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New fluorinated 1,2-diaminoarenes, quinoxalines, 2,1,3-arenothia(selena)diazoles and related compounds☆

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ABSTRACT

5,6,7,8-Tetrafluoroquinoxaline (**1**) and its previously unknown derivatives (**2**–**8**) were synthesized from glyoxal and polyfluorinated 1,2-diaminoarenes (**10**–**17**) obtained by reduction of corresponding 2,1,3-arenothiadiazoles (including new ones **21** and **22**). The thiadiazoles were prepared from polyfluorinated Ar–NH_2 via Ar–N=S=N–$SiMe_3$ (**34**–**37**) and their fluoride-induced nucleophilic *ortho*-cyclization. New approaches to Ar–N=S=N–$SiMe_3$ based on interaction between polyfluorinated Ar–N=SCl_2 (**32**) and $LiN(SiMe_3)_2$, and between $ArN(SiMe_3)Li$ and Me_3Si–N=S=O, were tried together with our previous synthetic method based on reaction of Ar–N=S=O with $Me_3SnLiN(SiMe_3)_2$. New polyfluorinated 2,1,3-arenoselenadiazoles (**26**–**28**) were prepared from corresponding diamines and SeO_2 and **26** also from the diamine and $SeCl_4$. Compounds synthesized were characterized by multinuclear NMR (particularly ^{1}H, ^{19}F, ^{77}Se), compounds **1**, **2**, **4**, **7**, **8**, **16** (salt with 2 HCl), **19**, **26**, **28** and **32** by single-crystal X-ray diffraction, and quinoxalines **1**–**8**, thiadiazole **22** and selenadiazoles **27** and **28** by UV-vis and fluorescence techniques.

1. Introduction

Aza-analogs of naphthalene, 10π-electron 6-6-bicyclic aromatic compound, play essentially important roles in many fields of chemistry, chemical technology and related disciplines. In particular, quinoxaline (benzopyrazine) and its derivatives represent one of the most significant groups of aza-aromatics for fundamental organic chemistry and its applications to biomedicine and materials science [1]. It is well known that in many cases hydrogen substitution by fluorine improves properties of both materials and pharmaceuticals [2], and preparation of low-fluorinated quinoxalines attracted considerable attention [3]. In this context it is rather astonishing that described polyfluorinated quinoxalines cover only 2,3,5,6,7,8-hexafluoroquinoxaline, 5,6,7,8-tetrafluoroquinoxaline (**1**, Chart 1) and a few 2,3-R_2 derivatives of the latter, and their properties are poor studied [4–6].

Polyfluorinated 2,1,3-benzochalcogenadiazoles (chalcogen: S, Se, Te), 10π-electron 5-6-bicyclic hetero analogs of (octafluoro) naphthalene, also received very limited attention [7,8] despite of the fact that the chemistry and numerous applications of their hydrocarbon congeners are extensively studied [9,10]. Only recently, persistent radical anions of polyfluorinated 2,1,3-benzochalcogenadiazoles were recognized as candidate building blocks for magnetically-active molecule-based functional materials [10a–c].

It should be noted that quinoxalines and 2,1,3-benzothia(selena)diazoles (structurally connected by mutual substitution of the C=C bond and S or Se atom) are closely related compounds since they have very similar π-electronic structure manifesting in similarity of their UV–vis [11] and HeI PES [12] spectra and spin

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density distribution in triplet state [13]. 2,1,3-Benzotelluradiazoles also fit the analogy [14].

In this work we report on atom-efficient one-step synthesis of compound **1** and its congeners **2**–**8** (Chart 1) from glyoxal and corresponding 1,2-diaminoarenes (**10**–**17**, Chart 1). The latter, including previously unknown **12**–**14** and **16**, were obtained by reduction of 4,5,6,7-tetrafluoro-2,1,3-benzothiadiazole [7a] and its easily accessible derivatives (**19**–**24**, Chart 1). The thiadiazoles were synthesized from polyfluorinated Ar–NH_2 via Ar–N=S=N–$SiMe_3$ (**34**–**37**) and their fluoride-induced nucleophilic *ortho*-cyclization. Two new approaches to polyfluorinated Ar–N=S=N–$SiMe_3$ compounds based on interaction between polyfluorinated Ar–N=SCl_2 (**32**, Chart 1) and $LiN(SiMe_3)_2$, and between $ArN(SiMe_3)Li$ and Me_3Si–N=S=O, were tried additionally to our previous synthetic method based on reaction of Ar–N=S=O with Me_3Sn-$LiN(SiMe_3)_2$. Besides quinoxalines, 1,2-diaminoarenes **13**, **14** and **17** were converted into polyfluorinated 2,1,3-arenoselenadiazoles (**26**–**28**, Chart 1) in the reaction with selenium dioxide and **13** also with selenium tetrachloride. Compounds synthesized were characterized by multinuclear NMR (particularly ^{1}H, ^{19}F, ^{77}Se), and compounds **1**, **2**, **4**, **7**, **8**, **16** (salt with 2 HCl), **19**, **26**, **28** and **31** by single-crystal X-ray diffraction (XRD; Table S1, Supporting Information). Additionally, fluorescence of quinoxalines **1**–**8** and chalcogenadiazoles **22**, **27** and **28** was measured to clarify applicability of optically-detected EPR (OD-EPR) technique to detecting their radical anions in the future work [15].

In the case of polyfluorinated 5-aminoindane, attempts to carry out the aforementioned functionalizations were unsuccessful for the reasons which are not entirely clear. Only N-sulfinylamine **31** was synthesized and isomeric thiadiazoles **25**a,b were observed in the reaction mixtures as minor components. Neither quinoxaline **9** nor diamine **18** and compound **38** (Chart 1) were prepared.

2. Results and discussion

In the hydrocarbon series, a classical approach to the synthesis of quinoxalines is condensation of aromatic 1,2-diamines with 1,2-diones (the Koerner-Hinsberg reaction) [16]. To the best of our knowledge, in the fluorocarbon series this approach was used only twice, namely, for preparing 2,3-R_2 derivatives of **1** [5] some of which are of interest as molecular tweezers.

The present work expands the discussed approach onto the synthesis of polyfluorinated quinoxalines via reaction between polyfluorinated 1,2-diaminoarenes and glyoxal. Previously, it was shown that polyfluorinated 1,2-diaminoarenes are easily accessible by reduction of corresponding 2,1,3-arenothiadiazoles [7]. The general synthetic route to those is based on transformation of fluorinated Ar–NH_2 into Ar–N=S=N–$SiMe_3$ and intramolecular cyclization of the latter by means of nucleophilic substitution of *ortho*-F atom under the action of CsF in MeCN [7,17].

In this work, three related approaches (Scheme 1) were used to convert polyfluorinated Ar–NH_2 into compounds Ar–N=S=N–$SiMe_3$ (**33**–**38**) based on transformation of the amines into: 1) Ar–N=S=O (**29**–**31**) by the Michaelis reaction followed by their interaction with $Me_3SiN(SiMe_3)_2$ (compounds **35** and **36**) or $LiN(SiMe_3)_2$ (cf. [7a,18]); 2) Ar–N=SCl_2 (**32**; via N=S=O derivative **29**) followed by their reaction with $LiN(SiMe_3)_2$ (compound **35**); and 3) $Ar–N(SiMe_3)Li$ followed by their reaction with Me_3Si–N=S=O (compound **34**).

