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The design of smectic liquid crystals with axially chiral biphenyl cores: in search of a proper ferroelectric liquid crystal phase

Ziauddin Ahmed,[†] Carsten Müller,[¶] Marcel Holzwarth,[¶] Christian Haege,[¶] Frank Giesselmann[¶] and Robert P. Lemieux[,†]*

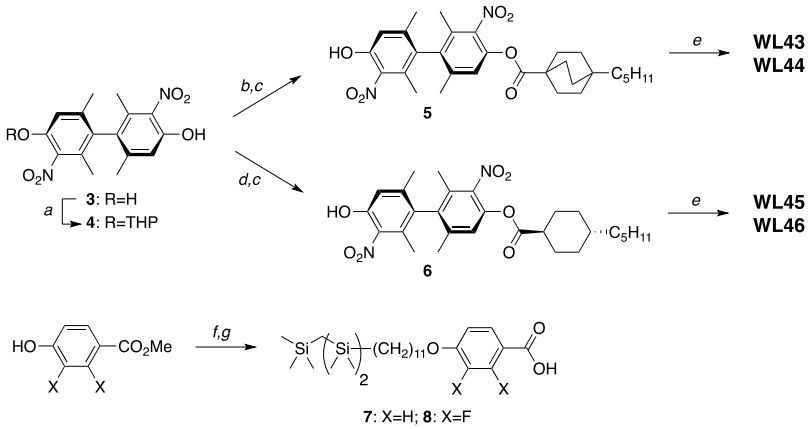
[†] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada
[¶] Institute of Physical Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

EXPERIMENTAL

General. Reactions were performed in oven-dried glassware under an atmosphere of argon unless otherwise stated. 1-Bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane and 4,4'-dihydroxy-2,2',6,6'-tetramethyl-3,3'-dinitrobiphenyl (**3**) were synthesized according to literature procedures and shown to have the expected physical and spectral properties.[1, 2] All reagent grade materials were purchased from Aldrich, TCI America, Combi-Blocks and Alfa Aesar, and used without further purification. Tetrahydrofuran (THF) and dichloromethane (DCM) were dried over 1/16" pellets of 3Å molecular sieves purchased from EMD Millipore and activated at 200 °C in a vacuum oven. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired in $CDCl_3$ on a Bruker Avance Spectrometer operating at 300, 75 and 282 MHz respectively. Chemical shifts are reported in units of δ (ppm) relative to residual solvent. Silica gel for chromatography was purchased from Silicycle with an estimated pore size of 60 Å formed from 40-63 mesh (particle size 230-400 μm) silica. Thin layer chromatography was performed on Merck Millipore aluminium plate with 200 μm thick layer of 10-12 μm 60G silica/ with manganese doped zinc silicate (F_{254}) particles. The purity of the final compounds was confirmed by high performance liquid chromatography using a Varian ProStar pump, D-Star Instruments DVW-10 variable wavelength detector and GL Sciences InertSustain HP reverse phase C18 column (250 mm × 4.6 mm, 5 μm particles, 100 Å pore size). Chiral resolution was performed on a Chiral Technologies Chiralpak AS column (50 cm x 5 cm, 20 μm particles) with a 9:1 mixture of hexane and ethanol as eluent. High resolution mass spectra were recorded at the Mass Spectrometry Facility at Queens University using a Thermo Fisher Orbitrap Velos Pro with electrospray ionization (ESI).

The thermal properties of the final compounds were analyzed by differential scanning calorimetry on a TA Instruments Q2000 instrument. These experiments were performed under nitrogen and the enthalpies measured against an internal reference. Texture analyses were performed on a Nikon Eclipse LV100N POL optical polarizing microscope fitted with a Nikon DS-Ri2 digital camera and Linkam LTS 350 hot stage and TMS 93 temperature controller. Induced optical tilt angles were measured in a rotating analyzer setup previously described in the literature;[3] the linearly polarized light of a He-Ne Laser (λ = 633 nm, Linos Photonics, Göttingen) was circularly polarized with a Glan-Thompson prism and a quarter-wave plate and sent through the sample cells (ITO glass, homogeneous alignment, rubbed nylon and polyimide coating, 1,6 μm cell gap, AWAT1, Poland), which were filled by capillary action in the isotropic phase; the sample temperature was controlled in a brass block with a Julabo FH-25HP thermostat; the analyzer was a second Glan-Thompson prism rotated at a frequency of 3-4 Hz with an Owis HeDL-5540 A02 motor fitted with Hall probes to detect the angular position of the analyzer; the transmitted light intensity was recorded using a Linos Photonics/Spindler & Hoyer

