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## Liquid Crystals

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### Liquid crystalline properties and dependence of transition temperatures on the length of the flexible alkylene spacer of symmetric dimers composed of bent-core units

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# Liquid crystalline properties and dependence of transition temperatures on the length of the flexible alkylene spacer of symmetric dimers composed of bent-core units

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Three new series of symmetric dimers composed of bent-core molecules connected by a flexible alkylene spacer have been synthesized and their mesomorphic properties studied. The effect of varying the length of the terminal chains for fixed odd and even spacers, as well as varying the spacer length for a fixed terminal chain length, on the mesomorphic properties has been investigated. Remarkably, all the dimers investigated show the same type of mesophase, which has been characterized as a  $Col_{ob}P_F$  phase, on the basis of X-ray diffraction and electro-optical measurements. It is found that for a fixed spacer length, the thermal range of the mesophase increases with increase in the number of methylene units in the terminal chain. On the other hand, interestingly an odd–even effect is observed when the length of the flexible spacer is varied; dimers having an odd number of methylene units possess higher clearing points.

## 1. Introduction

Banana-shaped mesogens, formed by compounds whose constituent molecules have a bent-core (BC) structure, have been the subject of intense investigations during the past decade. The main reason for interest in such compounds is the polar order [1] and the macroscopic chiral superstructures [2] formed by self-organization of the constituent achiral molecules. A beautiful demonstration of the mechanism of electro-optical switching in the mesophase of such an achiral BC molecule was given by Link *et al.* [3]. Following this, a large number of compounds with a BC structure were synthesized and their mesomorphic properties investigated. A detailed account of the different types of BC compounds synthesized, the mesophases exhibited by them and the physical properties investigated can be found in three review articles [4–6].

Liquid crystal dimers, which consist of two mesogenic units connected by a flexible spacer, have attracted much interest since they exhibit complex and novel phase behaviour different from that of the corresponding monomers [7]. A number of liquid crystalline dimers made up of two rod-like mesogenic units as well as disc-like units have been investigated [8]. On the basis of these studies, it has been established that the transition

temperatures and phase behaviour of these dimers depend on the length and parity of the flexible spacer, chemical nature of the spacer, chemical nature of the mesogenic group and the nature of terminal groups. A systematic study by Date *et al.* [9] on a series of symmetric dimers composed of two rod-like mesogenic units has revealed interesting behaviour regarding the dependence of mesomorphic behaviour on the length of the spacer unit and the terminal groups. In addition to the observation of a pronounced alternation (odd–even effect) of the clearing temperatures as a function of the spacer length, it was found that those with an even number of methylene units exhibit higher clearing temperatures.

Mesogenic dimers made of BC units are relatively new and have not been investigated in detail. Dantlgraber *et al.* [10] reported the first dimesogens in which two BC molecules are connected by flexible dimethylsiloxane units. Interestingly, a ferroelectric or an antiferroelectric polar smectic C phase was obtained as a function of spacer length in these dimers. Very recently, Kosata *et al.* [11] reported several liquid crystalline dimers composed of BC mesogenic units, which are terminally linked using three different types of spacers. Although they did not obtain a mesophase in a dimer with an alkylene spacer, it was concluded that the formation of mesophases mainly depends on the chemical structure of the spacer. Remarkably, we

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were able to show that using the same basic structure but with suitable lateral fluoro substituent, a switchable mesophase could be obtained [12].

In our previous study [12], we examined the influence of a lateral fluoro substituent in dimers composed of BC molecules with a fixed terminal chain length ( $m=14$ ) and connected by either an odd ( $n=9$ ) or even ( $n=12$ ) alkylene spacer. Herein, we describe the mesomorphic behaviour of three series of novel symmetric dimers having the same basic structure, **D**. The effect of varying the length of terminal chains for a fixed odd or even spacer ( $m=8-12, 14, 16, 18$  for spacers  $n=9$  or  $n=12$ ) and the influence of spacer length ( $n=7-12$  for  $m=14$ ) on the mesomorphic properties of these dimers are examined. The dimers investigated have the general molecular structure (**D**) shown in scheme 1.

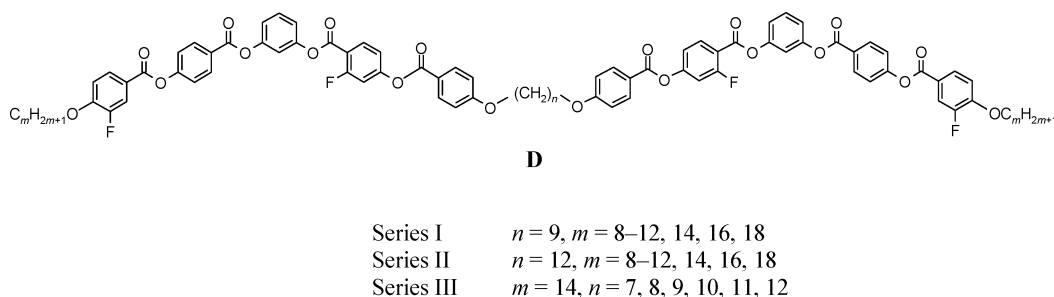
## 2. Experimental

### 2.1. Synthesis

The general procedure followed for the synthesis of symmetric dimers **D** has been reported previously [12]. All the dimers were purified through repeated crystallization using analytical grade solvents. The chemical structure of the dimers was determined using a combination of IR spectroscopy, NMR spectroscopy and elemental analysis techniques. IR (Shimadzu FTIR-8400 spectrophotometer) spectra for intermediate

