

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Table 2. Yields and analytical data for the new compounds.

| Compound  | Yield/% | Analysis: calc(found)/% |           |           |
|-----------|---------|-------------------------|-----------|-----------|
|           |         | C                       | H         | N         |
| <b>6</b>  | 47      | 77.5 (77.6)             | 8.5 (8.4) | 3.2 (3.3) |
| <b>7</b>  | 31      | 78.0 (78.1)             | 8.8 (8.8) | 3.0 (3.1) |
| <b>8</b>  | 52      | 78.4 (75.0)             | 9.1 (9.4) | 2.8 (2.6) |
| <b>9</b>  | 47      | 74.8 (75.0)             | 8.2 (8.4) | 3.1 (2.7) |
| <b>10</b> | 49      | 75.4 (75.5)             | 8.5 (8.7) | 2.9 (2.7) |



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