Synthesis of pentafluoro-λ⁶-sulfanyl substituted acetylenes for novel liquid crystals

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ABSTRACT

Synthetic routes towards SF_5-substituted acetylenes as novel liquid crystal molecules were studied. Key steps of the synthetic sequence were based upon radical addition of SF_5Cl to double and triple bonds of the corresponding liquid crystal precursors followed by dehydrochlorination of the corresponding products. The physical properties of the new liquid crystals **10a–c** were investigated.

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1. Introduction

The use of liquid crystals (LC) in active-matrix display devices has stimulated the development of synthetic approaches for their design as functional materials [1–4]. The study of fluorine-substituted liquid crystals has played an essential role in the development of various types of liquid crystal displays, because of the combination of polar and steric effects of the fluorine substituent as well as the strength of the C–F bond which confers thermal stability on fluorinated compounds [1,3,4]. In the design of polar liquid crystals the combination of high dielectric anisotropy ($\Delta\varepsilon$) with very low birefringence (Δn) is often favorable for LCDs [1–5].

The pentafluoro-λ⁶-sulfanyl (SF_5) group is one such fluorine-containing substituent that has attracted increasing interest, as it provides compounds with low surface energy, high chemical resistance, thermal stability, high electronegativity and lipophilicity [3–9]. The above mentioned properties were often compared with those of the CF_3-group, and the advantages of the SF_5-group were hence referred to as a "super CF_3 function" [3–5,8]. A number of patents and papers describing the synthesis and the properties of pentafluoro-λ⁶-sulfanyl derivatives as new liquid crystals with the suitable combination of physical properties have been published [10]. It was noticed that the pentafluoro-λ⁶-sulfanyl group is so far the most suitable group for the design of polar liquid crystals with high dielectric anisotropy [4,5,11].

These unique properties, a tendency towards the formation of nematic mesophases and the generation of large dielectric anisotropies in some terminal and substituted acetylenes have been reported in the literature, and the materials have been compared with their hydrogenated analogs [12,13]. However, only one Ref. [10d] is known for the synthesis of liquid crystals of the type SF_5–C≡C–R, using Pd-catalyzed coupling reactions of SF_5-acetylene with the corresponding phenyl-iodides. The disadvantage of this approach is the rather difficult preparation of the starting 1-pentafluoro-λ⁶-sulfanyl-acetylene by the reaction of acetylene with SF_5X (X = Br, Cl) followed by dehydrohalogenation [14–16].

Herein we present the results of studying such synthetic possibilities towards new types of SF_5–C≡C–R liquid crystal molecules, using radical addition of commercially available SF_5Cl to suitable unsaturated precursors (olefins and alkynes [16–24]) as a key step, followed by the transformation of the corresponding 1-pentafluoro-λ⁶-sulfanyl-2-chloro-substituted products into the target SF_5-acetylenes.

2. Results and discussion

We found that olefins **1** are not suitable for synthesizing the target SF_5-acetylenes (Scheme 1). A radical addition of SF_5Cl to olefins **1** upon irradiation with a low-pressure Hg lamp in a quartz

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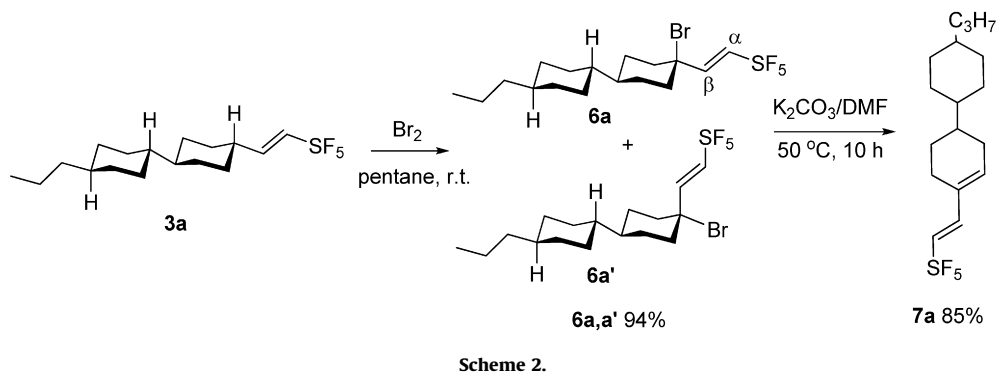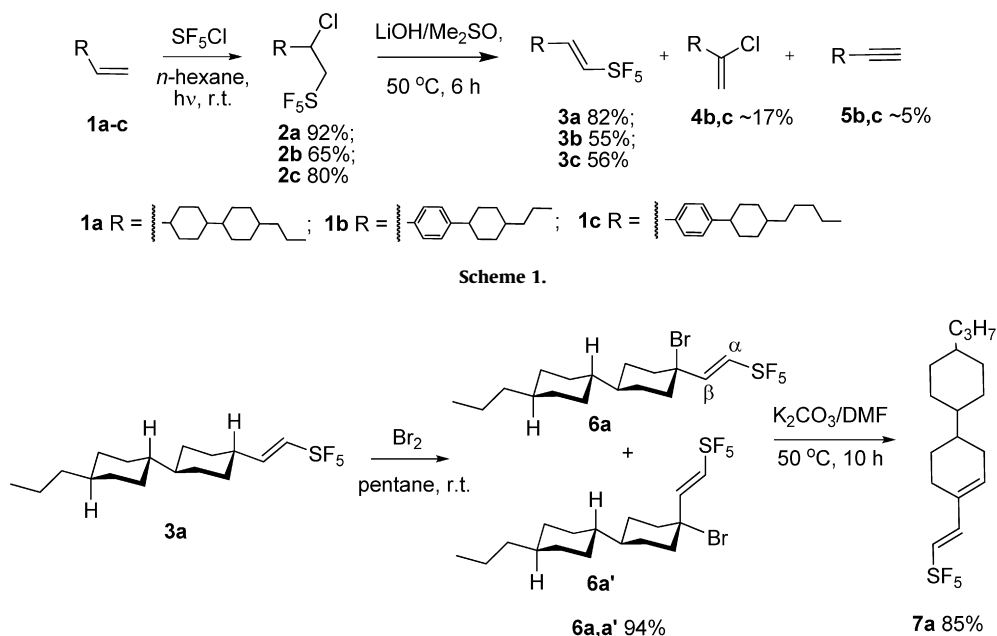
Scheme 1.