photodiode linked to a digital oscilloscope (Tektronix TDS460); unlike the setup described in literature, dc fields up to 10 V μm^{-1} were applied with alternating sign using a Kontron Elektronik 8021 waveform generator and a FLC Electronics F10A 10x voltage amplifier to slowly switch the sample between opposite tilt orientations, and to detect the optical signals separately for the two switching states; the setup was controlled and the data collected using a customized LabView 8.2 (National Instruments) program; the two optical signals were fitted according to the equations described by Langhoff *et al.,*[3] and the tilt angle was extracted. The same cells were used to perform polarization measurements by the triangular wave method using a LC-Vision LCAS1 instrument (5V μm^{-1}, 100Hz).[4] Small-angle X-ray scattering analyses were performed on a SAXSess system from Anton Paar GmbH. Unaligned samples (filled into Hilgenberg Mark capillary tubes of 0.7 mm diameter) were mounted in a temperature controlled sample holder unit (TSC 120). The X-ray beam was focused by a bent multilayer mirror and shaped by a line collimation block to receive CuK_α (1.5418 Å) radiation. The X-ray scattering was recorded with a CMOS detector (Dectris, Mythen 1K) and processed and analysed using the SAXSquant 3.5 software. 2D X-ray scattering analyses were performed on a Bruker Nanostar X-ray diffractometer (CuKα radiation, beam diameter 100 μm, HiStar 2D-detector). The samples were filled into Hilgenberg Mark capillary tubes of 0.7 mm in diameter and placed in a home-made temperature-controlled sample holder with a magnetic field of 0.7 T.



Scheme 1. *Reagents and conditions*: (a) 3,4-Dihydro-2*H*-pyran, pyridinium *p*-toluenesulfonate, CH_2Cl_2; (b) 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid, DIC, DMAP, CH_2Cl_2; (c) TsOH, 1:1 MeOH/CH_2Cl_2; (d) *trans*-4-pentylcyclohexane-1-carboxylic acid, DIC, DMAP, CH_2Cl_2; (e) **7** or **8**, DIC, DMAP, CH_2Cl_2; (f) 1-bromo-12,12,14,14,16,16-hexamethyl12,14,16-trisilylheptadecane, K_2CO_3, acetone, reflux; (g) NaOH, MeOH/THF/H_2O, reflux.

4-Hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((tetrahydro-2*H*-pyran-2-yl)oxy)-biphenyl (4). A mixture of **3** (0.48 g, 1.44 mmol) and pyridinium *p*-toluenesulfonate (0.036 g, 0.14 mmol) were dissolved in dry DCM under nitrogen. 3,4-Dihydro-2*H*-pyran (0.12 g, 0.14 mmol) was added dropwise and the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the mixture was extracted into EtOAc. The extract was washed successively with water (50 mL) and brine (50 mL), dried ($MgSO_4$) and concentrated. The product and unreacted starting material were separated by flash chromatography (1:1 hexane/EtOAc) to give **4** as a yellow solid (0.175 g, 29%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.10 (s, 1H), 6.98 (s, 1H), 5.58 (s, 1H), 3.91 (td, J = 11.1, 2.7 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H), 2.16 (d, J = 10.9 Hz, 3H), 1.98 (d, J = 35.3 Hz, 4H), 1.97 – 1.79 (m, 12H), 1.64 (s, 5H), 1.25 (t, J = 7.1 Hz, 1H).

