Inorg. Chem. **2006**, *45*, 2221–2228

Inorganic Chemistry
Article

5,6,7,8-Tetrafluoro-$3\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine, 5,6,7,8-Tetrafluoro-$1,3\lambda^4\delta^2$,2,4-benzodithiadiazine, and Their Hydrocarbon Analogues: Molecular and Crystal Structures

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Received September 8, 2005

5,6,7,8-Tetrafluoro-$3\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine (**1**) is prepared by the intramolecular nucleophilic cyclization of $C_6F_5SeN{=}S{=}NSiMe_3$ (**2**) mediated by CsF. According to an X-ray diffraction analysis, the heterocycle of **1** is bent along the Se(1)···N(4) line by 6.0(2)° in the crystal. Despite the obvious similarities between **1** and its 1,3-dithia analogue (**7**) with respect to molecular composition and shape, the crystal packing of **1** is substantially different from that of **7**. An interesting consequence of this is the inclusion of atmospheric N_2 in the crystal lattice of the selenium derivative **1**. The molecular structure and bonding of **1** have been investigated using quantum-chemical calculations at the DFT/B3LYP/6-311+G* level of theory, and the results have been compared to those of 5,6,7,8-tetrafluoro-$1,3\lambda^4\delta^2$,2,4-benzodithiadiazine (**7**) and their hydrocarbon analogues (**5** and **8**).

1. Introduction

The chemistry of chalcogen–nitrogen compounds has received much attention in recent years because of its fundamental and practical significance.[1] $1,3\lambda^4\delta^2$,2,4-Benzodithiadiazine and its derivatives (Figure 1) have been of particular interest because they can be seen as combinations of an organic and an inorganic ring into a 12π-electron system. The reactivity of the heteroatomic fragment is high and quite varied; consequently, a large number of unusual reactions have been identified, and several novel structures have been observed among the reaction products.[2–19] In particular, $1,3\lambda^4\delta^2$,2,4-benzodithiadiazine and its 5,6,7,8-tetrafluoro derivative, 6–6 bicyclic systems, can be easily transformed into differently fused polysulfur–nitrogen 5–5–6, 5–6–7, and 5–6–6–6 polycyclic systems that were previously unknown.[19] Thus, many useful new compounds

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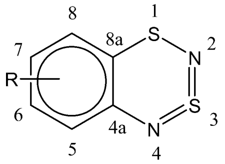

Figure 1. Representative structure of 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine and its derivatives.

can be prepared from 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines, which are not easily, if at all, accessible via other synthetic pathways.[5,7,9−11,16,18,19] Additionally, from a structural chemistry point of view, 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine and its derivatives have very different properties when compared with their hydrocarbon analogues. When, for example, naphthalene is compared with 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine [its analogue containing an $(SN)_2$ unit], we see that upon changing the −C═C−C═C− fragment into an −N═S═N−S− fragment the number of double bonds is retained, but one lone pair from the S(II) atom is added to the π system. While the latter is considerably delocalized in naphthalene, it is localized in the two S═N bonds of the heterocycle in 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine. This causes the latter to become a 12π-electron antiaromatic system, while naphthalene is a 10π-electron aromatic compound. These effects of electronic (de)localization combined with promising magnetic and electronic properties that result from the peculiar electronic structure make these new compounds very interesting systems for further theoretical and experimental investigations.

The analogues of these heterocyclic compounds with a selenium atom in the 1 position are as yet unknown. The present contribution deals with the synthesis and structural characterization of 5,6,7,8-tetrafluoro-3$\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine (**1**), the tetrafluorinated 1-selena analogue of 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine (**8**). This new selenium-containing compound **1** should be seen as the first of a series of new systems that are themselves useful starting materials for numerous interesting preparations.[20] Furthermore, the general reactivity and structure and bonding of systems such as **1** are of considerable fundamental importance.

In this paper, we report the molecular and crystal structure of compound **1** as determined by quantum-chemical calculations at the DFT/B3LYP/6-311+G* level of theory and single-crystal X-ray diffraction (XRD), respectively. The results are compared with those obtained for its 1,3-dithia analogue, 5,6,7,8-tetrafluoro-1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine (**7**), and the influence of the selenium atom in the 1 position is discussed. It appears that, even though the properties of the isolated molecules are quite comparable, those of the compounds in a crystal environment are not. The effects of the fluorine substitution are investigated by comparison with the structure and properties of the hydrocarbon analogues 3$\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine (**5**) and **8** determined by the same experimental and computational methods.

