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Chiral liquid crystalline *m*-nitrotolans and tolans: synthesis and mesomorphic properties

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Two homologous series, 4′-(4-*n*-alkoxybenzoyloxy)-4-substituted 3-nitrotolans (**Ia–d**) and 4′-(4-*n*-alkoxybenzoyloxy)-4-substituted tolans (**IIa–c**), with substituents (*S*)-2-methyl-1-butyl and *n*-alkyl, were synthesized by Sonogashira's coupling. Their mesomorphic behaviour is reported. The thermal stability of the series **II** is higher than that of series **I**. Series **I** melting points and clearing points are lower than those of series **II**. None of the chiral tolans or *m*-nitrotolans have an enantiotropic smectic C phase. When the chiral chains are changed to *n*-alkyl groups in compounds **Ia,b** and **IIa**, an enantiotropic smectic C phase is seen. All compounds have a nematic or cholesteric phase, and two homologues of series **II** present a monotropic smectic C phase with mosaic texture. The mesophases were characterized using optical polarized light microscopy and differential scanning calorimetry.

1. Introduction

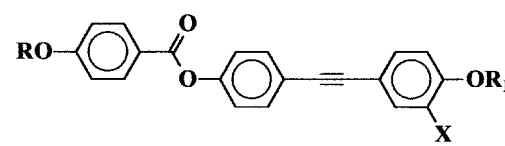
The liquid crystalline state combines the properties of both the solid and liquid states; it is characterized by anisotropic optical, electric, magnetic and mechanical properties. Until 1960, few compounds exhibiting liquid crystalline phases were known and few research groups interested in the anisotropic properties of liquid crystals. Since the discovery of the twisted nematic (TN) effect [1] in 1971, however, the fundamental and applied research effort has grown enormously.

In 1975, when Meyer and co-workers [2] discovered the phenomenon of ferroelectricity in chiral SmC mesophases and, later, Clark and Lagerwall [3] found a new electro-optic effect—surface stabilized ferroelectric liquid crystals (SSFLC), academic and technological research in ferroelectric liquid crystals has received much more attention, due to their practical applications in displays.

Many SmC* materials have benzoates, benzylideneanilines, phenylpyrimidines, and biphenylcarboxylates as the mesogenic core. More recently tolan (diphenylacetylene) has received attention because of its stability, linearity and phase behaviour [4]. In addition to showing SmC phases it displays twist grain boundary phases (TGB_A and TGB_C) [5], NLO properties [6], and an antiferroelectric smectic phase [7].

Our attention is focused on the design and synthesis of chiral liquid crystals with ferroelectrics properties [8]. The acetylene substructure of tolan increases the length of liquid crystalline molecules and therefore changes the thermal stability of mesophases. Moreover the introduction of a nitro substituent, with its large dipole moment at the *meta*-position to the acetylene unit, has a great effect on the electron distribution in the aromatic ring.

Based upon the considerations discussed above, we now report the design, synthesis and phase behaviour of some chiral *m*-nitrotolans and tolans derived from (*S*)-(−)-2-methyl-1-butanol. The compounds investigated are members of the series 4′-(4-*n*-alkoxybenzoyloxy)-4-substituted 3-nitrotolans (**Ia–d**) and 4′-(4-*n*-alkoxybenzoyloxy)-4-substituted tolans (**IIa–c**), with the substituents (*S*)-2-methyl-1-butyl and *n*-alkyl, respectively. The general structure of each series is shown below:



Series I X = NO_2; R = *n*-alkyl; R_1 = (*S*)-2-methyl-1-butyl, *n*-alkyl

Series II X = H; R = *n*-alkyl; R_1 = (*S*)-2-methyl-1-butyl, *n*-alkyl

2. Experimental

2.1. *Characterization*

^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with Varian-200 and 300 MHz spectrometers, using TMS as the internal standard. IR spectra were

