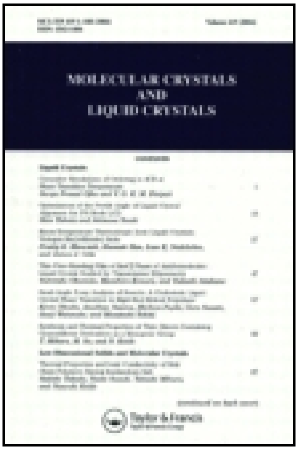

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bent - Shaped Achiral Azo Compounds Exhibiting Banana Mesophases

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Version of record first published: 24 Sep 2006

To cite this article: Veena Prasad (2001): Bent - Shaped Achiral Azo Compounds Exhibiting Banana Mesophases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 363:1, 167-179

To link to this article: http://dx.doi.org/10.1080/10587250108025267

Mol. Cryst. Liq. Cryst., Vol. 363, pp. 167-179
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Bent – Shaped Achiral Azo Compounds Exhibiting Banana Mesophases

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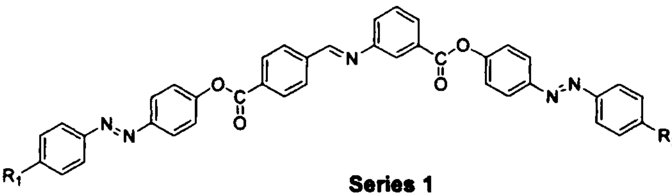
(Received November 25, 2000; In final form December 19, 2000)

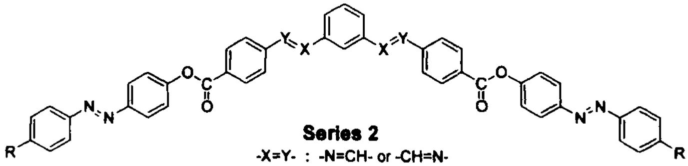
Two novel series of bent-shaped achiral azo compounds with the following molecular structures have been synthesised and characterised.



Series 1

$R_1 = R_2 = C_8H_{17}, C_{10}H_{21}, OC_8H_{17}, OC_{10}H_{21}$

$R_1 = C_{10}H_{21}; R_2 = OC_8H_{17}, OC_{10}H_{21}$



Series 2

$-X=Y-$: $-N=CH-$ or $-CH=N-$

$R = C_8H_{17}, C_{10}H_{21}$ and $OC_{10}H_{21}$

The object of the present work was to study the effect of molecular structure on the mesomorphic properties of bent-shaped molecules. The compounds of series 1 exhibit different types of banana mesophases. These compounds with unsymmetrical molecules exhibit mainly B_1 phase, in addition

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to other higher ordered smectic mesophases (X_2 and X_3, the optical textures of which are reminiscent of banana phases). The compounds of series 2, with symmetrical molecules exhibit only one type of mesophase i.e., B_7 when (-X=Y-) = (-N=CH-) and X4 (unidentified mesophase with textural features of a banana phase) when (-X=Y-) = (-CH=N-). From the studies carried out here, it has been found that, even minor modifications such as, the reversal of linkage groups in the molecules can lead to a considerable change in the mesomorphic properties.

Keywords: bent-shape; azo compounds; B_1 phase; B_7 phase

INTRODUCTION

Ferro/antiferroelectric liquid crystalline compounds composed of bent – shaped achiral molecules are very interesting subjects which have recently attracted much attention. Since the discovery[1] of such materials showing new type of mesophases, various structural variants of the parent compound i.e., 1,3-phenylene bis[4-(4-n-alkylphenyliminomethyl)benzoates] have been reported[2–12]. As a consequence of the sterically induced packing of the bent – molecules, smectic layers with C_{2v}, C_2 and possibly also C_{1n} or C_1 symmetry could occur[13], giving rise to ferro-, ferri-, or antiferroelectric properties. As the structure of the mesophases exhibited by these bent or banana – shaped compounds is not completely understood, a tentative classification scheme has been proposed in which the phases are labeled with the code letters B_1....B_7 according to the sequence of their discovery[4]. Among the physical properties of the "banana mesophases", the electrooptical behaviour is of particular interest which also gives some hints about the structure of these mesophases. Among the seven phases, the electrooptical switching has been observed only in B_2, B_5 and B_7 phases.