2. Experimental Section

^{1}H, ^{13}C, ^{15}N, ^{29}Si, and ^{77}Se NMR spectra were recorded on a Bruker DRX-500 spectrometer at frequencies of 500.13, 125.76, 50.68, 99.36, and 95.38 MHz, respectively, with tetramethylsilane (TMS), NH_3(liquid), and $(CH_3)_2Se$ as standards. ^{19}F NMR spectra were recorded with a Bruker AC-200 spectrometer at a frequency of 188.28 MHz with C_6F_6 as the standard. High-resolution mass spectra [electron impact (EI), 70 eV] were recorded on a Finnigan MAT MS-8200 instrument, and the UV−vis spectra were recorded on a HP 8453 spectrophotometer. IR spectra in KBr were measured on a Bruker Vector 22 spectrometer. Raman spectra were recorded on a Bruker IFS 66 spectrometer equipped with Nd:YAG laser with an excitation line of 1064 nm.

2.1. Syntheses. All syntheses were performed under argon in dry solvents with stirring. The reagents were added dropwise, and the solvents were distilled off under reduced pressure. CsF was calcinated and $SeCl_2$ was prepared directly before use. The authenticity of $SeCl_2$ was determined by ^{77}Se NMR in a tetrahydrofuran (THF) solution.[21] Compounds **3** and **4** are known[22,23] but were prepared by modified procedures.

2,2′,3,3′,4,4′,5,5′,6,6′-Decafluorodiphenyl Diselenide (4). At −60 °C, 13.43 g (0.17 mol) of finely powdered Se was added in small portions to a solution of 29.58 g (0.17 mol) of C_6F_5Li (prepared at the same temperature from C_6F_5H and BuLi) in 250 mL of Et_2O and 100 mL of hexane. After 1 h, the reaction mixture was warmed to 20 °C and an excess of I_2 was added. The reaction mixture was washed with aqueous $Na_2S_2O_3$ and dried with $CaCl_2$, and the solvent was distilled off. The residue was chromatographed on a silica column (heptane). After recrystallization from EtOH, compound **4** was obtained as orange-yellow crystals in a yield of 35.97 g (86%). Mp: 55−56 °C. MS *m*/*z*: 493.8172 [M^+, calcd (^{80}Se) for $C_{12}F_{10}Se_2$ 493.8170]. NMR ($CDCl_3$) δ: ^{19}F 36.84, 13.23, 2.53; ^{77}Se 369.8.

(2,3,4,5,6-Pentafluorophenyl)selenenyl Chloride (3). A mixture of 4.92 g (0.01 mol) of **4** and 5.50 g (0.04 mol) of SO_2Cl_2 was refluxed for 1 h. The excess of the solvent (SO_2Cl_2) was distilled off, and the residue was distilled under reduced pressure. Compound **3** was obtained as a red oil in a yield of 5.07 g (90%). Bp: 72−74 °C/7 mmHg. NMR ($CDCl_3$) δ: ^{19}F 39.81, 16.76, 3.19; ^{77}Se 799.1.

1-(2,3,4,5,6-Pentafluorophenyl)-4-(trimethylsilyl)-2,4-diaza-1-selena-3-thia-2,3-butadiene (2). At −30 °C, a solution of 2.25 g (0.008 mol) of **3** in 10 mL of hexane was added for 1 h to a solution of 2.01 g (0.01 mol) of $(Me_3SiN{=})_2S$[24] in 10 mL of hexane. After

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an additional 1 h, the reaction mixture was warmed to 20 °C and the solvent was distilled off. The residue was distilled under reduced pressure. Compound **2** was obtained as an orange oil in a yield of 2.06 g (68%). Bp: 143−145 °C/6 mmHg. MS *m*/*z*: 379.9345 [M^+, calcd (^{80}Se) for $C_9H_9F_5N_2SSeSi$ 379.9341]. NMR ($CDCl_3$) δ: ^{1}H 0.38; ^{15}N 320.4, 302.8; ^{19}F 36.55, 11.41, 1.52; ^{29}Si 4.6; ^{77}Se 812.3.

