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Hugo Gallardo[a]; Adailton J. Bortoluzzi[a]; Deise Maria Pereira De Oliveira Santos[a]
[a] Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil

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Synthesis, crystalline structure and mesomorphic properties of new liquid crystalline 1,2,3-triazole derivatives

Hugo Gallardo*, Adailton J. Bortoluzzi and Deise Maria Pereira De Oliveira Santos

Departamento de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil

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Two new [1,2,3]-triazole-based liquid crystalline compounds were synthesised through Cu(I)-catalyzed 1,3-dipolar cycloaddition of 1-azido-4-decyloxybenzene or 1,3-diazidobenzene with terminal acetylenes. Their mesophases were characterised by a combination of differential scanning calorimetry and polarising optical microscopy. The calamitic final compounds exhibited a smectic C phase over a wide temperature range. The crystal and molecular structure of compound **3a**, determined by X-ray analyses, is discussed in detail. Crystal packing of the mesogens is characterised by a parallel arrangement of the strongly intercalated molecules.

Keywords: 1,2,3-triazole derivatives; X-ray crystal structure; click chemistry

1. Introduction

Liquid crystals are fascinating materials with properties intermediate between those of solids and liquids. It is well known that molecular shape has a dominant influence on the existence of the liquid crystalline state (*1–3*). The design of novel thermotropic liquid crystals as advanced functional materials involves suitable selection of a core fragment, linking group and terminal functionality. Over many years a large number of liquid-crystalline compounds containing heterocyclic units have been synthesised (*4, 5*). This research field has grown even more in recent years because of improvements in synthetic methodologies. Heterocycles are of great importance as core units in thermotropic liquid crystals due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape (*6, 7*). Furthermore, the incorporation of heteroatoms can result in considerable changes in the corresponding liquid-crystalline phases and/or in the physical properties of the observed phases, because most of the heteroatoms (S, O and N) commonly introduced are chemically classified as more polarisable than carbon (*8*). In particular, 1,2,3-triazoles are useful targets in chemical synthesis because they have been associated with a wide variety of interesting properties. These unnatural N-heterocyclic compounds with high levels of biological activity exhibit great potential in materials chemistry, e.g. as dyes, corrosion inhibitors, photostabilisers and photographic materials (*9, 10*). However, to the best of our knowledge, little detailed research on the relationships between structure and mesomorphic properties of 1,2,3-triazole derivative has been reported.

The most general methodology described in literature for the synthesis of five-member ring heterocycles is the 1,3-dipolar cycloaddition reaction. In particular, when the reaction occurs between alkyl or aryl azides and terminal acetylenes, 1,2,3-triazoles are obtained (*11*). Combinations of substituents on the azide and the alkyne allow the preparation of many N-substituted structures. If the cycloaddition is thermally conduced, a 1:1 mixture of the 1,4- and 1,5-regioisomers is usually obtained. To improve the 1,4-regioselectivity, reactions are carried out using a catalytic amount of Cu(I) or Cu(II) salts and sodium ascorbate, with water as the solvent or even in encapsulated systems (*12*).

The click reaction has been applied successfully by our group in the synthesis of new 1,2,3-triazole derivative chiral mesogens, which exhibit smectic A (SmA), chiral smectic C (SmC*) and helical chiral nematic (N*, cholesteric) phases (*13*). Also, we have previously described a synthetic procedure for regioselective synthesis of 1,4-diaryl-[1,2,3]-triazole with a nonlinear shape (*14*). The aim of the present work was to continue with the investigation of structures based on this heterocyclic core, 1,4-disubstituted-[1,2,3]-triazole, in order to establish the influence of molecular structures on the mesomorphic properties in these compounds. The triazole unit plays an important role since it acts as a link between the conjugated segments of the compound and also because it has a good electron affinity, potentially acting as an electron-transporting material.

