Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 1449–1453
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis and characterisation of 3- and 4-(pentafluorosulfanyl) benzoic acid derivatives X-ray structure of 3–SF_5–C_6H_4–COOH

C. Zarantonello [a], A. Guerrato [a], E. Ugel [b], R. Bertani [b,*], F. Benetollo [c], R. Milani [d], A. Venzo [e], A. Zaggia [b]

[a] *MITENI, S.P.A., 36090 Trissino (VI), Italy*
[b] *Department of Chemical Processes of Engineering, Faculty of Engineering, University of Padova, via Marzolo 9, 35131 Padova, Italy*
[c] *ICTIMA, CNR, Corso Stati Uniti 4, Padova, Italy*
[d] *Dipartimento Scienze Chimiche, via Marzolo 1, 35131 Padova, Italy*
[e] *Istituto Scienze e Tecnologie Molecolari, C.N.R., Sezione di Padova, via Marzolo 1, 35131 Padova, Italy*

Received 23 March 2007; received in revised form 25 July 2007; accepted 30 July 2007
Available online 6 August 2007

Abstract

The high yield synthesis of 3- and 4-(pentafluorosulfanyl)benzoic acid derivatives is described starting from the NO_2-derivatives, which are reduced to the corresponding anilines. Then the NH_2– group is converted to bromide and subsequently to the HC═O moiety. The benzaldeydes are then oxidised to the corresponding benzoic acids. The X-ray structure of 3–SF_5–C_6H_4–COOH is also reported.

Keywords: 3- and 4-Pentafluorosulfanyl anilines; 3- and 4-Pentafluorosulfanyl bromobenzenes; 3- and 4-Pentafluorosulfanyl benzaldeydes; 3- and 4-Pentafluorosulfanyl benzoic acids

1. Introduction

About 40 years ago the first pertafluorosulfanyl aromatic compounds were prepared by Sheppard [1] through reaction of aryl disulfides or aryl-sulfur-trifluorides with AgF_2. Typically, the syntheses started from the corresponding nitro-derivatives [2], which, by subsequent reactions, were converted into a wide variety of functionalized SF_5-aromatic compounds. In particular the preparation of aromatic pentafluorosulfanyl derivatives involving direct fluorination using F_2 (10% in N_2) of bis(3- and 4-nitrophenyl)disulfides, has been described [3].

In order to test the biological effect of replacing other fluorinated moieties (i.e. CF_3 or OCF_3) with SF_5 many pentafluorosulfanyl aromatic derivatives have been patented [4,5].

Recently, new *ortho*-substituted pentafluorosulfanyl benzenes have been prepared as valuable intermediates for preparing medicaments, polymers, pesticides, herbicides, fungicides [6,7].

In comparison with CF_3, SF_5 is more strongly electron withdrawing [8] and, as a consequence, phenyl-sulfur pentafluoride has a larger dipole moment (3.44 D) than benzotrifluoride (2.60 D). Liquid crystals with very high dielectric anisotropy can be obtained with pentafluorosulfanyl-benzenes [9].

Here we report the synthesis of 3- and 4-SF_5–C_6H_4–COOH derivatives starting from the corresponding nitro-compounds, taking into account the optimisation of the experimental procedures in order to improve the yield.

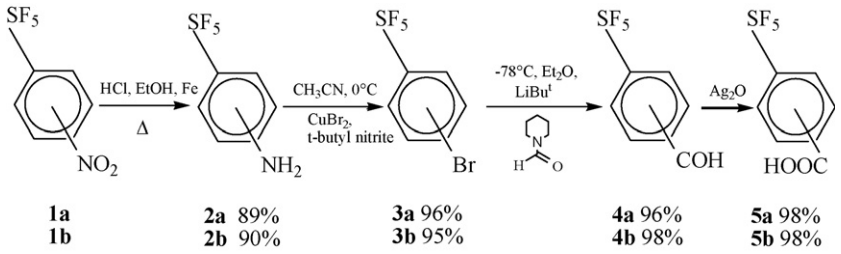
2. Results and discussion

2.1. Synthesis and characterisation

The synthesis of 3–SF_5–C_6H_4–COOH (**5a**) and 4–SF_5–C_6H_4–COOH (**5b**) was accomplished according to Scheme 1, which gives the products in very high yield with respect the starting nitro-derivatives.

