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Unexpected water addition to fluorinated 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines with the formation of 2-amino-*N*-sulfinylbenzenesulfenamides[†]

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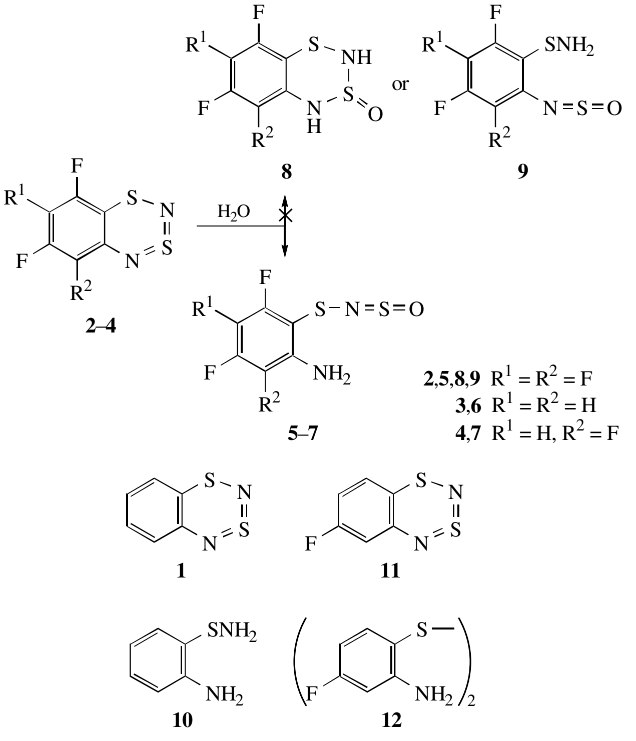
Fluoro-containing 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines 2–4 unexpectedly add water to give previously unknown 2-amino-*N*-sulfinylbenzenesulfenamides 5–7 as the first derivatives of still undescribed 2-aminobenzenesulfenamide 10.

Hyperelectronic (π- and σ-excessive) 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine[1] **1** and its derivatives[2–5] exhibit a nontrivial combination of antiaromaticity[6,7] with moderate thermal stability and photostability.[1–5,8–15]

The chemistry of these compounds is imperfectly understood.[1–5,8–16] Since both π-excessiveness and antiaromaticity are destabilising factors, one can believe that the heteroatom reactivity of **1** and its derivatives is high, and various new structural types can be observed among the reaction products.



Scheme 1

Indeed, we found that individual fluorine-containing compounds **2–4** (which are solids under normal conditions) unexpectedly add water to give previously unknown 2-amino-*N*-sulfinylbenzenesulfenamides **5–7** (Scheme 1)[‡] as the first derivatives of still undescribed 2-aminobenzenesulfenamide **10**.

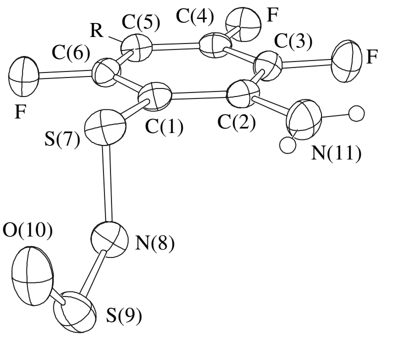


Figure 1 X-ray structures for the molecules of **5** (R = F) and **7** (R = H). Selected bond lengths (Å) and bond angles (°). **5**: S(7)–C(1) 1.756(4), S(7)–N(8) 1.676(3), N(8)–S(9) 1.529(3), S(9)–O(10) 1.454(3); C(1)–S(7)–N(8) 110.4(2), S(7)–N(8)–S(9) 121.5(2), N(8)–S(9)–O(10) 117.2(2). **7**: S(7)–C(1) 1.748(3), S(7)–N(8) 1.665(2), N(8)–S(9) 1.524(2), S(9)–O(10) 1.466(3); C(1)–S(7)–N(8) 100.2(1), S(7)–N(8)–S(9) 121.6(2), N(8)–S(9)–O(10) 116.7(2).

Taking into account high volatility of the title compounds,[8–10,15] it is believed that under macroscopically heterogeneous conditions the addition of water actually proceeded in a gas phase followed by the precipitation of products **5–7** as solids on the walls of the reaction vessel.[‡] Generally, the formation of **5–7** from **2–4** under the action of water is paradoxical since it is well known that RNSO derivatives are highly unstable toward hydrolysis to give corresponding RNH_2.[17] Seemingly, the kinetically unfavourable reaction conditions prevent compounds **5–7** from further hydrolysis. The homogeneous hydrolysis of **2** and other partially fluorinated compounds of this type in organic solvents gives corresponding 2,2′-diaminodiphenyl disulfides.[3]

According to the ΔH_f^0 PM3 calculations, compound **5** is less stable than its heterocyclic isomer **8** (Scheme 1) by

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[†] *Names.* According to the IUPAC rules, compounds **5–7** should be named 2-[(sulfinylamino)sulfanyl]anilines or 2-[(sulfinylamino)sulfanyl]phenylamines. This information was obtained using the ACD/IUPAC Lab Web service (ACD/IUPAC Name Free 6.04).

