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Structure–property study of new [1,2,3]-triazole liquid crystalline derivatives

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The synthesis of a new type of liquid crystalline compound derived from 1,2,3-triazole was achieved using Wittig reaction. Polarised microscopy studies, X-ray scattering and differential scanning calorimetry analysis revealed that the target compounds exhibit enantiotropic liquid crystalline properties. Their mesomorphic behaviour is closely related to the nature of substituents in position N1 of the heterocycle, the length of the mesogenic core as well as the isomerisation nature (E/Z) of the double bond.

Keywords: 1,2,3-triazole; mesogen; 1,3-dipolar cycloaddition; Wittig; smectic mesophases

1. Introduction

Mesogenic compounds containing heterocyclic rings are increasingly reported [1–5]. The incorporation of heterocyclic moieties as core units in liquid crystalline structures can result in large changes in their mesophases and physical properties due to the fact that most of the heteroatoms (S, O and N) commonly introduced are more polarisable than carbon. Heterocycle cores are thus able to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [6,7]. Among these derivatives, the five-membered heterocyclic rings, such as isoxazole [8], tetrazole [9] and 1,2,4-oxadiazole [10], have been studied as structural units to accede to liquid crystalline materials and to establish the relation between their molecular structure and the corresponding mesomorphic properties. Even if the disubstituted five-membered rings are not collinear which causes a significant loss of linearity disfavouring the mesophases formation, nematic, smectic C – smectic A mesophases were observed [11,12].

Since the discovery of the activated [2+3] dipolar cycloaddition reaction between an organic azide and terminal alkyne, also known as 'Click Chemistry', [1,2,3]-triazole compounds have attracted much more attention in different fields of material chemistry, supramolecular chemistry and pharmaceutical industry [13–16]. Examples of mesogen-based 1,2,3-triazoles have however been less described [17–19]. The position of the triazole ring within the rigid core and the nature of the substituents attached to the latter could induce dramatic effects on mesomorphic behaviour of the corresponding compounds. Thus, it was reported that compounds containing two phenyl rings and [1,2,3]-triazole unit at a terminal position were unable to exhibit liquid crystalline property while their homologues containing an additional polar alkoxy group at the terminal [1,2,3]-triazole ring displayed liquid crystallinity [20–22]. When the triazole unit is placed in a central core position and is linked directly to phenyl rings, smectic A or C mesophases were observed. We have previously reported that the introduction of an ester connector group within the triazole heterocycle leads to stable smectic A mesophases over a wide thermal domain [23].

In this article, the synthesis of novel 1,4-disubstituted [1,2,3]-triazole-based compounds was carried out by applying the Wittig reaction. The triazole core is linked through a double bond to the conjugated segments of the final derivatives leading to extended conjugated system which can potentially act as electron transporting materials.

2 Experimental section

2.1 Characterisation

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer (Wissembourg, France). Tetramethylsilane was used as an internal reference for chemical shifts. Infrared spectroscopies were carried out with a Jasco-4200 Fourier transform infrared spectrometer (Jasco, Inc., Easton, MD, USA) using KBr pellets. LC–MS identification was carried out by electrospray on HPLC Waters Alliance 2690 (Waters, Milford, MA, USA). Column chromatographies were carried out using E-Merck silica gel (Kieselgel 60, 230–400 mesh) as the stationary phase (Merck Millipore, Gernsheim, Germany). Thin-layer chromatography was carried out on aluminium plates

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pre-coated with Merck silica gel 60F254 and visualised by means of ultraviolet fluorescence quenching or iodine vapour.

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}. Mesomorophic textures were observed using an Olympus polarising microscope (Olympus corporation, Tokyo, Japan) equipped with Mettler Toledo heating stage.

X-ray diffraction experiments were performed by using a rotating anode generator (Rigaku, Kent, UK) having a wavelength of 1.54 Å, together with a home-made heating stage with a thermal stability of 0.1°C. The spectra were recorded with a bi-dimensional detector (Marresearch-345; Marreserche GmbH, Norderstedt, Germany) located at 309 mm from the sample, which was introduced as a powder in glass capillary tubes (Glas, Muller, Germany) having a diameter of 1.5 mm.

2.2 Synthesis

All the reagents were purchased from Aldrich (Sigma, Taufkirchen, Germany) 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.

2.2.1 (1-(4-Nitrophenyl)-1H-1,2,3-triazole-4-yl) methanol (2a)

A mixture of 4-azido-1-nitrobenzene 1a (1.19 g, 7.26 mmol), propargyl alcohol (0.4 g, 7.26 mmol), CuI (0.138 g, 0.726 mmol) and a catalytic amount of triethylamine in 30 ml of ethanol/water, 1/1, mixture was stirred at 70°C for 48 h. After cooling to room temperature, the reaction mixture was filtered and the obtained solid was washed with water and then recrystallised from hexane to give an orange powder.

The similar procedure was adopted for the preparation of (1-(4-bromophenyl)-1H-1,2,3-triazole-4-yl)methanol (2b) and (1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-yl)methanol (2c).

2a: Yield: 72 %, m.p. 210°C. IR (KBr) ν/cm^{-1}: 3223, 3120, 1490. ^{1}H NMR (300 MHz, $CDCl_3$): 2.33 (s, 1H, OH), 4.85 (s, 2H, CH_2), 7.93 (d, 2H, Ar–**H**, $^3J = 9.02$ Hz), 8.17 (s, 1H, H_5 triazole), 8.37 (d, 2H, Ar–**H**, $^3J = 9.02$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 59.61, 117.10, 120.42, 130.85, 135,71, 145.12, 148.27.

(1-(4-bromophenyl)-1H-1,2,3-triazole-4-yl)methanol (2b) : Yield: 87 %, m.p. 160°C. ^{1}H NMR (300 MHz, $CDCl_3$): 2.34 (s, 1H, OH), 4.85 (s, 2H, CH_2), 7.55 (d, 2H, Ar–**H**, $^3J = 9.31$ Hz), 7.61 (d, 2H, Ar–**H,** $^3J = 9.31$ Hz), 7.98 (s, 1H, H_5 triazole), ^{13}C NMR (300 MHz, $CDCl_3$): 59.55, 116.90, 123.10, 128.00, 131.73, 132.26, 144.50.