compounds were recorded as nujol mull and as KBr discs for target compounds.  $^1\text{H}$ NMR (Bruker AMX 400 spectrometer) spectra were recorded using deuteriochloroform ( $\text{CDCl}_3$ ) or deuterioacetone ( $\text{CD}_3\text{COCD}_3$ ) as solvents. Tetramethylsilane (TMS) was used as an internal reference. Elemental analysis (Carlo-Erba 1106 analyser) was performed using BBOT [2,5-bis-(5-*tert*-butyl-benzoxazol-2-yl)thiopene] and sulfanilamide as standards. As an example, the spectral and analytical data obtained for the dimer **DO9m8** are presented below. In the notation used for **DO9m8**, D=dimer, O9=odd number (9) of methylene units in the spacer, m8=number (8) of carbon atoms in the terminal chain; similarly **DE12m12** means D=dimer, E12=even number (12) of methylene units in the spacer, m12=number (12) of carbon atoms in the terminal chain. The analytical data obtained for the remaining dimers are presented in table 1.

**2.1.1. Dimer DO9m8.** m.p.  $142^\circ\text{C}$ . IR  $\nu_{\text{max}}$ : 2923, 2854, 1739, 1728, 1604, 1614, 1512, 1473, 1282,  $1240\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta_{\text{H}}$ : 8.28 (d,  $^3J$  8.72 Hz, 4H, Ar-H), 8.20–8.16 (m, 2H, Ar-H), 8.13 (d,  $^3J$  8.84 Hz, 4H, Ar-H), 7.97 (d,  $^3J$  8.64 Hz, 2H, Ar-H), 7.92–7.89 (dd,  $^3J$  11.4 Hz,  $^4J$  1.92 Hz, 2H, Ar-H), 7.49 (t,  $^3J$  8.16 Hz, 2H, Ar-H), 7.37 (d,  $^3J$  8.68 Hz, 4H, Ar-H), 7.22–7.16 (m, 10H, Ar-H), 7.07–7.03 (m, 2H, Ar-H), 6.99 (d,  $^3J$  8.92 Hz, 4H, Ar-H), 4.13 (t,  $^3J$  6.6 Hz, 4H,  $2 \times \text{Ar-OCH}_2$ -), 4.06 (t,



Scheme 1. Molecular structure of the investigated dimers.

Table 1. Elemental analysis data (%) obtained for all the dimers investigated.

Dimer	C calc. (found)	H calc. (found)	Dimer	C calc. (found)	H calc. (found)
<b>DO9m8</b>	69.74 (69.56)	5.50 (5.25)	<b>DE12m8</b>	70.18 (69.82)	5.76 (5.35)
<b>DO9m9</b>	70.01 (70.16)	5.68 (5.81)	<b>DE12m9</b>	70.40 (70.34)	5.90 (5.73)
<b>DO9m10</b>	70.28 (69.95)	5.83 (5.82)	<b>DE12m10</b>	70.66 (70.24)	6.04 (6.08)
<b>DO9m11</b>	70.53 (70.11)	5.97 (5.89)	<b>DE12m11</b>	70.90 (70.62)	6.17 (6.19)
<b>DO9m12</b>	70.78 (70.42)	6.11 (6.13)	<b>DE12m12</b>	71.13 (70.72)	6.31 (6.12)
<b>DO9m14</b>	71.25 (71.59)	6.37 (6.39)	<b>DE12m14</b>	71.59 (71.63)	6.56 (6.75)
<b>DO9m16</b>	70.78 (70.42)	6.11 (6.13)	<b>DE12m16</b>	72.0 (71.73)	6.79 (6.54)
<b>DO9m18</b>	72.11 (72.23)	6.84 (6.99)	<b>DE12m18</b>	72.41 (72.06)	7.01 (7.06)
<b>DO7m14</b>	71.02 (70.77)	6.25 (6.51)	<b>DE8m14</b>	71.14 (70.91)	6.25 (6.51)
<b>DO11m14</b>	71.47 (71.12)	6.50 (6.43)	<b>DE10m14</b>	71.36 (71.23)	6.44 (6.37)

$^3J$  6.52 Hz, 4H,  $2 \times \text{Ar-OCH}_2$ -), 1.91–1.80 (m, 8H,  $4 \times \text{Ar-OCH}_2\text{-CH}_2$ -), 1.50–1.31 [m, 30H,  $2 \times (-\text{CH}_2)_5 + (-\text{CH}_2)_5$ ], 0.88 (t,  $^3J$  6.88 Hz, 6H,  $2 \times -\text{CH}_3$ );  $\text{C}_{93}\text{H}_{88}\text{F}_4\text{O}_{20}$  requires C 69.74, H 5.50%; found C 69.56, H 5.25%.

## 2.2. Characterization

The mesomorphic properties were investigated using a combination of polarizing optical microscopy (POM), X-ray diffraction (XRD) and electro-optical measurements. Textural observations were made under a polarizing light microscope (Olympus BX50) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). The transition temperatures were determined from POM observations as well as from the thermograms obtained on a differential scanning calorimeter (DSC, Perkin-Elmer Calorimeter, Model Pyris 1D). Enthalpy values associated with the transitions were also determined from these thermograms. The apparatus was calibrated using pure indium ( $156.6^\circ\text{C}$ ;  $\Delta H = 28.56 \text{ J g}^{-1}$ ) as a standard and operated at a scanning rate of  $5^\circ\text{C min}^{-1}$  both on heating and cooling cycles.

