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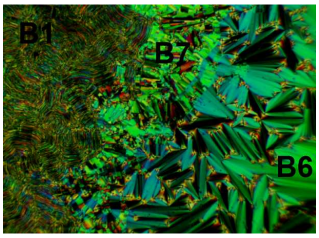

Novel bent-core mesogenic of 4-amino-triazole derivatives: synthesis, characterization and liquid crystalline study

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Abstract

The synthesis, characterization and mesomorphism of twelve new bent-shaped mesogens containing 4-amino-1,2,4-triazole as a central rigid core $(II)_n$ are reported. The amino triazole derivatives were characterized by ^1H, ^{13}C NMR spectroscopy, FT infrared, elemental analysis and one of them by mass spectrometry. The mesophase behavior was investigated using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The homologues with short alkoxy terminal groups $(II)_{a-d}$ do not show any mesomorphic properties and only crystal to isotropic transition was observed by POM, whilst the analogue with the longest alkoxy terminal groups $(II)_{e-l}$ exhibit enantiotropic S_mA, B_1, B_2, B_6 and B_7 phases with wide mesomorphic temperature ranges. The effect of the triazole ring and the length of the terminal alkoxy chains on the liquid crystals behavior of the compounds were discussed.

1. Introduction

The triazole ring, which has a five-membered ring of two carbon atoms and three nitrogen atoms, has two isomers, 1,2,3- and 1,2,4-triazole. Of these two types, the most important is 1,2,4-triazole. Substituted 1,2,4-triazoles and their derivatives are key skeletons of many biologically active molecules and important organic compounds.[1] They are in fact considered as the most important heterocycles among numerous five membered families. The electron-deficient nature and electron acceptors properties that are recognized in 1,2,4-triazoles have lead them to be excellent candidates used in many potential applications as organic and bio-active materials.[2]

Over the years, a long number of liquid crystalline compounds containing heterocyclic cores have been prepared.[3] The incorporation of heterocyclic moieties into the rigid core of thermotropic liquid crystals can result in large changes in their mesophases and physical properties, because they possess more polarizable heteroatoms, such as nitrogen, oxygen and sulfur atoms[4] Otherwise, heteroatoms may also participate in intermolecular interactions which are at the origin of mesomorphism thus affecting the type of mesophases.[5] The effect of non-linear shape, caused by a larger exocyclic angle, played an important key factor in generating mesophases. In general, the more linear molecules favored the appearance of liquid crystal phases, whereas, the more pronounced bent shapes proved detrimental to the mesomorphic phases.[6] Moreover, the incorporating of five-membered heteroaromatic rings into the center of the calamitic core results in a bent-shaped core.[7]

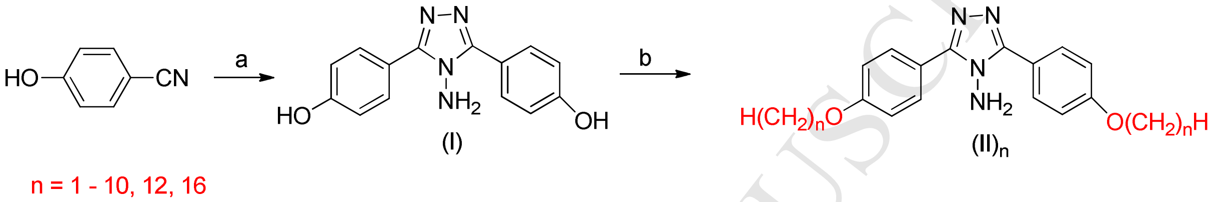
Banana-shaped molecules, also known as bent-shaped and/or bent-core molecules, have fascinated many researchers in the field of liquid crystal science.[8] In general; the mesophases formed by the banana-shaped compounds are termed as (Banana) (B_n) phases, designated as B_1-B_8 phases, the B_3 and B_4 phases are crystalline, while the others are mesomorphic.[9] Among these, the mysterious B_7 phase is well known for its beautiful and distinct polarized optical microscope textures such as myelinic, striped focal conic and checker board usually formed upon cooling from an isotropic liquid with varying temperature control.[8] Over the past decades, a large number of bent or banana-shaped compounds have been synthesized, and their mesophase behavior characterized. Most of these compounds contain five heteroaromatic rings which have been widely used as the central core.[10]

In the literature, 1,2,3-triazole derivatives exhibiting mesophases have been less often reported,[11] while we did not find any studies on liquid crystal properties of 4-amino-1,2,4-triazole as a bent central core. In the present paper, we describe the synthesis and mesomorphic properties of a novel series containing 4-amino-1,2,4-triazole as a central bent-core. S_mA, B_1, B_2, B_6 and B_7 phases were observed along the series of compounds $(II)_{e-l}$ with wide mesomorphic temperature ranges.

2. Results and Discussion

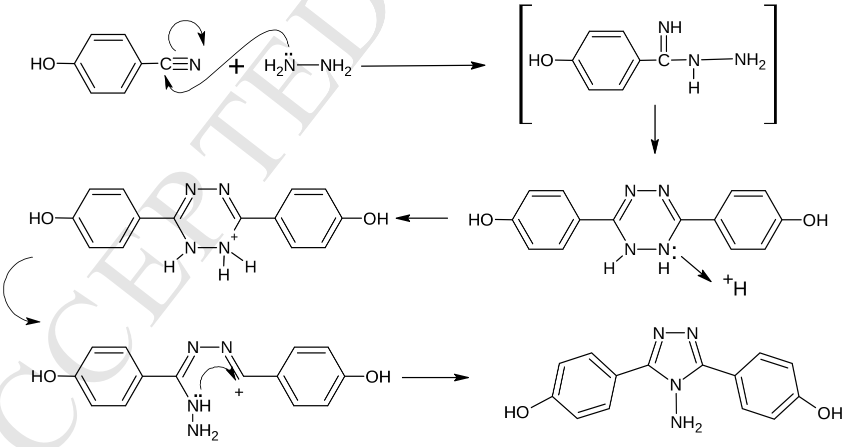
2.1. Synthesis

The synthetic route used for the synthesis of compounds $(II)_{a-l}$ is outlined in (Scheme 1).



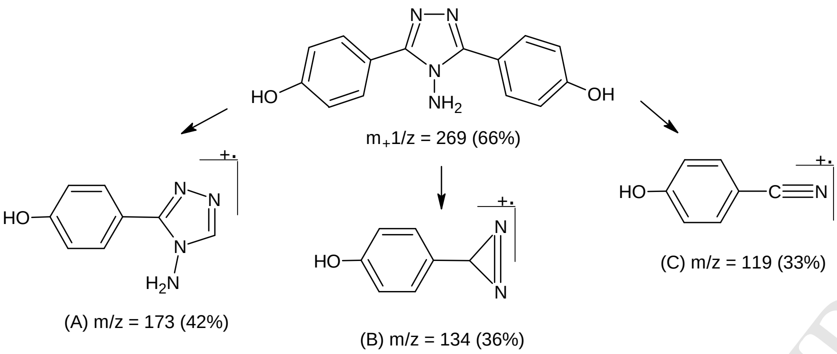
Scheme 1. Reactions and reagents: (a) hydrazine hydrate (3.0 equiv.), hydrazine hydrochloride (1.0 equiv.), stirred in ethylene glycol at 130 °C, 10 h, 84%; (b) n-alkyl bromide (2.0 equiv.), anhydrous potassium carbonate (2.0 equiv.), refluxing in dry acetone, 20 h, 72-89%.

4-Cyanophenol with hydrazine hydrate and hydrazine hydrochloride in ethylene glycol could be smoothly cyclized to afford the 3,5-di(4-hydroxyphenyl)-4-amino-1,2,4-triazole (I) in good yield. The mechanism[12] of the ring closing of 4-amino-1,2,4-triazole ring is described in (Scheme 2).



Scheme 2. The suggestion mechanism steps of compound (I).

