

Fluorinated 1,3λ⁴δ²,2,4-Benzodithiadiazines – A Synthetic, Structural and Theoretical Study

Alexander Yu. Makarov,^[a] Irina Yu. Bagryanskaya,^[a] Frank Blockhuys,^{*,[b]}
 Christian Van Alsenoy,^[b] Yuri V. Gatilov,^[a] Vladimir V. Knyazev,^[a]
 Alexander M. Maksimov,^[a] Tatiana V. Mikhulina,^[a] Vyacheslav E. Platonov,^[a]
 Makhmut M. Shakirov,^[a] and Andrey V. Zibarev^{*,[a]}

Dedicated to Professor Dr. Rüdiger Mews on the occasion of his 60th birthday

Keywords: Antiaromaticity / Fluorinated 1,3λ⁴δ²,2,4-benzodithiadiazines / Electrophilic cyclisation / Molecular structure / NICS / Nucleophilic cyclisation

The series of title compounds has been prepared through both electrophilic ($C_6H_nF_{5-n}-N=S=N-SiMe_3 + SCl_2$) and nucleophilic ($C_6HF_4-S-N=S=N-SiMe_3 + CsF$) intramolecular *ortho*-cyclisation reactions, and the former route seems to be the more effective. High regioselectivity of the ring-closing procedures is observed in both cases. The compounds were characterised by X-ray crystallography and multinuclear (¹H, ¹³C, ¹⁵N and ¹⁹F) NMR spectroscopy. In accordance with GIAO calculations, ¹⁵N{¹H} experiments and the effects observed on complete substitution of hydrogen by fluorine, the high-field signal in the ¹⁵N NMR spectra can be assigned to N-4 and the low-field signal to N-2. In the crystal, 5,6,7-trifluoro- (**5**) and 5,6,8-trifluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**6**) are planar, whereas the 6,8-difluoro derivative **3** is bent along the S1...N4 line by 8.3°. According to NICS calculations

the heterocycle moiety in this compound class is antiaromatic while the carbocycle is aromatic. The fluorine substituents increase the aromaticity – and in some cases (especially when a fluorine atom is present in the 8-position) the antiaromaticity – of the corresponding rings. The *ortho*-fluoro-containing starting material $C_6H_nF_{5-n}-N=S=N-SiMe_3$ ($n = 2$: **10**) cyclises to the fluorinated 2,1,3-benzothiadiazole **27** upon treatment with CsF instead of SCl₂. For starting compound 6- $HC_6F_4-S-N=S=N-SiMe_3$ (**14**) the planar (*Z,E*) configuration features a short intramolecular H...N contact, as evidenced by X-ray diffraction. Both the reaction pathways mentioned are also discussed.

(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2003)

1. Introduction

Hyperelectronic (π - and σ -excessive) 1,3λ⁴δ²,2,4-benzodithiadiazines^[1–4] **1** (Scheme 1) reveal a nontrivial combination of definite features of antiaromaticity^[5] with moderate thermal stability. In particular, the compounds in series **1** possess a cyclic 12 π -electron system with a notably low IE₁^[6–8] in planar or nearly planar molecular conformations observed both in the gas phase^[9] and in the crystal,^[1–4] low-lying π^* -excited states^[1–4,10] localised predominantly on the heterocycle,^[11] and enhanced magnetic shielding of the ¹H, ¹³C and ¹⁹F (for the monofluoro deriv-

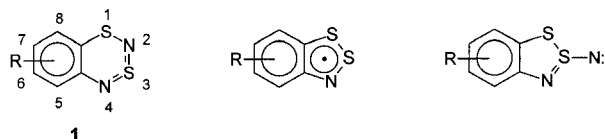
atives) nuclei attached to C-5 and C-8 – i.e., those closest to the heterocycle – with respect to those attached to C-6 and C-7,^[1,3,4] this probably being due to paratropic ring currents.^[5] At the same time, the compounds in series **1** are thermally stable up to ca. 100 °C. At higher temperatures and in dilute hydrocarbon solutions, compounds **1** quantitatively yield persistent 1,2,3-benzodithiazolyl radicals (Scheme 1),^[10,12] which are also the products of photolysis reactions of **1**.^[10,13] The key intermediates are singlet 1,2,3-benzodithiazol-2-yl nitrenes (Scheme 1), identified under matrix isolation conditions.^[13] The other aspects of the heteroatom reactivity of **1** have been studied only to a limited extent. Since both the π -excess and the antiaromaticity are destabilising factors, one might believe that the heteroatom reactivity of **1** should be high; consequently, many new reactions should be found in which this reactivity takes on many different forms. Additionally, several new structures should no doubt be observed among the reaction products of **1**. Currently, however, the only fact that is known is that the compounds in series **1** are able to imitate some S^{II} ^[4]

^[a] Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia
 Fax: (internat.) + 7-3832/344-752
 E-mail: zibarev@nioch.nsc.ru

^[b] Department of Chemistry, University of Antwerp (UIA), Universiteitsplein 1, 2610 Wilrijk (Antwerpen), Belgium
 Fax: (internat.) + 32-3/820-2310
 E-mail: Frank.Blockhuys@ua.ac.be

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

and P^{III} [14] derivatives oxidatively, another reaction most probably mediated by the nitrenes mentioned above. Reversible cycloaddition to norbornadiene^[1] as well as reduction and hydrolysis to 2-aminobenzenethiols (isolated in the form of their corresponding disulfides)^[3] have also been described.



In this work, compounds **1**: R = H (**2**), 6,8-F₂ (**3**), 6,7-F₂ (**4**), 5,6,7-F₃ (**5**), 5,6,8-F₃ (**6**), 5,6,7,8-F₄ (**7**)

Scheme 1

The fluorinated compounds in series **1** are all unknown except for the 5-, 6- and 7-fluoro derivatives^[3,4] and the 5,6,7,8-tetrafluoro derivative.^[2] Nevertheless, they are interesting not only from a general point of view, but also in the context of further investigation of the peculiarities of the molecular and electronic structures of these compounds. For instance, it was found by gas electron diffraction (GED) that a free molecule of the parent 1,3λ⁴δ²,2,4-benzodithiadiazine **2** is bent significantly, while a free molecule of its tetrafluoro derivative **7** is planar.^[9] The bent geometry of the former was attributed to pseudo-Jahn–Teller distortion to minimize the antiaromaticity,^[4,9] whereas the planar geometry of the latter was thought to be due to a conflict between the pseudo-Jahn–Teller effect and the perfluoro (or π-fluoro) effect, caused by the presence of a fluorine atom in the 8-position, resolved in favour of the latter.^[9] To verify this conclusion it is necessary to perform GED on 6,8-difluoro- (**3**) and 5,6,7-trifluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**5**), the free molecules of which would be expected to be planar and bent, respectively, and these experiments are currently underway.

This work deals with the preparation and X-ray structural characterisation of a number of new fluorinated derivatives of 1,3λ⁴δ²,2,4-benzodithiadiazine **2**, as well as with the quantitative estimation of the (anti)aromaticity of the compounds in series **1** for both the fluorocarbon and the hydrocarbon series, by application of the Nucleus-Independent Chemical Shift (NICS) concept.^[15] On the basis of the theoretical calculations, a more detailed structural study was also performed for all fifteen possible fluoro-substituted 1,3λ⁴δ²,2,4-benzodithiadiazines.

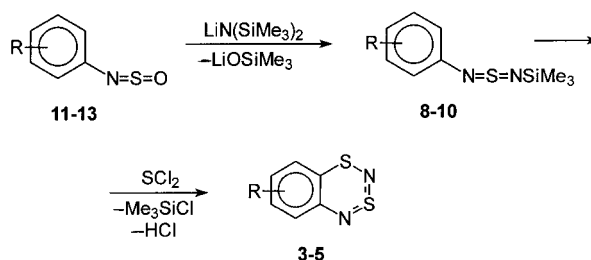
2. Results and Discussion

The monofluorinated compounds of series **1** had previously been synthesised by 1:1 condensation of the corresponding Ar–N=S=N–SiMe₃ with SCl₂, followed by the electrophilic *ortho*-cyclisation of the [Ar–N=S=N–S–Cl]

intermediates.^[3,4] The tetrafluoro derivative **7** was obtained by the nucleophilic ring-closure of the intermediate [Ph_F–S=N=S=N][–] anion generated from Ph_F–S=N=S=N–SiMe₃ and CsF.^[2] Both approaches were applied in this work.

