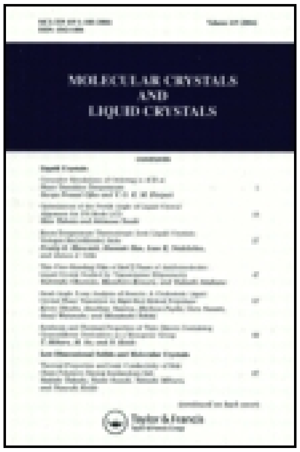

## Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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# New Liquid Crystalline Compounds of a T-Shape

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# New Liquid Crystalline Compounds of a T-Shape

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Three new dimesogenic compounds that are consisted of two mesogenic units connected through a polymethylene spacer in the shape of the letter T have been synthesized. The compounds were characterized for their liquid crystallinity by the differential scanning calorimetry (DSC), X-ray diffractometry and visual observation of the melts on a hot-stage attached to a polarizing microscope. All the compounds were found to form only nematic phase and to be enantiotropic.

*Keywords:* Dimesogenic compounds; DSC; T-shape molecules; polymethylene spacer

## INTRODUCTION

We and others have reported the liquid crystalline behavior of twin, dimesogenic compounds in which two same mesogenic units are connected linearly through a flexible spacer such as polymethylene or oligosiloxyl group [1–18]. These compound not only can be taken as model compounds for main chain liquid crystalline polymers (LCPs) containing flexible spacers, but also they can be taken as novel LC compounds revealing interesting phase-transition properties [19–22]. When the chemical structures of the two mesogenic units are not the same, their phase-transition behavior becomes even more complicated and intriguing as reported recently by us [23, 24].

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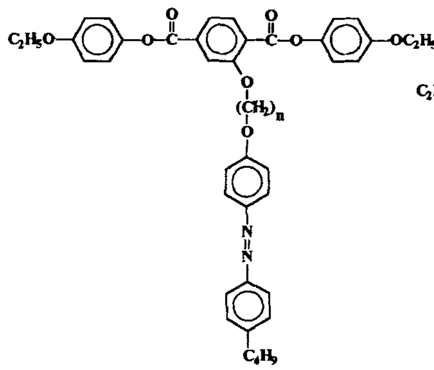
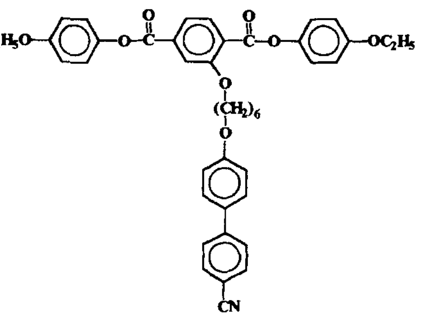
This investigation is a continuation of our efforts to establish structure-LC property relationships of dimesogenic compounds, and we would like to describe specifically the synthesis and LC characteristics of the following three compounds of the T shape:



