Synthesis of New Chiral Smectic Mesogenes with 4-(2-Phenylethyl)biphenyl and 4-[2-(3-Fluorophenyl)ethyl]biphenyl Molecular Cores

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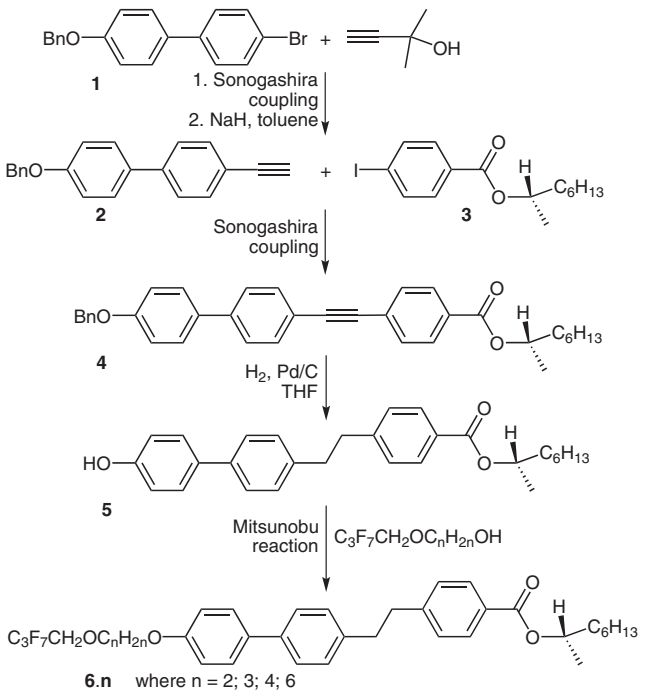
Abstract: Two methods of synthesis of chosen 1-[4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyalkoxy)biphenyl-4-yl]ethanes and 1-[3-fluoro-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyalkoxy)biphenyl-4-yl]ethanes have been proposed, checked and compared. The compounds were prepared by Sonogashira coupling of 4-benzyloxy-4′-ethynylbiphenyl with appropriate 4-halobenzoate esters followed by parallel hydrogenation of ethynylene bridge and debenzylation of hydroxyl group. The 1-[4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-hydroxybiphenyl-4-yl]ethane and 1-[3-fluoro-4-(methoxycarbonyl)phenyl]-2-[4′-hydroxybiphenyl-4-yl]ethane thus obtained has been transformed into final products by Mitsunobu reaction with ω-(2,2,3,3,4,4,4-heptafluorobutoxy)alkan-1-ols, followed by the replacing of an ester terminal chain in the case of second method.

Key words: coupling, Mitsunobu reaction, alkynes, biaryls, self-assembly

Great attention has been recently focused on searching new ferroelectric and antiferroelectric liquid crystals having high molecular tilt angle in smectic layers, long helicoidal structure, and reduced number of ester linking groups.[1] Such materials ensures very promising electrooptical properties leading to a new generation of orthoconic antiferroelectric liquid-crystal displays (OAFLCD).[2] Recently many new classes of highly tilted ferroelectric and antiferroelectric materials from the group of biphenyl benzoates, phenyl biphenylates, and terphenyl derivatives with partially fluorinated terminal chains have been synthesized and some utilitarian mixtures have been formulated and their properties determined.[3] However, all of them suffer from the problem of the too short helicoidal structure which has serious influence on the alignment quality of the liquid crystal in the display cell. The synthesis of presented two series of compounds is based on the idea of lower rigidity of 4-(phenylethyl)biphenyl molecular core in comparison with analogous terphenyl one.[4] Lower rigidity can have influence on the length of the helicoidal structure which is created in synclinic and anticlinic liquid-crystal phase.

For the preparation of 4-(2-phenylethyl)biphenyls and 4-[2-(3-fluorophenyl)ethyl]biphenyls, Sonogashira coupling between corresponding aryl halides and terminal acetylenes followed by the hydrogenation of etynylene bridge have been utilized, see Scheme 1 and Scheme 2. The main starting compound, 4-benzyloxy-4′-ethynylbiphenyl (**2**) has been prepared from 4-benzyloxy-4-bromobiphenyl by the Sonogashira coupling with 2-methyl-3-butyn-2-ol followed by the elimination with sodium hydride in toluene.[5] The experimental procedure is described in the literature.[6] The (*S*)-1-[4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-benzyloxybiphenyl-4-yl]ethyne (**4**) has been prepared by Sonogashira coupling between (*S*)-octan-2-yl 4-iodobenzoate and compound **3**. Then simultaneous reduction of triple bond and debenzylation, followed by the Mitsunobu etherification with corresponding ω-(2,2,3,3,4,4,4-heptafluorobutoxy)alkyl chain (**16.n**) resulted in final compounds, 1-[(*S*)-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyalkoxy)biphenyl-4-yl]ethanes (**6.n**).[7] The second series of compounds **12.n** differ from the first series by the fluorine atom in the proximal position to the chiral terminal chain so the same synthetic approach could be easily utilized (Scheme 1) but the more general method has been