2.1. Electrophilic Cyclisation

The Ar–N=S=N–SiMe₃ starting materials **8–10** (Scheme 2) for the electrophilic ring-closure procedure were synthesised by a general method^[3,4,16,17] from the corresponding Ar–N=S=O compounds and LiN(SiMe₃)₂. Earlier, the less common Me₃SnN(SiMe₃)₂ was used to transform the polyfluorinated Ar–N=S=O into Ar–N=S=N–SiMe₃.^[18,19] Further treatment of **8–10** with SCl₂ afforded the desired compounds **3–5** (Scheme 2). From these experiments it appears that the introduction of up to three fluorine atoms into the carbocycle does not deactivate Ar–N=S=N–SiMe₃ toward the electrophilic cyclisation needed to obtain **1**. It should be noted that only 75% of the stoichiometric amount of SCl₂ was used in these preparations, so as to suppress any further reaction of **3–5** with SCl₂, it having previously been found that the compounds in series **1** readily react with SCl₂ to yield 1,2,3-benzodithiazolium chlorides (Herz salts).^[4]



3: R = 6,8-F₂; **4**: R = 6,7-F₂; **5**: R = 5,6,7-F₃;
8, **11**: R = 3,5-F₂; **9**, **12**: R = 3,4-F₂; **10**, **13**: R = 2,3,4-F₃

Scheme 2

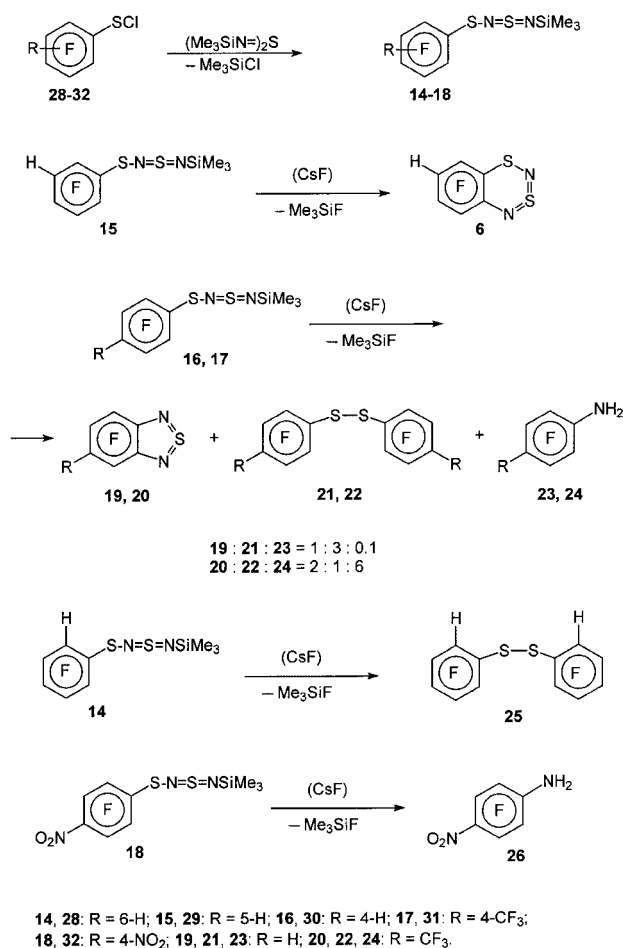
The cyclisation proved to be effectively regioselective in the case of **9**, which possesses two non-equivalent positions at which the ring-closure may occur (cf. refs.^[3,4]). Only **4** (Scheme 2) was isolated from the reaction mixture, and the second possible isomer was not detected. It had previously been shown^[3] that the regioselectivity in these types of cyclisation reactions is consistent with the thermodynamics of the corresponding intermediate σ complexes as well as with factors of kinetic control for an orbital-controlled electrophile-nucleophile reaction. At the same time, the ratio of the isomers observed in the reaction mixture is obviously affected by the difference in their rates of reaction with SCl₂.^[4] The structures of **3** and **5** were confirmed by X-ray crystallography (see below).

As reaction by-products, the corresponding sulfur diimides (Ar–N=)₂S were identified in all cases. One can explain their formation in terms of dimerisation of [Ar–N=

S=N–S–Cl] intermediates through [2π + 2π] cycloaddition reactions, followed by decomposition of the nonsymmetric dimers to (Ar–N=)₂S and the well-known [S₃N₂Cl]Cl.^[20] Dilution of the reaction solutions reduces the yields of the (Ar–N=)₂S by-products.

2.2. Nucleophilic Cyclisation

The Ar_F–S–N=S=N–SiMe₃ starting materials **14**–**18** (Scheme 3) for the nucleophilic cyclisation reactions were obtained through the known 1:1 condensation of the corresponding Ar_FSCl compounds with (Me₃SiN=)₂S.^[2,3,19] The structure of **14** was confirmed by X-ray crystallography (Figure 1). The planar (*Z,E*) configuration features a short intramolecular H⋯N contact or hydrogen bond (cf. hydrocarbon analogues^[21]).



Scheme 3

The compounds **14**–**18** were treated with CsF in boiling acetonitrile (cf. ref.^[2]) in an attempt to close the ring and obtain the target heterocycles; this was successful only in the case of **15** (Scheme 3). The cyclisation of **15** to **6** again proved to be highly regioselective, since the second possible isomer was not observed. It had previously been shown,^[19] for the closely related nucleophilic cyclisation reactions affording polyfluorinated naphtho[1,2-*c*][1,2,5]thiadiazoles,

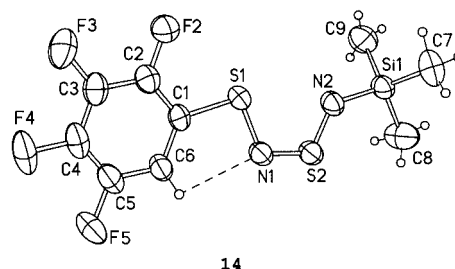


Figure 1. Molecular structure of **14**; selected bond lengths [Å] and bond angles [°]: C1–S1 1.762(3), S1–N1 1.662(3), N1–S2 1.552(3), S2–N2 1.494(3), N2–Si1 1.748(3), N1–H 2.504; C1–S1–N1 98.55(15), S1–N1–S2 116.19(15), N1–S2–N2 113.58(15), S2–N2–Si1 129.17(19)

that the preferred direction of the ring-closure is consistent with essentially the same factors as described above for the electrophilic cyclisation reactions. The structure of **6** was confirmed by X-ray crystallography (see below).

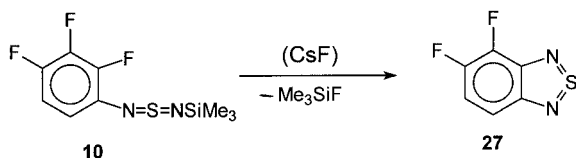
In the cases of **16** and **17**, only polyfluorinated 2,1,3-benzothiadiazoles **19** and **20** (i.e., the smaller-sized heterocycles) could be detected in the reaction mixtures, along with the corresponding Ar_FSSAr_F and Ar_FNH₂ derivatives (in different ratios). In the case of **14** (a potential precursor of **5**: see Scheme 2), however, only the disulfide **25** (Scheme 3) was identified by ¹⁹F NMR in the crude reaction product, and was subsequently isolated; in the case of **18** only amine **26** (Scheme 3) was obtained in high yield.

Similar thiadiazoles, disulfides and/or amines had previously been obtained from unsuccessful attempts to prepare fluorinated naphthalene- and pyridine-fused 1,3λ⁴δ²,2,4-dithiadiazines from the corresponding Ar_F–S–N=S=N–SiMe₃ derivatives upon treatment with CsF^[3,19] (cf. also the formation of the corresponding disulfide, rather than the target compound **2**, from 2-O₂NC₆H₄–S–N=S=N–SiMe₃ on treatment with CsF^[2]). The results were attributed then to both low nucleophilicity and thermal stability of the [Ar_F–S–N=S=N][–] anions and explained in terms of: (1) *ipso*-cyclisation followed by ring-opening reactions to form [Ar_F–N=S=N–S][–] anions, (2) elimination of sulfur and *ortho*-cyclisation of [Ar_F–N=S=N][–] anions to form thiadiazoles, or (3) decomposition to Ar_FNH₂. The decomposition of [Ar_F–S–N=S=N][–] anions before cyclisation yields Ar_FSSAr_F.^[3,19]

The same explanation is obviously valid for this work. The difference between the successful Ar_F–S–N=S=N–SiMe₃-based syntheses of the title compounds (Ar_F = C₆F₅,^[2] 5-HC₆F₄) and their failed counterparts (Ar_F = 6-HC₆F₄, 4-HC₆F₄) is in accordance with the known relative propensities of fluorine atoms in different positions of partially fluorinated aromatic compounds to nucleophilic substitution.^[22] In the case of **14** one can also consider that the intramolecular H⋯N interaction (see Figure 1) stabilises the [Ar_F–S–N–S=N][–] thiazylamide form of the intermediate anion (cf. refs.^[17,23,24]) more than the [Ar_F–S–N=S=N][–] sulfur diimide one, the former obviously being unable to cyclise in either *ortho* or *ipso* fashion. Taking into

account the high yield of cyclisation of the $[4\text{-F}_3\text{CC}_6\text{F}_4\text{NSN}]^-$ anion to the corresponding thiadiazole under the same conditions,^[25] one can also explain the predominant formation of amine **24** from compound **17** (Scheme 3) by the direct decomposition of the $[4\text{-F}_3\text{CC}_6\text{F}_4\text{NSNS}]^-$ anion to the radical anion $[4\text{-F}_3\text{CC}_6\text{F}_4\text{N}]^-$, followed by reaction with the solvent to give the final product **24**. This explanation is also applicable to the formation of **26** from **18** (Scheme 3).

Thus, the synthetic usefulness of the nucleophilic approach to fluorinated 1,3λ⁴δ²,2,4-benzodithiadiazines is limited. On the other hand, this type of cyclisation reaction is a convenient method for the synthesis of fluorinated 2,1,3-benzothiadiazoles.^[16,19,25] For example, compound **10** (the precursor of **5** under electrophilic cyclisation conditions; Scheme 2) afforded fluorinated thiadiazole **27** in good yield upon treatment with CsF (Scheme 4).



Scheme 4

2.3. X-ray Molecular Structures and Comparison with Calculated Gas-Phase Data

According to X-ray crystallography^[1–4] and gas electron diffraction^[9] data, as well as post-HF and DFT calculations,^[4,9,11] the compounds in series **1** are structurally nonrigid because they possess a low-energy vibrational mode that allows the molecule to be deformed easily upon going from the gas phase to the solid. For example, a molecule of **2** is significantly bent along the S1⋯N4 line in the gas phase^[9] and perfectly planar in the crystal.^[1] In contrast, a molecule of **7** is flat in the gas phase^[9] and folded in the solid state.^[2] (For an in-depth discussion of the structures of **2** and **7** in the two phases, including an analysis of the experimental gas-phase geometries, see ref.^[9]; the results of GED measurements on **3** and **5** will be published elsewhere.) The 6-fluoro derivative of **2** is nearly planar in the crystal.^[3] This structural dichotomy is also observed for compounds **3**, **5** and **6** in the crystal (Figure 2 and Table 1). According to X-ray diffraction data, molecules **5** and **6** are planar, whilst a molecule of **3** is bent along the S1⋯N4 line by 8.3°; this is the largest deviation from planarity so far found in the solid state for fluoro-containing compounds of series **1**.^[2,3] For compound **4** the crystals obtained were not suitable for X-ray diffraction.