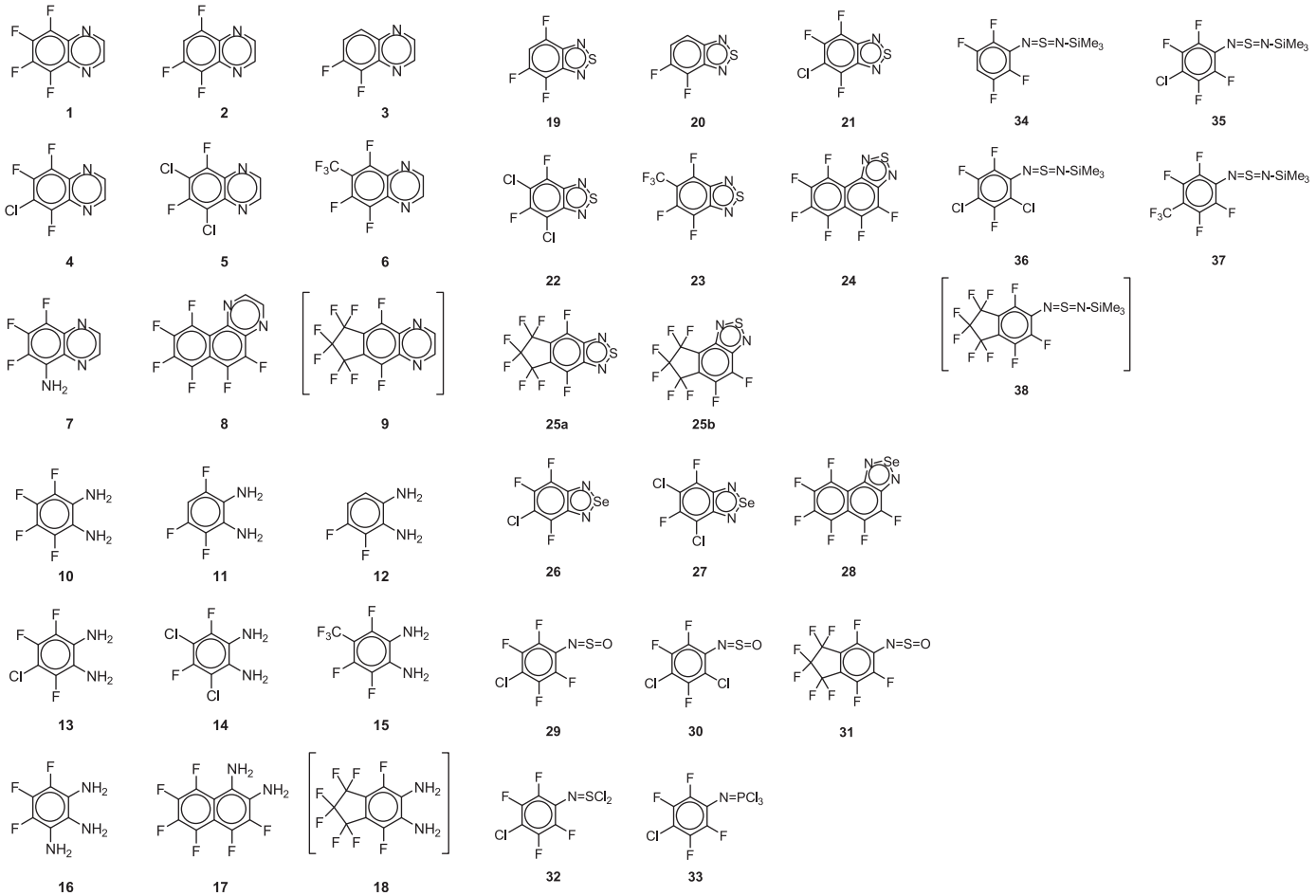
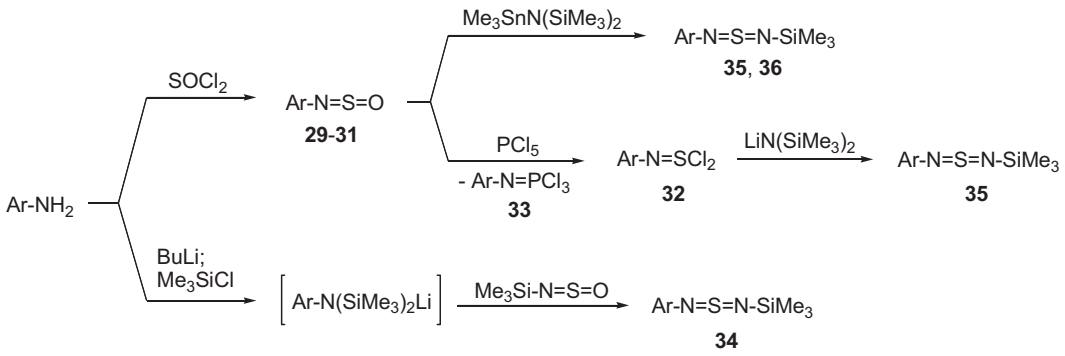


Chart 1. Compounds **1**–**38** (for chemical names see Table S2, Supporting Information).



Scheme 1. Synthesis of compounds **29**–**36**.

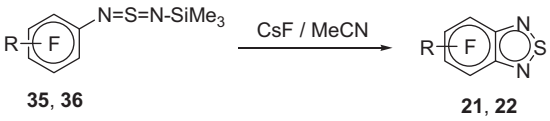
Previously approaches based on R–N=SCl_2 (R=t-Bu, Ar, $ArSO_2$) [19] and Me_3Si–N=S=O [20] derivatives were known only with a few examples in the hydrocarbon series.

It should be noted that all approaches tried have some limitations. Particularly, compound **38** was not prepared from compound **31** and $LiN(SiMe_3)_2$ in hexane/THF or $Me_3SnN(SiMe_3)_2$ in MeCN. Instead, a mixture of corresponding $ArNH–SiMe_3$ and isomeric thiadiazoles **25**a,b was observed (^1H and ^{19}F NMR, GC–MS) in the first case, and a complex mixture (^1H and ^{19}F NMR) of unidentified compounds in the second one. Synthesis of compound **32** was accompanied by formation of compound **33** (Scheme 1) isolated even in higher yield than the target **32**. The structure of the latter was defined by XRD (Fig. 1; Table S1, Supporting Information) for the first time for Ar–N=SCl_2 derivatives in both fluorocarbon and hydrocarbon series.

Compounds Ar–N=S=N–$SiMe_3$ were converted into corresponding thiadiazoles including previously undescribed derivatives **21** and **22** (Scheme 2) by the action of CsF in MeCN (cf. [7,17]). Structure of **19** (prepared earlier in the similar way [7a]) was confirmed by XRD (Fig. 2; Table S1, Supporting Information).

The polyfluorinared 2,1,3-arenothiadiazoles (both known **19**, **20**, **24** [7] and newly prepared **21** and **22**) were reduced into new 1,2-diaminoarenes (Scheme 3). Compound **16** was obtained by reduction of 4,5,6-trifluoro-2-nitro-1,3-phenylenediamine (**39**, Scheme 3) and its structure was confirmed by XRD in the form of salt with 2 HCl (Fig. 3; Table S1, Supporting Information).

The diamines synthesized together with some known derivatives [7] reacted with glyoxal taken as aqueous solution or solid hydrate to give polyfluorinated quinoxalines **1**–**8** (Scheme 4). Structures of compounds **1**, **2**, **4**, **7** and **8** were confirmed by XRD (Fig. 4; Fig. S1 and Table S1, Supporting Information).



Scheme 2. Synthesis of compounds **21** and **22**.

Diamines **13**, **14** and **17** were also converted into corresponding polyfluorinated selenadiazoles **26**–**28** by reaction with selenium dioxide which is widely used for this purpose in the hydrocarbon series. Additionally, selenadiazole **26** was synthesized from diamine **13** and selenium tetrachloride using approach suggested in [7a] (Scheme 5). Structure of **26** was confirmed by XRD (Fig. 5; Table S1, Supporting Information).

3. Conclusions

Conceptually/technically related synthetic protocols for preparation of new (poly) fluorinated quinoxalines, as well as 2,1,3-arenothia(selena)diazoles, 1,2-diaminoarenes and some other derivatives, are elaborated, in all cases with corresponding anilines as starting materials. The compounds synthesized, including –N=S=X (X=O, $NSiMe_3$, Cl_2) derivatives [22], are of obvious interest to organofluorine, aromatic and heterocyclic chemistry. For example, polyfluorinated 1,2-diaminoarenes, besides synthetic applications, are candidate analytical reagents for the GC-ECD determination of selenium including environmental [23]. Particularly, redox properties of polyfluorinated 2,1,3-arenothia(selena)-diazoles and quinoxalines, especially their ability to form long-lived radical anions (cf. [6,10]) and serve as electron acceptors for charge-transfer complexes (cf. [24]), are worth of special study.

