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H. N. Shreenivasa Murthy[a]; B. K. Sadashiva Corresponding author[a]
[a] Raman Research Institute, Sadashivanagar, India

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Banana-shaped mesogens: a new homologous series of compounds exhibiting the B_7 mesophase

H. N. SHREENIVASA MURTHY and B. K. SADASHIVA*

Raman Research Institute, C.V. Raman Avenue, Sadashivanagar,
Bangalore-560 080, India

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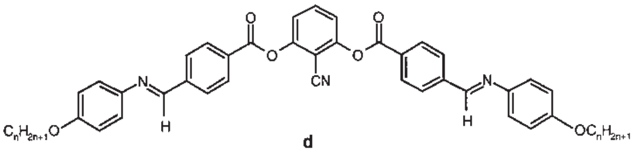
The synthesis and characterization of a new homologous series of compounds, the 2-cyano-1,3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates] derived from 2-cyanoresorcinol is reported. All the compounds are enantiotropic mesogens and exhibit the fascinating B_7 mesophase. The characterization of the mesophase was performed using polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction and electro-optical studies.

1. Introduction

The study of the physics and chemistry of liquid crystals composed of banana-shaped molecules has evoked great interest since the discovery of electro-optical switching [1] in such compounds. Over the last few years a number of such compounds have been synthesized and their mesomorphic properties studied [2–12]. Although at least eight different phases, assigned the general symbol B [1], have been reported, the B_3 and B_4 phases are now known to be crystalline phases. Amongst the six mesophases, the B_7 phase exhibits the most beautiful and complex optical textures. This mesophase was first observed in a series of Schiff's base compounds derived from 2-nitroresorcinol [13, 14]. One of the most common textures seen for this mesophase consists of helical filaments which may also be doubly or even triply wound. Such filamentary growth patterns have also been seen in a number of other banana-shaped mesogens which are not derivatives of 2-nitroresorcinol [15–19], and these phases are also assigned the symbol B_7. However, various other optical patterns seen for the 2-nitroresorcinol derivatives are not reported for these compounds; also the X-ray diffraction patterns are different. Moreover, the mesophases of many of these compounds show electro-optic switching behaviour, and both ferro- and antiferroelectric properties have been reported.

Recently we reported [20, 21] the synthesis and characterization of the mesophases of two homologous series of seven-ring esters derived from 2-cyanoresorcinol. The higher homologues of both the series of compounds exhibit the B_7 mesophase. In this paper, we report the synthesis and characterization of a new homologous series of five-ring Schiff's base esters derived from 2-cyanoresorcinol. All the compounds exhibit a single mesophase, whose characterization has been performed using polarizing optical microscopy (POM), X-ray diffraction (XRD) and electro-optical studies. The compounds investigated have the general molecular structure **d**.



d

2. Materials

The new symmetrical five-ring compounds, listed in the table, were synthesized following the pathway shown in figure 1. 2-Cyanoresorcinol, **a**, was prepared following a procedure we have described previously [21]. 4-Carboxybenzaldehyde, **b**, was obtained commercially and used without further purification. 4-*n*-Alkoxyanilines were prepared following a procedure already described [22]. A typical synthesis is described below.

2.1. *2-Cyano-1,3-phenylene bis(4-formylbenzoate)*, **c**

A mixture of 2-cyanoresorcinol **a** (1.0 g, 7.4 mmol), 4-carboxybenzaldehyde **b** (2.22 g, 14.8 mmol), and a catalytic amount of 4-(*N*, *N*-dimethylamino)pyridine in anhydrous dichloromethane (20 ml) was stirred for 10 min. To this mixture *N*,*N*′-dicyclohexylcarbodiimide

*Author for correspondence; e-mail: sadashiv@rri.res.in

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Table. Transition temperatures (°C) and associated enthalp changes (kJ mol^{-1}) for the series **d**.