* Corresponding author. Tel.: +39 049 8275731; fax: +39 049 8275525.
E-mail address: roberta.bertani@unipd.it (R. Bertani).

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.07.011



Scheme 1.

The reduction of the nitro group in **1a** and **1b** to the NH_2–moiety in **2a** and **2b** was performed according to the procedure previously reported for substituted pentafluorosulfanyl benzenes [2c,7b,10] with HCl in the presence of Fe. The $NO_2 \rightarrow NH_2$ conversion on pentafluorosulfanyl aromatic compounds was previously reported by employing 10% Pd on charcoal as the catalyst under an atmosphere of hydrogen in ethanol as solvent [3] or using PtO_2 in ethanolic HCl under H_2 pressure [1a]. NH_2 group of **2a** and **2b** was converted to Br by reaction with *t*-butyl nitrite and $CuBr_2$ according to one of the reported methods for aryl bromides preparation [11]. The bromo-derivatives **3a** and **3b** have been converted into the corresponding benzaldeydes **4a** and **4b** by reaction with 1-formyl-piperidine according to the procedure reported in ref. [9a]. The compounds **5a** and **5b** have been prepared by oxidation of **4a** and **4b**, respectively, with Ag_2O [12] under basic conditions. The reaction is quantitative and easily allows **5a** and **5b** as crystals. This experimental procedure must be compared with the synthesis of **5a** and **5b** previously reported occurring with about 55% yield, by reaction of the corresponding bromo-derivatives with methyl iodide, due to the fact that the Grignard reagent of bromo-pentafluorosulfanyl-benzene can not be prepared by reaction with Mg [1].

The compounds **2–5** have been characterised by analytical and spectroscopic determinations. In particular the ^{13}C NMR spectra of the compounds **2–5** are characterised by the presence of the C-SF_5 signals as a quintet of doublets due to the coupling ($^2J_{CF}$ 15–18 Hz) with the equatorial four fluorine atoms and with the axial one. The same feature is detected for the carbon atoms in *ortho* position with respect to the SF_5 group (the $^2J_{CF}$ and the $^3J_{CF}$ coupling constants values with the axial fluorine atom are not always reported having a value smaller than 2 and 1 Hz, respectively).

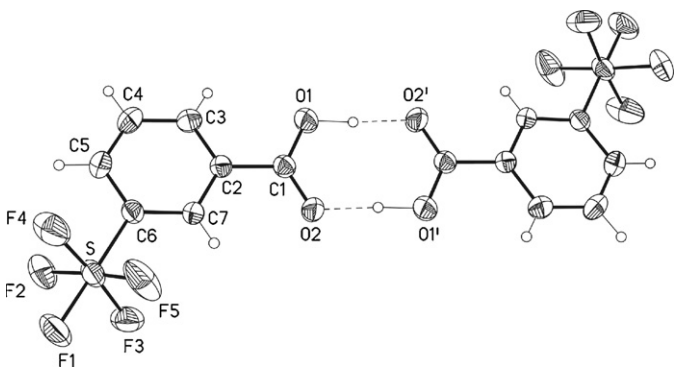


Fig. 1. An ORTEP drawing of the centrosymmetric structure of 1. The vibration ellipsoids are at 40% confidence level (symmetry codes: at $1-x, 1-y, 1-z$).