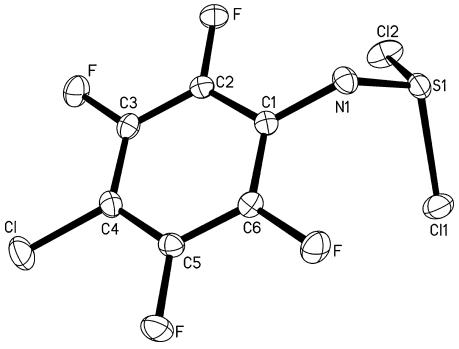


Fig. 1. XRD molecular structure of compound **32** (displacement ellipsoids at 30%). Selected bond lengths (Å), dihedral and torsion angles (°): C1–N1 1.402(1), N1–S1 1.501(1), S1–Cl1 2.0953(5), S1–Cl2 2.1244(5); C2–C1–N1 121.57(10), C1–N1–S1 129.29(8), N1–S1–Cl1 109.99(4), N1–S1–Cl2 111.59(4), Cl1–S1–Cl2 93.83(2); C2–C1–N1–S1 −92.72(13), C1–N1–S1–Cl1 −42.91(12), C1–N1–S1–Cl2 59.82(11).

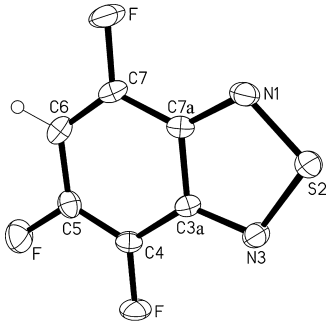
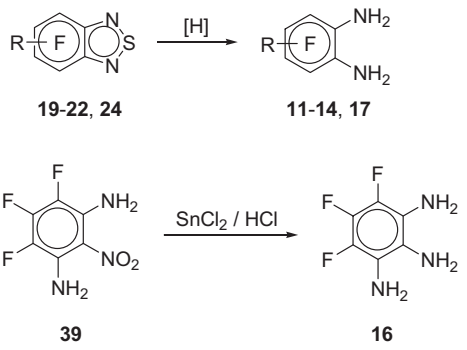


Fig. 2. XRD molecular structure of compound **19** (displacement ellipsoids at 30%). Selected bond lengths (Å) and bond angles (°) (two crystallographically independent molecules): N1–S2 1.617(2)/1.614(2), S2–N3 1.620(2)/1.622(2), N3–C3a 1.346(3)/1.339(3), C3a–C7a 1.432(4)/1.430(4), C7a–N1 1.340(3)/1.338(3); C7a–N1–S2 106.4(2)/106.6(2), N1–S2–N3 100.9(1)/100.5 (1), S2–N3–C3a 106.0(2)/106.3(2), N3–C3a–C7a 113.3(2)/113.4(2), C3a–C7a–N1 113.3(2)/113.3(2).



Scheme 3. Synthesis of compounds **11**–**14**, **16** and **17**.

Importantly, the chalcogenadiazoles and quinoxalines synthesized can be functionalized further at the C–F centers via nucleophilic substitution, and the quinoxalines also at the C–H centers via electrophilic substitution. N-Oxidation of these compounds is also of interest [10a].

The XRD structure of compound **32** provides the first example for Ar–N=SCl_2 derivatives in both fluorocarbon and hydrocarbon series.

Previously, it was shown that bicyclic aromatics and aza-aromatics with only one polyfluorinated ring create new possibilities for crystal engineering of organic solids [25]. In further work crystal structures of compounds **1**–**8**, **19**, **26** and **28** will be studied in detail and results will be published elsewhere.

4. Experimental

4.1. General

^{1}H NMR spectra were measured with Bruker AV-300 and Bruker AV-400 spectrometers at the frequencies of 300.1 and 400.1 MHz, respectively, and ^{19}F NMR spectra with a Bruker AV-300 spectrometer at the frequency of 282.4 MHz; the standards were TMS and C_6F_6 ($\delta^{19}F = -162.9$ ppm with respect to $CFCl_3$), respectively. The ^{31}P NMR spectra were taken with Bruker AV-300 machine at the frequency of 121.5 MHz, the standard was 85% H_3PO_4. The ^{77}Se NMR spectra were recorded with a Bruker AM-400 instrument at the frequency of 76.31 MHz, and a Bruker AV-600 at the frequency of 114.5 MHz; the standard was Me_2Se. The NMR spectra were obtained for solutions in $CDCl_3$ unless otherwise indicated.

High-resolution mass-spectra (EI, 70 eV) were taken with a Thermo Electron Corporation DFS mass-spectrometer. Gas-chromatography–mass-spectrometry experiments were performed with Hewlett-Packard G1800A instrument.

UV–vis and fluorescent (FL) spectra were collected with Varian Cary 5000 and Varian Cary Eclipse instruments for heptane solutions, respectively, unless otherwise indicated.

Glioxal (40% aqueous solution and solid hydrate) was received from Novokhim Co. Ltd., Tomsk, Russia, and $(Me_3Si)_2NH$, $SOCl_2$, BuLi, Me_3SiCl and $LiN(SiMe_3)_2$ from Aldrich. Starting compounds $Me_3SnN(SiMe_3)_2$ [18], $Me_3Si–N=S=O$ (0.56 M solution in $(Me_3Si)_2O$ [26]), and Ar–NH_2 (Ar = 5-C_9F_9 [27a], 4-HC_6F_4 [27b,c], 4-$F_3CC_6F_4$ [27d,e], 2,4-$Cl_2C_6F_3$ [27f]) were prepared by known methods.

Tables 1–3 contain physical, analytical and NMR data of the compounds synthesized. Compounds **1** [4a], **10**, **11**, **13**, **15**, **19**, **23** [7a], **20** [7c], **24** [7b], **29**, **31** and **37** [18] were known before. They present in the Tables in the cases they were prepared by new/improved approaches, or/and additionally characterized in this work.

4.2. X-ray diffraction

The XRD data (Table S1, Supporting Information) were collected on a Bruker Kappa Apex II CCD diffractometer using φ,ω-scans of narrow (0.5°) frames with Mo Kα (λ = 0.71073 Å) radiation with a graphite monochromator. Absorption corrections were applied using the empirical multi-scan method with the *SADABS* program [28]. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the *SHELX-97* programs set [29]. For **1**, **2**, **4**, **8** and **19**, the H atom positions were calculated with a riding model and those for NH_2 groups in **7** and **16** were located from difference Fourier maps and refined in isotropic approximation. The obtained structures were analyzed for exposing shortened contacts between nonbonded atoms with the programs *PLATON* [30] and *MERCURY* [31]. The bond lengths and bond angles of all compounds are typical [32].

Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Center as CCDC – 994919 (1), – 994920 (2), – 994921 (4), –994922 (7), –994923 (8), –994924 (16·2HCl), –994925 (19), – 994926 (26), –996836 (28), –994927 (32). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk

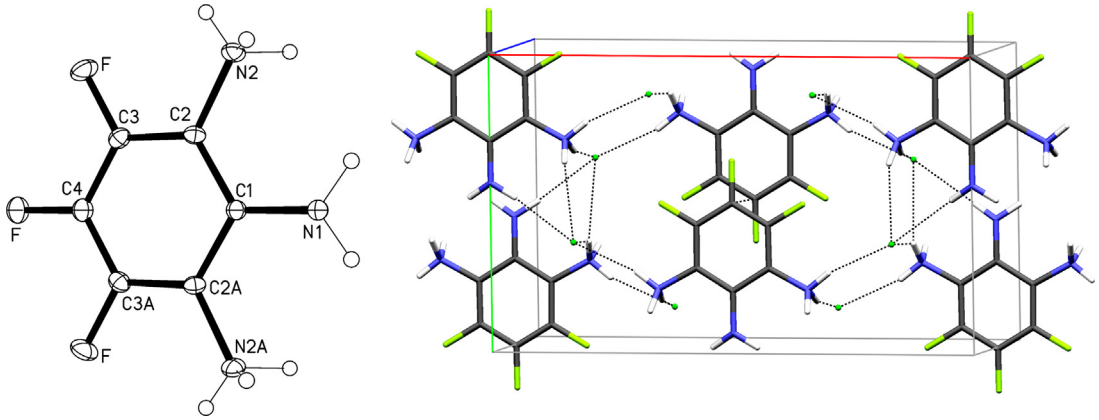
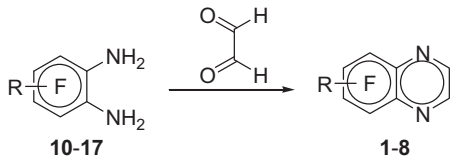


Fig. 3. XRD molecular (left, displacement ellipsoids at 30%) and crystal (right) structure of **16**·2HCl. Selected bond lengths (Å) and bond angles (°) (crystallographic numbering used): C1–N1 1.357(2), C2–N2 1.451(2), C1–C2 1.408(2), C2–C3 1.389(2), N1–C1–C2 121.55(8), C1–C2–N2 120.3(1). Cations and anions are connected by N–H...Cl contacts featuring shortened H...Cl distances (Å): H1...Cl1 2.46(2), H2...Cl1 2.36(1), H3...Cl1 2.30(2). Note, that normal H...Cl contact is 2.86 Å [21].