XRD patterns were obtained for unoriented samples and in some cases for oriented samples. In all cases,  $\text{Cu-K}_\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation generated from a 4 kW rotating anode X-ray source (Rigaku Ultrax-18) was used. The beam was monochromated using a graphite crystal. The powder samples held in Lindemann capillaries (diameter 0.7 mm, wall thickness 0.01 mm) and placed in a temperature-controlled heater were cooled slowly from the isotropic state to the mesophase and irradiated. Oriented patterns were obtained by slow cooling of a drop of the sample on a glass plate from the isotropic state. In each case, the sample temperature was controlled to within  $\pm 0.1^\circ\text{C}$ . The diffraction pattern of the mesophase was recorded on a two-dimensional (Marresearch) image plate.

Polarization measurements were carried out using ITO coated glass cells (with polyimide alignment layers and without any alignment layers) employing the standard triangular-wave method [13]. The glass cells of different thicknesses were either home made or obtained from EHC, Japan. Triangular waves were generated by a waveform generator (Wavetek, Model 39) connected to an amplifier (Trek Model 601B-3). The current was measured across a  $10 \text{ k}\Omega$  resistor and the current response traces were recorded using an oscilloscope (Agilent 54621A). Simultaneously the optical behaviour was observed under a polarizing microscope.

## 3. Results and discussion

As mentioned earlier, three different series of symmetric dimers have been investigated for their mesomorphic properties. In the first series of dimers, the terminal chain length has been varied by having an odd number of spacer units ( $n=9$ ). In the second series, the spacer unit was fixed to be an even number ( $n=12$ ) and the terminal chain length varied. In series III, for a fixed terminal chain length, the spacer length was varied to see if this has any bearing on the mesomorphic properties. The transition temperatures and the associated enthalpy values obtained for the dimers of series I are summarized in table 2. It can be seen that all the dimers are enantiotropic and exhibit the same type of mesophase. This mesophase has been characterized as a columnar phase with an oblique lattice that exhibits ferroelectric characteristics and is assigned the symbol  $\text{Col}_{\text{ob}}\text{P}_F$ . This assignment was made on the basis of XRD measurements and electro-optical studies, which are discussed below.

A plot of the dependence of transition temperature on the length of the terminal chain for this series is shown in figure 1. It can be seen from figure 1 that as the terminal chain length is increased, melting points decrease, clearing points increase and, as a result, the thermal range for the mesophase increases. For example, dimer **DO9m8** has a thermal range  $14^\circ\text{C}$  for the mesophase, which increases to  $38.5^\circ\text{C}$  for dimer **DO9m18**.

Interestingly, the variation in terminal chain length has no effect on the type of the mesophase observed.

Table 2. Transition temperatures ( $^\circ\text{C}$ ) and the associated enthalpy values ( $\text{kJ mol}^{-1}$ , in italics) for the dimers of series I.

Dimer	$m$	Cr	$\text{Col}_{\text{ob}}\text{P}_F$	I
<b>DO9m8</b>	8	.	142.0	156.0
			<i>49.5</i>	<i>24.5</i>
<b>DO9m9</b>	9	.	140.5	155.0
			<i>47.0</i>	<i>25.0</i>
<b>DO9m10</b>	10	.	140.0	155.0
			<i>39.0</i>	<i>24.5</i>
<b>DO9m11</b>	11	.	140.0	157.5
			<i>47.5</i>	<i>25.5</i>
<b>DO9m12</b>	12	.	139.0	159.5
			<i>48.0</i>	<i>26.0</i>
<b>DO9m14</b>	14	.	136.0	164.5
			<i>49.5</i>	<i>26.5</i>
<b>DO9m16</b>	16	.	135.5	169.5
			<i>57.5</i>	<i>26.5</i>
<b>DO9m18</b>	18	.	134.0	172.5
			<i>60.0</i>	<i>26.0</i>

Cr=crystalline phase;  $\text{Col}_{\text{ob}}\text{P}_F$ =columnar polar phase with an oblique lattice showing ferroelectric characteristics; I=isotropic liquid.

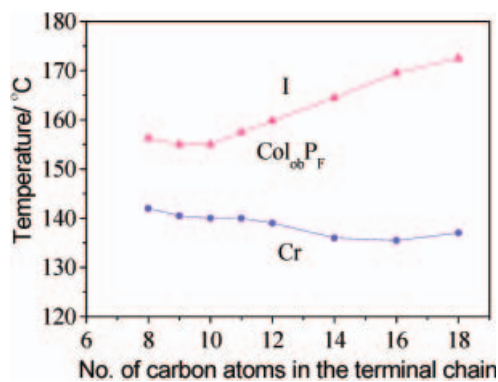
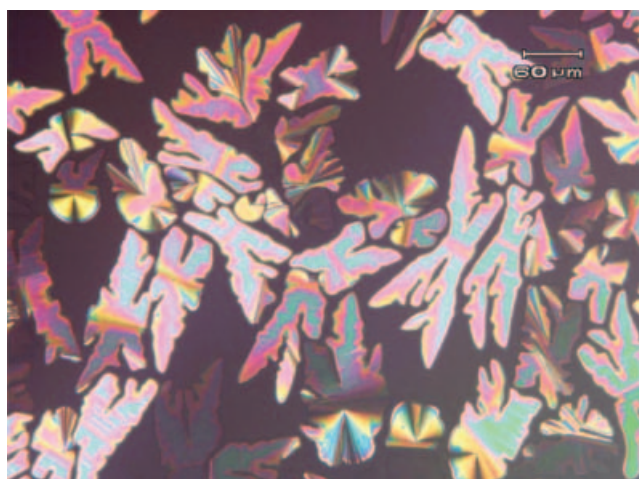


