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Synthesis and mesomorphic properties of novel [1,2,3]-triazole mesogenic based compounds

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HIGHLIGHTS

- Novel [1,2,3]-triazole based mesogenic derivatives were synthesized and characterized.
- The smectic A phase appeared to be the dominant phase in these structures.
- The incorporation of an ester function within the triazole unit could generate enough dipole which promotes the arrangement of molecules in smectic layer structures.
- The mesomorphic behavior is closely related to the nature of the substituent X present in N1 position of the heterocycle.
- The increase of the mesogenic length causes a decrease in the existence range of the smectic A mesophase in favor of a new nematic mesophase.

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ABSTRACT

A series of five-membered heterocyclic 1,2,3-triazole derivatives with different substituents in N1 position was synthesized. The heterocyclic moiety was connected through an ester function to a *p*-decyloxyphenyl or *p*-decyloxybiphenyl tails Polarized microscopy studies, X-ray scattering and differential scanning calorimetry (DSC) analysis revealed that the target compounds exhibit enantiotropic liquid crystalline properties. Their mesomorphic behavior is closely related to the nature of the substituent X present in N1 position of the heterocycle.

1. Introduction

Numerous heterocyclic liquid crystalline materials were designed and characterized during the past decades [1–5]. The presence of a heteroatom as nitrogen, oxygen or sulfur incorporated on such heterocyclic rings may have a strong effect on the polarity and polarizability of the molecule, the angle of rotation between its fragments, the planarity and thereby on the stability of mesophases and the temperatures of the phase transitions [6,7].

Heteroatoms may also participate in intermolecular interactions which are at the origin of mesomorphism (dipole–dipole interaction, dispersion, H-bonding, coordinative force, etc.) thus affecting the type of mesophases. Otherwise, by influencing the direction and magnitude of the dipole moment of the molecule, the heteroatom may affect the sign and magnitude of the dielectric anisotropy of the liquid crystal mesophase.

It was reported that compounds based on six membered aromatic rings containing one or two nitrogen atoms such as pyridine, tetrazine, pyridazine, give rise to interesting physical properties [8–12]. The lone pairs of electrons on the nitrogen atoms introduce attractive forces which induce smectic mesophase formation. The position of nitrogens may be important as layer formation depends significantly on how easily the molecules can pack together.

For example, the pyrimidine system as 5-alkyl 2-[4-alkoxyphenyl] pyrimidine exhibit Sc phase and was also used in smectic C ferroelectric mixtures [13].

Heterocyclic five-membered rings are not generally as conducive to liquid crystal phase formation as six-membered rings due

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to their relative deviation from linearity and planarity. Compounds containing pyrrolyl and 5-methylthienyl rings, described by Nash and Gray, promote nematic and smectic phases relative to phenyl homologous [14].

[1,2,3]-triazoles are important type of heterocyclic compounds and are known to exhibit a wide range of biological activities such as *anti*-HIV activity [15], antimicrobial activity against Gram positive bacteria [16], selective β_3 adrenergic receptor agonism [17] and antianxiety activity [18]. They have been used in a variety of research areas including non-linear optics (NLOs), organic light-emitting diodes (OLEDs) and polymeric materials [19]. However, 1,2,3-triazole derivatives exhibiting mesophases have been less often reported. Nematic and/or smectic C – Smectic A mesophases formed by these rod-like compounds were observed [20–23]. [1,2,3]-triazole ring is placed at the end of the rigid core or in central core position and is linked directly to phenyl rings.

In this paper, we report the synthesis, the characterization and the mesomorphism behavior of new series of 1,4-disubstituted [1,2,3] triazole derivatives where the central heterocyclic ring is connected through an ester function to 4-decyloxyphenyl or 4-decyloxybiphenyl unit leading to extended conjugated system which can potentially act as a electron transporting materials.

2. Experimental

2.1. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Brucker 300 MHz spectrometer. Tetramethylsi–lane was used as an internal reference for chemical shifts. Infrared spectroscopies were carried out with a Jasco-4200 Fourier transform infrared spectrometer using KBr pellets. Column chromatographies were carried out using E-Merck silica gel (Kieselgel 60, 230–400 mesh) as the stationary phase. Thin-layer chromatography was carried out on aluminum plates precoated with Merck silica gel 60F254 and visualized by means of ultraviolet fluorescence quenching or iodine vapor. Elemental analysis were obtained with a Perkin Elmer 2400 system.

The melting points, transition temperatures and phase transition enthalpies were determined using a differential scanning calorimetry (DSC) at a heating rate of 5 °C min^{-1}. Mesomorphic textures were observed using an Olympus microscope equipped with Mettler Toledo heating stage. Structural characterizations were performed by X-ray scattering using a Rigaku rotating anode generator working at a wavelength of 1.54 Å (Cu Kα emission). The spectra were recorded with a bidimensional detector located at 154 mm from the sample, which was introduced as a powder in glass capillary tubes (Glas, Muller, Germany) exhibiting a diameter of 1.5 mm. An in-house made heating stage having an accuracy of 0.01 K was used to monitor sample temperature.

2.2. Synthesis

All the reagents were purchased from Aldrich and used as received. The solvents were of commercial grade quality and were dried and distilled before use. Methylene chloride was distilled over calcium hydride.

4-azido-1-nitrobenzene (1a), 4-azido-1-bromobenzene (1b) and 4-azido-1-methoxybenzene (1c) were prepared according to Nolting and Michel method [24] with a yield of 79%, 92% and 82% respectively.

Methyl 5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carboxylate was prepare according to the procedure described in the literature [25].

4-decyloxyphenol (4) was synthesized according to Ref. [26].

