



Nematic phases in achiral unsymmetrical four-ring bent-core azo compounds possessing strongly polar cyano and nitro moieties as end substituents: Synthesis and characterization



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ABSTRACT

Achiral unsymmetrical four-ring bent-core liquid crystals with strongly polar cyano and nitro moieties as substituents at one end and alkyloxy group (butyl to dodecyl) at the other end have been synthesized by a simple and straight forward synthetic method. The four phenyl rings are connected through azo, ester and imine linkages respectively and bent unit is derived from 3-aminobenzoic acid with 2-methyl substituent in the transverse direction of the molecule. The molecular structure characterization is consistent with elemental and spectroscopic analysis data. The materials thermal behaviour and phase characterization have been investigated by differential scanning calorimetry and polarizing optical microscopy. All the compounds exhibit enantiotropic nematic phase over a wide temperature range. The light induced *cis–trans* isomerization is also discussed.

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1. Introduction

Bent-core or banana liquid crystals (BLCs) came into prominence in recent years due to their distinct properties viz., polar order, chirality, 2D splay modulated layer undulated phases etc. [1–7]. Most of these compounds consist of five or more aromatic rings and have in general higher transition temperatures. The attention had been focused to these BLCs exhibiting nematic phases with SmA or SmC type cybotactic clustered molecular arrangement (N_{CybA} or N_{CybA}) [8–16] and chiral nematic phases [17–19]. The recent observation of cluster picture of nematic phase [20] followed by the smectic layers in the nematic phase [21] made these class of materials exhibiting nematic phase is of special importance in BLCs. The search for ferroelectric switching in the nematic phases [14,15] as well as the biaxial characteristics [22] motivated further to synthesize new molecular systems exhibiting such nematic phases. However the bent-core molecules with five, six and seven aromatic ring compounds with different linking groups have been explored for the mesomorphism and most of these molecular structures are

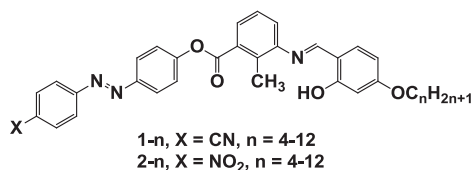
found to exhibit a variety of banana mesomorphic phases. In the last few years three and four-ring bent-core mesogens is a topical field [23,24] of bent-core liquid crystals. Recently we reported four-ring bent-core molecular structures [25–33] exhibiting banana phases, in particular polarization modulated layer undulated banana phases as well as nematic phases.

Azobenzene derivatives have found numerous applications in molecular devices such as prototype molecular switches, optical storage as trigger for protein folding etc and functional materials because of its photoisomerization properties [34–39]. The molecule when inserted with an azobenzene moiety can undergo *trans–cis* isomerization without detectable side reactions when irradiated with an appropriate wavelength in UV region. Similarly the reverse thermal *cis–trans* isomerization can be achieved spontaneously due to the formation of thermodynamically stable *trans* isomer in dark. Nematic phases are realized in symmetrical five-ring bent-core LCs with a lateral substituent in particular a cyano or chloro substituent in 4-position of the central phenyl ring [12,17,40]. Thus, in the present study to investigate the effect of a polar cyano or nitro substituent at one end of the four-ring bent-core LC consisting of an azobenzene group in the longer side arm and terminal alkoxy chains at the other end in the shorter side arm, we have synthesized two novel series of hockey-stick shaped bent molecules (see

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Fig. 1) derived from 2-methyl 3-amino benzoic acid as the central bent moiety. The methyl group at 2-position of the central phenyl unit make it possible not only to vary the bending angle but also disallow the formation of layered phases promoted by kinked structures. The compounds are (4'-cyanophenylazo) phenyl-4-yl 3-[N-(4'-n-alkoxy 2-hydroxy-benzylidene)amino]-2-methyl benzoate **1-n** ($n = 4$ to **12**) and (4'-nitrophenylazo) phenyl-4-yl 3-[N-(4'-n-alkoxy 2-hydroxybenzylidene)amino]-2-methyl benzoate, **2-n** ($n = 4$ to **12**).

