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Liquid Crystals

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Kan Wang; Hengfeng Li; Kegang Liu; Jianxun Wen

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Preliminary communication

Mesomorphic properties of 4-(polyfluoroalkoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoates

KAN WANG, HENGFENG LI, KEGANG LIU and JIANXUN WEN*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032, PR China

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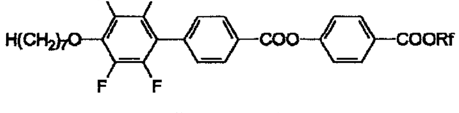
A series of 4-(polyfluoroalkoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)-benzoates were synthesized and observed using DSC and optical polarizing microscopy. The results show that they are not mesogens. Their mesomorphic properties were compared with similar compounds containing no aromatic fluorine substituents.

Fluorinated liquid crystals have attracted much attention since the 1970s owing to their excellent properties for LCD applications. More recently, polyfluorination on the aromatic mesogenic core in mesogenic molecules has been systematically studied. Earlier research of this group showed that lateral polyfluoro-substituted liquid crystals show low melting points and tend to form the nematic phase [1–5]. Biphenyl ester systems have good mesomorphic properties [6]; but when four fluorine atoms are substituted in the phenyl, far away from the centre in 4-(4-*n*-alkoxyphenyl)benzoic acids, their esters do not exhibit a mesophase [7]. We also know that fluorinated tails are advantageous to the formation of mesophases as compared with their hydrocarbon analogues [8–10]. We thus planned to introduce highly fluorinated tails into systems in order to observe the change of mesomorphic properties. In this work, we prepared three 4-(polyfluoroalkoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoates (compound **Ia**, **b**, **c**), which are described as structure **1**. They were prepared by an esetrification procedure between a 4-(polyfluoroalkoxycarbonyl)phenol [11] and 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoic acid [7] in the presence of dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP) as catalyst in anhydrous dichloromethane.

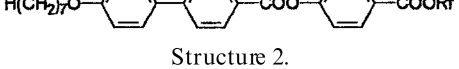


Structure 1.

The mesomorphic properties of the new compounds were studied by thermal optical polarizing microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a temperature control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literatures [12, 13]. Their transition temperatures are summarized below (°C).

Ia. $Rf = CH_2CH_2(CF_2)_4Cl$: Cr 155.09 I 138.38 Recr
Ib. $Rf = CH_2CH_2(CF_2)_4H$: Cr 156.69 I 137.54 Recr
Ic. $Rf = CH_2CH_2(CF_2)_6Cl$: Cr 158.91 I 145.92 Recr

From the observation of the mesomorphic properties of these compounds, some interesting results have been obtained. First, it is unfortunate that none of the target compounds exhibits a mesomorphic state; the highly fluorinated tail does not induce mesogenicity. Second, the melting points of all three compounds are very close. When a CF_2CF_2 unit was inserted in the tail, the melting point increased only by 3.82°C. The melting point of the compound containing a terminal hydrogen atom at the end of the fluorinated chain (**Ib**) is 1.60°C higher than that of the similar compound containing a chlorine atom (**Ia**). But in the similar compounds **IIa**,**b**,**c**,**d** (structure 2) [11, 14, 15], which have no fluoro substituents on the aromatic rings, the situation is different; phase transition



Structure 2.

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* Author for correspondence; e-mail: liukg@pub.sioc.ac.cn

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properties are listed below. When a CF_2CF_2 unit was inserted in the tail, the melting point increased by 17.2°C, and the clearing point increased by 11.9°C. The melting and clearing points of **IIa** are lower than those of **IIb**.

II-a. $Rf = CH_2CH_2(CF_2)_4Cl$: Cr 123.67 SmC 196.51 SmA 213.28 I 206.18 SmA 193.25 SmC 107.57 Recr.

II-b. $Rf = CH_2CH_2(CF_2)_4H$: Cr 119.65 SmC 181.83 SmA 204.30 I 198.79 SmA 177.33 SmC 109.69 SmB 91.96 Recr.

II-c. $Rf = CH_2(CF_2)_4H$: Cr 104.4 SmC 132.9 SmA 200.9 I 197.8 SmA 89.7 SmC 78.8 Recr.

II-d. $Rf = CH_2(CF_2)_6H$: Cr 121.6 SmC 187.6 SmA 212.8 I 210.4 SmA 186.2 SmC 102.3 Recr.

It can be seen from these results that fluorine substitution on the aromatic cores in this structure destroys the mesophase. First, the breadth-increasing effect of fluorine substituents destabilizes the mesophase; second, the symmetrical tetrafluorination of the biphenyl group destroys the coplanarity of the two phenyl rings [16, 17], which plays an important role in mesophase formation.