2.2.1. 1-(4-Nitrophenyl)-1-H-[1,2,3]-triazole 4-carboxylic acid, 1-(4-bromophenyl)-1H-[1,2,3]-triazole 4-carboxylic acid, 1-(4-methoxyphenyl)-1H-[1,2,3]-triazole) 4-carboxylic acid (2a–c)

One equivalent (4 mmol) of the appropriate p-X-arylazide and 1.1 equivalents (0.31 g, 4.4 mmol) of propargyl acid dissolved in 5 mL of acetone were stirred at 60 °C for 24 h. After solvent evaporation, the residue was washed with diethyl ether given the (1,4) regioisomer (2a–c). The filtrate was then evaporated and the solid obtained was triturated in hexane affording the (1,5)-regioisomer (2′a–c).

X = NO_2, yield: 68%, (2a)/(2′a) ratio: 66/34; X = Br, yield: 88%, (2b)/(2′b) ratio: 81/19; X = MeO, yield: 70%, (2c)/(2′c) ratio: 96/4.

2.2.1.1. 1-p-Nitrophenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (2a). mp: 220 °C, IR (KBr): 3138–3617, 3089, 1696, 1519.1H NMR (300 MHz, DMSO): 8.04 (d, 2H, Ar–**H** ortho triazole, J^3 = 9.20), 8.40 (d, 2H, Ar–**H** ortho NO_2, J^3 = 9.20), 8.74 (s, 1H, H-triazole), 12.32 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 167, 148, 143.2, 134.7, 129.7, 128.3, 123.7.

2.2.1.2. 1-p-Nitrophenyl-1-H-[1,2,3]-triazole 5-carboxylic acid (2a′). mp: 169 °C, ^{1}H NMR (300 MHz, DMSO): 7.72 (d, 2H, Ar–**H** ortho triazole, J^3 = 9.06), 8.28 (s, 1H, H-triazole), 8.33 (d, 2H, Ar–**H** ortho NO_2, J^3 = 9.06), 12.31 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 167.5, 148, 140, 134.7, 132.7, 130.3, 123.7.

2.2.1.3. 1-p-Bromophenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (2b). mp: 206 °C, 1H NMR (300 MHz, DMSO): 7.35 (d, 2H, Ar–**H** ortho triazole, J^3 = 9.01), 7.74 (d, 2H, Ar–**H** ortho Br, J^3 = 9.01), 8.73 (s, 1H, H-triazole), 12.61 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 167, 143, 132.5, 131.9, 128, 127.9, 123.1.

2.2.1.4. 1-p-Bromophenyl-1-H-[1,2,3]-triazole 5-carboxylic acid (2b′). mp: 170 °C, ^{1}H NMR (300 MHz, DMSO): 7.38 (d, 2H, Ar–**H** ortho triazole, J^3 = 8.83), 7.30 (d, 2H, Ar–**H** ortho Br, J^3 = 8.83), 8.21 (s, 1H, H-triazole), 12.31 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 166.9, 139.6, 132.7, 132, 131.5, 127, 122.9.

2.2.1.5. 1-p-Methoxyphenyl-1-H-[1,2,3]-triazole 4-carboxylic acid (2c). mp: 215 °C, ^{1}H NMR (300 MHz, DMSO): 3.81 (s, 3H, OCH_3), 6.99 (d, 2H, Ar–**H** ortho OCH_3, J^3 = 9.02), 7.63 (d, 2H, Ar–**H** ortho triazole, J^3 = 9.02), 8.47 (s, 1H, H-triazole), 12.68 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 167.9, 160, 143.6, 131.2, 129.2, 121.7, 115, 60.2.

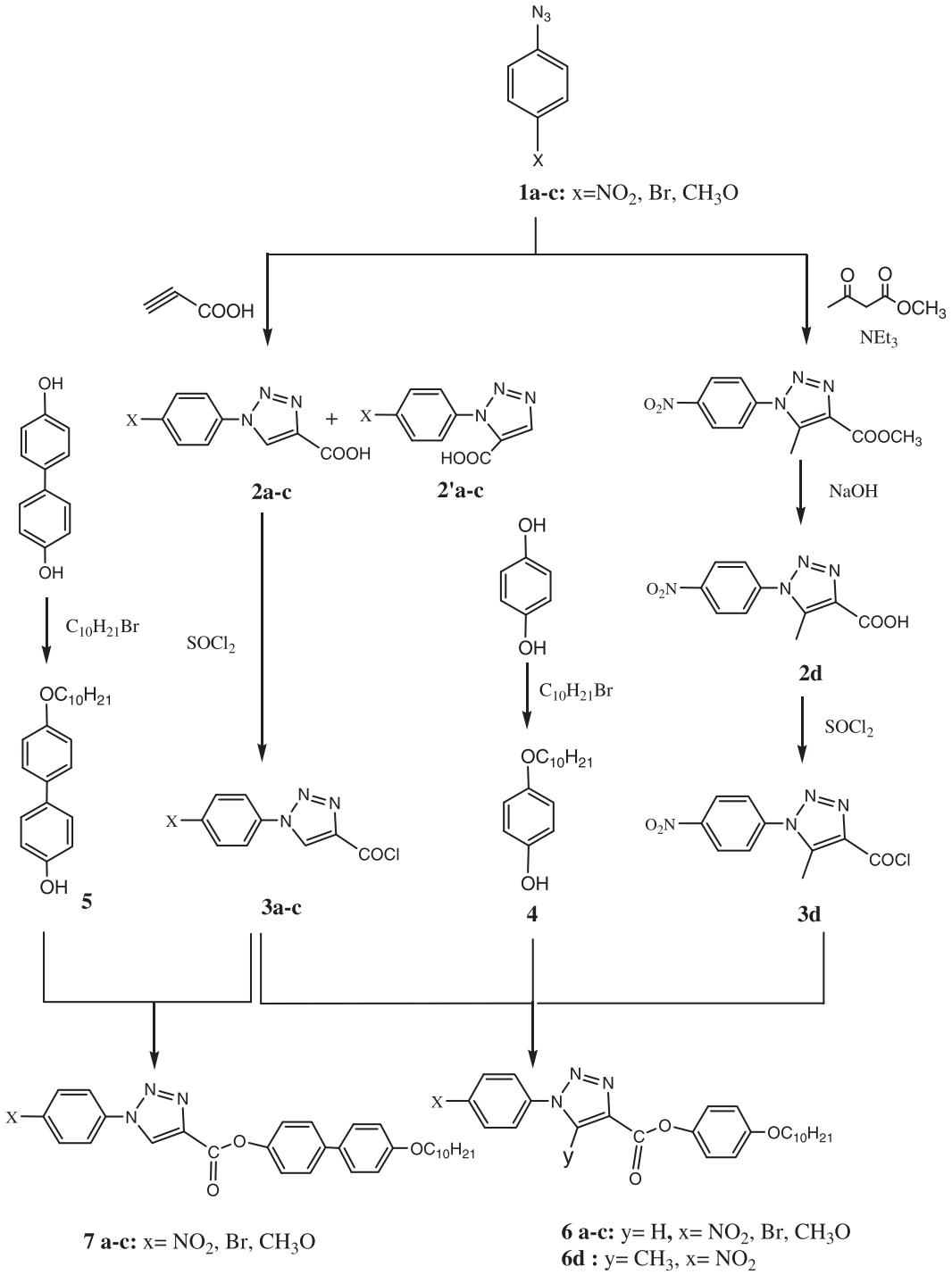
2.2.2. 5-Methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylic acid (2d)