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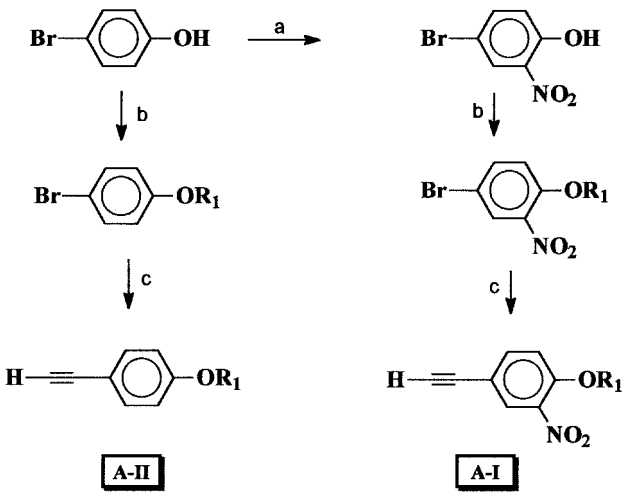
recorded in KBr discs or film with a 3000 Galaxy Series spectrometer. Elemental analyses were obtained with a Perkin Elmer 2400CHN. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter at the sodium D line.

The thermal transitions and the mesomorphic textures were identified using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP-52 hot stage and PL DSC differential scanning calorimeter. The rate of heating or cooling was 10°C min^{-1}.



R_1* = (*S*)-2-Methyl-1-butyl and R_1 = *n*-alkyl

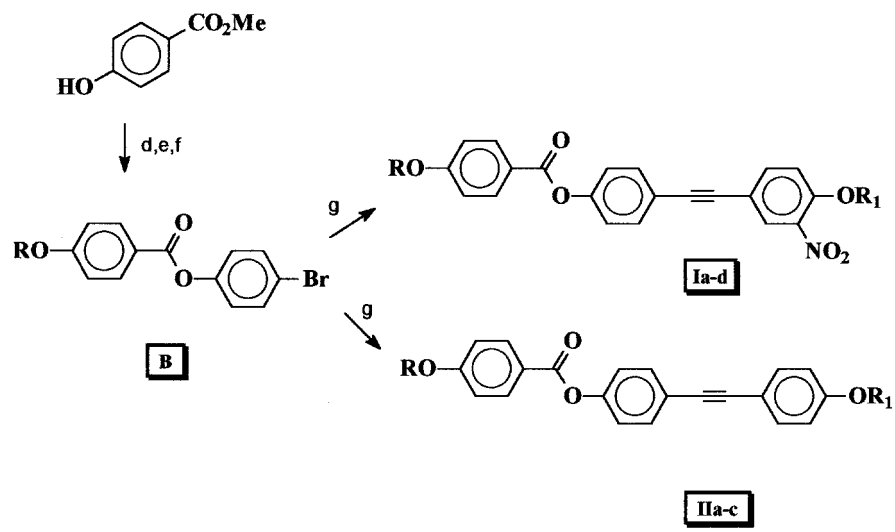
a. HNO_3/HOAc, RT; b. R_1Br or R_1*OTs, K_2CO_3, butanone;
c. i. $HC{\equiv}CCMe_2OH$, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N; ii. NaOH, toluene

Scheme 1.

2.2. *Synthesis*

The synthesis of the title compounds was carried out according to standard methods outlined in schemes 1 and 2. *p*-Bromophenol, was first nitrated with HNO_3/HOA_c at room temperature to give the corresponding 4-bromo-2-nitro phenol (scheme 1). If the temperature was raised to 70°C (under reflux) only 4-bromo-2,6-dinitrophenol was isolated, in quantitative yield. The nitration reaction with alkylated *p*-bromo-*n*-alkoxybenzenes gave the correct regioisomer but in low yield.

The chiral (*S*)-(−)-2-methyl-1-butyltosylate was prepared by functional interconvertion of (*S*)-(−)-2-methyl-1-butanol into the tosyl derivative in 89% yield and optical purity $[\alpha]_D^{20} = -3.59°$ (neat) [9]. The alkylation reaction was carried out with chiral and achiral alkylation reagent in butanone/K_2CO_3 in 95% yield. The key intermediates (**A–I**) and (**A–II**) were synthesized via Sonogashira's coupling method [10] between 2-methyl-3-butyn-2-ol and chiral/achiral 4-(substituted)-1-bromo-3-nitrobenzene or 4-(substituted)-1-bromobenzene followed by deprotection of the aromatic alkynol to yield 4-ethynyl-2-nitro-*n*-alkoxybenzene (**A–I**) and 4-ethynyl-*n*-alkoxybenzene (**A–II**), respectively, in 40–75% yield.