**MAZO-6 (n=6) and MAZO-10 (n=10)**



**MCN-6**

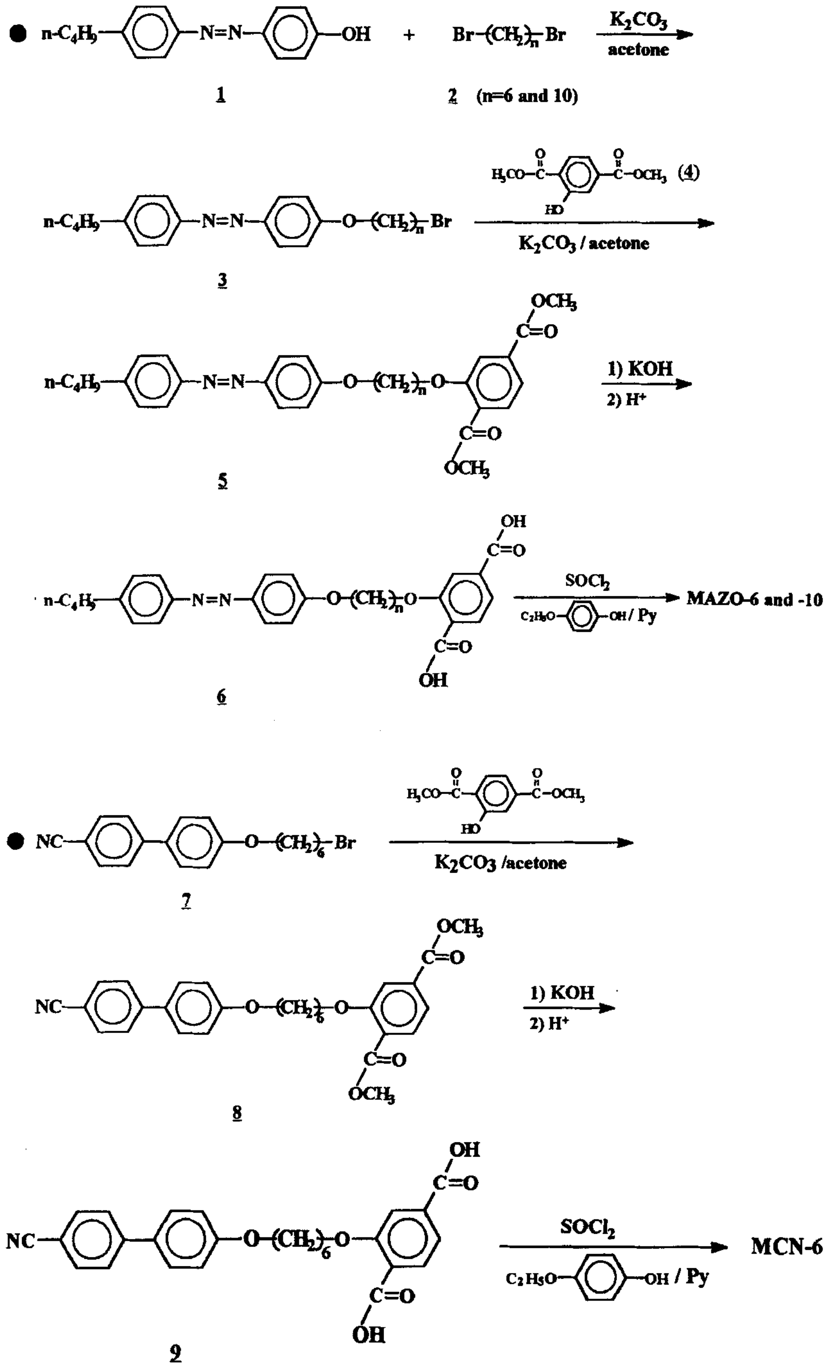
## RESULTS AND DISCUSSION

The compounds were synthesized via multi-step routes as schematically shown on the next page:

The structures of the final compounds, *i. e.*, MCN-6, MAZO-6 and MAZO-10 were confirmed by elemental analysis and $^1$H-NMR and IR spectra (see Experimental part). Their purity was checked with a high pressure liquid chromatograph and was found to be higher than $99.9^{+}$%.

These compounds possess a common, peculiar structural feature; the triad aromatic ester type mesogenic structure is linked to another mesogenic unit through a polymethylene spacer that is attached to its central terephthaloyl moiety. Overall shape of the molecule is therefore more or less in a T-shape disregarding the detailed conformation of the polymethylene spacer and is directly related to the repeating unit of one of the so-called combined type LCPs [25, 26].

Figure 1 shows their DSC thermograms and they reveal reversibly isotropization endotherms (see Tab. I). At the cooling rate of 10°C/min, all the three compounds froze in LC phases and did not crystallize when cooled down to room temperature. The optical textures of the melts shown in Figure 2 tell us that they all form nematic phases. This is rather surprising in



SCHEME 1 Synthetic schemes of MAZO and MCN compounds.