Scheme 2.

apparatus gave the corresponding products **2** with high regios-electivity and in high yields, but subsequent transformations [24] did not lead to the target $SF_5-C{\equiv}C$-products (Schemes 1 and 2).

The dehydrochlorination of **2a** [5] with LiOH in Me_2SO yields *trans*-SF_5-substituted olefin **3a**. It is known that tertiary hydrogens in allylic systems are reactive towards molecular bromine or N-bromosuccinimide, but in all such cases an initiator – either irradiation or high temperature was used [25]. Moreover, reactions of elemental bromine with olefins substituted with an electron withdrawing group (COOR, CN, CF_3, NO_2, etc.) without special initiation led to formation of the corresponding dibromides in excellent yields [26]. To our surprise, a reaction of the olefin **3a** with elemental bromine, carried out in pentane at ambient conditions without using any initiation, gave exclusively allylic bromination products, observed and isolated as a mixture of two such isomers **6a,a′** in a ~1/0.43 ratio observed by ^{19}F NMR (Scheme 2).

The most useful tool for the confirmation of the *equatorial* or *axial* position of substituents in the products **6a,a′** is ^{13}C NMR spectroscopy. It is known that the carbon nuclei in *equatorial* positions of cyclohexane ring almost always show downfield shifts relative to signals of the carbons in *axial* positions, explained by anisotropic effect of the cyclohexane ring [27]. We observed in ^{13}C NMR of the mixture of **6a,a′**, that a signal of the β-carbon atom to the SF_5 group of **6a** is more downfield shifted than for **6a′** {**6a**: δ 143.9 (quin, *J* = 6.7 Hz, β-carbon); **6a′**: δ 141.4 (quin, *J* = 7.7 Hz, β-carbon)}. In addition to the latter, in the ^{13}C NMR spectrum quintets of the α- and β-carbons with respect to the SF_5 group of **6a** have chemical shifts which are similar to signals of the corresponding carbons of the olefin **3a** {**6a**: δ 138.7 (quin, *J* = 21.2 Hz, α-carbon); **3a**: δ 139.4 (quin, *J* = 19.6 Hz, α-carbon), 144.3 (quin, *J* = 7.0 Hz, β-carbon)}. Moreover in general *equatorial* alkyls as well as alkenyl substituents determine downfield shifts of cyclohexane carbon atoms in contrast to the corresponding *axial* groups [27]. The latter regularly occurs in the ^{13}C NMR spectrum of the isomers **6a,a′**, a singlet of cyclohexane carbon atom of **6a**, bonded with bromine and the CH=CHSF$_5$ substituent is more downfield shifted (66.7 ppm) relative to the singlet of the corresponding carbon of **6a′** (63.1 ppm). This also supports the *equatorial* orientation of the CH=CHSF$_5$ group in the **6a** isomer.

Scheme 3.
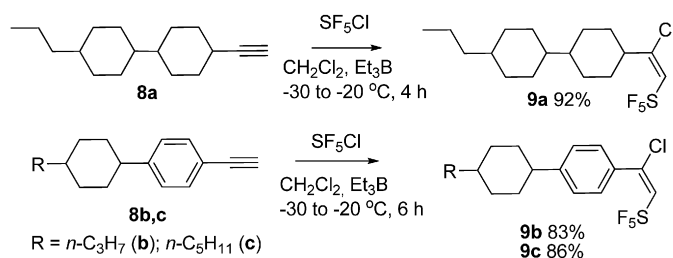
According to the data described above, it was established that the isomer **6a** is the major product in the bromination reaction of **3a**.
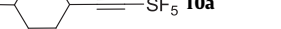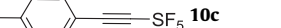
The next steps of dehydrobromination of the mixture of **6a,a′** using bases such as DBU, LiOH or K_2CO_3 led to the formation of the *s-trans*-1,3-diene **7a** in high yields (Table 1). We have recently reported this approach for the synthesis of 1,3-butadienes substituted with a terminal pentafluoro-λ^6-sulfanyl group [24].

In contrast to the dehydrochlorination of **2a**, the treatment of **2b,c** with LiOH in Me_2SO gave a mixture of products **3b,c–5b,c** (Scheme 1). Compounds **3b,c** were separated from the latter using column chromatography on silica gel. The use of DBU for HCl-elimination of **2b,c** did not increase the yields of **3b,c** (56–57%), but led to only one by-product **4b,c** (~17%), which facilitated the separation of the olefins **3b,c**. Bromination reactions of **3b** and subsequent dehydrobromination to form the corresponding SF_5-acetylene was unsuccessful. All reactions of **3b** with bromine under electrophilic (in *n*-hexane, acetic acid, chloroform, CCl_4) as well as radical (UV irradiation in *n*-hexane or benzene) conditions led to inseparable mixtures of products as observed by ^1H and ^{19}F NMR.

Table 1
Dehydrobromination of **6a,a′**.

