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# The *N*,*N′*-bis[4-(4-*n*-alkyloxybenzoyloxy)benzylidene]-phenylene-1,3-diamines: mesophase behaviour and physical properties

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A homologous series of banana-shaped compounds ($n = 1$–$12$) is described. The short-chain derivatives exhibit a $B_6$ phase, while $B_6/B_1$ dimorphism is found for the pentyloxy and hexyloxy homologues. The $B_1$ phase of the compounds having longer alkyloxy chains is changed to a $B_2$ phase for the compounds with $n = 11$ and 12. The phase characterization was performed using their optical textures and by means of X-ray investigations. Transition enthalpies were measured using DSC. In addition, density measurements were performed on one selected homologue. The compound $n = 8$ exhibiting a $B_1$ phase was investigated also by high-pressure DTA.

## 1. Introduction

Banana-shaped mesogens represent a new sub-field in thermotropic liquid crystals differing from conventional calamitic liquid crystals. As a consequence of the bent molecular shape, a polar packing of the molecules within the smectic layers is favoured giving rise to several new mesophases labelled by the code letters $B_n$ [1]. These mesophases are not compatible with the conventional smectic mesophases of calamitic compounds (SmA, SmC).

In this paper we describe the synthesis and characterization of 12 members of the homologous series of *N*,*N′*-bis[4-(4-*n*-alkyloxybenzoyloxy)benzylidene]phenylene-1,3-diamines. The mesophases were assigned by means of their optical textures and by using X-ray diffraction as $B_1$ and $B_6$ phases. Density measurements and high pressure measurements on the octyloxy homologue were performed to obtain the thermodynamic data associated with the phase transition.

## 2. Materials

The compounds were prepared by the condensation of the appropriate 4-(4-*n*-alkyloxybenzoyloxy)benzaldehyde with 1,3-phenylenediamine. In contrast to the usual conditions used for the preparation of azomethines, in these condensation reactions the addition of acetic acid or toluenesulphonic acid as catalyst is disadvantageous. In several cases impure products were obtained having temperature ranges of several degrees for the clearing process and which could not be purified by recrystallization. The substances were instead prepared by heating for a short time (about 2 minutes) equimolar amounts of the components without the addition of any catalytic protons, using absolute methanol or ethanol as solvent. The pure white products were obtained after recrystallization twice from ethanol in yields greater than 70%.

Transition temperatures and enthalpies are listed in table 1 along with the proposed phase assignments. It should be noted that the transition temperatures of the homologues with $n = 6$–$10$ have been reported already [1].

## 3. Experimental

The transition temperatures and corresponding enthalpies were determined using a differential scanning calorimeter (Perkin Elmer, DSC Pyris1). The mesophases were assigned from their characteristic textures using a polarizing microscope (Leitz Orthoplan) equipped with a Linkam hot stage (THM 600/S). The X-ray

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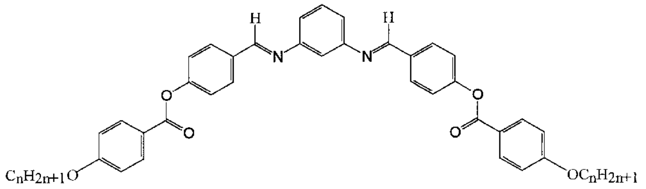
Table 1. Transition temperatures (°C) and transition enthalpies [kJ mol$^{-1}$] of the homologous series. DSC heating and cooling rate is 10 K min$^{-1}$; brackets denote monotropic phases.



