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Synthesis and transition temperatures of liquid crystals incorporating a 1,4-tetrafluorophenylene unit

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Synthesis and transition temperatures of liquid crystals incorporating a 1,4-tetrafluorophenylene unit

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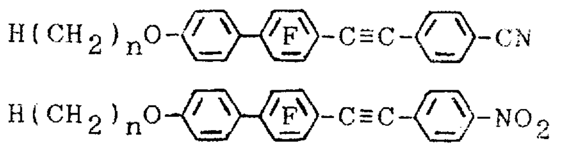
Two homologous series of mesogenic materials which incorporate a 1,4-tetrafluorophenylene moiety and a terminal cyano- or nitro-substituent have been synthesized by using palladium-catalysed coupling procedures. The compounds exhibit nematic and/or smectic A phases.

1. Introduction

Fluorination, it is well known, alters certain physical properties of organic compounds. For example, chemical and thermal stability, lower viscosity and lower birefringence are realized. The replacement of fluorine atom for the hydrogen atom in liquid crystal systems has a dramatic effect on mesomorphic behaviour and other physical properties, and hundreds of liquid crystalline molecules with monofluoro-, difluoro- or trifluoro-substituted phenyls [1–5] have been prepared. However, only a limited number of liquid crystalline molecules containing 1,4-tetrafluorophenylene moiety have been reported [6–11]. In our previous studies, we have reported several types of new liquid crystals with 2,3,5,6-tetrafluoro-1,4-phenylene units [12–17]. In this paper, we wish to report two novel types of liquid crystals containing 1,4-tetrafluorophenylene unit (compounds **A** and **B**), which were synthesized using 1-pentafluorophenyl-2-trimethylsilylacetylene as the starting material.



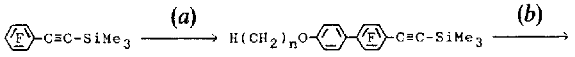
(*n* = 5–10) **A**
(*n* = 4, 6, 8, 10) **B**

2. Experimental

IR spectra were recorded on a Shimadzu IR-440 spectrophotometer. ^{1}H NMR spectra, with TMS as the internal standard, and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz) or FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra, the high field is positive, mass spectra were measured on a Finnigan-4021 spectrometer.

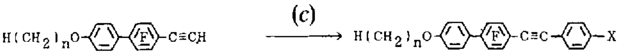
Transition temperatures were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a Metler FP 52 heating stage and FP 5 control unit, while phase identification was made by comparing the observed textures with those in the literatures [18, 19].

Compounds **A** and **B** have been obtained according to the following scheme.



1 **2a–g**

2a, *n* = 4; **2b**, *n* = 5; **2c**, *n* = 6; **2d**, *n* = 7;
2e, *n* = 8; **2f**, *n* = 9; **2g**, *n* = 10.



3a–g **4–13**

3a, *n* = 4; **3b**, *n* = 5: **3c**, *n* = 6;
3d, *n* = 7; **3e**, *n* = 8: **3f**, *n* = 9;
3g, *n* = 10.

X = CN: **4**, *n* = 5: **5**, *n* = 6; **6**, *n* = 7;
7, *n* = 8; **8**, *n* = 9; **9**, *n* = 10.

X = NO2: **10**, *n* = 4; **11**, *n* = 6;
12, *n* = 8; **13**, *n* = 10.

Reagents: (*a*) H $(CH_2)_nO–C_6H_4–MgBr$, THF, reflux. (*b*) CH_3OH/CH_3COCH_3, $NaOH/H_2O$, R. T. (*c*) $(Ph_3P)_2PdCl_2$, CuI, Et_3N and $I–C_6H_4–CN$ or $I–C_6H_4–NO_2$, reflux.

