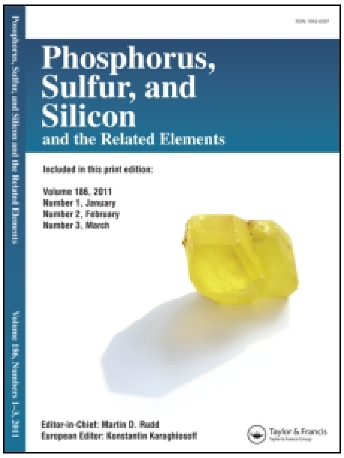

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NOVEL REACTIONS OF SPIROSULFURANE PRECURSOR SULFIDES AND SULFOXIDES

M. Kuti[a]; J. Rábai[a]; I. Kapovits[a]
[a] Department of Organic Chemistry, L. Eötvös University, Budapest, Hungary

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NOVEL REACTIONS OF SPIROSULFURANE PRECURSOR SULFIDES AND SULFOXIDES

M. KUTI, J. RÁBAI* and I. KAPOVITS

Department of Organic Chemistry, L. Eötvös University, H-1518 Budapest 112, PO Box 32, Hungary

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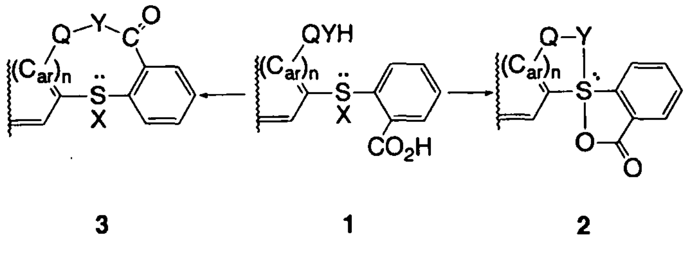
The S^{IV}[C,C,N,O] spirosulfurane **19** and the lactam-sulfoxides **21**, **22** and **23** with seven-, eight- and nine-membered rings have been prepared by oxidation and dehydration of trifluoroacetylaminoaryl-carboxyphenyl sulfides and sulfoxides, respectively. A mechanism is proposed for the formations of lactam-sulfoxides. The preparation of the starting sulfides and sulfoxides is also described.

Key words: Diaryl sulfides; diaryl sulfoxides; spirosulfurane; lactams; carboxyl activation; lactam-sulfoxide formation.

INTRODUCTION

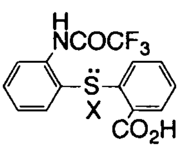
The first synthesis of a diaryldiacyloxyspirosulfurane was reported in 1971[1a] and since then a number of stable sulfuranes of different types have been prepared.[1,2] Spirosulfuranes of high stability are readily formed (**1** → **2**) from diaryl sulfides or diaryl sulfoxides having two functional groups near the sulfur centre (e.g. CO_2H, CH_2OH or $CONHCH_3$), by oxidation or by dehydration, respectively.[1,3]



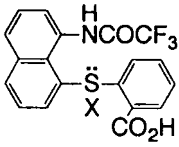
Q = C=O, CH_2
Y = O, NCH_3
X = O=, lone pair

Under given conditions, however, the dehydration of sulfoxides occurs on the reactive groups while saving the sulfinyl group (**1** → **3**) to yield a lactone (Q = CH_2, Y = O) or cyclic anhydride (Q = CO, Y = O).[3] These compounds may have eight-, nine- or ten-membered rings, depending on the 1,4 1,5 or 1,6 relative positions of the functional group and sulfur atom (*n* = 1, 2 and 3 for 1,2, 1,8 and 2,2′ disubstituted benzene, naphthalene and biphenyl derivatives, respectively).

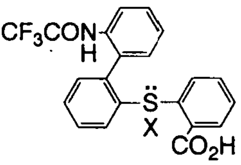
Now we report on the preparation of three diaryl sulfides with trifluoroacetylaminoaryl and 2-carboxyphenyl groups (**4**–**6**) together with the corresponding sulfoxides (**7**–**9**), in which the reactive trifluoroacetylamino group and the sulfur atom are in 1,4 1,5 and 1,6 relative positions, respectively.