| *n* | $Cr_1$ | | $Cr_2$ | | $B_1$ | | $B_6$ | | $B_2$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ● | 188<br>[13.6] | ● | 196<br>[36.1] | — | | (● | 125)<br>[][a] | — | | ● |
| 2 | ● | 166.5<br>[50.2] | — | | — | | (● | 143)<br>[5.0] | — | | ● |
| 3 | ● | 148.5<br>[45.3] | — | | — | | (● | 142)<br>[8.6] | — | | ● |
| 4 | ● | 165.5<br>[45.8] | — | | — | | (● | 156)<br>[11.2] | — | | ● |
| 5 | ● | 150<br>[30.9] | — | | (● | 125)<br>[][a] | ● | 152<br>[6.8] | — | | ● |
| 6 | ● | 136<br>[37.7] | — | | ● | 142.5<br>[0.1] | ● | 149.5<br>[14.0] | — | | ● |
| 7 | ● | 106.5<br>[13.7] | ● | 114<br>[20.5] | ● | 140<br>[15.7] | — | | — | | ● |
| 8 | ● | 104<br>[28.6] | ● | 114.5<br>[20.3] | ● | 134.5<br>[16.0] | — | | — | | ● |
| 9 | ● | 81.5<br>[29.8] | ● | 119<br>[20.7] | ● | 125<br>[15.6] | — | | — | | ● |
| 10 | ● | 89<br>[14.2] | ● | 123<br>[43.6] | (● | 117)<br>[12.1] | — | | — | | ● |
| 11 | ● | 121<br>[41.7] | — | | — | | — | | (● | 113)<br>[][a] | ● |
| 12 | ● | 119.5<br>[48.9] | — | | — | | — | | (● | 114)<br>[17.1] | ● |

[a] These transitions could not be detected by calorimetry and only by microscopic investigations on fast cooling.

studies were performed using a Guinier device (Huber Diffraktionstechnik GmbH, Germany) for non-oriented samples and a flat-film method for samples oriented by a magnetic field.

Electro-optical investigations were carried out using a typical experimental set-up in which the liquid crystal cells are placed on the hot stage of the polarizing microscope with a power supply (Hewlett-Packard, 8116A) generating the voltage signals.

The densities were measured with a vibrating tube densimeter (Anton Paar DMA 60), technical details are described elsewhere [2]. The densimeter was calibrated using octane, nonane, and decane. The temperature could be varied from room temperature to 150°C and was measured by a Pt-100 thermocouple to an accuracy of 0.05 K. The high pressure DTA instrument was developed in the laboratory of Schneider *et al.* [3] and recently applied to the investigation of laterally aryl-branched liquid crystals [4–7].

## 4. Results

### 4.1. *Phase assignment*

On cooling the isotropic liquid, the $B_6$ phase appears as a SmA-like fan-shaped texture (see figure 1). In contrast to the SmA phases, however, it was impossible to obtain a homeotropic texture either by shearing or by surface treatment. Sometimes schlieren-like texture was observed on the application of mechanical stress but this rapidly transformed into a non-specific texture. The monotropic I–$B_6$ transition of the compounds $n=2$–4 was shown to be a reversible transition both by microscopic observations and calorimetric measurements.

The $B_1$ phase forms a mosaic texture on slow cooling of the isotropic liquid (figure 2). On shearing, a fan-like texture develops. In the case of $B_6$–$B_1$ dimorphism, shown by the pentyloxy ($n=5$) and hexyloxy ($n=6$) derivatives, the fan-shaped texture of the $B_6$ phase remains unchanged at the $B_6$–$B_1$ transition. This transition can be easily seen, however, if the fan-shaped

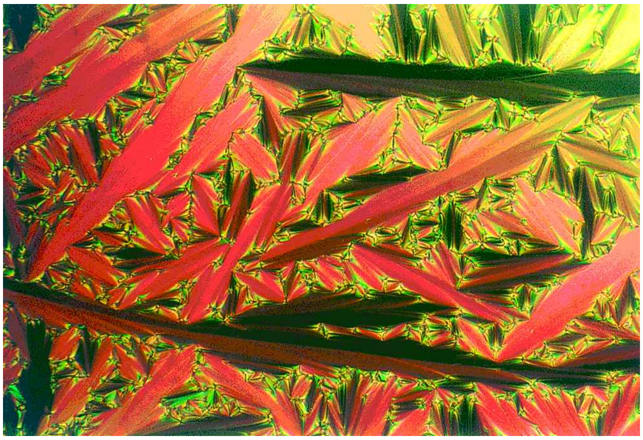


Figure 1. Fan-shaped texture of the $B_6$ phase of the pentyloxy homologue $n=5$ (148°C).