(1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-yl)methanol (2c): Yield: 85 %, m.p. 146°C. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.10 (s, 1H, OH), 3.70 (s, 3H, CH_3), 4.80 (s, 2H, CH_2), 6.93 (d, 2H, Ar–**H**, $^3J = 9.25$ Hz), 7.33 (d, 2H, Ar–**H,** $^3J = 9.25$ Hz), 7.88 (s, 1H, H_5 triazole), ^{13}C NMR (300 MHz, $CDCl_3$): 56.12, 59.65, 114.35, 116.95, 121.05, 130.90, 144.50, 160.78.

2.2.2 4-(bromomethyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (3a)

A 50-ml round bottom flask was charged with alcohol 2a (0.54g, 2.47 mmol), triphenylphosphine (0.70 g, 2.66 mmol) and 10 ml of CH_2Cl_2. The mixture was cooled to 0°C and stirred until the solution became homogeneous. N-bromosuccinimide (0.5 g, 2.82 mmol) was then added under nitrogen atmosphere. After 24 hours of vigorous stirring, solvent was evaporated and the crude product was purified by column chromatography ($CHCl_3$/ethyl acetate, 3/1) to yield 4-(bromomethyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (3a) as a yellow solid. The similar procedure was used for the preparation of 4-(bromomethyl)-1-(4-bromophenyl)-1H-1,2,3-triazole (3b) and 4-(bromomethyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3c)

3a: Yield: 78 %, m.p. 170°C. IR (KBr) ν/cm^{-c}: 3143, 1596, 747. ^{1}H NMR (300 MHz, $CDCl_3$): 4.94 (s, 2H, CH_2), 7.77 (s, 1H, H_5 triazole), 7.93 (d, 2H, Ar–**H**, $^3J = 9.31$ Hz), 8.37 (d, 2H, Ar–**H**, $^3J = 9.31$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 28.15, 119.22, 121.45, 130.85, 134,60, 145.15, 148.20.

4-(bromomethyl)-1-(4-bromophenyl)-1H-1,2,3-triazole (3b): Yield: 55 %, m.p. 140°C. ^{1}H NMR (300 MHz, $CDCl_3$): 4.56 (s, 2H, CH_2), 7.77 (s, 1H, H_5 triazole), 7.93 (d, 2H, Ar–**H,** $^3J = 9.31$ Hz), 8.37 (d, 2H, Ar–**H,** $^3J = 9.31$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 28.24, 119.30, 127.89, 131.13, 132.06, 132.15, 145.45.

4-(bromomethyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (3c): Yield : 70 %, m.p. 120°C. ^{1}H NMR (300 MHz, $CDCl_3$): 3.81 (s, 3H, CH_3), 4.59 (s, 2H, CH_2), 6.96 (d, 2H, Ar–**H,** $^3J = 9.00$ Hz), 7.55 (d, 2H, Ar–**H,** $^3J = 9.00$ Hz), 7.87 (s, 1H, H_5 triazole). ^{13}C NMR (300 MHz, $CDCl_3$): 28.10, 55.95, 114.33, 119.25, 120.84, 130.97, 145.77, 160.74.

2.2.3 Triphenylphosphoniums ylides (4a)

In a 50-ml round bottom flask was placed an equimolar quantity of 1-*p*-nitro-phenyl, *1H*, [1,2,3] triazole 4–bromomethyl (3a) (0.56g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in 10 ml of dichloromethane. After 5 days of vigorous stirring under nitrogen atmosphere at room temperature, the solvent was evaporated and the resulting crude mixture was washed with hexane to yield the phosphinium ylide (4a) as a pale yellow product.

The similar procedure was used for the preparation of compounds (4b) and (4c). In this case, the reaction time was 4 and 3 days, respectively.

4a:yield : 94 %, m.p. 260°C. ^{1}H NMR (300 MHz, $CDCl_3$): 5.50–5.57 (ds, 2H, CH_2), 7.56–7.87 (m, 15H, PPh_3), 7.93 (d, 2H, Ar–**H,** $^3J = 9.16$ Hz), 8.28 (d, 2H, Ar–**H,** $^3J = 9.16$ Hz), 9.44 (s, 1H, H_5 triazole).

4b:yield = 96%, m.p. 290°C. ^{1}H NMR (300 MHz, $CDCl_3$): 5.51–5.57 (ds, 2H, CH_2), 7.50–7.86 (m, 15H, PPh_3), 7.77 (d, 2H, Ar–**H,** $^3J = 8.45$ Hz), 8.45 (d, 2H, Ar–**H,** $^3J = 8.45$ Hz), 9.05 (s, 1H, H_5 triazole).

4c:yield = 93%, m.p. 270°C.

2.2.4 4-decyloxybenzaldehyde (5)

4-Hydroxybenzaldehyde (3 g, 20 mmol), K_2CO_3 (17.25 g, 120 mmol) and 1-decylbromide (5.4 g, 20 mmol) were dissolved in 50 ml of DMF and were stirred for 5 hours at 150°C under nitrogen atmosphere. The crude mixture was filtered and the filtrate was evaporated then extracted three times with diethyl ether, washed with water and finally dried under Na_2SO_4. The product was purified by column chromatography using chloroform as eluant to yield 90% of 4-decyloxybenzaldehyde as colourless oil.