4 X= lone pair
7 X= O=



5 X= lone pair
8 X= O=



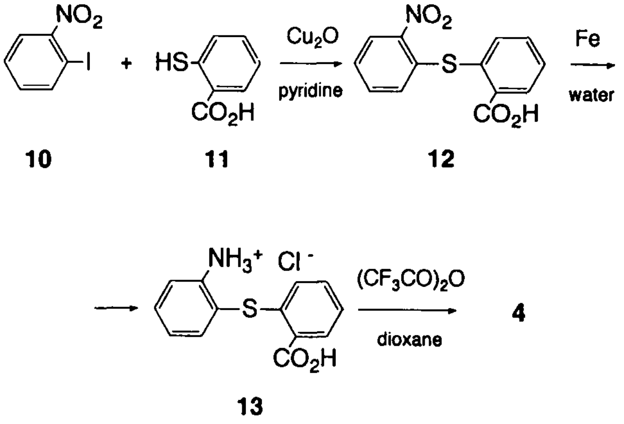
6 X= lone pair
9 X= O=

The spirosulfurane precursor sulfides **4**–**6** and sulfoxides **7**–**9** seemed to be suitable models to study how structural features influence the formation of the corresponding spirosulfuranes or lactam-sulfoxides (cf. **2** and **3** where $NCOCF_3$ or NH stands for QY). The methods applied were the oxidation of the sulfides with dichloramine-T in dry pyridine and the dehydration of the sulfoxides with trifluoroacetic anhydride in dry DMF.

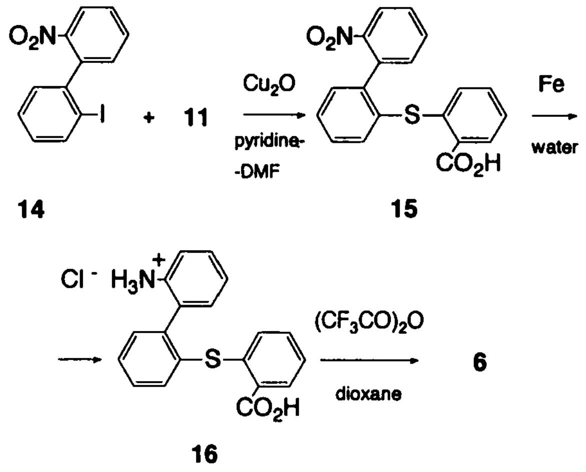
RESULTS AND DISCUSSION

Synthesis of Sulfides

2-Iodo-nitrobenzene (**10**) was coupled[4] with thiosalicylic acid (**11**) in the presence of copper(I) oxide to give 2-(2-nitrophenylthio)benzoic acid (**12**)[5] from which the sulfide **4** was obtained by reduction and subsequent acylation with trifluoroacetic anhydride (**12** → **13** → **4**).



Starting from 2-iodo-2′-nitrobiphenyl (**14**)[6] the sulfide **6** was prepared in a similar way as given for sulfide **4**(**14**, **11** → **15** → **16** → **6**).



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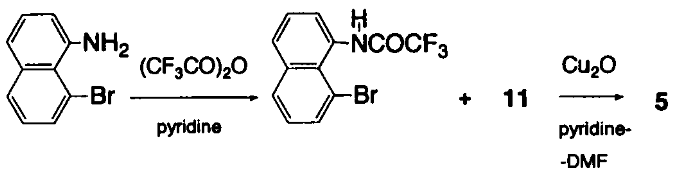
The synthesis of the sulfide **5** started from 8-bromo-1-aminonaphthalene (**17**)[7] which was acylated with trifluoroacetic anhydride, then coupled with thiosalicylic acid (**11**).



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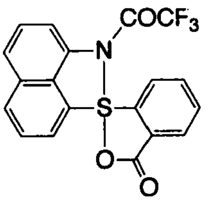
Synthesis of Sulfoxides

The sulfoxides **7** and **9** were obtained from the corresponding sulfide **4** and **6** by oxidation with *tert*-butyl hypochlorite. The oxidation of the sulfide **5** to the sulfoxide **8** was carried out by using phenyltrimethylammonium tribromide.[8]

Conversion of Sulfoxides

When the sulfoxides **7–9** were treated at 20°C with trifluoroacetic anhydride in DMF, only the dehydration of the compound **8** gave the expected crystalline spirosulfurane **19** with five-membered spiorings. Presumably the reaction proceeds through a monocyclic acyloxisulfonium salt intermediate (**20**; cf. Reference 1).



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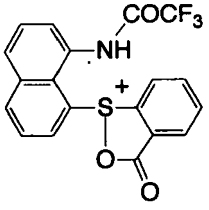

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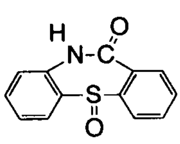
Both the mass spectrum and the elementary analysis are in accordance with the **19** spirosulfurane structure. The lack of ν_{OH} and ν_{NH} bands in the IR spectrum also supports the above structure. The verification of spirosulfurane structure was provided by the mild hydrolysis of compound **19** carried out in acetone-water at room temperature, resulting in the starting sulfoxide **8** (see the analogous reactions in Reference 1).

When the spirosulfurane was not isolated from the reaction mixture **8** → **19** at 20°C, but it was heated at 100°C, with subsequent addition of water, the lactam **22** crystallized from the mixture. Under such conditions from the sulfoxides **7** and **9** the lactam-sulfoxides **21**[9] and **23** were obtained, respectively.