Scheme 1 Preparation of 1-[(*S*)-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyalkoxy)biphenyl-4-yl]ethanes by the method I

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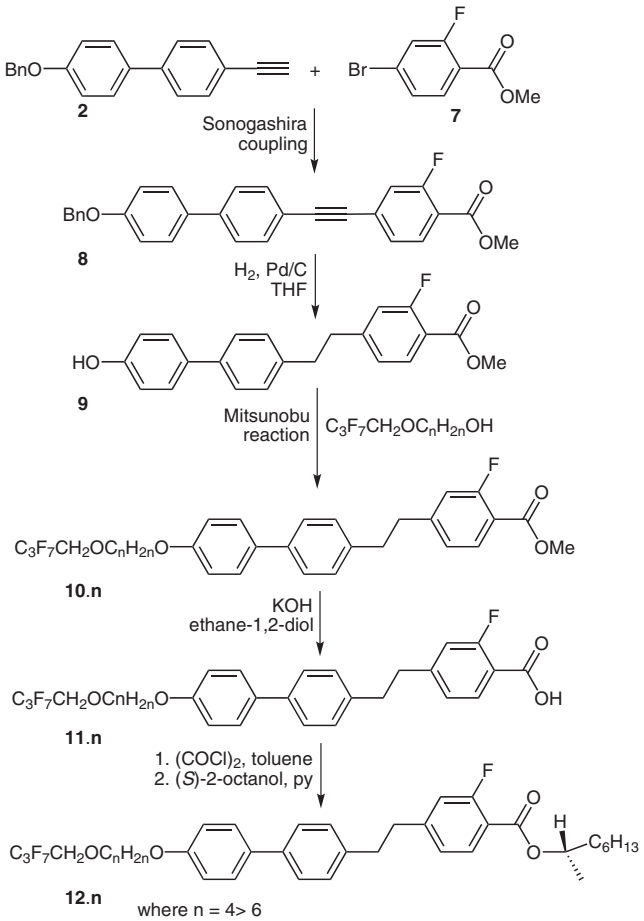
chosen, allowing easy introduction of different chiral terminal chain as well as the perfluorinated one, see Scheme 2.

The second method has a serious advantage over the first approach due to much easier purification of compound **8** than **4**. Compound **8** has been crystallized from THF with good yield. Spectroscopic data for compound **12.4** prepared according to method II (Scheme 2) is given in the literature.[8]

The preparation of ω-(2,2,3,3,4,4,4-heptafluorobutoxy) alkan-1-ols has been performed as depicted in Scheme 3. Compounds **13.n** have been prepared as described in the references,[9] the rest of the synthesis of **17.n** has been described in the literature.[10] The synthesis of compounds **5**, **6.n**, **9**, **10**, **11**, **12.n** were performed similarly to the reported method.[4]



Scheme 2 Preparation of 1-[(*S*)-3-fluoro-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyalkoxy)biphenyl-4-yl]ethanes by the method II

Temperatures and enthalpies of phase transitions for compounds **6.n** and **12.n** were determined by polarizing thermomicroscopy and DSC technique are described in Table 1. Electrooptical measurements and miscibility study were performed to confirm the type of the smectic phases.