IR (KBr) ν/cm^{-1}: 3094, 1738, 1205. ^{1}H NMR (300 MHz, $CDCl_3$): 0.85 (t, 3H, CH_3, $^3J = 6.70$ Hz), 1.35 (m, 14H, CH_2), 1.84 (tt,2H, O–CH_2CH_2–,$^3J = 7.35$ Hz, $^3J = 6.58$ Hz), 4.05 (t, 2H, O–CH_2, $^3J = 6.58$ Hz), 7.00 (d, 2H, Ar–**H,** $^3J = 8.75$Hz), 7.82 (d, 2H, Ar–**H,** $^3J = 8.75$), 9.88 (s, 1H, CHO). ^{13}C NMR (300 MHz, $CDCl_3$): 190.00, 164.22, 132.11, 129.95, 114.91, 68.50, 31.00, 29.65, 29.42, 29.37, 29.08, 26.15, 22.70, 14.35.

2.2.5 4-decyloxybenzoate benzaldehyde (6)

4-decyloxybenzoate benzaldehyde (6) was prepared in a two-step procedure. 4-Hydroxybenzoic acid (6 g, 40 mmol), potassium iodide (0.45 g, 2.7 mmol) and potassium hydroxide (4.64 g, 82 mmol) were dissolved in a mixture of water/ethanol, 30 ml/130 ml. 1-bromodecane (8.8 g, 40 mmol) was then added dropwise and the mixture was stirred at 80°C for 3 days. Solvent was evaporated and then a solution of concentrated HCl 37% was added. The precipitate formed was filtered, washed several times with water until neutralisation then with petroleum ether to eliminate impurities. 4-decyloxybenzoic acid was obtained as a white solid (yield = 68%, m.p. 92°C).

4-Decyloxybenzoic acid (2 g, 7 mmol), 4-hydroxybenzaldehyde (0.87 g, 7 mmol), dicyclohexycarbodiimide (1.44 g) and 4-dimethylaminopyridine (0.85 g) were dissolved in 100 ml of dichloromethane and were stirred for 3 days at 40°C under nitrogen atmosphere.

Precipitate urea was removed by filtration, then the solvent was evaporated and the residual product was purified by column chromatography using chloroform as eluant. 4-decyloxybenzoate benzaldehyde (6) was obtained as a white solid (yield = 70%, m.p. 56°C).

IR (KBr) ν/cm^{-1}: 3094, 1738, 1205. ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (t, 3H, CH_3, $^3J = 6.64$ Hz), 1.35 (m, 14H, CH_2), 1.84 (tt,2H, O–CH_2CH_2–,$^3J = 7.35$ Hz, $^3J = 6.56$ Hz), 4.07 (t, 2H, O–CH_2, $^3J = 6.56$ Hz), 7.00 (d, 2H, Ar–**H,** $^3J = 8.92$Hz), 7.42 (d, 2H, Ar–**H,** $^3J = 8.56$), 7.98 (d, 2H, Ar–**H,** $^3J = 8.56$), 8.16 (d, 2H, Ar–**H,** $^3J = 8.92$), 10.04 (s, 1H, CHO). ^{13}C NMR (300 MHz, $CDCl_3$): 191.00, 165.34, 162.72, 157.36, 133.71, 130.94, 130.35, 122.11, 121.93, 114.31, 68.90, 31.90, 29.71, 29.42, 29.37, 29.08, 26.15, 22.77, 14.15.

2.2.6 (E) and (Z)-1-(4-nitrophenyl)-4-(4-decyloxystyryl)-1H-1,2,3-triazole (7-7′a)

In a 50-ml bicolour round bottom flask was placed 1 equivalent of phosphonium ylide 4a (0.81 g, 1.49 mmol), 2.6 equivalents of 4-decyloxybenzaldehyde 5 (1.02 g, 3.91 mmol) and NaOH (0.55g) in a mixture of 2.8 ml of dichloromethane, 2 ml of water and 1.3 ml of hexane. After 48 hours of vigorous stirring at ambient temperature under nitrogen atmosphere, the reaction mixture was poured into a 30-ml HCl 1M solution and then extracted 4 times with dichloromethane. The organic fractions were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Methanol was added in order to separate the insoluble E-isomer product. The filtrate was then evaporated and the obtained solid was washed with hot hexane in order to yield the Z isomer as a solid. A purification of the filtrate by column chromatography using chloroform as eluant is also possible.

Total yield, 47%; 7a/7′a ratio = 50/50. IR (KBr) ν/cm^{-1}: 3094, 1470, 1346, 1205. ^{1}H NMR (300 MHz, $CDCl_3$): **Isomer E (7 a):** 0.90 (t, 3H, CH_3, $^3J = 6.53$ Hz,), 1.37 (m, 14H, CH_2), 1.82 (tt, 2H, O–CH_2CH_2, $^3J = 6.61$ Hz, $^3J = 6.03$ Hz), 4.00 (t,

2H, O–CH_2, ^3J = 6.61 Hz), 7.00 (d, 1H, = CH–Ar, $^3J_{trans}$ = 16.19 Hz), 7.39 (d, 1H, = CH–triazole, $^3J_{trans}$ = 16.19 Hz), 7.48 (d, 2H, Ar–**H**, ^3J = 8.34 Hz), 7.84 (d, 2H, Ar–**H**, ^3J = 8.34 Hz), 8.01 (d, 2H, Ar–**H**, ^3J = 9.11 Hz), 8.06 (s, 1H, H_5 triazole), 8.45 (d, 2H, Ar–**H**, ^3J = 9.11 Hz). ^{13}C NMR (300 MHz, $CDCl_3$):14.09, 22.66, 26.01, 29.21, 29.30, 29.37, 29.54, 29.55, 31.87, 68.17, 113.02, 114.79, 117.15, 120.17, 125.54, 127.97, 132.10, 141.11, 147.04, 148.01, 160.51. MS (ES +): calcd for $C_{26}H_{32}N_4O_3$: 448.25, found: 449.2 $[M + 1]^{+\cdot}$

