Synthesis and Structural Characterization of Highly Fluorinated Sulfimides and Sulfoximides as Functional Building Blocks for Materials Science

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Dedicated to Professor Gerd-Volker Röschenthaler on the occasion of his 60th birthday

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Several examples of highly fluorinated sulfimides and sulfoximides have been synthesized in order to assess their potential usefulness as functional materials, such as liquid crystals or as active components in molecular electronics. The polarity of liquid crystals with these types of functional groups was lower than expected, due to conformational effects. A new synthetic method provides a convenient access to *N*,*S*,*S*-triaryl sulfimides and sulfoximides, which were characterized by X-ray crystallography.

Introduction

N-(Trifluoromethylsulfonyl)sulfimides and -sulfoximides are among the strongest electron-withdrawing functional groups known.[1] For example, the -$SCF_3(=NSO_2CF_3)$ and the -$SCF_3(=O)(=NSO_2CF_3)$ groups have σ_p constants of +1.39 and +1.55, respectively, far exceeding the values for more common, highly polar groups, such as nitro (+0.78), cyano (+0.66) or trifluoromethylsulfonyl (+1.17).[2] Nevertheless, these remarkable electronic properties have never been put to practical use for materials science. Mostly due to preparative difficulties and potentially hazardous synthetic procedures,[3] only a limited number of organic compounds carrying these functionalities has been synthesized.[1,3,4]

For the design of liquid crystalline materials for liquid crystal display (LCD) applications, there is often a need for highly polar, so-called "super fluorinated materials" (SFM) [5] that can be used as additives for increasing the dielectric anisotropy ($\Delta\varepsilon$) of liquid crystal mixtures. In this context, the superpolar sulfimide and sulfoximide groups became the focus of our attention.

The performance of liquid crystalline materials for display applications relies critically on the absence of ionic impurities in the medium.[5] Ions can either be introduced by charge injection, i.e. by electrochemical oxidation or reduction, or by the extraction of ionic impurities from peripheral display components, such as UV-curable sealants or the polyimide orientation layer. Using suitable model systems, the propensity of new types of functional materials to generate ions or to mobilize them by coordinative solvation can be conveniently studied in detail in the gas phase by ion cyclotron resonance (ICR) mass spectrometry.

Synthesis and Characterization of the Liquid Crystals

For the design of suitable, highly polar liquid crystals we chose the 4-propyl-4′-phenylbicyclohexyl unit as the mesogenic core structure. The phenyl moiety should be substituted in the terminal position by the sulfimide or sulfoximide groups and flanked by two lateral fluorine atoms for an additional increase of the dielectric anisotropy. The synthesis started from the trifluoromethylthio derivative **3**,[6] which was oxidized to the sulfoxide **4** with 3-chloroperbenzoic acid (MCPBA). A by-product of the oxidation was the trifluoromethylsulfonyl-substituted compound **5**. The triflimide residue was introduced in analogy to the general procedure introduced by Yagupolskii and coworkers[1] by activation of the sulfoxide **4** with triflic anhydride, followed by reaction with triflic amide (see Scheme 1, box), to give the sulfimide **6** in 16% yield. Several failed attempts to oxidize *S*-aryl-*S*-trifluoromethyl-*N*-(trifluoromethylsulfonyl)sulfimides to the corresponding sulfoximides led Yagupolskii to the conclusion that the oxidation is not possible due to the extremely electron-deficient character of the sulfur atom.[1] In contrast to this result, we were able to achieve the oxidation of **6** to **7** with the $RuCl_3/NaIO_4$ system[7] in reasonable yield (41%), even in the presence of the two additional electron-withdrawing *ortho*-fluorine substituents.