4-Hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octane-1-carbonyl)oxy)biphenyl (5). A mixture of **4**, 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid (0.66 g, 2.9 mmol), N,N-diisopropylcarbodiimide (0.75 g, 5.9 mmol) and DMAP (0.19 g, 1.5 mmol) were dissolved in 50 mL of dry DCM under argon. The mixture was stirred at room temperature under darkness until completion by TLC. The solvent was removed *in vacuo* and the residue purified by flash chromatography (1:3 hexane/EtOAc) to give the THP-protected ester as a white solid (0.80 g, 84%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1H), 7.04 (s, 1H), 5.55 (s, 1H), 3.87 (t, J = 10.7 Hz, 1H), 3.64 (d, J = 11.2 Hz, 1H), 2.00 (s, 3H), 1.95 – 1.75 (m, 16H), 1.74 – 1.51 (m, 3H), 1.39 (dd, J = 16.3, 8.8 Hz, 6H), 1.33 – 1.00 (m, 8H), 0.84 (t, J = 7.0 Hz, 3H). The product was dissolved with *p*-toluenesulfonic acid (11 mg, 62.8 μmol) in 50 mL of 1:1 MeOH/DCM and stirred at room temperature until deprotection was complete. The solid residues were filtered off, the filtrate concentrated and redissolved in EtOAc. The solution was washed successively with 2 M aq HCl (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$) and concentrated. Purification by flash chromatography (2:1 hexane/DCM) gave **5** as a white solid (0.64 g, 95%): ^{1}H NMR (300 MHz,$CDCl_3$) δ 7.07 (s, 1H), 6.99 (s, 1H), 2.12 (s, 3H), 1.88 (3, J = 10.5 Hz, 14H), 1.40 (t, J = 20.4, 12.9 Hz, 6H), 1.33 – 1.01 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H).

4-Hydroxy-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((*trans*-4-pentylcyclohexane-1-carbonyl)oxy)biphenyl (6). The procedure used for the synthesis of **5** was repeated with **4** (0.1 g, 0.24 mmol) and *trans*-4-pentylcyclohexane-1-carboxylic acid (0.095 g, 0.48 mmol) to give **6** as a yellow oil (0.80 g, 99%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.99 (s, 1H), 2.47 (tt, J = 12.2, 3.5 Hz, 1H), 2.09 (dd, J = 11.1, 2.6 Hz, 5H), 1.98 – 1.77 (m, 10H), 1.51 (qd, J = 13.0, 3.2 Hz, 2H), 1.37 – 1.10 (m, 9H), 1.05 – 0.91 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H).

4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)benzoic acid (7). A mixture of methyl 4-hydroxybenzoate (0.51 g, 3.35 mmol), 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane (1.0 g, 2.21 mmol) and K_2CO_3 (0.92 g, 6.66 mmol) in acetone (30 mL) was stirred at reflux overnight. Solid residues were filtered off, the filtrate was concentrated and redissolved in EtOAc. The solution was washed successively with water (50 mL) and brine (50 mL), dried ($MgSO_4$) and concentrated. Purification by flash chromatography (1:1 hexane/DCM) gave the ester as colourless oil (0.96 g, 83%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.88 (s, 3H), 1.87 – 1.68 (m, 2H), 1.52 – 1.14 (m, 16H), 0.54 – 0.39 (m, 2H), 0.11 – -0.07 (m, 21H), -0.27 (d, J = 7.3 Hz, 4H). The ester was then mixed with a solution of KOH (0.51 g, 9.10 mmol) in water (5 mL) in 1:1 MeOH/THF (20 mL) and stirred at room temperature overnight. After refluxing for 1 hour to ensure complete hydrolysis, the mixture was poured onto a 1:1 mixture of ice and aq HCl (200 mL) and extracted with EtOAc. The extract was washed successively with water (200 mL) and brine (200 mL), dried and concentrated. The crude product was recrystallized form EtOH to give **7** as a white solid (0.93 g, 99%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 1.79 (m, 2H), 1.50 – 1.17 (m, 16H), 0.45 (s, 2H), -0.00 (t, J = 7.6 Hz, 21H), -0.29 (d, J = 7.2 Hz, 4H).