Herein, we report the synthesis and mesomorphic properties of some 1,4-disubstituted-[1,2,3]-triazoles,

*Corresponding author. Email: hugo@qmc.ufsc.br

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3a–**3b** and **4**. In addition, the results of an X-ray crystal structure determination of mesogen **3a** will be presented. The compounds were characterised by ^{1}H and ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC) and polarising optical microscopy (POM).

2. Experimental

Characterisation

Elemental analyses were carried out using a Perkin Elmer model 2400 instrument. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer in KBr discs. ^{1}H NMR spectra were obtained with a Varian Mercury Plus 400 MHz instrument using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded on a Varian Mercury Plus 100 MHz spectrometer. The melting points, thermal transitions and optical textures were determined using an Olympus BX50 polarising optical microscope equipped with a Mettler Toledo FP-82 HT heating stage and an exposure control unit PM-30. DSC measurements were carried out using a Shimadzu instrument with a DSC-50 module. The samples were prepared in a nitrogen atmosphere and hermetically closed in aluminium pans. The mass of the samples was 4–8 mg; heating and cooling rates of $5^{\circ}C\,min^{-1}$ were applied.

Materials

All the reagents were obtained from commercial sources and used without further purification. The organic solvents were commercial and all were dried by traditional methods. All the compounds were purified by column chromatography on silica gel (60–120 mesh), and crystallisation from analytical grade solvents. The purity of the sample was confirmed by thin layer chromatography (Merck Kieselgel 60F254).

General procedure for 1-azido-4-alcoxybenzenes, ***1a****.*

4-*N*-decyloxyaniline (4.00 g, 16.1 mmol) was dissolved in H_2O (22 ml) and HCl conc. (22 ml). $NaNO_2$ (1.55 g, 22.5 mmol) dissolved in H_2O (5 ml) was added dropwise to the mixture cooled at 0°C. The mixture was stirred for 10 min, then NaN_3 (1.60 g, 24.6 mmol) dissolved in H_2O (5 ml) was added slowly, keeping the temperature under 2°C. The resultant suspension was stirred for 20 min, and then the phases were separated. The aqueous phase was extracted with diethyl ether (3×50 ml). The combined organic phases were dried under Na_2SO_4 and the solvents evaporated. The residue was purified by column chromatography (silica gel, hexane), furnishing the 1-azido-4-decyloxybenzene (**1a**) as a yellow oil. Yield: 3.98 g (89.9%). IR (KBr, cm^{-1}): 2926, 2855, 2111, 1503, 1464, 1283, 1244, 825.

For 1,3-diazido-benzeno (**1b**): yield: 44%. Dark-red oil, very viscous. IR (KBr, cm^{-1}): 2406, 2253, 2114, 1591, 1259, 853.

General procedure for propynoic acid 4-alkoxyphenyl esters, ***2a*** *and* ***2b****.*

To a solution of 4-decyloxyphenol (2.00 g, 8.0 mmol) and propiolic acid (0.46 ml, 7.4 mmol, $d=1.138\,g\,ml^{-1}$) in dry CH_2Cl_2 at 0°C in inert atmosphere, a combined solution of DCC (1.53 g, 7.4 mmol) and DMAP (0.009 g, 0.074 mmol) in dry CH_2Cl_2 was added over a period of 1 h. The reaction was stirred for an additional 3 h. The reaction mixture was then filtered, and following evaporation of the solvent, the crude product was purified by silica gel chromatography (hexane) to give propynoic acid 4-decyloxyphenyl ester (**2a**) as a pale brown solid. m.p.=33.9–35.7°C. Yield: 2.00 g (88.9%). IR (KBr, cm^{-1}): 3488, 3287, 2920, 2852, 2139, 1718, 1506, 1225, 827. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (m, 3H), 1.30 (m, 3H), 1.76 (q, $J=6.8$ Hz, 2H), 3.05 (s, 1H); 3.93 (t, $J=5.6$ Hz, 2H), 6.88 (d, $J=9.2$ Hz, 2H), 7.04 (d, $J=9.2$ Hz, 2H).