Compound	n	Cr		B_7		I
1	6	●	177.0 *14.5*	●	190.0 *26.7*	●
2	7	●	172.0 *17.6*	●	192.5 *27.4*	●
3	8	●	*170.0* *14.5*	●	193.5 *26.9*	●
4	9	●	163.0 *16.6*	●	193.5 *28.2*	●
5	10	●	163.0 *35.1*	●	193.5 *27.9*	●
6	11	●	162.0 *42.8*	●	193.0 *30.8*	●
7	12	●	160.0 *33.6*	●	192.0 *33.6*	●
8	14	●	156.0 *43.8*	●	190.0 *33.9*	●
9	16	●	152.0 *52.5*	●	188.0 *34.7*	●
10	18	●	146.5 *58.8*	●	185.5 *35.3*	●

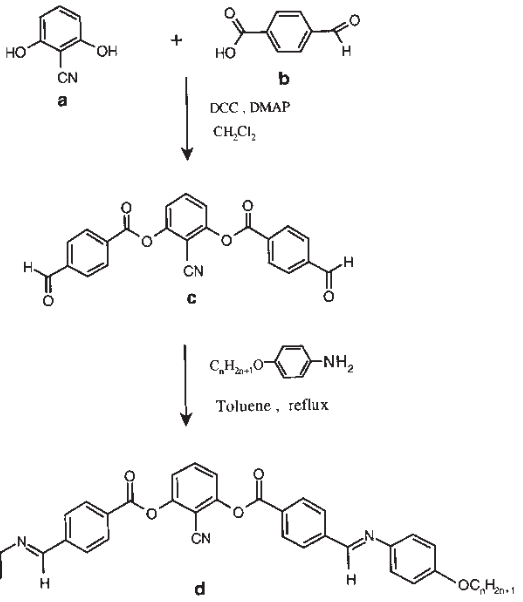

Figure 1. Synthetic pathway used to obtain the banana-shaped mesogens.

(3.35 g, 16.3 mmol) was added and stirring continued at room temperature overnight. The precipitated *N*,*N*′-dicyclohexylurea was filtered off and washed with dichloromethane (10 ml). The combined organic solution was washed with ice-cold aqueous 5% sodium hydroxide (2 × 30 ml), 5% aqueous acetic acid (2 × 30 ml) and water (3 × 40 ml), then dried over anhydrous sodium sulphate. The required compound was isolated by columning the residue obtained after removing the solvent on silica gel using a mixture of 2% ethylacetate in chloroform as eluent. It was further purified by crystallization from a mixture of chloroform and acetonitrile; yield 2.0 g (68%), m.p. >265°C. IR (nujol) ν_{max}: 2924, 2854, 2232, 1751, 1705 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.16 (s, 2H, Ar–CHO), 8.43–8.40 (d, $^3J = 8.2$ Hz, 4H, Ar–H), 8.07–8.05 (d, $^3J = 8.3$ Hz, 4H, Ar–H), 7.78–7.74 (t, $^3J = 8.4$ Hz, 1H, Ar–H), 7.50–7.48 (d, $^3J = 8.4$ Hz, 4H, Ar–H). Elemental analysis: $C_{23}H_{13}O_6N$ requires C 69.17, H 3.28, N 3.51; found C 68.92, H 3.38, N 3.41%.

2.2. *2-Cyano-1,3-phenylene bis[4-(4-n-dodecyloxyphenyliminomethyl)benzoate]*,**7**

A mixture of compound **c** (0.1 g, 0.25 mmol), *n*-dodecyloxyaniline (0.138 g, 0.5 mmol), and toluene (20 ml) was heated under reflux using a Dean–Stark apparatus for 4 h. The mixture was cooled to room temperature, and the precipitate formed was filtered off. The precipitate was passed through a column of neutral alumina using chloroform as an eluent. The product thus obtained was crystallized using a mixture of chloroform and acetonitrile followed by recrystallization from butan-2-one; yield 0.091 g (40%), m.p. 160.0°C. IR (KBr) ν_{max}: 2916, 2851, 2239, 1740 and 1736 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (s, 2H, –CH = N,), 8.35–8.33(d, $^3J = 8.3$ Hz, 4H, Ar–H), 8.07–8.05(d, $^3J = 8.3$ Hz, 4H, Ar–H), 7.77–7.73 (t, $^3J = 8.4$ Hz, 1H, Ar–H), 7.49–7.47(d, $^3J = 8.4$ Hz, 2H, Ar–H), 7.31–7.29(d, $^3J = 8.8$ Hz, 4H, Ar–H), 6.96–6.94(d, $^3J = 8.8$ Hz, 4H, Ar–H), 4.00–3.96 (t, $^3J = 6.6$ Hz, 4H, Ar–O–CH_2–), 1.84–1.77(quin, 4H, Ar–OCH_2–CH_2–), 1.36–1.27(m, 40H, $20 \times CH_2$), 0.90–0.86 (t, $^3J = 6.5$ Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 163, 158.6, 156, 153, 143.9, 141.8, 134.0, 130.9, 129.7, 128.7, 122.5, 120.2, 115.1, 111.6, 68.4, 31.9, 29.6, 29.4, 29.3, 26.0, 22.7, 14.0. Elemental analysis: $C_{59}H_{71}O_6N_3$ requires C 77.18, H 7.79, N 4.58; found C 76.78, H 7.67, N 4.31%.