The bond lengths and bond angles of **3**, **5** and **6** (Table 1) are typical.^[1–4,9] As in the parent compound **2** and the tetrafluoro derivative **7**, four of the π -electrons in the heterocycle are localised to some extent in two of the N–S bonds, giving rise to one long and two short bonds. We also note that the bond lengths in the N=S=N moiety of **5** are

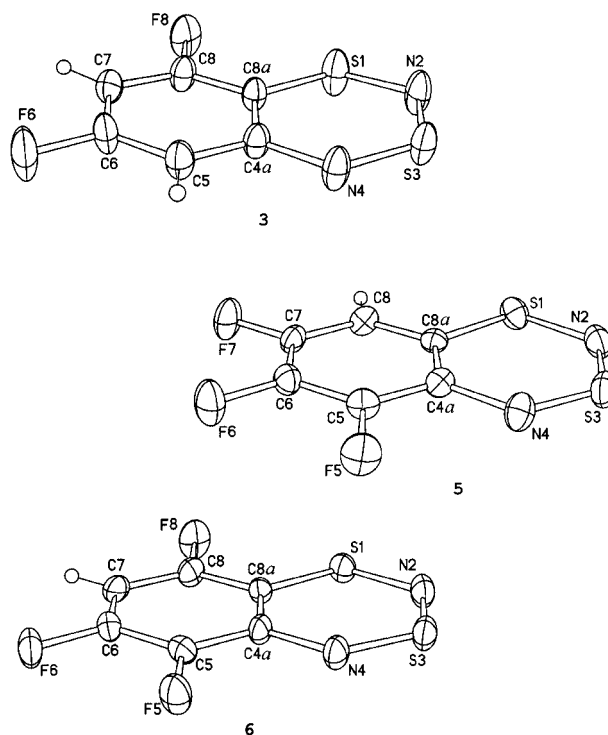


Figure 2. Molecular structures of **3**, **5** and **6**; for selected bond lengths and bond angles see Table 1

practically identical, as also found for **2**,^[1] whereas for **3** and **6** they are slightly different, as found for **7**.^[2]

Thus, in the crystal, compound **2** and its 5-F₃C, 6-F, 7-Br, 7-H₃CO, 5,6,7-F₃ (**5**) and 5,6,8-F₃ (**6**) derivatives are planar, whereas the 5-H₃CO, 5-Br, 6-H₃C, 8-Br, 6,8-F₂ (**3**) and 5,6,7,8-F₄ (**7**) derivatives are bent along the S1⋯N4 line by up to 10.8° (for the 5-H₃CO derivative) (see refs.^[1–4] and this work). Of the two crystallographically independent molecules of the 6-Br derivative, one is perfectly planar whereas the other is bent by 3.1°, which directly indicates the importance of packing effects.^[4]

Table 1 also compares the solid-state geometries with those obtained in the gas phase by calculation, for those derivatives for which crystal structures exist. The choice of the method/basis set combination was based on previous calculations on **2** and **7**, which showed that B3LYP/6-311+G* performs quite well for these systems, unlike MP2, which incorrectly reproduces the conformation of the heterocycle.^[9] (Cartesian coordinates and energies for **2** and its fifteen fluorinated derivatives can be found in the Supporting Information; symmetries and relative energies can be found in Table 3). The calculations rigorously maintain the equal bond lengths in the N=S=N fragment for all sixteen compounds; the largest difference is 0.005 Å. However, the localisation of the π -electrons in the heterocycle is adequately reproduced. The variation in the N=S bond lengths for the various derivatives is negligible: for N2–S3 this is limited to 0.005 Å, and for S3–N4 to 0.006 Å. The values in Table 1 illustrate this. For the S–N single bond,

Table 1. Selected data comparing solid-state (XRD) and calculated gas-phase (B3LYP, *r*_c) geometries for **3**, **5**, **6** and 6-fluoro-1,3λ⁴δ²,2,4-benzodithiadiazine^[3]

Parameter ^[a] ^[b]	5		3		6		6-Fluoro	
	XRD	B3LYP	XRD	B3LYP	XRD	B3LYP	XRD	B3LYP
S1–N2	1.683(5)	1.713	1.668(5)	1.697	1.677(6)	1.696	1.673(4)	1.713
N2–S3	1.539(5)	1.568	1.551(5)	1.565	1.537(7)	1.565	1.534(4)	1.568
S3–N4	1.532(4)	1.566	1.536(5)	1.567	1.552(5)	1.566	1.531(5)	1.568
N4–C4a	1.430(6)	1.402	1.425(6)	1.409	1.421(6)	1.401	1.425(6)	1.409
C4a–C8a	1.389(7)	1.410	1.398(7)	1.414	1.386(9)	1.415	1.405(6)	1.410
C8a–S1	1.786(5)	1.814	1.779(5)	1.826	1.784(6)	1.825	1.797(5)	1.813
S1–N2–S3	123.9(3)	121.7	123.9(3)	124.9	124.8(1)	125.0	124.3(3)	121.1
N2–S3–N4	119.7(2)	117.9	118.3(2)	118.5	119.1(3)	118.3	119.0(2)	118.0
S3–N4–C4a	121.4(4)	121.9	123.2(4)	122.9	121.2(5)	122.7	123.3(3)	121.9
N4–C4a–C8a	125.7(4)	125.6	123.6(4)	124.7	125.1(5)	125.6	123.7(5)	124.5
C4a–C8a–S1	123.9(4)	121.6	124.6(4)	125.1	125.4(4)	124.3	124.1(4)	122.0
C8a–S1–N2	105.3(2)	103.8	105.0(2)	103.9	104.1(3)	104.0	105.3(2)	103.6

^[a] Bond lengths in Å and bond angles in °. ^[b] For atomic numbering see Scheme 1 and Figure 2.

S1–N2, the variation is larger, amounting to 0.021 Å, and seems to depend on the presence of the fluorine atom in the 8-position and thus on the conformation of the heterocycle. If the atom is present and the compound has *C_s* symmetry, the S1–N2 bond is shorter, as is again illustrated in Table 1. The typical C–C double/single-bond alternation, as observed in the calculations on **2** and **7**,^[9] is found for all other compounds in the series and thus seems to be independent of the number and position of the fluorine atoms.

A closer look at the various C–F bond lengths displays some interesting patterns. The C–F distance for a particular position (i.e., C5, C6, C7 or C8) is shorter when that fluorine atom has another fluorine atom *ortho* to it than when it does not, which corresponds to the known shortening of the C–F bond in *r*₀ structures observed by microwave spectroscopy on going from fluorobenzene to 1,2-difluorobenzene.^[26] The difference in the bond lengths between these two situations depends on the position of the fluorine atom: for F5 and F8 the difference is limited to 0.009 Å on average and for F6 and F7 it is 0.012 Å on average. In any of the derivatives of **2**, the C8–F8 distance is always the largest, C7–F7 and C6–F6 are intermediate and the C5–F5 bond length is the shortest. The four torsion angles that define the conformation of the heterocycle (see ref.^[9] for further details) do not vary significantly with the number and the position of the fluorine atoms. The largest differences for each angle range from 1.0° for C5–C4a–C8a–S1 through 1.9° (N4–C4a–C8a–S1) and 2.4° (S3–N2–S1–C8a) to 3.8° for C4a–C8a–S1–N2.

2.4. Spectral Properties

The experimental assignment of the ¹H and ¹³C NMR spectra of compound **2**, the parent compound in the **1** series, is based on double resonance, COLOC and off-resonance techniques. For the fluorinated derivatives, mono-resonance and off-resonance techniques as well as analyses of ¹H–¹H, ¹H–¹⁹F, ¹³C–¹⁹F and ¹⁹F–¹⁹F spin-spin coupling

constants were used to obtain full assignments. These are given in Table 2.

In the ¹⁵N{¹H} NMR spectrum of **2**, the signal at δ = 263.1 ppm is a doublet on selective decoupling with 8-H, but a singlet on selective decoupling with 5-H. From this, it is possible to assign the signal at δ = 263.1 ppm to N-4 and the signal at δ = 269.2 ppm to N-2. This is also in agreement with an empirical analysis of the ¹⁵N NMR spectroscopic data for various 5-, 6-, 7- and 8-R substituted derivatives of **2**.^[3] Comparison of ¹⁵N and ¹⁵N{¹H} NMR spectra (see footnotes to Table 2; the latter feature the lack of the N⁴–H⁵ spin-spin coupling, cf. ref.^[3]) unambiguously identifies the high-field resonance of the 6-F derivative of **2** as well as of compounds **3** and **4** as N-4 and the low-field resonance as N-2. For the previously studied compounds of series **1**, the δ¹⁵N values lie in a narrow range of ca. 280–250 ppm (except for **7**^[2]), with a weak dependence on the nature of the carbocyclic substituent. In the case of polyfluorinated derivatives **5**, **6** (Table 2) and **7**,^[2] one nitrogen resonance is shifted to higher field (up to δ = 233 ppm for **7**^[2]). It is known for related heterocycles that replacement of the four hydrogen atoms by fluorines increases the ¹⁵N shielding in 2,1,3-benzothiadiazole but does not affect the δ¹⁵N of 1,3λ⁴δ²,5,2,4-benzotrithiadiazepine.^[27,28] Consequently, and in agreement with the discussion above, it is feasible that the high-field signal in the ¹⁵N NMR spectra of **5**–**7** belongs to N-4 and the low-field signal to N-2. In agreement with the experiment, the GIAO calculations systematically predict that the N-2 nucleus of the studied compounds should be definitely deshielded relative to the N-4 nucleus for all but the 5-fluoro derivative, since the calculations for this last compound fail to predict the coincidence of both signals. For the 7-fluoro derivative the experimental assignment is difficult, but from the excellent qualitative agreement between theory and experiment for the other derivatives, one can be confident in again assigning the high-field signal to N-4 and low-field signal to N-2. Quantitative prediction of the δ¹⁵N values, on the other hand, is prob-