5,6,7,8-Tetrafluoro-$3\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine (1). A solution of 0.76 g (0.002 mol) of **2** in 20 mL of MeCN was added for 1 h to a refluxed suspension of 0.30 g (0.002 mol) of CsF in 50 mL of MeCN. After an additional 1 h, the reaction mixture was cooled to 20 °C and filtered, and the solvent was distilled off. According to ^{19}F NMR, the residue was a mixture of the target compound **1**, 4,5,6,7-tetrafluoro-2,1,3-benzothiadiazole,[25] and compound **4**. Compound **1** was isolated and purified by three cycles of a vacuum sublimation followed by a recrystallization from hexane. It was obtained as black crystals in a yield of 0.04 g (7%). Mp: 46−47 °C. MS *m*/*z*: 287.8882 [M^+, calcd (^{80}Se) for $C_6F_4N_2SSe$ 287.8883]. NMR ($CDCl_3$): see Table 2. UV−vis (heptane) λ_{max} (nm) (log ϵ): 584 (2.49), 359 (3.36), 270 (4.09). IR ν (cm^{-1}): 1626 m, 1609 m, 1591 m, 1495 vs, 1467 vs, 1372 w, 1281 w, 1178 s, 1109 s, 1089 m, 1002 s, 977 m, 877 m, 776 m, 636 w, 558 w, 412 w. Raman ν (cm^{-1}): 1611 m, 1371 vs, 1284 m, 1255 m, 1185 s, 1052 m, 1003 s, 892 m, 480 m, 409 m, 367 m, 268 s.

2.2. X-ray Structure Determination. Crystal structure data for **1** were collected at 188 K on a Bruker P4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) with a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares methods on all F^2 in the anisotropic approximation using the *SHELX-97* program.[26] The obtained crystal structure was analyzed for short contacts between nonbonded atoms using the *PLATON* program.[27,28]

Crystal structure data for 1: $C_6F_4N_2SSe + 0.11N_2$, M = 290.21, rhombohedral, $a = b$ = 32.832(3) Å, c = 4.0616(6) Å, γ = 120°, V = 3791.5(8) Å^3, space group $R\bar{3}$, Z = 18, D_c = 2.288 g·cm^{-3}, μ(Mo Kα) = 4.727 mm^{-1}, F(000) = 2476, crystal size 0.8 × 0.14 × 0.1 mm, $2\theta_{max}$ = 29.98°, 2167 reflections measured, 1872 unique reflections (R_{int} = 0.0513) measured, integration method transmission 0.52 and 0.64, 131 parameters, R_1 [$1502F_0 \geq 2\sigma(F)$] = 0.0388, wR_2 = 0.1074, S = 1.027 for all data, residual electron density peaks of +0.678 and −0.607 e·Å^{-3}. The difference electron density peaks in the lattice cavities are interpreted as partial space filling by disordered N_2 molecules. Alternative interpretation of these peaks as O_2 or CO consistently led to higher values of the R factors. Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles are available as CCDC 282739 from the Cambridge Crystallographic Data Centre.

2.3. Calculations. Theoretical calculations were performed on isolated molecules using *Gaussian 03*[29] applying standard gradient techniques at the DFT/B3LYP level of theory using the 6-311+G* basis set on all atoms; the basis set was used as it is implemented in the program. Force-field calculations were used to ascertain whether the resulting structures were energy minima. All subsequent calculations of molecular properties were performed at the B3LYP/6-311+G* geometries. Chemical-shielding factors were calculated at all atomic positions at the DFT/B3LYP/6-311+G* level of theory using the GIAO method implemented in *Gaussian 03*. The chemical shifts of the hydrogen and carbon atoms were obtained by subtracting the chemical-shielding value of these atoms from the ones calculated for TMS, which are 32.2509 and 183.9810 ppm, respectively. Chemical shifts for the nitrogen atoms were obtained by subtracting the chemical-shielding values of the two atoms from that calculated for ammonia (NH_3), which is 258.7582 ppm. The chemical shift for the selenium atom was obtained by subtracting the chemical-shielding value of this atom from the one calculated for dimethyl selenide, which is 1623.1484 ppm (C_{2v} symmetry; anti,anti conformer). Chemical shifts for the fluorine atoms were obtained by subtracting the chemical-shielding values of these atoms from the one calculated for hexafluorobenzene (C_6F_6), which is 336.2740 ppm. Nucleus-independent chemical shifts (NICSs)[30] were calculated in the geometrical center of the ring [NICS(0)] and at a distance of 1 Å perpendicularly above [NICS(1)] and below [NICS(−1)] the ring center.[31] Bond orders (or rather overlap populations; see ref 32) were calculated according to the Hirshfeld scheme.[32]