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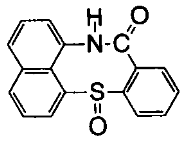

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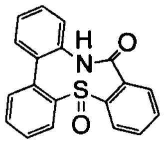

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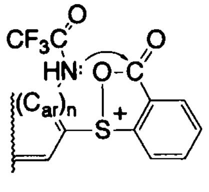
It seems very likely that the lactams **21**–**23** are formed from the corresponding monocyclic acyloxysulfonium intermediates (e.g. **22** from **20**) by an intramolecular S_N—C(Ad + E) reaction. The nucleophilic carbamoyl-nitrogen can approach and attack the sp^2-carbon of the cyclic acyloxy moiety activated by the positive sulfur atom. The splitting of the acyloxy ring results in the formation of a lactam ring and in regeneration of the sulfinyl group (**24** → **25**). Under the given conditions the diacylamino intermediate (**25**) undergoes partial hydrolysis to give a lactam (**26**) having no N-trifluoroacetyl group.



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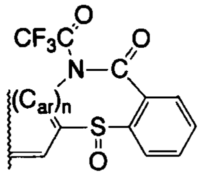

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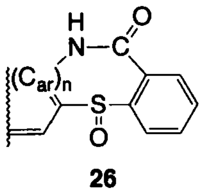

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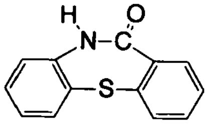
The mechanism proposed is supported by the following facts. (i) The acylation of a trifluoroacetamide derivative by acetyl chloride followed by the cleavage of the trifluoroacetyl group to yield an acetamide derivative as previously described.[10] (ii) Intramolecular acylation between amide and carboxyl groups leading to acyl-lactam accomplished by using acetic anhydride reactant.[11] (iii) In contrast with the sulfoxides **8** and **9**, the sulfides **5** and **6** when treated with trifluoroacetic anhydride under the same conditions, gave a mixture of products from which the lactam-sulfides corresponding to the **22** and **23** lactam-sulfoxides could not be isolated. However the sulfide **4** could be converted in part to the lactam-sulfide **27**[9], while an amount of the starting sulfide was detectable in the product. This difference between the reactivities of the corresponding sulfides and sulfoxides provides evidence for the role of the three-coordinated positive sulfur atom in the activation of the *ortho*-carboxyl group involved in the lactam formation. (iv) The lack of



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spirosulfurane formation in the conversion of the compounds **7** and **9** may be ascribed to the structure of four- or six-membered spiorings which are less favourable than the rings in the five-membered analogues.[2,3,12]

Conversion of Sulfides

When the sulfide **5** was treated with dichloramine-T in cold pyridine, the crystalline spirosulfurane **19** was formed immediately. Since under similar conditions we failed to isolate a crystalline product from the reaction of sulfides **4** and **6** with dichloroamine-T, the mixtures were treated with hot water to give the lactams **21** and **23**, respectively. All these products were also obtained by the dehydration of the corresponding sulfoxides, suggesting that both reactions may proceed through a common intermediate. As shown earlier,[1] cyclic acyloxysulfonium intermediates (see e.g. **20** and **24**) can also be formed from carboxy-sulfides by electrophilic Cl^+ addition to sulfur, followed by the intramolecular nucleophilic attack of the carboxyl group on the positive sulfur centre.

The molecular structure of the lactam-sulfoxide **23** has been determined by X-ray diffraction method. Results will be published elsewhere.[13]

EXPERIMENTAL

Melting points were determined with a Boetius microscopic melting point apparatus. Reaction courses and product mixtures were monitored by TLC on silica gel F254 plates with visualization by UV light. IR spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. Bruker AC-80 and Bruker WM-250 spectrometers were used to obtain NMR spectra. Mass spectra were determined at 70 eV on Kratos MS-50 and Kratos MS-25-RFA spectrometers through solid probe (SP/MS) introduction (only molecular ions are listed). In absence of clearly detectable molecular ions, CI was employed on the same instrument. Solvents were purified and dried by usual methods; pyridine by distillation over P_2O_5. All the substances were dried over P_2O_5 *in vacuo*.

2-(2-Trifluoracetylaminophenylthio)benzoic acid (**4**). 2-Iodo-nitrobenzene (**10**; 74.7 g, 0.3 mol) and thiosalicylic acid (**11**; 47.2 g, 0.3 mol) were dissolved in dry pyridine (270 cm^3) under N_2, and copper(I) oxide (21.5 g, 0.15 mol) was added to the solution. After boiling for 3 hours, the mixture was poured onto 5% aqueous HCl (2.5 L), and left standing for a day. The precipitate was thoroughly ground, filtered off, washed with water and dissolved in 2 M NaOH solution (1.5 L). After filtration the filtrate was poured onto 37% aqueous HCl. The precipitate was filtered off, washed with water and dried to yield *2-(2-nitrophenylthio)benzoic acid* (**12**; 70 g, 85%). The crude product was crystallized from ethanol, mp. 170–172.5° C (lit.,[5] 166–169°C).