4.2 mmol of methyl 5-methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazole-4-carboxylate and 35 mL of NaOH 2M were heated at 100 °C during 24 h. The mixture was then acidified with HCl 35% solution until pH = 1. The obtained precipitate was filtered, washed several times with water and dried.

Yield: 66%, mp: 220 °C, IR (KBr): 3381–3473, 3127, 1716, ^{1}H NMR (300 MHz, DMSO): 2.35 (s, 3H, CH_3), 8.02 (d, 2H, Ar–**H** ortho triazole, J = 9.1), 8.45 (d, 2H, Ar–**H** ortho NO_2, J = 9.1 Hz), 12.3 (s, 1H, COOH). ^{13}C NMR (300 MHz, DMSO): 167.8, 148.3, 139.8, 136.6, 134.6, 125.9, 125.2, 10.2.

2.2.3. [1-(4-X-phenyl)-1H-1,2,3-triazoyl chloride (3a–c) and 5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazoyl chloride (3d)

To a solution of compound 2a–d (2 mmol) was added (20 mmol) of thionyl chloride. The reaction mixture was stirred at 85 °C during 5–6 h under inert atmosphere. After evaporation of the excess of $SOCl_2$, the crude product was used for the next step without further purification.



Scheme 1. Synthesis of compounds.

2.2.4. 4,4′-(Decyloxy)biphenyl-4-ol (5)

(1 g, 5.4 mmol) of 4,4′-biphenol dissolved in 6 mL of dimethylsulfoxyde was added to 0.9 g of KOH. 1-bromodecane (1.32 g, 6 mmol) were then added dropwise so that the initial temperature was maintained. The reaction was stirred for 24 h at room temperature.

The resulting mixture was transferred into 60 mL of water, then acidified with HCl 35% until pH = 2–3. The precipitate was collected by filtration the purified by column chromatography (silica gel, dichloromethane/acetone 1/1) to give a white solid.

Yield: 78%, mp: 152 °C, IR (KBr): 3367, 2921, 1250. ^{1}H NMR (300 MHz, DMSO-d_6): 0.86 (t, 3H, CH_3, ^3J = 6.60 Hz), 1.29 (m, 14H, CH_2), 1.71 (m, 2H, OCH_2–$\underline{CH_2}$), 3.94 (t, 2H, OCH_2, J = 6.3 Hz), 6.81 (d, 2H, Ar–**H** ortho OH), 6.95 (d, 2H, Ar–**H** ortho OCH_2), 7.43 (m, 4H, Ar–**H**), 9.42 (s, 1H, OH).

2.2.5. 4-(Decyloxy)phenyl 1-(4-Xphenyl)-1H-1,2,3-triazole-4-carboxylate (6a–c)

In a typical procedure, 2 mmol of triazoyl chloride (3a–c), (0.57 g, 5.7 mmol) of triethylamine and 6 mL of freshly distilled

Table 1
Transition temperatures (°C) and transition enthalpies ΔH (kJ mole^{-1}) of compounds (6a–d) and (7a–c) determined by DSC (10 °C min^{-1}) during second cycle.

Compound	X	Transition temperatures (°C) [transition enthalpies ΔH/kJ mole^{-1}]
6a	NO_2	Cr (119.40 °C) [19.72] Cr′ (127.63 °C) [11.96] SmA (222.8 °C) [6.30] I
6b	Br	Cr (127.45 °C) [17.99] I
6c	MeO	Cr (51.89 °C) [17.6] SmA (125.32 °C) [17.22] I
6d	NO_2	Cr (152.50 °C) [12.72] SmA (162.18 °C) [9.87] I
7a	NO_2	Cr (105.5 °C) [18.03] Cr′ (169.65 °C) [27.54] SmA (182.14 °C) [broad] N (244 °C) [1.12] I
7b	Br	Cr (134.10 °C) [25.0] I
7c	MeO	Cr (155.02 °C) [47.19] SmA (237.46 °C) [1.48] N (248 °C) [broad] I

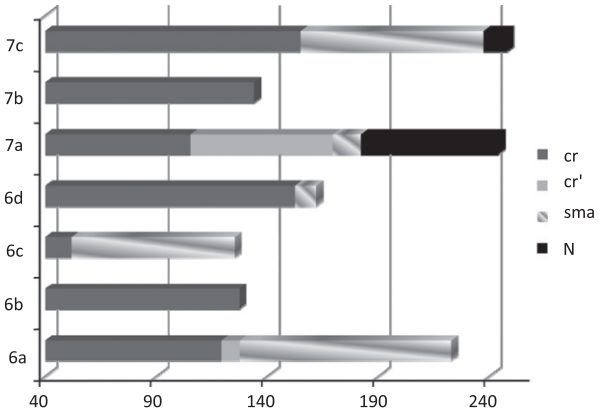


Fig. 1. Comparative thermal behavior of the final compounds.

dichloromethane were transferred in a round bottom three-necked flask placed in a ice bath. After purging with nitrogen gas, (0.5 g, 2 mmol) of 4-decyloxyphenol dissolved in 6 mL dichloromethane were added dropwise. The reaction mixture was heated under reflux for 48 h. Water was then added and the organic phase was extracted, washed three times with an aqueous solution of HCl 1M, then with water until neutrality and finally dried with $MgSO_4$. The residue obtained after solvent evaporation was purified with column chromatography (silica gel, dichloromethane/ethyl acetate 5:1).

