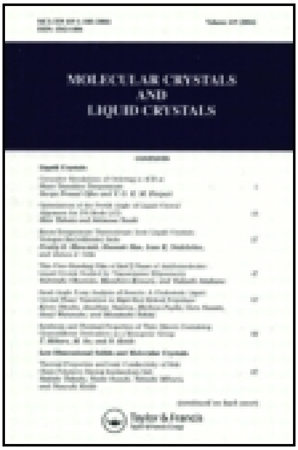

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis, Stability and Mesomorphic Behavior of a Liquid Crystal containing a CF_2 Unit Adjacent to a Thiophene Ring

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Synthesis, Stability and Mesomorphic Behavior of a Liquid Crystal containing a CF_2 Unit Adjacent to a Thiophene Ring

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The synthesis of a novel fluorinated liquid crystal 7 containing a thiophene ring in the aromatic core is discussed. Adjacent to the thiophene ring is a 1,1-difluoropentyl unit, which was introduced *via* DAST fluorination of an intermediate thienylketone. The difluoromethylene unit was incorporated with the aim of improving the stability of the electron-rich thiophene-containing core and increasing the dielectric biaxiality when compared to the non-fluorinated parent molecule. The material synthesized displays both the S_A and the S_F phases.

Keywords: thiophene; fluorinated; synthesis; tilted smectic

INTRODUCTION

Thiophene-containing liquid crystals are known to have lower viscosities than the corresponding phenyl derivatives and possess fast response times in the presence of an electric field. We were interested in examining the impact of incorporating a 2-(1,1-difluoroalkyl) substituent on the thiophene ring in such materials. The difluoromethylene unit was chosen to impart a high dielectric biaxiality (for use in ferroelectric display devices) and was also expected to increase the stability of the thiophene nucleus by electron-withdrawal from the π–electron rich heterocyclic ring. The material targeted in this initial study is achiral and has been designed to provide some insight into the types and breadth of mesophase transitions supported by the 2-(1,1-difluoroalkyl)thienyl unit. The thiophene ring is substituted in the 2- and 5-positions which gives the most linear architecture and therefore the highest clearing points[1].

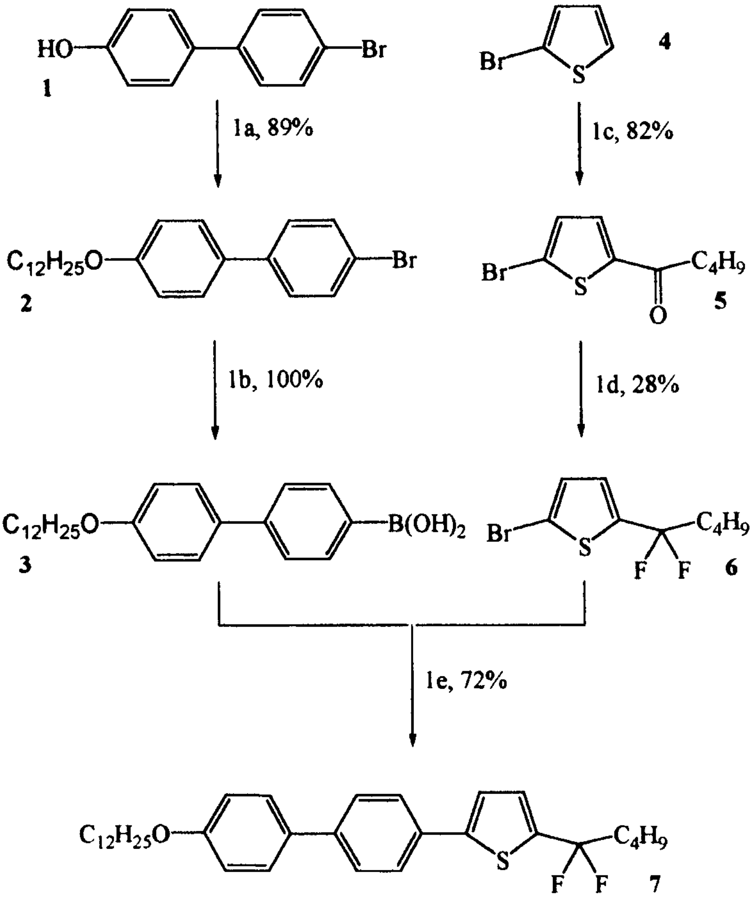
Until now there have been no publications that have reported the synthesis of the 2-(1,1-difluoroalkyl)thiophene unit as an entity for incorporation into a liquid crystal structure. Even in non-liquid-crystal chemistry there are remarkably few examples of the synthesis of such materials and, even then, chain lengths ($CF_2\mathbf{R}$) in excess of two carbon units are not known as far as we have been able to ascertain.