Scheme 4. Synthesis of compounds **1**–**8**.

4.3. Preparations

4.3.1. N-Sulfinylarylamines *29*–*31* and their precursors

(a) 4-HOC_6F_4–NO_2 [33] was treated with $SOCl_2$ in DMF to give 4-ClC_6F_4–NO_2 (**40**) [34], 52%, b. p. 91–92 °C/18 mm, m. p. 33–34 °C. ^{19}F NMR: 25.7, 16.6. MS, M^+ *m*/*z*, found (calculated): 228.9552 (228.9554, ^{35}Cl).

(b) A mixture of 5.30 g (23 mmol) of **40**, 18.40 g (82 mmol) of $SnCl_2{\cdot}2H_2O$ and 20 ml of concentrated HCl was refluxed for 5 h, neutralized with saturated solution of Na_2CO_3 to pH ~ 8, and extracted with 5 × 30 ml of methyl-*tert*-buthyl ether. Organic layer was dried with $MgSO_4$, solvent distilled off under reduced pressure, and the residue sublimed at 45 °C/1 mm and recrystallized from hexane. 4-ClC_6F_4–NH_2 [35] was obtained in the form of white crystals, 2.99 g (65%), m.p. 55–56 °C (54.3–55.4 °C [35b]). ^{1}H NMR: 3.94. ^{19}F NMR: 17.9, 0.9. MS, M^+ *m*/*z*, found (calculated): 198.9825 (198.9812, ^{35}Cl).

(c) Corresponding Ar–NH_2 [27a,f] (25 mmol) was refluxed with excess of $SOCl_2$ (3 ml) until evaluation of HCl ceased, the solvent was distilled off, and the residue was distilled under reduced pressure (**29**, **31**) or crystallized from hexane at −20 °C (**30**). Compound **29** [18b] was obtained in the form of yellow liquid solidified upon cooling to room temperature, crystallization of the product from hexane gave yellow crystals; compound **30** was obtained in the form of bright-yellow crystals and compound **31** in the form of orange-yellow liquid.

4.3.2. 1-Aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes *34*–*36*, attempted synthesis of compound *38*, and thiadiazoles *25*a,b

(a) At −60 °C and under argon, 12 ml of 2.5 M solution of n-BuLi in hexanes, 3.30 g (30 mmol) of Me_3SiCl, the same portion of n-BuLi, and 8.05 g of 56% solution of Me_3SiNSO (30 mmol) in $(Me_3Si)_2O$ were subsequently added, with 30-min periods between them, to a stirred solution of 5.00 g (30 mmol) of 4-HC_6F_4–NH_2 in 120 ml of Et_2O. The reaction mixture was warmed-up to −25 °C and kept at this temperature for 2 h. Then 3.30 (30 mmol) of Me_3SiCl was added, the reaction mixture warmed-up to 25 °C, filtered, the solvents were evaporated, and the residue was distilled under reduced pressure. Compound **34** [18] was obtained in the form of orange liquid.

(b) Stirred mixture of 4.86 g (0.015 mol) of $Me_3SnN(SiMe_3)_2$, 30 ml of MeCN and 0.015 mol of **29** or **30** was refluxed for 15 min. The solvent and volatile by-products were distilled off under reduced pressure, and the residue was distilled in vacuo. Compounds **35** and **36** were obtained in the form of orange-red oils.

(c) At −60 °C and under argon, solution of 1.41 g (4.7 mmol) of **32** in 15 ml of Et_2O was added dropwise to a stirred solution of 0.80 g (4.8 mmol) of $LiN(SiMe_3)_2$ in 30 ml of the same solvent during 15 min. Reaction mixture was warmed-up to ambient temperature during 2 h, filtered, the solvent was distilled off under reduced pressure, and the residue distilled in vacuo. Compound **35** was obtained in the yield of 0.83 g (56%).

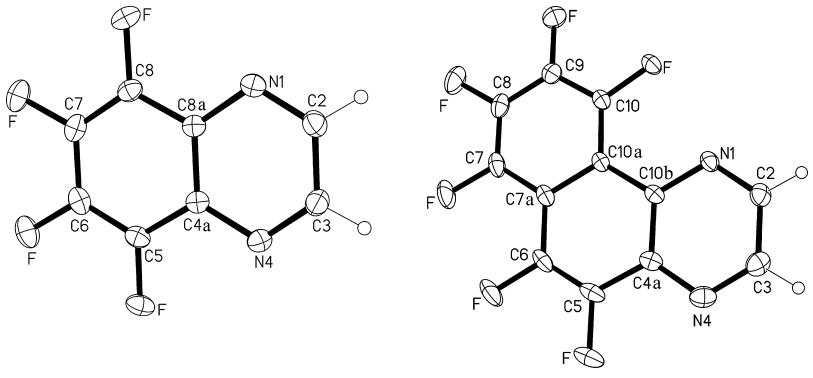
(d) Compound **38** was not synthesized from compound **31** and $LiN(SiMe_3)_2$ in hexane/THF; instead, a mixture of corresponding ArNH–$SiMe_3$ and isomeric thiadiazoles **25**a,b was observed (^{1}H and ^{19}F NMR, GC–MS). The 5: 1 mixture of **25**a: **25**b was separated from the ArNH–$SiMe_3$ by column chromatography (silica/hexane).

^{19}F NMR: **25**a: 53.6 (4F), 43.4 (2F), 30.4 (2F); **25**b: 55.4 (2F), 54.9 (2F), 33.2 (2F), 29.7 (1F), 17.7 (1F).

Interaction of **31** with $Me_3SnN(SiMe_3)_2$ under conditions described above gave a complex mixture (^{1}H and ^{19}F NMR) of unidentified compounds.

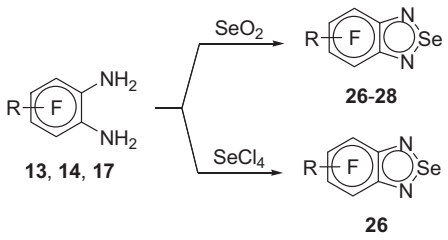
4.3.3. 2,1,3-Arenothiadiazoles *21* and *22*

(a) A solution of 3.16 g (0.01 mol) of **29** in 30 ml of MeCN was added dropwise during 2 h to refluxed and stirred suspension of 1.52 g (0.01 mol) of freshly calcinated CsF in 200 ml of MeCN. After additional 0.5 h, the reaction mixture was cooled to 20 °C and filtered. The solvent was distilled off under reduced pressure and the residue was chromatographed on alumina column (hexane – Et_2O 3:1) and sublimed in vacuo. Compound **21** was obtained in the form of colorless crystals.



1 **8**

Fig. 4. XRD molecular structures (displacement ellipsoids at 30%) of compounds **1** and **8** (for compounds **2**, **4** and **7** see Fig. S1, Supporting Information). Selected bond lengths (Å) and angles (°): **1**: N1–C2 1.312(2), C2–C3 1.414(2), C3–N4 1.311(2), N4–C4a 1.365(2), C4a–C8a 1.416(2), C8a–N1 1.361(2); C8a–N1–C2 115.7(1), N1–C2–C3 122.8(1), C2–C3–N4 123.0(1), C3–N4–C4a 115.6(1), N4–C4a–C8a 121.3(1); C4a–C8a–N1 121.6(1). **8**: N1–C2 1.320(2), C2–C3 1.403(2), C3–N4 1.315(2), N4–C4a 1.354(2), C4a–C10b 1.412(2), C10b–N1 1.358(2); C10b–N1–C2 116.8(1), N1–C2–C3 122.7(2), C2–C3–N4 122.0(2), C3–N4–C4a 116.3(2), N4–C4a–C10b 122.3(1); C4a–C10b–N1 119.8(1).