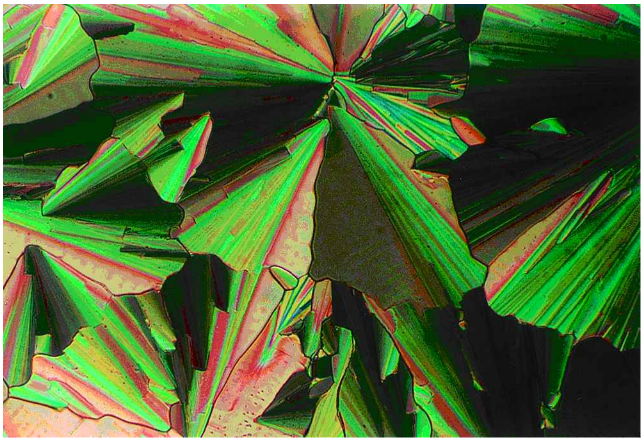
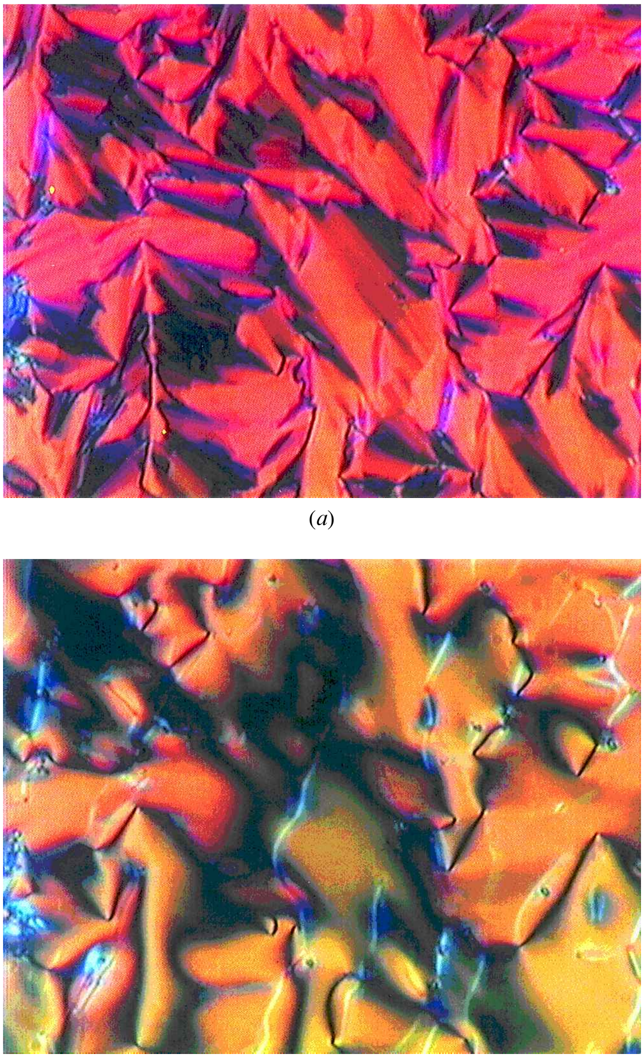


Figure 2. Mosaic texture of the $B_1$ phase of the nonyloxy homologue $n=9$ (122°C).

texture of the $B_1$ phase obtained by shearing the sample, figure 3 (*a*), is heated into the $B_6$ phase. In this case, the $B_6$ phase adopts a strong fluctuating schlieren texture, figure 3 (*b*), which rapidly transforms into a non-specific texture.

It is remarkable that the $B_1$–$B_6$ transition enthalpy is extremely low ($0.1\,\mathrm{kJ\,mol^{-1}}$). The $B_1$–I transition temperatures decrease on increasing the length of the terminal alkyl chains. The mesophase of the long chain homologues ($n=11$, 12) is monotropic and, unfortunately, crystallizes immediately after formation. Therefore, we investigated an equimolar mixture of these homologues. In this case, the mesophase remains monotropic but the melting point could be depressed so that microscopic observations and electro-optic studies were possible for a limited time. The mesophase of the two homologues under discussion exhibits a non-specific 'grainy' texture on cooling the isotropic liquid. On applying a sufficiently high electric field, the grainy texture is switched into a fan-shaped texture with irregular stripes parallel to the smectic layers. The field-induced texture change points to the $B_2$ phase. Since the monotropic $B_2$ mesophase has only a limited lifetime, neither quantitative electro-optical measurements nor X-ray investigations could be performed.