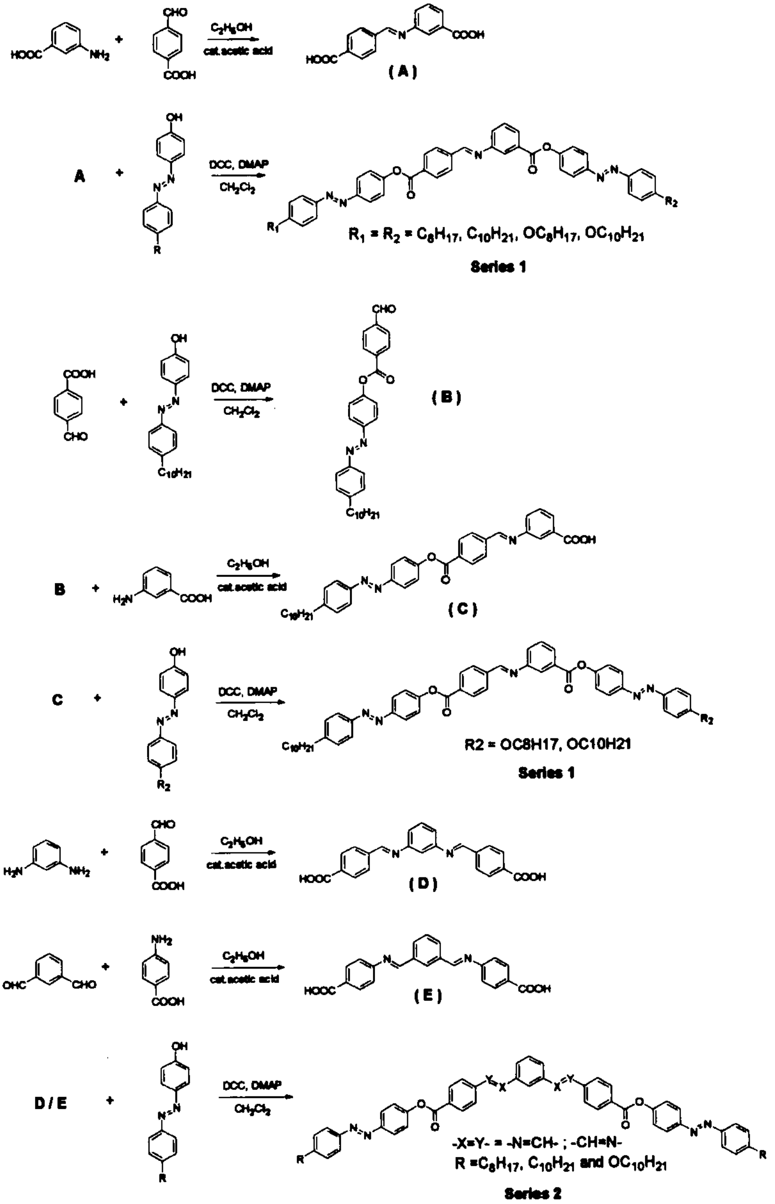
When we examined the literature of bent-shaped molecules we observed the following two important factors: (i) from the view point of the chemical structures, the molecules with five, six and seven aromatic rings have been found to exhibit banana phases; (ii) however, in all these compounds, one notices that, either the same type of linkages (-COO-) or two different types of linkages (-COO- and -CH=N- or -COS- or -C=C-) have been utilised. No compounds consisting of an azo linkage have been reported to form banana phases. The observation of banana phases in azo compounds assumes significance from the fact that, the introduction of -N=N- linkage brings in a new dimension to this field, namely, photochromism. Having this idea in mind, we aimed at the synthesis of bent – shaped molecules with an azo linkage in it. Towards this end, the first molecule which we synthesised was 1,3-phenylene bis[4-(4′-decyloxyphenylazo)benzoate][14]. But to our surprise, we found it to be non-mesomorphic. Therefore, we thought of introducing an imino linkage in this molecule, as it has been found that the -CH=N- linkage is more conducive to mesomorphism. As expected, we succeeded in obtaining banana phases in novel bent-shaped azo compounds (Series $ shown in figure 1) and we have made a report of this observation in our previous communication[15].

As a continuation of our investigation on bent-shaped azo compounds forming banana phases, we have further synthesised two more series of compounds. The molecular structures of these compounds are shown in figure 1. We have already reported[15] the mesomorphic properties of the compounds of series $. In this paper we are reporting the synthesis and liquid crystalline properties of the compounds of series 1 and 2. As we can see from figure 1, the compounds of series $ and series 1 are composed of unsymmetrical molecules, whereas the compounds of series 2 are composed of symmetrical molecules. All the compounds synthesised in these series are found to be liquid crystalline, forming textures reminiscent of banana phases.