2.2. X-Ray structure of 3–SF_5–C_6H_4–COOH

The compound **5a** crystallizes as a ''dimer'' via hydrogen bond interactions between the proton of hydroxyl proton of one molecule and the carboxylic oxygen of the centrosymmetrically related as shown in Fig. 1. The O(1)–H···O(2)' distance is 1.521(3) Å with an angle of 168(6)° (' at $1-x, 1-y, 1-z$). The sulfur atom of the SF_5 group has an octahedral coordination geometry. The sixth position is occupied by the phenyl carbon with the equatorial fluorine atoms staggered to the relative benzene moiety, as previously proposed by Sheppard [8] to be energetically favourable. The geometry of the SF_5 group [S–F_{ax} 1.587(3) Å, S–F_{eq} (average) 1.561(4) Å, F_{ax}–S–F_{eq} bond angles (average) 87.6(3)° and between two F_{eq}–S–F_{eq} 90.9(3)° with a C–S bond distances of 1.804(2)Å] is comparable to that of the analogous 3–SF_5–C_6H_4–$NHCOCH_3$ (3-acetamidopentafluorosulfanylbenzene) and 4–SF_5–C_6H_4–$NHCOCH_3$ (4-acetamidopentafluorosulfanylbenzene) [3].

The data can be also compared with those reported for $SF_5CH_2CH_2COOH$ [13] showing a slightly longer S–F_{ax} bond (1.574(14) Å) with respect the nearly identical S–F_{eq} bonds (1.571(14) Å) with F_{ax}–S–F_{eq} bond angles 88.1(10)° and a long S–C bond 1.791(6) Å.

The equatorial plane of the SF_5 group has an umbrella shape with the cant toward the fifth fluorine atom as previously reported. The observed twist of the equatorial atoms by roughly 2.4° out of the equatorial plane was proposed to explain the relatively high dipole moment of the aromatic pentafluorosulfanyl group resulting in an additional component to the overall dipole moment in the direction of the long molecular axis. Further contribution is represented by the S–F highly polarized bonds due to the hypervalence of the sulfur atom [9a].

3. Experimental

3.1. General procedures and materials

All experiments were carried out under nitrogen atmosphere using standard Schlenck techniques. Solvents were distilled prior to use; Et_2O and pentane were distilled before use on Na/benzophenone and CaH_2, respectively. Elemental analyses were performed by the Department of Chemical Sciences of the University of Padova. The compounds 3–SF_5–C_6H_4–NO_2 (**1a**)

and 4–SF_5–C_6H_4–NO_2 (**1b**) were purchased by MITENI and all the other reagents by Aldrich.

3.2. Instrumentation

IR spectra were taken on a FT-IR Nexus (range 4000-600 cm^{-1}) of the Nicolet Instrument Corporation (KBr films) spectrophotometer; the wavenumbers $\bar{\nu}$ are given in cm^{-1}. Oils were run neat between two CsI plates and solids were run as KBr films. ^1H and ^{13}C NMR spectra were recorded on a Bruker 200 AC spectrometer operating at 200.13 and 50.32 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^1H: CHD_2COCHD_2, $\delta_H = 2.04$ ppm) or the deuterated solvent multiplet (^{13}C: CD_3COCD_3, $\delta_C = 29.8$ ppm). ^{19}F NMR measurements were recorded on a Bruker 200 AC spectrometer operating at 188.30 MHz. Peak positions are reported relative to $CFCl_3$.

GC/MS spectra were measured on a CARLO ERBA INSTRUMENT MFC 500/QMD1000 using a silica fused capillary PS264 column (30 m × 0.25 mm) on a Finnigan Mat TSQ7000. Typical conditions were: temperature program 80 °C for 1 min, 10 °C/min to 280 °C; He as gas carrier 1 ml/min).