4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)-2,3-difluorobenzoic acid (8). The procedure used for the synthesis of **7** was repeated with methyl 4-hydroxy-2,3-difluorobenzoate (0.2 g, 1.06 mmol) and 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecane (0.53 g, 1.17 mmol) to give the ester as a colourless oil (0.28 g, 47%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (t, J = 7.2 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 4.08 (t, J = 6.5 Hz,

2H), 3.90 (s, 3H), 1.91 – 1.70 (m, 2H), 1.53 – 1.10 (m, 16H), 0.47 (d, *J* = 7.8 Hz, 2H), 0.00 (t, *J* = 7.6 Hz, 21H), -0.29 (d, *J* = 7.3 Hz, 4H). Hydrolysis of the ester and recrystallization from EtOH gave **11** as a white solid (0.20 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (t, *J* = 7.2 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 6.4 Hz, 2H), 1.79 (m, 2H), 1.50 – 1.09 (m, 16H), 0.45 (s, 2H), 0.00 (t, *J* = 7.6 Hz, 21H), -0.29 (d, *J* = 7.2 Hz, 4H).

(*R,S*)-4-((4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)benzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octane-1-carbonyl)oxy)biphenyl (WL43) The following procedure is representative: A mixture of **5** (0.22 g, 0.4 mmol), **7** (0.41 g, 0.82 mmol), N,N-diisopropylcarbodiimide (0.21 g , 1.7 mmol) and DMAP (0.05 g, 0.4 mmol) were dissolved in 40 mL of dry DCM under argon and stirred at room temperature, under darkness until completion by TLC. The solvent was removed *in vacuo* and the residue purified by flash chromatography (1:5 hexane/EtOAc). Recrystallization from EtOH gave **WL43** as a white solid (0.37 g, 85%): ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.07 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 5.8 Hz, 1H), 7.10 (d, *J* = 5.9 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.06 – 1.74 (m, 19H), 1.51 – 1.39 (m, 8H), 1.38 – 1.03 (m, 23H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.53 – 0.42 (m, 2H), 0.02 (t, *J* = 7.5 Hz, 21H), -0.27 (d, *J* = 7.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 175.6, 164.1, 163.6, 143.4, 142.0, 141.8, 140.0, 140.0, 136.1, 132.7, 129.7, 129.6, 123.6, 123.5, 119.9, 114.6, 68.4, 41.3, 39.6, 33.7, 32.8, 30.5, 30.2, 29.6, 29.4, 29.1, 28.5, 26.0, 24.0, 23.4, 22.7, 20.4, 20.3, 18.1, 15.1, 14.1, 5.8, 4.0, 2.5, 1.5, -0.42; HRMS *m/z* calcd for $C_{57}H_{88}NOSi_3$+Na 1051.5690, found 1051.5658; HPLC assay (80:20 MeCN/DCM) 98.78 %.

(*R,S*)-4-((4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)-2,3-difluorobenzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((4-pentylbicyclo[2.2.2]octane-1-carbonyl)oxy)biphenyl (WL44). White solid (0.06 g, 75%); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.76 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 7.09 (s, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 2.16 – 1.70 (m, 20H), 1.50 – 1.03 (m, 30H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.46 (t, 2H), 0.00 (t, 21H), -0.29 (d, *J* = 7.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 175.4, 160.4, 153.8, 153.7, 143.2, 143.1, 141.7, 141.3, 140.1, 139.8, 136.5, 135.9, 129.9, 129.4, 127.2, 127.1, 123.4, 109.8, 109.6, 108.52, 108.49, 71.4, 41.1, 39.4, 33.6, 32.6, 30.4, 30.1, 29.5, 29.4, 29.3, 29.2, 28.8, 28.4, 25.7, 23.9, 23.2, 22.6, 20.23, 20.17, 17.9, 15.0, 14.9, 14.0, 5.7, 3.9, 2.4, 1.4, -0.56; ^{19}F NMR (282 MHz, $CDCl_3$) *δ* -132.01 (dd, *J* = 19.2, 5.5 Hz), -157.79 (dd, *J* = 19.2, 5.5 Hz); HRMS *m/z* calcd for $C_{57}H_{86}F_2N_2O_9Si_3$+Na 1087.5501, found 1087.5543; HPLC assay (80:20 MeCN:DCM) 99.30 %.