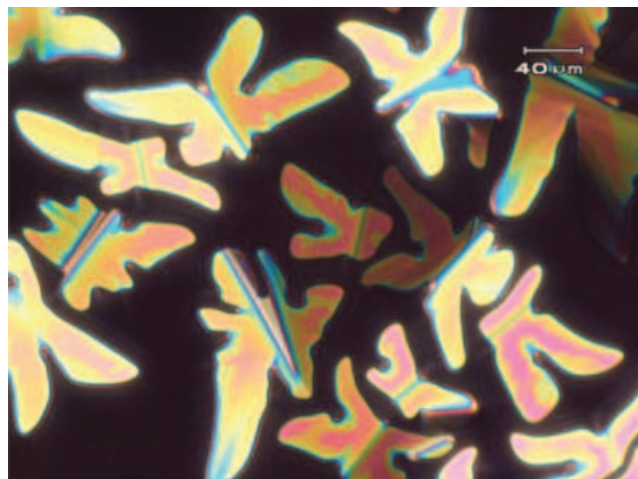
Figure 1. The dependence of transition temperature on the length of the terminal chain for the dimers of series I.

This is in complete contrast to the observation made in symmetric calamitic dimers where a phase change occurs as a function of terminal chain length [8, 9, 14–16] at least in a number of cases, although this is not a general phenomenon. In addition, in the present series the clearing temperatures follow a smooth curve relationship, whereas a strong odd–even effect for the nematic–isotropic transition is seen in dimers made of calamitic systems.

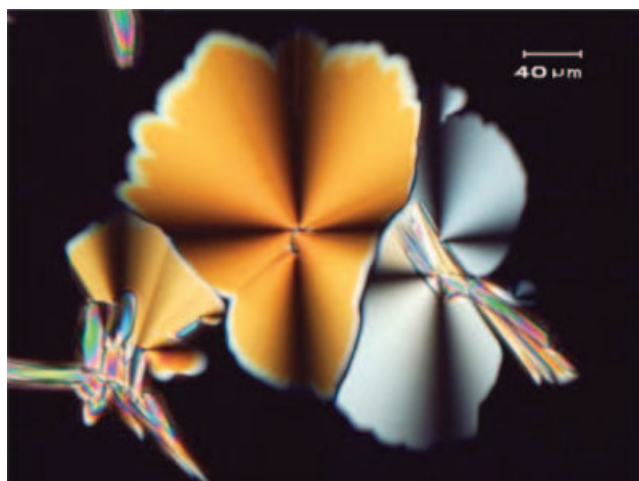
When a sample of dimer **DO9m8** is cooled slowly from the isotropic phase and observed using a polarizing microscope, different types of textures are seen to grow. Typical textures obtained for this dimer are shown in figures 2a and 2b. All the remaining homologues exhibit birefringent spherulitic domains and, as an example, those obtained for dimer **DO9m14** are depicted in figures 2c and 2d.



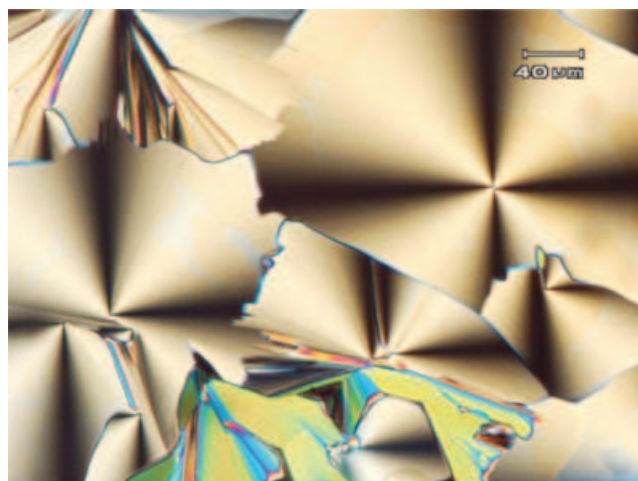
(a)



(b)



(c)



(d)

Figure 2. (a, b) Photomicrographs of the textures obtained for the mesophase of dimer **DO9m8** on cooling the isotropic liquid ( $T=155^{\circ}\text{C}$ ). (c, d) Photomicrographs obtained for the mesophase of dimer **DO9m14** at  $T=164^{\circ}\text{C}$  and  $T=163^{\circ}\text{C}$ , respectively.

The XRD patterns obtained for the mesophase of all the dimers were similar with many reflections in the small-angle region ruling out the possibility of a simple layer structure. As a matter of fact, the reflections obtained could be indexed to an oblique lattice. A partially oriented pattern obtained for the mesophase of dimer **DO9m14** along with the Miller indices is shown in figure 3. The lattice parameters obtained are  $a=19.9 \text{ \AA}$ ,  $b=53.5 \text{ \AA}$  and  $\beta=86.8^\circ$ . Previously we proposed [12] a structural model for the  $\text{Col}_{\text{ob}}\text{P}_F$  phase in which it is assumed that two BC units of a dimer are located at the opposite corners of the lattice. The possible overlap of the flexible spacer of a dimer with the terminal chains of the adjacent dimers was also considered in the model. The same model also holds good for the mesophase of these dimers.