The structure of this compound was confirmed by elemental analysis, mass spectrometry, FT IR, and ^1H NMR and ^{13}C NMR spectroscopy, and corresponds to the suggested structure of compound (I). In the mass spectrum, the molecular ion peak (m+1/z = 269) is prominent which corresponds to the molecular weight of the structure suggested to this compound. (Scheme 3) shows the fragmentation pattern of compound (I) and the ions (A, B and C) gives an excellent diagnostic for the 4-amino-1,2,4-triazole ring.[13]



Scheme 3. The fragmentation pattern of compound (I).

The compounds of series (II)$_n$ were synthesized by alkylation reaction of compound (I) with n-bromoalkanes in acetone in presence of anhydrous potassium carbonate. The structures of these compounds were confirmed by using elemental analysis, FT IR, and ^{1}H NMR and ^{13}C NMR spectroscopy, and are consistent with their proposed structures. The microanalytical data of carbon, hydrogen and nitrogen were formed to be satisfactory and within the permissible limit error. The disappearance of the peak at δ 9.99 ppm in compound (I), assigned to the phenolic hydroxyl group and appearance the peaks of alkyl groups (-CH$_3$, -CH$_2$- and -OCH$_2$-) in compounds (II)$_{a-l}$ are good conformation that the alkylation reaction occurred.

2.2. Mesomorphic properties of compounds (II)$_{a-l}$

The mesomorphic behavior of compounds (II)$_{a-l}$ was studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

2.2.1. DSC studies

The differential scanning calorimetry (DSC) was used to determine the phase transition temperatures (T/° C), phase transition enthalpy changes (ΔH/ KJ.mol^{-1}) and entropies (ΔS/ J.mole^{-1}.K^{-1}). The transition temperatures from first heating and cooling scans for all compounds have been collected in Table 1.

Table 1. Phase transition temperatures (T/° C), phase transition enthalpy changes (ΔH/ KJ.mol^{-1}) and entropies (ΔS/ J.mole^{-1}.K^{-1}) of the compounds (II)$_{a-l}$ in the first heating and cooling cycles.

Compound	**n**	**Phase transitions T °C (ΔH/ KJ.mol^{-1}) [ΔS/ J.mole^{-1}.K^{-1}] on first heating**	**Phase transitions T °C (ΔH/ KJ.mol^{-1}) [ΔS/ J.mole^{-1}.K^{-1}] on first cooling**
(II)$_a$	1	Cr-I^a > 300	-
(II)$_b$	2	Cr-I^a 289	-
(II)$_c$	3	Cr-I^a 281	-
(II)$_d$	4	Cr-I^a 276	-
(II)$_e$	5	Cr-B$_2$ 145.45 (13.31) [31.37] B$_2$-S$_m$A 215.20 (11.41) [23.37] S$_m$A-I^a 270	I-S$_m$A^a 267 S$_m$A-B$_2$ 205.35 (-11.90) [-24.89] B$_2$-Cr 125.65 (-11.12) [-27.88]
(II)$_f$	6	Cr-B$_2$ 147.00 (10.88) [25.90] B$_2$-S$_m$A 203.35 (11.18) [23.46] S$_m$A-I^a 261	I-S$_m$A^a 255 S$_m$A-B$_2$ 192.90 (-8.76) [-18.80] B$_2$-Cr 128.70 (-11.79) [-29.36]
(II)$_g$	7	Cr-B$_2$ 149.40 (18.82) [44.56] B$_2$-S$_m$A 187.85 (12.92) [28.03] S$_m$A-I^a 256	I-S$_m$A^a 244 S$_m$A-B$_2$ 175.00 (-8.25) [-18.42] B$_2$-Cr 120.85 (-23.29) [-59.13]
(II)$_h$	8	Cr-B$_1$ 148.80 (21.56) [51.12] B$_1$-B$_6$ 192.80 (12.54) [26.92] B$_6$-I^a 255	I-B$_6$^{a} 243 B$_6$-B$_7$ and B$_7$-B$_1$ 182.85 (-7.60) [-16.68] B$_1$-Cr 124.35 (-18.44) [-46.41]
(II)$_i$	9	Cr-B$_1$ 146.30 (13.24) [31.58] B$_1$-B$_6$ 165.85 (4.83) [10.99] B$_6$-I^a 253	I-B$_6$^{a} 241 B$_6$-B$_7$ and B$_7$-B$_1$ 176.25 (-4.97) [-11.85] B$_1$-Cr 124.05 (-17.08) [-43.01]
(II)$_j$	10	Cr-B$_1$ 145.15 (30.35) [72.59] B$_1$-B$_6$ 183.90 (11.07) [24.24] B$_6$-I^a 250	I-B$_6$^{a} 239 B$_6$-B$_7$ and B$_7$-B$_1$ 167.81 (-6.63) [-15.71] B$_1$-Cr 124.15 (-29.72) [-74.84]
(II)$_k$	12	Cr-B$_1$ 147.15 (37.09) [88.27] B$_1$-B$_6$ 178.95 (10.60) [23.45] B$_6$-I^a 241	I-B$_6$^{a} 233 B$_6$-B$_7$ and B$_7$-B$_1$167.85 (-8.73) [-19.82] B$_1$-Cr$_3$ 132.62 (-2.32) [-5.73] Cr$_3$-Cr$_2$ 123.90 (-6.29) [-15.85] Cr$_2$-Cr$_1$ 114.80 (-4.85) [-12.49]
(II)$_l$	16	Cr$_1$-Cr$_2$ 132.25 (2.49) [6.14] Cr$_2$-B$_1$ 145.80 (37.48) [89.49] B$_1$-B$_7$ 153.05 (2.02) [4.75] B$_7$-B$_6$ 168.70 (10.61) [24.01] B$_6$-I^a 220	I-B$_6$^{a} 215 B$_6$-B$_7$ and B$_7$-B$_1$160.50 (-8.13) [-18.76] B$_1$-Cr$_2$ 135.40 (-2.20) [-5.39] Cr$_2$-Cr$_1$ 127.25 (-46.04) [-115.03]

Abbreviations: Cr, Cr$_1$, Cr$_2$ = crystal phase; S$_m$A = smectic A phase; B$_1$, B$_2$, B$_6$ and B$_7$ = Banana phase; I = isotropic phase; a = data from POM.

The first four homologues (II)$_{a-d}$ exhibit no mesomorphic phase, and only crystal to isotropic liquid transition was observed on POM perhaps due to the short alkoxy terminal groups which cause the higher melting points and thus suppress the liquid crystal phases. The others (II)$_{e-l}$ with n = 5-10, 12 and 16 exhibit an enantiotropic LC phase and the mesomorphic temperature range tends to become wider with increasing alkoxy chain length. An increase in terminal length is often helpful to enhance dipole-dipole interaction between the terminal chains and facilitate the formation of a mesophase.[14]

The DSC thermographs of compounds (II)$_{e-k}$ show only two transitions on first heating (Cr-B$_2$ and B$_2$-S$_m$A) for homologues (II)$_{e-g}$ and (Cr-B$_1$ and B$_1$-B$_6$) for homologues (II)$_{h-k}$ while the homologue (II)$_l$ exhibit four transitions on heating (Cr$_1$-Cr$_2$, Cr$_2$-B$_1$, B$_1$-B$_7$ and B$_7$-B$_6$). The liquid crystal to isotropic transition (LC-I) in DSC thermograms of compounds $(II)_{e-l}$ did not show because it cannot heated the compounds higher than the isotropic phase due to the decomposition and this is the loss of liquid crystalline phases that appears on cooling. The transitions (LC-I) of all compound $(II)_{e-l}$ were observed on POM.

On first cooling from the isotropic phase, the compounds $(II)_{e-g}$ showed only two transitions in the DSC thermographs which corresponding to S_mA-B_2 and B_2-Cr transitions. Furthermore, more than two peaks were found in the DSC thermographs on first cooling the isotropic melts of compounds $(II)_{h-l}$, corresponding to different B phase transitions, (Table 1). Therefore, all compounds of this series show enantiotropic behavior, Figure 1 and 2 shows the DSC thermographs of some compounds as representative examples of series $(II)_{e-l}$.