In this paper, the synthesis of 2-(1,1-difluoropentyl)thiophene derivative **7** is reported, together with an evaluation of its hydrolytic stability and mesomorphic behavior.

SYNTHESIS

The synthesis of 2-(1,1-difluoropentyl)thiophene 7 is outlined in Scheme 1. Alkoxybiphenyl **2** was prepared from the corresponding hydroxybiphenyl **1** using standard Williamson ether synthesis conditions. Compound **2** was transformed into the boronic acid **3** following the procedure reported by Wakefield[2]. 2-Bromothiophene **4** was acylated[3] with exclusive substitution taking place at the 5-position (GC and NMR analyses) as expected. Conversion of **5** into **6** was effected using neat DAST[4,5] at 55 °C for 3-5 days. When the reaction was left for more than a week, the DAST appeared to be decomposing (based on the lack of an exothermic reaction with water during workup) and a black tar was obtained. We also attempted conversion of ketone **5** into the difluoro compound **6** *via* conversion to the corresponding 1,3-dithiolane and subsequent reaction with pyridinium poly(hydrogen fluoride)/1,3-dibromo-5,5-dimethylhydantoin[6]. This procedure gave low yields due to competitive ring bromination[7], even at −95 °C. The thiophene nucleus is highly reactive to electrophilic aromatic substitution and was brominated (NMR and GC-MS analyses) by the 1,3-dibromo-5,5-dimethylhydantoin during the reaction. Mixtures of mono- and di-brominated materials were produced together with the desired product **6**. Purification of **6** by careful column chromatography could not be achieved.

Palladium-catalyzed Suzuki cross-coupling of boronic acid **3** and bromothiophene **6** was used to obtain **7**. Chromatography of crude **7** using silica gel or basic alumina resulted in partial decomposition of the product to the corresponding ketone. Recrystallization of the crude product, however, yielded the desired target **7** in high purity. It is interesting to note that the synthetic intermediate **6** did not decompose when passed through a silica gel column, even though this material also contains the thienyl-CF_2 unit. Benzylic difluoro compounds with an electron-donating group in the *ortho* or *para* positions are known[8,9] to undergo hydrolysis to the corresponding ketones. Apparently, the remote alkoxy substituent in **7** can effectively stabilize a developing carbocation at the fluorine-bearing carbon, hence facilitating hydrolysis. In contrast, intermediate **6** has only a poorly electron-donating bromo substituent which does not facilitate hydrolysis of the difluoromethylene group.



1a...1-Bromododecane, K_2CO_3, butan-2-one, reflux.
1b...(i) n-Butyllithium, trimethyl borate, -78 °C; (ii) $HCl_{(aq)}$, room temp.
1c...Valeric anhydride, $FeCl_3$, room temp.
1d...Diethylaminosulfur trifluoride (neat), 55 °C.
1e...$PdCl_2$, $Na_2CO_{3(aq)}$, acetone, reflux.