The starting material (compound **1**) was prepared by the method reported previously [20]. The nucleophilic substitution [21] of para-substituted phenyl magnesium bromide on compound **1** in dry THF gave acetylenes **2a–g**, from which polyfluoro-substituted biphenyl acetylenes **3a–g**

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were obtained after the removal of trimethylsilyl group under the action of methanol and aqueous NaOH in acetone. The coupling procedure involving compound **3** and 1-cyano-4-iodobenzene or 1-nitro-4-iodobenzene yielded the desired polyfluoro-substituted systems (series **A** and **B**, compounds **4–13**). All of the final compounds were purified by chromatography on silica gel with petroleum ether (b.p. 60–90°C)/ethyl acetate mixtures as eluent and recrystallized from acetone–methanol. Their structures were identified by IR, MS, ^{1}H NMR and ^{19}F NMR spectra.

2.1. *Synthesis of 1-trimethylsilyl-2-[4-(4-*n*-alkoxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylenes*

The 1-trimethylsilyl-2-[4-(4-*n*-alkoxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylenes (compounds **2a–g**) were synthesized as in the following example. In a dry 50 ml round bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel and a reflux condenser attached to a bubbler, were placed 660 mg (27·2 mmol) of magnesium turnings, 6 ml of anhydrous THF and a little grain of iodine (as initiator). Under dry nitrogen, a solution of 5·43 g (18·2 mmol) of 1-*n*-nonyloxy-4-bromobenzene in 4 ml of anhydrous THF was added slowly, dropwise to the stirred reaction mixture over a period of 30 min. The reaction was initiated by heating till the brown red colour of iodine disappeared, and the mixture was maintained in a slight reflux by heat generated from the reaction. After the addition, the resulting mixture was heated in an oil bath and refluxed while stirring for 1 h, then cooled to room temperature, with a large quantity of white crystal precipitating from the gray turbid liquid.

In another dry 50 ml round bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel and a reflux condenser attached to a bubbler, were placed 4·0 g (15·1 mmol) of compound **1** and 3 ml of anhydrous THF. The above prepared Grignard reagent was transferred into the dropping funnel and dropwise to the stirred reaction mixture over a period of 30 min; meanwhile the solution colour gradually turned brown. The resulting mixture was stirred at room temperature for 3 h and then refluxed for 40 h. After cooling to room temperature, the product mixture was acidified by the addition of 30 ml of 5 per cent aqueous HCl. The product was extracted into ether (3 × 40 ml) and the combined ethereal extracts were washed with water, and dried over anhydrous sodium sulphate. The solvent was removed and the residue was purified by column chromatography on silica gel with petroleum ether (b.p. 60–90°C) as eluent to yield a pale yellow solid of 1-trimethylsilyl-2-[4-(4-*n*-nonyloxyphenyl)-2,3,5,6-tetrafluorophenyl}acetylene (compound **2f**) 3·73 g (53·1 per cent). ^{1}H NMR ($CDCl_3$): δ0·19 (s, 9 H), 0·80–1·90 (m, 17 H), 3·78 (t, 2 H, J = 6·3 Hz),7·02 (AA′ BB′, 4 H, H arom) ppm. ^{19}F NMR (CCl_4/TFA): δ 59·20 (m, 2 F), 66·60 (m, 2 F) ppm.

2.2. *synthesis of 4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-acetylenes*

4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-acetylenes were prepared as in the following example. In a 50 ml round-bottomed flask equipped with a magnetic stirring bar, were placed 1·70 g (3·66 mmol) of compound **2f**, 6 ml of methanol, 25 ml of acetone and 3 ml of 0·2 M aqueous NaOH. The reaction mixture was stirred at room temperature for 24 h. Then the organic solvent was removed in vacuum, and the product was extracted with ether. The ethereal extracts were washed with water, dried over anhydrous sodium sulphate. The solvent was removed in vacuum and the residue was recrystallized from acetone–methanol to give white flaky crystals of 4′-*n*-nonylowy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (compound **3f**) 1·28 g (88·9 per cent). ^{1}H NMR (CCl_4/TMS: δ 0·79–1·99 (m, 17 H), 3·42 (s, 1 H), 3·86 (t, 2 H, J = 6·3 Hz), 7·03 (AA′ BB′, 4 H, H arom) ppm.^{19}F NMR (CCl_4/TFA): δ 59·30 (m, 2 F), 66·33 (m, 2 F) ppm.