3.3. Syntheses

3.3.1. Synthesis of 3-SF_5-C_6H_4-NH_2 (*2a*)

To a pale yellow solution of **1a** (10.0 g; 0.040 mol) in EtOH (200 ml) HCl (37%, 8.00 ml) was added at room temperature. The reaction mixture was heated at 90 °C and Fe (11.22 g, 0.201 mol) were added. The suspension was refluxed for 3 h, then cooled at room temperature. By addition of NH_3(aq) (25% solution, 40 ml) the pH of the reaction mixture was turned up 9. The iron was filtered off on kieselgur and the filtrate was taken to dryness obtaining a yellow oil which slowly crystallized. The product as a white solid was purified by dissolution in $CHCl_3$ and treatment with Na_2SO_4 (2 g). Yield 7.83 g, 89%. mp 35–37 °C Anal. Calc. for $C_6H_6NF_5S$ (PM = 219.17): C, 32.88; H, 2.76; N, 6.39. Found: C, 32.12; H, 2.35; N, 6.25%.

IR ($\bar{\nu}$, KBr film): 3250 (m, CH_{Ph}); 1624 (m, CC_{Ph}); 820, 831 (vs, SF_5); 3367, 3498, 3438 (s, NH). ^1H NMR (CD_3COCD_3; δ, ppm; J, Hz): 6.89 (dd, $^3J_{HH}$ 9.0, $^4J_{HH}$ 2.0, C*H(4)*CNH_2, 1H); 7.00 (dm, $^3J_{HH}$ 8.1, C*H(6)*CSF_5, 1H); 7.19(dd, $^4J_{HH}$ 2.0, $^4J_{HH}$ 2.1, C*H(2)*CSF_5, 1H); 7.23(m, C*H(5)*, 1H), 5.11 (2H, NH) ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 155.2 (qt, $^2J_{CF}$ 15.5, *C(1)*-SF_5); 111.5 (qt, $^3J_{CF}$ 4.9, *C(2)*); 149.5 (*C(3)*-NH2); 117.7 (*C(4)*); 129.7 (*C(5)*); 113.9 (qt, $^3J_{CF}$ 4.7, *C(6)*). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 61.3 (d, $^2J_{FF}$ 148, 4F), 85.4 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 219 ($[M]^+$, 100%); 200 ($[M–F]^+$, 30%); 95 ($[C_6H_4F]^+$, 80%).

3.3.2. Synthesis of 4–SF_5–C_6H_4–NH_2 (*2b*)

The synthesis was performed starting from **1b** (10.0 g; 0.040 mol) following the same procedure described for **2a**. Yield 7.90 g, 90%. mp 57–59 °C.

Anal. Calc. for $C_6H_6NF_5S$ (PM = 219.17.): C, 32.88; H, 2.76; N, 6.39. Found: C, 32.30; H, 2.25; N, 5.99%.

IR ($\bar{\nu}$, KBr film): 3250 (m, CH_{Ph}); 1627 (m, CC_{Ph}); 800-850 (vs, SF_5); 3391, 3490 (s, NH). ^1H NMR (CD_3COCD_3; δ, ppm): 7.54, 7.49 and 6.65, 6.60 (AA′BB′ pattern, 4H, Ph); 5.39 (2H, NH). ^{13}C NMR (CD_3COCD_3 δ, ppm; J, Hz): 142.9 (qt, $^2J_{CF}$ 16.6, *C(1)*-SF_5); 127.6 (qt, $^3J_{CF}$ 4.5, *C(2)* and *C(6)*); 113.1 (*C(3)* and *C(5)*); 152.0 (*C(4)*-NH_2). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 63.9 (dt, $^2J_{FF}$ 146, $^4J_{HF}$ 2, 4F), 88.4 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 219 ($[M]^+$, 100%); 200 ($[M–F]^+$, 40; %); 95 ($[C_6H_4F]^+$, 70%).

3.3.3. Synthesis of 3–SF_5–C_6H_4–Br (*3a*)

$CuBr_2$ (7.70 g, 0.035 mol) and *t*-butyl-nitrite (8.8 g, 0.085 mol) were suspended in CH_3CN (50 ml). The mixture was cooled at 0 °C and a CH_3CN solution of **2a** (7.65 g, 0.035 mol) was added dropwise. The pale brown solution was stirred at 0 °C for 1 h, then it was heated at room temperature and stirred for additional 4 h. Deionised water (50.0 ml) was then added and the pH of the solution was turned down 2, by adding HCl (2 M, 10 ml). Then ethylacetate (50.0 ml) was added. The organic phase was separated and treated with Na_2SO_4 (10 g). By taking the solution to dryness a pale yellow oil was obtained which was purified by column chromatography using Floresil and eluting with 30% dichloromethane in hexane. Yield 9.5 g, 96%.