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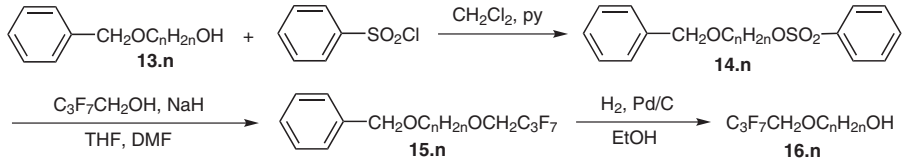
(6) **Synthesis of 4-Benzyloxy-4′-ethynylbiphenyl (3)**
4-Benzyloxy-4-bromobiphenyl (128.8 g, 0.38 mol), Et_3N (57.6 g, 0.57 mol), DBU (29 g, 0.19 mol), $PdCl_2(PPh_3)_2$ (2 g, 2.85 mmol), CuI (1 g, 5.27 mmol), and THF (400 mL) have been added in a 1 L nitrogen-filled flask. The mixture were heated(boiling) for 5 min, and 2-methyl-3-butyn-2-ol (38.3 g, 0.456 mol) has been dropped in slowly. After 4 h of stirring the GC-MS analysis was performed. To complete the reaction, 25% of the initial amount of 2-methyl-3-butyn-2-ol and 0.5g of $PdCl_2(PPh_3)_2$ were added and stirred for additional 8 h. Then the reaction mixture was poured onto H_2O and the solid was filtered off, dried and washed using CH_2Cl_2 (0.5 L). The obtained 4-[4′-(benzyloxy)biphenyl-4-yl]-2-methylbut-3-yn-2-ol (112 g, 0.33 mol), NaH (1.1 g, 46 mmol) and dry toluene (1 L) have been placed in a flask equipped with column and distillation head to distill off the emerging acetone. When the distillate temperature reached the bp of toluene, the reaction mixture was cooled down and poured onto the H_2O. The organic layer was separated and poured through active carbon pad and dried over anhyd $MgSO_4$. The toluene solution was concentrated and the final product crystallized in freezer. 4-Benzyloxy-4′-ethynylbiphenyl (**3**) was obtained in 57% yield (61.5 g, 0.217 mol). MS (EI 70eV): *m/z* = 284 [M^+], 193, 165, 139, 91, 65. IR (neat): 3282, 3061, 3036, 2861, 2359, 2340, 1600, 1488, 1454, 1380, 1284, 1246, 1026, 1008, 812, 738, 619. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.53 (m, 2 H, ArH), 7.51 (m, 5 H, ArH), 7.43 (m, 2 H, ArH), 7.39 (m, 2 H, ArH), 7.03 (m, 2 H, ArH), 5.10 (s, CH_2), 3.11 (s, 1 H C≡CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.89 (1 C), 141.31 (1 C), 137.04 (1 C), 133.15 (1 C), 132.74 (2 CH), 128.84 (2 CH), 128.32 (2 CH), 128.25 (2 CH), 127.69 (1 CH), 126.70 (2 CH), 120.49 (1 C),



Scheme 3 Preparation of ω-(2,2,3,3,4,4,4-heptafluorobutoxy)alkan-1-ols

Table 1 Comparison of Temperatures and Enthalpies of Phase Transitions for Compounds **6.n** and **12.n**

Compd	Cr	Temp (°C) [J/mol]	SmC_a*	Temp (°C) [J/mol]	SmC*	Temp (°C) [J/mol]	SmA	Temp (°C) [J/mol]	iso
6.2	+	110.9 59500	(+)	(95)[b]	–	–	(+)		+
6.3	+	102.0 48000	(+)	(93)[b]	–	–	(+)		+
6.6	+	47.2 27000	+	84.7 85	+	–	–	99.2 11150	+
12.4	+	67.6 27300	+	79.3 68	+	83.0 [a]	+	84.1 9800	+
12.6	+	40.8 24700	+	72.0 50	+	86.0 1600	+	88.0 7400	+

[a] Value of the SmC*–SmA transition enthalpy has been added to the enthalpy of SmA-Iso transition because it was impossible to separate.
[b] Extrapolated value from miscibility study diagram (polarizing thermomicroscope measurement); the presence of monotropic phase transitions are in brackets.

115.44 (2 CH), 83.87 (1 C), 77.87 (1 CH), 70.28 (1 CH_2). Mp 156.7–157.2 °C (dec.).

(7) **1-[(*S*)-4-(1-Methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxyhexyloxy)biphenyl-4-yl]ethane (6.6)**
MS (EI 70eV): 712 [M^+], 465, 183, 55. MS (ESI$^+$, MeOH–H_2O): 735 [M + Na^+], 615. IR (neat): 2934, 2856, 1710, 1608, 1499, 1354, 1222, 1103, 810, 736 cm^{-1}. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.29 (1 COO), 158.55 (1 CO), 146.94 (1 CEt), 139.63 (1 CEt), 138.69 (1 C), 133.38 (1 C), 129.67 (2 CH), 128.83 (2 CH), 128.75 (1 CCOO), 128.48 (2 CH), 127.95 (2 CH), 126.67 (2 CH), 114.74 (2 CH), 73.13 (1 COOC), 71.59 (1 CH_2O), 67.88 (1 CH_2O), 37.87 (1 CH_2Ar), 37.12 (1 CH_2Ar), 36.11 (1 CH_2), 31.77 (1 CH_2), 29.41 (1 CH_2), 29.19 (2 CH_2), 25.82 (1 CH_2), 25.60 (1 CH_2), 25.43 (1 CH_2), 22.61 (1 CH_2), 20.11 (CH_3), 14.08 (CH_3).

(8) **1-[(*S*)-3-Fluoro-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4′-(2,2,3,3,4,4,4-heptafluorobutoxybutoxy)biphenyl-4-yl]ethane (12.4)**
MS (EI, 70eV): *m/z* = 702 [M^+], 465, 183, 55. MS (ESI$^+$, MeOH–H_2O): *m/z* = 725 [M + Na^+], 605. IR (neat): 2950, 2859, 1699, 1622, 1499, 1354, 1219, 1117, 971, 817, 734.

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