A mixture of the nitro compound **12** (41.3 g, 0.15 mol), ferrum reductum (100.8 g, 1.8 mol), crystalline iron(III) chloride (10.1 g, 37.5 mmol) and water (250 cm^3) was stirred and heated on a steam bath for 12 hours. Then ethanol (200 cm^3) was added to the mixture, with heating continued for another 5 hours. Then 25% aqueous NH_4OH (100 cm^3) was added and the solution was decanted after boiling for a few minutes. The remaining paste was boiled three times with 5% aqueous NH_4OH solutions. The filtered solutions were poured onto 37% aqueous HCl. Next day the precipitate was filtered off, washed with water and dried to give *2-(2-aminophenylthio)benzoic acid hydrochloride* (**13**; 35.0 g, 83%), mp. 184–188° C (Found: C, 55.7; H, 4.3; N, 5.5; S, 10.8; Cl, 12.6. Calcd. for $C_{13}H_{12}ClNO_2S$(281.761): C 55.40; H 4.30; N 4.97; S 11.38; Cl, 12.60%); ν_{max}(KBr)/cm^{-1} 3265–1800br (NH_3^+, OH); 1678vs (C=O).

To a suspension of the amine hydrochloride **13** (21.1 g, 75 mmol) in dioxane (70 cm^3) was added trifluoroacetic anhydride (21.2 cm^3, 0.148 mol), and the mixture was stirred at room temperature for 18 hours, then poured onto water (300 cm^3). The precipitate was filtered off, washed with water and dried, yielding 25.4 g (95%) of crude **4**, which was crystallized from ethanol, mp. 231–232.5°C (Found: C, 52.7; H, 3.2; N, 4.2; S, 9.1%; M^+, 341. Calcd. for $C_{15}H_{10}F_3NO_3S$: C, 52.78; H, 2.95; N, 4.10; S, 9.39%; M, 341.304); δ_H [80 MHz; $(CD_3)_2SO$; DSS] 6.78 (1H, m, 3-H at NHAc-ring), 7.2–7.8 (6H, overlapping m's, ArH), 8.04 (1H, m, 6-H at CO_2H-ring), 11.08 (1H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 115.9 (q, J 289, CF_3CO), 125.1, 127.5, 127.7, 128.7, 128.7 overlapping, 129.6, 130.4, 130.8, 132.3, 136.7, 137.5, 140.0 (C_{Ar}), 155.4 (q, J 37, CF_3CO), 167.5 (CO_2H); ν_{max}(Kbr)/cm^{-1} 3335s (NH), 3300–2100br (OH), 1721vs, 1689vs (C═O), 1189vs (CF_3).

2-(8-Trifluoroacetylamino-1-naphthylthio)benzoic acid (**5**). 8-Bromo-1-aminonaphthalene (**17**[7]; 22.2 g, 0.1 mmol) was dissolved in pyridine (50 cm^3) and trifluoroacetic anhydride (40 cm^3, 0.28 mol) was added dropwise (1 hour) to the solution which was cooled with ice-salt and shaken occasionally; then the mixture was left standing in ice-water for 1 hour. Most of the pyridine was evaporated *in vacuo*, then water was added to the mixture which was left standing overnight. The precipitate was filtered off, washed with water and dried. Crystallization from methanol-water yielded *8-bromo-1-trifluoroacetylaminonaphthalene* (**18**; 26.0 g, 82%), mp. 106–109°C (crystallizes on the plate) and 115–118°C (Found: C, 45.1; H, 2.5; Br, 25.1; F, 17.2; N, 4.5. Calcd. for $C_{12}H_7BrF_3NO$(318.102): C, 45.31; H, 2.22; Br, 25.12; F, 17.92; N, 4.40%).

The mixture of the amide **18** (26 g, 81.7 mmol), thiosalicylic acid (**11**; 12.6 g, 81.7 mmol), copper(I) oxide (5.8 g, 40.9 mmol), dry pyridine (20 cm^3) and dry DMF (100 cm^3) was boiled for 8 hours under N_2. The reaction mixture was cooled and poured slowly onto 20% aqueous HCl (200 cm^3) with external ice-water cooling. The precipitate was powdered, then water (1 L) was added and the solid was filtered off, washed with water and stirred with a mixture of saturated $NaHCO_3$ solution (500 cm^3) and water (300 cm^3) at room temperature for 5 hours. After filtration the filtrate was added to 20% aqueous HCl (200 cm^3). The precipitate was filtered off, washed with water and dried, yielding 24.5 g (76%) of the crude sulfide **5**. After five recrystallizations from dry ethanol mp. 213–214.5°C (Found: C, 58.2, H, 3.5; N, 3.8; S, 8.3%, M^+, 391. Calcd. for $C_{19}H_{12}F_3NO_3S$: C, 58.31; H, 3.09; N, 3.58; S, 8.19%; M, 391.364); δ_H [80 MHz; $(CD_3)_2SO$; DSS] 6.35 (1H, dd, 4.7 Hz, 7-H at NHAc-ring), 7.2–7.4 (2H, overlapping m's, 3-H at CO_2H-ring and 2-H at NHAc-ring), 7.7–8.4 (7H, overlapping m's, ArH), 11.44 (1H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 119.8 (q, J 289, $COCF_3$), 128.4, 129.9, 130.3, 130.5, 130.7, 130.8, 130.9, 133.1, 133.4, 134.8, 135.7, 136.2, 139.8, 139.8 overlapping, 143.3, 146.2 (C_{AR}), 158.9 (q, J 36, $COCF_3$), 171.1 (CO_2H); ν_{max}(KBr)/cm^{-1} 3222m (NH), 3250–2150br (OH), 1725vs, 1685vs (C═O), 1195vs (CF_3)