Scheme 5. Synthesis of compounds **26–28**.

(b) A solution of 1.36 g (4.1 mmol) of **36** in 30 ml of MeCN was added dropwise during 2 h to refluxed and stirred suspension of 0.71 g (4.7 mmol) of freshly calcinated CsF in 200 ml of MeCN. After additional 0.5 h, the reaction mixture was cooled to 20 °C and filtered. The solvent was distilled off under reduced pressure and the residue was extracted with hexane (5 × 10 ml), the extract was evaporated and the residue sublimed in vacuo (110 °C/1 mm). Compound **22** was obtained in the form of light-yellow crystals. UV–vis, λ_{max}, nm, (log ε): 216 (4.15, sh.), 232 (4.25), 304 (4.07), 311 (4.05), 317 (3.14), 344 (3.49, sh.). FL, λ_{max} (λ_{exc}), nm: 406 (316).

4.3.4. 1,2-Diaminoarenes **12–14**, **16** and **17**

(a) A mixture of 285 mg (~0.002 mol) of **20**, 275 mg (~0.006 mol) of $NaBH_4$, 78 mg (0.0003 mol) of $Co(OAc)_2{\cdot}4H_2O$ and 5 ml of ethanol was refluxed for 9 h. After cooling to 20 °C, the reaction mixture was diluted with water, and precipitate was filtered off and washed with ether. The filtrate was extracted with ether (4 × 25 ml). The combined ether solution was dried over $MgSO_4$ and evaporated. Concentrated HCl (0.1 ml) was added to the residue, and the mixture was extracted with toluene (3 × 7 ml). Aqueous solution was neutralized with 353 mg of Na_2CO_3, evaporated to dryness and the residue sublimed at 75 °C/1 mm. Compound **12** was obtained in the form of colorless crystals.

(b) Compounds **13** and **14** were prepared by reduction of **21** and **22** by $SnCl_2$/HCl under conditions [35] similar to described above (item 4.3.1), and purified by sublimation in vacuo and crystallized from hexane. Compounds **13** and **14** were obtained in the form of colorless crystals.

(c) A mixture of 840 mg (~4 mmol) of **39** [36], 3.05 g (~14 mmol) of $SnCl_2{\cdot}2H_2O$ and of 4 ml (~50 mmol) of concentrated HCl was refluxed for 0.5 h. After cooling to room temperature, crystals of **16**·2HCl (0.133 g) were filtered off being suitable to XRD. Free **16** was obtained by treatment of **16**·2HCl with aqueous Na_2CO_3 followed by extraction with Et_2O. The filtrate was neutralized with 5.27 g of Na_2CO_3 and extracted with Et_2O (20 × 15 ml). Combined ether extract was dried over $MgSO_4$, evaporated to dryness and the residue was sublimed at 90 °C/1 mm. Compound **16** was obtained in the form of colorless crystals.

(d) (modified procedure [7b]) A mixture of 227 mg (0.0008 mol) of **24**, 503 mg (0.008 mol) of Zn dust, 1.5 ml (0.018 mol) of hydrochloric acid and 2.7 ml of ethanol was refluxed for 4 h. After cooling to 20 °C, 15 ml of water was added, the precipitate of was filtered off. The filtrate was evaporated to dryness and the residue sublimed at 120 °C/1 mm. Combined product was crystallized from ethanol. Compound **17** was obtained in the form of white crystals.

4.3.5. Quinoxalines **1–8**

(a) A mixture of 250 mg (1.4 mmol) of **10**, 116 mg (1.7 mol) of crystalline glyoxal (a), or 241 mg (1.7 mol) of 40% aqueous glyoxal (b), and 6 ml of ethanol was refluxed for 4 h. The solvent was distilled off at reduced pressure, and the residue was sublimed at 50 °C/1 mm and crystallized from hexane. Compound **1** [4a] was obtained in the form of colorless crystals suitable to XRD. UV–vis (EtOH), λ_{max}, nm, (log ε): 236 (4.49), 311 (3.58). FL, λ_{max} (λ_{exc}), nm: 410 (310).

(b) A mixture of 3.5 mmol of **11** or **12** and 514 mg (3.5 mmol) of 40% aqueous glyoxal in 15 ml of ethanol was refluxed for 5 h, the solvent was distilled off under reduced pressure, and the residue sublimed at 80 °C/1 mm.

Compound **2** was obtained in the form of white crystals. Single crystals suitable to XRD were obtained by crystallization from ethanol. UV–vis, λ_{max}, nm, (log ε): 239 (4.57), 310 (3.42). FL, λ_{max} (λ_{exc}), nm: 388 (310).

Compound **3** was obtained in the form of white crystals. UV–vis, λ_{max}, nm, (log ε): 234 (4.46), 313 (3.60). FL, λ_{max} (λ_{exc}), nm: 409 (310).

(c) A solution of 380 mg (2.6 mmol) of 40% aqueous glyoxal in 10 ml of ethanol was added during 2 h to refluxed solution of 2.6 mmol of **13**, or **14**, or **15** in 10 ml of the same solvent. The reaction mixture was refluxed for 3 h, the solvent was distilled off under reduced pressure, and the residue sublimed at 70 °C/1 mm and crystallized from hexane.

Compound **4** was obtained in form of yellowish crystals. UV–vis, λ_{max}, nm, (log ε): 242 (4.67), 318 (3.57). FL, λ_{max} (λ_{exc}), nm: 382 (318).

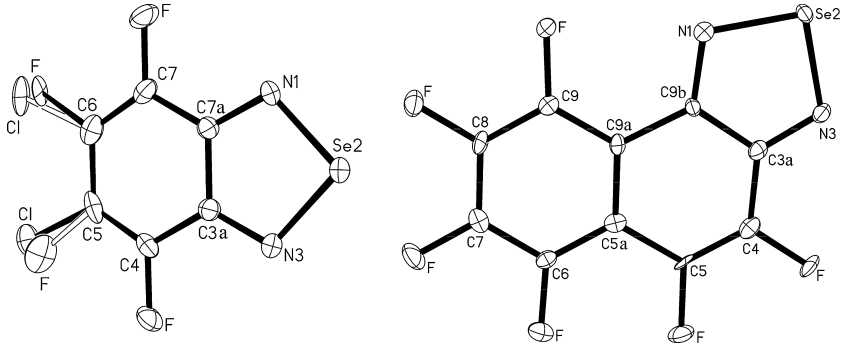


Fig. 5. XRD molecular structure (displacement ellipsoids at 30%) of **26** (Cl atoms are 0.60: 0.40(1) disordered over two positions) and **28.** Selected bond lengths (Å) and bond angles (°): **26**: Se2–N1 1.791(6), Se2–N3 1.798(6), N1–C7a 1.327(9), N3–C3a 1.323(9), C3a–C7a 1.440(10); N1–Se2–N3 93.4(3), Se2–N1–C7a 107.2(4), Se2–N3–C3a 106.8(5), N1–C7a–C3a 116.0(6), N3–C3a–C7a 116.5(6). **28**: Se2–N1 1.788(6), Se2–N3 1.803(7), N1–C9b 1.322(9), N3–C3a 1.311(11), C3a–C9b 1.431(11); N1–Se2–N3 92.9(3), Se2–N1–C9b 107.1(5), Se2–N3–C3a 107.1(5), N3–C3a–C9b 116.4(7), N1–C9b–C3a 116.4(7).

Table 1
Isolated yields, melting (boiling) points and MS data for compounds.

