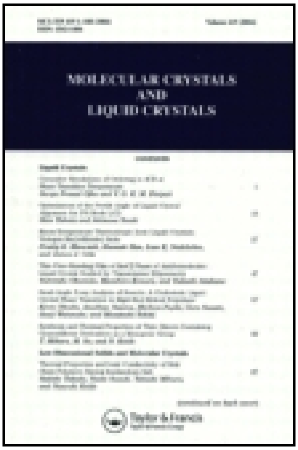

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Columnar Mesophase in a Novel Series of Banana-Shaped Compounds Consisting of Functional Nitro Groups

Veena Prasad [a] , D. S. Shankar Rao [a] & S. Krishna Prasad [a]

[a] Centre for Liquid Crystal Research, Jalahalli, Bangalore, 560 013, India

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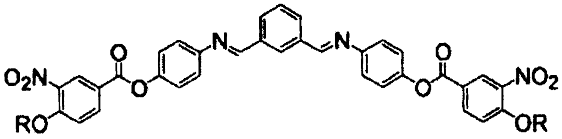
COLUMNAR MESOPHASE IN A NOVEL SERIES OF BANANA-SHAPED COMPOUNDS CONSISTING OF FUNCTIONAL NITRO GROUPS

Veena Prasad, D. S. Shankar Rao, and S. Krishna Prasad*
Centre for Liquid Crystal Research, Jalahalli,
Bangalore 560 013, India

A novel series of banana-shaped compounds with the following molecular structure has been synthesized and characterized.



$R = C_nH_{2n+1}$; n = 4, 6, 8, 10, 12, 16 and 18

All the compounds synthesized in this series are found to be liquid crystalline forming a B_1 phase, which has recently been designated as a columnar phase. the liquid crystalline behaviour of these compounds has been investigated by using the polarizing optical microscopy, differential scanning calorimetry and x-ray studies. the lower homologues of this series are monotropic whereas the higher ones are enantiotropic. we found that introduction of the nitro functional groups affects the mesomorphic properties in comparison to their respective unsubstituted compounds. the lower homologues of the unsubstituted ones exhibit a B_1 phase whereas the higher ones a B_2 phase.

Keywords: columnar phase; banana-shape; B_1 phase

INTRODUCTION

The molecular architecture is an important factor which governs the mesomorphic properties of the compounds in the field of thermotropic

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*Corresponding author. Tel: +91-80-8381119, Fax: +91-80-8382044, E-mail: clcr@vsnl.com

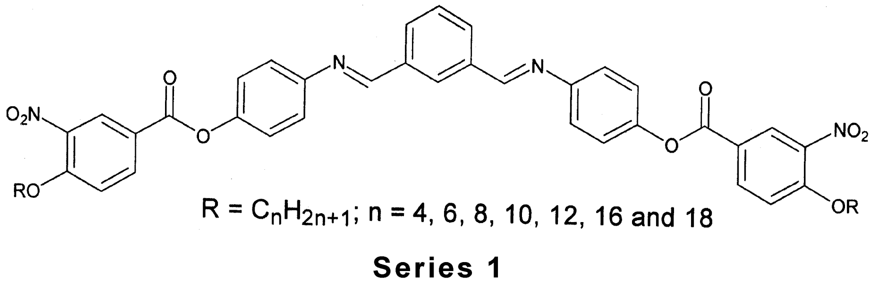


FIGURE 1 Molecular structure of the compounds synthesized.

liquid crystals. Although classical thermotropic liquid crystals are commonly composed of rod-like molecules, many other types of low molecular weight compounds with unconventional molecular structures have been shown to exhibit liquid crystalline properties [1]. Among these, the recent discovery [2] of liquid crystalline compounds with banana-shaped molecules are very interesting and have attracted a lot of attention [3–12]. In the literature, we find reports on the observation of a variety of mesophases with interesting physical properties in such banana shaped compounds. Till now at least seven phases have been described and designated by the code letters B_1–B_7 [4]. Among these some of the mesophases have been found to be electro-optically switchable. One of these banana phases viz., B_1 having a two dimensional order, has recently been designated as a columnar mesophase [13]. It may be mentioned that, the observation of columnar phase in “banana-shaped” compounds was first reported by Strzelecka et al. in 1988 [14,15].