R_1 = (*S*)-2-Methyl-1-butyl and *n*-alkyl
R = *n*-Alkyl

d. RBr, NaOH, benzene/DMF; e. i. NaOH, EtOH/H_2O; ii. HCl conc.;
f. *p*-BrPhOH, DCC, DMAP, CH_2Cl_2; g. (**A**), $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N

Scheme 2.

Purification of the intermediates **A–I** and **A–II** by distillation is not recommended because of their decomposition: they were therefore purified by chromatographic techniques. Reaction conditions for compounds without the nitro substituent were the same as described above. The yields of this reaction were not as reproducible as reported in the literature [4(*a*), 11]. Even when we used the conditions described by Thorand and Krause [12], with THF as solvent, the yields were not reproducible.

With molecule **A** in hand, the synthesis of chemical structure **B** was begun (scheme 2). Alkylation of methyl *p*-hydroxybenzoate with alkyl bromides, followed by hydrolysis, afforded the *p*-*n*-alkoxybenzoic acid (yield 65–80%) [13(*a*)].

Esterification using dicyclohexylcarbodiimide (DCC) as dehydrating agent, *N*,*N*-dimethylamine pyridine (DMAP) as catalyst and *p*-bromophenol, gave the target molecule 4′-bromophenyl 4-*n*-alkyoxybenzoate (**B**) in 70–95% yield [13(*b*)]. Our convergent synthesis terminated with the second Sonogashira's coupling between **A** and **B** yielding the title compounds 4′-(4-alkoxybenzoyloxy)-4-substituted 3-nitrotolans (**I**) and 4′-(4-alkoxybenzoyloxy)-4-substituted tolans (**II**), in 40–60% yields.

Purifications by column chromatography were carried out on 70–230 mesh Merck silica gel 60. (*S*)-(−)-2-Methyl-1-butanol (~95%), 2-methyl-3-butyn-2-ol, dimethylaminopyridine (DMAP), *p*-bromophenol, palladium(II) chloride, copper(I), iodide (CuI), dicyclohexylcarbodiimide (DCC), *p*-hydroxybenzoate and triphenylphosphine (PPh_3) were purchased from Aldrich, and used as received from the supplier unless otherwise specified. Triethylamine (Et_3N) was distilled over potassium hydroxide (KOH) under argon immediately before use. Analytical thin-layer chromatography (TLC) was conducted on Merck aluminium plates with 0.2 mm of silica gel 60F-254. All reactions involving Sonogashira's coupling were performed in three-neck round-bottom flasks equipped with septum stoppers and charged with triethylamine (Et_3N), aromatic bromide and alkyne under an argon atmosphere for 30 min. Copper(I) iodide (CuI), triphenylphosphine (PPh_3) and bis-(triphenylphosphine)palladium(II) chloride ($PdCl_2(PPh_3)_2$) were then added.

2.2.1. *(S)-(−)-Methyl-1-butyl toluenesulphonate* [9]

p-Toluenesulfonyl chloride (0.20 mol, 38 g) was added in small portions to a stirred solution of dried pyridine (60 ml) and (*S*)-(−)-2-methyl-1-butanol (0.20 mol, 17.6 g) at 0°C. The solution was stirred for 12 h at 0°C. Water and ice (100 g) were added and the mixture was extracted with diethyl ether (3 × 100 ml); the extract was washed with cold dilute hydrochloric acid (2 × 100 ml) and water (100 ml). The ether layer was dried over Na_2SO_4, filtered, and evaporated to yield 41.2 g of crude yellow oil (89%); $[\alpha]_D^{20} - 3.59°$ (neat) [9]. ^{1}H NMR ($CDCl_3$): 0.7 (t, 3H, $J = 7.8$ Hz, CH_3); 0.75 (d, 3H, $J = 7.5$ Hz, CH_3); 1.15 (m, 1H, CH_2); 1.4 (m, 1H, CH_2); 1.6 (m, 1H, CH); 2.3 (s, 3H, CH_3), 3.75 (m, 2H, CH_2), 7.25 (d, 2H, $J = 8$ Hz, Ar); 7.65 (d, 2H, $J = 8$ Hz, Ar). A representative procedure for series **I** compounds is now given.