EXPERIMENTAL

Synthesis

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. The synthesis of compounds of series $ has been described previously[15]. The compounds of series 1 and 2 were synthesised following the routes shown in Scheme 1. Thus, the first four compounds of series 1 are obtained by esterifying the intermediate **A** with the respective 4-alkyl / alkyloxy – 4′ – hydroxyazobenzenes. The last two compounds of this series are obtained by the esterification of the intermediate **C** with 4- alkyloxy – 4′ – hydroxyazobenzenes. The compounds of series 2 are obtained by the esterification of intermediates **D** and **E** with the respective 4-alkyl / alkyloxy – 4′ – hydroxyazobenzenes. All the required 4-alkyl / alkyloxy – 4′ – hydroxyazobenzenes were prepared following the procedure already reported[16]. All the intermediates and final compounds were purified either by column chromatography or recrystallisation, as per the requirement, using the appropriate solvents. The purities as well as the chemical structures of all the compounds synthesised were confirmed by spectral data. IR spectra were recorded on a Perkin-Elmer spectrum 1000 spectrometer. ^1H 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. The elemental analysis were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. The transition temperatures were determined using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarising microscope. The enthalpies of transitions were determined from thermograms obtained with a differential scanning calorimeter (DSC Perkin-Elmer). The heating and cooling rates were 10°C/min.



SCHEME 1

The analytical data obtained for all the intermediates and the final compounds were satisfactory. The intermediates **B** and **C** are also found to be liquid crystalline, which will be communicated elsewhere[17]. The analytical data obtained for the representative compounds of both the series are given below.

$R_1 = R_2 = -C_{10}H_{21}$ (Series 1)

IR ν_{max} cm^{-1} (nujol mull): 2920, 2852, 1744, 1594, 1462, 1377, 1286, 1233, 1097, 1081, 920, 884, 864; ^{1}H NMR δ_H: 0.88 (t, J = 6.6 Hz, 6H, $-CH_3$), 1.20–1.80 (m, 32H, $-CH_2-$), 2.69 (t, J = 7.4 Hz, 4H, Ar-CH_2-), 7.33 (d, J = 8.4 Hz, 4H, ArH), 7.42 (d, J = 8.4 Hz, 4H, ArH), 7.58 (m, 2H, ArH), 7.83 (d, J = 8.4 Hz, 4H, ArH), 8.03 (d, J = 8.4 Hz, 4H, ArH), 8.17 (m, 4H, ArH), 8.35 (d, J=8.4 Hz, 2H, ArH), 8.65 (s, 1H, -CH=N-). Elemental Analysis: Found, C, 78.11 %, H, 7.45 %, N, 7.74 %.

($C_{59}H_{67}O_4N_5$ requires, C, 77.89 %, H, 7.37 %, N, 7.70 %).

$R_1 = R_2 = -OC_{10}H_{21}$ (Series 1)

IR ν_{max} cm^{-1} (nujol mull): 2922, 2854, 1744, 1603, 1462, 1377, 1285, 1252, 1150, 1027, 920, 884, 842; ^{1}H NMR δ_H: 0.89 (m, 6H, $-CH_3$), 1.25–1.84 (m, 32H, $-CH_2-$), 4.05 (t, J = 6.6 Hz, 4H, Ar-OCH_2-), 7.03 (d, J = 8.8 Hz, 4H, ArH), 7.39 (d, J = 8.8 Hz, 4H, ArH), 7.57 (m, 2H, ArH), 7.92 (d, J = 9.0 Hz, 4H, ArH), 7.98 (d, J = 9.0 Hz, 4H, ArH), 8.12 (m, 4H, ArH), 8.35 (d, J = 8.4 Hz, 2H, ArH), 8.65 (s, 1H, -CH = N-). Elemental Analysis: Found, C, 75.28 %, H, 7.21 %, N, 7.41 %.

($C_{59}H_{67}O_6N_5$ requires, C, 75.24 %, H, 7.12 %, N, 7.44 %).

$R_1 = -C_{10}H_{21}$ and $R_2 = -OC_{10}H_{21}$ (Series 1)

IR ν_{max} cm^{-1} (nujol mull): 2928, 2854, 1744, 1604, 1462, 1377, 1286, 1254, 1151, 1076, 1025, 920, 884, 843; ^{1}H NMR δ_H: 0.88 (m, 6H, $-CH_3$), 1.28–1.82 (m, 32H, $-CH_2-$), 2.69 (t, J = 7.2 Hz, 2H, Ar-CH_2-), 4.05 (t, J = 6.6 Hz, 2H, Ar-OCH_2-), 7.02 (d, 9.0 Hz, 2H, ArH), 7.29–7.42 (m, 8H, ArH), 7.54 (m, 2H, ArH), 7.81–8.12 (m, 10H, ArH), 8.33 (d, J = 8.4 Hz, 2H, ArH), 8.64 (s, 1H, -CH = N-).

Elemental Analysis: Found: C, 76.14 %, H, 7.16 %, N, 7.59 %.