Method:base/solvent/°C	Time, h	Yields of **7a** after SiO$_2$, %
K_2CO_3 (5 equiv.)/DMF/50	10	85
LiOH (5 equiv.)/Me_2SO/50	10	79
DBU (1.1 equiv.)/*n*-heptane/reflux	5	68

Scheme 4.

Table 2
The physical properties [28] of the new SF$_5$-LCs **10a–c** in comparison to some of the known SF$_5$ analogs [5].

Structure	Phase sequence[a]	$\Delta\varepsilon_{virt}$-dielectric anisotropies	Δn_{virt}-birefringences
⬡⬡=–SF$_5$ [5]	C 51 S$_G$? 65 I	10.5	0.0704
⬡⬡–⬡=–SF$_5$ [5]	C 145 S$_B$ 173 N 194.1 I	10.1	0.0641
⬡⬡≡–SF$_5$ **10a**	C 49 I	10.4	0.084
C$_5$H$_{11}$–⬡⬡≡–SF$_5$ **10c**	C 38 I	14.5	0.131
⬡⬡≡–SF$_5$ **10b**	C 41 I	15.5	0.134

[a] The phase transition temperatures are cited in °C. C: crystalline, S$_B$: smectic B, S$_G$: smectic G, N: nematic, I: isotropic. In the cases marked by a question mark the mesophase assignment is not clear.
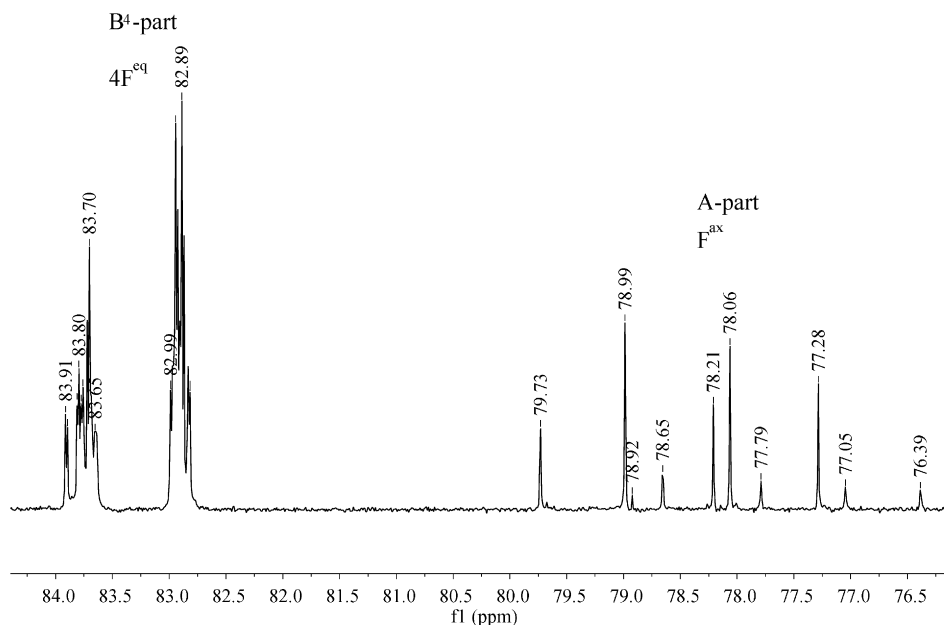

Fig. 1. ^{19}F NMR for 1,3-diene **7a**.

Fig. 2. ^{19}F NMR for acetylene **10a**.

Treatment of the latter with bases such as DBU, LiOH or K_2CO_3 did not even give trace amount of the target SF$_5$–C≡C substituted products (^{19}F NMR).

After the condensation of SF$_5$Cl into solutions of acetylenes **8a–c** in CH$_2$Cl$_2$ at approximately–30 °C the reaction mixture turned brown within a few minutes, indicating the beginning of reactions without initiation. The conversion after 6 h was very low and addition products **9a–c** were observed by ^{19}F and ^{1}H NMR only as admixture (~1–2%). Moreover, a signal for SF$_4$ (~74.5 ppm) was observed in the ^{19}F NMR spectrum of the reaction mixture before workup, and a large amount of black polymer was filtered off, indicating side reactions [19,23]. The use of UV-irradiation during 5 h for the analogous reactions in *n*-hexane and with 1.5-fold excess of SF$_5$Cl increases the yields of the corresponding products **9a–c** slightly to 7–11% as observed by ^{19}F and ^{1}H NMR. Reactions of **8a–c** with 2.5 equivalents of SF$_5$Cl induced by triethylborane at −20 to −30 °C gave exclusively the terminal pentafluorosulfanyl substituted *E*-olefins **9a–c** in good yields (Scheme 3) similar to literature data [20–22].

The dehydrohalogenation of **9a–c** with lithium hydroxide powder at 50 °C in Me$_2$SO gave the desired acetylenes **10a–c**, which were separated in pure form after column chromatography in yields of more than 65% (Scheme 4).

The birefringences (Δn) of the SF$_5$-acetylenes **10a–c**, which were synthesized for the first time, are rather low and useful for reflective type LCDs [1,2,5,11]. Most important are the observed high dielectric anisotropies ($\Delta \varepsilon$) of **10b,c** compared to known LCs based on hypervalent sulfur fluorides (Table 2 and [5,11]) and alkynes [12,13]. Caused by the presence of the aromatic ring the birefringence in **10b,c** is increased when compared to **10a** but the polarity is also significantly higher.