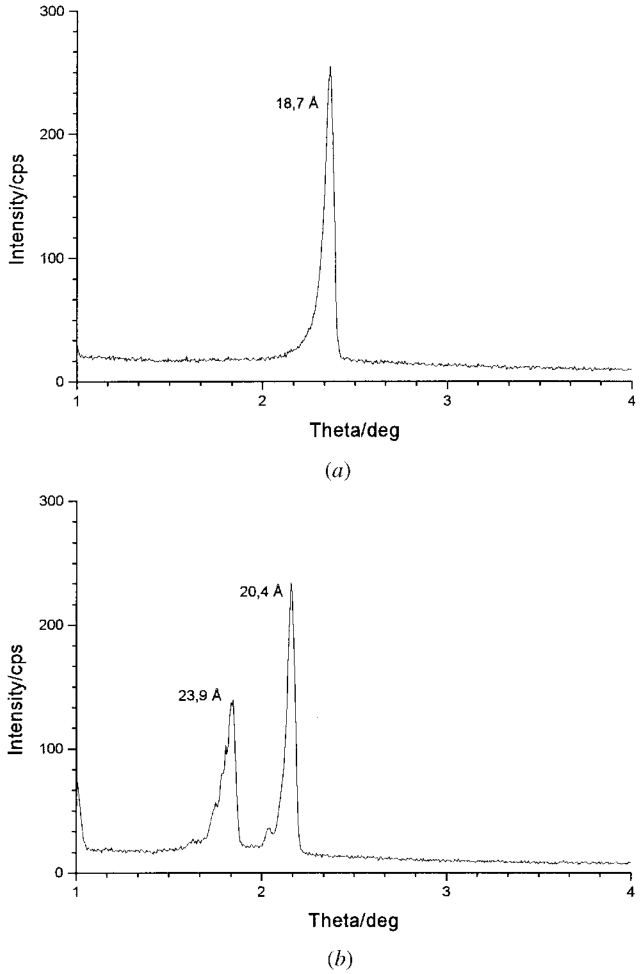
(*a*)

(*b*)

Figure 3. Textures of the hexyloxy homologue $n=6$: (*a*) fan-like texture of the $B_1$ phase obtained by shearing the mosaic texture (141°C); (*b*) schlieren-like texture of the $B_6$ phase obtained on fast heating of the fan-shaped texture of the $B_1$ phase (143°C).

### 4.2. *X-ray investigations*

The X-ray studies supported the changes in liquid crystalline phase diffraction behaviour on increasing the chain length as found by microscopic observations. The diffraction pattern for the low members of the series ($n=5$, 6) in the high temperature $B_6$ phase contain only one reflection in the small angle region, figure 4 (*a*). The corresponding period is smaller than half the molecular



(*a*)

(*b*)

Figure 4. Intensity scans of the X-ray patterns of non-oriented samples in the small angle region: (*a*) the $B_6$ phase of the compound $n = 5$ (145°C); (*b*) the $B_1$ phase of the compound $n = 7$ (120°C).

length. This suggests an intercalation of the molecules by the length of one leg and additionally, a tilt of the molecules in the layer. The molecular length was estimated as the end-to-end distance between the outer hydrogen atoms of the bent molecule. The bend angle was measured by $^{13}C$ and $^{1}H$ NMR spectroscopy to be about 120°, experimental detail will be given by Grande elsewhere [8]. With these structural data and the experimentally obtained layer spacing, a tilt of the molecules of approximately 25°–27° can be estimated. For the hexyloxy homologue ($n = 6$) an oriented sample could be obtained in the $B_6$ phase by slow cooling in a magnetic field. The pattern obtained for this sample (figure 5) supports the discussion above. The positions of the outer diffuse maxima in the pattern clearly point to a tilt angle (30° ± 3°), which can be measured without any assumptions being made. Furthermore, the small extent of the outer crescents suggest only limited fluctuations of the molecules around a preferred axis which seems to be a characteristic feature of an intercalated structure.

On cooling the sample into the $B_1$ phase the orientation is lost. In no case could an oriented sample of the $B_1$ phase of these compounds be obtained. The powder-like patterns of the $B_1$ phase display two reflections in the small angle region, which have been evaluated on the basis of a rectangular cell by analogy to the $B_1$ phase of other compounds, see figure 4 (*b*). The values are summarized in table 2. Again, a comparison of the lattice