The electro-optical investigations of the mesophase were carried out by employing a triangular-wave method which revealed ferroelectric characteristics. For instance, on application of a triangular-wave electric field, the mesophase of dimer **DO9m14** showed a single peak per half period of the applied voltage. The single peak did not split even on reducing the frequency down to 0.1 Hz. The current response trace obtained for the mesophase of compound **DO9m14** under a triangular-wave field of 400 V<sub>PP</sub> and a frequency of 3 Hz is shown in figure 4. The switching polarization value calculated from the trace is about  $770 \text{ nC cm}^{-2}$ . On the basis of these results, the assignment of the symbol  $\text{Col}_{\text{ob}}\text{P}_F$  for the mesophase appears to be reasonable.

The transition temperatures and the associated enthalpy values obtained for dimers belonging to series II are presented in table 3. These dimers contain an even number of methylene units ( $n=12$ ) in the spacer. All the homologues of this series also exhibit the same type of mesophase, which has been characterized as a  $\text{Col}_{\text{ob}}\text{P}_F$  phase. Dimer **DE12m8** exhibits an enantiotropic phase. However, on ascending the series, for dimers with terminal chain lengths  $m=9-11$ , the melting point

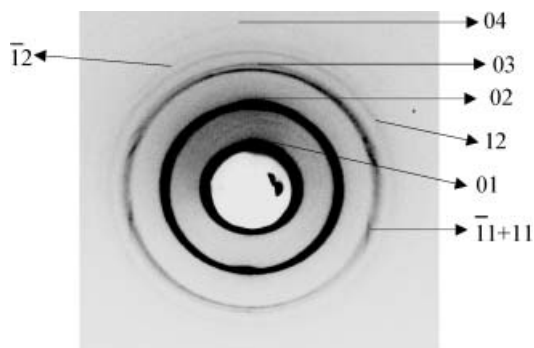


Figure 3. X-ray diffraction pattern obtained in the small-angle region for dimer **DO9m14** at  $150^\circ\text{C}$ .

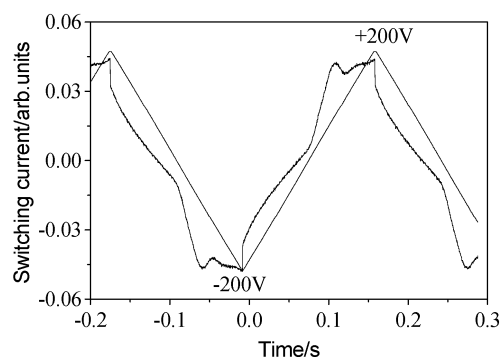


Figure 4. Current response trace obtained for the mesophase of dimer **DO9m14** ( $T=150^\circ\text{C}$ , 400 V<sub>PP</sub>, 3 Hz, cell thickness  $8.68 \mu\text{m}$ ,  $P_S \sim 770 \text{ nC cm}^{-2}$ ).

increases slightly and the mesophase becomes monotropic. Interestingly, on increasing the chain length further, the dimers **DE12m12**, **DE12m14**, **DE12m16** and **DE12m18** display an enantiotropic phase.

Dimer **DE12m8** exhibits an additional metastable phase at  $127.5^\circ\text{C}$  with a low enthalpy of  $0.3 \text{ kJ mol}^{-1}$ . When a sample of this dimer is cooled slowly from the isotropic phase, the mesophase appears as dendrites which coalesce to give rise to a mosaic texture. On cooling further, at  $127.5^\circ\text{C}$  a clear textural change could be observed which is reversible. The photomicrographs of the textures obtained for this dimer at  $138^\circ\text{C}$  and  $125^\circ\text{C}$  are shown in figure 5a and 5b, respectively. Although a transition to this metastable phase could be clearly seen both under a polarizing microscope as well as in a DSC thermogram, it could not be characterized

Table 3. Transition temperatures ( $^\circ\text{C}$ ) and the associated enthalpy values ( $\text{kJ mol}^{-1}$ , in italics) for the dimers of series II.

Dimer	$m$	Cr	$\text{Col}_{\text{ob}}\text{P}_F$	I
<b>DE12m8</b> <sup>a</sup>	8	.	137.0	<i>145.5</i>
			50.0	<i>21.0</i>
<b>DE12m9</b>	9	.	142.0	(138.0)
			70.0	23.5
<b>DE12m10</b>	10	.	142.5	(138.0)
			65.0	22.0
<b>DE12m11</b>	11	.	143.0	(140.5)
			63.5	24.5
<b>DE12m12</b>	12	.	142.0	145.0
			43.7	26.0
<b>DE12m14</b>	14	.	138.5	149.0
			45.5	25.5
<b>DE12m16</b>	16	.	138.5	154.0
			82.0	26.0
<b>DE12m18</b>	18	.	137.0	157.5
			94.0	26.5

<sup>a</sup>Dimer exhibits a monotropic transition at  $127.5^\circ\text{C}$ , and the mesophase could not be characterized as the sample crystallizes rapidly; ( ) indicate monotropic transitions.