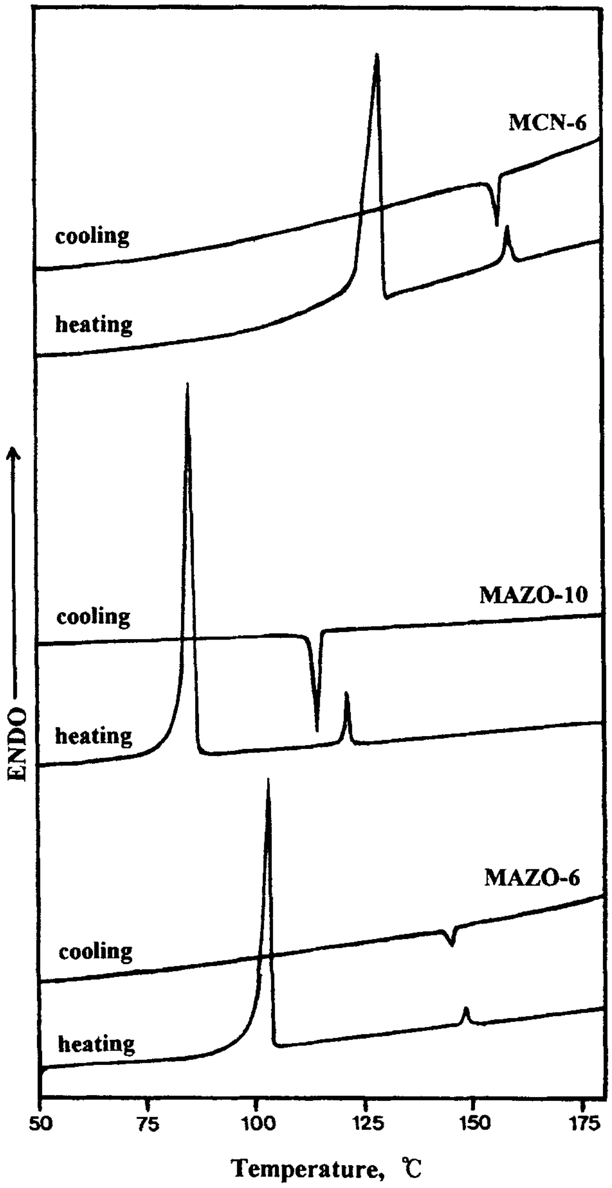


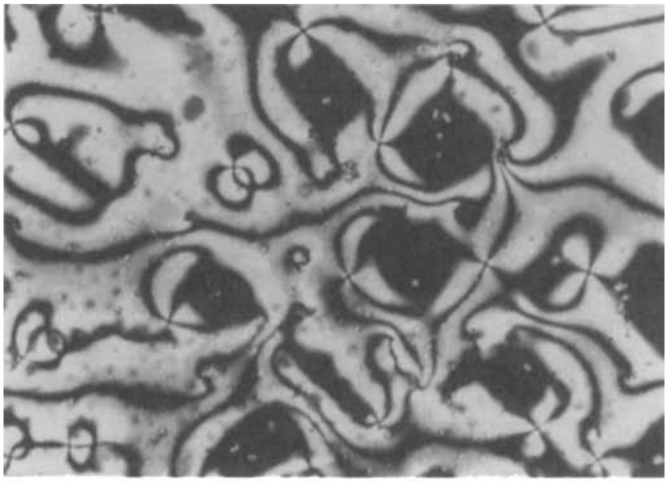
FIGURE 1 DSC thermograms of liquid crystalline compounds.

light of the fact that their chemical structures predict a high possibility for the formation of layered LC phases, especially if the compounds maintain a T-shaped geometry in LC phases.