2.2.2. *4-Bromo-2-nitrophenol*

To a solution of *p*-bromophenol (10 mmol, 1.73 g) in acetic acid (25 ml) was added concentrated nitric acid (2.75 ml) dropwise; the temperature of the reaction mixture was kept below 22°C. After 50 min the reaction mixture was poured into water (100 ml), and the suspension left at room temperature overnight. The resulting yellow solid was filtered and dried under vacuum; yield 1.7 g (77%). M.p. = 88–89°C, lit [14] 90–94°C. IR (KBr): 3500, 3090, 1580, 1530, 1350, 1050, 850, 780, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.1 (d, 1H, $J = 8.9$ Hz, Ar); 7.7 (dd, 1H, $J = 8.9$ Hz, $J = 2.5$ Hz, Ar); 8.3 (d, 1H, $J = 2.5$ Hz, Ar); 10.5 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): 145.6; 143.0; 130.0; 129.5; 124.5; 114.5.

2.2.3. *(S)-(+)-4-(2-Methyl-1-butyloxy)-1-bromo-3-nitrobenzene*

A mixture of 4-bromo-2-nitrophenol (0.078 mol, 16.35 g), powdered potassium carbonate (0.148 mol, 16.30 g) and *N*,*N*-dimethylformamide (DMF) (50 ml) was stirred at 60°C for 30 min. A solution of (*S*)-(−)-2-methyl-1-butyl toluenesulfonate (0.08 mol) in DMF (20 ml) was slowly added, and the resulting mixture was stirred for 8 h at 65°C. The resulting white precipitate was filtered off and washed with diethyl ether (200 ml). After the addition of 250 ml water the layers were separated and the aqueous solution was extracted with diethyl ether. The organic layers were combined and dried over sodium sulfate. The diethyl ether was evaporated and the remaining oil distilled to give 21.4 g of light yellow oil (95%). B.p. 125–130°C, 0.3 mm Hg; $[\alpha]_D^{20} + 12°$ (1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.0 (t, 3H, $J = 7.5$ Hz, CH_3); 1.1 (d, 3H, $J = 6.7$ Hz, CH_3); 1.35 (m, 1H, CH_2); 1.6 (m, 1H, CH_2); 1.95 (m, 1H, CH); 3.87 (dd, 1H, $J = 8.8$ Hz, 6.4 Hz, C<u>H</u>HO); 3.97 (dd, 1H, $J = 8.8$ Hz, 5.8 Hz, CH<u>H</u>O); 7.0 (d, 1H, $J = 8.9$ Hz, Ar); 7.65 (dd, 1H, $J = 8.9$ Hz, $J = 2.5$ Hz, Ar); 7.95 (d, 1H, $J = 2.5$ Hz, Ar). ^{13}C NMR: 151.8; 140.0; 136.7; 128.1; 116.0; 111.3; 74.5; 34.6; 25.8; 16.4; 11.3.

2.2.4. *(S)-1-Ethynyl-4-(2-methyl-1-butyloxy)-3-nitrobenzene (**A–I**)*

An argon-filled three-neck round-bottom flask was charged with Et_3N (31.6 ml), (*S*)-(+)-4-(2-methyl-1-butyloxy)-1-bromo-3-nitrobenzene (0.037 mol, 10.84 g) and 2-methyl-3-butyn-2-ol (0.055 mol, 4.68 g); CuI