($C_{59}H_{67}O_5N_5$ requires, C, 76.54 %, H, 7.24 %, N, 7.57 %)

$R = -C_{10}H_{21}$ and -X=Y- = -N=CH- (Series 2)

IR ν_{max} cm^{-1} (nujol mull): 2920, 2852, 1744, 1594, 1462, 1377, 1280, 1230, 1076, 914, 876, 852; ^{1}H NMR δ_H: 0.88 (m, 6H, $-CH_3$), 1.28–1.82 (m, 32H, $-CH_2-$), 2.69 (t, J = 8.0Hz, 4H, Ar-OCH_2-), 7.14–7.45 (m, 12H, ArH), 7.83 (d, J = 8.4Hz, 4H, ArH), 7.98 (d, J= 8.4 Hz, 4H, ArH), 8.07 (d, J = 8.4 Hz, 4H, ArH), 8.32(d, J = 8.4 Hz, 4H, ArH), 8.62 (s, 2H, -CH=N-).

Elemental Analysis: Found, C, 78.50 %, H, 7.20 %, N, 8.37 %.
($C_{66}H_{72}O_4N_6$ requires, C, 78.26 %, H, 7.12 %, N, 8.30 %).

RESULTS AND DISCUSSION

The transition temperatures and the associated enthalpies for the compounds of series 1 and 2 are given in the table I and II respectively. The mesomorphic properties of the compounds of series $ are discussed previously[15]. They mainly exhibit the B_1 phase. The lower homologues with n = 4 and 6, exhibit a high temperature phase (X_1) as well above the B_1 phase. They show focal conic texture for the X_1 phase. Since the X_1 phase appears above B_1 phase and it exhibits focal conic texture with the features of B_6 phase[2], we opined that the phase X_1 may be either B_6 or a new banana phase.

TABLE I Trasition temperatures (°C) and the enthalpies of trasitions (kJ mol^{-1}), in *italics* for the compounds of series 1

R_1	R_2	Cr^a	–	X_3		$X_2{}^b$		B_1		I
$-C_8H_{17}$	$-C_8H_{17}$	•	152.0	–		–		•	220.0	•
			43.76						*18.03*	
$-C_{10}H_{21}$	$-C_{10}H_{21}$	•	146.5			–		– •	216.0	•
			45.1						*17.12*	
$-OC_8H_{17}$	$-OC_8H_{17}$	•	200.5	–		•	(185.5)	•	229.5	•
			59.74						*19.6*	
$-OC_{10}H_{21}$	$-OC_{10}H_{21}$	•	189.0	–		•	206.0	•	232.5	•
			50.25						*17.02*	
$-C_{10}H_{21}$	$-OC_8H_{17}$	•	169.5	•	(152.0)	•	(167.0)	•	232.0	•
			54.98		*26.0*				*19.26*	
$-C_{10}H_{21}$	$-OC_{10}H_{21}$	•	172.5	•	(159.5)	•	187.0	•	230.0	•
			58.42		*29.6*				*21.23*	

a. Cr – Cr transitions are observed before melting for all the compounds.
b. This transition is seen only under the microscope and in DSC thermogram there is no peak corresponding to this transition.

Table I gives the transition temperatures for the compounds of series 1. Now let us discuss the mesomorphic properties of these homologues. The compounds with $R_1 = R_2 = C_8H_{17}$ and $C_{10}H_{21}$ show only the B_1 phase. The mesophase ranges for these two compounds are 68°C and 69.5°C respectively. The compounds with $R_1 = R_2 = OC_8H_{17}$ and $OC_{10}H_{21}$ show two mesophases. The high temperature mesophase is a B_1 phase and the optical texture observed for the low temperature phase (X_2) did not resemble any of the known banana phases. The compounds with $R_1 = C_{10}H_{21}$ and $R_2 = OC_8H_{17}$ and $OC_{10}H_{21}$ exhibit three different types of smectic phases. The mesophase sequence for these two compounds is I – B_1 – X_2 – X_3. While the X_3 phase is monotropic for both the compounds, the X_2 phase is monotropic for the compound with $R_2 = OC_8H_{17}$ and enantiotropic for the compound with $R_2 = OC_{10}H_{21}$.