TABLE I General Properties of T-Shaped Liquid Crystalline Compounds

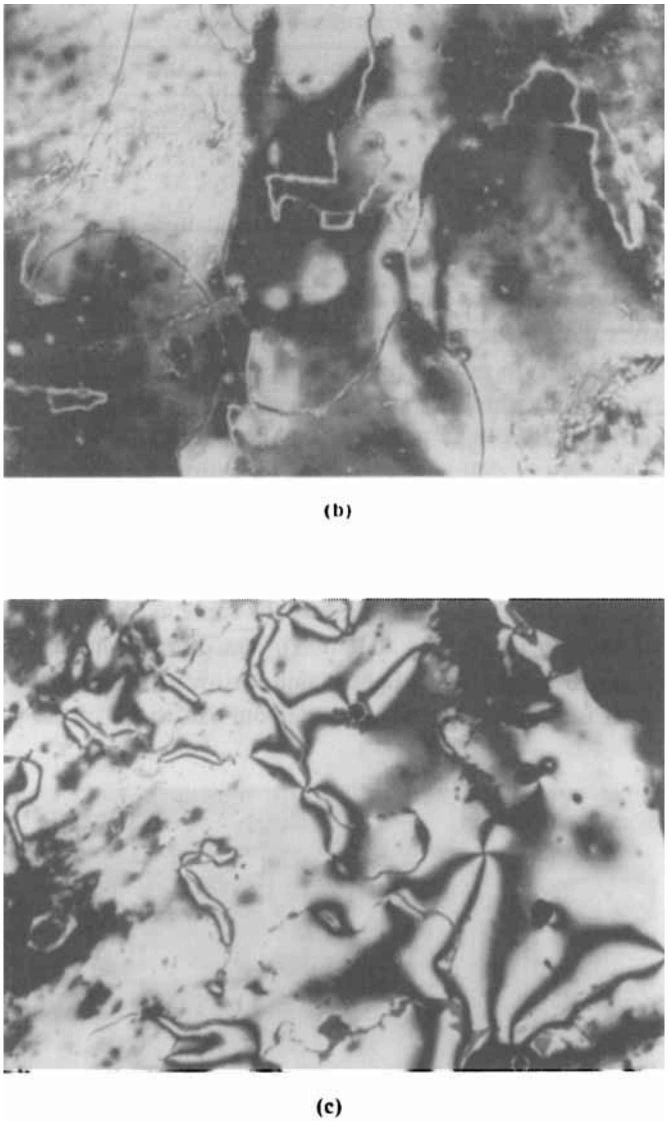
| *Compound* | $T_m$ | $T_i$ | $\Delta H_m$ | $\Delta S_m$ | $\Delta H_i$ | $\Delta S_i$ | $\Delta H_m/\Delta H_i$ |
|---|---|---|---|---|---|---|---|
| | *°C* | *°C* | *KJ/mol* | *J/mol·K* | *KJ/mol* | *J/mol·K* | % |
| MAZO-6 | 101 | 149 | 55.2 | 148 | 2.6 | 6.2 | 4.7 |
| MAZO-10 | 90 | 124 | 63.3 | 174 | 3.2 | 8.1 | 5.1 |
| MCN-6 | 131 | 160 | 42.3 | 105 | 2.4 | 5.5 | 5.7 |

Figure 3–5 compare the X-ray diffractograms of the compounds obtained in LC phases with those taken for crystalline powders. The diffractograms taken in LC phases do not show any sharp peak in the small-angle region, but they commonly show a rather diffuse peak in the wide-angle region centered around $2\theta = 18.5°$ (4.8 Å), which corresponds to intermolecular distance. These X-ray diffraction patterns reconfirm the observation results through the polarizing microscope that tell us these compounds form nematic phases. Figures 3–5 also compare the X-ray diffractograms of LC phases of the three compounds with those obtained for the corresponding isotropic liquids. The formers are almost the same as the latters, with only the difference lying in the fact that maximum diffraction positions of the isotropic liquids appear very slightly shifted toward small-angle side and also that their half widths are broadened (from 6.0° to 6.4°, from 6.0° to 6.3°



(a)

FIGURE 2 Optical photomicrographs of (a) MAZO-6 (148°C), (b) MAZO-10 (105°C) and MCN-6 (158.5°C) (magnification 200*x*). (See Color Plate III).


(b)

(c)

FIGURE 2 (Continued).

and from 6.7° to 7.6°, respectively for MCN-6, feature of the diffractograms shown in Figure 5 for MAZO-10 is that they reveal weak diffractions centered around $2\theta = 5°$ (ca. 20 Å) both for LC and isotropic phase. Although the origin of this diffraction is not yet clear, it can be conjectured that there are some remnant of long range order persistent in LC as well as isotropic