(25.3 mg), PPh_3 (0.158 g) and $PdCl_2(PPh_3)_2$ (82.23 mg) were then added to the stirred solution [4(*a*)]. The mixture was heated for 6 h at 90°C. After cooling, precipitated solid was filtered off and washed with diethyl ether (50 ml). The filtrates were evaporated and the resulting dark yellow viscous oil dissolved in diethyl ether (150 ml); the organic phase was washed with water (4 × 100 ml) and cold 10% hydrochloric acid (100 ml). The final solution was filtered over celite and the solvent evaporated to yield a pale yellow oil. The deprotection reaction was carried out with KOH in toluene. The chiral alkynol (9.5 g, 0.0017 mol) was added in anhydrous toluene (200 ml) under argon and stirred for 20 min. Potassium hydroxide (1.9 g) was added and the solution slowly heated to (100°C), held for 3 h, and the acetone distilled off. After cooling, the solution was filtered. The filtrate was concentrated, dissolved in diethyl ether (100 ml), washed with water (4 × 100 ml) and dried over sodium sulfate. The ether layer was filtered and evaporated. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane = 1:9) to yield 3.4 g of (**A–I**) (46%) as a yellow oil. IR (film): 3300, 2110, 1600, 1530, 1400, 1080, 780, 720 cm^{-1}. ^1H NMR ($CDCl_3$): 0.95 (t, 3H, J = 7.5 Hz, CH_3); 1.05 (d, 3H, J = 6.7 Hz, CH_3); 1.35 (m, 1H CH_2); 1.6 (m, 1H, CH_2); 1.95 (m, 1H, CH); 3.1 (s, 1H, CH); 3.9 (dd, 1H, J = 8.8 Hz, 6.4 Hz, C<u>H</u>HO); 3.95 (dd, 1H, J = 8.7 Hz, 5.8 Hz, CH<u>H</u>O); 7.0 (d, 1H, J = 8.8 Hz, Ar); 7.6 (dd, 1H, J = 8.8 Hz, 2 Hz, Ar); 7.95 (d, 1H, J = 2 Hz, Ar).

2.2.5. *4′-Bromophenyl 4-n-decyloxybenzoate (**B**)*

p-n-Decyloxybenzoic acid was first prepared [13(*a*)]. Methyl *p*-hydroxybenzoate (15.2 g, 0.1 mol) and potassium hydroxide (6.17 g, 0.11 mol) were added to benzene/DMF (1:1, 100 ml) and heated at 50°C for 20 min. *n*-Decylbromide (22.1 g, 0.1 mol) was added dropwise and the mixture heated under reflux for 6 h. The solid was filtered off and the filtrate concentrated. The residue was dissolved in diethyl ether (200 ml) and washed with 10% sodium bicarbonate solution (2 × 100 ml), water (100 ml); the solvent was then removed by evaporation. The solid obtained was hydrolysed by adding methanol (70 ml) and water (70 ml) and heated under reflux for 5 h. The solution was cooled, and concentrated hydrochloric acid (50 ml) added carefully. The resulting solid was filtered off and recrystallized in ethanol to yield *p-n*-decyloxybenzoic acid, yield 74%. (The octyl and heptyl compounds were prepared in 65% and 78% yield, respectively.)

The title compound (**B**) was synthesized according to [13(*b*)]. *p*-Bromophenol (3.46 g, 0.02 mol) and *p-n*-decyloxybenzoic acid (5.56 g, 0.02 mol) were added to dried CH_2Cl_2 (40 ml) under argon and the solution was stirred at room temperature for 10 min. DCC (4.54 g, 0.022 mol) and DMAP (0.216 g, 0.002 mol) were then added, and the mixture was stirred for 24 h at room temperature. The resulting solution was filtered over celite and the solvent evaporated. The remaining solid was recrystallized from ethanol to give 6.1 g of the compound 4′-bromophenyl 4-*n*-decyloxybenzoate (**B**) as a white solid (70%) (Cr 81.0°C SmA 86.0°C I). (Yield for *n*-octyl: 7.5 g, 93%, m.p. 85.5°C; yield for *n*-heptyl: 6.3 g, 80%, m.p. 85°C). IR (KBr): 2930, 1720, 1604, 1510, 1460, 1370, 1160, 710 cm^{-1}. ^1H NMR (*n*-decyl) ($CDCl_3$): 0.95 (t, 3H, J = 8 Hz, CH_3); 1.4 (m, 14H, CH_2); 1.85 (m, 2H, CH); 4.05 (t, 2H, J = 6.6 Hz, CH_2O); 6.95 (d, 2H, J = 8.9 Hz, Ar); 7.1 (d, 2H, J = 8.9 Hz, Ar); 7.55 (d, 2H, J = 8.6 Hz, Ar); 8.1 (d, 2H, J = 8.6 Hz, Ar). ^{13}C NMR (*n*-decyl) ($CDCl_3$): 164.5; 163.6; 150.0; 132.4; 132.2; 123.6; 121.0; 118.7; 114.3; 68.3; 31.8; 29.8; 29.3; 29.2; 29.0; 28.7; 25.9; 22.6; 14.1.