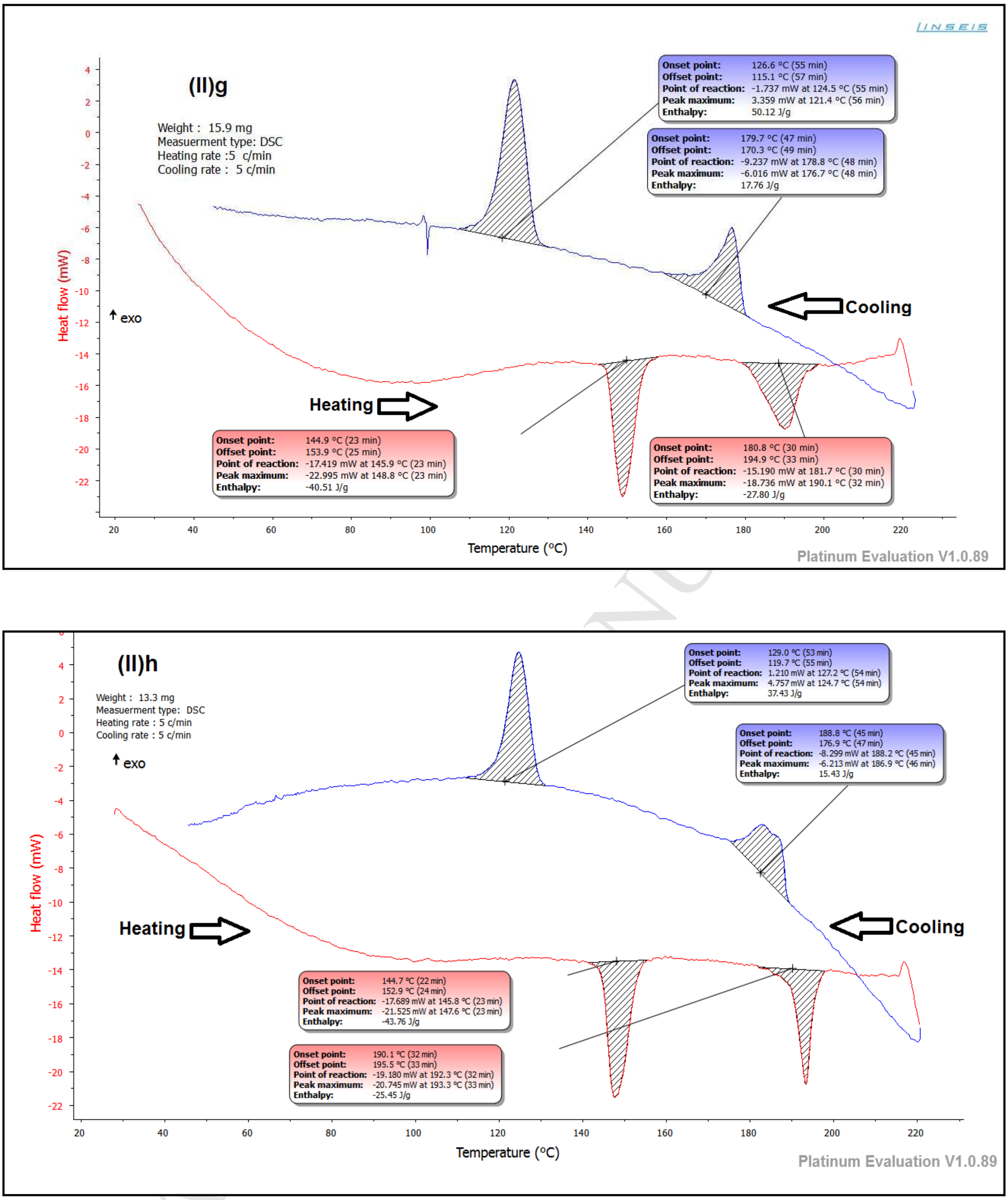


Figure 1. (Color online) DSC thermograms for compounds **(II)**$_g$ and **(II)**$_h$ on first heating and cooling scans.

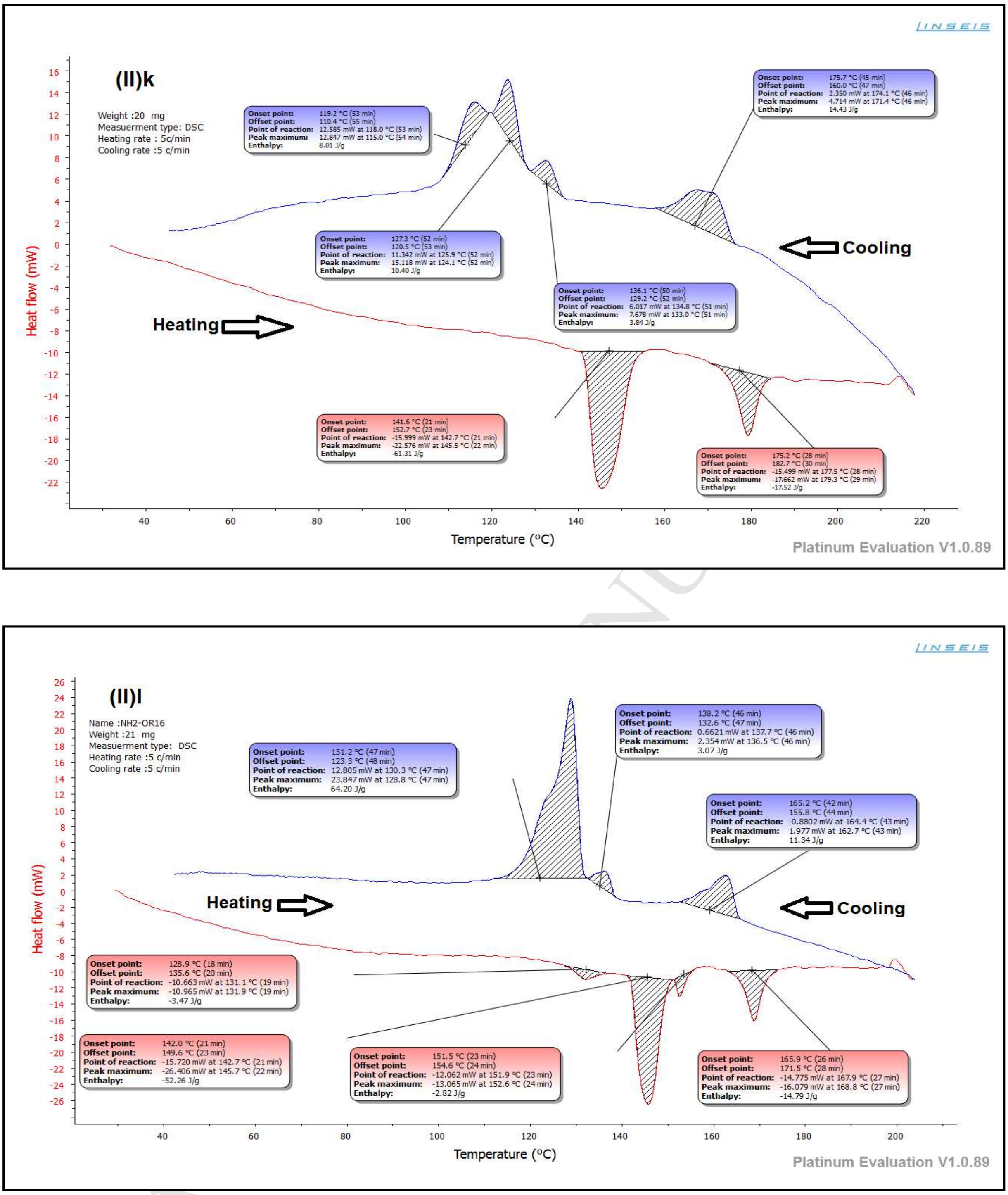
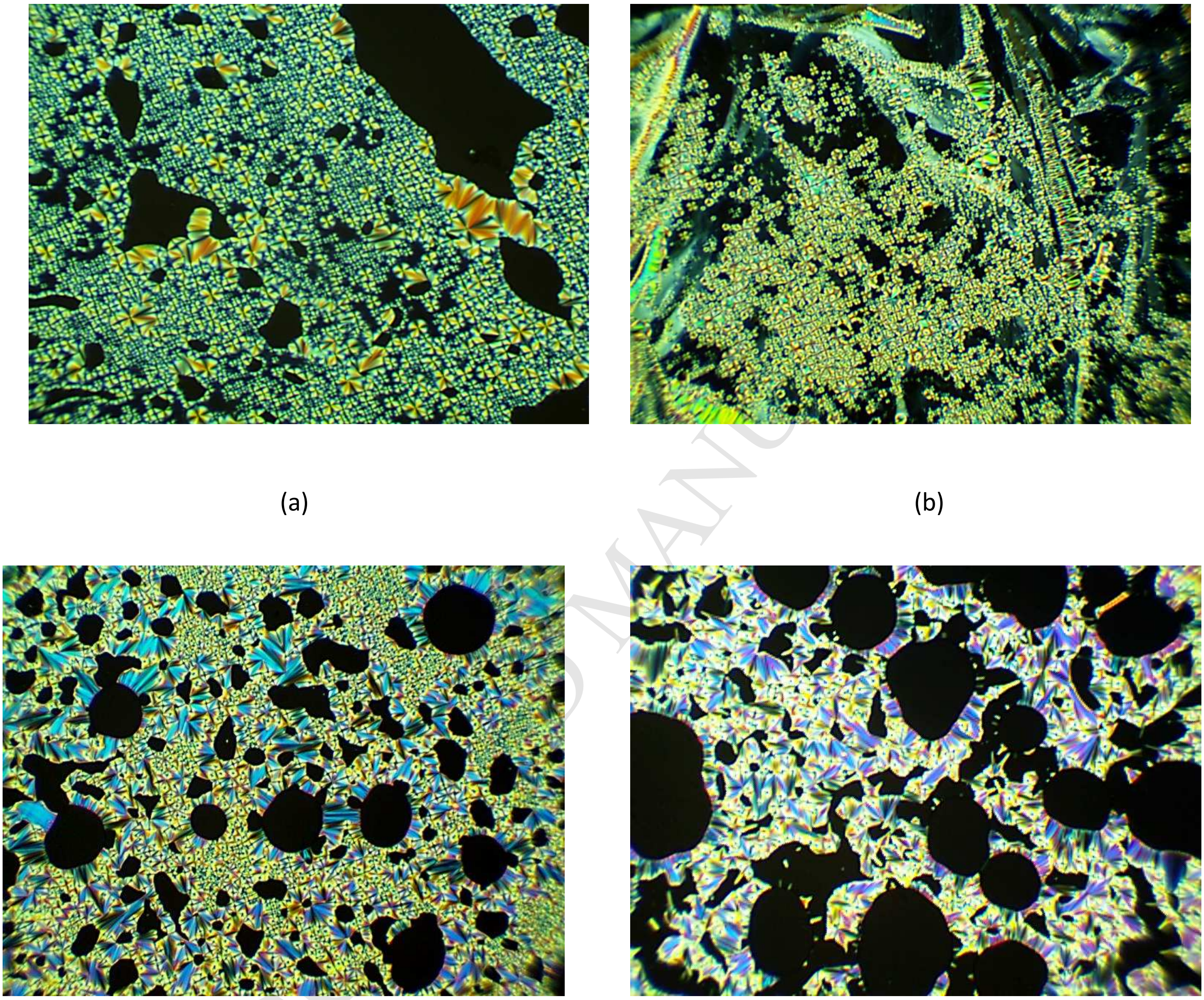