Isomer Z (7′a): 0.90 (t, 3H, CH_3, ^3J = 6.52 Hz), 1.29 (m, 14H, CH_2), 1.82 (tt,2H, O–CH_2CH_2, ^3J = 7.11 Hz, ^3J = 6.57 Hz,), 4.00 (t, 2H, O–CH_2, ^3J = 6.57 Hz), 6.74 (dd, $\sum$AA′, 2H, CH = CH, $^3J_{cis}$ = 12.24 Hz), 6.92 (d, 2H, Ar–**H**, ^3J = 8.59 Hz), 7.35 (d, 2H, Ar–**H**, ^3J = 8.59 Hz), 7.71 (s, 1H, H_5 triazole), 7.84 (d, 2H, Ar–**H**, ^3J = 9.17 Hz), 8.39 (d, 2H, Ar–**H**, ^3J = 9.17 Hz). ^{13}C NMR (300 MHz, $CDCl_3$):14.09, 22.66, 26.04, 29.25, 29.30, 29.41, 29.55, 29.68, 31.88, 68.15, 114.69, 114.80, 118.77, 120.34, 125.47, 127.98, 129.54, 132.99, 141.13, 146.09, 147.08, 158.96. MS (ES +): calcd for $C_{26}H_{32}N_4O_3$: 448.25, found: 449.2 $[M + 1]^{+\cdot}$

The same procedure was used to prepare (E) and (Z)-4-(4-(decyloxy)styryl)-1-(4-bromophenyl)-1*H*- [1,2,3]-triazole (7-7′b) and (E)-4-(4-(decyloxy) styryl)-1-(4-methoxyphenyl)-1*H*- [1,2,3]-triazole (7c).

(E) and (Z)-1-(4-bromophenyl)-4-(4-decyloxystyryl) -1H-1,2,3-triazole (7-7′b): Total yield obtained was 41%, 7b/7′b ratio = 78/23.

Isomer E (7 b): 0.90 (t, 3H, ^3J = 6.64 Hz, CH_3), 1.35 (m, 14H, CH_2), 1.81 (tt,2H, O–CH_2CH_2, ^3J = 7.31, ^3J = 6.52 Hz), 4.00 (t, 2H, O–CH_2, ^3J = 6.52 Hz,), 6.92 (d, 2H, Ar–**H**, ^3J = 8.70 Hz), 7.01 (d, 1H, –CH = CH–Ar, $^3J_{trans}$ = 16.36 Hz,), 7.38 (d, 1H, –CH = CH–triazole, $^3J_{trans}$ = 16.36 Hz), 7.47 (d, 2H, Ar–**H**, ^3J = 8.70 Hz), 7.68 (s, 4H, Ar–**H**), 7.95 (s, 1H, H_5 triazole). ^{13}C NMR (300 MHz, $CDCl_3$):14.10, 22.67, 27.61, 29.27, 29.29, 29.54, 29.68, 29.77, 31.15, 68.10, 114.76, 121.74, 122.48, 124.77, 127.86, 129.72, 131.32, 132.90, 137.32, 149.57, 157.59.

Isomer Z (7′b): 0.90 (t, 3H, CH_3,^3J = 6.68 Hz), 1.35 (m, 14H, CH_2), 1.81 (tt,2H, O–CH_2CH_2, ^3J = 7.31 Hz, ^3J = 6.63 Hz), 3.99 (t, 2H, O–CH_2, ^3J = 6.63), 6.71 (dd, 2H, CH = CH–, $^3J_{cis}$ = 12.14 Hz), 6.90 (d, 2H, Ar–**H**, ^3J = 8.67), 7.34 (d, 2H, Ar–**H,** ^3J = 8.67 Hz), 7.50 (d, 2H, Ar–**H,** ^3J = 8.86 Hz), 7.59 (s, 1H, H_5 triazole), 7.62 (d, 2H, Ar–**H**, ^3J = 8.86 Hz). ^{13}C NMR (300 MHz, $CDCl_3$):14.10, 22.66, 26.02, 29.23, 29.30, 29.38, 29.56, 29.67, 31.87, 68.10, 113.67, 121.74, 121.83, 122.27, 127.87, 129.05, 131.31, 132.89, 138.13, 147.46, 158.81.

(E)-1-(4-methoxyphenyl)-4-(4-decyloxystyryl)-1H-1,2, 3-triazole (7c): Total yield, 42%; 7c/7′c ratio = 100/0.

Isomer E (7 c): 0.90 (t, 3H, CH_3, ^3J = 6.62 Hz,), 1.45 (m, 14H, CH_2), 1.81 (tt,2H, O-CH_2CH_2, ^3J = 7.28 Hz, ^3J = 6.59 Hz), 3.89 (s, 3H, OCH_3), 3.99 (t, 2H, O–CH_2, ^3J = 6.59 Hz), 6.91 (d, 2H, Ar–**H**, ^3J = 8.67 Hz), 7.02 (d, 1H, –CH = CH–Ar, $^3J_{trans}$ = 16.43 Hz,), 7.05 (d, 2H, Ar–**H**, ^3J = 8.99 Hz), 7.35 (d, 1H, –CH = CH–triazole, $^3J_{trans}$ = 16.43 Hz), 7.46 (d, 2H, Ar–**H**, ^3J = 8.67 Hz), 7.67 (d, 2H, Ar–**H**, ^3J = 8.99 Hz), 7.90 (s, 1H, H_5 triazole). ^{13}C NMR (300 MHz, $CDCl_3$):14.03, 22.66, 26.02, 29.24, 29.31, 29.38, 29.55, 29.69, 31.88, 55.62, 68.08, 114.56, 117.97, 122.08, 126.08, 127.78, 128.04, 130.72, 133.68, 135.96, 159.96, 163.17. MS (ES +): calcd for $C_{27}H_{35}N_3O_2$: 433.27, found: 434.3 $[M + 1]^{+\cdot}$

2.2.7 (E) and (Z)-1-(4-nitrophenyl)-4-(4-decyloxy benzoatestyryl)-1H-1,2,3-triazole (8-8′a)

These compounds were prepared by a similar procedure to that described for compounds (7-7′a) from compound (4a) and 4-decyloxybenzoate benzaldehyde (6).
Total yield 66%, 7c/7′c ratio = 49/51.