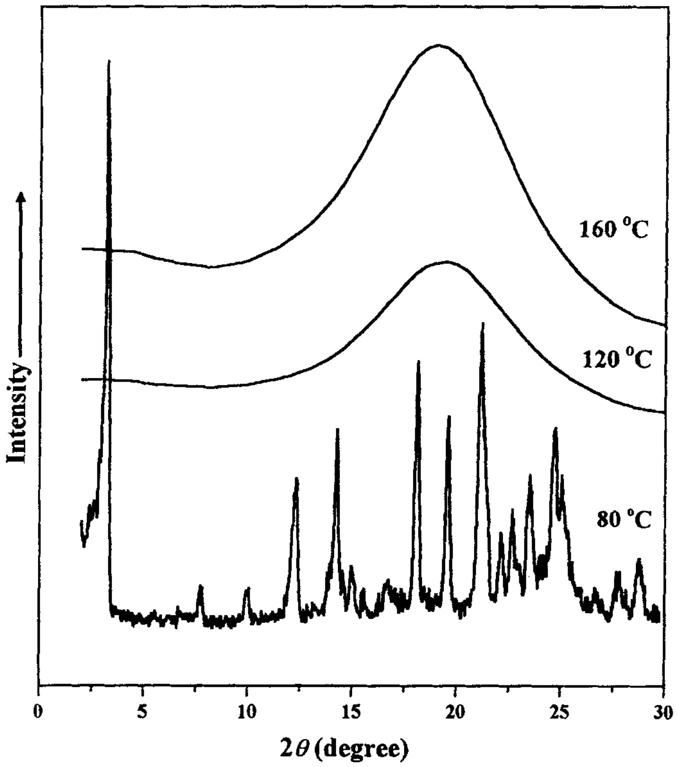


FIGURE 3 X-ray diffractograms of MAZO-6.

phases. This diffraction is not so clear for the compounds with shorter spacers between the two mesogenic units, i.e., MCN-6 and MAZO-6.

All of the observations and discussions described for the nature of the mesophases formed by the present compounds lead us to the temporary conclusion that they form uniaxial nematic melts, although their chemical structures imply a genuine possibility for the formation of a biaxial nematic or layered order in LC phases. Such a uniaxial nematic ordering is possible only when the two mesogenic units are more or less paralleld to each other. This can be achieved if the polymethylene spacers are bent via conformational adjustment. In other words, the methylene groups in the spacers are not fully in trans conformation; some of them are of gauche conformation as was claimed earlier by Ringsdorf and coworkers [27] for the mesophase structure of the so-called combined type LC polyesters consisting of main chain polyesters carrying pendant mesogenic side groups that are attached to the main chain through polymethylene spacers.

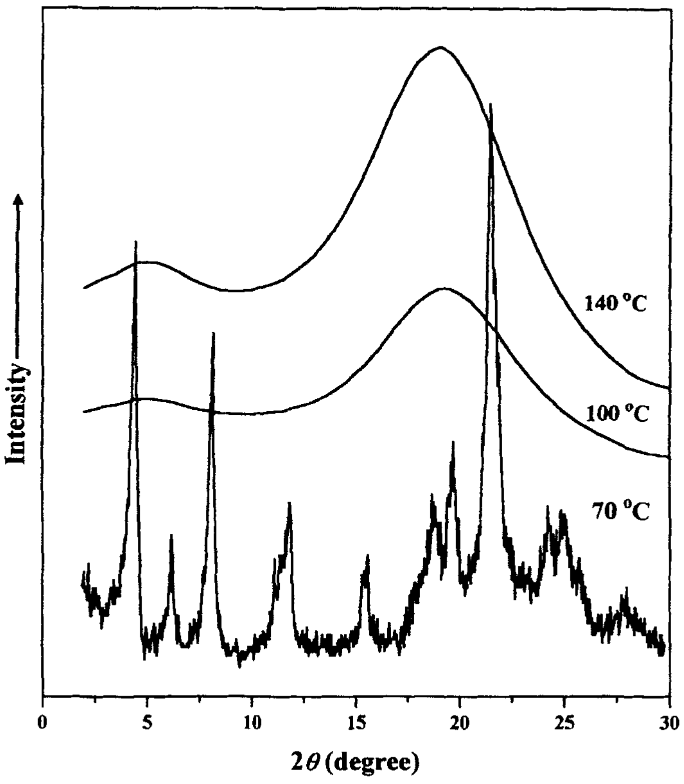


FIGURE 4 X-ray diffractograms of MAZO-10.