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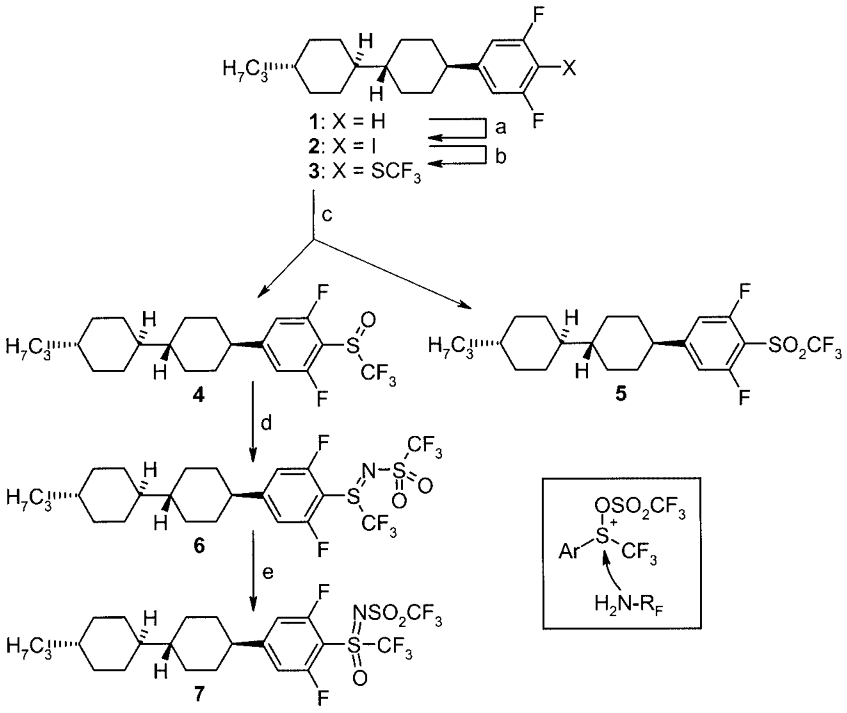


Scheme 1. Synthesis of the liquid crystals **3**–**7**: a) 1. BuLi, THF, –70 °C. 2. I_2, THF, –40 °C (78%); b) $CuSCF_3$, NMP, 120–150 °C, 18 h (56%); c) MCPBA, CH_2Cl_2, room temp., 3 d (**4**: 28%; **5**: 7%); d) Tf_2O, $TfNH_2$, CH_2Cl_2, room temp., 18 h (16%); e) $NaIO_4$, $RuCl_3$ (0.1 mol%), CH_3CN, H_2O, CCl_4, room temp., 18 h (41%). The inset illustrates the reaction of the nucleophile (H_2N-R_F, in this case triflic amide) with the sulfoxide activated by triflic anhydride.

None of the newly synthesized materials exhibits a mesophase. Nevertheless, as a component of a nematic host mixture, they behave like typical liquid crystalline additives and contribute to the anisotropic properties of the overall mixture. This behaviour can be quantified by so-called "virtual" parameters, such as the clearing point ($T_{\mathrm{NI,virt}}$), the dielectric anisotropy ($\Delta\varepsilon_{\mathrm{virt}}$), and birefringence ($\Delta n_{\mathrm{virt}}$),[8] which are summarized in Table 1.

Table 1. Physical properties of the liquid crystals **3**–**7**.[8] Due to its limited solubility in the nematic host mixture ZLI-4792, the virtual parameters for sulfone **5** were only extrapolated from a 5% w/w solution. The solubility for sulfoximide **6** was too low to obtaining extrapolated mixture data. The melting points and virtual clearing temperatures are given in degrees Celsius.

	M.p.	$T_{\mathrm{NI,virt}}$	$\Delta\varepsilon_{\mathrm{virt}}$	Δn_{virt}
3	69	27.6	9.8	0.086
4	101	32.5	16.4	0.098
5	146	14.4	25.8	0.100
6	166	–	–	–
7	101	–14.9	20.0	0.141