Isomer E (8 a): 0.90 (t, 3H,, CH_3, ^3J = 6.65 Hz), 1.30 (m, 14H, CH_2), 1.85 (tt,2H, O–CH_2CH_2, ^3J = 7.44 Hz, ^3J = 6.55 Hz), 4.07 (t, 2H, O–CH_2, ^3J = 6.55 Hz), 7.03 (d, 2H, Ar–**H**, ^3J = 8.79 Hz), 7.13 (d, 1H, –CH = CH–Ar, $^3J_{trans}$ = 16.39 Hz), 7.26 (d, 2H, Ar–**H**, ^3J = 8.64 Hz), 7.52 (d, 1H, –CH = CH–triazole, $^3J_{trans}$ = 16.39 Hz), 7.61 (d, 2H, Ar–**H**, ^3J = 8.64 Hz), 8.03 (d, 2H, Ar–**H**, ^3J = 9.11 Hz), 8.12 (s, 1H, H triazole), 8.19 (2H, Ar–**H**, ^3J = 8.79 Hz), 8.46 (d, 2H, Ar–**H**, ^3J = 9.11 Hz). ^{13}C NMR (300 MHz, $CDCl_3$):14.10, 22.66, 25.97, 29.07, 29.30, 29.34, 29.53, 29.68, 31.87, 68.34, 114.43, 120.25, 122.23, 122.77, 125.49, 127.68, 131.51, 132.29, 133.92, 134.49, 135.71, 142.58, 143.97, 150.74, 155.32, 165.92.

Isomer Z (8′a): 0.90 (t, 3H,, CH_3, ^3J = 6.65 Hz), 1.30 (m, 14H, CH_2), 1.85 (tt,2H, O–CH_2CH_2, ^{3} J = 7.44 Hz, *J* = 6.55 Hz), 4.07 (t, 2H, O–CH_2, ^3J = 6.55 Hz), 6.89 (dd ($\sum$AA′), 2H,, –CH = CH– $^3J_{cis}$ = 11.41 Hz), 6.99 (d, 2H, Ar–**H**, ^3J = 8.80 Hz), 7.26 (d, 2H, Ar–**H,** ^3J = 8.32 Hz), 7.42 (d, 2H, Ar–**H**, ^3J = 8.32 Hz), 7.35 (s, 1H, H–triazole), 7.89 (d, 2H, Ar–**H,** ^3J = 9.12 Hz), 8.16 (d, 2H, Ar–**H**, ^3J = 8.80 Hz), 8.39 (d, 2H, Ar–**H,** ^3J = 9.12 Hz) . ^{13}C NMR (300 MHz, $CDCl_3$): 14.10, 22.66, 25.96, 29.07, 29.30, 29.34, 29.53, 29.68, 31.87, 68.39, 114.43, 120.32, 122.22, 122.77, 125.48, 127.68, 129.17, 132.29, 132.37, 133.92, 135.36, 140.82, 145.65, 150.74, 153.61, 165.19.

The same procedure was used to prepare (E)-1-(4-bromophenyl)-4-(4-decyloxybenzoatestyryl)-1H-1,2,3-triazole (8b) and (E)-1-(4-methoxyphenyl)-4-(4-decyloxybenzoatestyryl)-1H-1,2,3-triazole (8c) from the appropriate phosphonium ylides (4b) and (4c), respectively.

Isomer E (8b): 0.90 (t, 3H, CH_3, $^3J = 6.69$ Hz), 1.30 (m, 14H, CH_2), 1.85 (tt,2H, O–CH_2CH_2–, $^3J = 7.36$ Hz, $^3J = 6.61$ Hz,), 4.06 (t, 2H, O–CH_2, $^3J = 6.61$ Hz), 6.99 (d, 2H, Ar–**H**, $^3J = 8.90$ Hz), 7.13 (d, 1H, –CH = CH–Ar, $^3J_{trans} = 16.43$ Hz), 7.24 (d, 2H, Ar–**H**, $^3J = 8.63$ Hz), 7.46 (d, 1H, CH = CH–triazole, $^3J_{trans} = 16.43$ Hz), 7.59 (d, 2H, Ar–**H**, $^3J = 8.63$ Hz), 7.69 (s, 4H, Ar–**H**), 8.01 (s, 1H, H–triazole), 8.16 (2H, Ar–**H**,$^3J = 8.90$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 14.10, 22.67, 25.96, 29.08, 29.30, 29.34, 29.53, 29.68, 31.09, 68.33, 114.30, 121.79, 122.17, 123.15, 123.75, 127.60, 129.28, 130.26, 132.29, 132.84, 132.93, 134.20, 134.72, 141.76, 147.45, 153.86, 161.97.