2.2.5.1. 4-(Decyloxy)phenyl 1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (6a). Yield: 76%, m.p. 127.63 °C, IR (KBr): 3096, 1727, 1245. ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.64 Hz), 1.35 (m, 14H, CH_2), 1.81 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 6.55 Hz, ^3J = 7.25 Hz), 3.98 (t, 2H, OCH_2, ^3J = 7.25 Hz), 6.96 (d, 2H, Ar–**H** ortho OR, ^3J = 9.06 Hz), 7.18 (d, 2H, Ar–**H** ortho OCO, ^3J = 9.06 Hz), 8.08 (d, 2H, Ar–**H** ortho triazole, ^3J = 9.09 Hz), 8.50 (d, 2H, Ar–**H** ortho NO_2, ^3J = 9.09 Hz), 8.81 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 13.25, 21.55, 25.01, 28.22, 30.94, 31.18, 68.90, 114.15, 120.04, 121.19, 124.31, 127.84, 129.86, 143.20, 143.10; 148.32, 154.30, 156.29. Anal. Calcd for $C_{25}H_{30}N_4O_5$: C, 64.36; H, 6.48; N, 12.02. Found: C, 64.30; H, 6.23; N, 11.99.

2.2.5.2. 4-(Decyloxy)phenyl 1-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (6b). Yield: 63%, m.p. 127.45 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.64 Hz), 1.34 (m, 14H, CH_2), 1.81 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 6.52 Hz, ^3J = 7.35 Hz), 3.97 (t, 2H, OCH_2, ^3J = 6.52 Hz), 6.95 (d, 2H, Ar–**H** ortho OR, ^3J = 9.04 Hz), 7.18 (d, 2H, Ar–**H** ortho OCO, ^3J = 9.04 Hz), 7.71 (d, 2H, Ar–**H** ortho triazole, ^3J = 9.19 Hz), 7.75 (d, 2H, Ar–**H** ortho Br, ^3J = 9.19 Hz), 8.66 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 12.64, 21.86, 25.97, 29.71, 31.92, 67.56, 114.81, 122.04, 123.0, 127.51, 130.68, 132.93, 134.58, 143.10, 143, 22, 154.32, 156.34. Anal. Calcd for $C_{25}H_{30}BrN_3O_5$: C, 60.00; H, 6.04; N, 8.40. Found: C, 59.88; H, 6.14; N, 8.32.

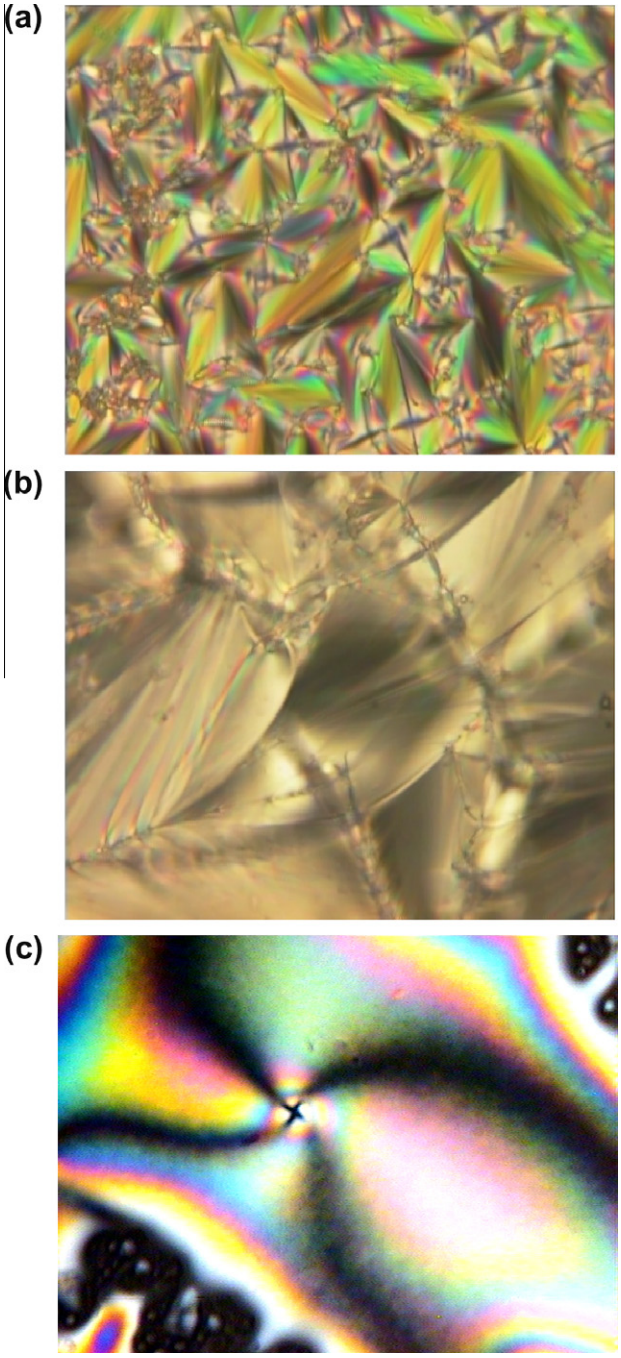


Fig. 2. The representative photomicrographs of (a) the focal conic texture of the SmA phase for compound **6c** at 120 °C, (b) the SmA polygonal texture for compound **6d** at 160 °C and (c) the nematic schlieren texture for compound **7c** at 241 °C (240 * 300 μm^2).