For propynoic acid 4-heptyloxyphenyl ester (**2b**): yield: 92%. IR (KBr, cm^{-1}): 3488, 3287, 2920, 2852, 2139, 1718, 1506, 1225, 827. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (m, 3H), 1.77 (m, 2H), 3.06 (s, 1H), 3.93 (t, $J=5.4$ Hz, 2H), 6.88 (d, $J=9.2$ Hz, 2H), 7.04 (d, $J=9.2$ Hz, 2H).

General procedure for synthesis of 1,2,3-triazole rings ***3a****,* ***3b*** *and* ***4****.*

A mixture of acrylic acid 4-decyloxyphenyl ester (**2a**, 0.21 g, 0.69 mmol), CuI (12.7 mg, 0.067 mmol) and triethylamine (9 ml, 0.069 mmol) in 20 ml of ethanol/water 1:1 was stirred vigorously for 30 min. Then, 1-azido-4-decyloxybenzene (**1a**, 0.186 g, 0.676 mmol) dissolved in 5 ml of ethanol/water 1:1 was added dropwise, and the resultant heterogenic mixture kept at 60°C for 48 h. After cooling, the suspension was poured into water (30 ml). The solid was filtered, washed with water and purified by recrystallisation from acetonitrile giving 4-decyloxyphenyl 1-(4-decyloxyphenyl)-[1,2,3]-triazole-4-acetate (**3a**) as a yellow powder. Yield: 0.29 g (74%). IR (KBr, cm^{-1}): 3142, 2920, 2851, 1723, 1518, 1250, 827. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (m, 6H), 1.27 (m, 4H), 1.45 (m, 2H), 1.80 (m, 4H), 3.5 (t, $J=6.6$ Hz, 2H), 4.02(t, $J=6.6$ Hz, 2H), 6.93 (d, $J=9.2$ Hz, 2H), 7.10

(d, J=9.2 Hz, 2H), 7.16(d, J=9.2 Hz, 2H), 7.66 (d, J=9.2 Hz, 2H), 8.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.419, 18.98, 22.29, 22.34, 25.42, 25.63, 25.68, 25.86, 28.19, 64.68, 64.82, 111.36, 111.73, 118.62, 118.68, 122.61, 125.68, 136.19, 139.78, 153.40, 155.77, 156.32. Elemental analysis: calculated for $C_{35}H_{51}N_3O_4$, C 72.70, H 8.90, N 7.27, O 11.08; found, C 72.91, H 8.41, N 7.34, O 11.43%.

For 4-heptyloxyphenyl 1-(4-decyloxyphenyl)-[1,2,3]-triazole-4-acetate (**3b**): yield: 74.3%. IR (KBr, cm^{-1}): 3141, 2921, 2851, 1725, 1519, 1252, 829. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (m, 6H), 1.28 (m, 4H), 1.34 (m, 2H), 1.90 (m, 4H), 3.95 (t, J=6.7 Hz, 2H), 4.15 (t, J=6.5 Hz, 2H), 6.93 (d, J=9.2 Hz, 2H), 7.04 (d, J=9.2 Hz, 2H), 7.15 (d, J=9.2 Hz, 2H), 7.66 (d, J=9.2 Hz, 2H), 8.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.35, 22.90, 26.22, 26.27, 29.34, 29.49, 29.59, 29.79, 32.05, 32.12, 68.65, 68.78, 115.33, 115.71, 122.57, 122.71, 126.53, 129.63, 140.18, 143.72, 157.37, 159.72, 16.31. Elemental analysis: calculated for $C_{32}H_{45}N_3O_2$, C 71.74, H 8.47, N 7.84, O 11.95; found, C 71.50, H 8.12, N 7.91, O 12.49%.