It is a well-known fact in the chemistry of liquid crystals that even a small change in the molecular structure can lead to a drastic change in the mesomorphic properties. Thus, to investigate the relationship between the molecular structure and mesomorphic properties in banana-shaped molecules, we synthesised several such compounds and some of the results have already been reported [16–19]. As a continuation of our study on the bent-shaped molecules, we are reporting here, the synthesis and mesomorphic properties of a novel series of compounds, the molecular structure of which is shown in Figure 1. Here, we have introduced a bulky nitro functional group on the terminal aromatic rings on either sides of the molecule. Interestingly, all the compounds in this series are found to be liquid crystalline forming only one type of mesophase, i.e., the B_1 phase throughout the series, which has recently been designated as a columnar mesophase [13].

EXPERIMENTAL

General

Chemicals and solvents (AR quality) were obtained locally and used as such without further purification. All the intermediate compounds and final products were purified, either by column chromatography on silica gel or repeated recrystallisations using suitable solvents, as per the requirement. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). The chemical structures of all the intermediates and final compounds were confirmed by spectral data. ^{1}H NMR spectra were recorded in $CDCl_3$ on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer, using Me_4Si as an internal standard. Mass spectra were recorded on a JEOL JMS-600H spectrometer. The transition temperatures were determined using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarising microscope. The enthalpies of transitions were determined from thermograms recorded on a differential scanning calorimeter (DSC 7 Perkin-Elmer). The heating and cooling rate was 10°/min.

Synthesis

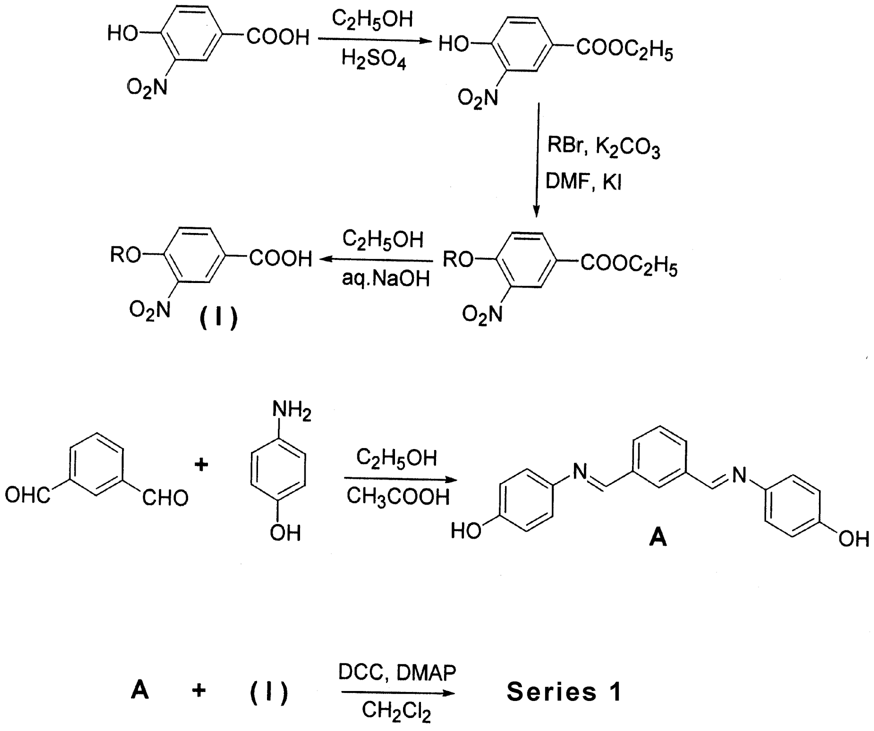
All these new banana shaped compounds were synthesised following the routes shown in Scheme 1. Thus, 4-alkyloxy-3-nitro benzoic acids (I) were prepared starting from 4-hydroxy-3-nitro benzoic acid. The intermediate **A** was obtained by a known method [20]. The synthesis of final compounds were achieved by the esterification of **A** with the substituted acids I. All the intermediate and final compounds were well characterised using the spectral data. The analytical data obtained for one of the representative compounds of this series are given below.