2-(2'-Trifluoroacetylamino-2-biphenylylthio)benzoic acid (**6**). A mixture of crude 2-iodo-2'-nitrobiphenyl (**14**[6]; 31.5 g, 97 mmol), thiosalicylic acid (**11**; 15 g, 97 mmol), copper(I) oxide (6.95 g, 48.5 mmol), dry pyridine (35 cm^3) and dry DMF (160 cm^3) was boiled for 12 hours under N_2, then poured onto the mixture of water (1 L) and 20% aqueous HCl (120 cm^3). The precipitate was filtered off, washed with water and dissolved in 2 M NaOH solution (1.5 L). After filtration the solution was poured onto 37% aqueous HCl. The precipitate was filtered off, washed with water and dried to yield crude *2-(2'-nitro-2-biphenylylthio)benzoic acid* (**15**; 30.1 g, 88%) which was crystallized from acetic acid, mp. 244–246.5°C (Found: C, 65.0; H, 3.6; N, 4.2; O, 19.3; S, 8.9. Calcd. for $C_{19}H_{13}NO_4S$(351.368): C, 64.94; H, 3.73; N, 3.99; O, 18.21; S, 9.13%); ν_{max}(KBr)/cm^{-1} 3300-2000br (OH), 1682vs (C═O), 1525s, 1353s (NO_2).

A mixture of the nitro compound **15** (38.9 g, 0.11 mol), ferrum reductum (37.2 g, 0.66 mol), crystalline iron(III) chloride (3.7 g, 14 mmol) and water (150 cm^3) was heated on a steam bath for 12 hours. Then ethanol (150 cm^3) was added and the mixture was heated for 3 hours. Finally 25% aqueous NH_4OH (100 cm^3) was added to the mixture, and after heating for 5 minutes, the solution was decanted. The remaining paste was boiled three times with 5% aqueous NH_4OH solutions. The filtered solutions were poured onto 37% aqueous HCl. Next day the precipitated *2-(2'-amino-2-biphenylylthio)benzoic acid hydrochloride* (**16**) was filtered off, washed with water and dried. Yield: 33.0 g (84%), mp. 177–187°C (Found: C, 62.3; H, 4.8; Cl, 11.3; N, 5.2; S, 8.3. Calcd. for $C_{19}H_{16}ClNO_2S$(357.849): C, 63.77; H, 4.50; Cl, 9.92; N, 3.92; S, 8.96%); ν_{max}(KBr)/cm^{-1} 3265–1750br (NH_3^+, OH), 1696s (C═O).

2-(2'-Amino-2-biphenylylthio)benzoic acid hydrochloride (**16**; 14.3 g, 40 mmol) was suspended in dry dioxane (40 cm^3) and trifluoroacetic anhydride (11.0 cm^3, 78 mmol) was dropped to the stirred mixture at 0°C. With the addition complete, external cooling was stopped and stirring continued for 3 hours. The mixture was left standing overnight, then water was added. The precipitate was filtered off, washed with water and dried to yield the crude carboxy-sulfide **6** (14.8 g, 89%) which was crystallized from ethanol-water mp. 183–195°C (M^+, 417. Calcd. for $C_{21}H_{14}F_3NO_3S$: M, 417.396); δ_H [80 MHz;

$(CD_3)_2SO$; DSS] 6.97 (1H, dd, 7.7 Hz, 1.5 Hz, 3′-H), 7.2–7.7 (10H, overlapping m's, ArH), 7.98 (1H, dd, 7.4 Hz, 2.0 Hz, 6-H at CO_2H-ring), 10.89 (1H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 115.8 (q, *J* 288, $COCF_3$), 124.6, 126.8, 127.0, 128.1, 128.4, 128.5, 128.7, 129.2, 130.2, 130.5, 131.1, 132.0, 132.4, 132.6, 135.8, 137.3, 141.6, 142.2 (C_{Ar}), 154.9 (q, *J* 36, $COCF_3$), 167.2 (CO_2H); ν_{max}(KBr)/cm^{-1} 3419m (NH), 3250–2150br (OH), 1723vs, 1692vs ($C{=}O$), 1179vs (CF_3). TLC analysis indicated some contamination which could not be removed with crystallization. The purified product was examined by RP-HPLC analysis and two unidentified by-products were found (less than 4 – 4%). RP-HPLC: ODS-Hypersil-5 column (125 × 4 mm), eluent: methanol-0.02 M sodium-acetate buffer (pH 4.0) 60:40 (v/v), flow speed: 1.1 cm^3/minute, detection: UV, 254 nm, instrument: Knauer Model.