Compound	Yield %	M. p. °C, b. p. °C/mm	MS, *m/z*, found/calc.
1	59 (a), 64 (b)	95–97 °C	202.0145/202.0149
2	89	115–117	184.0239/184.0243
3	74	85–86	166.0335/166.0337
4	77	94–95	217.9857/217.9853
5	84	107–108	233.9552/233.9558
6	88	81–82	252.0114/252.0117
7	35	158–159	199.0355/199.0352
8	66	162–163	288.0115/288.0117
12	44	60–61	144.0493/144.0494
13	86	139–140	196.0018/196.0015, ^{35}Cl
14	90	143–144	211.9718/211.9714
16	39	143–145	177.0504/177.0508
17	65	137–139	–
21	82	36–37	223.9419/223.9423, ^{35}Cl
22	82	59–61	239.9126/239.9122
26	92 (a), 88 (b)	181–182 (sealed capillary)	271.8903/271.8867, ^{35}Cl, ^{80}Se
27	64	178–179	283.8590/283.8593 ^{76}Se
28	95	197–198	339.9140/339.9133, ^{78}Se
29	96	52–53, 105–106/20	–
30	80	47–48	–
31	90	103–104/1	–
32	23	41–42	–
33	44	93–94	332.8451/332.8453, ^{35}Cl
34	83	91–93/1	–
35	38	85–86/2	315.9877/315.9880, ^{35}Cl
36	62	80–82/0.2	331.9582/331.9579

Compound **5** was obtained in form of yellowish crystals. UV–vis, λ_{max}, nm, (log ε): 245 (4.63), 321 (3.71). FL, λ_{max} (λ_{exc}), nm: 393 (320).

Compound **6** was obtained in form of white crystals. UV–vis, λ_{max}, nm, (log ε): 240 (4.60), 289 (3.30), 325 (3.32). FL, λ_{max} (λ_{exc}), nm: 399 (325).

(d) A mixture of 100 mg (~0.5 mmol) of **16** in 1.5 ml of water, 105 mg (~0.6 mmol) of $Na_2S_2O_5$ in 0.5 ml of water and 79 mg (~0.5 mmol) of 40% aqueous glyoxal was refluxed for 3 h. After cooling, the solution was made basic with 20% NaOH and extracted with chloroform (9 × 7 ml). The combined chloroform solution was dried over $MgSO_4$, evaporated to dryness and the residue sublimed at 75 °C/1 mm. Compound **7** was obtained in the form of yellow crystals. UV–vis, λ_{max}, nm, (log ε): 262 (4.47), 324 (3.01), 384 (3.21). FL, λ_{max} (λ_{exc}), nm: 491 (385).

Crystals suitable to XRD were obtained by crystallization from 1: 1 mixture of hexane and CH_2Cl_2.

(e) A mixture of 60 mg (0.2 mmol) of **17**, 40 mg (0.3 mmol) of 40% aqueous glyoxal and 2 ml of ethanol was refluxed for 2 h. After cooling to 20 °C, the crystalline precipitate was filtered off and sublimed at 120 °C/1 mm. Compound **8** was obtained in the form of colorless crystals suitable to XRD. UV–vis (EtOH), λ_{max}, nm, (log ε): 226 (4.60), 269 (4.26), 350 (3.80), 366 (3.82). FL, λ_{max} (λ_{exc}), nm: 409 (365).

Table 2
Analytical data for compounds.[a,b]

Compound	Found/calculated %			
	C	H	N	F
2	52.05/52.19	1.61/1.64	14.97/15.21	30.85/30.96
3	57.87/57.84	2.47/2.43	16.87/16.86	22.80/22.87
4	44.05/43.96	1.03/0.92	12.88/12.82	26.22/26.08
5	41.04/40.88	1.10/0.86	11.68/11.92	16.19/16.17
6	42.43/42.88	0.86/0.80	11.09/11.11	45.32/45.21
7	47.97/48.25	2.07/2.02	20.81/21.10	28.38/28.62
8	50.40/50.02	0.61/0.70	9.71/9.72	39.46/39.56
12	50.09/50.00	4.30/4.20	19.36/19.44	26.28/26.36
13	36.68/36.66	2.07/2.05	13.77/14.25	29.74/29.00
14	34.10/33.83	1.90/1.89	13.05/13.15	17.61/17.84
16	40.41/40.69	3.47/3.41	23.53/23.72	31.88/32.18
21	32.14/32.09	–	12.05/12.47	25.83/25.38
22	30.07/29.90	–	11.26/11.62	15.40/15.76
26	26.50/26.54	–	10.31/10.32	20.94/20.99
27	25.02/25.03	–	9.58/9.73	13.18/13.20
28	34.88/35.21	–	8.21/8.21	33.32/33.42
30	27.88/27.50	–	5.41/5.35	21.90/21.75
32	23.80/23.98	–	4.59/4.66	25.46/25.29
33	21.23/21.52	–	4.34/4.18	22.86/22.69

[a] S: **29**, 13.32/13.06; **32**, 10.41/10.67. Cl: **13**, 19.72/18.04; **22**, 29.00/29.42; **26**, 12.92/13.06; **27**, 24.40/24.63; **30**, 26.62/27.06; **32**, 35.09/35.40; **33**, 42.06/42.35. Se: **28**, 23.40/23.15. P: **33**, 9.51/9.25.

[b] Vacuum distillation gave compound **36** with purity of ~92–94% only according to the data of elemental analysis for C, H, Cl, F and N. The sample was characterized by MS and NMR (Tables 1 and 3) and used in the synthesis of compound **22**.

4.3.6. 2,1,3-Arenoselenadiazoles ***26–28***

(a) At 0 °C and under argon, a solution of 0.66 g (3 mmol) of $SeCl_4$ in 5 ml of monoglyme was added to a stirred solution of 0.59 g (3 mmol) of **13** and 0.95 g (12 mmol) of pyridine in 15 ml of the same solvent. After additional 1 h at 20 °C, the reaction mixture was filtered, the solvent distilled off under reduced pressure, the residue crystallized from EtOH and sublimed in vacuo. Compound **26** was obtained in the form of yellow crystals.

(b) Mixture of 0.18 g (0.9 mmol) of **13**, 0.11 g (1.0 mmol) SeO_2 and 10 ml of EtOH was refluxed for 2 h, evaporated to dryness, and the residue was sublimed at 90 °C/1 mm and crystallized from hexane Compound **26** was obtained in the form of yellow crystals. Crystals suitable for XRD were obtained by crystallization from EtOH.

(c) Mixture of 139 mg (0.7 mmol) of **14**, 99 mg (0.9 mmol) SeO_2 and 20 ml of EtOH was refluxed for 1.5 h, evaporated to dryness, and crystallized from hexane. Compound **27** was obtained in form of light-yellow crystals. UV–vis, λ_{max}, nm, (log ε): 223 (3.97), 251 (3.64, sh.), 328 (4.14), 334 (4.19), 340 (4.19), 371 (3.41, sh.). FL, λ_{max} (λ_{exc}), nm: 370 (334).

Table 3
NMR chemical shifts, δ, for compounds.

Compound	^{1}H	^{19}F
1[a]	8.99	10.0 (4F)
2	8.96, 8.91, 7.42	36.4, 30.9, 7.5
3	8.86, 8.84, 7.87, 7.62	28.5, 11.7
4	8.95, 8.94	34.5, 28.6, 9.7
5	9.02, 8.95	55.1, 39.1
6	9.08, 9.03	105.7, 38.3, 25.9, 10.2
7	8.86, 8.71, 4.6 (NH_2)	8.0, 6.0,–3.7
8	9.07 (t), 9.02 (d)	26.1, 21.9 (J_{peri} = 70.8 Hz), 17.9 (J_{peri} = 70.8 Hz), 11.4, 11.2, 9.2
12	6.30 (1H), 6.40 (1H), 3.56 (2H)	12.8, 3.5
13	3.45	21.3, 11.5, 0.1
14	3.6 (s, $\Delta_{1/2}$ 240 Hz)	36.0, 26.3
16	3.23	−4.8 (2F), −11.0 (1F)
21	–	40.2, 26.9, 14.1
22	–	52.3, 43.4
26[b]	–	39.5, 20.9, 13.3
27[b]	–	51.6, 44.3
28[b]	–	25.4, 19.4 (J_{peri} = 71 Hz), 18.2 (J_{peri} = 71 Hz), 15.8, 11.7, 9.9
29	–	22.9 (2F), 21.9 (2F)
31	–	55.3 (2F), 55.1 (2F), 45.0 (1F), 39.0 (1F), 32.6 (2F), 22.8 (1F)
32	–	22.2, 17.5
33[c]	–	Two groups of signals: at 22.3, 17.8 (minor); and at 19.0, 12.6 (major)
34	6.84, 0.18	22.1, 17.4
35	0.20	20.0 (2F), 18.8 (2F)
36	0.20	44.3, 25.0, 20.9

[a] The ^{19}F NMR spectra are solvent-dependent, and for EtOH solution δ^1H are 10.5 (2F) and 9.0 (2F) (this work) whereas for acetone solution 15.4 and 13.7 [4a].
[b] δ^{77}Se: **26**: 1592; **27**: 1550; **28**: 1554.
[c] δ^{31}P: Two singlets: at 10.7 (minor), and at −29.9 (major).