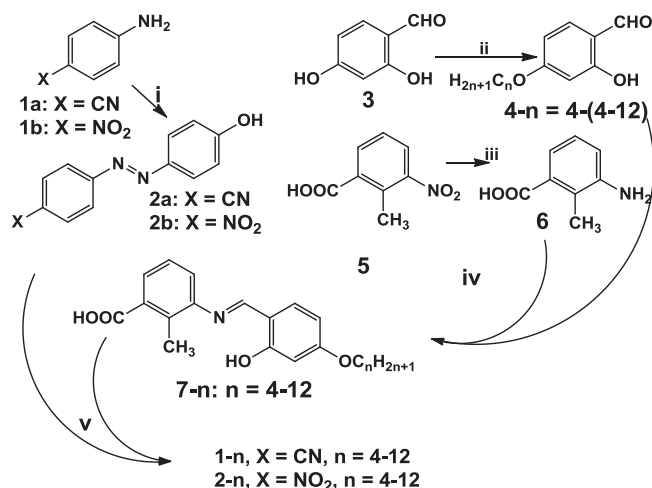


2. Experimental

All the chemicals were procured from M/s Alfa Aesar/Aldrich/Tokyo Kasei Kogyo Co. Ltd. The solvents and reagents are of AR grade and were distilled and dried before use. Micro analysis of C and H elements were determined on Perkin–Elmer 2400 elemental analyzer. IR spectra were recorded on Shimadzu IR Prestige-21, FTIR-8400S (ν_{\max} in cm^{-1}) on KBr disks. The ^1H nuclear magnetic resonance spectra were recorded on Bruker DPX-400 spectrometer in CDCl_3 (chemical shift δ in parts per million) solution with TMS as internal standard. The liquid crystalline properties were observed and characterized using polarizing microscope (Nikon optiphot-2-pol attached with hot and cold stage HCS402, with STC200 temperature controller configured for HCS402 from INSTEC Inc. USA). The phase transition temperatures and associated enthalpies were recorded on differential scanning calorimetry (Perkin–Elmer Pyris-1 system) with a heating/cooling rate of $5^\circ\text{C}/\text{min}$.

3. Synthetic procedures

All the homologues have been synthesized following the same procedure reported earlier [27]. 4-hydroxy 4'-cyano azobenzene, 4-hydroxy 4'-nitro azobenzene were synthesized using the appropriate starting materials following the procedure reported [27]. Similarly 4-n-alkoxy 2-hydroxy benzaldehyde i.e. (Scheme 1, alkoxy: $n = 4$ to **12**) have been synthesized using 2,4-dihydroxy



Scheme 1. Synthetic details of compounds **1-n**, **2-n**. Reagent and conditions: i. HCl, NaNO_2 , $0-5^\circ\text{C}$, Phenol, NaOH; ii. Dry acetone/ KHCO_3 , $\text{C}_n\text{H}_{2n+1}\text{Br}$; KI. iii. 5%Pd/C, H_2 , EtOAc stirring 48 h; iv. Abs EtOH, AcOH, Δ , 6 h; v. DCC, DMAP, DCM, stirring 48 h.

benzaldehyde, appropriate 1-bromoalkane, KHCO_3 , and catalytic amount of KI in dry acetone. 2-methyl 3-N-(4-n-alkoxy-salicylidene)amino benzoic acid (with alkyl group from butyl to dodecyl) was also synthesized by the condensation of 4-n-alkoxy salicylaldehyde and the 2-methyl 3-aminobenzoic acid similar to the reported pentyloxy homologue [27]. (4'-cyano phenyl azo) phenyl-4-yl 3-[N-(4'-n-alkoxy 2-hydroxybenzylidene)amino]-2-methyl benzoate **1-n** ($n = 4$ to **12**) and (4'-nitro phenyl azo) phenyl-4-yl 3-[N-(4'-n-alkoxy 2-hydroxybenzylidene)amino]-2-methyl benzoate, **2-n** ($n = 4$ to **12**) were synthesized using the DCC-DMAP esterification. The elemental analyses, ^1H NMR data are presented below.

1-4: 13.50 (s, ^1H , $-\text{OH}$), 8.45 (s, 1H, $-\text{CH}=\text{N}-$), 8.06 (dd, 2H, $J = 2.0\text{ Hz}, J = 8.8\text{ Hz}$, ArH), 8.01 (d, 3H, $J = 8.4\text{ Hz}$, ArH), 7.83 (dd, 2H, $J = 2.0\text{ Hz}, J = 8.4\text{ Hz}$, ArH), 7.43 (dd, 2H, $J = 2.0\text{ Hz}, J = 8.8\text{ Hz}$, ArH), 7.40 (t, 1H, $J = 7.6\text{ Hz}$, ArH), 7.30 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 6.52 (dd, 1H, $J = 2.4\text{ Hz}, J = 6.8\text{ Hz}$, ArH), 6.51 (d, 1H, $J = 2.4\text{ Hz}$, ArH), 4.02 (t, 2H, $J = 6.8\text{ Hz}$, $-\text{OCH}_2-$), 2.69 (s, 3H, Ar- CH_3), 1.82–1.48 (m, 4H, $-(\text{CH}_2)_2-$), 0.99 (t, 3H, $J = 6.4$ $-\text{CH}_3$). Elemental Analysis calculated for $\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_4$: C, 72.16; H, 5.30% Found: C, 71.88; H, 5.16%.