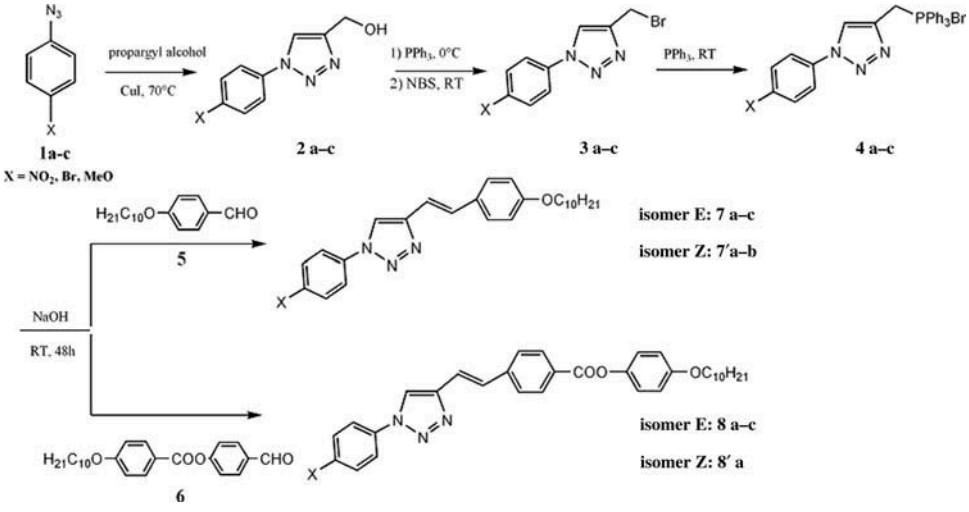
Isomer E (8 c): 0.90 (t, 3H, CH_3,$^3J = 6.38$ Hz), 1.40 (m, 14H, CH_2), 1.84 (tt,2H, O–CH_2CH_2–, $^3J = 7.34$ Hz, $^3J = 6.59$ Hz), 3.90 (s, 3H, CH_3O), 4.06 (t, 2H, O–CH_2, $^3J = 6.59$ Hz), 6.99 (d, 2H, Ar–**H**, $^3J = 8.97$ Hz), 7.06 (d, 2H, Ar–**H**, $^3J = 8.95$ Hz), 7.14 (d, 1H, –CH = CH–Ar, $^3J_{trans} = 16.41$ Hz), 7.43 (d, 1H, CH = CH–triazole, $^3J_{trans} = 16.41$ Hz), 7.47 (d, 2H, Ar–**H**, $^3J = 8.56$ Hz), 7.59 (d, 2H, Ar–**H**, $^3J = 8.56$ Hz), 7.68 (2H, Ar–**H**, $^3J = 8.97$ Hz), 7.96 (s, 1H, H–triazole), 8.16 (d, 2H, Ar–**H**, $^3J = 8.95$Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 14.10, 22.66, 25.96, 29.07, 29.30, 29.34, 29.53, 29.68, 31.87, 55.62, 68.33, 114.30, 114.72, 118.50, 121.39, 122.10, 122.60, 127.51, 129.37, 130.14, 130.43, 132.28, 134.35, 135.26, 146.53, 150.50, 159.72, 164.87.

3 Results and discussion

3.1 Synthesis

The synthetic procedures for the triazole derivatives 7a–c and 8a–c and their corresponding Z isomers 7′ and 8′ are summarised in Scheme 1. The triazole-based mesogenic compounds were prepared according to the Wittig reaction by reacting the appropriate triphenylphosphoniums ylides (4a–c) with 4-decyloxybenzaldehyde (5) or 4-decyloxybenzoate benzaldehyde (6). Triphenylphosphoniums ylides were synthesised in four-stage process. In the first instance, we have attempted to prepare the bromomethyl substituted triazoles (3a–c) directly by the reaction of propargylbromide with different azide derivatives (1a–c), previously prepared according to Nolting and Michel method [24]. The yields were low (lower than 30%) whatever the experimental conditions employed, i.e. by refluxing in water or through click chemistry conditions in the presence of CuI using a mixture of water/ethanol as a solvent at 70°C.

Thus, we opted for a two-step procedure involving the bromination of the hydroxymethyl triazole derivatives (2a–c) synthesised by catalytic 1,3-dipolar cycloaddition between the arylazides (1a–c) with propargyl alcohol in the presence of CuI. The reaction is highly regioselective since only the 1,4 regioisomers were obtained. Their structures were supported by ^{1}H and ^{13}C NMR analysis and the examination of relevant literature. The reaction of (2a–c) with N-triphenylphosphine and bromosuccinimide afforded the brominated compounds (3a–c) with good yield. They were then condensed with triphenylphosphine in dichloromethane to produce the active Wittig reagents (4a–c) which were further coupled with 4-decyloxybenzaldehyde (5) or 4-decyloxybenzoate



Scheme 1. Synthesis of the compounds.

Table 1. Transition temperatures (°C) and transition enthalpies ΔH (KJ mole^{-1}) of compounds (7/7′ a–c) and (8/8′ a–c) determined by DSC (5°C min^{-1}) during the second cycle.

Compound	X	Isomer	Transition temperatures (°C) [transition enthalpies ΔH (KJ mole^{-1})]
7a	NO_2	E	Cr (76.03°C) [14.11] SmA(165.51°C) [3.69] I
7′a	NO_2	Z	Cr (78.70°C) [1.90] Cr′(110.35°C) [17.14] I
7b	Br	E	Cr (159.91°C) [19.27] SmA(241°C) [4.24] I
7′b	Br	Z	Cr (110.59°C) [9.62] SmA(162.58°C) [2.47] I
7c	MeO	E	Cr (81.24°C) [1.23] Cr′(102.66) [1.93]Cr″(123.64°C)[35.20] SmC (185.56°C) [0.03] N(193.97)[0.48] I
8a	NO_2	E	Cr (121.69°C) [11.15] SmA(158.38°C) [0.96] I
8′a	NO_2	Z	Cr (84.60°C) [2.27] Cr′(127.19°C)[7.34] SmA(159.52°C) [0.74] I
8b	Br	E	Cr (99.80°C) [28.09] Cr′(141,50°C) [11.09]SmC (>250°C)I
8c	MeO	E	Cr (85.98°C) [6.37] Cr′(142.24°C)[8.86]N(165.04°C) [0.56] I

benzaldehyde (6) to give the desired derivatives with good yields. Depending on the nature of the substituent X present in position N1 of the heterocycle, we observed the formation of one isomer (E isomer) or two isomers (E and Z). These isomers were easily separated by washing the crude products with methanol then hexane or by column chromatography.

3.2 *Mesomorphic properties*

The mesomorphic behaviour of compounds 7/7′ a–c and 8/8′ a–c was studied using polarised optical microscopy, DSC and X-ray scattering. The phase transitions and thermodynamic data are summarised in Table 1 and in the bar-graph chart (Figure 1).

Expected for compound 7a′, all studied derivatives exhibit enantiotropic liquid crystalline behaviour. The dominant mesophase was the smectic A mesophase which was clearly identified by optical texture as shown in Figure 2a. On slow cooling from the isotropic liquid, tiny batonnets developed at the edge of melted substance and grew up to the focal conic fan texture. Polygonal textures were also observed for some samples.