Anal. Calc. for $C_6H_4F_5SBr$ (PM = 283.05.): C, 25.46; H, 1.42; Found: C, 25.15; H, 1.33%.

IR ($\bar{\nu}$, KBr film): 1578 (m, CC_{Ph}); 842 (vs, SF_5). ^1H NMR (CD_3COCD_3; δ, ppm; J, Hz): 7.99 (dd, $^4J_{HH}$ 2.0, $^4J_{HH}$ 2.1, C*H(2)*CBr, 1H); 7.78(dm, $^3J_{HH}$ 8.0, C*H(4)*, 1H), 7.53 (tm, $^3J_{HH}$ 8.0, C*H(5)*, 1H); 7.85(ddd, $^3J_{HH}$ 8.0, $^4J_{HH}$ 2.0, $^4J_{HH}$ 1.0, C*H(6)*CBr, 1H). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 154.7 (qt, $^2J_{CF}$ 18.0, *C(3)*-SF_5); 129.1 (qt, $^3J_{CF}$ 4.8, *C(2)*); 122.4 (*C(1)*-Br); 125.3 (qt, $^3J_{CF}$ 4.8, *C(4)*); 131.3 (*C(5)*); 135.66(*C(6)*);. ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 61.7 (dt, $^2J_{FF}$ 149, $^4J_{HF}$ 2, 4F), 82.1 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 283 ($[M]^+$, 50%); 285 (48%); 264 ($[M–F]^+$, 8%); 266 (7%); 156 ($[M–SF_5]^+$, 20%); 158 (19%); 95 ($[C_6H_4F]^+$, 100%).

3.3.4. Synthesis of 4–SF_5–C_6H_4–Br (*3b*)

The synthesis was performed starting from **2b** (7.65 g; 0.035 mol) following the same procedure described for **3a**. Yield 9.4 g, 95%.

Anal. Calc. for $C_6H_4F_5SBr$ (PM = 283.05.): C, 25.46; H, 1.42; Found: C, 25.20; H, 1.25%.

IR ($\bar{\nu}$, KBr film): 1579 (m, CC_{Ph}); 843 (vs, SF_5). ^1H NMR (CD_3COCD_3; δ, ppm; J, Hz): 7.75 (s, 4H, Ph). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 152.9 (qt, $^2J_{CF}$ 17.4, *C(3)*-SF_5); 128.2 (qt, $^3J_{CF}$ 4.6, *C(3)* and *C(5)*); 132.6 (*C(2)* and *C(6)*); 126.5 (*C(1)*-Br). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 61.9 (d, $^2J_{FF}$ 149, 4F), 82.7 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 283 ($[M]^+$, 60%); 285 (48%); 264 ($[M–F]^+$, 15%); 266 (7%); 156 ($[M–SF_5]^+$, 15%); 158 (19%); 95 ($[C_6H_4F]^+$, 100%).

*3.3.5. Synthesis of 3–SF_5–C_6H_4–COH (**4a**)*

An Et_2O solution (15 ml) of **3a** (7.0 g, 0.024 mol) was cooled at −78 °C. Then LiBu^t pentane solution (25.2 ml, 1.6 M) was added dropwise. The solution turned from pale brown to red. The solution was stirred at low temperature for 1 h. 1-Formyl-piperidine (4.20 ml, 0.035 mol) was then added dropwise and the mixture was stirred for additional 30 min. Then the solution was stirred at room temperature for 4 h. Deionised water (70.0 ml) was added to the solution, which was also treated three times with HCl (140 ml, 2,5% solution). Organic phase was collected, treated with Na_2SO_4 and taken to dryness obtaining a reddish oil which slowly crystallized. Yield 5.5 g, 96%.