## EXPERIMENTAL

### Synthesis of MAZO-6 and -10

These compounds were prepared following the synthetic route shown in Scheme 1. Since synthetic methods for the two compounds were the same, only the procedure for the preparation of MAZO-6 is given. 4-Butyl-4′-hydroxyazobenzene, 1, (18.0 g; 7.08 × $10^{-2}$ mol) and 1,6-dibromohexane, 2, (54 mL; 0.344 mol) and 11.2 g (0.2 mol) of KOH were dissolved in 50 mL of ethanol. The mixture was refluxed for 6 hours under a nitrogen atmosphere. Another 600 mL of ethanol was added to the mixture, which was then heated to its boiling temperature. The KBr residue was quickly removed by filtration and washed with ethanol. The filtrate was cooled down to room temperature and the precipitate was collected on a filter. The crude product thus obtained was purified by recrystallization from ethanol. The yield of

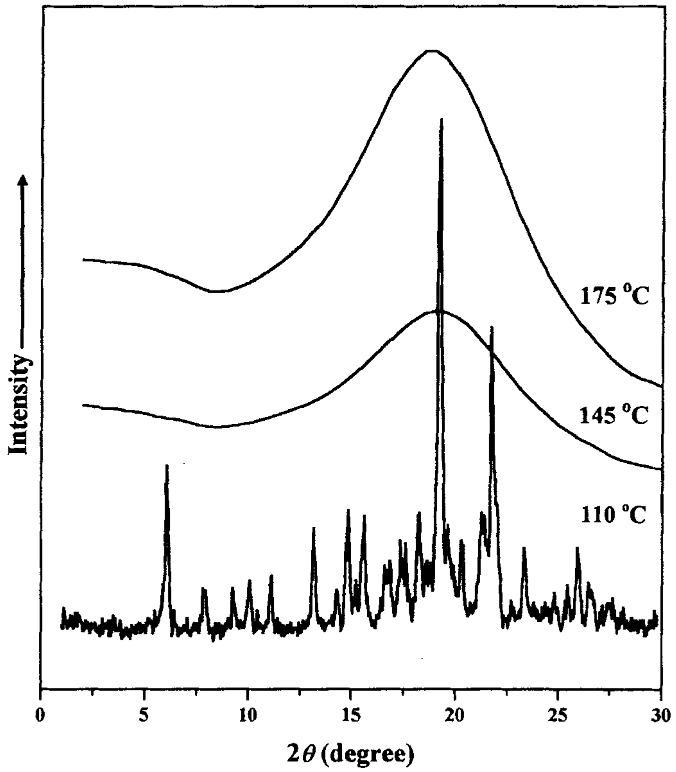


FIGURE 5 X-ray diffractograms of MCN-6.

4-(6-bromohexyloxy)-4′-butylazobenzene, 3, was 11.7 g (40%), mp 73°C. Anal: Cald. for $C_{22}H_{29}BrN_2O$; C 63.31, H 7.00 and N 6.71%; Found, C 63.25, H 6.99 and N 6.77%. $^1$H-NMR spectrum (acetone-$d_6$, ppm) : $\delta$ 0.9 (*t*, 3H, $CH_3$), 1.3–1.5 (*m*, 2H, $\text{-}CH_2\text{-}$), 1.5–1.8 (*m*, 10H, $Ar\text{-}CH_2\text{-}\underline{CH_2}\text{-}$ and $\text{-}OCH_2(\underline{CH_2})_4CH_2O\text{-}$), 2.7–2.8 (*t*, 2H, $\text{-}\underline{CH_2}\text{-}Ar$), 3.5–3.7 (*t*, 2H, $\text{-}\underline{CH_2}Br$), 4.1–4.3 (*t*, 2H, $\text{-}O\text{-}CH_2$), and 9.0–8.0 ppm (*m*, 8H, aromatic Hs); IR spectrum (KBr, $cm^{-1}$), 2394 (aliphatic C-H stretching), 1253 (ether C-O-stretching).

Compound 3 (2.0 g; $4.79 \times 10^{-3}$ mol) and dimethyl 2-hydroxyterephthalate, 4, (1.01 g; $4.81 \times 10^{-3}$ mol), potassium carbonate (0.99 g; $7.2 \times 10^{-3}$ mol), and tetrabutylammonium bromide (0.015 g) were dissolved in 30 mL of acetone. The mixture was refluxed for 5 hours. After the reaction mixture was cooled down to room temperature, the solid residue was removed by filtration. The filtrate was subjected to distillation using a rotatory evaporator. The oily residue was run through a silica gel column utilizing a mixture of *n*-hexane and ethyl acetate (3:1 by volume) as a eluent. By evaporating the eluent, dimethyl 2-[(4-butylphenylazo)phenoxy]terephthalate, 5, was obtained.