The most useful tool to confirm the formation of a triple bond in products **10a–c** is ^{19}F NMR spectroscopy. The typical appearance of the AB$_4$-spin system for structurally nonequivalent fluorine atoms [5,9] of the SF$_5$-substituent of olefins (**3a,b**, **7a**, **9b,c**) or bonded to saturated carbon atoms (**2a–c**, **6a**) was observed with nine lines for the *trans* fluorine atom (A-part) at 84.3–90.0 ppm and a doublet of multiplets of the *cis* fluorines (B$_4$-part) at 64.3–69.5 ppm (J_{FF} = 148–150 Hz) (Fig. 1 for **7a**). The typical ^{19}F NMR of the AB$_4$-spin system of SF$_5$-substituted acetylenes showed on Fig. 2, the B$_4$-part in the ^{19}F NMR of

alkynes **10a–c** is more downfield shifted (83.3 ppm) with higher multiplicity.

3. Conclusion

We have studied synthetic routes to SF$_5$-substituted acetylenes as novel liquid crystal molecules, based upon radical addition of SF$_5$Cl to double (**1a–c**) and triple (**8a–c**) bonds of the corresponding LCs-precursors. It was shown that interaction of SF$_5$Cl with alkynes **8a–c** initiated by Et$_3$B and followed by dehydrochlorination of the adducts is a convenient approach for preparation of such SF$_5$–C≡C-substituted liquid crystals. The physical properties of the new liquid crystals **10a–c** were investigated. The latter showed very high dielectric anisotropies ($\Delta \varepsilon$). In summary the SF$_5$-group is one of the most useful terminal groups for polar LCs with low birefringence (Δn).

4. Experimental

The ^{1}H (200.13 MHz), ^{13}C (50.32 MHz) and ^{19}F (188.31 MHz) NMR spectra were recorded on a Bruker DPX-200 spectrometer using CDCl$_3$ as solvent and TMS or CCl$_3$F as internal standards. MS (EI) and HRMS spectra were obtained on a Varian MAT CH7A instrument at 70 eV.

Column chromatography was performed on Kieselgel Merck 60 (230–400 mesh).

4.1. Reactions of olefins 1a–c with SF$_5$Cl: general procedure

A mixture of **1a–c** (12 mmol), F$_5$SCl (18 mmol) in anhydrous *n*-hexane (20 mL) contained in a Pyrex reactor, which was equipped with an immersed low pressure mercury lamp, was irradiated for 4–6 h at ambient temperature. The reaction mixture was freed from solvent by evaporation leaving light yellow oil of **2a–c**. The oil was purified by column chromatography on silica gel using *n*-hexane or pentane as the eluent, giving **2a–c**.

4.1.1. 4-[1-Chloro-2-(pentafluoro-λ^6-sulfanyl)ethyl]-4'-propyl-1,1'-bi(cyclohexyl) (2a)

Colourless solid (92% yield), mp 46–47 °C (EtOH); ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.55–1.50 (m, 18H), 1.53–1.90 (m, 9H), 3.98

(m, 2H), 4.32 (m, 1H); ^{13}C NMR (CDCl$_3$): δ 14.8, 20.5, 27.4, 29.6, 29.8, 30.5, 33.9, 38.0, 40.2, 43.3, 43.6, 44.3, 61.1 (quin, J = 4.0 Hz), 76.4 (quin, J = 13.1 Hz); ^{19}F NMR (188 MHz, CDCl$_3$): δ 67.6 (dm, 4F, J = 146.0 Hz, B$_4$-part), 88.5 (9 lines, 1F, A-part). Anal. Calcd. for C$_{17}$H$_{30}$ClF$_5$S: C, 51.44; H, 7.62; Cl, 8.93; S, 8.08. Found: C, 51.49; H, 7.64; Cl, 8.99; S, 8.12.

4.1.2. 1-[1-Chloro-2-(pentafluoro-λ^6-sulfanyl)ethyl]-4-(4-propylcyclohexyl)benzene (2b)

Colourless oil (65% yield); ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.92 (t, 3H, J = 7.8 Hz), 1.00–1.70 (m, 9H), 1.89 (m, 4H), 2.50 (tm, 1H, J = 12.2 Hz), 4.30 (m, 2H), 5.37 (t, 1H, J = 6.4 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.33 (d, 2H, J = 8.0 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.5, 20.5, 33.8, 34.5, 37.4, 40.1, 44.9, 56.7 (quin, J = 4.6 Hz), 77.5 (quin, J = 13.6 Hz), 127.2, 128.0, 136.3, 149.8; ^{19}F NMR (188 MHz, CDCl$_3$): δ 67.7 (dm, 4F, J = 143.1 Hz, B$_4$-part), 82.3 (9 lines, 1F, A-part). Anal. Calcd. for C$_{17}$H$_{24}$ClF$_5$S: C, 52.24; H, 6.19; Cl, 9.07; S, 8.20. Found: C, 52.27; H, 6.22; Cl, 9.17; S, 8.25.

4.1.3. 1-[1-Chloro-2-(pentafluoro-λ^6-sulfanyl)ethyl]-4-(4-pentylcyclohexyl)benzene (2c)

Colourless oil (80% yield); ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.92 (t, 3H, J = 7.8 Hz), 1.00–1.70 (m, 13H), 1.89 (m, 4H), 2.50 (tm, 1H, J = 12.2 Hz), 4.31 (m, 2H), 5.37 (t, 1H, J = 6.4 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.5, 23.1, 27.1, 32.7, 34.0, 34.6, 37.7, 44.8, 56.8 (quin, J = 4.6 Hz), 77.5 (quin, J = 13.6 Hz), 127.2, 128.0, 136.3, 149.8; ^{19}F NMR (188 MHz, CDCl$_3$): δ 65.8 (dm, 4F, J = 148.0 Hz, B$_4$-part), 82.2 (9 lines, 1F, A-part); HRMS for [M$^+$] (C$_{19}$H$_{28}$ClF$_5$S): calcd. 418.1521, found 418.1521.