Anal. Calc. for $C_7H_5F_5OS$ (PM = 232.17.): C, 36.21; H, 2.17; Found: C, 36.10; H, 2.08%.

IR ($\bar{\nu}$, KBr film): 1606 (m, CC_{Ph}), 842 (vs, SF_5); 1707 (vs, CO). ^{1}H NMR (CD_3COCD_3; δ, ppm; J, Hz): 7.76 (t, $^3J_{HH}$ 8.0, C*H(5)*, 1H); 8.10 (ddd, $^3J_{HH}$ 8.0, $^4J_{HF}$ 2.0, $^4J_{HH}$ 1.0, C*H(6)*, 1H); 8.26 (d, $^3J_{HH}$ 8.0, C*H(4)*, 1H); 8.40 (dd, $^4J_{HH}$ 2.0, $^4J_{HH}$ 2.1, C*H(2)*, 1H), 10.15 (1H, CHO). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 154.5 (qt, $^2J_{CF}$ 18.6, *C(1)*-SF_5); 126.2 (qt, $^3J_{CF}$ 5.0, *C(2)*); 137.8 (*C(3)*-CHO); 132.9 (*C(4)*); 130.7 (*C(5)*); 131.4 (qt d, $^3J_{CF}$ 4.7, *C(6)*); 190.9 (*C*H=O). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 61.4 (d, $^2J_{FF}$ 147, 4F), 82.7 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 232 ([M]$^+$, 80%); 231 ([M–H]$^+$, 100%); 213 ([M–F]$^+$, 5%); 203 ([M–CHO]$^+$, 10%); 105 ([M–SF_5]$^+$, 25%); 95 ([C_6H_4F]$^+$, 60%).

*3.3.6. Synthesis of 4–SF_5–C_6H_4–COH (**4b**)*

The synthesis was performed starting from **3b** (7.0 g; 0.024 mol) following the same procedure described for **4a**. Yield 5.6 g, 98%.

Anal. Calc. for $C_7H_5F_5OS$ (PM = 232.17.): C, 36.21; H, 2.17; Found: C, 36.10; H, 1.99%.

IR ($\bar{\nu}$, KBr film): 1601 (m, CC_{Ph}), 845 (vs, SF_5); 1712 (vs, CO). ^{1}H NMR (CD_3COCD_3; δ, ppm; J, Hz): 8.15-8.02 (m, 4H, Ph); 10.16 (1H, CHO). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 157.5 (qt, $^2J_{CF}$ 17.1, *C(1)*-SF_5); 127.3 (qt, $^3J_{CF}$ 6.3, *C(2)* and *C(6)*); 130.4(*C(3)* and *C(5)*); 139.2 (*C(4)*–CHO), 191.3 (*C*H=O). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 61.1 ppm (d, $^2J_{FF}$ 151, 4F), 81.9 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 232 ([M]$^+$, 75%); 231 ([M–H]$^+$, 100%); 213 ([M–F]$^+$, 8%); 203 ([M–CHO]$^+$, 15%); 105 ([M–SF_5]$^+$, 20%); 95 ([C_6H_4F]$^+$, 65%).

*3.3.7. Synthesis of 3–SF_5–C_6H_4–COOH (**5a**)*

An H_2O solution (25 ml) of **4a** (5.0 g, 0.02 mol) was reacted with Ag_2O (7.0 g, 0.030 mol) and NaOH (15.0 ml, 10% solution). The reaction mixture was stirred at room temperature in the dark for 20 h. The mixture was then treated with charcoal; the solids filtered off and the solution was acidified with HCl (37%, ca. 5 ml) until **5a** precipitates. Yield 4.9 g, 98%. mp 153–155 °C.

Anal. Calc. for $C_7H_5F_5O_2S$ (PM = 248.17.): C, 33.88; H, 2.03; Found: C, 33.50; H, 2.00%.