Compound with n = 10

IR (KBr pellet) ν_{max}cm^{-1}: 2925, 2851, 1731, 1615, 1529, 1503, 1468, 1352, 1273, 1234, 1190, 1158, 1102, 1088, 917, 869, 753; ^{1}H NMR δ: 8.67 (s, 2H, -CH =N-), 6.7–8.6 (m, 18H, ArH), 4.21 (t, $\mathbf{J}$ = 8.0Hz, 4H, $-OCH_2-$), 1.27–1.89 (m, 32H, $-CH_2-$), 0.87 (m, 6H, $-CH_3$); Mass (FAB) m/z 928 $(M+2)^+$(calcd. for $C_{54}H_{62}O_{10}N_4$).

RESULTS AND DISCUSSION

We have synthesised seven new compounds in series 1, with n = 4, 6, 8, 10, 12, 16 and 18. All the compounds synthesised are found to be



SCHEME 1

liquid crystalline. The transition temperatures of the different transitions and the associated enthalpies for these compounds are given in the Table 1.

Interestingly, throughout series 1, starting from the compound $n=4$ to $n=18$, we observed only one type of mesophase B_1 which has recently been designated as a columnar phase [13]. This phase is monotropic for lower homologues with $n=4$ and 6 and it became enatiotropic in nature for the compounds with $n=8$ onwards. Under the polarizing optical microscope, we observed two different textural variants for the B_1 phase. The lower homologues exhibit a dendritic pattern and the higher ones show a focal-conic texture without having sharp edges. The photomicrograph of these two textural variants are shown in Figures 2 (a) and 2 (b), taken for the compounds with $n=6$ at 138.5°C and $n=12$ at 154°C respectively. However, we have carried out X-ray studies on both lower (with $n=8$) and higher (with $n=16$) homologues, which will be discussed later. We found from these studies, that both the lower and higher

TABLE 1 Transition Temperatures (°C) and the Enthalpies of Transitions (kJ mol^{-1}) in *Italics*, for the Compounds of Series 1

n	Cr		B_1		I
4	●	156.0	●	(118.5)	●
		47.48		*9.88*	
6	●	153.5	●	(140.5)	●
		52.50		*13.11*	
8	●	135.0	●	145.0	●
		43.6		*12.18*	
10*	●	113.0	●	154.0	●
		25.74		*15.86*	
12*	●	111.7	●	158.0	●
		28.44		*18.62*	
16	●	110.5	●	160.5	●
		68.48		*17.06*	
18	●	103.5	●	158.7	●
		21.72		*15.1*	

*Cr-Cr transition was observed.

homologues exhibit only one type of mesophase, i.e., B_1. The compound with n = 8 has two different melting points depending on whether the solid is solvent-crystallised or melt-crystallised. Some of the homologues even show a Cr-Cr transition before melting. One can see from Table 1 that, the mesophase exists over a large temperature range (nearly 50°C) for the higher homologues with n = 10 onwards. Although, the molecules in these compounds have two imino linkages, they have been found to be thermally very stable, as confirmed by the repeated DSC scans that is shown in Figure 3. All the compounds in this series have fairly low transition temperatures thus making them suitable candidates for the physical studies.

We made a comparison of the mesomorphic properties of the present series with similar compounds [20] without the nitro substitution. We found that, when there is no nitro substitution [20] the compounds exhibit B_1 and B_2 banana phases. However, when we substitute a nitro group on the terminal phenyl rings (series 1), we observe only one type of mesophase i.e., B_1, throughout the series. According to an observation in a detailed studies on the B_1 phase [13], as the chain length is increased the "ribbon structure" of this B_1 phase becomes unstable due to the highly unfavourable chain-core interaction in the border line regions. Hence, either the phase becomes monotropic or it completely disappears for higher homologues. However, in the present series 1, we have synthesized compounds