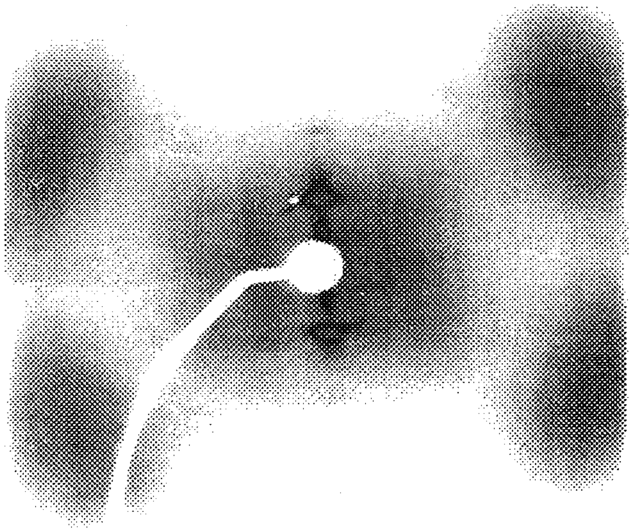


Figure 5. X-ray pattern of an oriented sample of compound $n = 6$ in the $B_6$ phase.

Table 2. Structural parameters of the compounds under investigation. $d_1$, $d_2$ are the periodicities measured in the small angle region; $L_{120}$ is the estimated molecular length; $a$ and $b$ are as shown in figure 6; $\delta_{\mathrm{ber}}$ and $\delta_{\mathrm{exp}}$ are the calculated and experimental molecular tilts, respectively.

| Compound $n$ | Phase type | $d_1$/nm | $d_2$/nm | $L_{120}$/nm | $a$/nm | $b$/nm | $\delta_{\mathrm{ber}}$/° | $\delta_{\mathrm{exp}}$/° |
|---|---|---|---|---|---|---|---|---|
| 5 | $B_6$ | — | 1.90 | 4.12 | — | — | 22 | — |
| 6 | $B_6$ | — | 1.96 | 4.36 | — | — | 25 | 30 |
| 6 | $B_1$ | 2.24 | 1.96 | 4.36 | 2.73 | 3.92 | 25 | — |
| 7 | $B_1$ | 2.40 | 2.07 | 4.56 | 2.82 | 4.14 | 26 | — |
| 8 | $B_1$ | 2.54 | 2.14 | 4.78 | 3.15 | 4.28 | 26 | — |
| 9 | $B_1$ | 2.77 | 2.22 | 5.0 | 3.55 | 4.44 | 27 | — |

parameter (*b*-axis) with the molecular structure supports the assumption of a tilt of the molecules with respect to the *c*-axis, that is a tilt out of the *ac*-plane. Therefore, the transition from the $B_6$ phase into the $B_1$ phase can be explained by the appearance of a period perpendicular to the layer normal caused by clusters of molecules aligned in a parallel fashion (figure 6). Also for the small value of the transition enthalpy.

### 4.3. *Density and high pressure DTA measurements*

For the first time density measurements on a B phase have been performed, and to do this, we used the $B_1$ phase of the octyloxy homologue $n = 8$. It can be seen in figure 7 that, at the transition from the isotropic liquid to the $B_1$ phase, there is a continuous increase of density within a temperature interval of 2–3 degrees. The density values appear relatively low in comparison with conventional calamitic compounds and laterally-substituted mesogens measured using the same equipment by ourselves or with that described in the literature.

For the same homologue, i.e. $n = 8$, the dependence of the phase transition temperatures on pressure have been determined using high pressure DTA. Figure 8 shows a typical DTA curve. In the first DTA run a peak appears at 373 K before the main transition at 385 K. When the heating of the sample is interrupted between these two peaks, and the sample cooled and reheated, the lower transition is no longer observed. Therefore, it is concluded that the lower peak is associated with a monotropic transition (denoted as $Cr_1'$–$Cr_1$). Increasing the pressure yields similar behaviour, but the lower temperature transition approach and coincide at ~80 MPa. At higher pressures two transitions below the clearing point are again observed, however they are enantiotropic. Thus, a new stable high pressure phase, denoted as $Cr_2$, has been detected (figure 9).

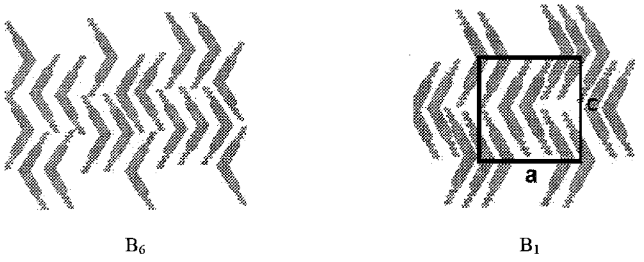


Figure 6. Sketch of the molecular packing in the $B_6$ and $B_1$ phases.