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Appendix

The following are results of identification analyses on the target compounds.

Ia: 4-(6-chloro-3,3,4,4,5,5,6,6-octafluorohexoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoate. MS (*m/z*): 767 ($M+1^+$, 1.27), 367 ($H(CH_2)_7O{-}C_6F_4{-}C_6H_4{-}CO^+$, 100.00), 269 ($O{-}C_6F_4{-}C_6H_4{-}CO^+$, 35.02). Anal. for $C_{33}H_{27}ClF_{12}O_5$ calc. C 51.58, H 3.55; found C 51.54, H 3.38%. ^1H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 0.90 (3H, t, $J = 6.4$ Hz, CH_3), 1.10–1.60 (m, 8H, RH), 1.60–2.00 (m, 2H, CH_2), 2.54–2.70 (m, 2H, CF_2CH_2), 4.27 (t, 2H, $J = 6.5$ Hz, OCH_2), 4.65 (t, 2H, $J = 6.5$ Hz, OCH_2), 7.10–7.70 (m, 4H, ArH), 8.00–8.40 (m, 2H, ArH). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): -9.0 (2F, t, $J = 13$ Hz, CF_2Cl), 36.7 (m, 2F, CH_2CF_2), 42.9 (m, 2F, CF_2), 46.0 (m, 2F, CF_2), 67.6 (m, 2F, ArF), 79.0 (m, 2F, ArF). IR (KBr, ν_{max}, cm^{-1}): 2929, 2857, 1737, 1482, 1266, 1206, 1185, 1070, 985, 889, 864, 842, 767, 501.

Ib: 4-(3,3,4,4,5,5,6,6-octafluorohexoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoate. MS (*m/z*): 733 ($M+1^+$, 1.67), 367 ($H(CH_2)_7O{-}C_6F_4{-}C_6H_4{-}CO^+$, 100.00), 269 ($O{-}C_6F_4{-}C_6H_4{-}CO^+$, 34.42). Anal. for $C_{33}H_{28}F_{12}O_5$ calc. C 54.11, H 3.85; found C 55.15, H 3.76%. ^1H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 0.90 (3H, t, $J = 6.4$ Hz, CH_3), 1.10–1.60 (m, 8H, RH), 1.60–2.00 (m, 2H, CH_2), 2.54–2.70 (m, 2H, CF_2CH_2), 4.27 (t, 2H, $J = 6.5$ Hz, OCH_2), 4.65 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.06 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5.5$ Hz, CF_2H), 7.10–7.70 (m, 4H, ArH), 8.00–8.40 (m, 2H, ArH). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): 36.3 (m, 2F, CH_2CF_2), 48.3 (m, 2F, CF_2), 52.8 (m, 2F, CF_2), 60.1 (d, 2F, $J = 52$ Hz, CF_2H), 67.6 (m, 2F, ArF), 79.0 (m, 2F, ArF). IR (KBr, ν_{max}, cm^{-1}): 2930, 1737, 1713, 1608, 1482, 1266, 1169, 1070, 1020, 984, 889, 864, 811, 767, 704, 630, 501.

Ic: 4-(8-chloro-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorooctoxycarbonyl)phenyl 4-(4-*n*-heptoxy-2,3,5,6-tetrafluorophenyl)benzoate. MS (*m/z*): 867 ($M+1^+$, 0.44), 367 ($H(CH_2)_7O{-}C_6F_4{-}C_6H_4{-}CO^+$, 100.00), 269 ($O{-}C_6F_4{-}C_6H_4{-}CO^+$, 34.19). Anal. for $C_{35}H_{27}ClF_{16}O_5$ calc. C 48.49, H 3.14; found C 48.31, H 2.88%. ^1H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 0.90 (m, 3H, CH_3), 1.10–1.60 (m, 8H, RH), 1.60–2.00 (m, 2H, CH_2), 2.54–2.70 (m, 2H, CH_2CF_2), 4.27 (t, 2H, $J = 6.5$ Hz, OCH_2), 4.65 (t, 2H, $J = 6.5$ Hz, OCH_2), 7.10–7.70 (m, 4H, ArH), 8.00–8.40 (m, 2H, ArH). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): -9.5 (2F, t, $J = 13$ Hz, CF_2Cl), 36.3 (m, 2F, CH_2CF_2), 42.3–45.0 (m, 6F, $(CF_2)_3$), 46.3 (m, 2F, CF_2), 67.4 (m, 2F, ArF), 79.3 (m, 2F, ArF). IR (KBr, ν_{max}, cm^{-1}): 1737, 1714, 1643, 1482, 1406, 1267, 1206, 1169, 1070, 1021, 984, 888, 767, 501.

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