IR ($\bar{\nu}$, KBr film): 1606 (m, CC_{Ph}), 836, 803 (vs, SF_5); 1697 (vs, CO). ^{1}H NMR (CD_3COCD_3; δ, ppm; J, Hz): 7.84 (tm, $^3J_{HH}$ 8.0, C*H(5)*, 1H); 8.15 (ddd, $^3J_{HH}$ 8, $^4J_{HH}$ 2, $^4J_{HF}$ 1, C*H(6)*CSF_5, 1H); 8.18 (d, $^3J_{HH}$ 8.0, C*H(4)*, 1H); 8.35 (dd, $^4J_{HH}$ 2.1, C*H(2)*, 1H), 11.40 (1H, COOH). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 153.9 (qt, $^2J_{CF}$ 17.1, *C(1)*-SF_5); 127.2 (qt, $^3J_{CF}$ 4.8, *C(2)*); 132.2 (*C(3)*–COOH); 133.5 (*C(4)*); 130.2 (*C(5)*); 130.5 (qt d, $^3J_{CF}$ 4.7, *C(6)*); 165.54 (*C*=O). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 60.9 (dt, $^2J_{FF}$ 149, $^4J_{HF}$ 2.0, 4F), 84.3 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 248([M]$^+$, 100%); 229 ([M–F]$^+$, 5%); 231 ([M–OH]$^+$, 60%); 203 ([M–CO_2H]$^+$, 10%); 121([M–SF_5]$^+$, 20%).

*3.3.8. Synthesis of 4-SF_5-C_6H_4-COOH (**5b**)*

The synthesis was performed starting from **4b** (5.0 g; 0.02 mol) following the same procedure described for **3b**. Yield 4.8 g, 98%. mp 192–193 °C.

Anal. Calc. for $C_7H_5F_5O_2S$ (PM = 232.17.): C, 33.88; H, 2.03; Found: C, 33.75; H, 1.98%.

IR ($\bar{\nu}$, KBr film): 1603 (m, CC_{Ph}), 843 (vs, SF_5); 1706 (vs, CO). ^{1}H NMR (CD_3COCD_3; δ, ppm; J, Hz): 8.26, 8.21 and 8.06, 7.99 (AA′BB′ pattern, 4H, Ph); 11.05 (1H, COOH). ^{13}C NMR (CD_3COCD_3; δ, ppm; J, Hz): 156.9 (qt, $^2J_{CF}$ 18.1, *C(1)*-SF_5); 126.7 (qt, $^3J_{CF}$ 4.8, *C(2)* and *C(6)*); 130.9 (*C(3)* and *C(5)*); 134.4 (*C(4)*), 165.6 (C=O). ^{19}F NMR (CD_3COCD_3; δ, ppm; J, Hz): 62.7 (dt, $^2J_{FF}$ 140, $^4J_{FH}$ 1, 4F), 83.58 (quintet, 1F). MS (EI+, 70 eV, *m/z*, rel.ab.%): 248([M]$^+$, 100%); 229 ([M–F]$^+$, 10%); 231 ([M–OH]$^+$, 50%); 203 ([M–CO_2H]$^+$, 8%); 121 ([M–SF_5]$^+$, 30%).

4. X-ray measurements and structure determination

*4.1.1. Crystal data for compound 3–SF_5–C_6H_4–COOH (**5a**)*

Empirical formula $C_7H_4F_5O_2S$, M_r = 247.16, monoclinic, space group $P2_1/n$, with a = 8.723(2), b = 9.682(2), c = 11.641(3) Å, β = 111.44(2)°, V = 915.1(4) Å^3, Z = 4, ρ_{calc} = 1.794 Mg/m^3, F (0 0 0) = 492, λ = 0.71073 Å, T = 293(2) K, μ (Mo Kα) = 0.410 mm^{-1}.

A prismatic colorless crystal was centered on a four-circle Philips PW1100 (Febo System) diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), following standard procedures at room temperature. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-Polarization effects and for absorption, as described by North et al. [14].