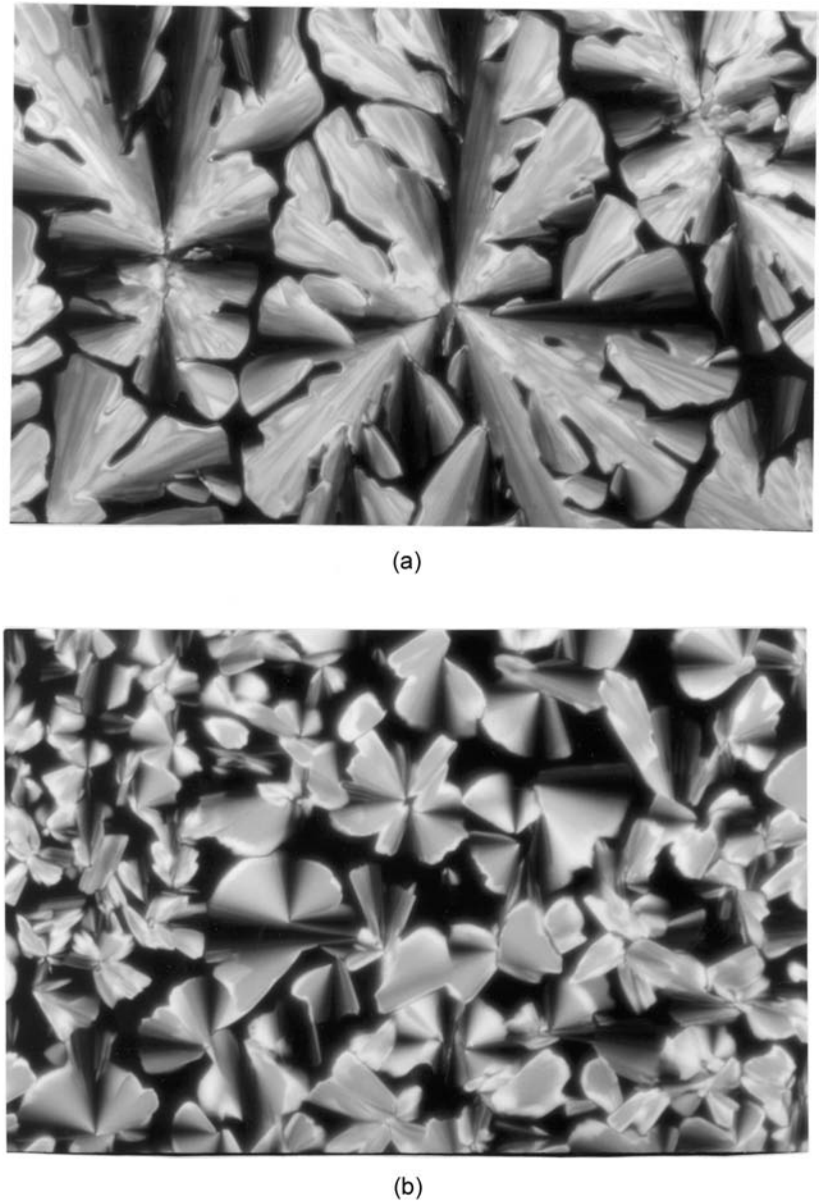


FIGURE 2 Photomicrographs showing (a) the dendritic pattern of the B_1 phase exhibited by the compound with $n = 6$ at 138.5°C and (b) the focal conic texture of the B_1 phase without having sharp edges exhibited by the compound with $n = 12$ at 154°C. (See Color Plates VI & VII).