For the 1,3-bis-[1-(4-decyloxyphenyl)-[1,2,3]-triazole-4-acetate of decyloxyphenylbenzene (**4**): yield, 47%. IR (KBr, cm^{-1}): 2921, 2851, 1754, 1504, 1220, 861. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (m, 6H), 1.48 (m, 6H), 1.81 (m, 4H), 3.96 (t, J=6.2 Hz 4H), 6.94 (d, J=8.8 Hz, 4H), 7.17 (d, J=8.8 Hz, 4H), 7.83 (t, J=8.0 Hz, 1H), 7.98 (d, J=8.0 Hz, 2H), 8.41 (s, 1H), 8.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.13, 22.69, 26.05, 29.27, 29.33, 29.40, 29.58, 31.91, 68.44, 113.07, 115.15, 121.12, 122.24, 126.24, 131.89, 137.56, 140.71, 143.37, 157.27, 159.03. Elemental analysis: calculated for $C_{44}H_{56}N_6O_6$, C 69.09, H 7.38, N 10.99, O 12.55; found, C 68.67, H 7.43, N 11.10, O 12.82%.

X-ray crystallographic analysis

Colourless single crystals of **3a** were obtained by recrystallisation in dichloromethane. The crystallographic analysis was carried out on a Bruker Kappa X8 Apex II CCD area detector with graphite monochromatised Mo K_α radiation (λ=0.71073 Å) at room temperature. Intensities were integrated from all collected frames with SAINT (*15*) to generate the final intensity data corrected for polarisation and Lorentz effects. The structure was solved using direct methods with SHELXS-97 (*16*) and refined by full-matrix least-squares procedures using SHELXL-97 (*16*). All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added at their calculated positions and included in the structure factor calculations with C–H distances and U_{eq} taken from the default of the refinement program. Further crystallographic information is shown in Table 1.

Table 1. Selected crystal data and structure refinement for **3a**, 1-(4-decyloxyphenyl)-1*H*-[1,2,3]-triazole-4-carboxylic acid 4-decyloxyphenyl ester.

Empirical formula	$C_{35}H_{51}N_3O_4$
Molecular weight/g mol^{-1}	577.79
Measurement temperature/K	293(2)
Crystal system; space group	Triclinic; $P\bar{1}$
Unit cell dimensions	a=10.2612(13) Å α=75.052(4)°
	b=12.2203(14) Å β=88.409(4)°
	c=14.3799(18) Å γ=77.839(4)°
Volume	1702.4(4) Å^3
Z; density (calculated)	2; 1.127 Mg m^{-3}
Absorption coefficient (μ)	0.073 mm^{-1}
Crystal size	0.23 × 0.15 × 0.05 mm^3
Theta range for data collection	2.47 to 28.34°
Index ranges	$-12 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 16$,
	$-19 \leqslant l \leqslant 18$
Reflections collected	26 102
Independent reflections	8321 [R(int)=0.0456]
Refinement method	Full-matrix least-squares on F^2
R indices [$I>2\sigma$ (I)]	R_1=0.0654, wR_2=0.1854
R indices (all data)	R_1=0.2101, wR_2=0.2519