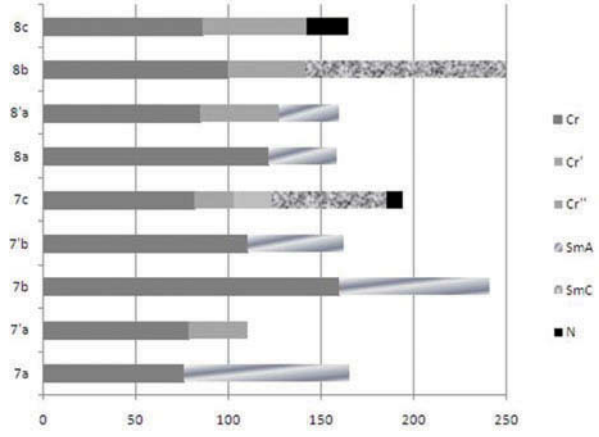


Figure 1. (colour online) Comparative thermal behaviour of the final compounds.

The thermal stability range of the smectic A mesophase varied from 81 to 89°C for the first series (7a–b) and is thus independent of the nature of substituent X. Compounds with electron-donating substituent (OCH_3) (compounds 7c) exhibit a smectic C mesophase instead of the smectic A mesophase observed for the majority of the studied compounds. The smectic C mesophase was clearly evidenced in polarised optical microscopy by the broken-fan-shaped textures as presented in Figure 2b. An additional nematic phase was also observed which was confirmed by optical microscopy by the formation of droplets with Schlieren optical texture.

The elongation of the aromatic rigid core by the introduction of an additional phenyl group (8a–c) has a drastic effect on the stability of mesophases in comparison with those of the series (7a–c) with shorter mesogens. The stability range of the smectic A mesophase was reduced by a factor of 2.5 for compounds 8a in comparison with the corresponding shorter structure 7a, whereas for compound 8c, the smectic C mesophase disappears completely in favour of a more stable nematic phase. A typical DSC thermogram of compound 8c is presented in Figure 3.

It is interesting to note that the nematic–isotropic enthalpy changes obtained for compounds 7c and 8c are rather smaller than would be expected for a conventional low molar mass liquid crystals consisting of a single mesogenic unit. These small values for the clearing enthalpy may be attributed to the increased molecular biaxiality arising from both the triazole core and the double bound connector. Similar observations have been made for other types of non-linear cores [25,26].

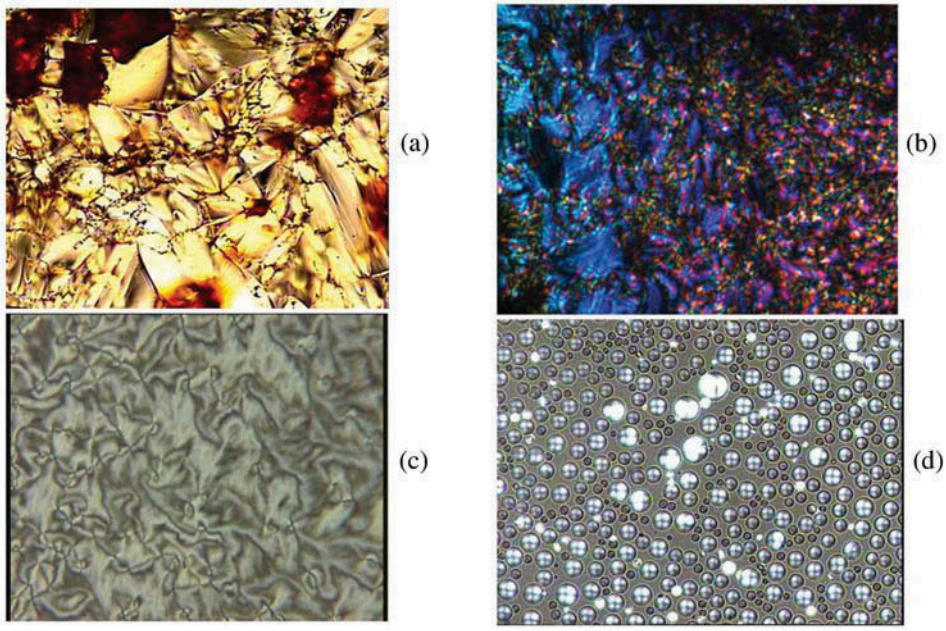


Figure 2. The representative photomicrographs of (a) the SmA polygonal texture for compound 7b at 218°C and (b) SmC broken-fan-shaped texture SmC for compound 7c at 150°C, (c) Schlieren texture for compound 8b at 145°C and (d) the nematic droplets texture for compound 8c at 159°C. In each case, the image size is 240 μm × 300 μm.

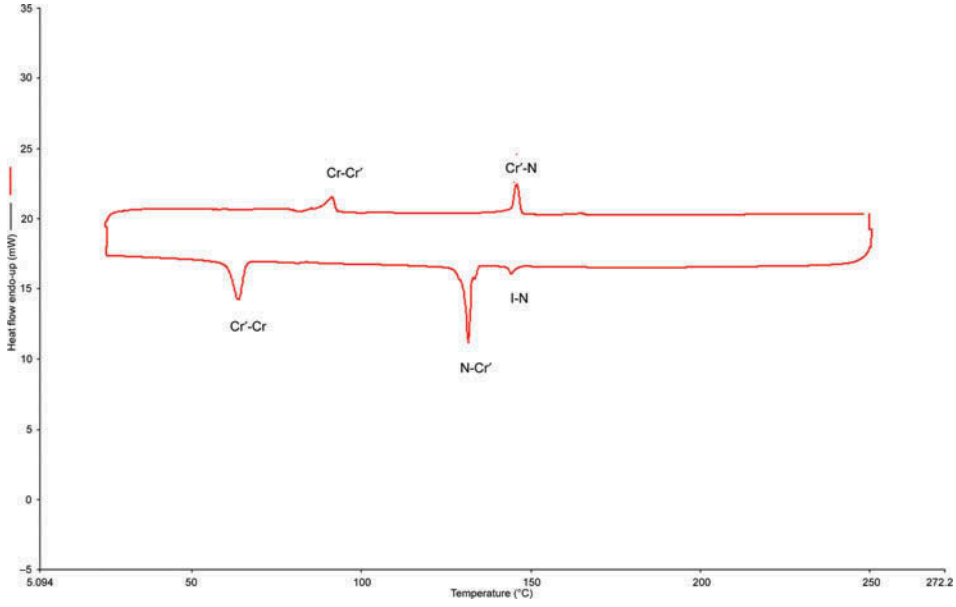


Figure 3. (colour online) Thermogram of compound 8c during the second cycle. The heating and cooling rates are 5°C min^{-1}.