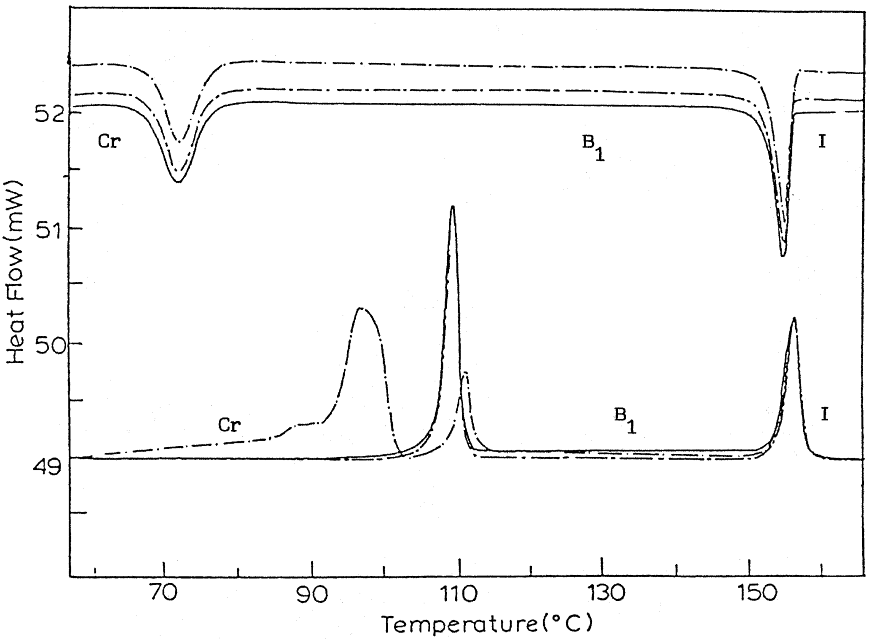


FIGURE 3 DSC thermogram of the compound with n = 12. Heating and cooling scans were done at a rate of 5°C/min. Note that the B_1–I and I–B_1 peaks in all the three consecutive heating and cooling runs respectively, are perfectly overlapping, thus proving the thermal stability of this compound.

starting from n = 4 to n = 18. Surprisingly, even on increasing the chain length to n = 18, the B_1 phase was quite stable, with a mesophase range of 55°C. In the case of corresponding unsubstituted compounds [20], the B_1 phase was stabilized up to n = 9, and n = 10 onwards the B_2 phase was observed. Therefore, we strongly believe that the polar nature of the nitro functional group has a bearing on the stabilization of the B_1 phase throughout series 1.

We have also prepared a contact mixture of the n = 12 compound of the present series with P-10-PIMB, a well-characterised banana compound [3], exhibiting B_2 and B_3 mesophases. Observations under the microscope, shows the growth of double-helical ribbons in the contact region (see Fig. 4), which is normally a characteristic feature of the B_7 banana phase. However, very recently, there is a report on the observation of this type of helical domains even in the B_2 banana mesophase [21].

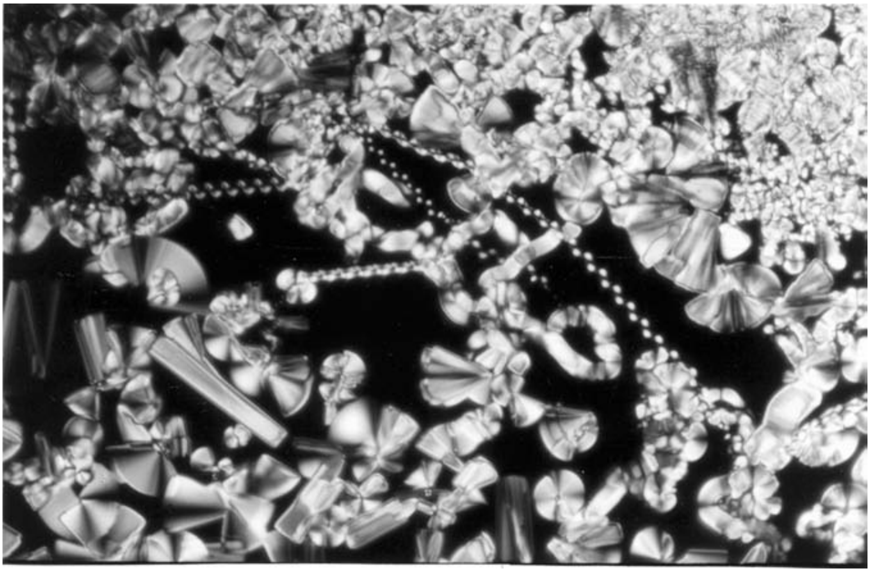


FIGURE 4 Photomicrograph of the texture observed at 146.5°C for the contact mixture prepared using the compound with n = 12 and P-10-PIMB. The upper region is B_2 phase of P-10-PIMB and the lower region is the B_1 phase of the compound with n = 12. Notice the appearance of the double–spiral helical domains in the contact region which is generally observed for the B_7 banana mesophase. (See Color Plate VIII).