1-6: 13.48 (s, ^1H , $-\text{OH}$), 8.45 (s, 1H, $-\text{CH}=\text{N}-$), 8.06 (dd, 2H, $J = 2.0\text{ Hz}, J = 7.6\text{ Hz}$, ArH), 8.00 (dd, 3H, $J = 2.0\text{ Hz}, J = 8.8\text{ Hz}$, ArH), 7.83 (dd, 2H, $J = 2.0\text{ Hz}, J = 8.4\text{ Hz}$, ArH), 7.43 (dd, 2H, $J = 2.0\text{ Hz}, J = 7.2\text{ Hz}$, ArH), 7.40 (t, 1H, $J = 8.0\text{ Hz}$, ArH), 7.30 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 6.52 (dd, 1H, $J = 2.4\text{ Hz}, J = 7.6\text{ Hz}$, ArH), 6.51 (d, 1H, $J = 2.0\text{ Hz}$, ArH), 4.01 (t, 2H, $J = 6.8\text{ Hz}$, $-\text{OCH}_2-$), 2.69 (s, 3H, Ar- CH_3), 1.85–1.25 (m, 8H, $-(\text{CH}_2)_4-$), 0.89 (t, 3H, $J = 6.4$ $-\text{CH}_3$). Elemental Analysis calculated for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_4$: C, 72.84; H, 5.75% Found: C, 72.46; H, 5.68%.

1-7: 13.48 (s, ^1H , $-\text{OH}$), 8.45 (s, 1H, $-\text{CH}=\text{N}-$), 8.06 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 8.00 (d, 3H, $J = 8.4\text{ Hz}$, ArH), 7.83 (d, 2H, $J = 8.4\text{ Hz}$, ArH), 7.43 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 7.38 (t, 1H, $J = 8.0\text{ Hz}$, ArH), 7.30 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 6.53 (s, 1H, ArH), 6.51 (s, 1H, ArH), 4.01 (t, 2H, $J = 6.8\text{ Hz}$, $-\text{OCH}_2-$), 2.69 (s, 3H, Ar- CH_3), 1.82–1.27 (m, 10H, $-(\text{CH}_2)_5-$), 0.89 (t, 3H, $J = 6.4$ $-\text{CH}_3$). Elemental Analysis calculated for $\text{C}_{35}\text{H}_{34}\text{N}_4\text{O}_4$: C, 73.15; H, 5.96% Found: C, 72.99; H, 5.86%.

1-8: 13.49 (s, ^1H , $-\text{OH}$), 8.45 (s, 1H, $-\text{CH}=\text{N}-$), 8.07 (dd, 2H, $J = 2.0\text{ Hz}, J = 6.8\text{ Hz}$, ArH), 8.00 (dd, 3H, $J = 2.0\text{ Hz}, J = 8.4\text{ Hz}$, ArH), 7.83 (d, 2H, $J = 7.2\text{ Hz}$, ArH), 7.43 (dd, 2H, $J = 2.4\text{ Hz}, J = 8.8\text{ Hz}$, ArH), 7.39 (t, 1H, $J = 8.0\text{ Hz}$, ArH), 7.30 (d, 2H, $J = 8.8\text{ Hz}$, ArH), 6.53 (dd, 1H, $J = 2.4\text{ Hz}, J = 7.6\text{ Hz}$, ArH), 6.51 (d, 1H, $J = 2.0\text{ Hz}$, ArH), 4.01 (t, 2H, $J = 6.8\text{ Hz}$, $-\text{OCH}_2-$), 2.69 (s, 3H, Ar- CH_3), 1.82–1.27 (m, 12H, $-(\text{CH}_2)_6-$), 0.89 (t, 3H, $J = 6.4$ $-\text{CH}_3$). Elemental Analysis calculated for $\text{C}_{36}\text{H}_{36}\text{N}_4\text{O}_4$: C, 73.45; H, 6.16% Found: C, 73.12; H, 6.14%.

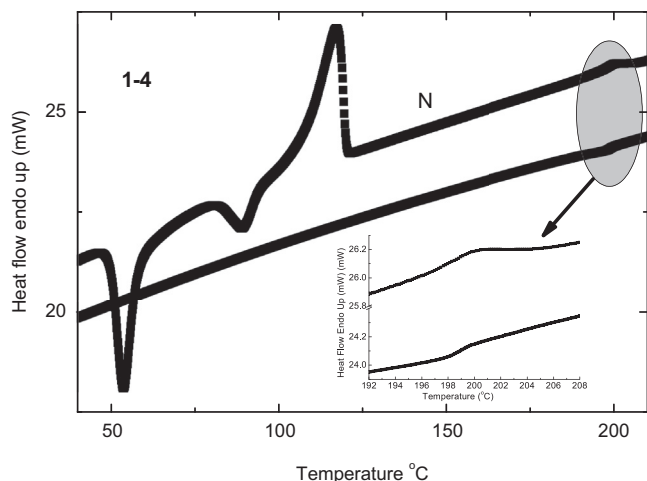


Fig. 1. DSC thermogram of 1–4 in the third heating and cooling cycle at $5^\circ\text{C}/\text{min}$.

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