Figure 2. (Color online) DSC thermograms for compounds **(II)$_k$** and **(II)$_l$** on first heating and cooling scans.

2.2.2. POM studies

Under the polarizing microscope, upon heating, a focal conic like texture of B_2 phase and fan-shaped texture of S_mA phase were observed in compounds $(II)_{e\text{-}g}$ with a shorter terminal chain (n = 5-7). The B_2 phase of compounds (II)$_e$ and (II)$_f$ are shown in Figure 3$_a$ and 3$_b$, Figure 3$_d$ and 3$_e$ taken at 234 °C and 236 °C possesses a mixture of B_2 phase and fan-shaped of S_mA phase in compounds (II)$_f$ and (II)$_g$ respectively.

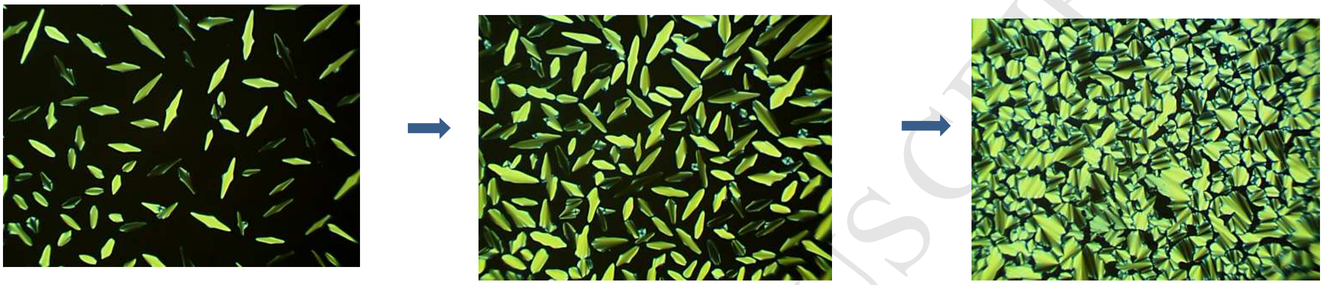


(a) (b)

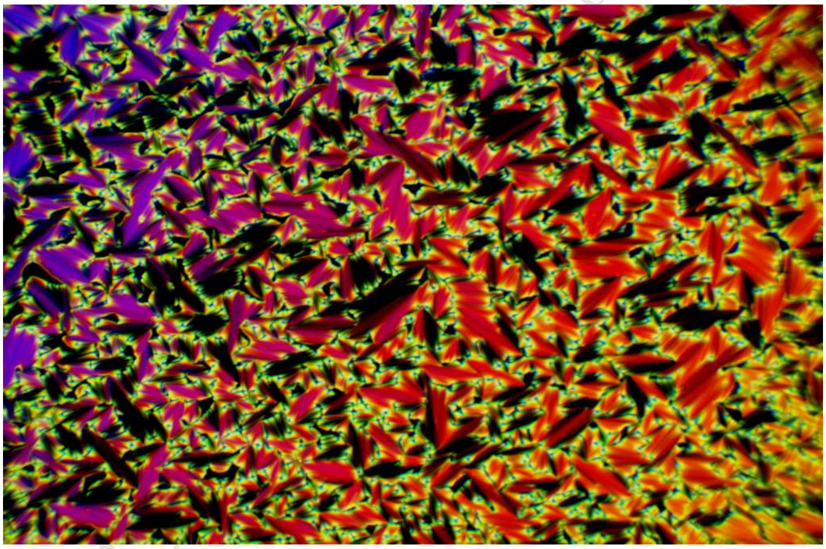
(c) (d)

Figure 3. (Color online) Photomicrographs of (a) the focal conic like texture of the B_2 phase at 166 °C on heating for compound **(II)$_e$**, (b) the focal conic like texture of the B_2 phase at 191 °C on heating for compound **(II)$_f$**, (c) a mixture of B_2 phase and fan-shaped of S_mA phase in compounds **(II)$_f$** on heating at 234 °C, (d) a mixture of B_2 phase and fan-shaped of S_mA phase in compounds **(II)$_g$** on heating at 236 °C (33x).