TABLE II Transition temperatures (°C) and the enthalpies of transitions (kJ mol^{-1}) in *italics*, for the compounds of series 2

R	*-X=Y-*	*Cr*[a]		*X_4*		*B_7*		*I*
$-C_8H_{17}$	-N=CH-	•	171.5 *34.23*	–		•	271.0[b]	•
$-C_{10}H_{21}$	-N=CH-	•	166.5 *45.8*	–		•	271.5[b]	•
$-OC_{10}H_{21}$	-N=CH-	•	210.5 *42.38*	–		•	280.0[b]	•
$-C_8H_{17}$	-CH=N-	•	173.0 *35.32*	•	244.0 *14.04*	–		•
$-C_{10}H_{21}$	-CH=N-	•	168.5 *36.25*	•	245.0 *14.32*	–		•
$-OC_{10}H_{21}$	-CH=N-	•	180.0 *35.08*	•	226.0 *13.02*	–		•

a. Cr – Cr transitions are observed for all the compounds before melting.
b. Partial decomposition is there at this temperature.

The DSC thermogram for the compound with $R_1 = C_{10}H_{21}$ and $R_2 = OC_8H_{17}$, which exhibits all the three types of mesophases (B_1, X_2 and X_3) is shown in figure 2. In heating cycle (a), we see a strong peak at 169.5°C which corresponds to the melting of crystal to mesophase (B_1) as observed under the optical polarising microscope and the second peak at 232°C is for the transition of B_1 mesophase to isotropic liquid. In cooling cycle (b) we see three peaks. The first peak corresponds to I – B_1 and the second peak to X_2 – X_3 transitions. Note that there is no peak at 167°C corresponding to B_1 – X_2 transition. The last broad peak corresponds to X_3 – Cr transition. Now let us discuss the microscopic textural observations of this compound in connection with the cooling cycle of DSC themogram obtained. On cooling from the isotropic liquid it forms a texture shown

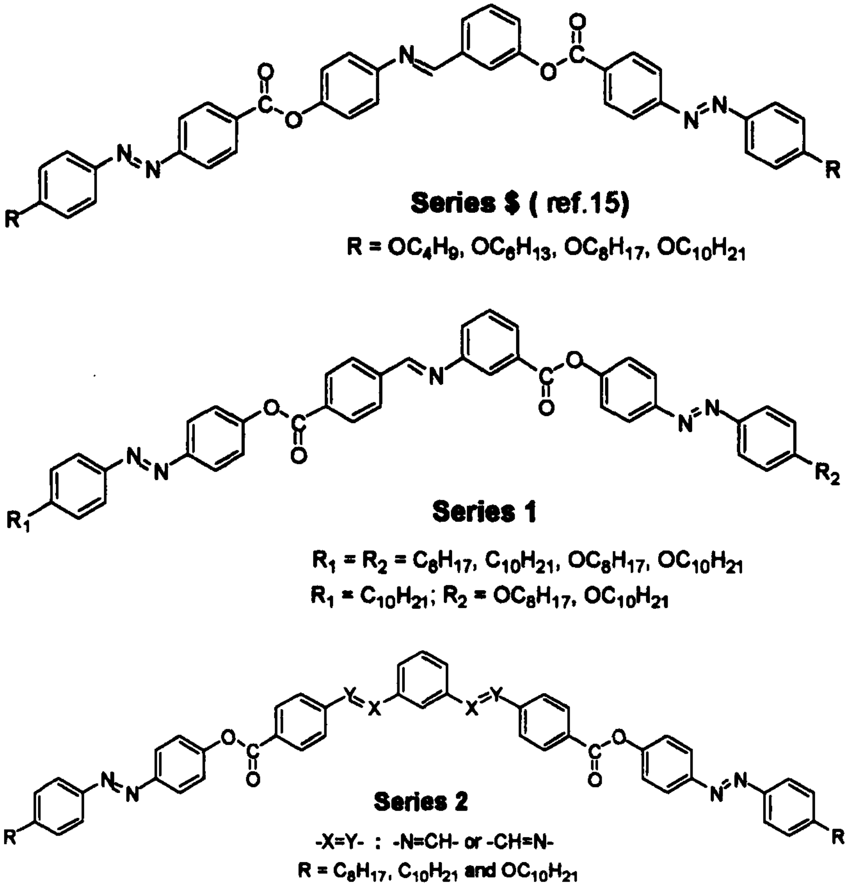


FIGURE 1 Molecular structures of different series of compounds synthesised

in figure 3(a). The preliminary x-ray measurements indicated that the phase is of the B_1 type. On further cooling, around 167°C coloured wrinkles start appearing on this texture (shown in figure 3(b)) and it looks as if the texture is broken (X_2 phase). We do not see any peak for this transition in the DSC thermogram in the cooling cycle. When we tried to disturb the coverslip, it moved easily. Further cooling of this mesophase, showed a pattern (X_3 phase, shown in figure 3(c)) which is reminiscent of the texture of a B_2 / B_3 mesophase (since both the B_2 and B_3 phases have similar textural features, only eletrooptical switching studies can differentiate between the two phases). To understand the exact nature of these mesophases (X_2 and X_3), physical studies are required for structural characterisation, which is proposed to be undertaken in the future.

