# Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

## A novel class of banana-shaped azo compounds exhibiting antiferroelectric switching behaviour

Veena Prasad; D. S. Shankar Rao; S. Krishna Prasad

**To cite this Article** Prasad, Veena , Rao, D. S. Shankar and Prasad, S. Krishna(2001) 'A novel class of banana-shaped azo compounds exhibiting antiferroelectric switching behaviour', Liquid Crystals, 28: 4, 643 — 646

**To link to this Article: DOI:** 10.1080/02678290010020887

**URL:** http://dx.doi.org/10.1080/02678290010020887

LIQUID CRYSTALS, 2001, VOL. 28, NO. 4, 643–646

# Preliminary communication

# A novel class of banana-shaped azo compounds exhibiting antiferroelectric switching behaviour

VEENA PRASAD*, D. S. SHANKAR RAO and S. KRISHNA PRASAD
Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

(*Received 9 August 2000; accepted 20 October 2000*)

The first banana-shaped liquid crystal materials with photo-active azo linkages are reported. The higher temperature mesophase $X_1$ (believed to be $B_6$) above the $B_1$ phase exhibited by these azo compounds shows antiferroelectric switching characteristics. The observation of banana phases in azo compounds assumes significance from the point of view of photochromic studies.

About 25 years ago, Meyer *et al.* [1] discovered ferroelectricity in tilted smectic phases of chiral compounds. Later, antiferroelectric properties were also found in chiral materials [2]. Theoretical work has however shown that to exhibit these properties the molecules need not be chiral [3, 4]. Indeed, in 1996, Niori *et al.* [5] reported ferroelectric behaviour in a smectic phase formed by 'banana-shaped' non-chiral molecules. Observation of antiferroelectric switching properties in such materials followed almost immediately [6–8]. Since then, this new liquid crystal field has attracted the interest of a number of research groups [9–14]. As the structure of the mesophases exhibited by these banana-shaped molecules is not completely understood, a tentative classification scheme has been proposed in which the phases are labelled with the code letters $B_1 \ldots B_7$ according to the sequence of their discovery [12]. Among the physical properties of the 'banana mesophases', the electro-optical behaviour is of particular interest and gives some hints about the structure of these phases. Among the seven phases, electro-optical switching [12] has been observed only in the $B_2$, $B_3$ and $B_5$ phases.

From the view point of chemical structure, molecules with five, six and seven aromatic rings have been found to form this type of mesophase. However, in all the banana-shaped mesogens reported so far, the bent-shape of the molecules is achieved by either the same type of linkage (−COO−) or two different types of linkages (−COO− and −CH=N− or −COS− or −C≡C−) [12]. In this communication we report the first example of azo compounds exhibiting banana-mesophases. This observation assumes significance from the fact that the introduction of the −N=N− linkage brings in a new dimension to this field, namely photochromism.