2-(2-Trifluoroacetylaminophenylsulfinyl)benzoic acid (**7**). 2-(2-trifluoroacetylaminophenylthio)benzoic acid (**4**; 6.82 g, 20 mmol) was dissolved in a mixture of dichloromethane (500 cm^3) and trifluoracetic acid (60 cm^3), then *tert*-butyl hypochlorite (3 cm^3, 24 mmol) was added to the stirred solution at 0°C. After 1.5 hours water (2 cm^3) and *tert*-butyl hypochlorite (0.3 cm^3, 2.4 mmol) were added and stirring was continued for a few minutes. The solvent was removed *in vacuo*. The crude product (7.13 g) was crystallized from methanol-water to give the pure sulfoxide **7** (5.25 g, 74%), mp. 222–229°C (Found: C, 50.4; H, 2.8; F, 16.2; N, 4.2; S, 9.0%; M^+, 357. Calcd. for $C_{15}H_{10}F_3NO_4S$: C, 50.42; H, 2.82; F, 15.95; N, 3.92; S, 8.97%; M, 357.304); δ_H [80 MHz; $(CD_3)_2SO$; DSS] 7.3–8.1 (7H, overlapping m's, ArH), 8.43 (1H, d, 7.7 Hz, 6-H at CO_2H-ring), 11.19 (1H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 117.6 (q, *J* 289, $COCF_3$), 126.9, 127.1, 129.4, 129.5, 129.8, 132.8, 133.2, 133.6, 135.3, 135.7, 141.1, 148.2 (C_{Ar}), 156.6 (q, *J* 37, $COCF_3$), 168.4 (CO_2H); ν_{max}(KBr)/cm^{-1} 3450–2200br (NH), (OH), 1716vs ($C{=}O$), 1235–1149br (CF_3), 1014vs ($S{=}O$).

2-(8-Trifluoroacetylamino-1-naphthylsulfinyl)benzoic acid (**8**). To the solution of 2-(8-trifluoroacetylamino-1-naphthylthio)benzoic acid (**5**; 1.56 g, 4 mmol) in pyridine (7 cm^3) was added water (2 cm^3). The solution was cooled to −5°C and phenyltrimethylammonium tribromide (1.58 g, 4.2 mmol) was added. The mixture was stirred for 2 hours, left to warm up to room temperature, then poured onto 1 M H_2SO_4 (200 cm^3). Next day the crystals were filtered off, washed with water and dried. The crude product (1.6 g) was crystallized from methanol-water, then from methanol and finally from acetone. Yield: 0.94 g (58%), mp. 188–190°C (Found: C, 55.8; H, 3.0; F, 14.0; S, 7.7%; M^+, 407. Calcd. for $C_{19}H_{12}F_3NO_4S$: C, 56.02; H, 2.97; F, 13.99; S, 7.87%; M, 407.364); δ_H [250 MHz; $(CD_3)_2SO$; DSS] 7.5–7.8 (5H, overlapping m's, ArH), 8.0 (1H, t, 7.5 Hz, 5-H at CO_2H-ring), 8.2–8.4 (4H, overlapping m's, ArH), 11.38 (1H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 117.8 (q, *J* 289, $COCF_3$), 127.8, 128.0, 128.3, 129.8, 131.0, 131.7, 132.8, 133.4, 134.3, 135.0, 135.5, 136.5, 145.2, 148.7 (C_{Ar}), 157.7 (q, *J* 37, $COCF_3$), 168.6 (CO_2H); ν_{max}(KBr)/cm^{-1} 3330 m (NH), 3200–2100br (OH), 1725vs, 1691vs ($C{=}O$), 1265–1153br (CF_3), 984s ($S{=}O$).