SCHEME 1 The synthesis of 2-(1,1-difluoropentyl)-5-(4'-dodecyloxybiphenyl-4-yl)thiophene

4-Bromo-4'-dodecyloxybiphenyl (2). A mixture of 1-bromododecane (18.68 g, 0.075 mol), 4-bromo-4'-hydroxybiphenyl (15 g, 0.060 mol) and potassium carbonate (31 g, 0.225 mol) in butan-2-one (120 ml) was heated under reflux for 24 h (GC revealed a complete reaction) and the potassium carbonate was filtered off. The solvent was removed *in vacuo* and the crude product was recrystallized from petroleum ether (bp 35-60 °C) to afford colorless crystals which were dried *in vacuo* (P_2O_5, 24 h). Yield 22.18 g (89%); purity (GC) >99%; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, ^{3}J=6.8 Hz), 1.27-1.40 (16H, m), 1.46 (2H, m), 1.79 (2H, quint., ^{3}J=6.6 Hz), 3.97 (2H, t, ^{3}J=6.6 Hz), 6.94 (2H, d, ^{3}J=8.7 Hz), 7.39 (2H, d, ^{3}J=8.4 Hz), 7.45 (2H, d, ^{3}J=8.7 Hz), 7.51 (2H, d, ^{3}J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 29.2, 29.3, 29.5, 31.8, 68.0, 114.8, 120.6, 127.8, 128.1, 131.6, 132.1, 139.7, 158.9.

4'-Dodecyloxybiphenyl-4-ylboronic acid (3). n-Butyllithium (1.6 ml, 10M in hexanes, 0.016 mol) was added dropwise at -78 °C to a stirred, cooled (-78 °C) solution of compound **2** (4.17 g, 0.010 mol) in anhydrous THF (220 ml). The reaction mixture was maintained under these conditions for a further 2 hours (GC revealed a complete reaction) before previously cooled (0 °C) trimethyl borate (2.32 g, 0.022 mol) was added dropwise at –78 °C. The reaction mixture was allowed to warm to room temperature (overnight) and was stirred for 45 min with hydrochloric acid (10%, 80 ml). The resulting mixture was extracted with diethyl ether (3 x 60 ml). The combined organic phases were washed with water (2 x 50 ml), a further aliquot of water (50 ml) was added and the organic solvent was evaporated from this biphasic mixture *in vacuo*. The white suspension was filtered and the resulting white solid was washed with petroleum ether and briefly dried before being used directly in the next step. Yield 3.82 g (100%); ^{1}H NMR (DMSO-d_6) δ 0.87 (3H, t, ^{3}J=6.9 Hz), 1.26-1.39 (16H, m), 1.46 (2H, m), 1.76 (2H, quint, ^{3}J=6.6 Hz), 3.99 (2H, t, ^{3}J=6.6 Hz), 6.96 (2H, d, ^{3}J=8.7 Hz), 7.50-7.57 (4H, m), 7.45 (2H, d, ^{3}J=8.7 Hz), 8.09 (2H, d, ^{3}J=8.4 Hz).

2-Bromo-5-pentanoylthiophene (5). Iron (III) chloride (9.95g, 0.0613 mol) was added all at once to a stirred mixture of 2-bromothiophene (50.0g, 0.307 mol) and valeric anhydride (65.7g, 0.353 mol) under dry nitrogen at room temperature (a temperature rise to 100 °C was noted). The reaction mixture was stirred at room temperature for a further 2 h (TLC and GC analyses confirmed a complete reaction) and was then poured into water (300 ml). The organic layer was separated and the aqueous layer was washed with ether (2 x 50 ml). The combined organic extracts were washed with sodium carbonate (2M, 2 x 200 ml). The organic layer was dried ($MgSO_4$) and the drying agent was filtered off before the solvent was removed *in vacuo* to give a black liquid. The crude product was distilled to give a colorless liquid. Yield 62.36 g (82%); bp 128-133 °C at 0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.94 (3H, t, ^{3}J=7.2 Hz), 1.39 (2H, sext, ^{3}J=7.5 Hz), 1.70 (2H, quint, ^{3}J=7.5 Hz), 2.82 (2H, t, ^{3}J=7.2 Hz), 7.09 (1H, d, ^{3}J=3.9 Hz), 7.44 (1H, d, ^{3}J=3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.6, 26.6, 38.3, 122.2, 130.5, 132.8, 145.9, 192.3.