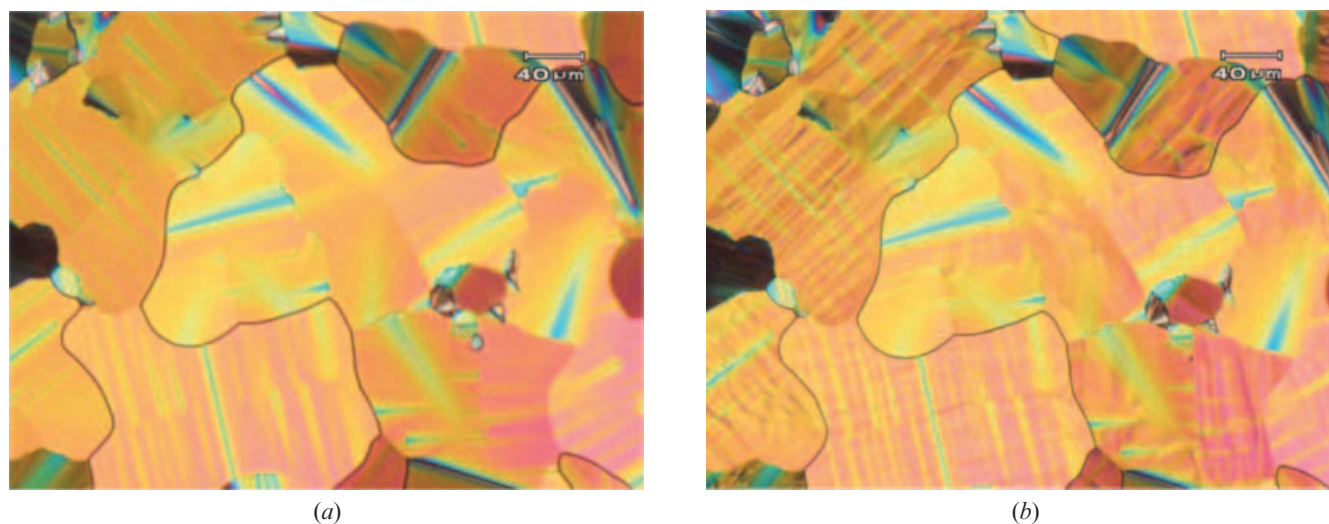


Figure 5. Textures observed on cooling the isotropic liquid of a sample of dimer **DE12m8** sandwiched between a glass slide and a coverslip: (a)  $T=138^{\circ}\text{C}$ ; (b)  $T=125^{\circ}\text{C}$ .

by XRD as the phase transforms to a crystalline state quite rapidly.

The other homologues of the series exhibit spherulitic and other patterns that are normally obtained for non-layered mesophases of BC compounds. The XRD patterns of all the dimers are similar and the reflections obtained could be indexed to a columnar phase with an oblique lattice. A partially oriented pattern obtained for the mesophase of dimer **DE12m14** and the indexing of the reflections has been discussed previously [12].

Electro-optical studies carried out on the mesophase of all these dimers clearly indicate a ferroelectric type of behaviour. When a sample of dimer **DE12m8** was cooled from the isotropic phase to the mesophase and a triangular-wave electric field applied, beyond a threshold voltage a single current peak per half period of the applied voltage was observed. This single peak persisted when the frequency was reduced to 0.1 Hz suggesting a ferroelectric switching. On further cooling under the field, although the single peak persists, a clear textural change could be observed at  $127.5^{\circ}\text{C}$ . This clearly indicates a phase transition and this is reversible. The current response traces obtained for this dimer at  $136^{\circ}\text{C}$  and  $123^{\circ}\text{C}$  are shown in figures 6a and 6b, respectively. The corresponding optical photomicrographs obtained are also shown in figures 6c and 6d below the traces.

A plot of the dependence of transition temperature on the length of the terminal chain for series II is shown in figure 7. It can be seen from the plot that as the terminal chain length ( $m$ ) increases, there is a decrease in the clearing temperature initially which increases rapidly on ascending the series further. This results in a wider thermal range of the mesophase for higher homologues.

A comparison of dependence of clearing temperature on the length of the terminal chain for the two series I and II is shown in figure 8. It is quite clear from this plot that the clearing temperatures of the dimers with an even number of methylene units in the spacer are lower than those with an odd number. Again, this behaviour is in complete contrast to the observations made in symmetric dimers [8, 9, 14–16] made of calamitic mesogenic units, in which dimers with even spacer units have higher clearing temperature as compared to those with odd ones. It must be pointed out that the shape of the clearing curves for the two series show some unusual tendency and this is not seen for monomers of BC compounds where a change of phase structure (e.g. columnar to lamellar phase) is generally observed on ascending the series.

This difference in transition temperatures has been attributed to the shape of the dimers. It has been suggested [9] that for even numbered spacers the two mesogenic moieties are almost parallel/antiparallel, whereas for odd numbered spacers they are no longer parallel and instead form an angle. In the case of dimers exhibiting layered phases, the shape of the connecting unit determines the arrangement of molecules in adjacent layers. Thus, for dimers with optically active mesogenic units, linear spacers give rise to ferroelectric properties, whereas the odd spacers favour antiferroelectric properties [17, 18]. If we use the same analogy for the symmetric BC dimers being discussed here, then for dimers containing an odd number of spacer units, the long axes of the bent mesogenic units will be in the same direction. In such a conformation, the molecules can pack more efficiently than in dimers with an even