As expected, the dielectric anisotropy ($\Delta\varepsilon_{\mathrm{virt}}$) of the materials **3**–**5** increases with the oxidation state of sulfur. Due to the poor solubility of the sulfoximide **6**, no meaningful data could be extrapolated from the nematic host mixture ZLI-4792.[8] Interestingly, the dielectric anisotropy of sulfoximide **7** is significantly lower than that of the sulfone **5** in spite of the far stronger electron-withdrawing character of the sulfoximide terminal group. This counterintuitive finding illustrates that the dielectric anisotropy ($\Delta\varepsilon$), as a characteristic of the supramolecular arrangement in the nematic phase, depends not only on the absolute molecular dipole moment, μ, but also on the orientation of the dipole moment vector relative to the director of the nematic phase, which can be approximated by the long molecular axis.[9,10] An orientation of the molecular dipole moment vector exactly parallel to the long molecular axis is most effective for achieving a high dielectric anisotropy in the nematic phase. More oblique orientations result in reduced or even negative $\Delta\varepsilon$ values.

The sulfoximide **7** can assume three basic conformers, which are interchangeable by a threefold rotation around the nitrogen–sulfur single bond. Their relative energies are estimated to be within a range of 2.8 kcal mol^{-1} (Figure 1).[11] In the energetically preferred conformer (**B**, 0 kcal mol^{-1}), the local dipole moment of the terminal trifluoromethyl moiety is pointing roughly perpendicular to the long molecular axis of the liquid crystal. Further rotation around the central nitrogen–sulfur bond gives the other conformers, **A** with similar energy (0.2 kcal mol^{-1}) and **C** with a significantly higher energy (2.8 kcal mol^{-1}), neither of which has its dipole moment oriented in the direction of the long molecular axis. The absolute dipole moments of all three conformers are rather high (around 8.2 D)[11] and quite similar. Nevertheless, their oblique orientation relative to the long molecular axis of the liquid crystal is the main reason for the lower than expected dielectric anisotropy of **7**.

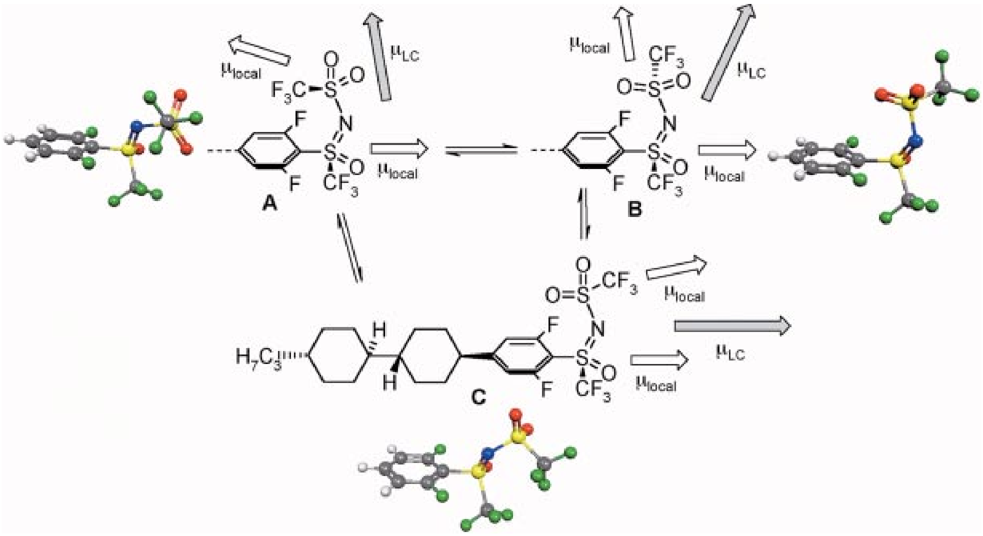


Figure 1. The three major conformers of 2,6-difluoro-1-[*S*-trifluoromethyl-*N*-(trifluoromethylsulfonyl)sulfoximido]benzene as a simplified model for the polar head-group of the liquid crystal **7** (B3LYP/6-31G*//B3LYP/6-31G* level of theory),[11] a schematic representation of the equilibrium between the three conformers **A** (0.2 kcal mol^{-1}), **B** (0 kcal mol^{-1}) and **C** (2.8 kcal mol^{-1}) and the different orientation of their dipole moments relative to the long molecular axis of the liquid crystal.