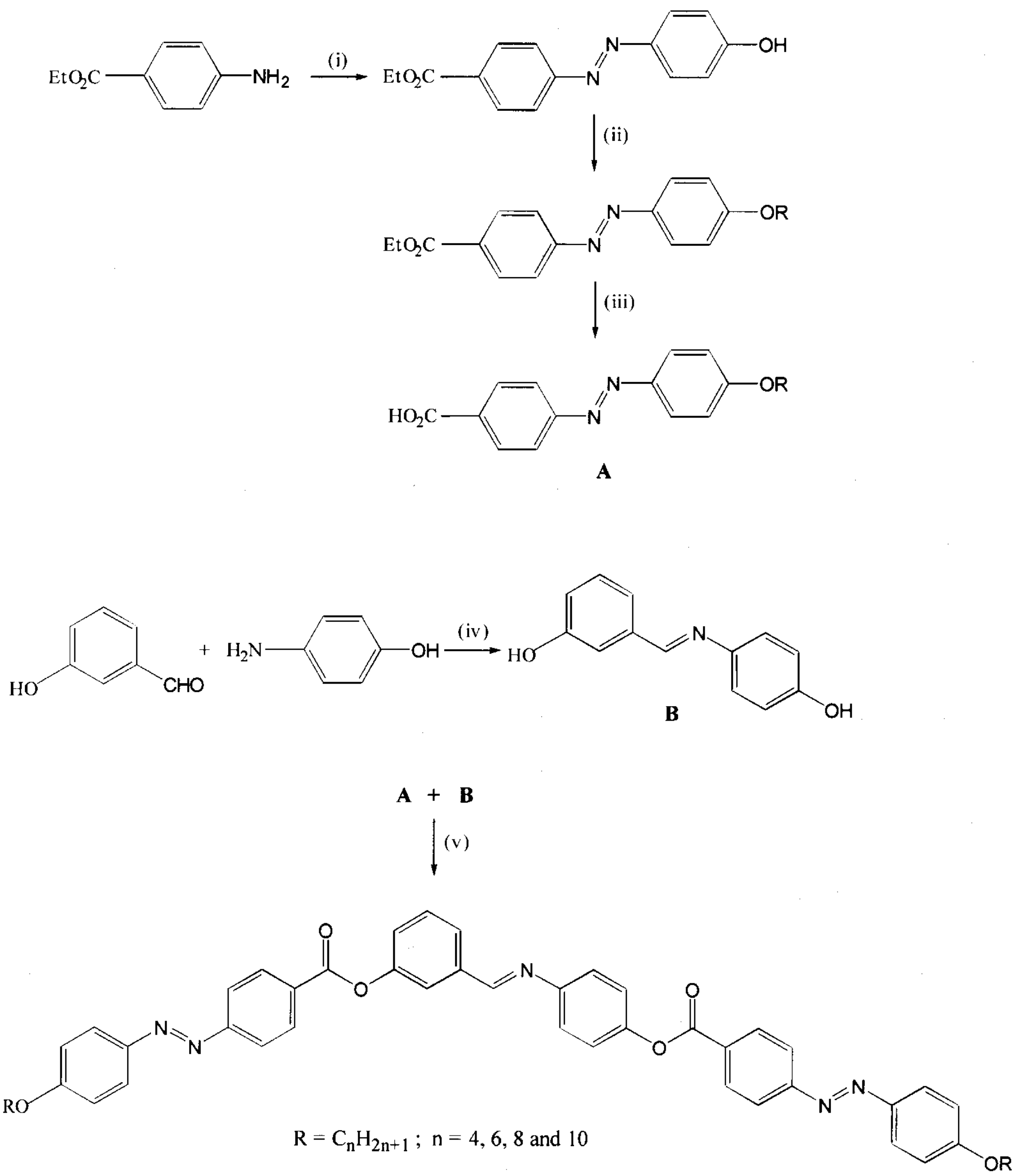
The synthesis of these banana-shaped azo compounds was achieved by following the synthetic routes shown in the scheme. Details of the synthesis will be reported in a forthcoming paper. The spectral data for all the intermediate compounds were satisfactory. Selected data for compound $C_6$: $\nu_{max}/\mathrm{cm}^{-1}$ (KBr pellet): 2937, 2870, 1731 and 1600; $\delta_H$ (200 MHz, $CDCl_3$, $SiMe_4$): 0.92 (t, $J = 6.0$ Hz, 6H, $CH_3$), 1.35–1.87 (m, 16H, $CH_2$), 4.06 (t, $J = 6.4$ Hz, 4H, Ar−$OCH_2$), 7.03 (d, $J = 8.0$ Hz, 4H, ArH), 7.3 (d, $J = 8.0$ Hz, 4H, ArH), 7.42 (m, 2H, ArH), 7.57 (m, 1H, ArH), 7.79–8.01 (m, 9H, ArH), 8.33 (d, $J = 8.8$ Hz, 2H, ArH), 8.38 (d, $J = 8.8$ Hz, 2H, ArH), 8.52 (s, 1H, −CH=N−); $m/z$ (FAB): 829 $[M]^+$ (calcd. for $C_{51}H_{51}O_6N_5$).