2-(2′-Trifluoroacetylamino-2-biphenylylsulfinyl)benzoic acid (**9**). 2-(2′-Trifluoroacetylamino-2-biphenylylthio)benzoic acid (**6**; 2.08 g, 5 mmol) was dissolved in a mixture of dichloromethane (100 cm^3) and trifluoroacetic acid (20 cm^3). To the solution *tert*-butyl hypochlorite (0.74 cm^3, 6 mmol) was added dropwise at 0°C. After stirring for 1.5 hours water (2 cm^3) was added, and the solvent was removed *in vacuo*. The remaining solid was crystallized from methanol-water. Yield: 1.5 g (70%), mp. 167–184°C (Found: C, 58.5; H, 3.6; F, 13.4; N, 3.2; S, 7.6%; $M^{\bullet}$, 433. Calcd. for $C_{21}H_{14}F_3NO_4S$: C, 58.19; H, 3.26; F, 13.15; N, 3.23; S, 7.40%; M, 433.396); δ_H [250 MHz; $(CD_3)_2SO$; DSS] 6.83 (1H, d, 7.5 Hz, 3′-H), 7.1–8.2 (10H, overlapping m's, ArH), 8.33 (1H, d, 7.5 Hz, 6-H at CO_2H-ring), 9.87 (1H, s, NH), 10.44 (1 H, s, CO_2H); δ_C [20 MHz; $(CD_3)_2SO$; DSS] 117.3 (q, *J* 289, $COCF_3$), 125.5, 127.1, 128.4, 128.9, 130.4, 132.3, 132.7, 132.9, 134.4, 135.2, 137.0, 139.0, 139.8, 145.3, 146.3, 146.8 (C_{Ar}), 156.8 (q, *J* 37, $COCF_3$), 167.5 (CO_2H); ν_{max}(KBr)/cm^{-1} 3450–3200br (NH), 3200–2100br (OH), 1737vs, 1699vs ($C{=}O$), 1275–1153br (CF_3), 993s ($S{=}O$).

2′-Trifluoroacetyl-spiro[3H-2,1-benzoxathiol-1,1′λ⁴-2H-naphtho[1,8-cd]isothiazol]-3-one (**19**). (a) To the solution of 2-(8-trifluoroacetylamino-1-naphthylsulfinyl)benzoic acid (**8**; 0.19 g, 0.47 mmol) in dry DMF (1.5 cm^3) was added trifluoroacetic anhydride (0.6 cm^3, 4.3 mmol) at room temperature. The crystals obtained were filtered off under Ar and washed with dry benzene. Yield: 0.14 g (76%) of **19**, mp. 163–166°C (Found: C, 58.6; H, 3.1; F, 14.9; S, 8.1%; M^+, 389. Calcd. for $C_{19}H_{10}F_3NO_3S$: C, 58.61; H, 2.59; F, 14.64; S, 8.24%; M, 389.344); δ_H [80 MHz; $CDCl_3$; TMS] 7.4–8.6 (overlapping m's, ArH); δ_C [20 MHz, $CDCl_3$, TMS]: 110.2 (7-C_n), 119.6 (5-C_n), 133.0 and 133.2 (9a-C_n and 10a-C_n), 134.8 (2-C_b), 137.6 (1-C_n), 138.9 (1-C_b), 143.8 (6-C_b); 170.0 (COO) {benzene (*b*) and naphthalene (*n*) peaks characteristic for sulfurane structure were assigned by DEPT}; ν_{max}(KBr)/cm^{-1} 1715vs, 1685vs ($C{=}O$), 1210s, 1197s, 1186s, 1151s, 1139s, 1129s (CF_3).

(b) To the solution of 2-(8-trifluoroacetylamino-1-naphthylthio)benzoic acid (**5**; 0.2 g, 0.5 mmol) in dry pyridine (0.4 cm^3) was added dichloramine-T (0.062 g, 0.26 mmol) at 0°C. Then the crystals were filtered off under Ar, washed with dry pyridine and dry benzene, then dried. Yield: 0.1 g, (49%) of **19**, mp. 162–165°C.

Hydrolysis of the spirosulfurane **19**. 0.01 g (0.023 mmol) of the spirosulfurane **19** was dissolved in acetone-water mixture (4:1 v/v; 1 cm^3), and the solution was kept at room temperatures for an hour. After evaporation a drab coloured material remained containing 5–10% baseline by-product (tlc) and *2-(8-trifluoroacetylamino-1-naphthylsulfinyl)benzoic acid* (**8**) (tlc and IR) Yield: 0.01 g (about 100%), mp. 187–189°C.

Dibenzo[b,f][1,4]thiazepin-11(10H)one 5-oxide (**21**). (a) To a solution of 2-(2-trifluoroacetylaminophenylsulfinyl)benzoic acid (**7**; 0.46 g, 1.3 mmol) in DMF (5cm^3) was added trifluoroacetic anhydride (1.2 cm^3, 8.5 mmol). The mixture was heated on a steam bath for 1 hour and after 12 hours at room temperature poured onto water. The precipitate was filtered off, washed with water and dried to yield 0.23 g (74%) of the lactam **21**. After crystallization from acetic acid-water mp. 302–310°C (lit.,[9] 314–316°C) (Found: C, 64.0; H, 3.6; N, 5.8; O, 14.0; S, 13.0%; M^+, 243. Calcd. for $C_{13}H_9NO_2S$: C, 64.20; H, 3.70; N, 5.76; O, 13.15; S, 13.16%; M, 243.276); δ_H [80 MHz; $(CD_3)_2SO$; DSS]: 7.3–7.9 (8H, m, overlapping m's, ArH), 10.97 (1H, s, NH); ν_{max}(KBr)/cm^{-1} 3300–2850br (NH), 1673s (C=O), 1030m, 1023m (S=O).