(d) A solution of 111 mg of SeO_2 (1.0 mmol) in 0.3 ml of water was added to refluxing solution of 266 mg of **17** (1.0 mmol) in 6 ml of EtOH. After 20 min, the reaction mixture was cooled to room temperature, and the precipitate was filtered off, washed with EtOH and dried. Compound **28** was obtained in the form of pale-yellow crystalline powder.

UV–vis (EtOH), λ_{max}, nm, (log ε): 224 (4.49), 253 (3.90), 281 (4.05), 331 (3.70), 364 (4.11), 381 (4.07). FL, λ_{max} (λ_{exc}), nm: 406 (363).

*4.3.7. Reaction of compound **29** with PCl_5. Compounds **32** and **33***

At ambient temperature, solution of 6.14 g (25 mmol) of **29** in 9 ml of CCl_4 was added to a stirred suspension of finely powdered 5.25 g (25 mmol) of PCl_5 in 3 ml of the same solvent. Reaction mixture was heated to 60 °C and kept at this temperature until true solution formed (~30 min). The solvent was distilled off under reduced pressure, and the residue washed on a glass filter with 2 ml of hexane. Compound **33** was obtained in the form of white crystals.

Filtrate was evaporated under reduced pressure and the residue sublimed at 60 °C/1 mm and crystallized from hexane. Compound **32** was obtained in the form of yellow crystals suitable to XRD.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.06.019.

References

[1] Relevant literature is too abundant to be cited completely. Selected references:
(a) M.P. Cabal, in: J. Alvarez-Builla, J.J. Vaquero, J. Barluengo (Eds.), Modern Heterocyclic Chemistry, vol. 3, Wiley-VCH, Weinheim, 2011, pp. 1683–1776;
(b) N. Sato, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, vol. 6, Pergamon Press, Oxford, 1996, pp. 233–278;
(c) A.E.A. Porter, in: A.R. Katritzky, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, vol. 3, Pergamon Press, Oxford, 1984, pp. 157–198;
(d) A.S. Patidar, M. Jeykandan, A.K. Mobiya, G. Selvam, Int. J. PharmaTech Res. 3 (2011) 386–392;
(e) R.M. Rajurkar, V.A. Agrawal, S.S. Thonte, R.G. Ingale, Pharmacophore 1 (2010) 65–76;
(f) G.K. Dutta, S. Patil, Org. Electron. 13 (2012) 1266–1276;
(g) J.Y. Lee, W.S. Shin, J.R. Haw, D.K. Moon, J. Mater. Chem. 19 (2009) 4938–4945.
[2] Relevant literature is too abundant to be cited completely. Selected recent books and review articles:
(a) V. Gouverneur, K. Mueller (Eds.), Molecular Medicine and Medicinal Chemistry. Vol. 6: Fluorine in Pharmaceuticals and Medicinal Chemistry: From Biophysical Aspects to Clinical Applications, World Scientific, London, 2012;
(b) M.L. Tang, Z. Bao, Chem. Mater. 23 (2011) 446–453;
(c) D. O'Hagan, J. Fluor. Chem. 131 (2010) 1071–1081;
(d) S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, Chem. Soc. Rev. 37 (2008) 320–330;
(e) W.K. Hagmann, J. Med. Chem. 51 (2008) 4359–4369;
(f) F. Babudri, G.M. Farinola, F. Naso, R. Ragni, Chem. Commun. (2007) 1003–1022;
(g) K.L. Kirk, J. Fluor. Chem. 127 (2006) 1013–1029;
(h) J.-P. Begue, D. Bonnet-Delpon, J. Fluor. Chem. 127 (2006) 992–1012;
(i) C. Isanbor, D. O'Hagan, J. Fluor. Chem. 127 (2006) 303–319.
[3] With the *Chemical Abstracts Plus* and *Reaxys* databases, ~1000 low-fluorinated quinoxalines were retrieved being mostly 6-F and 6,7-F_2 derivatives bearing various other functions. Selected recent references:
(a) E.V. Nosova, T.V. Trashakhova, V.S. Ustyugov, N.N. Mochulskaya, M.S. Valova, G.N. Lipunova, V.N. Charushin, Russ. Chem. Bull. 60 (2011) 942–947;
(b) N.N. Mochulskaya, E.N. Nagibina, Yu.S. Volchenkova, L.P. Sidorova, V.N. Charushin, Russ. J. Org. Chem. 41 (2005) 1694–1701;
(c) V.N. Charushin, G.A. Mokrushina, A.V. Tkachev, J. Fluor. Chem. 107 (2001) 71–80.
[4] (a) C.G. Allison, R.D. Chambers, J.A.H. MacBride, W.K.R. Musgrave, J. Fluor. Chem. 1 (1971/1972) 59–67;
(b) R.D. Chambers, C.W. Hall, J. Hutchinson, R.W. Millar, J. Chem. Soc. Perkin Trans. 1 (1998) 1705–1713;
(c) A. Costa, M. Tato, R.S. Matthews, Magn. Reson. Chem. 24 (1986) 547–548.
[5] (a) M. Etzkorn, J.C. Timmerman, M.D. Brooker, X. Yu, M. Gerken, Beilstein J. Org. Chem. 6 (2010), http://dx.doi.org/10.3762/bjoc.6.39;
(b) A. Heaton, M. Hill, F. Drake, J. Fluor. Chem. 81 (1997) 133–138.
[6] D.M.V. van den Ham, G.F.S. Harrison, A. Spaans, D. van der Meer, Rec. Trav. Chim. 94 (1975) 168–173.