2.2.6. *(S)-(+)-4′-(4-n-Decyloxybenzoyloxy)-4-(2-methyl-1-butyloxy)-3-nitrotolan (**Id**)*

A three-neck round-bottom flask was charged with Et_3N (12 ml), (*S*)-1-ethynyl-4-(2-methyl-1-butyloxy)-2-nitrobenzene (0.0036 mol, 0.85 g) and 4′-bromophenyl 4-*n*-decyloxybenzoate (0.0035 mol, 1.5 g) under argon. CuI (2.4 mg), PPh_3 (0.015 g) and $PdCl_2(PPh_3)_2$ (7.8 mg) were then added to the stirred solution [14(*a*)]. The mixture was heated for 6 h at 90°C. After cooling, the solid was filtered off and washed with diethyl ether (50 ml). The filtrates were evaporated and the resulting dark yellow solid was dissolved in diethyl ether (150 ml) and the organic phase was washed with water (4 × 100 ml) and cold 10% hydrochloric acid (100 ml). The final solution was filtered over celite and the solvent evaporated to yield a pale yellow solid. The solid was chromatographed on silica gel using hexane/diethyl ether (95:5) as eluent. Recrystallization from acetonitrile or hexane gave pale yellow crystals of compound **Id**, yield 0.82 g (40%); $[\alpha]_D^{20}$ + 2.5° (1.16, $CHCl_3$). IR (KBr): 2954, 2924, 2853, 1725, 1609, 1463, 1377, 1050, 780, 722 cm^{-1}. ^1H NMR ($CDCl_3$): 0.85 (t, 3H, J = 6 Hz, CH_3); 0.95 (t, 3H, J = 7.4 Hz, CH_3); 1.05 (d, 3H, J = 6.7 Hz, CH_3); 1.4 (m, 16H, CH_2); 1.85 (m, 3H, CH); 4.0 (m, 4H, OCH_2); 7.0 (d, 2H, J = 8.9 Hz, Ar); 7.06 (d, 1H, J = 8.9 Hz, Ar); 7.24 (d, 2H, J = 8.6 Hz, Ar); 7.6 (d, 2H, J = 8.6 Hz, Ar); 7.65 (dd, 1H, J = 8.4 Hz, 2 Hz, Ar); 8.0 (d, 1H, J = 2 Hz, Ar); 8.15 (d, 2H, J = 8.4 Hz, Ar). ^{13}C NMR: 164.5; 163.6; 152.3; 151.1; 139.4; 136.8; 132.7; 132.2; 128.5; 122.0; 121.0; 120.0; 115.2; 114.3; 89.17; 86.87; 74.3; 68.3; 34.5; 31.8; 29.5; 29.4; 29.3; 29.0; 25.9; 25.8; 22.6; 16.3; 14.1; 11.3. Elemental analysis calculated for **Id** $C_{36}H_{43}NO_6$ (585 g mol^{-1}): C 73.85, H 7.35, N 2.4; found: C 73.88, H 7.09, N 2.9%.

The compounds of series **II** were prepared by similar procedures to those described above for series **I**.

2.2.7. *(S)-(+)-1-Bromo-4-(2-methyl-1-butyloxy) benzene*

Yellow oil; b.p. 70–72°C, 0.5 mmHg, $[\alpha]_D^{20} + 7°$ (1, $CHCl_3$). ^1H NMR ($CDCl_3$): 0.9 (t, 3H, $J = 7.5$ Hz, CH_3); 1.0 (d, 3H, $J = 6.7$ Hz, CH_3); 1.25 (m, 1H, CH_2); 1.5 (m, 1H, CH_2); 1.8 (m, 1H, CH); 3.6 (dd, 1H, $J = 8.8$ Hz, 6.4 Hz, CHHO); 3.7 (dd, 1H, $J = 8.7$ Hz, 5.8 Hz, CHHO); 6.75 (d, 2H, $J = 9$ Hz, Ar); 7.3 (d, 2H, $J = 9$ Hz, Ar).