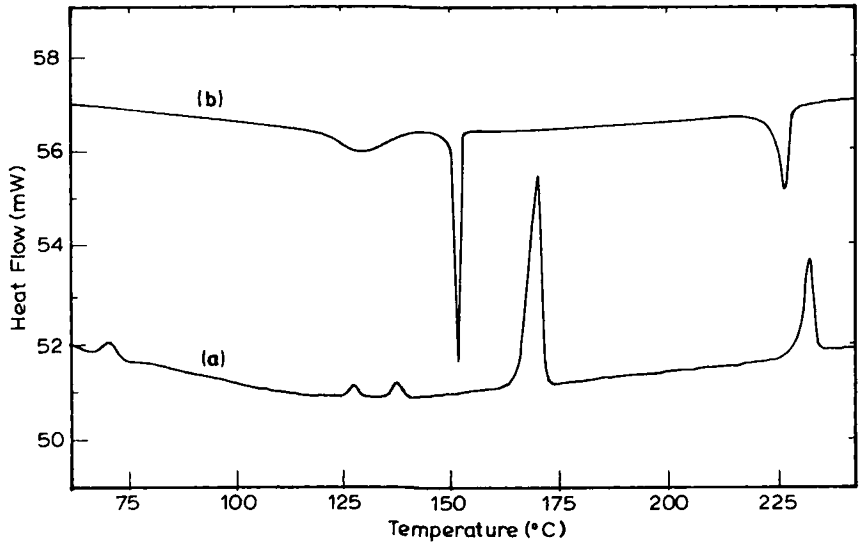


FIGURE 2 DSC thermograms for the compound with $R_1 = C_{10}H_{21}$ and $R_2 = OC_8H_{17}$ (series 1). The heating and cooling rate was 10°C/min. The scan (a) represents the heating cycle. The first three small peaks represent Cr-Cr transitions. The strong peaks at 169.5°C and 232.0°C represent the Cr – B_1 and B_1- I transitions respectively. The scan (b) represents the cooling cycle. The three peaks seen here corresponds to I – B_1, $X_2 - X_3$ and X_3 – Cr transitions respectively. Notice that no peak is observed for $B_1 - X_2$ transition

We made a comparison of the molecular structure and mesomorphic properties of compounds of series \$ and 1. We have done very minor changes in the molecular structures of series 1 with respect to those of series \$. We find that, even a small structural change can give rise to a considerable effect on the mesomorphic properties in such banana shaped molecules. In series \$, we observe the highest temperature mesophase X_1, above the B_1 phase. But in series 1, we observe B_1 as the highest temperature phase. In series \$, we observe only one phase i.e., B_4 below the B_1 phase. But in series 1, we observe two mesophases (X_2 and X_3) below the B_1 phase, for some of the homologues. Though the mesomorphic properties are affected even by small structural changes for the compounds of series 1, the transition temperatures are not much affected, compared to the compounds of series \$.

Table II gives the transition temperatures for the compounds of series 2. As can be seen, all the compounds in this series are mesomorphic. Each compound show only one type of mesophase enantiotropically. The first three compounds in this series, i.e., with – X = Y – linkage being – N = CH – show only B_7 mesophase. The mesophase range is found wider for the alkyl substituted compounds (100