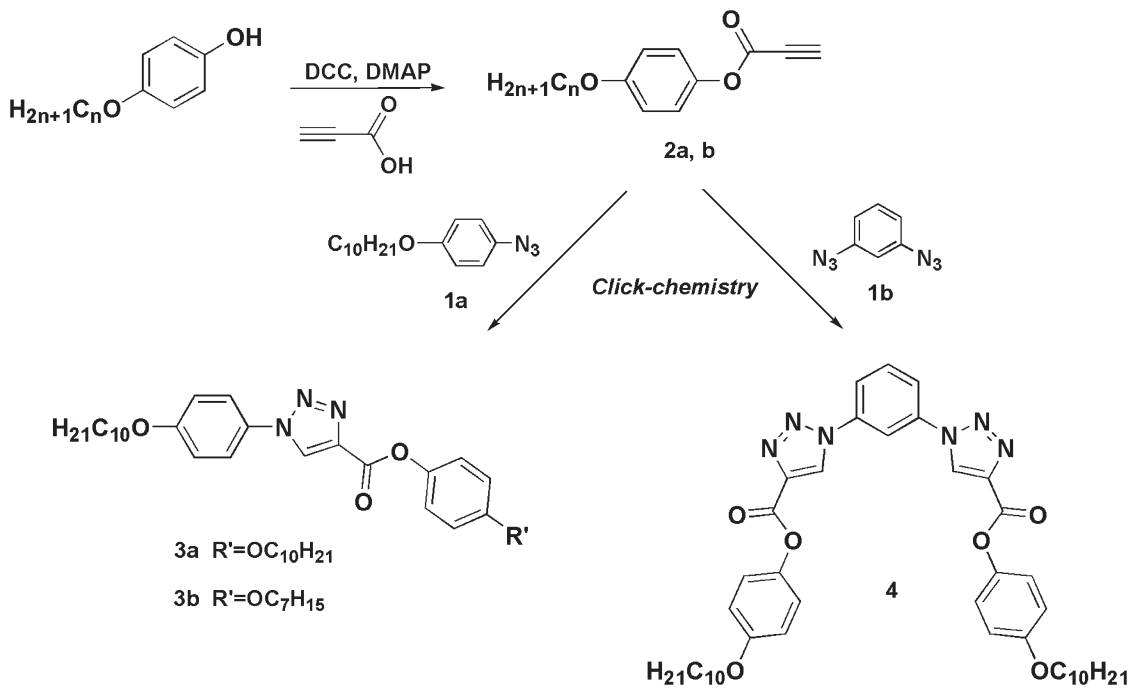
Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under supplementary publication number CCDC 678640. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: 207+44(0) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)].

3. Results and discussion

Synthesis

The synthesis of the targets was carried out as described in Scheme 1. The aryl azide **1a** was prepared by nucleophilic displacement from the diazonium salt of 4-*N*-alkoxyaniline. The propynoic acid 4-alkoxyphenyl esters (**2a** and **2b**) were synthesised through an esterification reaction using dicyclohexylcarbodiimide (DCC) as the dehydrating agent, *N*,*N*-dimethylaminepyridine (DMAP) as the catalyst and their respective alkoxyphenols with the commercial propargylic acid in dichloromethane gave the target molecule in 70–90% yield.

The final compounds, **3a, 3b** and **4**, were prepared with a high degree of purity and in good chemical yields through the Cu(I)-catalyzed 'click reaction' between 1-azido-4-decyloxybenzene (**1a**) or 1,3-diazidobenzene (**1b**) and the respective terminal acetylenes, propynoic acid 4-alkoxyphenyl ester (**2a** or **2b**), using a mixture of ethanol/water and catalytic



Scheme 1. Synthetic pathway to obtain **3a**, **3b** and **4**. Reagents and procedure for click chemistry: 10% CuI, 10% TEA, EtOH/H_2O, 1:1.

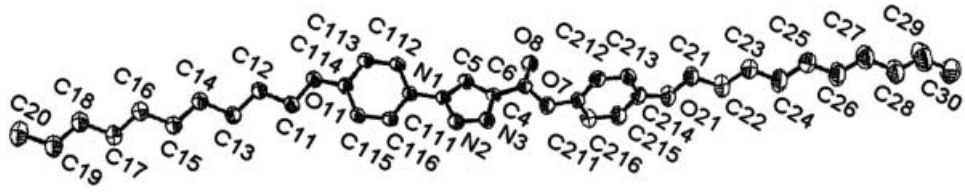


Figure 1. ORTEP plot of compound **3a** with atom numbering scheme. Ellipsoids are shown with 40% probability level. Hydrogen atoms are omitted for clarity.

amounts of Cu(I) and triethylamine (TEA) as the additive (*13*).

X-ray diffraction study of 3a

The molecular structure of compound **3a** is shown in Figure 1. Selected parameters of the molecular geometry are summarised in Table 2.

Table 2. Selected bond lengths and angles in compound **3a**.