Synthesis and Characterization of the Model Compounds

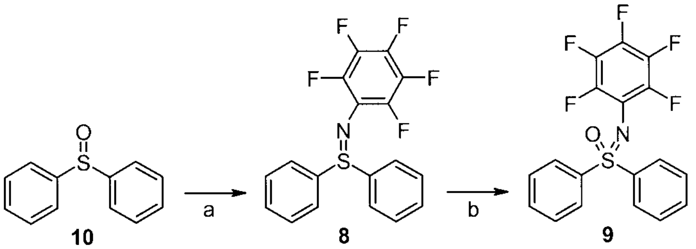
In order to explore and extend the scope of our synthetic methodology, a study was conducted with the aim to prepare compounds **8** and **9** as models for other structural motifs that are of potential interest for organic materials' design. There have been several reports on different synthetic routes leading to the basic *N*,*S*,*S*-triphenyl sulfimide structure,[12] but none of them uses the convenient activation of diphenyl sulfoxide (**10**) in situ. In analogy to the synthesis of **6** with triflic amide as the nucleophilic component, pentafluoroaniline acts here as the nucleophile (Scheme 2). In contrast to **6**, however, the resulting *N*-(pentafluorophenyl)-*S*,*S*-diphenylsulfimide (**8**) is hydrolytically unstable, and the work-up has therefore to be done under neutral or mildly basic conditions. Oxidation to the corresponding sulfoximide **9** can be achieved under the same conditions as for **7**.

For both compounds **8** and **9** it was possible to obtain single crystals suitable for X-ray crystallography from a solution in *n*-heptane.[13] Both molecules have a T-like shape with a planar Ph–S=N–PhF$_5$ subunit as the top bar and one phenyl moiety perpendicular (Figure 1 and Figure 2). Arene–arene interactions in the crystal packing of **8** seem to play a dominant role for the stabilization of the structure: in one dimension PhF$_5$-PhF$_5$-Ph triads are a recurrent motif (Figure 2).[2,14] The two pentafluorophenyl rings are parallel and eclipsed with an interplanar distance of about 3.6 Å. In the phenyl-pentafluorophenyl pair the rings are roughly parallel, with a distance of around 3.4 Å, but are shifted relative to each other.

All the aromatic and pentafluoroaromatic moieties are oriented parallel to two of the three crystallographic planes, with all pentafluorophenyl residues in the crystal coplanar with only one of these planes.

The structure of the single molecules of **9** (Figure 3) is very similar to that of **8**, and the space group is the same ($P\bar{1}$). In one dimension, parallel but shifted PhF$_5$-Ph pairs with a greater interplanar distance of 3.9 Å are apparently stabilizing the arrangement. Again, all pentafluorophenyl moieties are coplanar with only one crystallographic plane, and all the aromatic and fluoroaromatic moieties are parallel to only two of the three planes.

A detailed study of the gas-phase ion chemistry and proton affinities of the two model compounds **8** and **9** by FT-ICR mass spectrometry will be the subject of a forthcoming publication.[15]



Scheme 2. Synthesis of compounds **8** and **9**: a) 1. Tf$_2$O, CH$_2$Cl$_2$, –70 °C, 1 h. 2. pentafluoroaniline, CH$_2$Cl$_2$, –70 °C to room temp. (62%); b) NaIO$_4$, RuCl$_3$ (0.1 mol%), CH$_3$CN, CCl$_4$, H$_2$O, room temp., 3 d (34%).