4.2. 4-[E-2-(pentafluorol-λ^6-sulfanyl)vinyl]-4'-propyl-1,1'-bicyclohexyl (3a)

A solution of **2a** (2 g, 5.00 mmol) in Me$_2$SO (50 mL) was stirred with LiOH powder (1.2 g, 50.0 mmol) at 50–55 °C in a bath 24 h, with monitoring by ^{19}F NMR. Then the reaction mixture was diluted with 200 mL of water, extracted with pentane (5× 30 mL). The combined extracts were washed with water (5× 50 mL) and dried (Na$_2$SO$_4$). Pentane was removed by evaporation and the crude product was purified by chromatography (silica gel; pentane) giving 1.49 g of **3a** (82% yield), colourless solid.

The NMR spectra and others physical constants correspond to the literature data [5].

4.3. 1,2-Elimination of hydrogen chloride form 2b,c: general procedure

A solution of **2b,c** (8.8 mmol) and DBU (9.0 mmol) in n-heptane (30 mL) was stirred 4 h at room temperature. Then the reaction mixture was diluted with 50 mL of hexane, washed with water (5× 20 mL) and dried (Na$_2$SO$_4$). The solvents were removed by evaporation giving the crude mixture. After separation by column chromatography (silica gel; hexane) **3b,c** were obtained.

4.3.1. 1-[(E)-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4-(4-propylcyclohexyl)benzene (3b)

Colourless oil (55% yield). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.89 (t, 3H, J = 6.8 Hz), 1.00–1.70 (m, 9H), 1.87 (m, 4H), 2.47 (tm, 1H, J = 12.2 Hz), 6.94 (dquin, 1H, J_{HH} = 14.1 Hz, J_{HF} = 6.4 Hz), 7.23 (d, 2H, J = 8.2 Hz), 7.30 (m, 1H), 7.34 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.5, 20.5, 33.9, 34.5, 37.4, 45.2, 128.1, 128.2, 129.7, 137.0 (quin, J = 7.4 Hz), 139.0 (quin, J = 18.9 Hz), 151.4; ^{19}F NMR (188 MHz, CDCl$_3$): δ 63.9 (dm, 4F, J = 148.2 Hz, B$_4$-part), 84.3 (9 lines, 1F, A part); HRMS for [M$^+$] (C$_{17}$H$_{23}$F$_5$S): calcd. 354.1441, found 354.1756.

4.3.2. 1-[(E)-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4-(4-pentylcyclohexyl)benzene (3c)

Colourless solid (56% yield), mp 42–43 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.89 (t, 3H, J = 6.8 Hz), 1.00–1.70 (m, 13H), 1.87 (m, 4H), 2.48 (tm, 1H, J = 12.2 Hz), 6.96 (dquin, 1H, J_{HH} = 14.1 Hz, J_{HF} = 6.4 Hz), 7.23 (d, 2H, J = 8.2 Hz), 7.30 (m, 1H), 7.34 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.5, 23.1, 27.1, 32.6, 33.9, 34.6, 37.7, 45.0, 128.1, 128.2, 129.7, 136.9 (quin, J = 7.4 Hz), 138.8 (quin, J = 18.9 Hz), 151.4; ^{19}F NMR (188 MHz, CDCl$_3$): δ 64.0 (dm, 4F, J = 148.2 Hz, B$_4$-part), 84.3 (9 lines, 1F, A part); HRMS for [M$^+$] (C$_{19}$H$_{27}$F$_5$S): calcd. 382.1754, found 382.1769.

4.4. 4-Bromo-4-[(E)-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4'-propyl-1,1'-bi(cyclohexyl) (6a,a')

A solution of **3a** (3.9 g, 10.8 mmol) in pentane (50 mL) was stirred with Br$_2$ (1.73 g, 10.8 mmol) at ambient temperature 12 h. Volatiles were removed by evaporation and the crude product was purified by chromatography (silica gel; pentane) giving 4.84 g of **6a,a'** (94% yield) as mixture of two isomers by ^{19}F NMR in the ratio 1/0.43.

Colourless oil. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.55–1.45 (m, 13H, **6a,a'**), 1.45–1.80 (m, 10H, **6a,a'**), 2.05–2.45 (m, 3H, **6a,a'**), 6.48–6.80 (m, 2H, J_{HH} = 14.1 Hz, CH=CH, **6a,a'**); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.5, 20.1, 25.9, 28.0, 30.1, 30.2, 33.4, 33.5, 33.6, 37.5, 37.6, 39.1, 39.8, 40.7, 41.6, 42.2, 42.9, 63.1 (**6a'**), 66.7 (**6a**), 138.7 (quin, J = 21.2 Hz, **6a**), 140.9 (quin, J = 21.2 Hz, **6a'**), 141.4 (quin, J = 7.7 Hz, **6a'**), 143.9 (quin, J = 6.7 Hz, **6a**); ^{19}F NMR (188 MHz, CDCl$_3$): δ = 62.6 (dm, 4F, J = 154.4 Hz, B$_4$-part, **6a'**), 62.7 (dm, 4F, J = 148.8 Hz, B$_4$-part, **6a**), 80.0–83.4 (9 lines, 1F, A-part, **6a,a'**). Anal. Calcd. for C$_{17}$H$_{28}$BrF$_5$S: C, 46.47; H, 6.42; Br, 18.19; S, 7.30. Found: C, 46.50; H, 6.48; Br, 18.39; S, 7.55.