[7] (a) A.V. Zibarev, A.O. Miller, J. Fluor. Chem. 50 (1990) 359–363;
(b) I.Yu. Bagryanskaya, Yu.V. Gatilov, A.O. Miller, M.M. Shakirov, A.V. Zibarev, Heteroatom Chem. 5 (1994) 561–565;
(c) 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, A.V. Zibarev, Eur. J. Inorg. Chem. 2003 (2003) 77–88.
[8] (a) J. Fajer, B.H.J. Bielski, R.H. Felton, J. Phys. Chem. 72 (1968) 1281–1288;
(b) V.N. Kovtonyuk, A.Yu. Makarov, M.M. Shakirov, A.V. Zibarev, J. Chem. Soc. Chem. Commun. (1996) 1991–1992;
(c) A.F. Cozzolino, P.S. Whitfield, I. Vargas-Baca, J. Am. Chem. Soc. 132 (2010) 17265–17270.
[9] Selected recent review articles and book chapters:
(a) B.A.D. Neto, A.A.M. Lapis, E.N. da Silva Junior, J. Dupont, Eur. J. Org. Chem. 2013 (2013) 228–255;
(b) A.F. Cozzolino, P.J.W. Elder, I. Vargas-Baca, Coord. Chem. Rev. 225 (2011) 1426–1438;
(c) S. Yamazaki, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven, R.J.H. Taylor (Eds.), Comprehensive Heterocyclic Chemistry III, vol. 6, Wiley, New York, 2008, pp. 518–581;
(d) P.A. Koutentis, Sci. Synth. 13 (2004) 297–348;
(e) R.A. Aitken, Sci. Synth. 13 (2004) 777–822;
(f) S. Grivas, Curr. Org. Chem. 4 (2000) 707–726;
(g) Shinkai I., Reider P., in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, vol. 4, Pergamon Press, Oxford, 1996, pp. 355–377.
[10] (a) A.V. Lonchakov, O.A. Rakitin, N.P. Gritsan, A.V. Zibarev, Molecules 18 (2013) 9850–9900;
(b) A.V. Zibarev, R. Mews, in: J.D. Woollins, R.S. Laitinen (Eds.), Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials, Springer, Berlin, 2011, pp. 123–149;
(c) N.V. Vasilieva, I.G. Irtegova, N.P. Gritsan, A.V. Lonchakov, A.Yu. Makarov, L.A. Shundrin, A.V. Zibarev, J. Phys. Org. Chem. 23 (2010) 536–543;
(d) S.N. Konchenko, N.P. Gritsan, A.V. Lonchakov, U. Radius, A.V. Zibarev, Mendeleev Commun. 19 (2009) 7–9;
(e) R.T. Boere, T.L. Roemmele, Coord. Chem. Rev. 210 (2000) 369–445;
(f) C.L. Kwan, M. Carmack, J.K. Kochi, J. Phys. Chem. 80 (1976) 1786–1792.
[11] (a) V.G. Pesin, Khim. Geterotsikl. Soed. (1969) 235–242 (in Russian);
(b) E. Sawicki, B. Chastein, H. Bryant, A. Carr, J. Org. Chem. 22 (1957) 625–629.
[12] (a) R.A.W. Johnstone, F.A. Mellon, J. Chem. Soc. Faraday Trans. (1973) 1155–1163;
(b) M.H. Palmer, S.M.F. Kennedy, J. Mol. Struct. 43 (1978) 33–48;
(c) N.E. Petrachenko, V.I. Vovna, A.V. Zibarev, G.G. Furin, Khim. Geterotsikl. Soed. (1991) 563–567 (in Russian).
[13] T.S. Lin, Chem. Phys. Lett. 43 (1976) 338–343.
[14] A.F. Cozzolino, N.E. Gruhn, D.L. Lichtenberer, I. Vargas-Baca, Inorg. Chem. 47 (2008) 6220–6226.
[15] According to preliminary data, under CVA conditions compound **1** reduces into persistent radical anion detectable at ambient temperature by conventional EPR. However, it was not the case for compound **8** whose radical anion was detected only by OD-EPR (on this technique applied to radical anions of polyfluorinated aromatics, see, for example, M.M. Barlukova, I.V. Beregovaya, V.P. Vysotsky, L.N. Snchegoleva, V.A. Bagryansky, Yu.N. Molin, J. Phys. Chem. A 109 (2005) 4404–4409.)
[16] Y.T. Pratt, in: R.C. Elderfield (Ed.), Heterocyclic Compounds, vol. 6, Wiley, New York, 1957, pp. 377–409.
[17] E. Lork, R. Mews, M.M. Shakirov, P.G. Watson, A.V. Zibarev, Eur. J. Inorg. Chem. 2001 (2001) 2123–2134.
[18] (a) A.V. Zibarev, A.O. Miller, Yu.V. Gatilov, G.G. Furin, Heteroatom Chem. 1 (1990) 443–453;
(b) A.O. Miller, A.V. Zibarev, M.A. Fedotov, G.G. Furin, Zh. Obshch. Khim. 59 (1989) 586–590 (in Russian).
[19] (a) O.J. Scherer, G. Wolmershaeuser, Angew. Chem. Int. Ed. Engl. 14 (1975) 485–486;
(b) R. Lux, G. Kresze, Liebig's Ann. Chem. (1989) 605–606;
(c) A.Yu. Makarov, I.Yu. Bagryanskaya, Yu.V. Gatilov, T.V. Mikhalina, M.M. Shakirov, L.N. Shchegoleva, A.V. Zibarev, Heteroatom Chem. 12 (2001) 563–576.
[20] (a) O.J. Scherer, G. Wolmershaeuser, R. Jotter, Z. Naturforsch. B 37 (1982) 432–436;
(b) A.W. Cordes, M. Hojo, H. Koenig, M.C. Noble, R.T. Oakley, W.T. Pennington, Inorg. Chem. 25 (1986) 1137–1145.
[21] R.S. Rowland, R. Taylor, J. Phys. Chem. 100 (1996) 7384–7391.
[22] The heteroatom chemistry of –N=S=O and –N=S=N– functions is very rich. Selected books and review articles:
(a) R. Bussas, G. Kresze, H. Muensterer, A. Schwoebel, Sulfur Rep. 2 (1983) 215–377;
(b) S. Bleisch, R. Mayer, Methoden der Organischen Chemie (Houben-Weyl), Thieme, Stuttgart, 1985, E11/1;
(c) A.V. Zibarev, G.G. Yakobson, Usp. Khim. (Russ. Chem. Rev.) 54 (1985) 1706–1737 (in Russian);
(d) T. Chivers, A Guide to Chalcogen-Nitrogen Chemistry, World Scientific, Singapore, 2005;
(e) T. Chivers, R.S. Laitinen, in: F. Devillanova (Ed.), Handbook of Chalcogen Chemistry. New Perspectives in Sulfur, Selenium and Tellurium, RSC Press, Cambridge, 2007.
[23] V.L. Salenko, M.M. Troshkov, A.V. Zibarev, J. Chromatogr. 549 (1991) 429–433.
[24] N.A. Pushkarevsky, A.V. Lonchakov, N.A. Semenov, E. Lork, L.I. Buravov, L.S. Konstantinova, T.G. Silber, N. Robertson, N.P. Gritsan, O.A. Rakitin, J.D. Woollins, E.B. Yagubskii, A.V. Zibarev, Synth. Met. 162 (2012) 2267–2276.
[25] (a) I.Yu. Bagryanskaya, Yu.V. Gatilov, A.M. Maksimov, V.E. Platonov, A.V. Zibarev, J. Fluor. Chem. 126 (2005) 1281–1287;
(b) F. Cozzi, S. Bacchi, G. Filippini, T. Pilati, A. Gavezzotti, Chem. Eur. J. 13 (2007) 7177–7184;
(c) I.Yu. Bargyanskaya, M.A. Grishina, L.Yu. Safina, G.A. Selivanova, V.A. Potemkin, Yu.V. Gatilov, Zh. Strukt. Khim. 49 (2008) 933–941 (in Russian).
[26] J.D. Davis, L.D. Spicer, Inorg. Chem. 19 (1980) 2191–2192.
[27] (a) G.G. Furin, N.G. Malyuta, V.E. Platonov, G.G. Yakobson, Zh. Org. Khim. 10 (1974) 830–838 (in Russian);
(b) T.A. Vaganova, S.Z. Kusov, V.I. Rodionov, I.K. Shundrina, E.V. Malykhin, Russ. Chem. Bull. 56 (2007) 2239–2246;
(c) G.A. Selivanova, L.Yu. Gurskaya, L.M. Pokrovskii, V.F. Kollegov, V.D. Shteingarts, J. Fluor. Chem. 125 (2004) 1829–1834;
(d) G.A. Selivanova, T.V. Chuikova, A.A. Shtark, V.D. Shteingarts, Zh. Org. Khim. 24 (1988) 2513–2518 (in Russian);
(e) A.O. Miller, G.G. Furin, J. Fluor. Chem. 36 (1987) 247–272;
(f) G.A. Selivanova, L.M. Pokrovskii, V.D. Shteingarts, Russ. J. Org. Chem. 38 (2002) 1023–1029.
[28] SADABS, Version 2008-1, Bruker AXS, Madison, WI, 2008.
[29] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 122–127.
[30] (a) A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, Version 10M, Utrecht University, The Netherlands, 2003;
(b) A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.
[31] C.F. Macrae, P.R. Edgington, P. McCane, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Stree, J. Appl. Crystallogr. 39 (2006) 453–457.
[32] F.H. Allen, O. Kenard, D.G. Watson, L. Bramer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) S1–S19213.
[33] (a) A.O. Miller, G.G. Furin, Zh. Org. Khim. 25 (1989) 355–357 (in Russian);
(b) A.G. Budnik, N.V. Kalinichenko, V.D. Shteingarts, Zh. Org. Khim. 10 (1974) 1923–1927 (in Russian).
[34] A.A. Shtark, V.D. Shteingarts, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk. (1976) 123–128 (in Russian).
[35] (a) G.A. Selivanova, L.M. Pokrovskii, V.D. Shteingarts, Russ. J. Org. Chem. 37 (2001) 404–409;
(b) H. Kobayashi, T. Sonoda, K. Takuma, N. Honda, T. Nakata, J. Fluor. Chem. 27 (1985) 1–22;
(c) G.M. Brooke, R.D. Chambers, J. Heyes, W.K.R. Musgrave, Proc. Chem. Soc. (1963) 213.
[36] G.M. Brooke, J. Burdon, J.C. Tatlow, J. Chem. Soc. (1961) 802–807.