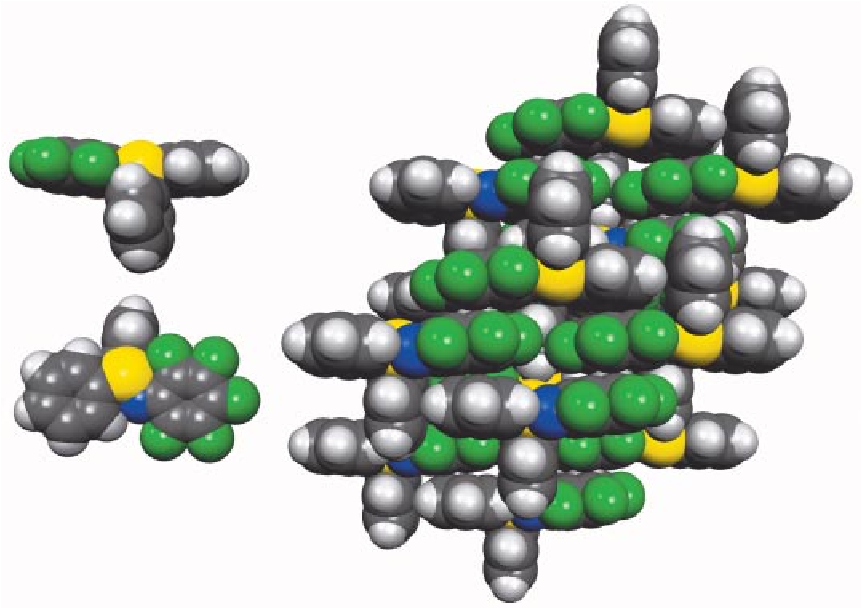


Figure 2. X-ray structure of **8** [13] showing two views of the single molecule, one frontal of the T-like shape (top left), and one of the Ph-S=N-PhF_5 heterostilbene-like substructure (bottom left) with one *S*-phenyl moiety pointing away from the viewer. The packing model on the right indicates a stabilization of the arrangement by arene–arene interactions, particularly by PhF_5-PhF_5-Ph triads.

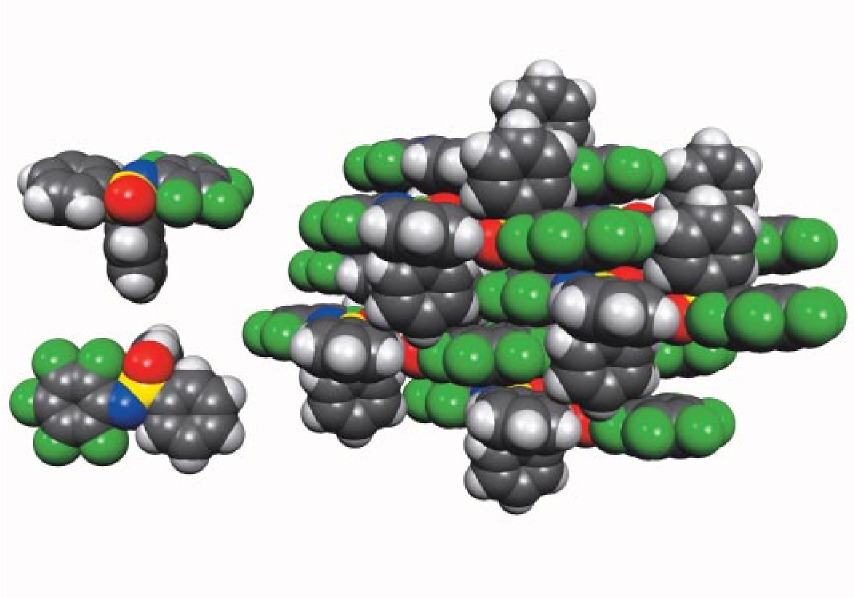


Figure 3. X-ray structure of **9** [13] showing two views of the single molecule, one frontal of the T-like shape (top left), and one of the Ph-S=N-PhF_5 heterostilbene-like substructure (bottom left) with one *S*-phenyl moiety pointing away from the viewer. As for **8**, the packing model on the right indicates a stabilization of the arrangement by arene–arene interactions, although here by PhF_5-Ph dimers.

Conclusions

An improved synthetic methodology has been developed that allows the convenient preparation of highly fluorinated sulfimides and sulfoximides. This method was subsequently applied to the synthesis of the highly polar, fluorinated liquid crystals **6** and **7**. The syntheses of **8** and **9** illustrate the general scope of the method and its applicability for the synthesis of structural motifs of interest for organic materials. The crystal packing of the T-shaped molecules of **8** and **9** demonstrates how supramolecular arrangements can be stabilized by electrostatic arene–perfluoro-arene interactions.