2-Bromo-5-(1,1-difluoropentyl)thiophene (6). Compound **5** (1.00 g, 0.004 mol) was added dropwise to stirred DAST (2.40g, 0.015 mol) under dry argon at room temperature. The reaction mixture was heated at 55 °C for 4 days. The cooled reaction mixture was diluted with petroleum ether (40 ml, bp 35-60 °C) and washed with saturated sodium bicarbonate until free of acid. The extract was filtered through a short column of silica gel [eluent - petroleum ether (bp 35-60°C)] and the solvent was removed *in vacuo* to give a colorless liquid. Yield 0.302g (28%); ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, ^{3}J=6.9 Hz), 1.33-1.52 (4H, m), 2.17 (2H, m), 6.95 (1H, dt, ^{3}J=3.6 Hz, $^4J_{H\text{-}F}$=1.5 Hz), 6.99 (1H, dt, ^{3}J=3.6 Hz, $^5J_{H\text{-}F}$=0.9 Hz); ^{13}C NMR

(CDCl$_3$) δ 13.6, 22.2, 24.5, 38.3 (t, $^2J_{C\text{-}F}$=26.4 Hz), 114.1, 120.5 (t, $^1J_{C\text{-}F}$=238.4 Hz), 126.1 (t, $^3J_{C\text{-}F}$=5.7 Hz), 129.5, 140.8 (t, $^2J_{C\text{-}F}$=32.0 Hz); ^{19}F NMR (CDCl$_3$) δ −85.1(t, $^3J_{F\text{-}H}$= 16.2 Hz).

2-(4'-Dodecyloxybiphenyl-4-yl)-5-(1,1-difluoropentyl)thiophene (7). Palladium (II) chloride (0.1M solution in water, 0.2 ml, 0.02 mmol) was added all at once to a stirred mixture of compound **3** (0.500 g, 1.30 mmol), compound **6** (0.210 g, 0.74 mmol) and sodium carbonate (2.0M, 1.68 ml, 3.36 mmol) in acetone (10 ml) under an argon atmosphere. The reaction mixture was heated under reflux for 40 h, diluted with hydrochloric acid (10%, 10 ml) and extracted with dichloromethane (3 x 20 ml). The combined organic extracts were washed with water (100 ml) and dried (Na$_2$SO$_4$). The extract was filtered through a column of silica gel (eluent - petroleum ether (bp 35-60 °C):dichloromethane, 3:1) and the solvent was removed *in vacuo*. The crude product was recrystallized from ethyl acetate followed by petroleum ether (bp 35-60 °C) to afford a white solid, which was dried *in vacuo* (P$_2$O$_5$, CaCl$_2$, 24 h). Yield 0.280g (72%). Transitions (°C) K 155.9 S$_F$ 160.4 S$_A$ 172.4 I; ^{1}H NMR (CDCl$_3$) δ 0.88 (3H, t, ^3J=6.9 Hz), 0.93 (3H, t, ^3J=7.2 Hz), 1.27-1.56 (22H, m), 1.81 (2H, quint, ^3J=6.6 Hz), 2.25 (2H, m), 4.00 (2H, t, ^3J=6.6 Hz), 6.98 (2H, d, ^3J=9.0 Hz), 7.17 (1H, dt, ^3J=3.9 Hz, $J_{H\text{-}F}$=1.5 Hz), 7.22 (1H, dt, ^3J=3.6 Hz, $J_{H\text{-}F}$=1.2 Hz), 7.54 (2H, d, ^3J=8.7 Hz), 7.57 (2H, d, ^3J=9.0 Hz), 7.63 (2H, d, ^3J=8.7 Hz); ^{19}F NMR (CDCl$_3$) δ −84.9 (t, $^3J_{F\text{-}H}$= 15.3 Hz).

CONCLUSIONS

We have successfully synthesized the first liquid crystal to contain a thiophene ring with a CF$_2$ unit adjacent to the heterocycle. Although we did not obtain a material that displayed a smectic C phase that would be required for use in a ferroelectric device (the structure could easily be modified to include a stereogenic center that would impart the required molecular symmetry), we do observe that the structure supports a tilted mesophase (S_F). The S_F phase was identified by optical microscopy and exhibited the typical mosaic texture[10] on cooling from the homeotropic S_A phase. The paramorphotic 'chunky' focal conic texture was also observed on cooling from the focal conic S_A.

We are currently working on modifications to the structure that should reduce the melting point and introduce a S_C phase.

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