4.5. 4-[(E)-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4'-propyl-1,1'-bi(cyclohexan)-3-ene (7a)

To a solution of **6a** (4.58 g, 8.8 mmol) in DMF (40 mL) was added K$_2$CO$_3$ (5 equiv., 44 mmol). The mixtures were stirred for 10 h at 50 °C, and then the mixtures were poured into ice water (~100 mL), extracted with n-hexane (4× 20 mL). The organic layers were combined, washed with brine, and dried over NaSO$_4$. The solvent was removed under reduced pressure, and then the residues were purified by chromatography (silica gel; n-hexane), giving 2.49 g of 1,3-dienes **7a** (85% yield).

Colourless solid, mp 47–48 °C (EtOH); ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.55–1.50 (m, 15H), 1.65–2.40 (m, 9H), 6.13 (bs, 1H), 6.39 (dquin, J_{HH} = 14.7 Hz, J_{HF} = 6.8 Hz, 1H, SF$_5$CH), 6.89 (d, 1H, J_{HH} = 14.7 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ 14.3, 20.0, 24.5, 25.5, 29.9, 30.1, 30.3, 33.4, 37.6, 38.9, 39.8, 42.3, 131.9, 136.3 (quind, CSF$_5$, J = 20 Hz, J = 1.5 Hz), 139.3 (quin, J = 7.0 Hz), 139.5; ^{19}F NMR (188 MHz, CDCl$_3$): δ 69.5 (d, 4F, J = 152.0 Hz, B$_4$-part), 90.4 (9 lines, 1F, A-part); MS (EI, 70 eV, 200 °C): m/z (%) 358 (86, M$^+$), 329 (5, M$^+$–Et), 315 (52, M$^+$–Pr), 301 (14), 231 (14, M$^+$–SF$_5$), 219 (13), 123 (100), 109 (50), 83 (60), 69 (100); HRMS for [M$^+$] (C$_{17}$H$_{27}$F$_5$S): calcd. 358.1754, found 358.1748.

4.6. Reactions of acetylenes 8a–c with SF$_5$Cl: general procedure

Into a three-necked flask equipped with a dry ice reflux condenser and a nitrogen inlet alkyne **8a–c** (11.79 mmol) in anhydrous CH$_2$Cl$_2$ (40 mL) was added and cooled to −40 °C. Then SF$_5$Cl (29.5 mmol, 2.5 equiv.) was condensed to the solutions. The solutions were stirred at −40 °C for 5 min and Et$_3$B (0.1 equiv., 1 M in n-hexane) was added slowly using a syringe. The solution was vigorously stirred for 4 h at −30 to −20 °C, and then the mixture was warmed to room temperature. The mixture was hydrolyzed

with aqueous $NaHCO_3$ and the organic layer dried over $NaSO_4$. The solvent was removed and the crude product was purified by filtration through a short column of silica gel (*n*-hexane). Removal of solvent provided white crystals of **9a–c**.

4.6.1. 4-[(E)-1-chloro-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4'-propyl-1,1'-bi(cyclohexyl) (9a)

Colourless solid, mp 51–52 °C (92% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.70–1.45 (m, 17H), 1.55–1.80 (m, 9H), 3.06 (m, 1H), 6.53 (m, 1H, J_{HF} = 8.8 Hz, $HCSF_5$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.8, 20.5, 29.3, 30.4, 30.5, 33.9, 38.0, 40.2, 42.8, 43.3, 43.7, 135.9 (quin, CSF_5, J = 20.6 Hz), 152.7 (quin, J = 7.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ 67.1 (dm, 4F, J = 152.0 Hz, B_4-part), 83.1 (9 lines, 1F, A-part); MS (EI, 70 eV, 200 °C): *m/z* (%) 394 (19, M$^+$), 359 (3, M$^+$–Cl), 231 (11), 125 (81), 83 (61), 69 (100); HRMS for [M$^+$] ($C_{17}H_{28}ClF_5S$): calcd. 394.1520, found 394.1534.

4.6.2. 1-[(E)-1-chloro-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4-(4-propylcyclohexyl)benzene (9b)

Colourless solid, mp 52–55 °C (83% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.92 (t, 3H, J = 7.2 Hz), 1.00–1.70 (m, 9H), 1.91 (m, 4H), 2.51 (tm, 1H, J = 12.2 Hz), 6.93 (q, 1H, J = 7.8 Hz), 7.24 (d, 2H, J = 8.8 Hz), 7.30 (d, 2H, J = 8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.8, 20.4, 33.9, 34.5, 37.4, 40.1, 44.9, 127.1, 128.0, 133.3, 138.0 (q, J = 21 Hz), 142.7 (q, J = 6.8 Hz), 150.4; ^{19}F NMR (188 MHz, $CDCl_3$): δ 68.6 (dm, 4F, J = 150.1 Hz), 81.2 (p, 1F); HRMS for [M$^+$] ($C_{17}H_{22}ClF_5S$): calcd. 388.1051, found 388.1056.

4.6.3. 1-[(E)-1-chloro-2-(pentafluoro-λ^6-sulfanyl)vinyl]-4-(4-pentylcyclohexyl)benzene (9c)

Colourless solid, mp 54–57 °C (86% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.92 (t, 3H, J = 7.2 Hz), 1.00–1.70 (m, 13H), 1.91 (m, 4H), 2.51 (tm, 1H, J = 12.2 Hz), 6.93 (q, 1H, J = 7.8 Hz), 7.24 (d, 2H, J = 8.8 Hz), 7.30 (d, 2H, J = 8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.5, 23.1, 27.1, 32.7, 33.9, 34.5, 37.7, 44.9, 127.1, 128.0, 133.3, 138.0 (q, J = 21 Hz), 143.7 (m, J = 6.8 Hz), 150.4; ^{19}F NMR (188 MHz, $CDCl_3$): δ 68.6 (dm, 4F, J = 150.1 Hz), 81.2 (p, 1F); HRMS for [M$^+$] ($C_{19}H_{26}ClF_5S$): calcd. 416.1364, found 416.1367.