Table 2. Calculated and experimentally determined NMR chemical shifts (ppm) for 1,3λ⁴δ²,2,4-benzodithiadiazine **2** and its fluoro-substituted derivatives

δ		2 HF		DFT		δ		5-Fluoro HF		DFT	
7-H	6.78	7-H	7.17	7-H	6.58	7-H	6.70	7-H	7.18	7-H	6.48
6-H	6.63	6-H	7.10	6-H	6.41	6-H	6.38	6-H	6.88	6-H	6.08
5-H	5.90	5-H	6.67	5-H	5.59	8-H	5.53	8-H	6.12	8-H	5.12
8-H	5.79	8-H	6.44	8-H	5.42	5-F	36.4	5-F	31.5	5-F	40.1
C-4a	138.5	C-4a	143.3	C-4a	141.4	C-5	152.1	C-5	149.5	C-5	148.5
C-7	133.2	C-7	130.7	C-7	129.5	C-7	133.3	C-7	132.7	C-4a	130.4
C-6	130.5	C-6	129.5	C-6	125.8	C-4a	126.9	C-4a	130.9	C-7	129.3
C-8	124.0	C-8	124.8	C-8	119.5	C-8	119.4	C-8	118.5	C-6	115.9
C-5	123.0	C-5	123.0	C-5	119.1	C-6	119.0	C-6	118.1	C-8a	115.6
C-8a	115.3	C-8a	113.8	C-8a	114.2	C-8a	116.4	C-8a	117.2	C-8	114.4
N-2	269.2	N-2	396.7	N-2	354.2	N-2	268.0	N-2	390.7	N-2	350.1
N-4	263.1	N-4	353.5	N-4	313.3	N-4	268.0	N-4	338.3	N-4	297.3
δ		6-Fluoro HF		DFT		δ		7-Fluoro HF		DFT	
7-H	6.48	7-H	6.87	7-H	6.21	6-H	6.25	6-H	6.74	6-H	5.92
8-H	5.76	5-H	6.47	5-H	5.39	5-H	5.90	5-H	6.68	5-H	5.53
5-H	5.71	8-H	6.45	8-H	5.34	8-H	5.59	8-H	6.22	8-H	5.20
6-F	50.5	6-F	37.6	6-F	45.8	7-F	55.5	7-F	40.3	7-F	54.0
C-6	163.9	C-6	161.7	C-6	161.4	C-7	165.2	C-7	162.3	C-7	163.8
C-4a	140.2	C-4a	146.0	C-4a	143.0	C-4a	134.5	C-4a	137.9	C-4a	136.9
C-8	124.9	C-8	127.2	C-8	120.4	C-5	124.6	C-5	125.9	C-5	120.5
C-7	118.4	C-7	115.7	C-7	115.4	C-8a	117.5	C-8a	118.3	C-8a	116.4
C-5	111.4	C-5	110.8	C-8a	108.2	C-6	115.4	C-6	114.4	C-6	111.5
C-8a	110.1	C-8a	106.8	C-5	108.1	C-8	112.3	C-8	112.5	C-8	108.6
N-2 ^[a]	275.7	N-2	415.8	N-2	362.6	N ^[b]	260.7	N-2	373.3	N-2	335.9
N-4 ^[a]	259.6	N-4	341.8	N-4	308.9	N ^[b]	256.5	N-4	352.6	N-4	309.7
δ		3 HF		DFT		δ		4 HF		DFT	
7-H	6.23	7-H	6.26	7-H	5.39	5-H	5.86	5-H	6.57	5-H	5.43
5-H	5.53	5-H	5.76	5-H	4.58	8-H	5.72	8-H	6.33	8-H	5.23
6-F	53.6	6-F	41.7	6-F	49.0	7-F	29.7	7-F	18.9	7-F	29.9
8-F	47.4	8-F	36.6	8-F	41.5	6-F	25.4	6-F	17.1	6-F	22.3
C ^[b]	163.8	C-8	162.5	C-6	161.3	C-6,C-7 ^[b]	152.2	C-7	148.9	C-7	151.8
C ^[b]	155.5	C-6	154.5	C-8	152.3	C-6,C-7 ^[b]	150.0	C-6	147.7	C-6	148.4
C-4a	139.0	C-4a	143.2	C-4a	137.9	C-4a	135.0	C-4a	139.9	C-4a	137.6
C-5	107.8	C-8a	106.3	C-5	104.3	C-5,C-8 ^[b]	113.6	C-8	115.4	C-8	110.3
C-7	107.1	C-7	103.3	C-7	103.7	C-5,C-8 ^[b]	113.2	C-5	113.7	C-5	110.0
C-8a	97.6	C-5	94.8	C-8a	96.1	C-8a	111.0	C-8a	109.8	C-8a	109.0
N-2 ^[c]	265.4	N-4	298.3	N-2	324.2	N-2 ^[d]	265.0	N-2	394.6	N-2	347.3
N-4 ^[c]	250.1	N-2	391.5	N-4	270.6	N-4 ^[d]	258.8	N-4	342.8	N-4	307.4
δ		5 HF		DFT		δ		6 HF		DFT	
8-H	5.51	8-H	6.06	8-H	4.99	7-H	6.29	7-H	6.37	7-H	5.39
7-F	30.1	7-F	23.1	7-F	31.4	8-F	41.6	8-F	30.0	8-F	35.7
5-F	16.3	5-F	17.9	5-F	23.6	5-F	32.0	6-F	24.8	6-F	30.3
6-F	3.3	6-F	-0.4	6-F	3.1	6-F	10.7	5-F	6.7	5-F	12.8
C-7	152.8	C-7	150.3	C-7	152.2	C-6,C-8 ^[b]	152.4	C-6	151.4	C-6	151.4
C-5	142.2	C-5	140.6	C-6	140.1	C-6,C-8 ^[b]	150.4	C-8	148.7	C-8	147.3
C-6	140.6	C-6	138.4	C-5	139.9	C-5	138.7	C-5	134.5	C-5	135.4
C-4a	124.5	C-4a	128.5	C-4a	127.7	C-4a	127.2	C-4a	131.3	C-4a	128.3
C-8a	110.8	C-8a	112.3	C-8a	109.4	C-7	107.7	C-7	105.3	C-7	104.2
C-8	108.1	C-8	108.5	C-8	104.5	C-8a	97.5	C-8a	96.6	C-8a	96.1
N-2	265.1	N-2	388.3	N-2	343.4	N-2	264.2	N-2	386.7	N-2	320.8
N-4	240.9	N-4	328.0	N-4	291.4	N-4	232.8	N-4	287.4	N-4	257.0
δ		7 HF		DFT		δ		7 HF		DFT	
8-F,5-F ^[b]	18.5	8-F	11.2	8-F	15.8	7-H	6.29	7-H	6.37	7-H	5.39
5-F,8-F ^[b]	12.2	5-F	11.0	5-F	14.3	8-F	41.6	8-F	30.0	8-F	35.7
6-F,7-F ^[b]	9.9	6-F	3.9	7-F	8.1	5-F	32.0	6-F	24.8	6-F	30.3
7-F,6-F ^[b]	6.9	7-F	2.9	6-F	5.3	6-F	10.7	5-F	6.7	5-F	12.8
C-6,C-7 ^[b]	143.0	C-6	139.8	C-7	141.9	C-6,C-8 ^[b]	152.4	C-6	151.4	C-6	151.4
C-7,C-6 ^[b]	141.3	C-7	139.3	C-6	141.1	C-6,C-8 ^[b]	150.4	C-8	148.7	C-8	147.3
C-8,C-5 ^[b]	140.4	C-8	139.0	C-8	138.9	C-5	138.7	C-5	134.5	C-5	135.4
C-5,C-8 ^[b]	139.5	C-5	136.3	C-5	136.9	C-4a	127.2	C-4a	131.3	C-4a	128.3
C-4a	122.0	C-4a	125.2	C-4a	122.9	C-7	107.7	C-7	105.3	C-7	104.2
C-8a	98.9	C-8a	100.4	C-8a	98.1	C-8a	97.5	C-8a	96.6	C-8a	96.1
N-2	255.5	N-2	368.5	N-2	309.0	N-2	264.2	N-2	386.7	N-2	320.8
N-4	233.1	N-4	289.7	N-4	256.7	N-4	232.8	N-4	287.4	N-4	257.0

^[a] The doublet at δ = 275.7 ppm is not changed on going to the ¹⁵N{¹H} spectrum; thus, the corresponding spin-spin coupling constant (ca. 2.2 Hz) is not ³J(N⁴-H⁵) (cf. ref.^[3]) and the signal does not belong to N-4. ^[b] Uncertain experimental assignments. ^[c] The doublet of doublets of doublets at δ = 250.1 ppm becomes a doublet of doublets on going to the ¹⁵N{¹H} spectrum while the triplet at δ = 265.4 ppm is not affected. ^[d] The quadruplet at δ = 258.8 ppm becomes a triplet on going to the ¹⁵N{¹H} spectrum while the signal at δ = 265.0 ppm is not affected.

lematic: DFT performs better than HF but the rms deviation for all the compounds under consideration in Table 2 is still $\delta = 103.9$ ppm for HF and 60.0 ppm for DFT.