(*R,S*)-4-((4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)benzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((*trans*-4-pentylcyclohexane-1-carbonyl)oxy)biphenyl (WL45). White solid (0.9 g, 56%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.01 (m, 2H), 7.31 (d, *J* = 4.7 Hz, 1H), 7.11 (d, *J* = 4.6 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.18 – 1.70 (m, 18H), 1.63 – 0.92 (m, 30H), 0.87 (t, *J* = 6.6 Hz, 3H), 0.47 (d, *J* = 7.8 Hz, 2H), 0.11 – -0.10 (m, 21H), -0.29 (d, *J* = 7.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30, 164.03, 163.47, 143.31, 143.13, 141.87, 141.57, 139.92, 139.87, 136.14, 136.03, 135.96, 132.56, 129.61, 129.57, 123.44, 123.41, 119.86, 114.45, 68.32, 43.24, 36.95, 36.68, 33.59, 32.01, 29.51, 29.49, 29.44, 29.27, 28.94, 28.66, 26.37, 25.86, 23.87, 22.55, 20.30, 20.25, 20.22, 20.17, 17.95, 15.00, 14.97, 13.97, 5.69, 3.92, 2.35, 1.35, -0.55; HRMS *m/z* calcd for $C_{55}H_{86}N_2O_9Si_3$ +Na 1025.5533, found 1025.5497. Assay (HPLC, C18, MECN:DCM 80:20) = 98.70 %

(*R,S*)-4-((4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)-2,3-difluorobenzoyl)oxy)-2,2',6,6'-tetramethyl-3,3'-dinitro-4'-((*trans*-4-pentylcyclohexane-1-carbonyl)oxy)biphenyl (WL46). White solid (0.022 g, 34%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 7.12 (s, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 4.12 (t, *J* = 6.2 Hz, 2H), 2.45 (d, *J* = 12.2 Hz, 1H), 2.10 (d, *J* = 12.7 Hz, 2H), 2.03 – 1.91 (m, 10H), 1.87 (d, *J* = 8.9 Hz, 4H), 1.65 – 0.75 (m, 34H), 0.46 (s, 2H), 0.11 – -0.07 (m, 21H), -0.23 – -0.35 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.44, 153.92, 153.79, 143.30, 143.18, 141.72, 141.45, 140.23, 139.98, 136.57, 136.12, 129.98, 129.68, 127.28, 127.23, 123.57, 123.54, 109.78, 109.70, 108.58, 108.55, 70.04, 43.34, 37.07, 36.78, 33.71, 32.11, 29.60, 29.51, 29.39, 29.29, 28.89, 28.77, 26.49, 25.79, 23.98, 22.68, 20.38, 20.34, 18.05, 15.17, 15.10, 14.10, 5.77, 4.00, 2.46, 1.46, -0.44; ^{19}F NMR (282 MHz, $CDCl_3$) δ -132.01 (dd, *J* = 19.2, 5.5 Hz), -157.79 (dd, *J* = 19.2, 5.5 Hz). HRMS *m/z* calcd for $C_{55}H_{84}F_2N_2O_9Si_3$ +Na 1061.5350, found: 1061.5304. Assay (HPLC, C18, MECN:DCM 80:20) = 99.54 %

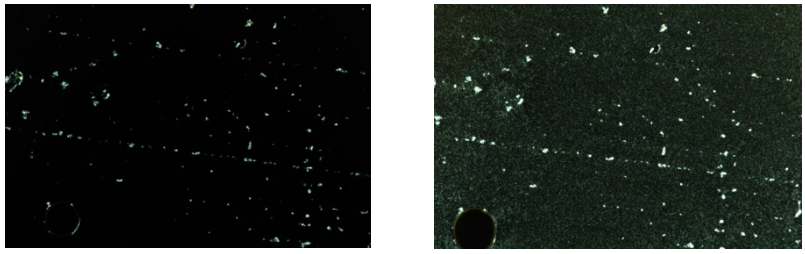


Figure S1. Polarized photomicrographs of **(*R,S*)-WL43** in a homeotropic alignment in the SmA phase at 81 °C (left) and in the SmI/F phase at 42 °C (right).

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