Compound 5 thus obtained was dissolved in 30 mL of ethanol, to which added was 1.7 g of potassium hydroxide (0.030 mol). The mixture was refluxed for 3 hours and cooled to room temperature. Insoluble residue was removed by filtration and the filtrate was acidified with 5 M HCl. The precipitate was redissolved in a hot mixture of water and ethanol (5:2 by volume) and filtered through a filter paper. The filtrate was cooled and, the precipitate was cooled on a filter and dried. The yield of 2-[6-{4-(4-butylphenylazo)phenoxy}hexyloxy]terephthalic acid, 6 was 2.1 g (84.3% for the last two steps), mp 224–225°C. Anal.: Calcd. for $C_{30}H_{34}N_2O_6$, C 69.48, H 6.61 and N 5.40%; Found, C 69.46, H 6.54 and N 5.41%. $^1$H-NMR spectrum (DMSO-$d_6$, ppm), $\delta$ 0.9 (*t*, 3H, -$CH_3$), 1.25–1.5(*m*, 2H, $\underline{CH_2}$-$CH_3$), 1.4–1.95 (*m*, 10H, -Ar$CH_2\underline{CH_2}$- and -$OCH_2$-$(\underline{CH_2})_4$-$CH_2O$-), 2.6–2.8 (*t*, 2H, $\underline{CH_2}$-Ar), 4.2–4.8 (*m*, 4H, Ar-O-$\underline{CH_2}$) and 7.1–8.0 (*m*, 11H, aromatic). IR spectrum (KBr, $cm^{-1}$), 3300–2000 (acidic -OH stretching), 1692 (C=O stretching), 1301 and 1244 (ether C-O stretching).

A solution of dicarboxylic acid, 6 (2.0 g; $3.86 \times 10^{-3}$ mol) and 20 mL of thionyl chloride was refluxed for 2 hours. Excess thionyl chloride was removed by distillation under a reduced pressure. The acid chloride formed was dissolved in 14 mL of an ice-chilled mixture of dry tetrahydrofuran (THF) and pyridine (5:2 by volume) to which added was a solution of ethoxyphenol (2.66 g; $19.3 \times 10^{-3}$ mol) dissolved in 5 mL of dry THF. The mixture was stirred for 12 hours at room temperature and then 1 hour at 60°C. The mixture was cooled down to room temperature and poured into excess methanol. The precipitate was collected on a filter. The product, MAZO-6, was purified by recrystallization from ethanol. The yield was 1.4 g (62%), mp 101°C. Anal.:Calcd. for $C_{44}H_{50}N_2O_6$, C 72.80, H 6.64 and N 3.69%; Found, C 72.75, H 6.70 and N 3.69%. $^1$H-NMR spectrum ($CD_2Cl_4$, ppm) : $\delta$ 0.95 (*t*, 3H, -$CH_3$), 1.3–1.95 (*m*, 2H, -$\underline{CH_2}$-$CH_3$), 1.3–1.95 (*m*, 13H, -Ar-$CH_2$-$\underline{CH_2}$-, Ar-O-$CH_2\underline{CH_3}$ and -$OCH_2$-$(\underline{CH_2})_4$-$CH_2$-), 2.6–2.8 (*t*, 2H, -$\underline{CH_2}$-Ar), 4.0–4.3 (*m*, 8H, Ar-O-$\underline{CH_2}$-), 7.1–8.1 (*m*, 19H, aromatic). IR spectrum (KBr, $cm^{-1}$) : 2936 (aliphatic C-H stretching), 1738 (C=0 stretching) and 1190 (ether C-O stretching).