2.2.5.3. 4-(Decyloxy)phenyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (6c). Yield: 80%, m.p. 51.89 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.62 Hz), 1.32 (m, 14H, CH_2), 1.80 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 6.54 Hz, ^3J = 7.29 Hz), 3.91 (s, 3H, OCH_3), 3.97 (t, 2H, OCH_2, ^3J = 6.54 Hz), 6.95 (d, 2H, Ar–**H** ortho OCH_3, ^3J = 9.02 Hz), 7.08 (d, 2H, Ar–**H** ortho OR, ^3J = 8.99 Hz), 7.17 (d,

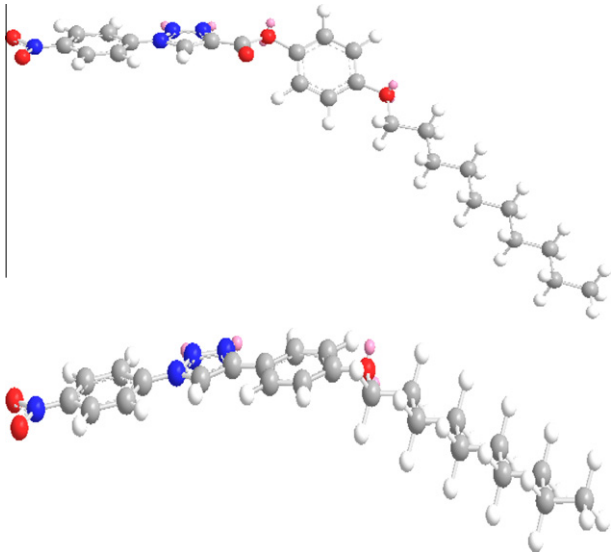


Fig. 3. Energy minimized structures of compound 6a (top) and homologous structure without ester function connector (bottom).

2H, Ar–**H** ortho OCO, ^3J = 8.99 Hz), 7.70 (d, 2H, Ar–**H** ortho triazole, ^3J = 9.02 Hz), 8.58 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 13.09, 21.74, 28.39, 28.53, 30.94, 54.66, 69.81, 113.94, 114.351, 120.08, 121.45, 124.31, 128.20, 143.20, 146.00, 154.32, 156.30, 160.71. Anal. Calcd for $C_{26}H_{33}N_3O_4$: C, 69.16; H, 7.37; N, 9.31. Found: C, 69.13; H, 8.12; N, 9.16.

2.2.6. 4-(Decyloxy)phenyl 5-methyl 1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (6d)

This compound was prepared by a similar procedure to that described for compounds (6a–c) from compound 3d and 4-decyloxyphenol (4).

Yield: 50%, m.p. 152.50 °C, IR (KBr): 3094, 1738, 1205. ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, 3H, CH_3, ^3J = 6.73 Hz), 1.29 (m, 14H, CH_2), 1.80 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 6.55 Hz, ^3J = 7.14 Hz), 2.74 (s, 3H, CH_3), 3.97 (t, 2H, OCH_2, ^3J = 6.55 Hz), 6.94 (d, 2H, Ar–**H** ortho O, ^3J = 8.92 Hz), 7.17 (d, 2H, Ar–**H** ortho OCO, ^3J = 8.92 Hz), 7.78 (d, 2H, Ar–**H** ortho triazole, ^3J = 8.83 Hz), 8.50 (d, 2H, Ar–**H** ortho NO_2, ^3J = 8.83 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 4.20, 13.10, 21.66, 24.98, 28.24, 28.37, 28.54, 28.69, 29.95, 30.87, 67.70, 114,10, 121.37, 124.26, 124.88, 134.61, 136.50, 139.32, 143.02, 148.00, 154.30, 160.76. Anal. Calcd for $C_{26}H_{32}N_4O_5$: C, 64.98; H, 6.71; N, 11.66. Found: C, 64.85; H, 6.82; N, 11.35.

2.2.7. 4-(Decyloxy)biphenyl 1-(4-Xphenyl)-1H-1,2,3-triazole-4-carboxylate (7a–c)

These compounds were prepared by a similar procedure to that described for compounds (6a–c) from compound (2a–c) and 4,4′-(decyloxy)biphenyl-4-ol (5). They were isolated by column chromatography (silica gel, dichloromethane/ethyl acetate 10:1).

2.2.7.1. 4-(Decyloxy)biphenyl 1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (7a). Yield: 76%, m.p. 169.65 °C, IR (KBr): 3135, 1725, 1166. ^{1}H NMR (300 MHz, $CDCl_3$): 0.84 (t, 3H, CH_3, ^3J = 6.43 Hz), 1.21 (m, 14H, CH_2), 1.76 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 6.66 Hz, $3J$ = 5.56 Hz), 3.93 (t, 2H, OCH_2, ^3J = 6.66 Hz), 6.91 (d, 2H, Ar–**H** ortho O, ^3J = 8.70 Hz), 7.22 (d, 2H, Ar–**H** ortho OCO, ^3J = 8.62 Hz), 7.54 (d, 2H, Ar–**H**, ^3J = 8.62 Hz), 7.46 (d, 2H, Ar–**H**, ^3J = 8.70 Hz), 8.02 (d, 2H, Ar–**H** ortho triazole, ^3J = 9.07 Hz), 8.42 (d, 2H, Ar–**H** ortho NO_2, ^3J = 9.07 Hz), 8.75 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 14.09, 22.66, 26.04, 29.30, 31.88, 68.11, 114.84, 121.07, 121.65, 125.75, 127.83, 127.90, 128.08, 128.10, 133.31, 134.61, 14.31, 148.00, 150.32, 156.31, 158.89. Anal. Calcd for $C_{31}H_{34}N_4O_5$: C, 68.62; H, 6.32; N, 10.33. Found: C, 69.78; H, 6.52; N, 10.09.