The transition temperatures for the azo compounds were determined using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope. The enthalpies of transitions were determined from thermograms recorded on a differential scanning calorimeter (DSC7 Perkin-Elmer). The heating and cooling rate was 10°C $\mathrm{min}^{-1}$. X-ray measurements were carried out using a MAC Science image plate set-up [15]. The lowest homologue (with $n = 4$, $n$ being the number of carbon atoms in the alkyl chains, $R$) showed only one mesophase while the compound with $n = 6$ exhibited two mesophases, both of which are enantiotropic. In contrast the two higher homologues, with $n = 8$ and 10, showed one enantiotropic and one monotropic mesophase. Hereafter, we refer to these compounds as $C_n$, $n$ being 4, 6, 8 and 10 for the four homologues.

---

*Author for correspondence;
e-mail: uclcr@giasbg01.vsnl.net.in or clcr@vsnl.com

*Liquid Crystals* ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010020887



Scheme. (i) $NaNO_2$, HCl, $C_6H_5OH$, 0–5°C, 2 h; (ii) *R*Br, anhydrous $K_2CO_3$, cat.KI, acetone, 65°C, 24 h; (iii) aq. NaOH, EtOH, 90°C, 2 h; (iv) EtOH, cat. acetic acid, 90°C, 4 h; (v) DCC, DMAP, $CH_2Cl_2$, r.t., 24 h.

On cooling from the isotropic phase, the $C_4$ compound first shows the formation of bâtonnets which coalesce to a focal-conic fan-shaped texture, very similar to the texture seen in classical smectic A phases. The alignment which can be obtained by shearing, is birefringent, but is unstable and relaxes back to the fan texture; no schlieren texture was observed. Similar features were also seen for the higher temperature mesophase of the $C_6$ compound. The X-ray pattern for this mesophase consists of only one sharp reflection at small angles (with $d = 2.24$ nm) and a diffuse ring at wide angles (0.46 nm). Compared with the length of the molecule in the all-*trans*-configuration and using a bending angle of 120°, which is typical for such systems, the *d* value suggests an intercalated structure. Although the X-ray data are equally compatible with an interdigitated smectic A phase, in view of the texture observations mentioned above we rule out the possibility of a smectic A phase. These observations are signatures of the banana $B_6$ phase, which to our knowledge, has been reported in only a few systems [10, 12]. It may be recalled that no electro-optic switching has been reported for the $B_6$ mesophase. However, we have observed electro-optic switching in the high temperature mesophase of the $C_6$ compound. Figure 1 shows the electro-optic switching profile obtained with a 7.5 V $\mu m^{-1}$, 20 Hz triangular wave field at a temperature of 215°C. To obtain this profile, the sample contained in a glass sandwich cell coated

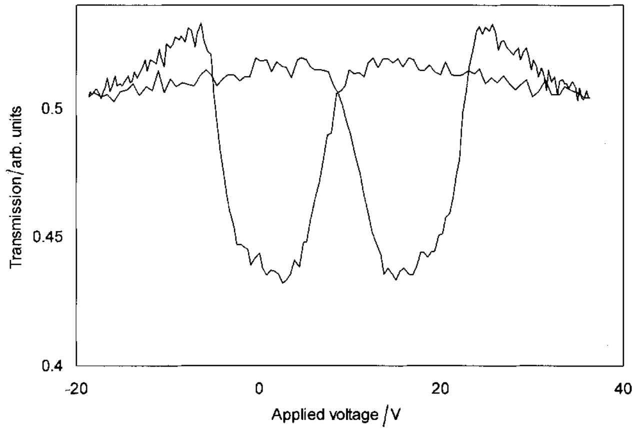


Figure 1. Electro-optic response of the compound $C_6$ obtained with an applied field of 7.5 V $\mu m^{-1}$ and a 20 Hz triangular wave taken at a temperature of 215°C. The profile is typical of antiferroelectric switching.

with ITO and with a cell gap of 3.6 µm was used. The sample was rotated by 22.5° from the point of minimum transmitted intensity in the absence of the applied field. The electro-optical profile obtained on application of the electric field is very similar to those obtained for materials exhibiting an antiferroelectric type of switching [16, 17]. Hence, although the texture and X-ray observations seem to suggest a $B_6$ phase, due to the presence of the electro-optic switching, we are not certain whether it is in fact a $B_6$ phase or another new phase, and therefore we tentatively call it the $X_1$ phase.