These results indicate the potential usefulness of sulfoximide-based functional materials in particular in electrically passive devices, such as LCDs, as well as in active devices, such as organic light-emitting diodes (OLED) or organic field-effect transistors (OFET).

Experimental Section

***N*-(Trifluoromethylsulfonyl)sulfimide (6):** Triflic anhydride (2.02 mL, 12 mmol) and then, 10 min later, trifluoromethane sulfonamide (2.24 g, 15 mmol) were added to a solution of **4** (4.37 g, 10 mmol) in 20 mL of CH_2Cl_2 whilst maintaining the temperature of the mixture at room temperature. After stirring at this temperature for 18 h, the mixture was poured into 200 mL of ice-water and extracted three times with 30 mL of CH_2Cl_2. The combined extracts were washed with saturated aqueous $NaHCO_3$ solution, with water and brine, and subsequently dried with $MgSO_4$. After evaporation to dryness, the crude product was chromatographed (*n*-heptane/ethyl acetate, 50:1) on silica gel and crystallized once from *n*-heptane. Yield: 0.9 g (16 %), colourless crystals, m.p. 166 °C (purity 99.7% by HPLC). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.3 Hz, 3 H), 0.90–1.47 (m, 15 H), 1.68–1.81 (m, 4 H), 1.86–2.01 (m, 4 H), 2.5–2.63 (m, 1 H), 7.04 (d, J = 8.8 Hz, 2 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$; standard $CFCl_3$): δ = –102.8 (m$_c$, 2 F, ar-*F*), –78.1 (m$_c$, 3 F, NSO_2CF_3), –63.1 (m$_c$, 3 F, SCF_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 498 (100) [$M^+ - CF_3$], 420 (11), 240 (7), 159 (9), 123 (10), 109 (13), 95 (8). HRMS for [$M^+ - CF_3$] ($C_{22}H_{29}F_5NO_2S_2$): calcd. 498.1560; found 498.1572. $C_{23}H_{29}F_8NO_2S_2$ (567.6): calcd. C 48.2, H 5.2, N 2.3, S 10.7; found C 48.6, H 4.9, N 2.3, S 10.4.

***N*-(Trifluoromethylsulfonyl)sulfoximide (7):** A mixture of **6** (800 mg, 1.41 mmol), $NaIO_4$ (900 mg 4.21 mmol), $RuCl_3{\cdot}H_2O$ (10 mg), 4 mL of acetonitrile, 4 mL of CCl_4 and 8 mL of water was stirred at room temperature for 3 d. The solution was extracted three times with 50 mL of methyl *tert*-butyl ether, the combined organic phases were dried with Na_2SO_4, and the solvents evaporated to dryness. The crude product was chromatographed over silica gel (*n*-heptane/toluene, 1:1) and subsequently crystallized once from ethanol and once from *n*-heptane to yield 340 mg (41 %) of pure **7** as colourless crystals, m.p. 101 °C (purity 99.5% by HPLC). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3 H), 0.93–1.48 (m, 15 H), 1.70–1.80 (m, 4 H), 1.89–1.99 (m, 4 H), 2.53–2.63 (m, 1 H), 7.07 (d, J = 9.7 Hz, 2 H) ppm. ^{19}F NMR (235 MHz, $CDCl_3$; standard $CFCl_3$): δ = –101.0 (m$_c$, 2 F, ar-*F*), –78.9 (m$_c$, 3 F, NSO_2CF_3), –76.5 (m$_c$, 3 F, SCF_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 583 (30) [M^+], 563 (5), 514 (6), 203 (10), 125 (55), 83 (68), 69 (100).