A similar observation can be made for the $\delta^{19}\text{F}$ values. Here, the rms differences are 8.6 and 3.6 ppm respectively. The spread in the specific values of the different compounds is larger for this nucleus, but HF seems to do better when the number of fluorine atoms increases. Both methods do, however, qualitatively reproduce the spectrum of all compounds, except for **6**, in which 5-F and 6-F have been switched. The assignments of the ^{19}F NMR spectrum of **7**, previously uncertain,^[2] can now be confidently made, on the basis of the superior DFT shifts.

For the ^1H NMR spectrum, the difference in performance of the two methods is a considerably smaller: the rms values are now 0.56 ppm for HF and 0.49 ppm for DFT, with HF performing better than DFT for compounds with a larger number of fluorine atoms. The only false prediction found for this nucleus, by both methods, is for the 6-fluoro derivative, in which 5-H and 8-H have been switched, but since both the calculated and the experimental differences in chemical shifts are very small, solvent effects can be used to account for this discrepancy.

For the $\delta^{13}\text{C}$ values, the rms differences for both methods are comparable: 2.6 ppm for HF and 2.7 ppm for DFT, but, in contrast to what was found for hydrogen, the performance of HF deteriorates relative to that of DFT when the number of fluorine atoms increases. The rather surprising fact that DFT falters slightly in the case of the carbon chemical shifts, when it had been clearly superior for the other nuclei, may be explained in terms of basic density functional theory. This indicates that the usual theorems do not hold in the presence of an external magnetic field and the functional has to depend both on the electron density ρ and the current density j , induced by the magnetic field.^[29] The functionals used here, including B3LYP, do not, and this may explain why DFT would be less reliable for compounds or specific fragments of compounds in which the effect of the current density J is logically larger, such as the aromatic ring in these 1,3λ⁴δ²,2,4-benzodithiadiazines. Only for the parent compound **2** and its 6-fluoro and 7-fluoro derivatives are the ^{13}C chemical shifts reproduced perfectly by both methods. For both **4** and **6** the two methods agree on the chemical shifts and the previously uncertain experimental assignments can be confidently made. For the 5-fluoro derivative of **2**, DFT switches C-4a and C-7 and incorrectly reproduces the shifts of C-6, C-8 and C-8a – the small difference calculated for C-8 and C-6 might explain this, even though the HF calculation displays the same small difference yet makes a correct prediction. In the case of compound **5**, DFT switches C-5 and C-6 but the small calculated difference may again be the cause. For **7** the assignments of C-5 and C-8 can now be made unambiguously, from the results of both methods, but those of C-6 and C-7 remain doubtful. Compound **3** fares the worst where HF is concerned, since only C-4a is correctly predicted and the rest is switched; even though DFT per-

forms better, the correct assignment of C-6 and C-8 remains a problem.

Despite the small problems that remain, the two methods used here perform generally well on a qualitative and sometimes even on a quantitative level. More sophisticated computational methods were not evaluated since computational time and efficiency become an important factor in those cases, and an evaluation of that type is beyond the scope of this study.

The most interesting feature of the NMR spectra of previously studied compounds of series **1**^[1,3,4] is the enhanced shielding of the ^1H , ^{13}C and ^{19}F nuclei (for the monofluoro derivatives) attached to C-5 and C-8 – i.e., those closest to the heterocycle – as compared to those attached to C-6 and C-7, probably due to paratropic ring currents. However, this is not the case for **3–6** (Table 2) and **7**.^[2] The GIAO calculations at HF and B3LYP levels of theory (Table 2) reproduce these shielding patterns. However, the results of these calculations cannot be interpreted in chemical terms. One can only think that for **3–7** the mutual influence of the fluorine atoms dominates all other effects on $\delta^{19}\text{F}$.

The long-wavelength absorption maxima in the UV/Vis spectra of compounds **3–6** (Table 5) and **7**^[2] are found in the 620–635 nm range (i.e., essentially the same as for the non-fluorinated analogues),^[1,3,4] with only a weak dependence upon the number and positions of the fluorine substituents. These results are in agreement with the conclusion,^[11] based on resonance Raman data, that the low-energy electronic transition in the UV/Vis spectra, responsible for the blue colour of solutions of the compounds in series **1**, is localised mainly on the sulfur–nitrogen chain.

2.5. Antiaromaticity

The aromaticity or antiaromaticity of π -systems is characterised by a combination of energetic, geometric and magnetic criteria. Application of these criteria usually yields different, and very frequently contradictory, results.^[5] In these situations the Nucleus-Independent Chemical Shift (NICS) concept^[15] appears to be a useful criterion for the quantification of (anti)aromaticity. For all 15 possible (poly)fluorinated compounds, and also the parent, the NICS values both of the carbocycle and of the heterocycle were calculated at the HF level of theory, together with a selected number at the DFT/B3LYP level, and studied as a function of the number and the position of fluorine atoms.

The heterocyclic ring of the parent compound **2** has a positive NICS value and is antiaromatic, whilst the carbocyclic ring has a negative value and is aromatic (Table 3). In comparison, at the same level of theory, but with the B3LYP/6-31G* geometry, the NICS values for benzene, naphthalene and *D*_{4h}-cyclooctatetraene are $\delta = -9.7$, -9.9 and 30.1 ppm^[15] (for a minireview on the antiaromaticity of planar cyclooctatetraene, see ref.^[30]). For 1,3λ⁴δ²,5,2,4-trithiadiazepine (10 π -electron sulfur–nitrogen heterocycle) this value is $\delta = -9.3$ ppm.^[31] The NICS values (Table 3) also show that fluorination increases the aromaticity of the carbocyclic moieties of the compounds in series **1**. These effects have been discussed previously with respect to fluor-

Table 3. Calculated NICS values (ppm) for all possible fluoro-substituted 1,3λ⁴δ²,2,4-benzodithiadiazines and the parent compound **2** in their minimum energy conformations [B3LYP/6-311+G* geometries and energies, except for *C*₇-**7** for which the MP2/6-31G* geometry was used (see ref.^[9] for details)]; values at HF/6-31+G* and B3LYP/6-31+G* levels and relative energies Δ*E* [kJ·mol^{−1}] are given for each isomer

Compound	Δ <i>E</i>	Conformation	HF/6-31+G*		B3LYP/6-31+G*	
			Carbocycle	Heterocycle	Carbocycle	Heterocycle
Parent (2)	0.00	<i>C</i> ₁	−6.70	10.74	−1.64	14.99
	1.72	<i>C</i> _s (TS)	−5.21	16.48		
5-Fluoro	8.46	<i>C</i> ₁	−8.14	11.02	−2.80	15.32
6-Fluoro	0.00	<i>C</i> ₁	−8.55	10.41	−3.42	14.63
7-Fluoro	0.08	<i>C</i> ₁	−8.24	11.12	−3.00	15.32
8-Fluoro	3.39	<i>C</i> _s	−6.99	16.02		
5,6-Difluoro	19.46	<i>C</i> ₁	−9.97	10.66		
5,7-Difluoro	4.86	<i>C</i> ₁	−9.56	11.31		
5,8-Difluoro	2.25	<i>C</i> _s	−8.57	15.81		
6,7-Difluoro (4)	9.42	<i>C</i> ₁	−10.30	10.64	−4.96	14.77
6,8-Difluoro (3)	0.00	<i>C</i> _s	−8.62	15.67	−2.49	21.68
7,8-Difluoro	14.57	<i>C</i> _s	−8.75	15.37		
5,6,7-Trifluoro (5)	10.88	<i>C</i> ₁	−11.58	10.85	−6.03	15.01
5,6,8-Trifluoro (6)	0.04	<i>C</i> _s	−10.13	15.36	−3.63	21.05
5,7,8-Trifluoro	0.00	<i>C</i> _s	−10.19	15.09		
6,7,8-Trifluoro	6.28	<i>C</i> _s	−10.41	15.32		
5,6,7,8-Tetrafluoro (7)	—	<i>C</i> _s	−11.77	14.94	−5.24	20.35
	—	<i>C</i> ₁ (TS)	−14.16	5.90		

inated pyridines and pyridones and were explained in terms of the increased π-electron density in the ring system due to the positive mesomeric effect from the fluorine substituents.^[32] The antiaromaticity of the heterocyclic moieties of the compounds in series **1** also depends on the number of fluorine substituents, but in a more complicated way. In some cases fluorine substituents increase the antiaromaticity (Table 3), whereas in some other cases (cf. **2**, **4** and **5**) fluorination does not affect the NICS value for the heterocycle.

The positions of the fluorine substituents seem to be of importance, especially the presence of a fluorine atom in the 8-position (cf. **2** and its 8-F, 5,8-F₂ and 6,7,8-F₃ derivatives **3**, **6** and **7** in Table 3): the very position responsible for the flattening of the heterocyclic ring on going from **2** to **7**.^[9] It is clear from the results of the HF calculations in Table 3 that the presence of the fluorine atom in the 8-position and the resulting increase in symmetry to *C*_s reduces the aromaticity of the carbocycle and increases the antiaromaticity of the heterocycle, roughly by about 1 and 5 ppm, respectively. This effect can also be seen in the DFT calculations, but the shifts in NICS values are larger there. There is no relation between NICS values and energetic stabilisation.

The NICS values of the carbocycle at the DFT level seem unexpectedly low, at least in comparison with the data of other compounds described above, while those at the HF level “fit” better. However, from the discussion of the performance of both levels of theory in the prediction of NMR shifts it is difficult to assess which of the two methods generates the more “reasonable” values. On the other hand, if the value for **2** at the DFT level is taken at face value, one might be inclined to assume the compound’s carbocycle is non-aromatic (NICS close to zero), which is clearly incor-

rect. Apart from the difference in scale, this is the only item that distinguishes the two methods.

Table 3 also lists data for two transition states (TS): the planar conformation of **2** and the nonplanar one of **7**. Even though the differences between TSs and ground states are not extreme, the values for the TSs – especially those for the heterocycle – are clearly located outside the set of the values for the ground states; this may be seen as an additional criterion for the assignment of the electronic states of a given conformer.