[‡] *Syntheses.* Compounds **5–7**, **12**. Under vacuum, 9 mg (0.5 mmol) of water was condensed into a 500 ml flask containing 0.5 mmol of corresponding **2–4**[1–5] as solids. After storage for 30 days at ambient temperature, the solid products were dissolved in CCl_4, the solution was filtered, the filtrate was evaporated under reduced pressure, and the residue (consisted of unreacted starting materials **2–4** and corresponding final products **5–7**) was fractionally sublimed in a vacuum and recrystallised from hexane. Compounds **5–7** were obtained as colourless (**5**) or yellow (**6**,**7**) crystals.

Compound **5**, 25 % (45% conversion of **2**), mp 97–98 °C. ^{1}H NMR ($CDCl_3$), δ: 4.47. ^{19}F NMR (C_6F_6) δ: 29.7, 11.9, 1.8, –9.5. ^{13}C NMR, δ: 147.1, 143.7, 136.2, 134.3, 132.7, 100.5. ^{14}N NMR [NH_3 (liq.)], δ: 336, 45. UV (heptane) λ_{max}/nm (log ε): 314 (3.96), 257 (3.57), 252 (3.59), 232 (3.84). MS, *m/z*: 257.9537 (M$^+$; calc. for $C_6H_2F_4N_2OS_2$: 257.9545).

Compound **6**, 28% (35% conversion of **3**), mp 102–104 °C. ^{1}H NMR ($CDCl_3$) δ: 6.27, 6.27, 4.64. ^{19}F NMR (C_6F_6) δ: 61.8, 60.0. ^{13}C NMR, δ: 166.3, 163.3, 150.7, 99.4, 97.7, 94.0. ^{15}N NMR [NH_3 (liq.)] δ: 341.0, 64.3. UV (heptane) λ_{max}/nm (log ε): 313 (3.88), 242 (3.86), 219 (4.20). MS, *m/z*: 221.9732 (M$^+$; calc. for $C_6H_4F_2N_2OS_2$ 221.9733).

Compound **7**, 64% (83% conversion of **4**), mp 88–90 °C. ^{1}H NMR ($CDCl_3$) δ: 6.37, 4.71. ^{19}F NMR (C_6F_6) δ: 54.8, 31.1, –0.5. ^{13}C NMR, δ: 157.9, 152.8, 139.5, 135.9, 100.5, 93.5. ^{15}N NMR [NH_3 (liq.)] δ: 337.5, 54.0 (t, *J* 88 Hz). UV (heptane) λ_{max}/nm (log ε): 312 (3.93), 219 (4.18). MS, *m/z* 239.9638 (M$^+$; calc. for $C_6H_3F_3N_2OS_2$: 239.9639).

Only 4,4′-difluoro-2,2′-diaminodiphenyl disulfide **12**[3] was obtained from **11**[3] under the same conditions (13%; 41% conversion of **11**). After the sublimation of unreacted **11**, compound **12** was isolated as a salt by treatment of the residue with HCl. After conversion into a free base, **12** was identified by a comparison of its mp and ^{1}H and ^{19}F NMR spectra with data for an authentic[3] sample. In the case of **1**,[1] the reaction resulted in unidentified tar containing no 2,2′-diaminodiphenyl disulfide (comparison with an authentic sample).[22]