3. Characterization

The phase transition temperatures and associated enthalpies were determined from thermograms obtained by differential scanning calorimetry (DSC) (Perkin-Elmer, Model Pyris 1D). The optical textures were observed using a polarizing microscope (Leitz Laborlux 12POL/Olympus BX50) equipped with a heating stage (Mettler FP 82 HT) and a controller. XRD experiments on non-oriented samples were carried out using a 4 kW rotating anode X-ray source (Rigaku Ultrax-18) and graphite monochromatic CuK_α radiation (1.54 Å). The diffraction patterns were collected on a two-dimensional detector (imaging plate system, Marresearch). The

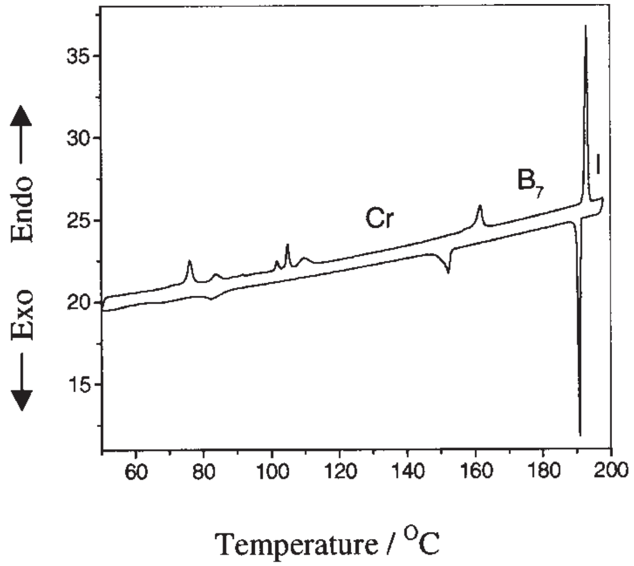

Figure 2. DSC thermogram of compound **7** (heating and cooling cycles, rate 5°C min^{-1}).

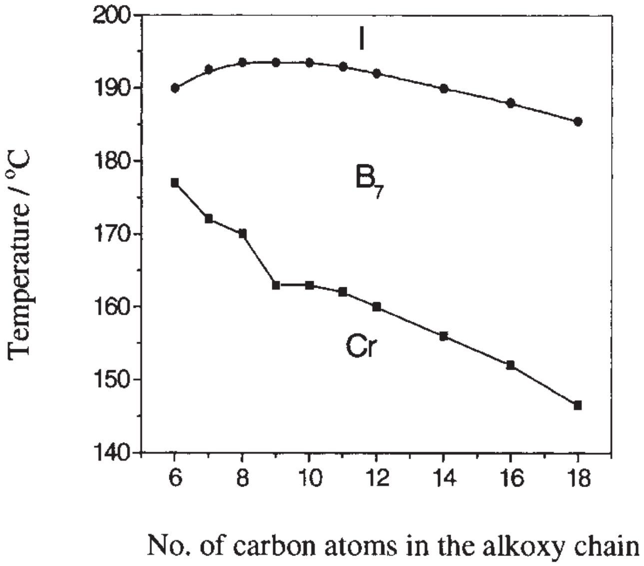

Figure 3. Plot of transition temperature as a function of the length of the *n*-alkoxy chain.

electro-optical experiments were performed using polyimide-coated ITO glass cells.