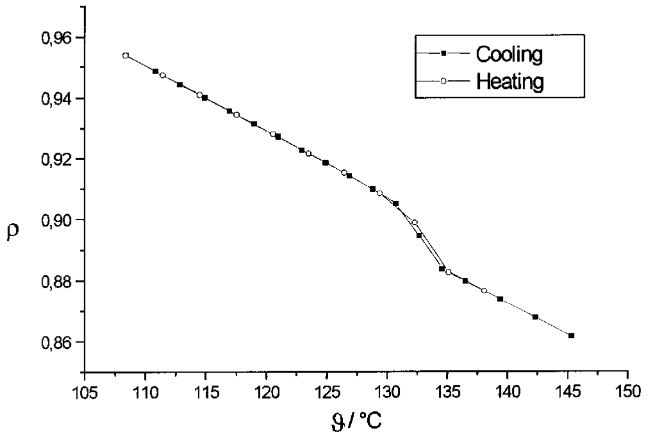


Figure 7. Temperature dependence of the density in the isotropic and $B_6$ phases of the octyloxy compound $n = 8$.

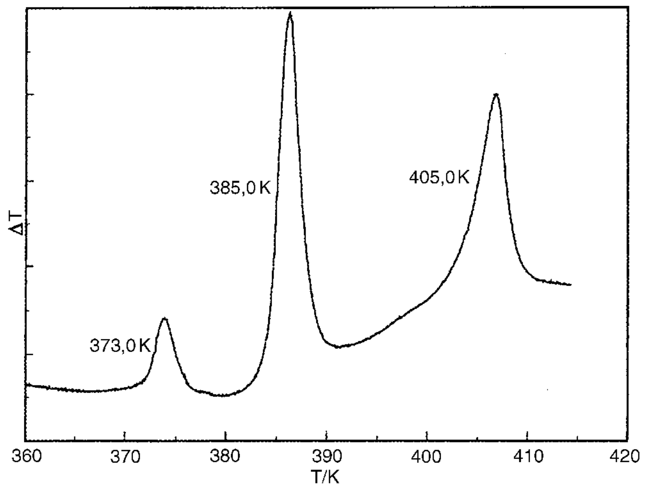


Figure 8. DTA curve of the octyloxy compound, $n = 8$, at atmospheric pressure. Note that the transition temperatures obtained by DSC are systematically higher because of the higher heating rate used.

The phase diagram for $n = 8$ is shown in figure 10. It seems as if the monotropic $Cr_1'$–$Cr_1$ transition in the low pressure region is the continuation of the enantiotropic $Cr_2$–$B_1$ transition of the high pressure region.

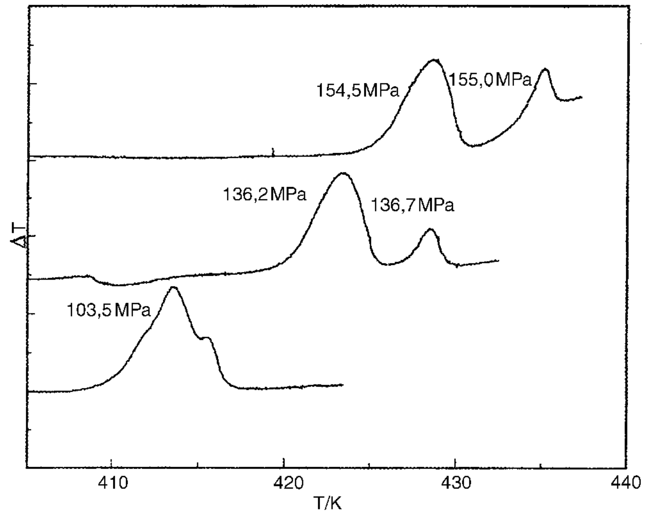


Figure 9. DTA curves of the octyloxy compound $n = 8$ at different pressures.