It seems that the four-membered rings (series 8a–c) are not as conducive to liquid crystalline packing as the compounds of series (7a–c). This observation could be due to the deviation from the linearity induced by the elongation of the rigid core.

Unexpected behaviour was observed for the compound 8b since it exhibits a smectic C mesophase stable above 250°C instead of the smectic A mesophase observed for the corresponding short-mesogen-based compound 7b . The smectic C mesophase was identified both by the schlieren textures as presented in Figure 2c and by X-ray scattering (Figures 4 and 5). The compound 8b shows two distinct crystalline phases with a strong lamellar organisation at low temperature and a smectic phase at high temperature

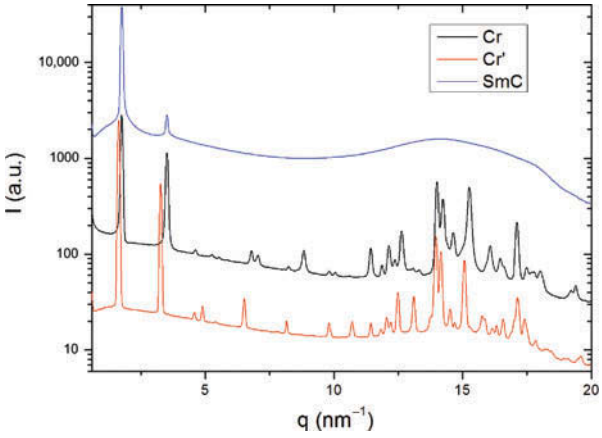


Figure 4. (colour online) X-ray diffractograms of 8b as a function of temperature showing two cristalline phases and a smectic mesophase. The spectra have been measured at 80, 120 and 170°C, respectively.

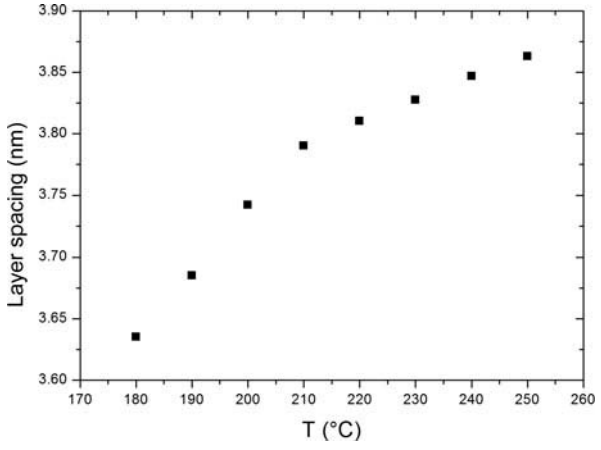


Figure 5. Temperature dependence of the smectic layer spacing of 8b measured by X-ray scattering. This increase of the layer spacing with temperature is characteristic of a mesophase exhibiting tilted molecules in the layers, i.e. of a smectic C local order.

characterised by the main Bragg peaks $q_{100} = 1.7\ nm^{-1}$ and the second-order reflection (200). The signal of the disordered aliphatic chains corresponds to the broad reflection at about 14 nm^{-1} and is characteristic of a liquid-like order. In order to determine the nature of the local smectic order, the dependence of the smectic layer spacing $d = 2\pi/q_{100}$ with temperature is displayed Figure 5. A rise of temperature in smectic C phases induces an increase of the fluctuations in the tilt angle of the molecular director, which leads to an increase of the average layer distance.

The mesomorphic behaviour was found to be also related to the nature (E/Z) of the double bond which has been introduced in the central position of the synthesised derivatives. The nature (E/Z) of the double bond changes the conformation of the mesogenic core substantially. It results in significantly higher stability of the smectic A mesophase and higher melting points for compounds with a *trans* double bond (E). This behaviour is much more pronounced for the molecules of the first series (7/7′), especially for compounds bearing a nitro group (7a and 7′a) where a *cis* double bond (Z) appears to be detrimental to the liquid crystalline behaviour since any mesophase was observed for the corresponding product.

The dependence of smectic-isotropic enthalpy transitions on the conformation of mesogenic core could also be stressed. E isomers (compounds 7b and 8a) exhibit greater enthalpy values then their corresponding Z isomers 7′b and 8′a, respectively. This behaviour is attributed to the increase in molecular biaxiality for Z isomers which can induce a reduction of enthalpy for the clearing transitions. Similary, enthalpy dependence of the equilibrium ratio of the *cis* to *trans* isomers derivatives has been observed for symmetric and non-symmetric liquid crystalline dimers [27,28].

4. Conclusion

Two novel series of 1,2,3-triazole-based mesogens were synthesised and characterised. An unsaturated carbon–carbon double bond has been introduced as a connector in the mesogenic core by applying a Wittig reaction of different triphenylphosphoniums ylides of triazole derivatives with 4-decyloxybenzaldehyde or 4-decyloxybenzoate benzaldehyde.

The effects of substituents in position N1 of the heterocycle, the length of the mesogenic core and the nature (E/Z) of the double bond on the mesomorphic behaviour were systematically studied. Most compounds exhibit smectic A mesophase. Compounds with methoxy terminal group promote additional nematic phase. Shorter mesogens as well as compounds with a *trans* double bond (E) are more conducive to liquid crystalline packing. This behaviour could be related to the changes in the geometry, i.e. linearity of the final molecules.

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