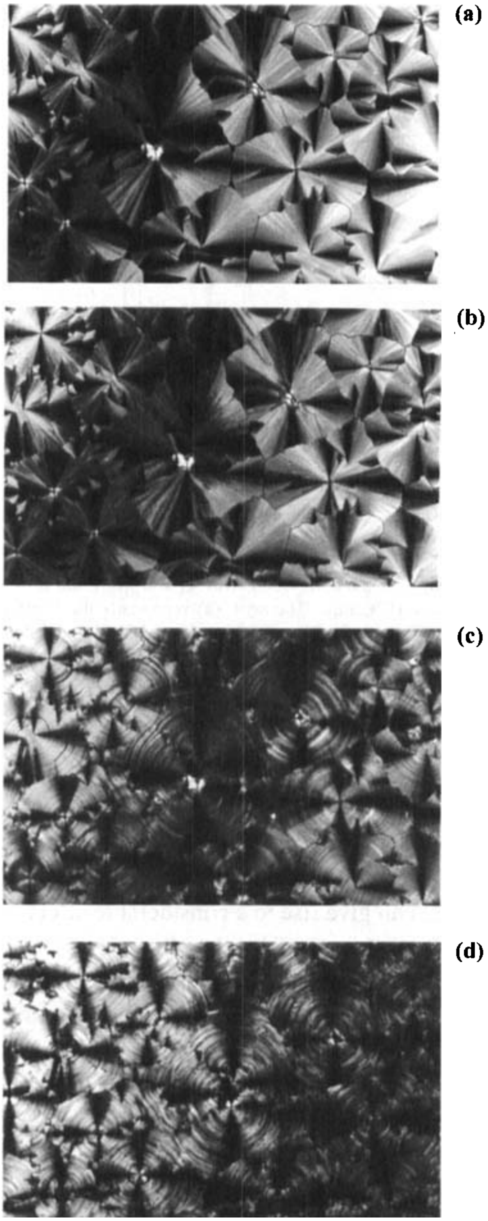


FIGURE 3 Photomicrographs showing the three different mesophases and the crystalline phase exhibited by the compound with $R_1 = C_{10}H_{21}$ and $R_2 = OC_8H_{17}$ (series 1). (a) B_1 phase at 225°C, (b) X_2 phase at 164°C (observe the wrinkles developed on B_1 phase), (c) X_3 phase at 150.5°C (reminds the texture of B_2 / B_3 phases) and (d) the crystalline phase obtained on cooling the phase X_3 (See Color Plate IV at the back of this issue)

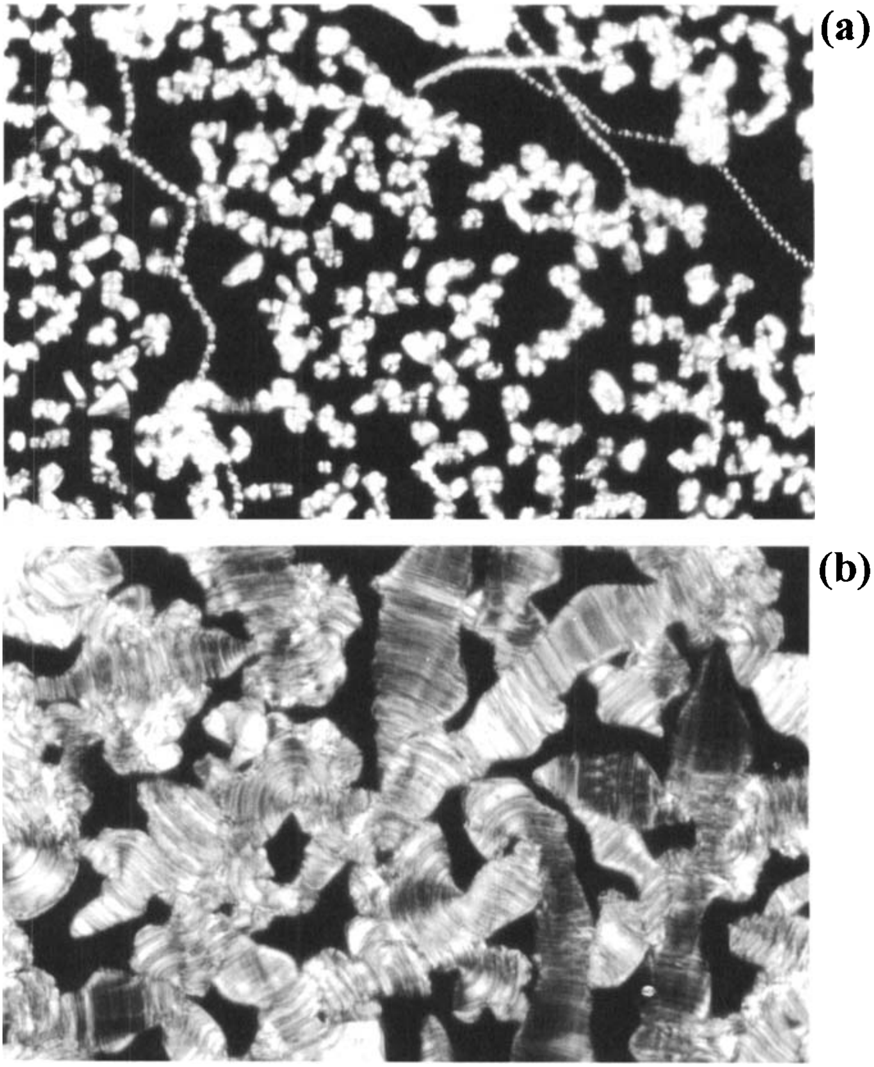


FIGURE 4 Photomicrographs showing the two different mesophases shown by the two different compounds of series 2. (a) B_7 phase shown by the compound R = $C_{10}H_{21}$ and (-X=Y-) = (-N=CH-) at 265.5°C and (b) X_4 phase shown by the compound R = $C_{10}H_{21}$ and (-X=Y-) = (-CH=N-) at 238.0°C (See Color Plate V at the back of this issue)

–105°C) than the alkyloxy substituted ones (69.5°C). The last three compounds, with – X = Y – linkage being – CH = N – (notice that, the imino linkages have been reversed in these compounds with respect to the previous three compounds), show only one mesophase X_4, enantiotropically. In this case mesophase range is being 71 – 76.5 °C for alkyl substituted compounds and 46°C for alkyloxy substituted compound. Once again, the mesophase range has been found wider for the alkyl substituted compounds than for the alkyloxy substituted compounds.