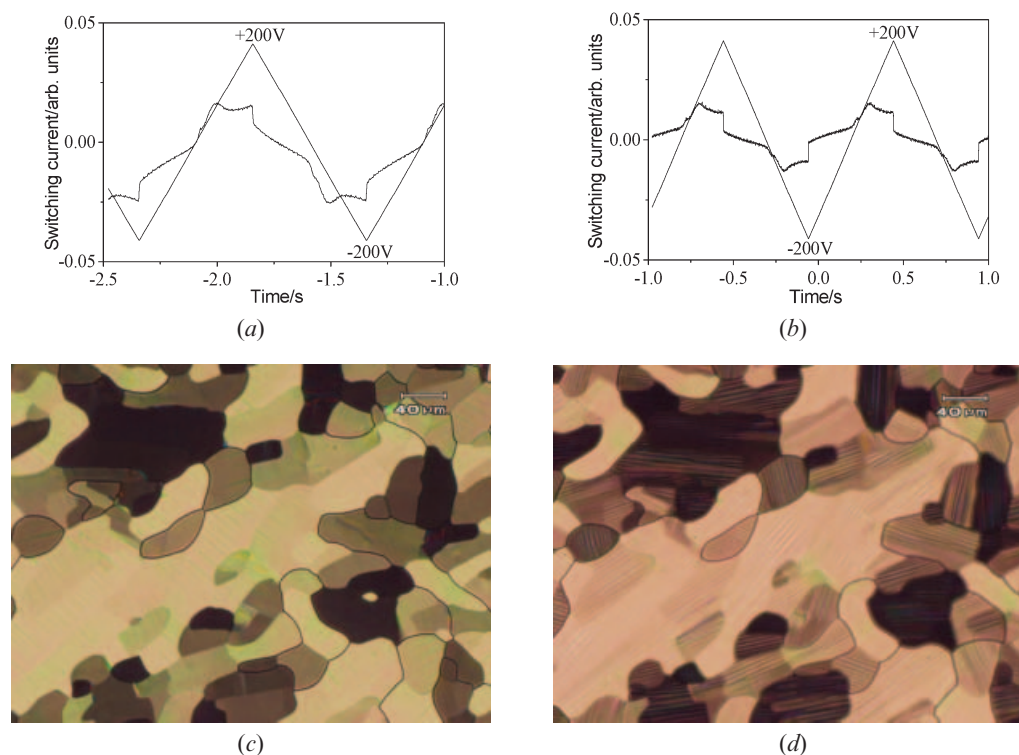


Figure 6. Current response traces obtained for the mesophase of dimer **DE12m8** in an ITO coated cell of thickness  $8\ \mu\text{m}$ : (a)  $T=136^\circ\text{C}$ ,  $400\ \text{V}_{\text{pp}}$ ,  $1\ \text{Hz}$ ,  $P_{\text{S}} \sim 180\ \text{nC cm}^{-2}$ ; (b)  $T=123^\circ\text{C}$ ,  $400\ \text{V}_{\text{pp}}$ ,  $1\ \text{Hz}$ ,  $P_{\text{S}} \sim 123\ \text{nC cm}^{-2}$ . (c, d) Corresponding optical textures obtained under the electric field.

number spacer where these axes make an angle. This results in an enhanced molecular association and hence higher clearing temperatures in dimers with an odd number spacer. Thus, the influence of the parity in the case of dimers with BC units is the reverse of that found in dimers made of calamitic mesogenic units.

Finally, in order to examine the influence of the length ( $n=7-12$ ) of the spacer unit for a fixed terminal chain length ( $m=14$ ), the mesomorphic properties of dimers belonging to series III were investigated. The transition temperatures and the associated enthalpy

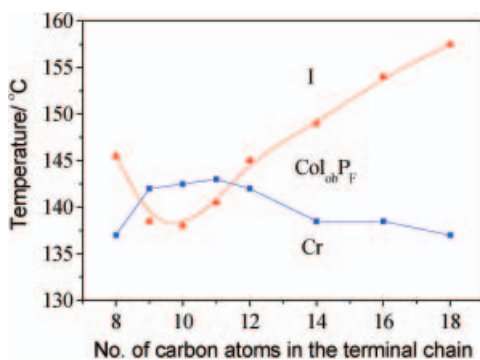


Figure 7. The dependence of transition temperature on the length of the terminal chain for the dimers series II.

values obtained for this series are summarized in table 4. All the dimers are enantiotropic except for dimer **DE8m14**, which has a metastable mesophase. The optical textures, XRD data and electro-optical measurements are all similar to those obtained for the dimers of series I and II and hence the mesophase has been identified as a  $\text{Col}_{\text{ob}}\text{P}_{\text{F}}$  phase.

The textural patterns obtained on slow cooling the isotropic liquid of dimer **DE10m14** are shown in

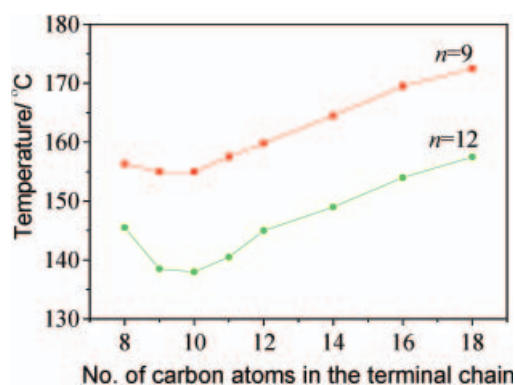


Figure 8. The dependence of clearing temperature on the length of the terminal chain for series I (spacer length  $n=9$ ) and II (spacer length  $n=12$ ).



Table 4. Transition temperatures ( $^{\circ}\text{C}$ ) and the associated enthalpy values ( $\text{kJ mol}^{-1}$ , in italics) for the dimers of series III.