4.7. Dehydrochlorination of 9a–c: general procedure

To a solution of **9a–c** (4.23 mmol) in Me_2SO (35 mL) was added LiOH (5 equiv.). The mixture was stirred for 12 h at 50 °C, then poured into ice water (~100 mL), extracted with *n*-hexane (4× 20 mL). The organic layers were combined, washed with brine, and dried over $NaSO_4$. The solvent was removed under reduced pressure, and then the residue was purified by chromatography (silica gel; *n*-hexane), giving alkynes **10a–c**.

4.7.1. 4-[(Pentafluoro-λ^6-sulfanyl)ethynyl]-4'-propyl-1,1'-bi(cyclohexyl) (10a)

Colourless solid, mp 49–50 °C (65% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.70–2.15 (m, 26H), 2.29 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.7, 20.4, 29.1, 29.5, 30.3, 32.1, 33.9, 38.0, 40.2, 42.6, 43.5, 82.2 (quind, CSF_5, J = 40.8 Hz, J = 4.0 Hz), 84.1 (m, J = 7.5 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ 76.4–79.7 (9 lines, 1F, A-part), 82.8–83.9 (m, 4F, B_4-part); MS (EI, 70 eV, 200 °C): *m/z* (%) 358 (4, M$^+$), 315 (15, M$^+$–Pr), 231 (9, M$^+$–SF$_5$), 123 (33), 83 (63), 69 (100); HRMS for [M$^+$] ($C_{17}H_{27}F_5S$): calcd. 358.1754, found 358.1752.

4.7.2. 1-[(Pentafluoro-λ^6-sulfanyl)ethynyl]-4-(4-propylcyclohexyl)benzene (10b)

Colourless solid, mp 43–48 °C (70% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.91 (t, 3H, J = 6.8 Hz), 1.00–1.70 (m, 9H), 1.89 (m, 4H), 2.51 (tm, 1H, J = 12.2 Hz), 7.25 (d, 2H, J = 8.8 Hz), 7.50 (d, 2H, J = 8.8 Hz); ^{13}C NMR (50 MHz, acetone-d$_6$): δ 14.2, 20.2, 33.6, 34.1,

37.2, 39.9, 45.0, 79.9 (q, J = 8.1 Hz), 88.9 (qd, J = 41.3 Hz, J = 4.0 Hz), 114.1, 128.0, 133.2, 152.8; ^{19}F NMR (188 MHz, $CDCl_3$): δ 75.5–78.9 (9 lines, 1F, A-part), 82.9–83.9 (m, 4F, B_4-part); HRMS for [M$^+$] ($C_{17}H_{21}F_5S$): calcd. 352.1284, found 352.1283.

4.7.3. 1-[(Pentafluoro-λ^6-sulfanyl)ethynyl]-4-(4-pentylcyclohexyl)benzene (10c)

Colourless solid, mp 48–52 °C (72% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.91 (t, 3H, J = 6.8 Hz), 1.00–1.70 (m, 13H), 1.89 (m, 4H), 2.51 (tm, 1H, J = 12.2 Hz), 7.25 (d, 2H, J = 8.8 Hz), 7.50 (d, 2H, J = 8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.5, 23.1, 27.1, 32.0, 32.6, 33.8, 34.4, 37.7, 45.2, 78.9 (q, J = 8.0 Hz), 89.8 (qd, J = 41.3 Hz, J = 4.3 Hz), 115.0, 127.7, 133.1, 152.1; ^{19}F NMR (188 MHz, $CDCl_3$): δ 75.5–78.9 (p, 1F), 82.9–83.9 (m, 4F); HRMS for [M$^+$] ($C_{19}H_{25}F_5S$): calcd. 380.1597, found 380.1595.