Now, we discuss the microscopic textural observations for the above compounds. On cooling from isotropic liquid, the first three compounds of this series wherein – X = Y – linkage is – N = CH – showed the characteristic texture[11,18] of B_7 mesophase (shown in figure 4(a) for the compound with $R = C_{10}H_{21}$). Along with some unspecified texture there start forming elongated thread-like germs. In some regions, we also see the growth of helical ribbons. All these textural features are expected for the mesophase B_7. When we cooled the isotropic liquid of the last three compounds wherein – X = Y – linkage is -CH = N-, they form a mesophase (X_4), the texture of which is shown in figure 4(b) for the compound with $R = C_{10}H_{21}$. The texture is more reminiscent of a banana mesophase. Here, one should notice that, even a small change such as, reversing the direction of imino linkage, has caused a drastic change, not only in the mesomorphic properties of these compounds but also in the transition temperatures.

CONCLUSIONS

We have synthesised two novel series of bent – shaped compounds consisting of azo linkages. All the compounds synthesised in both the series are found to be liquid crystalline. They exhibit different types of smectic phases. Among these, two of the phases are assigned unambiguously, viz., B_1 (by preliminary x-ray studies) and B_7 (by the optical microscopic observation of its typical textural features). The remaining phases X_2, X_3 and X_4 exhibit textures reminiscent of banana mesophases. To understand and assign the exact nature of these mesophases, we propose to carry out physical studies. From the studies carried out here, it has been found that, even the small structural modifications, such as the reversal of the direction of linkage groups in such molecules can lead to a drastic change in the mesomorphic properties, though the transition temperatures are less affected. Efforts to bring down the transition temperatures of these bent-shaped azo compounds by modifying their molecular structures, so that they are better suited for physical studies, are presently under progress.

Acknowledgements

The author is indebted to prof. S. Chandrasekhar for his constant encouragement and many valuable suggestions. Thanks are due to Dr. S. Krishna Prasad for the preliminary x-ray studies on one of the compounds.

References

1. T. Niori, T. Sekine, J. Watanabe, T. Furukava and H. Takezoe, *J. Mater. Chem.*, **6**, 1231 (1996).
2. D. Shen, S. Diele, I. Wirth and C. Tschierske, *Chem. Commun.*, 2573 (1998).
3. D. Shen, S. Diele, G. Pelzl, I. Wirth and C. Tschierske, *J. Mater. Chem.*, **9**, 661 (1999).
4. G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, **11**, 707 (1999), and the references therein.
5. Veena Prasad, D.S. Shankar Rao and Krishna Prasad, *Liq. Cryst.*, **27**, 585 (2000).
6. J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, M.F. Achard and H.T. Nguyen, *Liq. Cryst.*, **27**, 103 (2000).
7. G. Heppke, D.D. Parghi and H. Sawade, *Liq. Cryst.*, **27**, 313 (2000).
8. L. Kovalenko, W. Weissflog, S. Grande, S. Diele, G. Pelzl and I. Wirth, *Liq. Cryst.*, **27**, 683 (2000).
9. W. Weissflog, L. Kovalenko, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss and H. Kresse, *Liq. Cryst.*, **27**, 677 (2000).
10. R. Prathibha, N.V. Madhusudana and B.K. Sadashiva, *Science*, **288**, 2184 (2000).
11. D.M. Walba, E. Korblova, R. Shao, J.E. Maclennan, D.R. Link, M.A. Glaser, N.A. Clark, *Science*, **288**, 2181 (2000).
12. Veena Prasad, D.S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.* (in press).
13. H.R. Brand, P.E. Cladis and H. Pleiner, *Eur. Phys. J.*, **B 6**, 347 (1998).
14. Veena Prasad, *Liq. Cryst.*, (in press).
15. Veena Prasad, D.S. Shankar Rao, S. Krishna Prasad, *Liq. Cryst.*, (in press).
16. T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, **182B**, 357 (1990).
17. Veena Prasad, (in preparation).
18. G. Pelzl, S. Diele, A. Jakli, CH. Lischka, I. Wirth and W. Weissflog, *Liq. Cryst.*, **26**, 135 (1999).