When cooling from isotropic phase of compounds (II)$_{e-g}$, a fan-shaped texture of S$_m$A phase appeared. Also, the B$_2$ phase was easily observed under optical polarized microscope. Figure, 4$_{a-c}$ shows the growth of the fan-shaped texture from isotropic melt of compound (II)$_e$ and Figure 4$_d$ shows the S$_m$A phase from cooling the isotropic phase of compound (II)$_f$ at 223 °C.



(a) 290 °C (b) 273 °C (c) 255 °C



(d)

Figure 4. (Color online) (a-c) Growth of a fan-shaped texture upon cooling of the isotropic liquid of compound **(II)$_e$** and (d) S$_m$A phase from cooling the isotropic phase of compound **(II)$_f$** at 223 °C

On increasing the terminal alkyl chain length to n = 8-10, 12 and 16 atoms in compounds (II)$_{h-l}$, B$_1$, B$_6$ and B$_7$ phases appeared on heating and cooling. These mesomorphisms were strongly dependent on the number and length of the terminal alkyl chains. Increasing the carbon length often enhanced van der Waals forces between the alkoxy chains, leading to the formation of more types of B phase. When the alkoxy chain length is increased, the evolution of the isotropic temperatures as well as of the phase sequence strongly depends on the series of banana materials. With a varing of the carbon atoms (n) in the terminal chains, the temperatures can regularly decrease:

this is the case of the $(II)_n$ series, where a S_mA phase exists in the whole series and a B phases sequence is observed for long chains.

Under an optical microscope, on heating, the compound $(II)_h$ exhibited two phases only, B_1 at 152 °C and B_6 at 201 °C then converted to isotropic melt at 262 °C, while on cooling, three phases were observed (B_1, B_6 and B_7). When the second cooling of compound $(II)_h$ from the isotropic melt to the temperature between 188-205 °C, three liquid crystalline phases overlapping with each others were observed (B_1, B_6 and B_7). In the DSC thermogram of this compound, we found that there is a broad peak (not completely separate) between 177-189 °C that was attributed to these transitions. The mesophase assignments according to the POM observations of compound $(II)_h$ are in good agreement with the corresponding DSC thermograph. Figure 5 shows the DSC thermogram and the textures of this compound. The remaining compounds of this series (II_{i-l}) showed similar behavior to the compound $(II)_h$. Figure 6 shows some polarizing optical photomicrographs of compounds $(II)_{i-l}$ on heating and cooling. Also, only three compounds of this series $(II)_e$, $(II)_f$ and $(II)_g$ showed a S_mA phase in POM on heating, while only B phases appeared in other compounds $(II)_{h-l}$. This was similar when cooling the isotropic melt of these compounds on POM.

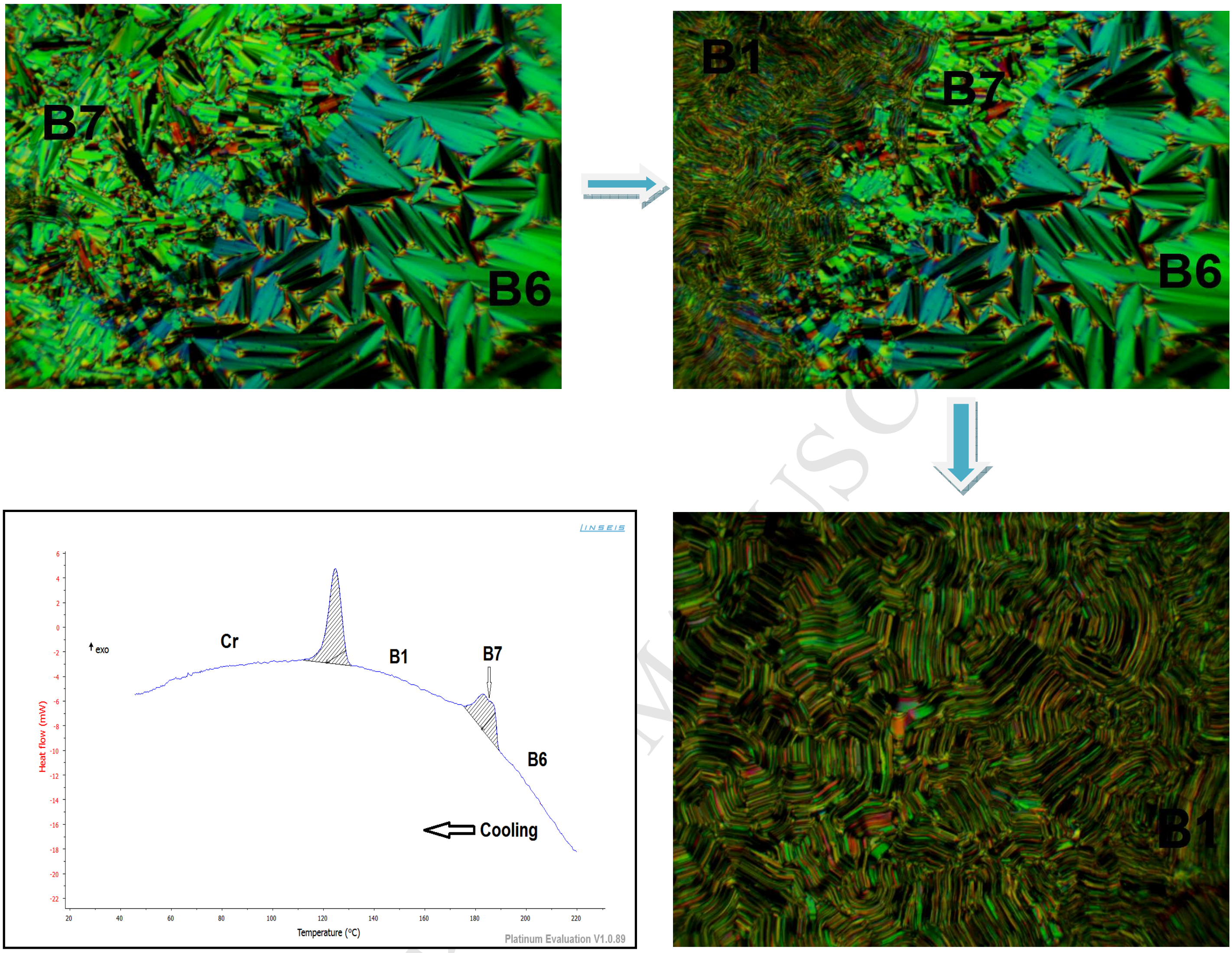
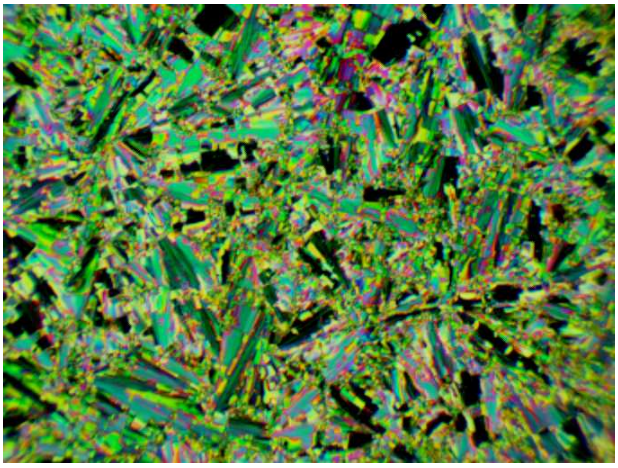
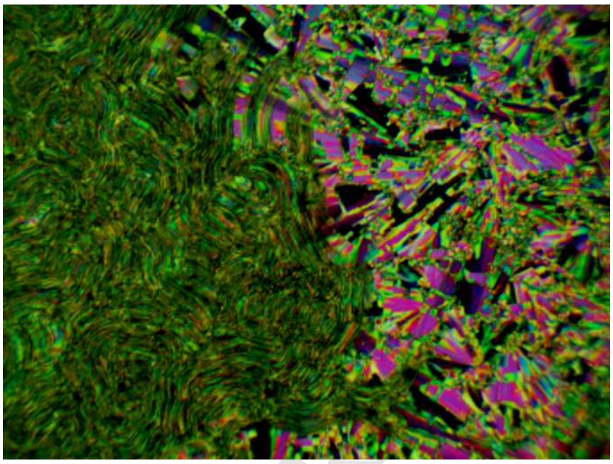