Bond length/Å		Bond angle/°	
N1–C5	1.330(3)	C5–N1–N2	109.5(2)
N1–N2	1.361(3)	C5–N1–C111	129.9(2)
N1–C111	1.427(3)	N2–N1–C111	120.6(2)
N2–N3	1.304(3)	N3–N2–N1	107.7(2)
N3–C4	1.359(3)	N2–N3–C4	108.3(2)
C4–C5	1.355(3)	C5–C4–N3	108.4(2)
C4–C6	1.457(4)	C5–C4–C6	127.4(2)
		N3–C4–C6	124.2(3)
		N1–C5–C4	106.1(2)

The molecular geometry of the molecule under discussion is not planar but consists of structural fragments (benzene rings, carboxylic group, triazole ring and alkoxy chains) with more or less perfect planarity (Figure 2). The overall molecular conformation results from dihedral angles between these fragments, and described in an equivalent manner by the appropriate torsion angle (Table 3).

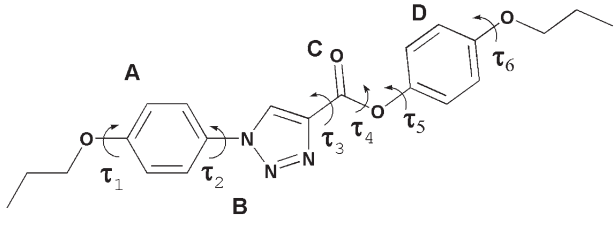


Figure 2. Labelling of torsion angles and structural (core) fragments used in discussion.

Table 3. Torsion angles in structural (core) fragments in compound **3a** (estimated values in parenthesis)

	Atoms	Angles/°
τ_1	C11–O11–C114–C115	2.1(4)
τ_2	C112–C111–N1–C5	−27.1(4)
τ_3	O7–C6–C4–C5	−175.5 (2)
τ_4	C4–C6–O7–C211	175.7(3)
τ_5	C212–C211–O7–C6	83.6(3)
τ_6	C21–O21–C213–C214	2.0(5)

Note that the torsion angle values for planes A (benzene ring), B (triazole ring) and C (carboxylic group) are either around 0 or 180°, and thus the planes are practically coplanar. However, a deviation from coplanarity was observed between planes C and D, where the value of the torsion angle, τ_5, is 83°. Therefore, planes C and D ((benzene ring) are practically orthogonal.

The molecular packing in the crystal lattice of compound **3a** is illustrated in Figure 3. The parallel alignment of the molecules is consistent with three lattice translations and the inversion centres of the space group $P\bar{1}$. The crystal structure consists of lamellar sheets parallel to the crystallographic *c* axis, in which the parallel-aligned molecules are strongly intercalated.

The crystal packing analysis shows that pairs of molecules are formed through weak C–H…O intermolecular interactions and related by an inversion centre. This is due to a biforked interaction between the carbonyl and the hydrogen of the triazole ring and the hydrogen of the aromatic ring (Figure 4). The non-bridged-hydrogen intermolecular atomic distances (3.166 and 3.438 Å) observed are indicative of normal van der Waals forces within the crystal lattice. The three-dimensional structure analysis shows that the formation of the couples is benefited when the molecular organisation assumes the lamellar arrangement. The interactions between the alkoxy chains are weak when compared with the rigid parts, which would also lead to the formation of such an arrangement.

The mesomorphic behaviour is consistent with the crystal packing analysis. The molecule has calamitic behaviour due to the triazole ring bend being compensated by a carboxylic group and, thus, compound **3a** exhibits only smectogenic behaviour.

Mesomorphic behaviour

The phase transition temperatures of the target compounds **3a–3b** were measured visually by POM and also by DSC. The optical observations were performed using clean untreated glass slides. The transition temperatures reported in this paper were obtained from the two peak values of the transition observed through DSC (Figure 5) and are summarised in Table 4.