2.3. *Synthesis of 1-(4-cyanophenyl)-2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylenes*

The 1-(4-cyanophenyl)-2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylenes (compounds **A**) were prepared Pd(0)/Cu(I) catalysed arylacetylene coupling reaction as in the following example. Under dry nitrogen, to a mixture of **3f** (179 mg, 0·46 mmol), 1-cyano-4-iodobenzene (103 mg, 0·46 mmol), bis(triphenylphosphine)palladium dichloride (35 mg, 0·05 mmol) and copper (I) iodide (17 mg, 0·089 mmol), was added 15 ml of anhydrous triethylamine. The resulting mixture was stirred reflux for 4 h. TLC analysis revealed a complete reaction. Then the formed precipitate was filtered off, washed with ether and filtrate washed with water, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure with a rotary evaporator and the residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (30 : 1) as eluent to yield yellow crystals. Recrystallization from acetone–methanol gave pale white crystals of 1-(4-cyanophenyl)-2-(4′-*n*-nonyloxy-2,3, 5,6-tetrafluorobiphenyl-4-yl)acetylene (compound **8**) 200 mg (89·3 per cent); C 102·7°C N 185·2°C I. ^{1}H NMR ($CDCl_3$): δ 0·84–1·92 (m, 17 H), 4·08 (t, 2 H, J = 6·3 Hz), 7·06 (d, 2 H, J = 8·1 Hz), 7·18 (d, 2 H, J = 8·1 Hz), 7·74 (s, 4 H) ppm. ^{19}F NMR ($CDCl_3$): δ 60·04 (m, 2 F), 67·02 (m, 2 F) ppm. IR (KBr): υ 2900, 2810, 2200, 1604, 1502, 1470, 1408, 1284, 1256, 1180, 1160, 1020, 980, 620 cm^{-1}: MS (*m/z*): (M^{+}, 31·36), 367 (100·00); Elemental analysis, found: C, 73·05; H, 5·58; N, 2·66; F 15·03; calculated; (for $C_{30}H_{27}F_4NO$) C 73·02; H, 5·48; N, 2·84; F, 15·42 per cent.

2.4. *Synthesis of 1-(4-nitrophenyl)-2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylenes*

1-(4-Nitrophenyl)-2-(4′-*n*-alkoxy-2, 3, 5, 6-tetrafluorobiphenyl-4-yl)acetylenes (compounds **B**) was prepared as described in § 2.3. Quantities: compound **3 a** (200 mg, 0·62 mmol), 1-nitro-4-iodobenzene (155 mg, 0·62 mmol), $Pd(PPh_3)_2Cl_2$(35 mg, 0·05 mmol), CuI (17 mg, 0·089 mmol). The experimental procedure was as described for the preparation of compound 8. The crude product was purified by column chromatography to yield a pale yellow solid of 1-(4-nitrophenyl)-2-(4′-*n*-butyloxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylene (compound 10) 177 mg (64·4 per cent); C, 139·0°C N 204·1°C I. ^{1}H NMR ($CDCl_3$): δ 0·97–2·00 (m, 7·H), 4·04 (t, 2 H, $J = 6{\cdot}3$ Hz), 7·02 (d, 2 H, $J = 8{\cdot}1$ Hz), 7·76 (d, 2 H, $J = 8{\cdot}1$ Hz), 7·44 (d, 2 H, $J = 8{\cdot}1$ Hz), 8·27 (d, 2 H, $J = 8{\cdot}1$ Hz) ppm; ^{19}F NMR ($CDCl_3$): δ 59·64 (m, 2 F), 66·75 (m, 2 F) ppm. IR (KBr):υ 2950, 2850, 1610, 1600, 1520, 1505, 1485, 1420, 1345, 1300, 1260, 1185, 1165, 990, 865, 620 cm^{-1}; MS (*m/z*): 443 (M^+, 50·99), 387 (100·00); Elemental analysis, found: C, 65·10; H, 3·82; N, 3·06; F, 17·15; calculated (for $C_{24}H_{17}F_4O_3N$): C, 65·01; H, 3·84; N, 3·16; F, 17·16 per cent.

3. Results and discussion

The phase behaviours of the series **A** and **B** are given in tables 1 and 2.