***N*-(Pentafluorophenyl)-*S,S*-diphenylsulfimide (8):** A solution of **10** (3.0 g, 14 mmol) in 20 mL of CH_2Cl_2 was treated dropwise with triflic anhydride (2.6 mL 15 mmol) at –70 °C. After 1 h, a solution of pentafluoroaniline (4.0 g, 21 mmol) in 50 mL of CH_2Cl_2 was added dropwise at the same temperature. The mixture was stirred at –70 °C for 1 h and then warmed up to room temperature over 4 h. The mixture was then poured into 500 mL of saturated aqueous $NaHCO_3$ solution. The organic phase was separated, and the aqueous phase was extracted twice with 100 mL of CH_2Cl_2. The combined organic phases were dried with Na_2SO_4 and the solvents evaporated to dryness. The crude product was chromatographed over silica gel (toluene) and subsequently crystallized once from ethanol and once from *n*-heptane to yield 3.5 g (62 %) of pure **8** as yellowish crystals, m.p. 79.6 °C (purity 99.8% by HPLC). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.50 (m$_c$, 6 H, ar-*H*), 7.78 (m$_c$, 4 H, ar-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.5, 129.5, 131.4, 140.5 ppm. ^{19}F NMR (235 MHz, $CDCl_3$; standard $CFCl_3$): δ = –172.6 (m$_c$, 1 F, ar-*F*), –166.7 (m$_c$, 2 F, ar-*F*), –156.0 (m$_c$, 2 F, ar-*F*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 367 (8) [M^+], 258 (7), 186 (100), 109 (6), 97 (5), 77 (13).

***N*-(Pentafluorophenyl)-*S,S*-diphenylsulfoximide (9):** A mixture of **8** (1.2 g, 3.2 mmol), $NaIO_4$ (2.14 g, 10 mmol), 30 mg of $RuCl_3{\cdot}H_2O$, 10 mL of acetonitrile, 10 mL of CCl_4 and 20 mL of water was stirred at room temperature for 3 d. The solution was extracted three times with 100 mL of methyl *tert*-butyl ether, the combined organic phases were dried with Na_2SO_4, and the solvents evaporated to dryness. The crude product was chromatographed over silica gel (toluene) and subsequently crystallized once from ethanol and once from *n*-heptane to yield 420 mg (34 %) of pure **9** as slightly yellowish crystals, m.p. 105.6 °C (purity 99.8% by HPLC). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.53 (m$_c$, 6 H, ar-*H*), 8.05 (m$_c$, 4 H, ar-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.1, 129.3, 133.1, 140.3 ppm. ^{19}F NMR (235 MHz, $CDCl_3$; standard $CFCl_3$): δ = –164.9 (m$_c$, 1 F, ar-*F*), –164.3 (m$_c$, 2 F, ar-*F*), –148.1 (m$_c$, 2 F, ar-*F*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 383 (100) [M^+], 258 (55), 238 (19), 202 (17), 186 (30), 173 (11), 154 (39), 125 (27), 97 (26). HRMS for $[M]^+$ ($C_{18}H_{10}F_5NOS$): calcd. 383.0403, found 383.0407.

Acknowledgments

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[13] a) Crystal structure data for **8**: $C_{182}H_{10}F_5NS$, crystallization from *n*-heptane: triclinic, $P\bar{1}$, a = 8.1970(10) Å, b = 9.2450(10) Å, c = 11.038(2) Å, α = 105.180(10)°, β = 93.350(10)°, γ = 106.080(10)°, V = 767.93(19) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.589 g cm^{-1}, $R(F)$ = 4.90% for 3075 observed independent reflections (4.35° ≤ θ ≤ 26.37°); b) Crystal structure data for **9**: $C_{18}H_{10}F_5NOS$, crystallization from *n*-heptane: triclinic, $P\bar{1}$, a = 8.0797(7) Å, b = 9.4506(8) Å, c = 10.5817(9) Å, α = 99.177(7)°, β = 91.672(7)°, γ = 93.878(7)°, V = 795.17(12) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.601 g cm^{-1}, $R(F)$ = 5.55% for 4096 observed independent reflections (3.16° ≤ θ ≤ 30.05°); c) CCDC-242383 (**8**) and -242384 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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