2.2.7.2. 4-(Decyloxy)biphenyl 1-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (7b). Yield: 46%, m.p. 134.10 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.83 (t, 3H, CH_3, $^{3J = 6.67\ Hz)}$, 1.26 (m, 14H, CH_2), 1.67 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 7.17 Hz, $3J$ = 6.84 Hz), 3.92 (t, 2H, OCH_2, ^3J = 6.84 Hz), 6.91 (d, 2H, Ar–**H** ortho O, ^3J = 8.72 Hz), 7.24 (d, 2H, Ar–**H** ortho OCO, ^3J = 8.75 Hz), 7.43 (d, 2H, Ar–**H** ortho triazole, ^3J = 8.65 Hz), 7.58 (d, 2H, Ar–**H** ortho Br, ^3J = 8.65 Hz), 7.65 (s, 4H, Ar–**H**), 8.53 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 13.10, 21.66, 25.04, 28.30, 30.88, 67.10, 113.82, 120.73, 121.24, 126.79, 127.10, 131.7, 132.22, 133.31, 147.52, 150.37, 157.86. Anal. Calcd for $C_{31}H_{34}BrN_3O_3$: C, 64.58; H, 5.94; N, 7.29. Found: C, 64.24; H, 5.83; N, 7.13.

2.2.7.3. 4-(Decyloxy)biphenyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (7c). Yield: 48%, m.p. 155.02 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.81 (t, 3H, CH_3, ^3J = 6.67 Hz), 1.35 (m, 14H, CH_2), 1.72 (tt, 2H, OCH_2–$\underline{CH_2}$, ^3J = 7.48 Hz, $3J$ = 6.49 Hz), 3.82 (s, 3H, OCH_3), 3.93 (t, 2H, OCH_2, ^3J = 6.49 Hz), 6.95 (d, 2H, CH_{bz}-O, ^3J = 8.70 Hz), 7.00 (d, 2H, Ar–**H** ortho OCH_3, ^3J = 9.04 Hz), 7.24 (d, 2H, Ar–**H**, ^3J = 8.70 Hz), 7.45 (d, 2H, Ar–**H**, ^3J = 8.74 Hz), 7.54 (d, 2H, Ar–**H** ortho OCO, ^3J = 8.70 Hz), 7.63 (d, 2H, $CH_{bz\text{-}N}$, ^3J = 9.04 Hz), 8.53 (s, 1H, triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 13.10, 21.66, 25.04, 28.30, 30.88, 54.68, 67.09, 113.80, 113.99, 120.79, 121.51, 125.38, 127.09, 128.51, 131.54, 130.9, 131.54, 138.07, 138.86, 143.20, 148.08, 157.82, 158.15, 159.47. Anal. Calcd for $C_{32}H_{37}N_3O_4$: C, 72.84; H, 7.07; N, 7.96. Found: C, 71.80; H, 7.28; N, 7.31.

3. Results and discussion

3.1. Synthesis

Synthesis of the 1-*H*-[1,2,3] triazole-based mesogenic derivatives (6a–d) and (7a–c) and the principal key intermediates is outlined in Scheme 1. Aromatic azides (1a–c) were prepared according to Nolting and Michel method from para-substituted anilines (p-NO_2, p-Br, p-MeO) by reacting with sodium nitrite in HCl media to accede to diazonium salts which were then transformed into aryl azides by the addition of sodium azide.

1,3-dipolar cycloaddition was conducted by heating the aryl azides with propargyl acid at 60 °C during 24 h using acetone as solvent. Two regioisomers corresponding to the anti (1,4-triazole) and syn (1,5-triazole) were obtained with unequal proportions. The 1,4-regioisomers (2a–c) were easily separated by washing the reaction residues with diethyl ether. The filtrates were then evaporated and the solids obtained were triturated in hexane affording the 1,5-regioisomers (2′a–c).

The structures of the two isomeric derivatives were supported by ^{1}H and ^{13}C NMR analysis and examination of relevant literature [27–29].

Comparison with ^{1}H NMR data described in literature shows similar single signal of the triazole-H_5 (1,4-regioisomer) which varied from 8.47 to 8.74 ppm whereas the H_4 proton of 5-substituted triazole (1,5-regioisomer) is shifted to lower frequency.

The 5-methyl substituted corresponding acid derivative for x = NO_2 (2d) was prepared by another methodology. First, the 4-nitroazide (1a) was reacted with acetylacetone in the presence of triethylamine to afford the methyl-1*H*-[1,2,3]-triazole-4-carboxylate [25] which is then hydrolyzed in basic media to afford the corresponding acid (2d) with a good yield.