The structure was solved by direct methods SIR-97 [15]. Refinement was carried out by full-matrix least-squares procedures using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 Uequiv of the parent carbon atom). For a total of 157 parameters and for 1968 reflections having ($I \geq 2\sigma(I)$), $wR'([\sum w(Fo^2 - Fc^2)2/\sum w(Fo^2)^2]^{1/2}) = 0.158$, S = 1.140 and conventional R = 0.059.

Structure refinement and final geometrical calculations were carried out with SHELXL-97 [16] and PARST [17] programs, drawings were produced using ORTEP II [18]. Crystallographic data for the structures here reported have been

deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 627133. Copies of the available material can be obtained, free of charge from CCDC,12 Union Road, Cambridge,CH2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) W.A. Sheppard, J. Am. Chem. Soc. 84 (1962) 3064;
(b) W.A. Sheppard, US Patent 3,219,690 (1965).

[2] (a) A.G. William, N.R. Forster, Patent WO 94 22817 (1994).;
(b) W.R. Dolbier Jr., S. Ait-Mohand, Patent US, 2004/0106827 A1 (2004).
(c) T.A. Sergeeva, W.R. Dolbier Jr., Org. Lett. 6 (2004) 2417.

[3] R.D. Bowden, P.J. Comina, M.P. Greenhall, B.M. Kariuki, A. Loveday, D. Philp, Tetrahedron 56 (2000) 3399.

[4] (a) H.W. Kleemann, Patent US 2003/0216476 A1 (2003).;
(b) R. Bowden, M.P. Greenhall, Patent WO 02/42263 A1 (2002).;
(c) B. Bossenmaier, W.G. Friebe, G. Georges, M. Rueth, E. Voss, Patent US, 2005/0197370 A1 (2005).

[5] (a) P.J. Crowley, G. Mitchell, R. Salmon, P.A. Worthington, Chimia 58 (2004) 138;
(b) R. Salmon, Patent WO 93/06089 (1993).
(c) F.M. Carlini, Chimica Oggi (2003) 14.

[6] D.W. Hawkins, US Patent 6,140,528 (2000).

[7] (a) H.W. Kleemann, R. Weck, Patent US 2005/0148652 A1 (2005).
(b) A.M. Sipyagin, C.P. Bateman, Y.-T. Tan, J.S. Thrasher, J. Fluorine Chem. 112 (2001) 287.

[8] W.A. Sheppard, J. Am. Chem. Soc. 84 (1962) 3072.

[9] (a) P. Kirsch, M. Bremer, M. Heckmeier, K. Tarumi, Angew. Chem. Int. Ed. Engl. 38 (1999) 1989;
(b) V. Reiffenrath, R. Eidenschink, G. Weber, Patent WO 88/10251 (1988).
(c) 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;
(d) P. Kirsch, J.T. Binder, E. Lerk, G.V. Rosachenthaler, J. Fluorine Chem. 127 (2006) 610.

[10] A.M. Sypyagin, V.S. Enshov, S.A. Kashtanov, C.P. Bateman, B.D. Mullen, Y.-T. Tan, J.J. Thrasher, J. Fluorine Chem. 125 (2004) 1305.

[11] (a) .P. Doyle, B. Siegfried, J.F. Dellaria Jr., J. Org. Chem. 42 (1977) 2426;
(b) H.W. Kleemann, R. Weck, Patent WO 2005/047240 A1 (2005).

[12] S.C. Thomason, D.G. Kubler, J. Chem. Ed. 45 (1968) 546.

[13] A.F.T. Yokochi, R. Winter, G. Gard, Acta Crystallogr. E 58 (2002) o1133.

[14] A.T.C. North, D.C. Philips, F.S. Mathews, Acta Crystallogr. A24 (1968) 351.

[15] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[16] G.M. Sheldrick, ‘‘SHELXL–97’’, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[17] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[18] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.