The enantiotropic mesophases of compounds $C_8$ and $C_{10}$ have a similar behaviour, which we shall describe now. On cooling from the isotropic phase, both exhibit a dendritic growth pattern which finally leads to a mosaic pattern with spherulitic domains (see figure 2). The texture seen for the lower temperature phase of the $C_6$ compound is similar to this, but not so well defined.

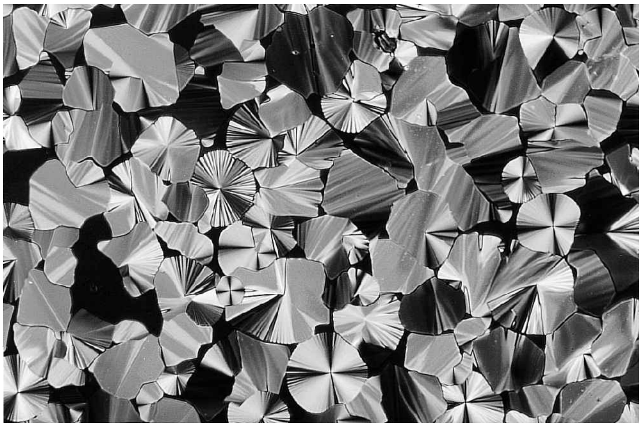


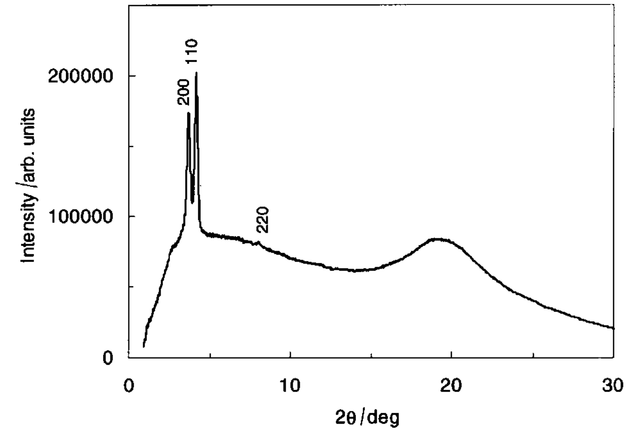
Figure 2. Optical microscopic texture showing the mosaic pattern for the $B_1$ phase of compound $C_{10}$ at a temperature of 189°C (magnification: × 100).

The X-ray powder pattern along with a '1D cut' obtained for compound $C_6$ at a temperature of 190°C is shown in figure 3. Three small angle reflections are seen at angles of 1.84°, 2.07° and 4.01° which can be indexed as the (2 0 0), (1 1 0) and (2 2 0) reflections of a centred 2D rectangular lattice, with unit cell dimensions of $a = 5.1$ nm, $c = 2.5$ nm. Further, a diffuse reflection is seen at wide angles corresponding to a spacing of 0.46 nm. Similar results were obtained for the enantiotropic mesophase of the $C_8$ and $C_{10}$ compounds. Thus, the texture and X-ray data conclusively prove that this mesophase is of the $B_1$ type.

The monotropic phase obtained on cooling the $B_1$ phase of compounds $C_8$ and $C_{10}$ shows a texture with intense blue coloured domains characteristic of the Sm blue or $B_4$ phase. This phase is supposed to have a twistgrain boundary structure, but possessing a three-dimensional order. A summary of the phases, transition temperatures and the associated enthalpy changes for all four homologues is given in the table.

In conclusion, we have observed banana-type mesophases in a novel type of molecular structure containing an azo linkage. This type of molecule is particularly attractive for photochromic studies, as the azo moiety undergoes *trans*-*cis*-isomerization in the presence of UV light.