From the NICS values (Table 3 and ref.^[15]), one can conclude that the antiaromaticity of the heterocycle moiety in compound **2** is about 1/3 of the antiaromaticity of *D*_{4h} cyclooctatetraene. According to recent estimations of resonance energy, however, the destabilization of *D*_{4h} cyclooctatetraene due to the cyclic interaction of the π bonds (i.e., the antiaromaticity) is negligible.^[30] Taking these findings into account, along with the fact that only the heterocyclic moieties of the compounds in series **1** are antiaromatic, whereas the carbocyclic moieties are aromatic (and the C4a–C8a) bond belongs to both moieties at the same time), as well as other available data on these compounds’ molecular and electronic structures^[1–4,6–9,11] and thermal stabilities,^[10,12] one can speculate that, in terms of the aromaticity/antiaromaticity concept,^[5] 1,3λ⁴δ²,2,4-benzodithiadiazines could reasonably be classified on the whole as conjugated non-aromatic substances.

3. Conclusions

Novel fluorinated derivatives of 1,3λ⁴δ²,2,4-benzodithiadiazines (series **1**) have been prepared and characterised structurally. They are interesting not only from structural

and theoretical points of view, the latter including an extension of the aromaticity/antiaromaticity concept to non-traditional compounds, but also for applications in synthesis. As noted above, hydrolysis of the compounds in series **1** produces 2,2'-diaminodiphenyl disulfides.^[3] The latter are well-known starting materials in the preparation of 1,5-benzothiadiazepines with anti-anginal and anti-hypertensive activities.^[33] In this context one can believe that these fluorinated derivatives (from this work and refs.^[2–4]) have some prospects in the synthesis of currently unknown fluorinated 1,5-benzothiadiazepines with potentially useful pharmacological properties.

Experimental Section

General: The ¹H, ¹³C and ¹⁵N NMR spectra were measured in CDCl₃ (unless otherwise indicated) with a Bruker DRX 500 spectrometer at frequencies of 500.13, 125.76 and 50.68 MHz, respectively, with TMS and NH₃ (liq.) as standards; the ¹⁹F NMR spectra were recorded with a Bruker AC 200 machine at a frequency of 188.28 MHz with C₆F₆ as the standard. The high-resolution mass spectra (EI, 70 eV) were collected with a Finnigan MAT MS-8200 instrument, and the UV/Vis spectra were recorded with Specord M40 and HP 8453 spectrophotometers. The GC-MS measurements of solutions in CH₂Cl₂ were performed with a Hewlett–Packard G1800A GCD apparatus.

The X-ray structure determinations (Table 4) were carried out with a Bruker P4 diffractometer with the use of Mo-*K*_α radiation with a graphite monochromator, at –30 °C for **5** and **6**, and at 20 °C for **3** and **14**. The structures were solved by direct methods by use of the SHELXS-97 program and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation by use of the SHELXL-93 and SHELXL-97 programs. The structure of **6** was refined as a merohedric twin (the

law of twinning is 100, 0–10, 00–1). Hydrogen atoms were located on difference Fourier maps for **5** and **14**, or geometrically for **3** and **6**. Atomic coordinates, thermal parameters, bond lengths and bond angles; CCDC-178645 (**3**), -178646 (**5**), -178647 (**6**), and -178648 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical calculations were performed with Gaussian98,^[34] by application of standard gradient techniques at the DFT/B3LYP level of theory using the 6-31G* and the 6-311+G* basis sets on all atoms; all basis sets were used as implemented in the program. Initially, the geometries of all compounds were optimised at the B3LYP/6-31G* level in C_s symmetry and force field calculations were used to ascertain whether the resulting structures were energy minima. When necessary, the symmetry was reduced in the subsequent B3LYP/6-311+G* calculation. Chemical shielding factors were calculated at all atomic positions and at both ring centres (non-weighted mean of the heavy-atom coordinates) for the NICS values, both at the HF/6-31+G* and B3LYP/6-31+G* levels, at the B3LYP/6-311+G* geometry, by use of the GIAO method implemented in Gaussian 98. Chemical shifts for the carbon and hydrogen atoms were obtained by subtracting the chemical shielding values of these atoms from those calculated for tetramethylsilane (TMS), which are δ = 200.7499 and 32.6074 ppm, respectively, at the HF/6-31+G* level, and δ = 191.6496 and 32.1776 ppm, respectively, at the B3LYP/6-31+G* level, based on a B3LYP/6-311+G* geometry. Chemical shifts for the fluorine atoms were obtained by subtracting the chemical shielding values of these atoms from that calculated for hexafluorobenzene (C₆F₆), which is δ = 388.5052 ppm at the HF/6-31+G* level and 347.9219 ppm at the B3LYP/6-31+G* level, based on a B3LYP/6-311+G* geometry. Chemical shifts for the nitrogen atoms were obtained by subtracting the chemical shielding values of these atoms from that calculated for ammonia (NH₃), which is 266.1027 ppm at the HF/6-

Table 4. Crystal and refinement data of compounds **3**, **5**, **6** and **14**

	3	5	6	14
Empirical formula	C ₆ H ₂ F ₂ N ₂ S ₂	C ₆ HF ₃ N ₂ S ₂	C ₆ HF ₃ N ₂ S ₂	C ₉ H ₁₀ F ₄ N ₂ S ₂ Si
Formula mass	204.22	222.21	222.21	314.40
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	13.521(4)	3.8936(8)	3.8743(16)	11.6965(12)
<i>b</i> [Å]	7.7464(19)	5.8300(13)	7.1529(18)	17.253(2)
<i>c</i> [Å]	7.202(2)	32.738(6)	27.115(8)	7.1838(7)
β [°]	99.99(3)	90.60(2)	90.59(2)	99.768(8)
<i>V</i> [Å ³]	742.9(3)	743.1(3)	751.4(4)	1428.7(3)
<i>Z</i>	4	4	4	4
<i>D</i> _c [g cm ^{–3}]	1.826	1.986	1.964	1.462
μ [mm ^{–1}]	0.687	0.714	0.707	0.484
<i>F</i> (000)	408	440	440	640
Crystal size [mm]	3.20 × 0.09 × 0.07	1.40 × 0.20 × 0.04	5.00 × 0.24 × 0.06	0.90 × 0.14 × 0.09
Scan mode	0–20	0–20	ω	0–20
2θ range [°]	< 50	< 50	< 52.38	< 50
Measured reflections	1315	1195	1173	2500
<i>F</i> _o > 4σ _{<i>F</i>}	712	843	909	1439
Transmission	0.2171–0.9535	0.8668–0.9717	0.844–0.958	0.9258–0.9631
<i>R</i> (obsd.)	0.0700	0.0497	0.0615	0.0463
<i>wR</i> ₂ (all)	0.1824	0.1571	0.2183	0.1271
<i>S</i>	0.876	1.065	1.034	1.006

31+G* level and 263.9129 ppm at the B3LYP/6-31+G* level, based on a B3LYP/6-311+G* geometry.

The $\text{Ar}_\text{F}\text{SCl}$ compounds **28** ($\text{Ar}_\text{F} = 6\text{-HC}_6\text{F}_4$)^[35] and **30** ($\text{Ar}_\text{F} = 4\text{-HC}_6\text{F}_4$)^[36] were prepared by known methods. The syntheses described below were carried out under argon (except for **29**, **31** and **32**) in absolute solvents with stirring. The reagents were added dropwise, and the solvents were distilled off at reduced pressure. CsF was calcinated and SCl_2 was distilled directly before use. Tables 5 and 6 list the physical and analytical data for the compounds synthesised.

6,8-Difluoro- (3), 6,7-Difluoro- (4) and 5,6,7-Trifluoro-1,3,4,8,2,4-benzodithiadiazine (5): Solutions of the corresponding $\text{Ar}-\text{N}=\text{S}=\text{N}-\text{SiMe}_3$ compounds (**8–10**, 0.010 mol) and SCl_2 (0.77 g, 7.50 mmol) in CH_2Cl_2 (30 mL) were mixed by adding them to 300 mL (600 mL in the preparation of **5**) of CH_2Cl_2 at 40 °C over a period of 1 h. After an additional hour, the reaction mixture was cooled to 20 °C and filtered, the solvent was distilled off, and the residue was sublimed under vacuum and recrystallised from hexane (to purify **5** at least three sublimation-recrystallisation cycles were necessary). Compounds **3–5** were obtained as black crystals.

5,6,8-Trifluoro-1,3,4,8,2,4-benzodithiadiazine (6): A solution of compound **15** (1.57 g, 0.005 mol) in MeCN (20 mL) was added over 1 h to a refluxing suspension of CsF (0.76 g, 0.005 mol) in MeCN (80 mL). After an additional 1/2 h, the reaction mixture was cooled to 20 °C and filtered, the solvent was distilled off, and the residue was sublimed under vacuum and recrystallised from hexane. Compound **6** was obtained as black crystals.

1-Fluoroaryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes 8–10: A solution of the corresponding ArNSO compound **11–13** (0.060 mol) in hexane (25 mL) was added at –30 °C to a suspension of $\text{LiN}(\text{SiMe}_3)_2$ (10.00 g, 0.060 mol) in hexane (50 mL). The temperature was allowed to rise to 20 °C over 2 h, and Me_3SiCl (6.60 g, 0.060 mol) in hexane (10 mL) was added. The precipitate was filtered off, the solvent was distilled off, and the residue was distilled under vacuum. Compounds **8–10** were obtained as orange oils.