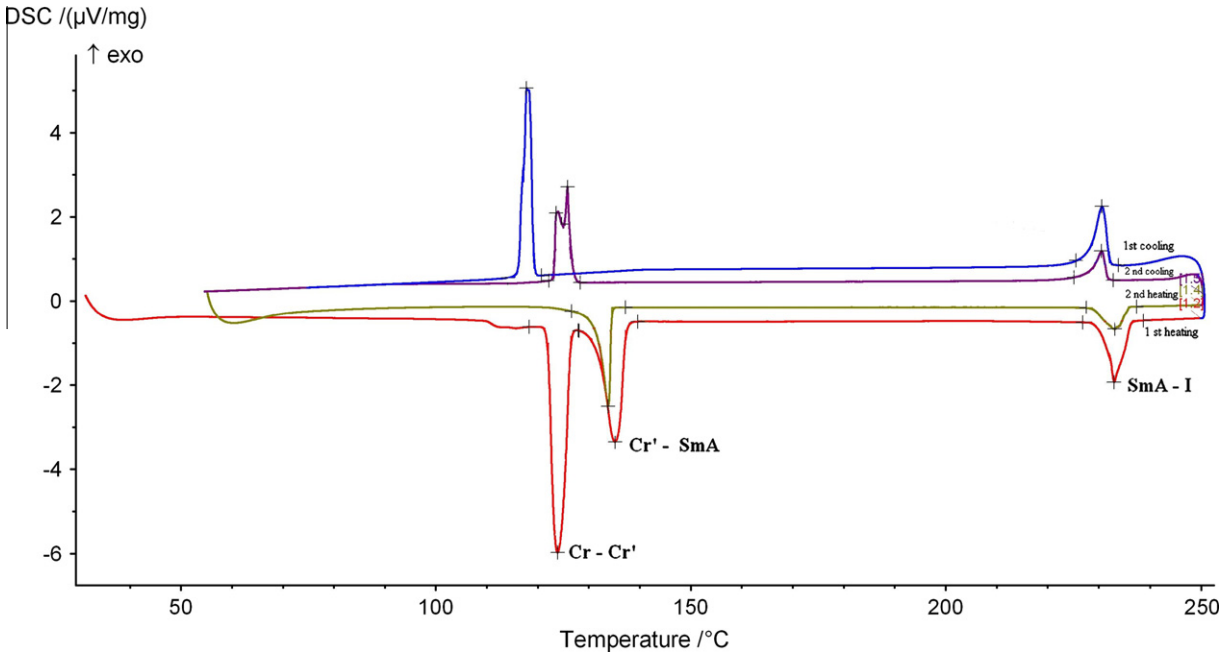


Fig. 4. Thermogram of compound 6a obtained by DSC during the first cycle at 10 °C/mn and during the second cycle at 5 °C/mn.

The resulting 1*H*-[1,2,3]-triazole-4-carboxylic acids (2a–d) were converted to the corresponding triazoyl chlorides (3a–d) with thionyl chloride then reacted with 4-decyloxyphenol (4) or 4,4′-(decyloxy)biphenyl-4-ol (5) in dichloromethane to give the aimed [1,2,3] triazole containing mesogens (6a–d) and (7a–c).

3.2. Mesomorphic properties

The transition temperatures and phase assignments for the synthesized materials were investigated by thermal polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The results are given in Table 1 and in the bar-graph chart (Fig. 1).

Compounds (6a), (6c), (6d) exhibit enantiotropic liquid crystalline behavior. The smectic A phase (SmA) appeared to be the dominant phase in these structures. On slow cooling from the isotropic liquid, tiny batonnets developed at the edge of melted substance and grow up to the focal conic fan texture as showed in Fig. 2a and b which is characteristic of SmA texture.

The linearity deviation caused by the triazole core (148.9 °C) seems to be, in our case, not sufficient to destroy calamitic mesomorphic behavior even for compound bearing only three aromatic rings. The presence of ester polar flexible group within triazole polar unit could not assist the recovery of linearity lost by triazole ring as seen when comparing, for instance the energy minimized structure obtained using MM2 method of compound 6a and the homologous structure without ester connector group (Fig. 3). Though the mesogen was a non-linear, the ester polar group shall generate enough dipole in addition to triazole ring unit which promotes the formation of smectic A mesophases.

Differential scanning calorimetry investigations confirm the mesomorphic behavior. Two sharp endothermic peaks, corresponding to melting temperature (high enthalpy) and isotropic temperature (low enthalpy) were observed. A typical thermogram obtained by DSC analysis of compound (6a) is presented in Fig. 4.

The mesomorphic behavior of the target compounds is closely related to the nature of the substituent X present in N1 position of the heterocycle. The introduction of a bromo substitution is detrimental to the liquid crystalline behavior since any mesophase was observed for the corresponding products. The large volume of this atom could be at the origin of such luck of mesomorphic packing since it reduces the dipolar interactions which lead to smectic phase.

In the same manner, the existence of a methyl group in the position 5 of the heterocycle (compound 6d) reduced the thermal stability of the smectic phase. The stability of the SmA phase was reduced by a factor of 10 and the clearing temperature was lowered by about 60 °C. The main factor contributing to this may be also the steric effect which is less pronounced than previously.

The elongation of the aromatic rigid core by the introduction of biphenyl group (7a–c), increases the melting points in comparison with compounds containing a phenyl group (6a–c). The mesomorphic behavior is found to be related to the number of aromatic rings in the mesogenic core. The introduction of an additional aromatic ring (benzene ring) in the series (7a–c) along with the 1,2,3-triazole heterocyclic favored the formation of a new nematic mesophase, which does not appear in the series (6a–c), to the detriment of the smectic A mesophase.

The occurrence of nematic phases in compounds 7a and c was evidenced by observation of Schlieren texture of nematic phase.

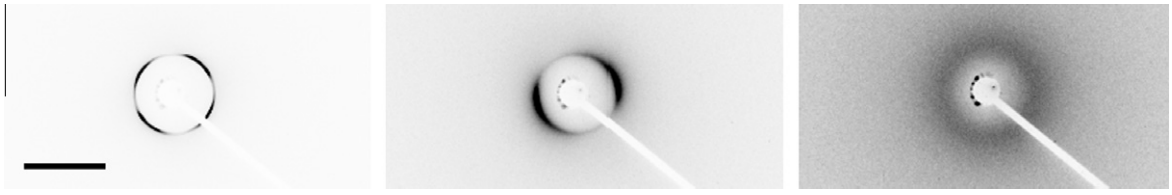


Fig. 5. X-ray diffraction pattern of the smectic (left), nematic (middle), and isotropic liquid (right) of the **BiPhMeO**, recorded at T = 170, 235 and 245 °C, respectively. The scale bar indicates 3 nm^{-1}.

As a representative case of nematic phase, the texture of (7c) is illustrated in Fig. 2c. Upon cooling the isotropic liquid, the appearance of colorful birefringence domains was noted. By cooling the isotropic liquid phase, Schlieren texture showing a network of black brushed connecting centers of point and line defects, was observed. On further cooling the nematic phase, more ordered SmA phase was observed at lower temperature. The co-existence of the homogeneous (fan-shaped texture) and homeotropic (dark area) textures confirmed the presence of SmA.