Dimer	n	Cr	$\text{Col}_{\text{ob}}\text{P}_{\text{F}}$	I
<b>DO7m14</b>	7	.	171.0	172.5
		.	<i>80.5</i>	<i>25.0</i>
<b>DE8m14</b>	8	.	170.0	(161.0)
		.	<i>81.5</i>	<i>21.0</i>
<b>DO9m14</b>	9	.	136.0	164.5
		.	<i>49.5</i>	<i>26.5</i>
<b>DE10m14</b>	10	.	137.0	156.7
		.	<i>65.0</i>	<i>24.5</i>
<b>DO11m14</b>	11	.	142.0	157.8
		.	<i>45.0</i>	<i>27.0</i>
<b>DE12m14</b>	12	.	138.5	149.0
		.	<i>45.5</i>	<i>25.5</i>

figure 9. These highly birefringent patterns are indicative of a columnar phase. A plot of dependence of transition temperature as a function of the spacer length for this series of dimers is shown in figure 10. A fairly pronounced odd–even effect on the clearing points can be clearly seen. Interestingly, the phase type is not affected as the spacer length is varied. It is also evident from this plot that homologues containing an odd number spacer have higher clearing points. This is the first example of a series of symmetric dimers containing BC units with flexible alkylene spacer where an odd–even effect is observed for the parity of the spacers. Remarkably, the parity has no influence on the type of mesophase obtained. This is in complete contrast to those dimers formed using rod-like mesogenic units, where odd–even effects are observed and also the parity

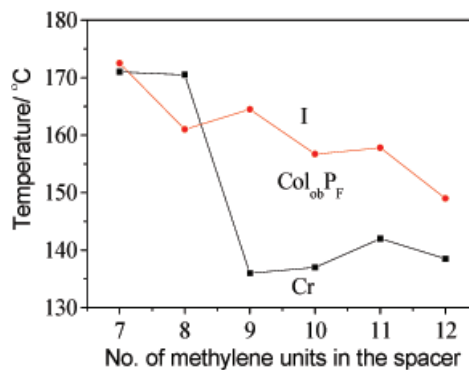
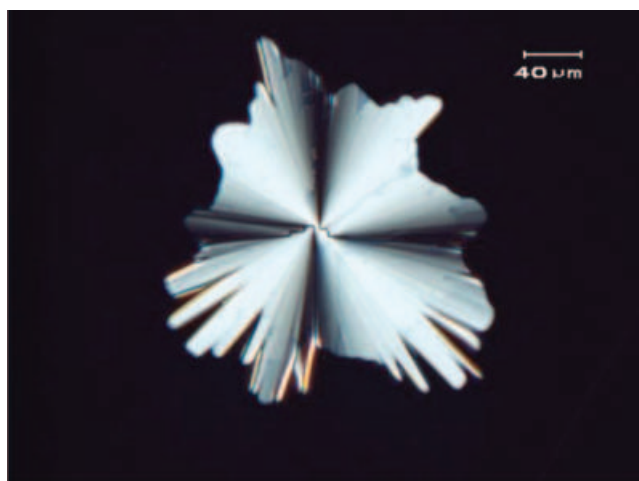


Figure 10. The dependence of transition temperature on the length of the flexible spacer for the dimers of series III.

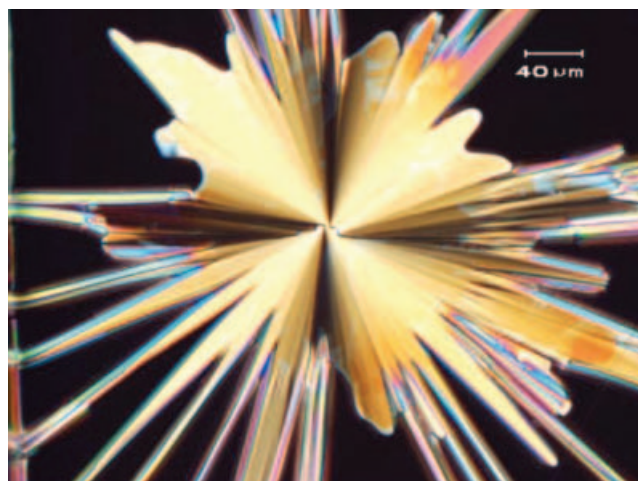
has a strong influence on the type of the mesophase obtained.

#### 4. Conclusions

Three series of mesogenic symmetric dimers composed of bent-core (BC) molecules and linked by an alkylene spacer were synthesized and their mesomorphic behaviour investigated. In order to study the structure–property relationships, the length of the terminal chain was varied for a fixed spacer unit and the length of the flexible spacer was varied for a fixed terminal chain length. Remarkably and surprisingly all the dimers investigated show the same type of mesophase. From partially oriented XRD patterns and electro-optical investigations, this mesophase has been characterized as a columnar phase with an oblique lattice that exhibits ferroelectric characteristics. Hence, this phase has



(a)



(b)

Figure 9. Photomicrographs of textures ( $\text{Col}_{\text{ob}}\text{P}_{\text{F}}$  phase) developing on slow cooling of the isotropic liquid of dimer **DE10m14**; (a) and (b) represent different regions of the same sample ( $T=156.2^{\circ}\text{C}$ ).

been designated as a Col<sub>ob</sub>P<sub>F</sub> phase. These studies reveal that in such dimers, for a fixed spacer the thermal range of the mesophase increases with increase in terminal chain length particularly for longer chain members of series II. In series III, the dimers with an odd number of methylene units in the spacer have higher clearing temperatures than those with an even number. This is the first example of a BC dimer, where an odd-even effect of the clearing transition temperature is observed when the length of the flexible spacer is varied. The results also suggest that the parity of the alkylene spacer has no effect on the nature of the mesophase obtained at least in the dimers investigated.

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