References

[1] M. Hird, Chem. Soc. Rev. 36 (2007) 2070–2095.
[2] H. Takatsu, Mol. Cryst. Liq. Cryst. 458 (2006) 17–26.
[3] P. Kirsch, Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, Germany, 2004.
[4] P. Kirsch, G.-V. Röschenthaler, in: V.A. Soloshonok, K. Mikami, T. Yamazaki, J.T. Welch, J.F. Honek (Eds.), Current Fluoroorganic Chemistry – New Synthetic Directions, Technologies, Materials and Biological Applications, 949, ACS Press, Washington, 2007, pp. 221–243.
[5] P. Kirsch, J.T. Binder, E. Lork, G.-V. Röschenthaler, J. Fluorine Chem. 127 (2006) 610–619.
[6] Ch. Ye, G.L. Gard, R.W. Winter, R.G. Syvret, B. Twamley, J.M. Shreeve, Org. Lett. 9 (2007) 3841–3844, and references therein.
[7] R.W. Winter, R.A. Dodean, G.L. Gard, in: V.A. Soloshonok (Ed.), ACS Symposium Series, 911: Fluorine-Containing Synthons, ACS Press, Washington, DC, 2005, pp. 87–118.
[8] G.S. Lal, R.G. Syvret, Chim. Oggi 26 (2008) 26–27.
[9] D. Lentz, K. Seppelt, in: K. Akiba (Ed.), Chemistry of Hypervalent Compounds, Wiley-VCH, 1999, pp. 295–325.
[10] (a) R. Salmon, WO 9306089 (1993).;
(b) M.N. Howard Jr., T.M. Sevenson, WO 9516676 (1995).;
(c) N. Shigeyoshi, S. Hidetaka, WO 2009028514 (2009).;
(d) P. Kirsch, K. Tarumi, J. Krause, DE19748108 (1999).;
(e) M.J. Goulding, W. Duffy, K. Adlem, P. Kirsch, A. Hahn, E. Poetsch, W. Binder, V. Meyer, M. Klasen-Memmer, M. Heckmeier, G. Lüssem, EP 1482022 A1 (2004).
(f) J.A. Smith, R.A. DiStasio Jr., N.A. Hannah, R.W. Winter, T.J.R. Weakley, G.L. Gard, S.B. Rananavare, J. Phys. Chem. B 108 (2004) 19940–19948.
[11] P. Kirsch, A. Hahn, Eur. J. Org. Chem. (2005) 3095–3100.
[12] M. Petrzilka, Mol. Cryst. Liq. Cryst. 111 (1984) 347–358.
[13] R. Buchecker, G. Marck, M. Schadt, Mol. Cryst. Liq. Cryst. 260 (1995) 93–105.
[14] R.J. Terjeson, J.A. Canich, G.L. Gard, M.R. Colsman, M.A. Uremovich, S.H. Strauss, Inorg. Synth. 27 (1990) 329–332.
[15] (a) J.A.M. Canich, M.M. Ludvig, W.W. Paudler, G.L. Gard, J.M. Shreeve, Inorg. Chem. 24 (1985) 3668–3670;
(b) G.S. Lal, K.E. Minnich, US 6479645B1 (2002).
[16] F.W. Hoover, D.D. Coffman, J. Org. Chem. 29 (1964) 3567–3570.
[17] V.K. Brel, J. Fluorine Chem. 128 (2007) 862–867.
[18] V.K. Brel, Synthesis (2005) 1245–1250.
[19] J.R. Case, N.H. Ray, H.L. Roberts, J. Chem. Soc. (1961) 2066–2070.
[20] S. Aït-Mohand, W.R. Dolbier Jr., Org. Lett. 4 (2002) 3013–3015.
[21] W.R. Dolbier Jr., A. Mitani, W. Xu, I. Ghiviriga, Org. Lett. 8 (2006) 5573–5575.
[22] W.R. Dolbier Jr., S. Aït-Mohand, T.D. Schertz, T.A. Sergeeva, J.A. Cradlebaugh, A. Mitani, G.L. Gard, R.W. Winter, J.S. Thrasher, J. Fluorine Chem. 127 (2006) 1302–1310.
[23] M.V. Ponomarenko, Y.A. Serguchev, G.-V. Röschenthaler, J. Fluorine Chem. 131 (2010) 270–273.
[24] M.V. Ponomarenko, Y.A. Serguchev, G.-V. Röschenthaler, Synthesis (2010) 3906–3912.
[25] (a) W.D. Pfeiffer, in: E. Schaumann (Ed.), Science of Synthesis, vol. 35, Thieme, Stuttgart, 2007, pp. 423–434;
(b) H. Dauben, L. McCoy, J. Org. Chem. 24 (1959) 1577–1579;
(c) H. Stetter, E. Tresper, Chem. Ber. 104 (1971) 71–74.
[26] (a) W. Quaglia, M. Pigini, S.K. Tayebati, A. Piergentili, M. Giannella, G. Marucci, C. Melchiorre, J. Med. Chem. 36 (1993) 1520–1528;
(b) F. Grellepois, F. Chorki, M. Ourévitch, B. Crousse, D. Bonnet-Delpon, J.-P. Bégué, Tetrahedron Lett. 43 (2002) 7837–7840;

(c) R. Seo, T. Ishizuka, A.A.-M. Abdel-Aziz, T. Kunieda, Tetrahedron Lett. 42 (2001) 6353–6355;
(d) G.V. Oreshko, L.T. Eremenko, Russ. Chem. Bull. 38 (1989) 1003–1006;
(e) S. Hu, Y. Huang, M.A. Poss, R.G. Gentles, J. Heterocycl. Chem. 42 (2005) 661–667;
(f) J. Paleček, J. Kvičala, O. Paleta, J. Fluorine Chem. 113 (2002) 177–183;
(g) T. Troll, in: E. Schaumann (Ed.), Science of Synthesis, vol. 35, Thieme, Stuttgart, 2007, pp. 439–501.
[27] (a) K. Endo, K. Seya, H. Hikino, Tetrahedron 43 (1987) 2681–2688;
(b) I.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, N.Y., 1972, p. 550;
(c) I.W. Wehrli, T. Wirihlin, Interpretation of Carbon-13 NMR Spectra, Heyden, London, 1976, p. 310;
(d) E. Breimaier, W. Voelier, Carbon-13 NMR Spectroscopy, 2nd ed., Verlag Chemie, Weinheim, Ist End, 1978, p. 344;
(e) R.J. Abraham, P. Loitus, Proton and Carbon-13 NMR Spectroscopy, Heyden, London, 1978, p. 230.
[28] The application oriented evaluation of liquid crystals for use in LCDs is centered around "virtual" clearing temperatures, electrooptical parameters and viscosities. These data are obtained by extrapolation from a standardized nematic host mixture: $T_{NI,virt}$, $\Delta\varepsilon_{virt}$ and Δn_{virt} were determined by linear extrapolation from a 10% (w/w) solution in the commercially available Merck mixture ZLI-4792 (T_{NI} = 92.8 °C, $\Delta\varepsilon$ = 5.27, Δn = 0.0964). The values thus obtained are empirically corrected for changes in the order parameter. For the pure substances the mesophases were identified by optical polarization microscopy, and the phase transition temperatures by differential scanning calorimetry (DSC). The helical twisting power (HTP) of 21 was measured at 20 °C in a 1% (w/w) solution of the analyte in the Merck liquid crystal mixture MLC-6260 (T_{NI} = 103.5 °C, $\Delta\varepsilon$ = 4.0, Δn = 0.088).