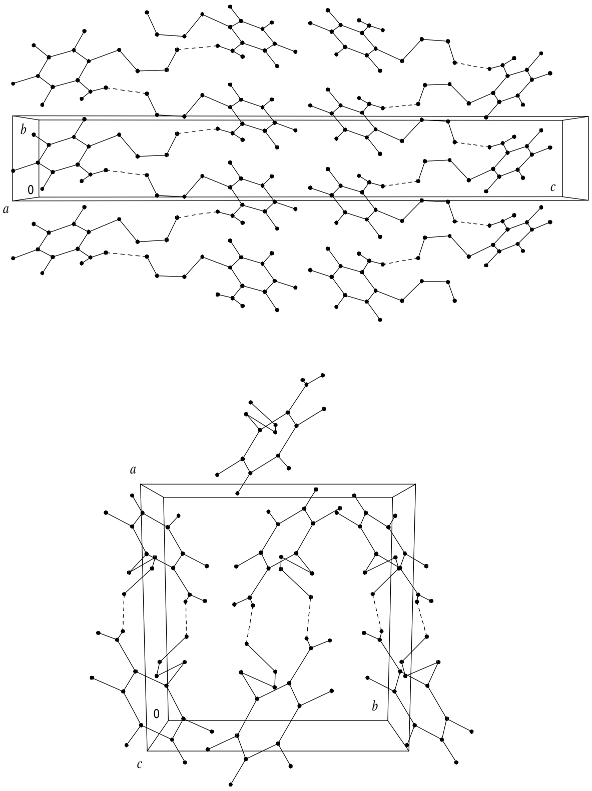

Figure 2 Molecular packing of compounds **5** (upper) and **7** (lower) in crystals.

20–24 kcal mol^{-1} (for various conformations of **8**) and more stable than acyclic isomer **9** by ~4 kcal mol^{-1}. We can speculate that the transformation of **2** into **5** is kinetically controlled and does not include the intermediate participation of **8**.

In contrast to **2**–**4**, parent compound **1** and its derivative **11** give only unidentified tar and disulfide **12**, respectively, under the same conditions.[‡] Intermediate compounds were neither isolated nor detected in the reaction mixtures by GC-MS or ^{1}H and ^{19}F NMR spectroscopy. The reason for this difference between **1**, **11** and **2**–**4** is unclear. For example, the $\Delta\Delta H^0_\mathrm{f}$ (PM3) for the hydrocarbon analogues of compounds **5**, **8** and **9** is almost the same as that for **5**, **8** and **9** themselves.

The structures of **5** and **7** were confirmed by X-ray diffraction analysis (Figure 1).[§] The crystals of compound **6** were not suitable for an X-ray study. The –S–N=S=O moiety is planar (within 0.004 Å for **5** and 0.006 Å for **7**) and virtually orthogonal to an aromatic ring [the dihedral angle is 83.9(1)° for **5** or 97.5(1)° for **7**].

Although the molecules of **5** and **7** are structurally similar, their crystal packings exhibited different supramolecular motifs (Figure 2). In the case of **5**, a hydrogen-bonded 1D network was observed as infinite zigzag chains along the crystallographic axis *b* featured a shortened[18] N–H···O contact of 2.31(4) Å and an N–H···O angle of 157(4)°. For **7**, 0D network was found as hydrogen-bonded centrosymmetric dimers with an N–H···O distance of 2.50(4) Å and an N–H···O angle of 163(4)°. Additionally, the molecules of neighbouring hydrogen-bonded dimers of **7** demonstrated a parallel-slipped arrangement of aromatic rings with an interplanar separation of 3.43 Å and a distance between ring centroids of 4.10 Å, thus forming pseudo-π-stacked centrosymmetric dimers. It is well known that weak non-covalent interactions[19] play significant roles in controlling molecular conformations, packing structures in crystals, and molecular recognition. In particular, both π-stacking interactions and hydrogen bonds are known to be general supramolecular synthons of significant importance with regard to new developments in crystal engineering.[18–20]

Thus, first derivatives **5**–**7** of unknown 2-aminobenzenesulfenamide **10** were prepared by unusual water addition to $1,3\lambda^4\delta^2,2,4$-benzodithiadiazines **2**–**4** and structurally characterised. Significantly, neither **10** (*a priori* useful synthon) nor its derivatives can be prepared in an obvious way, for example, by the reduction of 2-nitrobenzenesulfenamides or 1,2,3-benzothiadiazoles, due to the well-known instability of sulfenamide S–N linkages under the mildest reductive conditions.[21]

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References

1 A. W. Cordes, M. Hojo, H. Koenig, M. C. Noble, R. T. Oakley and W. T. Pennington, *Inorg. Chem.*, 1986, **25**, 1137.

2 A. V. Zibarev, Yu. V. Gatilov and A. O. Miller, *Polyhedron*, 1992, **11**, 1137.

3 I. Yu. Bagryanskaya, Yu. V. Gatilov, A. Yu. Makarov, A. M. Maksimov, A. O. Miller, M. M. Shakirov and A. V. Zibarev, *Heteroatom Chem.*, 1999, **10**, 113.

4 A. Yu. Makarov, I. Yu. Bagryanskaya, Yu. V. Gatilov, T. V. Mikhalina, M. M. Shakirov, L. N. Shchegoleva and A. V. Zibarev, *Heteroatom Chem.*, 2001, **12**, 563.