(*a*)



(*b*)

Figure 3. (*a*) X-ray diffraction pattern in the $B_1$ phase of compound $C_6$. (*b*) $\chi$-averaged one-dimensional intensity vs. $2\theta$ profile derived from (*a*). The two intense sharp peaks, along with a less intense third peak at low angles, confirm a two-dimensional rectangular packing. The diffuse peak at higher angles is due to the liquid-like packing of the molecules within the smectic layers.

Table. Transition temperatures (°C) and enthalpies of transitions (kJ mol$^{-1}$), in italics for the banana-shaped azo compounds: parentheses indicate monotropic transitions.

| *n* | Cr | | $B_4$ | | $B_1$ | | $X_1$ | | Iso |
|---|---|---|---|---|---|---|---|---|---|
| 4 | • | 196.5<br>*37.8* | — | | — | | • | 243.0<br>*15.7* | • |
| 6 | • | 166.5<br>*34.1* | — | | • | 206.0[a] | • | 224.5<br>*16.7* | • |
| 8 | • | 168.0<br>*40.0* | • | (136.5)<br>*39.8* | • | 209.0<br>*20.5* | — | | • |
| 10 | • | 166.5<br>*38.5* | • | (144.0)<br>*40.2* | • | 195.0<br>*19.0* | — | | • |

[a] This phase transition was seen only under the microscope.

We are indebted to Prof. S. Chandrasekhar for many useful discussions and suggestions.

## References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys.*, **36,** L-69.

[2] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., and Fukuda, A., 1989, *Jpn. J. appl. Phys.*, **28,** L1265.

[3] Prost, J., and Barois, P., 1983, *J. chim. Phys.*, **80,** 65.

[4] Petschek, R. G., and Wiefling, K. M., 1987, *Phys. Rev. Lett.*, **59,** 343.

[5] Niori, T., Sekine, F., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 1231; Sekine, F., Takanashi, Y., Niori, T., Watanabe, J., and Takezoe, H., 1997, *Jpn. J. appl. Phys.*, **36,** L1201.

[6] Heppke, G., Jakli, A., Krüerke, D., Löhning, C., Lötzsch, D., Paus, S., Rauch, S., and Sharma, N. K., 1997, in Abstracts of the European Conference on Liquid Crystals, Zakopane, Poland, p. 34.

[7] Weissflog, W., Lischka, C., Benne, L., Scharf, T., Pelzl, G., Diele, S., and Kruth, H., 1998, *Proc. SPIE*, **3319,** 14.

[8] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., and Walba, D. M., 1997, *Science*, **278,** 1924.

[9] Shen, D., Diele, S., Wirth, I., and Tschierske, C., 1998, *Chem. Commun.*, 2573.

[10] Shen, D., Diele, S., Pelzl, G., Wirth, I., and Tschierske, C., 1999, *J. mater. Chem.*, **9,** 661.

[11] Nguyen, H. T., Rouillon, J. C., Marcerou, J. P., Bedel, J. P., Barois, P., and Sarmento, S., 1999, *Mol. Cryst. liq. Cryst.*, **328,** 177.

[12] Pelzl, G., Diele, S., and Weissflog, W., 1999, *Adv. Mater.*, **11,** 707.

[13] Prasad, V., Shankar Rao, D. S., and Krishna Prasad, S., 2000, *Liq. Cryst.*, **27,** 585.

[14] Prasad, V., Shankar Rao, D. S., and Krishna Prasad, S., *Liq. Cryst.* (submitted).

[15] Kumar, S., Shankar Rao, D. S., and Krishna Prasad, S., 1999, *J. mater. Chem.*, **9,** 2751.

[16] Shilov, S. V., Rauch, S., Skupin, H., Heppke, G., and Kremer, F., 1999, *Liq. Cryst.*, **9,** 1409.

[17] Pociecha, D., Gorecka, E., Glogarova, M., and Mieczkowski, J., 1999, *Mol. Cryst. liq. Cryst.*, **328,** 75.