2.2.8. *(S)-4-Ethynyl-(2-methyl-1-butyloxy)benzene (**A-II**)*

IR (film): 3290, 2108, 1600, 1530, 1430, 1350 and 720 cm^{-1}. ^1H NMR ($CDCl_3$): 0.95 (t, 3H, $J = 7.5$ Hz, CH_3); 1.05 (d, 3H, $J = 6.7$ Hz, CH_3); 1.35 (m, 1H, CH_2); 1.6 (m, 1H, CH_2); 1.95 (m, 1H, CH); 3.1 (s, 1H, CH); 3.9 (m, 2H, CH_2O); 7.0 (d, 2H, $J = 9$ Hz, Ar); 7.6 (d, 2H, $J = 9$ Hz, Ar).

2.2.9. *(S)-(+)-4′-(4-Decyloxybenzoyloxy)-4-(2-methyl-1-butyloxy)tolan (**IIc**)*

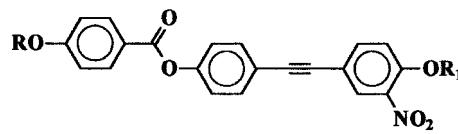
$[\alpha]_D^{20} + 2.4°$ (1.16; $CHCl_3$). IR (KBr): 2925, 2853, 1730, 1606, 1463, 1377, 722 cm^{-1}. ^1H NMR ($CDCl_3$): 0.94 (t, 3H, $J = 7.8$ Hz, CH_3); 0.96 (t, 3H, $J = 7.4$ Hz, CH_3); 1.05 (d, 3H, $J = 6.7$ Hz, CH_3); 1.4 (m, 16H, CH_2); 1.95 (m, 3H, CH, CH_2); 3.6 (dd, 1H, $J = 8.8$ Hz, 6.4 Hz, CHHO); 3.7 (dd, 1H, $J = 8.7$ Hz, 5.8 Hz, CHHO); 4.05 (t, 2H, $J = 6.6$ Hz, CH_2O); 6.95 (d, 2H, $J = 8.9$ Hz, Ar); 7.0 (d, 2H, $J = 9$ Hz, Ar); 7.2 (d, 2H, $J = 8.9$ Hz, Ar); 7.55 (d, 2H, $J = 8.6$ Hz, Ar); 7.6 (d, 2H, $J = 8.8$ Hz, Ar); 8.2 (d, 2H, $J = 8.6$ Hz, Ar). ^{13}C NMR ($CDCl_3$): 164.6; 163.6; 159.4; 150.6; 132.9; 132.5; 132.2; 121.8; 121.2; 121.1; 114.9; 114.5; 114.3; 89.5; 87.3; 68.3; 66.4; 34.7; 31.9; 29.5; 29.3; 29.1; 26.1; 26.0; 25.0; 22.7; 22.6; 16.5; 14.1; 11.3. Elemental analysis calculated for **IIc** $C_{36}H_{44}O_4$ (540 g mol^{-1}): C 80.0, H 8.15; found: C 80.23, H 8.01%.

3. Phase behaviour of the liquid crystals

The mesomorphic properties were studied by polarization microscopy and DSC. The textures of the mesophase [15] were identified by microscopy. On cooling the isotropic liquid forms of the tolans, a nematic phase was formed exhibiting schlieren and cholesteric textures with oily streaks; smectic A and B phases showed focal-conic fan and mosaic textures, respectively. The smectic C phase textures, were schlieren and blurred schlieren.

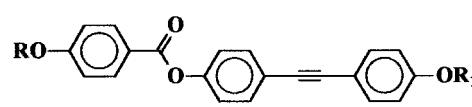
The sequence of phases and corresponding transition temperatures for tolans **I** and **II** are shown in the tables 1 and 2, respectively. The polymorphism shown by homologues of series **I** is dependent on the alkoxy chain

Table 1. Transition temperatures for *m*-nitrotolans **I** (°C).