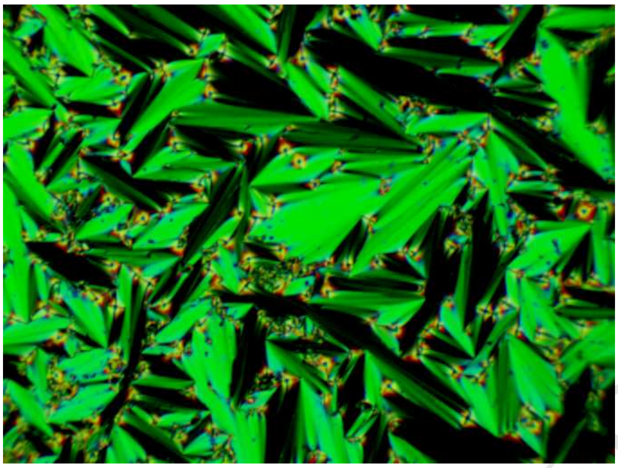
Figure 5. (Color online) Photomicrographs of the transitions between three phases (B_1, B_6 and B_7) on second cooling from isotropic at the range 188-205 °C (33x) and DSC thermogram of compound **(II)$_h$**.



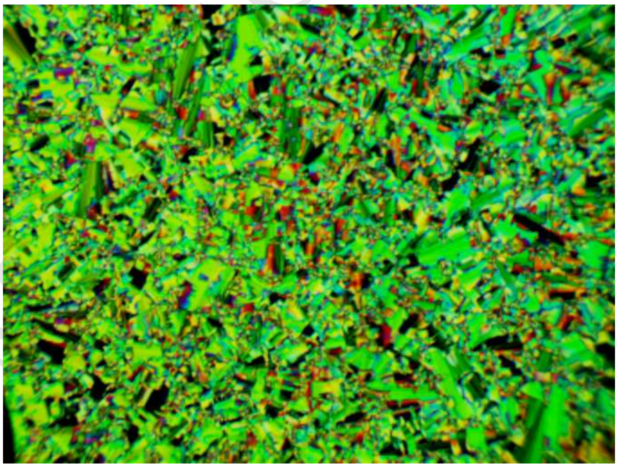
(a)



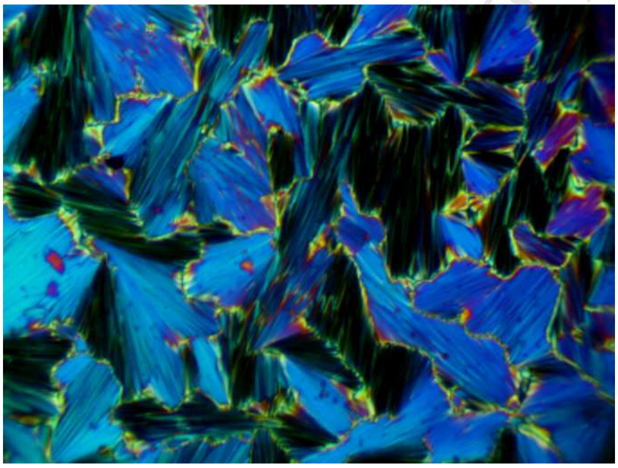
(b)



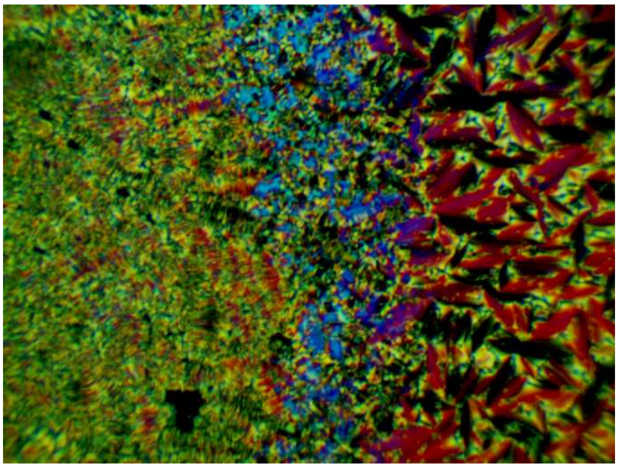
(c)



(d)



(e)



(f)

Figure 6. (Color online) Photomicrographs of (a) B_7 texture at 183 °C on second cooling for compound **(II)$_j$**, (b) B_7 and B_1 textures at the range 185-190 °C on second cooling for compound **(II)$_j$**, (c) B_6 texture at 232 °C on second cooling for compound **(II)$_j$**, (d) B_7 texture at 174 °C on second cooling for compound **(II)$_k$**, (e) B_6 texture at 227 °C on third heating for compound **(II)$_k$**, (f) B_1, B_6 and B_7 textures at the range 175-167 °C on second cooling for compound **(II)$_l$** (33x).

The L.C phase's stabilising of mesomorphic compounds is dependent mainly on the intermolecular interactions, in which molecular polarizibility, polarity and electronic factors play an important role.[15] In this research, the amino group in the 1,2,4-triazole ring plays an important role in the liquid crystalline phases of compounds (II)$_e$ – (II)$_l$. The intermolecular hydrogen bonding of the amino group in the heterocyclic ring[16-17] makes the distances between the molecules less; therefore the ease of packing in the mesomorphic state is more effective. The hydrogen bonding effect in this case is responsible for formation of the S_mA and B phases. Figure 7 show the schematic representation of the H-bonded amino triazole moiety in this homologues.

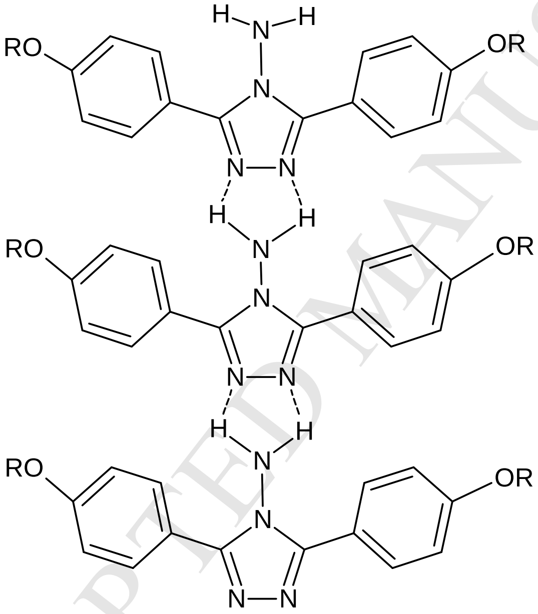


Figure 7. The schematic representation of H-bonded amino triazole moiety in the series **(II)$_n$**.

3. Conclusion

The new derivatives containing the 4-amino-1,3,4-triazole moiety in the center of the molecule were prepared by a cyclization reaction of 4-cyanophenol in the presence of hydrazine hydrate and hydrazine hydrochloride. The structure of all synthesized compounds was confirmed by ^{1}H and ^{13}C NMR, and FTIR spectroscopy and CHN analysis methods. The mesomorphic properties of these compounds were studied by DSC and POM. The effects of heterocycle and the length of alkoxy chains on the mesomorphic behavior were systematically studied. Most compounds exhibit SmA and different B mesophases. Compounds with shorter alkoxy chains (n = 1-4) did not show any liquid crystalline properties. The increase of the mesogenic length causes increase in the existence range of the smectic A mesophase, in favor of a new B mesophase.