1-Polyfluoroaryl-4-trimethylsilyl-2,4-diaza-1,3-dithia-2,3-butadienes 14–18: A solution of the corresponding $\text{Ar}_\text{F}\text{SCl}$ compound **29–33** (0.025 mol) in CH_2Cl_2 (10 mL) was added at 20 °C (this temperature was –30 °C in the syntheses of **17** and **18**, followed by slow warming to 20 °C) over a period of 1 h to a solution of $\text{Me}_3\text{SiN}=\text{S}^{[19]}$ (5.15 g, 0.025 mol) in CH_2Cl_2 (25 mL). After an additional 16 h, the solvent was distilled off, the residue was distilled under vacuum (for **15** and **16**) or recrystallised from hexane (for **14**, **17** and **18**), followed (for **18**) by vacuum sublimation. Compounds **15** and **16** were obtained as red oils, and compounds **14**, **17** and **18** as transparent yellow crystals.

Transformations of Compounds 14 and 16–18 by Treatment with CsF : A solution of the corresponding compound **14** or **16–18** (0.050 mol) in MeCN (20 mL) was added over a period of 1 h to a refluxing suspension of CsF (0.76 g, 0.005 mol) in MeCN (80 mL). After an additional 1/2 h, the reaction mixture was cooled to 20 °C and filtered, and the solvent was distilled off. The residue was worked up as follows:

Starting Compound 14: The residue was chromatographed on a silica column with hexane as the eluent. 2,2',3,3',4,4',5,5'-Octafluoro-

Table 5. Spectroscopic data of the compounds

Compound	NMR ($\delta^{[a]}$ [ppm])			UV/Vis	
	^1H	^{19}F	^{13}C	^{15}N (J [Hz])	λ_{max} [nm] (log ϵ) ^[b]
3	6.23, 5.53	53.6, 47.4	163.8, 155.5, 139.0, 107.8, 107.1, 97.6	265.4 (t, 2), 250.1 (ddd, 2.5, 1.5)	632 (2.70), 365 (3.37), 277 (4.23), 264 (4.03)
4	5.86, 5.72	29.7, 25.4	152.5, 150.0, 135.0, 113.6, 113.2, 111.0	265.0 (t, 2), 258.8 (q, 2.5)	625 (2.60), 291 (4.18), 284 (4.18), 247 (3.81)
5	5.51	30.1, 16.3, 3.3	152.8, 142.2, 140.6, 124.5, 110.8, 108.1	265.1, 240.9	620 (2.58), 369 (3.12), 283 (4.11), 246 (3.79)
6	6.29	41.6, 32.0, 10.7	152.4, 150.4, 138.7, 127.2, 107.7, 97.5	264.2, 232.8	631 (2.61), 377 (3.45), 265 (4.10)
8	7.21, 6.56, 0.29	52.3			334 (3.81)
9	7.75, 7.36, 7.02, 0.24	26.4, 25.5			344 (4.13)
10	7.55, 6.89, 0.23	26.0, 25.0, 2.7			340 (3.92)
11	7.60, 7.09	58.0			309 (4.13)
12	7.46, 7.30, 6.89	33.5, 30.4			
13	8.08, 6.99	36.1, 30.3, 6.9			316 (3.95)
14	7.41, 0.33	24.3, 22.6, 7.1, 4.4			376 (4.12)
15	6.85, 0.29	54.8, 38.0, 34.5, –0.9			347 (4.06)
16	7.14, 0.32	29.1, 24.2			349 (4.11)
17	0.39	105.1, 30.7, 22.2			352 (4.18)
18	0.34	32.5, 15.4			362 (4.24)
27	7.63, 7.42	24.9, 15.9	152.4, 148.7, 145.9, 139.3, 121.2, 116.9	333.3, 323.4 (dd, 6.5, 2.7)	306 (4.04)
29	6.89	58.7, 42.5, 39.5, 0.6			
31		105.2, 35.3, 23.0			
32		37.2, 16.9			
33	6.76, 3.48	50.0, 33.2, 26.4, –1.5			
34	7.01, 6.69	53.5			411 (4.03)
35	7.46, 7.17–7.04	27.3, 25.4			418 (4.09)
36	7.20, 6.89	27.8, 24.9, 3.6			415 (3.91)

^[a] Solvents: CCl_4 (**8–18**, **32**, **33**, **36–38**), neat liquid (**30**, **35**). ^[b] In heptane.

Table 6. Characterisation of the compounds

Compound	M.p. [°C], b.p. [°C/Torr]	Yield (%)	Empirical formula	MS: <i>m/z</i> [M ⁺] found (calcd.)
3	59–60	32	C ₆ H ₂ F ₂ N ₂ S ₂	203.9625 (203.9628)
4	73–74	29	C ₆ H ₂ F ₂ N ₂ S ₂	203.9636 (203.9628)
5	60–61	9	C ₆ HF ₃ N ₂ S ₂	221.9579 (221.9533)
6	58–59	55	C ₆ HF ₃ N ₂ S ₂	221.9535 (221.9533)
8	65–67/1	40	C ₉ H ₁₂ F ₂ N ₂ SSi	246.0458 (246.0458)
9	98–100/5	50	C ₉ H ₁₂ F ₂ N ₂ SSi	246.0459 (246.0458)
10	90–91/4	56	C ₉ H ₁₁ F ₃ N ₂ SSi	264.0363 (264.0364)
11	73–75/1, 38–39	90	C ₆ H ₃ F ₂ NOS	174.9913 (174.9915)
12	55–56/2	90	C ₆ H ₃ F ₂ NOS	174.9918 (174.9915)
13	64–65/10	92	C ₆ H ₂ F ₃ NOS	192.9809 (192.9809)
14	97–99/1, 57–58	70	C ₉ H ₁₀ F ₄ N ₂ S ₂ Si	313.9986 (313.9991)
15	107–108/1	93	C ₉ H ₁₀ F ₄ N ₂ S ₂ Si	313.9994 (313.9991)
16	115–117/1	73	C ₉ H ₁₀ F ₄ N ₂ S ₂ Si	313.9985 (313.9991)
17	111–113/2, 36–38	84	C ₁₀ H ₉ F ₇ N ₂ S ₂ Si	381.9868 (381.9865)
27	52–53	58	C ₆ H ₂ F ₂ N ₂ S	171.9904 (171.9907)
29	70–72/11	81	C ₆ HCIF ₄ S ^[a]	
31	71–72/15	90	C ₇ ClF ₇ S ^[a]	
32	86–87	90	C ₆ ClF ₄ NO ₂ S ^[a]	
33	41–43/12	57	C ₆ H ₂ F ₄ S	181.9808 (181.9808)
34	99–101		C ₁₂ H ₆ F ₄ N ₂ S	286.0179 (286.0188)
35	84–85		C ₁₂ H ₆ F ₄ N ₂ S	286.0188 (286.0188)
36	88–89		C ₁₂ H ₄ F ₆ N ₂ S	322.0003 (321.9999)

Found (calcd.) % Cl: **29**: 16.22 (16.40); **31**: 12.25 (12.48); **32**: 13.70 (13.58).

diphenyl disulfide (**25**,^[37] identified by high-resolution MS and ¹H and ¹⁹F NMR) was obtained as yellow oil in a 10% yield.

Starting Compound 16: The residue was distilled under vacuum, yielding, according to GC-MS and ¹⁹F NMR, 0.10 g of a 1:3:0.1 mixture of 4,5,7-trifluoro-2,1,3-benzothiadiazole (**19**)^[25] 2,2',3,3',5,5',6,6'-octafluorodiphenyl disulfide (**21**)^[38] and 2,3,5,6-tetrafluoroaniline (**23**).^[39]

Starting Compound 17: The residue was distilled under vacuum, yielding, according to GC-MS and ¹⁹F NMR, 0.35 g of a 2:1:6 mixture of 4,6,7-trifluoro-5-trifluoromethyl-2,1,3-benzothiadiazole (**20**),^[25] 4,4'-bis(trifluoromethyl)-2,2',3,3',5,5',6,6'-octafluorodiphenyl disulfide (**22**),^[40] and 2,3,5,6-tetrafluoro-4-(trifluoromethyl)-aniline (**24**).^[41]

Starting Compound 18: The residue was sublimed under vacuum and recrystallised from hexane/CHCl₃. 2,3,5,6-Tetrafluoro-4-nitroaniline (**26**,^[42] identified by comparison of its m.p. and ¹H and ¹⁹F NMR spectra with those of an authentic^[42] sample) was obtained as yellow crystals in 74% yield.

4,5-Difluoro-2,1,3-benzothiadiazole (27): A solution of compound **10** (1.32 g, 0.005 mol) in MeCN (20 mL) was added over 1 h to a refluxing suspension of CsF (0.76 g, 0.005 mol) in MeCN (80 mL). After an additional hour, the reaction mixture was cooled to 20 °C and filtered, the solvent was distilled off, and the residue was chromatographed on a silica column (with CHCl₃ as the eluent) and sublimed under vacuum followed by recrystallisation from hexane. Compound **27** was obtained as colourless crystals.

Polyfluorinated *N*-Sulfinylarylamines 11–13: The Ar–N=S=O compounds were prepared by Michaelis reaction from the corresponding ArNH₂ (Aldrich) and SOCl₂ in benzene. After the usual workup, compound **11** was obtained as yellow crystals (from hexane), and compounds **12** and **13** as yellow oils.

2,3,4,6-Tetrafluoro- (29), 2,3,5,6-Tetrafluoro-4-trifluoromethyl- (31) and 2,3,5,6-Tetrafluoro-4-nitrophenylsulfenyl Chloride (32): An ex-

cess of dry Cl₂ was slowly passed through a solution of the corresponding Ar₂SH [Ar₂ = 5-HC₆F₄ (**33**), 4-F₃CC₆F₄,^[41,43] 4-O₂NC₆F₄^[44]] in CCl₄ (40 mL) at ambient temperature. The solvent was distilled off and the residue was distilled (for **29** and **31**) or sublimed (for **32**) under vacuum. Compounds **29** and **31** were obtained as red oils, and compound **32** as yellow crystals.