Compounds **3a** and **3b** exhibit only a SmC phase over a wide temperature range, with a schlieren texture observed by microscopy. The typical thermograms obtained by DSC analysis of compounds **3a** and **3b** (Figure 5) are very similar. On heating, compound **3a** melts at 117.2°C to the SmC phase and it becomes an isotropic liquid at 155.5°C; the results agree well with POM observations. The same pattern is observed on cooling. In both cases, the isotropic–SmC transition enthalpy is well defined and indicated the first-order character for this transition,

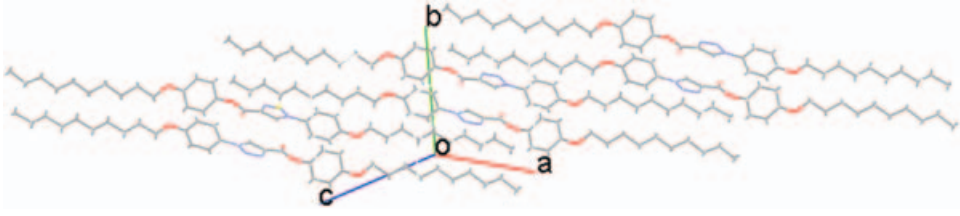


Figure 3. Crystal packing of compound **3a**.

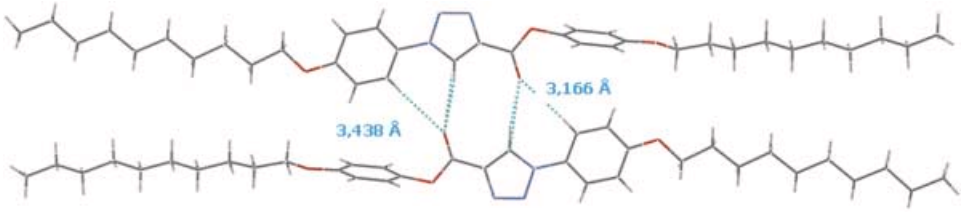


Figure 4. Pair formed by bifurcated carbonyl–hydrogen–hydrogen interactions in the crystal structure of compound **3a**. Symmetry code: $1-x$, $1-y$, $-z$.

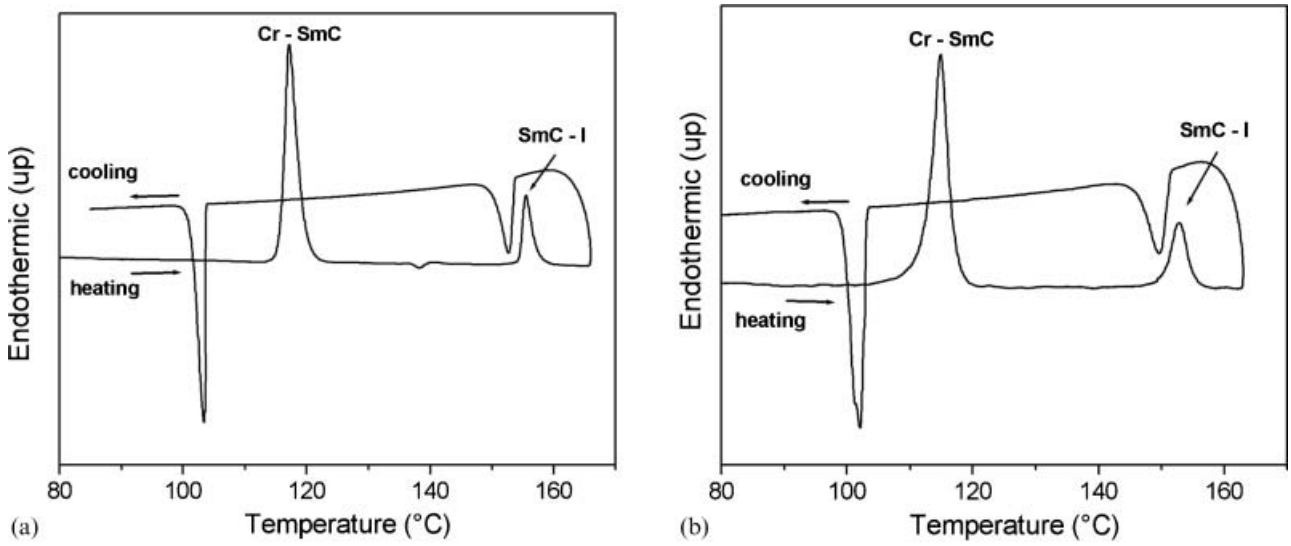


Figure 5. DSC thermograms for the heating and cooling cycles of (a) **3a** and (b) **3b**, showing the separation of Cr–SmC and SmC–I transition peaks. Heating rate=5°C min^{-1}.