4. Experimental

4.1. Characterization

All the chemicals used were procured from Sigma-Aldrich, and used without further purification. Melting points were determined on electrothermal capillary apparatus and are uncorrected. Elemental analysis for carbon, hydrogen and nitrogen were conducted using a Perkin-Elmer model 2400 instrument. FT-IR spectra of solid samples using the ATR technique was recorded on a Shimadzu 8400S. ^{1}H and ^{13}C NMR spectra were measured on a Bruker spectrometer model Ultra-Shield at 300 MHz using DMSO-*d6* as a solvent for all compounds and TMS as internal reference standard. Mass spectrum of compound (I) was recorded on a Shimadzu QP1000EX using the electron impact (EI) method. DSC thermographs were carried out on a Linseis instrument STA PT-1000, Ramp rate: 5 °C/ min. on heating and cooling, temperature and heat flow calibrated with standard indium. POM was carried out on a microscope model PW-BK 5000 PR equipped with a hot-stage system of HS-400 (KER 3100-08S).

4.2. Synthesis

4.2.1. 3,5-Di(4-hydroxyphenyl)-4-amino-1,2,4-triazole (I)

This compound was prepared according to the procedure that described by Wang.[18] A mixture of 4-cyanophenol (11.9 g, 0.1 mol), hydrazine dihydrochloride (10.5 g, 0.1 mol) and hydrazine hydrate (15 g, 0.3 mol) in (75 ml) ethylene glycol was heated to reflux at 130 °C for 10 h. After cooling to room temperature, the reaction mixture was diluted with (250 ml) water. The precipitate thus obtained was filtered off, washed with water, dried and recrystallized from methanol as a white powder. Yield: 84%, mp 296-297 °C (lit. 296 °C).[19] FTIR (ATR, cm^{-1}), υ_{max}: (3319, 3205, N-H, NH_2), (3110, O-H), (1610, C=N). ^{1}H NMR ($DMSO_{d6}$), δ, ppm: 9.99 (s, 2H, br, 2OH), 7.84 (d, *J* = 7.2 H_z, 4H, Ar-H), 6.90 (d, *J* = 7.1 H_z, 4H, Ar-H), 6.11 (s, 2H, NH_2). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 158.6, 153.9, 129.7, 127.5, 118.1, 115.5, 115.1. MS (EI) (relative intensity %): m/z = 269 (M^++1, 38%). Elemental analysis: calculated for $C_{14}H_{12}N_4O_2$ (268.27 g/mol): C 62.68, H 4.51, N 20.88., found C 62.63, H 4.48, N 20.84.

4.2.2. 3,5-Di(4-alkoxyphenyl)-4-amino-1,2,4-triazole $(II)_{a\text{-}l}$

A mixture of compound I (2.68 g, 0.01 mol) and anhydrous potassium carbonate (3.32 g, 0.04 mol) was suspended in acetone (50 ml). The relevant n-alkyl bromide (0.024 mol) was added to the mixture and refluxed for 20 h. After cooling, the mixture was added to ice-cold water. The crude solid product was filtered, washed with 5% aqueous sodium bicarbonate solution and with water several times. The white products obtained were dried and recrystallized from ethanol.

4.2.2.1. 3,5-Di(4-methoxyphenyl)-4-amino-1,2,4-triazole $(II)_a$

Yield: 88%, mp 279-281 °C. FTIR (ATR, cm^{-1}), υ_{max}: (3302, 3180, N-H, NH_2), (2933, 2839, aliph. C-H), (1614, C=N). ^{1}H NMR ($DMSO_{d6}$), δ, ppm: 7.99 (d, *J* = 6.9 H_z, 4H, Ar-H), 7.08 (d, *J* = 6.9 H_z, 4H, Ar-H), 6.14 (s, 2H, NH_2), 3.83 (s, 6H, $2OCH_3$). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 160.2, 152.9, 129.5, 129.6, 119.5, 113.7, 113.8, 55.3. Elemental analysis: calculated for $C_{16}H_{16}N_4O_2$ (296.32 g/mol): C 64.85, H 5.44, N 18.91., found C 64.67, H 5.37, N 18.77.

4.2.2.2. 3,5-Di(4-ethoxyphenyl)-4-amino-1,2,4-triazole $(II)_b$

Yield: 87%, mp 277-278 °C. FTIR (ATR, cm^{-1}), υ_{max}: (3333, 3163, N-H, NH_2), (2978, 2929, 2879, aliph. C-H), (1612, C=N). ^{1}H NMR ($DMSO_{d6}$), δ, ppm: 7.96 (d, *J* = 7.1 H_z, 4H, Ar-H), 7.07 (d, *J* = 7.2 H_z, 4H, Ar-H), 6.16 (s, 2H, NH_2), 4.15 (qt, 4H, $2OCH_2$), 1.37 (t, 6H, $2CH_3$). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 159.7, 153.7, 130.1, 129.6, 119.6, 114.7, 114.3, 63.3, 14.6. Elemental analysis: calculated for $C_{18}H_{20}N_4O_2$ (324.38 g/mol): C 66.65, H 6.21, N 17.27., found C 66.56, H 6.19, N 17.21.

4.2.2.3. 3,5-Di(4-propoxyphenyl)-4-amino-1,2,4-triazole (II)$_c$

Yield: 81%, mp 274-277 °C. FTIR (ATR, cm^{-1}), υ_{max}: (3338, 3157, N-H, NH_2), (2966, 2939, 2875, aliph. C-H), (1610, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.95 (d, *J* = 6.9 H$_z$, 4H, Ar-H), 7.08 (d, *J* = 6.9 H$_z$, 4H, Ar-H), 6.15 (s, 2H, NH_2), 4.01 (t, 4H, 2OCH$_2$), 1.76 (m, 4H, 2CH$_2$), 1.00 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.6, 153.7, 130.1, 129.6, 128.9, 119.6, 114.7, 114.3, 69.1, 20.9, 10.31. Elemental analysis: calculated for $C_{20}H_{24}N_4O_2$ (352.43 g/mol): C 68.16, H 6.86, N 15.90., found C 68.10, H 6.81, N 15.81.

4.2.2.4. 3,5-Di(4-butoxyphenyl)-4-amino-1,2,4-triazole (II)$_d$

Yield: 89%, mp 272-273 °C. FTIR (ATR, cm^{-1}), υ_{max}: (3354, 3153, N-H, NH_2), (2953, 2870, aliph. C-H), (1612, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.98 (d, *J* = 7.0 H$_z$, 4H, Ar-H), 7.06 (d, *J* = 7.1 H$_z$, 4H, Ar-H), 6.16 (s, 2H, NH_2), 4.03 (t, 4H, 2OCH$_2$), 1.72 (m, 4H, 2CH$_2$), 1.46 (m, 4H, 2CH$_2$), 0.94 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.6, 153.8, 129.9, 129.6, 119.4, 115.4, 114.5, 67.3, 30.7, 18.6, 10.31. Elemental analysis: calculated for $C_{22}H_{28}N_4O_2$ (380.48 g/mol): C 69.45, H 7.42, N 14.73., found C 69.38, H 7.29, N 14.59.

4.2.2.5. 3,5-Di(4-pentyloxyphenyl)-4-amino-1,2,4-triazole (II)$_e$

Yield: 82%. FTIR (ATR, cm^{-1}), υ_{max}: (3354, 3167, N-H, NH_2), (2956, 2937, 2868, aliph. C-H), (1614, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.94 (d, *J* = 8.3 H$_z$, 4H, Ar-H), 7.07 (d, *J* = 8.3 H$_z$, 4H, Ar-H), 6.17 (s, 2H, NH_2), 4.04 (t, 4H, 2OCH$_2$), 1.74 (m, 4H, 2CH$_2$), 1.39 (m, 8H, 4CH$_2$), 0.92 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.5, 153.6, 129.6, 129.5, 119.1, 114.9, 114.6, 69.1, 29.9, 28.5, 20.6, 13.8. Elemental analysis: calculated for $C_{24}H_{32}N_4O_2$ (408.54 g/mol): C 70.56, H 7.90, N 13.71., found C 70.49, H 7.83, N 13.69.