MAZO-10 was synthesized by the exact same route with the only difference lying in the fact that compound 1 was reacted with 1,10-dibromodecane instead of 1,6-dibromohexane in the first step. Anal.: Calcd. for $C_{50}H_{58}N_2O_8$, C 73.70, H 7.17 and N 3.44 %; Found, C 72.63, H 7.53 and N 3.60%. $^1$H-NMR spectrum ($CDCl_3$, ppm) : $\delta$ 0.95 (*t*, 3H, -$CH_3$), 1.3–1.95 (*m*, 2H, -$\underline{CH_2}$-$CH_3$, *m*, 3H, -Ar-$CH_2$-$\underline{CH_3}$-, and *m*, 16H, -$OCH_2$-$(\underline{CH_2})_4$-$CH_2$-), 2.6–2.7 (*t*, 2H, -$\underline{CH_2}$-Ar), 4.0–4.3 (*m*, 8H, Ar-O-$CH_2$-), 7.0–8.1 (*m*, 19H, aromatic). IR spectrum (KBr, $cm^{-1}$) : 2924 (aliphatic C—H stretching), 1738 and 1718 (C=O stretching) and 1187 (ether C—O stretching).

## Synthesis of MCN-6

4′-(6-Bromohexyloxy)-4-cyanobiphenyl (5.0 g; $13.9 \times 10^{-3}$ mol), dimethyl 2-hydroxyterephthalate (4; 2.92 g; $13.9 \times 10^{-3}$ mol), potassium carbonate (2.88 g; $20.9 \times 10^{-3}$ mol), and tetrabutylammonium bromide (0.3 g) were dissolved in 100 mL of acetone. The mixture was refluxed under a nitrogen atmosphere for 5 hours. After the reaction mixture was cooled down to room temperature, the insoluble were removed by filtration. Acetone in the filtrate was distilled out under a reduced pressure. The residue and potassium hydroxide (4.0 g) were then dissolved in 80 mL of ethanol. The mixture was refluxed for 3 hours. The mixture, after being cooled down to room temperature, was filtered through a filter paper. The filtrate was acidified with 5 M HCl. The yield of compound 9 thus obtained was 2.9 g (45.3%). Anal.: Calcd. for $C_{27}H_{25}NO_6$, C 70.58, H 5.48 and N 3.05%; Found, C 70.25, H 6.07 and N 3.13%. $^1$H-NMR spectrum (DMSO-$d_6$, ppm); $\delta$ 1.4–1.9 (*m*, 8 H, $OCH_2$-($\underline{CH_2}$)$_4$$CH_2$O-), 4.0–4.2 (*m*, 4H, -O$\underline{CH_2}$-) and 7.0–8.0 (*m*, 11H, aromatic H). IR spectrum (KBr, $cm^{11}$) : 3500-2100 (O-H stretching), 2932 (aliphatic C-H stretching), 2224 (C≡N stretching) and 1741 (C=O stretching).

Compound 9 was converted to the corresponding dichloride by reacting with thionyl chloride using the same method applied to compound 6, which was then reacted with 4-ethoxyphenol resulting in the formation of MCN-6. This step was exactly the same as the last reaction utilized for the preparation of MAZO-6. The yield was 79%, mp 131°C. Anal.: Calcd. for $C_{43}H_{41}NO_8$, C 73.80, H 5.90 and N 2.00%; Found, C 73.72, H 5.95 and N 2.12%. $^1$H-NMR spectrum ($CD_2Cl_4$, ppm); $\delta$ 1.3–1.7 (*m*, 6H, -$CH_3$, *m*, 4H, -$OCH_2$($\underline{CH_2}$)$_4$$CH_2$O-), 3.9–4.2 (*m*, 8H, -O$\underline{CH_2}$-) and 6.9–8.2 (*m*, 19H, aromatic H). IR spectrum (KBr, $cm^{-1}$), 2978 (aliphatic C-H stretching), 2219 (C≡N stretching), 1750 (C=O stretching) and 1190 (C-O-C stretching).

## Characterization of LC Properties

Thermal properties of the compounds were studied by differential scanning calorimetry on a Perkin Elmer DSC 7 at the heating rate of 10°C/min. Optical textures were observed on a hot-stage (Mettler FP-82) with a central control system (Mettler FP-90) attached to a polarizing microscope

(Olympus, BH-2). X-ray diffraction measurements were performed in transmission mode with a Ni-filtered CuK$\alpha$ radiation (0.1542 nm) from a Rigaku Denki generator operating at 40 KV and 40 mA. The samples were held in an aluminum sample holder sealed with a window of 8 μm thick Kapton films on both sides. The sample holder was heated with two cartridge heaters and temperature was monitored by a thermocouple. Background scattering corrections were made by subtracting the scattered intensity from the Kapton windows.

## Acknowledgement

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