Table 4. Transition temperatures, T (°C), and enthalpy changes, ΔH (kJ mol^{-1}, in parenthesis), of final compounds **3a**, **3b** and **4** determined by POM and DSC measurements at 5°C min^{-1}.

Compound	Transition	T, heating (ΔH)	T, cooling (ΔH)
3a	Cr–SmC	117.2 (−32.7)	103.4 (32.4)
	SmC–I	155.5 (−7.8)	152.7 (9.42)
3b	Cr–SmC	114.9 (−27.0)	102.1 (27.3)
	SmC–I	152.8 (−7.36)	149.6 (7.5)
4	Cr I–Cr II	95.4 (10.5)	84.0 (9.3)
	Cr II–Cr I	172.1 (19.9)	167.2 (26.9)
3a	Cr–SmC	117.2 (−32.7)	103.4 (32.4)
	SmC–I	155.5 (−7.8)	152.7 (9.42)

Cr=crystal; SmC=smectic C; I=isotropic.

possessing a narrow phase coexistence region and temperature hysteresis (the difference between the phase transition temperatures on heating and on cooling).

For both compounds, on cooling from the isotropic liquid a schlieren texture with singularities of $s=\pm 1$ was observed (see Figure 6). Compound **4** presented no mesomorphic proprieties, and only a crystal–crystal transition.

The mesomorphic behaviour of compounds **3a** and **3b** shows no substantial differences when compared with that of the structurally related [1,2,3]-based materials (*14*). In a previous study we reported that displacement of the heterocycle 1,2,3-triazole to the central position in a chiral liquid crystal resulted in it showing the SmA* phase, and the melting point lowered significantly in comparison with compounds containing the 1,2,3-triazole in the terminal position (*11*). However, the thermal results

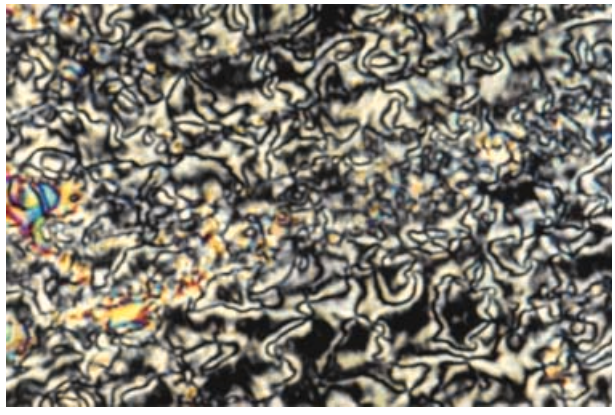


Figure 6. Photomicrograph of schlieren texture of the SmC phase for **3a** observed at 132.5°C, (33×) upon cooling.

for compounds **3a**–**3b** indicated that, even though the rigid core is shorter, with only three aromatic rings, the interaction in the crystal lattice is sufficient to stabilise the mesophase SmC.

4. Conclusions

In summary, two new [1,2,3]-triazole-based liquid crystalline compounds were synthesised through Cu(I)-catalyzed 1,3-dipolar cycloaddition of 1-azido-4-decyloxybenzene (**1a)** with terminal acetylenes, propynoic acid 4-alkoxyphenyl esters, via a click reaction. These compounds exhibit only a SmC phase over a wide temperature range, as observed by optical microscopy and DSC. The crystal structure consists of lamellar sheets in which the parallel-aligned molecules are strongly intercalated.

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