(b) To a solution of 2-(2-trifluoroacetylaminophenylthio)benzoic acid (**4**; 0.17 g, 0.5 mmol) in dry pyridine (0.4 cm^3) was added dichloramine-T (0.062 g, 0.26 mmol) at 0°C. No crystallization occurred. After 30 minutes water (5 cm^3) was added. The mixture containing an oily phase was heated on a steam bath for 1 hour, then the crystals formed were filtered off, washed with water, dried, and mixed with a small amount of dry acetone. After 1 hour the mixture was filtered, and the crystals were washed with acetone to yield the lactam **21** (0.02 g, 16%) mp. 304–312°C.

Benzo[b]naphtho[1,8-fg][1,5]thiazocin-8(7H)-one 13-oxide (**22**). (a) To a solution of 2-(8-trifluoroacetylamino-1-naphthylsulfinyl)benzoic acid (**8**; 0.2 g, 0.48 mmol) in dry DMF (1.5 cm^3) was added trifluoroacetic anhydride (0.6 cm^3, 4.3 mmol). The spirosulfurane **19** crystallized rapidly. The mixture was heated on a steam bath for an hour. The clear solution obtained was poured onto water. The precipitate was filtered off, washed with water and acetone, then dried to yield the lactam **22** (0.09 g, 66%) mp. 287–291°C (Found: C, 68.7; H, 3.5; N, 4.6; S, 10.7%; M^+, 293. Calcd. for $C_{17}H_{11}NO_2S$: C, 69.60; H, 3.79; N, 4.77; S, 10.93%; M, 293.332); ν_{max}(KBr)/cm^{-1} 3350–2800m (NH), 1666vs (C=O), 1073s, 1026m (S=O).

Tribenzo[b,f,h][1,5]-thiazonin-10(9H)-one 15-oxide (**23**). (a) To a solution of 2-(2′-trifluoroacetylamino-2-biphenylylsulfinyl)benzoic acid (**9**; 0.12 g, 0.27 mmol) in dry DMF (2 cm^3) was added trifluoroacetic anhydride (0.5 cm^3, 3.5 mmol). The mixture was heated on a steam bath for an hour then poured onto water. The precipitate was filtered off, washed with water and dried, yielding 0.08 g (97%) of the lactam **23**, mp. 208–216°C (Found: C, 70.8; H, 4.1; N, 4.3; O, 10.3; S, 9.8%; M^+, 319. Calcd. for $C_{19}H_{13}NO_2S$: C, 71.47; H, 4.07; N, 4.38; O, 10.02; S, 10.03%; M, 319.368); δ_H [250 MHz; $(CD_3)_2SO$; DSS] 7.21 (1H, ≈d, 7.5 Hz, 8-H), 7.4–7.7 (9H, overlapping m's, ArH), 7.9 (1H, td, 7.5 Hz, 1.5 Hz, 12-H), 8.12 (1H, ≈d, 7.5 Hz, 11-H), 10.56 (1H, s, NH); ν_{max}(KBr)/cm^{-1} 3250–2900br (NH), 1681s (C=O), 1015s (S=O).

(b) To a solution of 2-(2′-trifluoroacetylamino-2-biphenylylthio)benzoic acid (**6**; 0.21 g, 0.5 mmol) in dry pyridine (0.4 cm^3) was added dichloramine-T (0.062 g, 0.26 mmol) at 0°C. No crystallization occurred. After 30 minutes water (5 cm^3) was added. The mixture containing an oily phase was heated on a steam bath for an hour. The solid obtained was ground, then filtered off, washed with water, dried and mixed with a small amount of acetone. After standing for an hour the product was filtered off and washed with acetone to yield the lactam **23** (0.05 g, 32%) mp. 218–223°C.

Dibenzo[b,f][1,4]thiazepin-11(10H)one (**27**). To a solution of 2-(2-trifluoroacetylaminophenylthio)benzoic acid (**4**; 0.44 g, 1.3 mmol) in dry DMF (5 cm^3) was added trifluoracetic anhydride (1.2 cm^3, 8.5 mol). The mixture was heated on a steam bath for an hour, left standing overnight and poured onto water. The precipitate was filtered off, washed with water and dried to yield 0.35 g crude product, which was stirred with 1 M $KHCO_3$ solution for a day. The suspension was filtered to give 0.15 g (55%) of the lactam **27**, mp. 261–264°C (lit.,[9] 263–265°C); ν_{max}(KBr)/cm^{-1} 2700–3300br (NH), 1641s (C=O).

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