4. Results and discussion

In the table, the phase transition temperatures together with the associated transition enthalpies for the 2-cyano-1,3-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates], **d**, are listed. All the compounds show enantiotropic mesomorphic behaviour. Some interesting observations can be made from the data. Compounds **1–4** have a lower melting enthalpy than clearing enthalpy. However for homologues **5–10**, the melting enthalpies are higher. The DSC thermogram obtained for compound **7** is shown in figure 2. In addition to a gradual increase of the thermal range of the mesophase, there is a reduction in melting point on ascending the series. In the series, compound **10** has the largest temperature range for the mesophase, *c.* 39°C. A plot of transition temperature as a function of the number of carbon atoms in the alkoxy chain is shown in figure 3. The clearing temperatures fall on a smooth curve as observed previously for two other series of seven-ring esters [21].

As reported and observed previously [14, 20, 21], one of the most interesting features of the B_7 mesophase is its beautiful optical texture. For example, when a thin film of compound **9** sandwiched between two glass plates is cooled slowly from the isotropic phase, both single and doubly wound helices are seen under POM. A typical texture obtained for this compound is shown in figure 4. In addition, various other patterns can be seen to grow in other parts of the same sample. The textural variants include elongated worms, a myelinic texture and two-dimensional periodic patterns; these are shown in figure 5. All these textures are very typical for the B_7 mesophase.

In order to confirm the identity of this mesophase, XRD experiments were carried out on a non-oriented sample using an image plate arrangement. A sample of compound **10** in the isotropic phase was placed in a Lindemann capillary and cooled slowly to the mesophase. The temperature of the sample was controlled to within ±1°C. The X-ray angular intensity profile obtained for this compound at 160°C is shown in figure 6. The diffuse scattering in the wide angle region at 4.8 Å is indicative of the absence of in-plane order. In the small angle region, six reflections could be seen corresponding to $d_1=47.6$ Å, $d_2=27.8$ Å, $d_3=16.7$ Å, $d_4=12.5$ Å, $d_5=9.9$ Å and $d_6=7.6$ Å. Although these

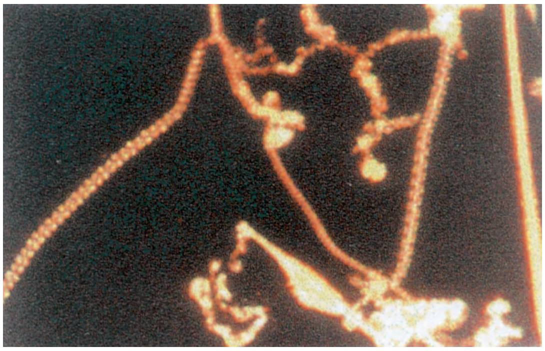

Figure 4. Helical pattern obtained for the B_7 mesophase of compound **9**.