Entry	*R*	R_1	*m-X*	Cr		SmC		SmB		SmA		N		I
Ia	C_7H_{15}	C_7H_{15}	NO_2	•	67.0	•	112	•	—	•	—	•	161	•
Ib	C_7H_{15}	C_8H_{17}	NO_2	•	66.0	•	87.5	•	—	•	—	•	137	•
Ic	C_7H_{15}	$*C_5H_{12}$	NO_2	•	71.0	•	—	•	—	•	98.5	•	127	•
Id	$C_{10}H_{21}$	$*C_5H_{12}$	NO_2	•	48.0	•	—	•	—	•	133.5	•	—	•

Table 2. Transition temperatures for tolans **II** (°C): () denotes monotropic transition.



Compound	*R*	R_1	*m-X*	Cr		SmC		SmB		SmA		N		I
IIa	C_7H_{15}	C_7H_{15}	H	•	85.0	•	112	•	(79.5)	•	—	•	199.5	•
IIb	C_8H_{17}	C_8H_{17}	H	•	88.5	•	—	•	(81.5)	•	—	•	199	•
IIc	$C_{10}H_{15}$	$*C_5H_{12}$	H	•	104.5	•	—	•	—	•	—	•	180	•

length. The smectic C phase appears when the alkoxy chain increases to $n = 7$ and 8. The mesogens (**Ic**,**d**), with a chiral alkoxy chain, do not exhibit SmC but only the SmA phase. The nematic (N/N*) phase appeared for **Ia–c**, not for **Id**.

Table 2 shows the thermal transitions of series **II**. There is no regular trend in the transition temperatures between **IIa** and **IIb**. **IIa** has an enantiotropic smectic C phase while **IIb** does not; however they both have a monotropic smectic B phase.

From the tables 1 and 2, we see that compounds of series **I** show enantiotropic phases, while compounds of series **II** show enantiotropic and monotropic phases. In addition, the homologues with a nitro group show a decrease in melting and clearing points when compared with homologues without a nitro group. The thermal stability of the phases increases in the homologous series without a nitro group (**II**). For example, $\Delta T_{\text{N-SmC}}$ is 49°C for **Ia**, 49.5°C for **Ib** and 87.5°C for **IIa**. The clearing point (c.p. = N*/N–isotropic transition) of the compounds of series **I** are at least 20°C lower than those for series **II**; the enthalpy data shows the same trend from DSC studies. For example, compounds **Ia** and **Id** exhibit $\Delta H_{\text{iso}} = 0.28$ and 0.34 kJ mol^{-1}, respectively, while **IIb** and **IIc** display $\Delta H_{\text{iso}} = 0.55$ and 0.79 kJ mol^{-1}, respectively. It is quite clear that thermal transitions are drastically changed when a nitro group is bonded laterally to the aromatic ring.

The thermal behaviour of the chiral homologues follows the same analysis. However, the data of table 2 shows little difference between **IIa** and **IIb**; probably an odd–even effect is operating.

The presence of the nitro group at the *meta*-position of the acetylenic unit significantly changes the liquid crystal phase and transition temperatures. According to Osman [16] the van der Waals volume of a substituent connected laterally to the rigid core is usually a more important factor for liquid crystalline behaviour than dipolar interactions. The decrease in the melting and clearing points of series **I** is probably associated with the steric effects that the nitro group exerts on molecular packing in the mesophase or crystal. The van der Waals volume of the lateral substituent disrupts the macroscopic molecular alignment of the rod-like molecules. The strong dipole moment is insufficient to maintain the packing in the crystal or mesophase.

4. Conclusions

Two homologous series of chiral liquid crystals, *m*-nitrotolans (**I**) and tolans (**II**) were synthesized via Sonogashira's protocol. Series **II** has higher thermal stability than series **I** with a lateral nitro group. Series **I** compounds exhibit melting and clearing points lower than series **II**. None of the chiral tolans or *m*-nitrotolans show the enantiotropic smectic C* phase. A comparison of the data of series **I** and **II** revealed that the presence of the nitro group at the *meta*-position relative to the acetylenic unit destabilizes the smectic phases.

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