2,3,4,6-Tetrafluorobenzenethiol (33): A solution of BuLi (4.78 g, 0.075 mol) in hexane (50 mL) was added at –80 °C to a solution of 1,2,3,5-tetrafluorobenzene (11.32 g, 0.075 mol) in Et₂O (70 mL). After 1 h, finely powdered sulfur (2.40 g, 0.075 mol) was added to the reaction solution at the same temperature. The temperature was allowed to rise to 20 °C, and the reaction mixture was quenched with 1:2 diluted HCl (25 mL). The organic layer was separated, washed with H₂O (20 mL) and dried with CaCl₂. The solvent was distilled off and the residue was distilled under vacuum. Compound **33** was obtained as a colourless liquid.

Fluorinated 1,3-Diaryl-1,3-diaza-2-thiaallenes (34–36): The (Ar–N=)₂S compounds [Ar = 3,5-F₂C₆H₃ (**34**), 3,4-F₂C₆H₃ (**35**), 2,3,4-F₃C₆H₂ (**36**)] were obtained as by-products in the preparations of compounds **3–5**, respectively, and were isolated as orange-yellow crystals by fractional sublimation followed by recrystallisation from hexane.

Acknowledgments

The Novosibirsk authors are grateful to Mrs. Nina F. Yakusheva for her assistance in the preparations, and to the Russian Foundation for Basic Research for financial support of their work (grants 99-03-33115 and 01-03-06190) including instrumental facilities at the Collective Analytical Center of the Siberian Division of the Russian Academy of Sciences (grant 00-03-40135), and for access to the Cambridge Structural Database (grant 99-07-90133) and to the STN International databases via the STN Center at their Institute (grant 00-03-32721). A.Yu. M. is also grateful to the Siberian Division of the Russian Academy of Sciences for the N. N. Vo-

rozhtsov Award for young scientists. F. B. and C. V. A. gratefully acknowledge support by the University of Antwerp under grant GOA-BOF-UA No. 23.

- [1] A. W. Cordes, M. Hojo, H. Koenig, M. C. Noble, R. T. Oakley, W. T. Pennington, *Inorg. Chem.* **1986**, 25, 1137–1145.
- [2] A. V. Zibarev, Yu. V. Gatilov, A. O. Miller, *Polyhedron* **1992**, 11, 1137–1141.
- [3] I. Yu. Bagryanskaya, Yu. V. Gatilov, A. Yu. Makarov, A. M. Maksimov, A. O. Miller, M. M. Shakirov, A. V. Zibarev, *Heteroatom Chem.* **1999**, 10, 113–124.
- [4] A. Yu. Makarov, I. Yu. Bagryanskaya, Yu. V. Gatilov, T. V. Mikhailina, M. M. Shakirov, L. N. Shchegoleva, A. V. Zibarev, *Heteroatom Chem.* **2001**, 12, 563–576.
- [5] [5a] V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley, New York, **1994**, 336 pp. [5b] K. B. Wiberg, *Chem. Rev.* **2001**, 101, 1317–1331 (and other articles of this special issue). [5c] M. K. Cyranski, T. M. Krygowsky, A. R. Katritzky, P. von R. Schleyer, *J. Org. Chem.* **2002**, 67, 1333–1338.
- [6] A. P. Hitchcock, R. S. DeWitte, J. M. Van Esbroek, P. Aebi, C. L. French, R. T. Oakley, N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.* **1991**, 57, 165–187.
- [7] N. E. Petrachenko, Yu. V. Gatilov, A. V. Zibarev, *J. Electron Spectrosc. Relat. Phenom.* **1994**, 67, 489–492.
- [8] A. V. Manaev, A. Yu. Makarov, Yu. V. Gatilov, J. N. Latosinska, V. V. Shcherbukhin, V. F. Traven, A. V. Zibarev, *J. Electron Spectrosc. Relat. Phenom.* **2000**, 107, 33–38.
- [9] F. Blockhuys, S. L. Hinchley, A. Yu. Makarov, Yu. V. Gatilov, A. V. Zibarev, J. D. Woollins, D. W. H. Rankin, *Chem. Eur. J.* **2001**, 7, 3592–3602.
- [10] I. V. Vlasjuk, V. A. Bagryansky, N. P. Gritsan, Yu. N. Molin, A. Yu. Makarov, Yu. V. Gatilov, V. V. Shcherbukhin, A. V. Zibarev, *Phys. Chem. Chem. Phys.* **2001**, 3, 409–415.
- [11] M. Schettino, R. M. Romano, C. O. Della Vedova, A. Yu. Makarov, A. V. Zibarev, *Phys. Chem. Chem. Phys.* **2001**, 3, 1411–1418.
- [12] V. A. Bagryansky, I. V. Vlasjuk, Yu. V. Gatilov, A. Yu. Makarov, Yu. N. Molin, V. V. Shcherbukhin, A. V. Zibarev, *Mendeleev Commun.* **2000**, 5–7.
- [13] N. P. Gritsan, V. A. Bagryansky, I. V. Vlasjuk, Yu. N. Molin, A. Yu. Makarov, M. S. Platz, A. V. Zibarev, *Russ. Chem. Bull., Int. Ed.* **2001**, 50, 2064–2070.
- [14] A. V. Zibarev, Yu. V. Gatilov, I. Yu. Bagryanskaya, A. M. Maksimov, A. O. Miller, *J. Chem. Soc., Chem. Commun.* **1993**, 298–299.
- [15] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, 118, 6317–6318.
- [16] E. Lork, R. Mews, M. M. Shakirov, P. G. Watson, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2001**, 2123–2134.
- [17] T. Borrmann, E. Lork, R. Mews, W. D. Stohrer, P. G. Watson, A. V. Zibarev, *Chem. Eur. J.* **2001**, 7, 3504–3510.
- [18] A. V. Zibarev, A. O. Miller, Yu. V. Gatilov, G. G. Furin, *Heteroatom Chem.* **1990**, 1, 443–453.
- [19] I. Yu. Bagryanskaya, Yu. V. Gatilov, A. O. Miller, M. M. Shakirov, A. V. Zibarev, *Heteroatom Chem.* **1994**, 5, 561–565.
- [20] T. Chivers, *Chem. Rev.* **1985**, 85, 314–365.
- [21] A. V. Zibarev, Yu. V. Gatilov, I. Yu. Bagryanskaya, S. N. Konchenko, *Polyhedron* **1992**, 11, 2787–2793.
- [22] G. M. Brooke, *J. Fluorine Chem.* **1997**, 86, 1–76.
- [23] A. V. Zibarev, E. Lork, R. Mews, *Chem. Commun.* **1998**, 991–992.
- [24] T. Borrmann, A. V. Zibarev, E. Lork, G. Knitter, S. J. Chen, P. G. Watson, E. Cutin, M. M. Shakirov, W. D. Stohrer, R. Mews, *Inorg. Chem.* **2000**, 39, 3999–4005.
- [25] A. V. Zibarev, A. O. Miller, *J. Fluorine Chem.* **1990**, 50, 359–363.
- [26] [26a] S. Doraiswamy, S. D. Sharma, *J. Mol. Struct.* **1983**, 102, 81–92. [26b] L. Nygaard, E. R. Hansen, R. L. Hansen, J. Rastrup-Andersen, G. O. Soerensen, *Spectrochim. Acta A* **1967**, 23, 2813–2819.
- [27] M. M. Shakirov, I. V. Beregovaya, A. V. Zibarev, *Khim. Geterotsikl. Soedin.* **1995**, 262–265 [*Chem. Abstr.* **1995**, 123, 55291j].
- [28] I. Yu. Bagryanskaya, H. Bock, Yu. V. Gatilov, A. Haas, M. M. Shakirov, B. Solouki, A. V. Zibarev, *Chem. Ber./Recueil* **1997**, 130, 247–253.
- [29] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, New York, **2001**, chapter 11.
- [30] F. G. Klaerner, *Angew. Chem. Int. Ed.* **2001**, 40, 3977–3981.
- [31] S. Martin-Santamaria, B. Lavan, H. S. Rzepa, *Chem. Commun.* **2000**, 1089–1090.
- [32] P. A. Hunt, T. Fisher, P. Schwerdtfeger, *J. Org. Chem.* **1997**, 62, 8063–8070.
- [33] A. R. Katritzky, B. V. Rogovoy, C. Chassaing, V. Vvedensky, B. Forood, B. Flatt, H. Nakai, *J. Heterocycl. Chem.* **2000**, 37, 1655–1658.
- [34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzales, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian Inc., Pittsburgh PA, **1998**.
- [35] T. P. Culbertson, *J. Heterocycl. Chem.* **1991**, 28, 1701–1703.
- [36] P. F. Butler, M. E. Peach, *J. Fluorine Chem.* **1987**, 35, 489–496.
- [37] G. M. Brooke, M. A. Quasem, *J. Chem. Soc. C* **1967**, 865–869.
- [38] P. Robson, M. Stacey, R. Stephens, J. C. Tatlow, *J. Chem. Soc.* **1960**, 4754–4760.
- [39] G. M. Brooke, J. Burdon, M. Stacey, J. C. Tatlow, *J. Chem. Soc.* **1960**, 1768–1771.
- [40] G. G. Furin, T. V. Terentieva, G. G. Yakobson, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk* **1972**, 6, 78–88 (in Russian).
- [41] D. J. Alsop, J. Burdon, J. C. Tatlow, *J. Chem. Soc.* **1962**, 1801–1805.
- [42] G. M. Brooke, J. Burdon, J. C. Tatlow, *J. Chem. Soc.* **1961**, 802–807.
- [43] A. M. Maksimov, V. E. Platonov, *Fluorine Notes* **1999**, 4, www.fluorine.ru/Notes/archive.html
- [44] D. J. Hupe, E. R. Pohl, *Isr. J. Chem.* **1985**, 26, 395–399.

Received May 3, 2002
[I02284]