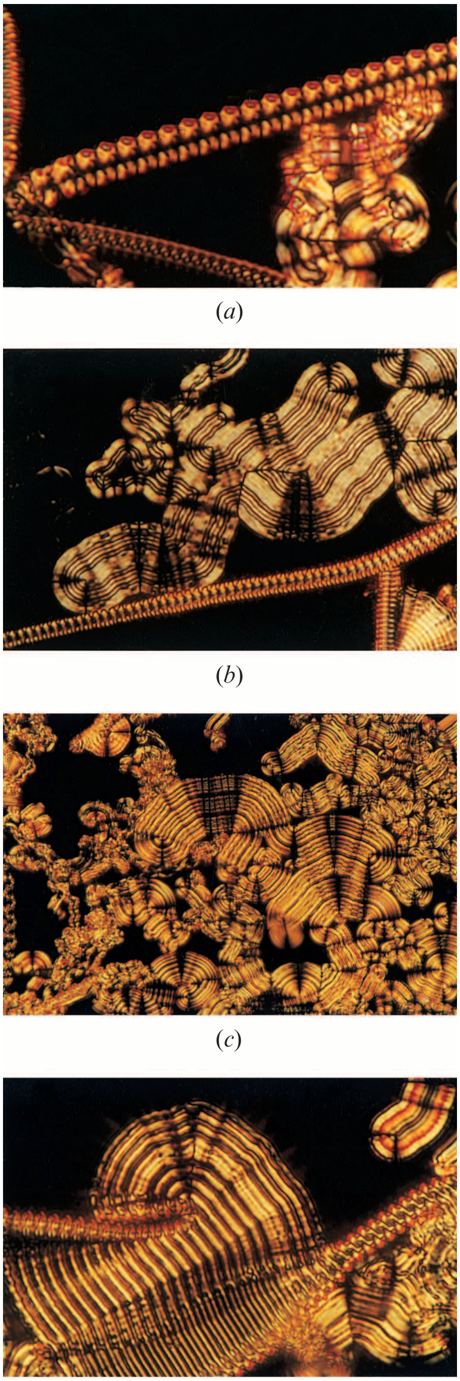

Figure 5. Various textural patterns obtained for the B_7

reflections cannot be indexed easily, a simple layered structure for the mesophase can be excluded; they perhaps instead point to a two- or three-dimensional structure.

We have also carried out electric field experiments on this mesophase. For example, a sample of compound **10** was taken into an ITO coated cell with a thickness of 9 μm. This was coated with polyimide and unidirectionally rubbed for homogeneous alignment of the sample. On applying a triangular wave electric field $V_{pp} = 44\,V\,\mu m^{-1}$, no evidence of switching could be seen.

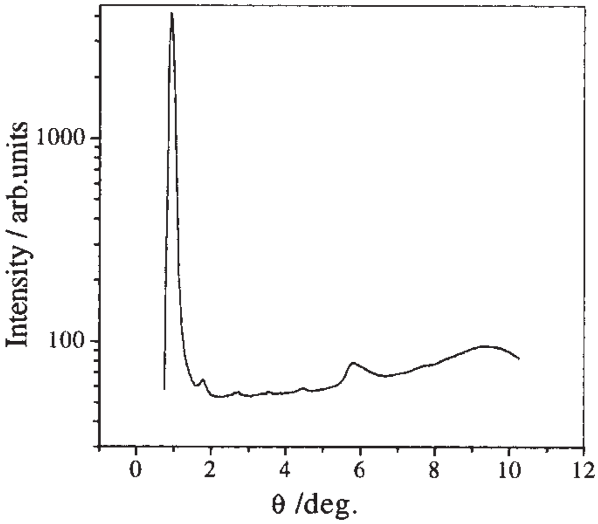

Figure 6. X-ray angular intensity profile obtained for the mesophase of compound **10** at 160°C.

In recent years, the mesophases of a number of different compounds have been assigned the symbol B_7 based on optical textures, and these have been discussed in some detail in our previous publication [21]. The various optical textures and X-ray data obtained for the mesophase of compounds presented here can be compared to those of the 2-nitroresorcinol derivatives which represent the standard materials for the B_7 mesophase. Moreover we observed no switching behaviour for the mesophase of compounds **1**–**10** like those of the standard materials. We can therefore safely conclude that the mesophase of these compounds is indeed B_7. As pointed out earlier, a strongly polar substituent such as a nitro or a cyano group in the 2-position of the central phenyl ring will certainly induce a B_7 mesophase.

Although the structure of the B_7 mesophase has not been established completely, Clark *et al.* have made considerable progress in this regard [23]. Using synchrotron XRD and freeze-fracture electron microscopy measurements, they have suggested a two- or three-dimensional structure for the B_7 phase in which the polarization is spontaneously splay modulated. Obviously such experiments are necessary on a variety of compounds exhibiting this phase to arrive conclusively at the structure of this fascinating mesophase.

5. Conclusions

A new homologous series of symmetrically substituted five-ring Schiff's base esters derived from 2-cyanoresorcinol and exhibiting the B_7 mesophase is reported. The optical textures, XRD measurements, and electro-optical studies are comparable to those observed for the standard 2-nitroresorcinol derivatives, which confirm that the mesophase is indeed B_7. A strongly polar substituent, such as a cyano group, in the angular position of these compounds is responsible for inducing a B_7 mesophase.

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