X-ray scattering has been done to confirm the mesomorphic structure of the different compounds. Fig. 5 displays the typical patterns obtained for biPhMeO by increasing temperature: sharp Bragg reflection characteristic of long range positional order in the smectic phase; "butterflies" anisotropic pattern arising from nematic ordering, where the large radial width reflects a liquid-like order; isotropic broad ring characteristic of a liquid order at high temperature. Despite a study of the smectic layer spacing as a function of temperature (data not shown), the nature of the smectic phase (smectic A or smectic C) was difficult to assign by X-ray scattering study [30].

4. Conclusion

Two series of novel [1,2,3]-triazole based mesogenic derivatives were synthesized using the reaction of esterification of 4-decyloxyphenol or 4,4′-(decyloxy)biphenyl-4-ol with 1*H*-[1,2,3]-triazo-4-yl chlorides (3a–d). The 1*H*-[1,2,3]-triazole-4-carboxylic acids key intermediates were obtained by 1,3-cyloaddition reaction between aryl azides and propargyl acid. The structure of all synthesized compounds was confirmed by ^{1}H NMR, ^{13}C NMR and IR analysis methods. Final compounds having only two rings in the mesogenic core and the triazole in a central position showed smectic A mesophases. The incorporation of an ester function within the triazole unit could generates enough dipole which promotes the arrangement of molecules in smectic layer structures. The introduction of a bromophenyl substituent in para position to the triazole was detrimental to the liquid crystalline phases. The increase of the mesogenic length, second series (7a–c), causes a decrease in the existence range of the smectic A mesophase, in favor of a new nematic mesophase.

References

[1] S. Sharma, D. Lacey, P. Wilson, Liq. Cryst. 30 (2003) 451.
[2] Y.-D. Zhang, K.G. Jespersen, M. Kempe, J.A. Kornfield, S. Barlow, B. Kippelen, S.R. Marder, Langmuir 19 (2003) 6534.
[3] R. Mcdonald, D. Lacey, P. Watson, S. Cowling, P. Wilson, Liq. Cryst. 32 (2005) 319.
[4] A. Mori, A. Sekiguchi, K. Masui, T. Shimada, M. Horie, K. Osakada, M. Kawamoto, T. Ikeda, J. Am. Chem. Soc. 125 (2003) 1700.
[5] V.F. Petrov, V.I. Yashkichev, Mol. Cryst. Liq. Cryst. 518 (2010) 12.
[6] B.Y. Zhang, Y.G. Jia, D.S. Yao, X.W. Dong, Liq. Cryst. 31 (2004) 339.
[7] P.J. Colling, M. Hird, Introduction to liquid crystals: chemistry and physics, Taylor & Francis Ltd, Bristol, 1998.
[8] M.P. Aldred, P. Vlachos, D. Dong, S.P. Kitney, W.C. Tsoi, M. O'Neill, S.M. Kelly, Liq. Cryst. 32 (2005) 951.
[9] T. Lifka, G. Zerban, P. Seus, A. Oehlhof, H. Meier, Tetrahedron 64 (2008) 6551.
[10] K.C. Majumdar, S. Mondal, N. Pal, R.K. Sinha, Tetrahedron Lett. 50 (2009) 1992.
[11] V.V. Titov, A.I. Pavlyuchenko, Chem. Heterocycl. Comp. 16 (1980) 11.
[12] J. Barbera, M. Marcos, E. Melendez, B. Ros, J.L. Serrano, Mol. Cryst. Liq. Cryst. 123 (1985) 159.
[13] W. Guang, J. Han, W. Wan, K. Zhao, L. Zhang, Liq. Cryst. 30 (2003) 1259.
[14] J.A. Nash, G.W. Gray, Mol. Cryst. Liq. Cryst. 25 (1974) 299.
[15] S. Velazquez, R. Alvarez, C. Perez, F. Gago, C. De, J. Balzarini, M. Camaraza, J. antivir. Chem. Chemoth. 9 (1998) 481.
[16] A.P. Oludotun, E. Udo Edet, M.E. Abdelhamid, R. Varghese Reny, Eur. J. Med. Chem. 44 (2009) 3217.
[17] L.L. Brockunier, E.R. Parmee, H.O. Ok, M.R. Candelore, M.A. Cascieri, L.F. Colwell Jr., L. Deng, W.P. Feeney, M.J. Forrest, G.J. Hom, D.E. MacIntyre, L. Tota, M.J. Wyvratt, M.H. Fisher, A.E. Weber, Bioorg. Med. Chem. Lett. 10 (2000) 2111.
[18] H.K. Seung, L. Kee-Jung, J. Heterocycl. Chem. 41 (2004) 613.
[19] K.K. Myoung, K. Jongchul, K. Tae-Hyuk, H. Jong-In, New J. Chem. 34 (2010) 1317.
[20] R. Cristiano, D.M. Pereira De Oliveira Santos, G. Conte, H. Gallardo, Liq. Cryst. 33 (2006) 997.
[21] G. Conte, F. Ely, H. Gallardo, Liq. Cryst. 32 (2005) 1213.
[22] D. Srividhya, S. Manjunathan, S. Thirumaran, E-J. Chem. 6 (2009) 958.
[23] D. Srividhya, S. Manjunathan, S. Thirumaran, C. Saravanan, S. Senthil, J. Mol. Struct. 927 (2009) 7.
[24] E. Nolting, O. Michel, Chem. Ber. 26 (1893) 86.
[25] G.L. 'Abbe, W. Dehaen, Tetrahedron 44 (1988) 461.
[26] E. Białecka-Florjańczyk, Synth. Comm. 30 (2000) 4417.
[27] E. Mayot, C. Gérardin-Charbonnier, C. Selve, J. Fluorine Chem. 126 (2005) 715.
[28] V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Edit. 41 (2002) 2596.
[29] C.W. Tornoe, C. Chritensen, M. Medal, J. Org. Chem. 67 (2002) 3057.
[30] E. Grelet, B. Pansu, H.T. Nguyen, Liq. Cryst. 28 (2001) 1121.