To confirm the existence of the B_1 phase, X-ray diffraction measurements were carried out on two homologues of the series 1. Experiments were done using an Image Plate Detector (MAC Science, Japan) system with the sample contained in a Lindemann capillary tube. The diffraction patterns and the corresponding intensity vs. diffraction angle profiles obtained for the compound with n = 16 (at 155°C) and n = 8 (at 140°C) are shown in Figures 5(a) and 5(b) respectively. In the low angle region we observe a few peaks, one strong and others relatively weak and in the wide-angle region a diffuse peak characteristic of the intermolecular separation of about 0.45 nm is seen. The low angle reflections can be indexed as (20), (11), (60) and (62) for the compound with n = 16, and (20), (11) and (60) for the compound with n = 8 sample. These indices conform to a two-dimensional rectangular lattice, a feature typically seen for the B_1 phase of banana shaped molecules. It may be remarked that Tschierske et al. [13] have recently attributed such a feature to the existence of a columnar structure.

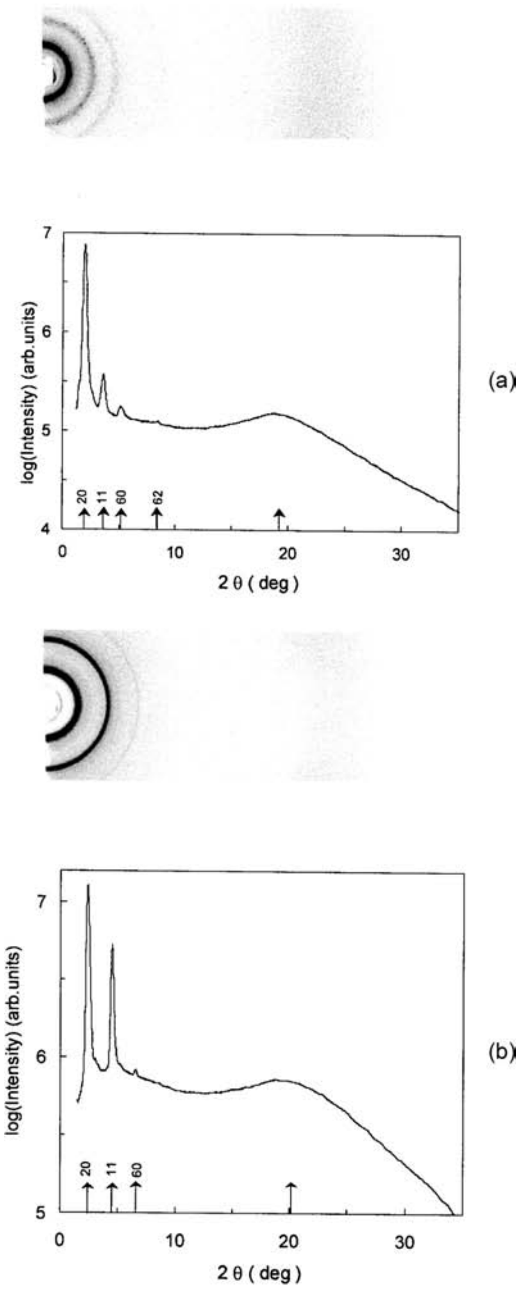


FIGURE 5 One dimensional cut of the X–ray diffraction pattern showing the χ-averaged intensity plotted as a function of 2θ angle, obtained in the B_1 phase of the (a) compound with $n = 16$ at 155°C and (b) compound with $n = 8$ at 140°C.

CONCLUSIONS

In summary, we have reported a novel series of banana shaped compounds consisting of nitro functional groups. All the compounds synthesized are found to be liquid crystalline. Interestingly, throughout this series we observed only one type of mesophase viz. B_1 which has recently been designated as a columnar phase. Introduction of nitro groups at the lateral position of terminal phenyl rings does affect the mesomorphic properties in comparison to their respective unsubstituted compounds.

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