4.2.2.6. 3,5-Di(4-hexyloxyphenyl)-4-amino-1,2,4-triazole (II)$_f$

Yield: 79%. FTIR (ATR, cm^{-1}), υ_{max}: (3340, 3151, N-H, NH_2), (2953, 2935, 2864, aliph. C-H), (1612, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.91 (d, *J* = 8.4 H$_z$, 4H, Ar-H), 7.05 (d, *J* = 8.3 H$_z$, 4H, Ar-H), 6.14 (s, 2H, NH_2), 4.02 (t, 4H, 2OCH$_2$), 1.72 (m, 4H, 2CH$_2$), 1.38-1.30 (m, 12H, 6CH$_2$), 0.86 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.6, 153.7, 130.1, 129.6, 119.4, 115.1, 114.6, 67.5, 31.8, 28.5, 24.4, 22.6, 13.7. Elemental analysis: calculated for $C_{26}H_{36}N_4O_2$ (436.59 g/mol): C 71.53, H 8.31, N 12.83., found C 71.43, H 8.22, N 12.77.

4.2.2.7. 3,5-Di(4-heptyloxyphenyl)-4-amino-1,2,4-triazole (II)$_g$

Yield: 86%. FTIR (ATR, cm^{-1}), υ_{max}: (3354, 3149, N-H, NH_2), (2955, 2929, 2862, aliph. C-H), (1614, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.94 (d, *J* = 8.6 H$_z$, 4H, Ar-H), 7.07 (d, *J* = 8.6 H$_z$, 4H, Ar-H), 6.16 (s, 2H, NH_2), 4.03 (t, 4H, 2OCH$_2$), 1.74 (m, 4H, 2CH$_2$), 1.43-1.30 (m, 16H, 8CH$_2$), 0.87 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.4, 153.6, 129.9, 129.3, 119.6, 115.1, 114.3, 66.6, 31.2, 28.6, 28.4, 25.4, 22.0, 13.9. Elemental analysis: calculated for $C_{28}H_{40}N_4O_2$ (464.64 g/mol): C 72.38, H 8.68, N 12.06., found C 72.29, H 8.55, N 11.98.

4.2.2.8. 3,5-Di(4-octyloxyphenyl)-4-amino-1,2,4-triazole (II)$_h$

Yield: 74%. FTIR (ATR, cm^{-1}), υ_{max}: (3355, 3157, N-H, NH_2), (2955, 2920, 2854, aliph. C-H), (1614, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.93 (d, *J* = 8.5 H$_z$, 4H, Ar-H), 7.06 (d, *J* = 8.5 H$_z$, 4H, Ar-H), 6.16 (s, 2H, NH_2), 4.02 (t, 4H, 2OCH$_2$), 1.76 (m, 4H, 2CH$_2$), 1.42-1.28 (m, 20H, 10CH$_2$), 0.86 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.8, 155.2, 130.1, 129.7, 119.6, 115.3, 114.7, 68.8, 31.7, 28.7, 28.2, 25.4, 23.3, 22.4, 13.3. Elemental analysis: calculated for $C_{30}H_{44}N_4O_2$ (492.70 g/mol): C 73.13, H 9.00, N 11.37., found C 73.06, H 8.89, N 11.28.

4.2.2.9. 3,5-Di(4-nonyloxyphenyl)-4-amino-1,2,4-triazole (II)$_i$

Yield: 77%. FTIR (ATR, cm^{-1}), υ_{max}: (3352, 3169, N-H, NH_2), (2955, 2918, 2850, aliph. C-H), (1612, C=N). ^{1}H NMR (DMSO$_{d6}$), δ, ppm: 7.95 (d, *J* = 8.4 H$_z$, 4H, Ar-H), 7.05 (d, *J* = 8.4 H$_z$, 4H, Ar-H), 6.15 (s, 2H, NH_2), 4.03 (t, 4H, 2OCH$_2$), 1.75 (m, 4H, 2CH$_2$), 1.41-1.30 (m, 24H, 12CH$_2$), 0.85 (t, 6H, 2CH$_3$). ^{13}C NMR (DMSO$_{d6}$), δ, ppm: 159.6, 154.2, 130.2, 129.6, 119.7, 115.2, 114.5, 67.4, 31.4, 28.7, 28.5, 25.1, 23.3, 22.2, 22.9 13.8. Elemental analysis: calculated for $C_{32}H_{48}N_4O_2$ (520.75 g/mol): C 73.81, H 9.29, N 10.76., found C 73.77, H 9.21, N 10.68.

4.2.2.10. 3,5-Di(4-decyloxyphenyl)-4-amino-1,2,4-triazole $(II)_j$

Yield: 72%. FTIR (ATR, cm^{-1}), υ_{max}: (3347, 3155, N-H, NH_2), (2951, 2920, 2853, aliph. C-H), (1614, C=N). ^1H NMR ($DMSO_{d6}$), δ, ppm: 7.93 (d, *J* = 8.1 H_z, 4H, Ar-H), 7.02 (d, *J* = 8.2 H_z, 4H, Ar-H), 6.13 (s, 2H, NH_2), 4.00 (t, 4H, $2OCH_2$), 1.77 (m, 4H, $2CH_2$), 1.43-1.33 (m, 28H, $14CH_2$), 0.82 (t, 6H, $2CH_3$). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 159.4, 154.7, 130.7, 129.5, 119.4, 115.5, 114.6, 67.3, 31.8, 28.6, 28.3, 25.8, 23.3, 23.9, 22.7, 22.2 13.8. Elemental analysis: calculated for $C_{34}H_{52}N_4O_2$ (548.80 g/mol): C 74.41, H 9.55, N 10.21., found C 74.33, H 9.51, N 10.16.

4.2.2.11. 3,5-Di(4-dodecyloxyphenyl)-4-amino-1,2,4-triazole $(II)_k$

Yield: 74%. FTIR (ATR, cm^{-1}), υ_{max}: (3359, 3163, N-H, NH_2), (2943, 2916, 2859, aliph. C-H), (1613, C=N). ^1H NMR ($DMSO_{d6}$), δ, ppm: 7.94 (d, *J* = 8.2 H_z, 4H, Ar-H), 7.04 (d, *J* = 8.2 H_z, 4H, Ar-H), 6.14 (s, 2H, NH_2), 4.04 (t, 4H, $2OCH_2$), 1.75 (m, 4H, $2CH_2$), 1.42-1.34 (m, 36H, $18CH_2$), 0.86 (t, 6H, $2CH_3$). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 159.9, 154.8, 130.6, 129.6, 119.3, 115.8, 114.3, 67.7, 31.9, 28.5, 28.3, 25.7, 23.2, 23.5, 23.8, 22.7, 22.4, 22.3 13.7. Elemental analysis: calculated for $C_{38}H_{60}N_4O_2$ (604.90 g/mol): C 75.45, H 9.99, N 9.26., found C 75.29, H 9.91, N 9.23.

4.2.2.12. 3,5-Di(4-hexadecyloxyphenyl)-4-amino-1,2,4-triazole $(II)_l$

Yield: 81%. FTIR (ATR, cm^{-1}), υ_{max}: (3362, 3155, N-H, NH_2), (2941, 2921, 2864, aliph. C-H), (1612, C=N). ^1H NMR ($DMSO_{d6}$), δ, ppm: 7.96 (d, *J* = 8.6 H_z, 4H, Ar-H), 7.07 (d, *J* = 8.5 H_z, 4H, Ar-H), 6.16 (s, 2H, NH_2), 4.02 (t, 4H, $2OCH_2$), 1.76 (m, 4H, $2CH_2$), 1.43-1.31 (m, 52H, $26CH_2$), 0.85 (t, 6H, $2CH_3$). ^{13}C NMR ($DMSO_{d6}$), δ, ppm: 159.5, 154.4, 130.3, 129.7, 119.4, 115.6, 114.1, 67.8, 31.3, 28.4, 28.5, 25.6, 23.8, 23.5, 23.2, 22.8, 22.6, 22.4, 22.2 13.4. Elemental analysis: calculated for $C_{46}H_{76}N_4O_2$ (717.12 g/mol): C 77.04, H 10.68, N 7.81., found C 77.18, H 10.55, N 7.93.

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