Compounds **A** show enantiotropic nematic phases and exhibit very high N–I transition temperatures. The N–I transition temperatures against the number of carbons (*n*) in the *n*-alkyl chain show the usual odd–even alternation. The melting points are rather irregular in their distribution along the series, the lowest being 101–101·3°C for the *n*-decyloxy compound. Four members of the series of compounds **B** were prepared. Compounds with $n = 10$ exhibit an enantiotropic smectic A phase and nematic phase, and other show enantiotropic nematic phase only. The thermal stabilities of liquid crystal phases for compounds **A** are larger than those of compounds **B**.

4. Conclusions

A homologous series of 1-(4-cyanophenyl)-2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylenes and four members of 1-(4-nitrophenyl)-2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylenes were prepared via Pd-catalysed coupling reaction. Thermal optical microscopy showed that these compounds were liquid crystalline, and each exhibited a wide nematic phases.

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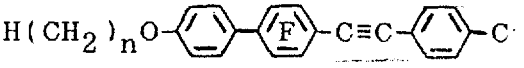
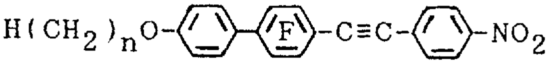
Table 1. Transition temperatures of compounds **A**.



n	Transition temperatures/°C
5	$\mathrm{C}\ \underset{101\cdot2}{\overset{119\cdot5}{\rightleftharpoons}}\ \mathrm{N}\ \underset{216\cdot0}{\overset{216\cdot3}{\rightleftharpoons}}\ \mathrm{I}$
6	$\mathrm{C}\ \underset{93\cdot9}{\overset{113\cdot9}{\rightleftharpoons}}\ \mathrm{N}\ \underset{191\cdot8}{\overset{192\cdot5}{\rightleftharpoons}}\ \mathrm{I}$
7	$\mathrm{C}\ \underset{109\cdot8}{\overset{128\cdot6}{\rightleftharpoons}}\ \mathrm{N}\ \underset{200\cdot7}{\overset{201\cdot4}{\rightleftharpoons}}\ \mathrm{I}$
8	$\mathrm{C}\ \underset{86\cdot9}{\overset{107\cdot0}{\rightleftharpoons}}\ \mathrm{N}\ \underset{192\cdot1}{\overset{192\cdot1}{\rightleftharpoons}}\ \mathrm{I}$
9	$\mathrm{C}\ \underset{84\cdot7}{\overset{102\cdot7}{\rightleftharpoons}}\ \mathrm{N}\ \underset{184\cdot9}{\overset{185\cdot2}{\rightleftharpoons}}\ \mathrm{I}$
10	$\mathrm{C}\ \underset{85\cdot5}{\overset{101\cdot3}{\rightleftharpoons}}\ \mathrm{N}\ \underset{177\cdot5}{\overset{177\cdot8}{\rightleftharpoons}}\ \mathrm{I}$

Table 2. Transition temperatures of compounds **B**.



n	Transition temperatures/°C
4	$\mathrm{C}\ \underset{105\cdot3}{\overset{139\cdot0}{\rightleftharpoons}}\ \mathrm{N}\ \underset{204\cdot0}{\overset{204\cdot1}{\rightleftharpoons}}\ \mathrm{I}$
6	$\mathrm{C}\ \underset{77\cdot3}{\overset{103\cdot8}{\rightleftharpoons}}\ \mathrm{N}\ \underset{190\cdot6}{\overset{190\cdot9}{\rightleftharpoons}}\ \mathrm{I}$
8	$\mathrm{C}\ \underset{89\cdot2}{\overset{96\cdot0}{\rightleftharpoons}}\ \mathrm{N}\ \underset{176\cdot9}{\overset{177\cdot6}{\rightleftharpoons}}\ \mathrm{I}$
10	$\mathrm{C}\ \underset{68\cdot2}{\overset{84\cdot8}{\rightleftharpoons}}\ \mathrm{S_A}\ \underset{147\cdot7}{\overset{147\cdot7}{\rightleftharpoons}}\ \mathrm{N}\ \underset{168\cdot4}{\overset{168\cdot6}{\rightleftharpoons}}\ \mathrm{I}$

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