5 A. Yu. Makarov, I. Yu. Bagryanskaya, F. Blockhuys, C. van Alsenoy, Yu. V. Gatilov, V. V. Knyazev, A. M. Maksimov, T. V. Mikhalina, V. E. Platonov, M. M. Shakirov and A. V. Zibarev, *Eur. J. Inorg. Chem.*, 2003, 77.

6 V. I. Minkin, M. N. Glukhovtsev and B. Ya. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley, New York, 1994.

7 K. B. Wiberg, *Chem. Rev.*, 2001, **101**, 1317 (and other articles of this special issue).

8 A. P. Hitchcock, R. S. DeWitte, J. M. van Esbroek, P. Aebi, C. L. French, R. T. Oakley and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 1991, **57**, 165.

9 N. E. Petrachenko, Yu. V. Gatilov and A. V. Zibarev, *J. Electron Spectrosc. Relat. Phenom.*, 1994, **67**, 489.

10 A. V. Manaev, A. Yu. Makarov, Yu. V. Gatilov, J. N. Latosinska, V. V. Shcherbukhin, V. F. Traven and A. V. Zibarev, *J. Electron Spectrosc. Relat. Phenom.*, 2000, **107**, 33.

11 M. Schettino, R. M. Romano, C. O. Della Vedova, A. Yu. Makarov and A. V. Zibarev, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1411.

12 F. Blockhuys, S. L. Hinchley, A. Yu. Makarov, Yu. V. Gatilov, A. V. Zibarev, J. D. Woollins and D. W. H. Rankin, *Chem. Eur. J.*, 2001, **7**, 3592.

13 V. A. Bagryansky, I. V. Vlasyuk, Yu. V. Gatilov, A. Yu. Makarov, Yu. N. Molin, V. V. Shcherbukhin and A. V. Zibarev, *Mendeleev Commun.*, 2000, 5.

[§] *X-ray structure data for* **5** *and* **7**.

Compound **5**: $C_6H_2F_4N_2OS_2$, *M* 258.22, monoclinic, *a* = 6.376(1), *b* = 4.515(1), *c* = 30.798(5) Å, *β* = 91.89(1)°, *U* = 886.1(3) Å^3, space group $P2_1/n$, *Z* = 4, d_calc = 1.936 g cm^{-3}, μ(MoKα) = 0.637, 1685 reflections measured, 1532 unique (R_int = 0.051) reflections were used in the calculations. The final *R* (obs.) was 0.0472.

Compound **7**: $C_6H_3F_3N_2OS_2$, *M* 240.22, monoclinic, *a* = 9.7545(6), *b* = 9.3840(6), *c* = 9.8699(7) Å, *β* = 104.855(5), *U* = 873.3(1) Å^3, space group $P2_1/c$, *Z* = 4, d_calc = 1.827 g cm^{-3}, μ(MoKα) = 0.623, 1630 reflections measured, 1537 unique (R_int = 0.035) which were used in all calculations. The final *R* (obs.) was 0.0379.

The data were measured on a Bruker P4 diffractometer with graphite-monochromated MoKα radiation using $\theta/2\theta$ scans. The structures were solved by the direct methods using the SHELXS-97 program and refined in the full-matrix anisotropic (isotropic for H atoms) approximation by the SHELXL-97 program.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 184073 (**5**) and 184074 (**7**). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

14 I. V. Vlasyuk, V. A. Bagryansky, N. P. Gritsan, Yu. N. Molin, A. Yu. Makarov, Yu. V. Gatilov, V. V. Shcherbukhin and A. V. Zibarev, *Phys. Chem. Chem. Phys.*, 2001, **3**, 409.
15 N. P. Gritsan, V. A. Bagryansky, I. V. Vlasyuk, Yu. N. Molin, A. Yu. Makarov, M. S. Platz and A. V. Zibarev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1973 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2064).
16 A. V. Zibarev, Yu. V. Gatilov, I. Yu. Bagryanskaya, A. M. Maksimov and A. O. Miller, *J. Chem. Soc., Chem. Commun.*, 1993, 298.
17 R. Bussas, G. Kresze, H. Muensterer and A. Schwoebel, *Sulfur Reports*, 1983, **2**, 215.
18 L. N. Kuleshova and M. Yu. Antipin, *Usp. Khim.*, 1999, **68**, 3 (*Russ. Chem. Rev.*, 1999, **68**, 3).
19 K. Mueller-Detlefs and P. Hobza, *Chem. Rev.*, 2000, **100**, 143.
20 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
21 E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co., New York, 1958, vol. 1, p. 283.
22 M. A. T. Rogers and W. A. Sexton, *J. Chem. Soc.*, 1947, 1619.

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