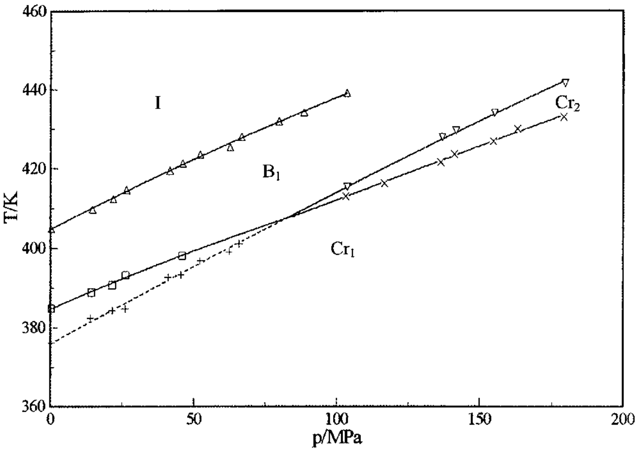


Figure 10. *P–T* phase diagram of the octyloxy compound $n = 8$.

The stability of the $Cr_2$ phase was proved through appropriate annealing experiments. Thus there exists a triple point (408 K, 84 MPa) between the three stable phases $Cr_1$, $Cr_2$, $B_1$. The phase transition lines have been fitted to polynomials of second order:

$$T/\mathrm{K} = a + bP/\mathrm{MPa} + c(P/\mathrm{MPa})^2. \qquad (1)$$

The values of *a*, *b* and *c* are given in table 3. Using the enthalpy changes determined by DSC and the slopes of the transition lines, volume changes can be calculated using the Clausius–Clapeyron equation, see table 4. The thermodynamic data can be compared with recent results reported for other liquid crystals [4–7, 9]. The initial slope of the clearing line is comparable with $\mathrm{d}T_{\mathrm{NI}}/\mathrm{d}P$ of rod-like nematic liquid crystals ($\sim 0.4\ \mathrm{K\,MPa^{-1}}$), but significantly larger than that for aryl-branched liquid crystals [4, 5]. The $\Delta H_m$ and $\Delta V_m$ values for the two transitions are not very different, pointing to the high degree of order in the $B_1$ phase. For conventional nematic liquid crystals, the thermodynamic changes at the clearing temperature are significantly smaller [9–11].

Table 3. Fitting parameters for the phase transition lines given by equation (1) and shown in figure 10.

| Phase transition | $a$/K | $b$/K MPa$^{-1}$ | $c/10^{-4}$ K MPa$^{-2}$ |
|---|---|---|---|
| $Cr_1 \rightarrow B_1$ | 385 | 0.303 | −2.76 |
| $Cr_1 \rightarrow Cr_2$ | 383 | 0.303 | −1.15 |
| $Cr_2 \rightarrow B_1$ | 367 | 0.537 | −6.80 |
| $B_1 \rightarrow Is$ | 404.8 | 0.368 | −3.64 |

Table 4. Thermodynamic parameters associated with the phase transitions for $n = 8$.

| Phase transition | $T$/K | $\Delta H_m$/kJ mol$^{-1}$ | $\Delta V_m$/cm$^3$ mol$^{-1}$ |
|---|---|---|---|
| $Cr_1 \rightarrow B_1$ | 385 | 25.6 | 20.1 |
| $B_1 \rightarrow Is$ | 405 | 16.3 | 14.8 |

## 5. Discussion

To date, several homologous series of bent-core mesogens (particularly five-ring compounds) have been reported in the literature. In some cases, only one liquid crystalline modification occurs irrespective of the chain length. In other cases, a characteristic change in the mesophase behaviour is observed within the homologous series. It must be remembered, however, that in general a limited number of homologues are available and those having very short or very long terminal chains are missing.

In the parent series of banana-shaped compounds described by Sekine *et al.* [12, 13] and in other series [14, 15], it was found that the short-chain homologues form the two-dimensional $B_1$ phase whereas for the long-chain members the switchable $B_2$ phase dominates. The homologous series presented here behaves in a quite similar fashion, but in addition the homologues having the shortest terminal chains ($n = 1$–$6$) form a $B_6$ phase and the pentyloxy and hexyloxy compounds exhibit $B_1$–$B_6$ dimorphism. Analogous phase behaviour was recently reported for a homologous series of seven-ring banana-shaped compounds [16]. Recently, the dielectric behaviour of the $B_6$ phase was investigated by Kresse *et al.* [17]. The density and high pressure DTA behaviour of the $B_1$ phase under investigation is similar to that of conventional smectic phases.

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