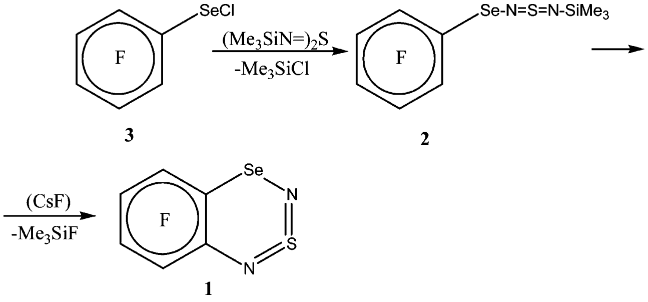

Figure 2. Synthesis of **1**.

3. Results and Discussion

3.1. Syntheses. Previously, polyfluorinated $1,3\lambda^4\delta^2$,2,4-benzodithiadiazines were prepared by the nucleophilic ring-closure reaction of $Ar_FSN{=}S{=}NSiMe_3$ precursors in MeCN under the action of CsF, with [Ar_FSNSN] anions as the key intermediates.[4,15] The same methodology was used in this work, leading to **1** (Figure 2) in four steps starting from pentafluorobenzene. The low isolated yield (7%) of compound **1** can be explained based on the numerous side reactions that have been described for the intermediate

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Table 1. Selected Data Comparing Solid-State (XRD) and Calculated Gas-Phase (B3LYP, r_e) Geometries for **1** (X = Se), **5** (X = Se), 7 (X = S), and 8 (X = S)[a]

	1		5	7		8	
	XRD	B3LYP	B3LYP	XRD[b]	B3LYP	XRD[c]	B3LYP
X(1)−N(2)	1.844(4)	1.876	1.862	1.651(4)	1.699	1.693(3)	1.717
N(2)−S(3)	1.541(3)	1.566	1.561	1.553(4)	1.565	1.547(4)	1.570
S(3)−N(4)	1.538(3)	1.564	1.562	1.513(3)	1.564	1.544(4)	1.566
N(4)−C(4a)	1.408(5)	1.408	1.397	1.432(4)	1.402	1.423(5)	1.411
C(4a)−C(8a)	1.401(5)	1.408	1.412	1.400(5)	1.414	1.394(5)	1.409
C(8a)−X(1)	1.941(4)	1.955	1.965	1.781(5)	1.825	1.796(4)	1.814
X(1)−N(2)−S(3)	123.5(2)	119.7	123.4	125.1(2)	125.0	122.7(2)	120.9
N(2)−S(3)−N(4)	121.1(2)	120.2	120.3	118.9(2)	118.3	119.9(2)	118.1
S(3)−N(4)−C(4a)	123.9(3)	124.8	125.4	121.7(2)	122.8	122.5(3)	122.1
N(4)−C(4a)−C(8a)	126.8(3)	125.4	126.3	125.1(3)	125.6	124.6(3)	124.5
C(4a)−C(8a)−X(1)	123.9(3)	121.8	124.2	124.1(3)	124.4	124.3(3)	122.1
C(8a)−X(1)−N(2)	100.4(2)	100.5	100.4	104.8(2)	104.0	105.8(2)	103.7

[a] Bond lengths are in angstroms, and bond angles are in degrees. For atomic numbering, see Figure 1. [b] See ref 4. [c] See ref 2.

[Ar$_F$SNSN] anions.[10,15,24] Additionally, the formation of long-lived [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl radical anions has been observed as the products of the unexpected reaction between [ArXNSN] anions (X = S and Se) and the solvent MeCN, even at low temperatures.[33] In this work, 4,5,6,7-tetrafluoro-2,1,3-benzothiadiazole and the decafluorodiphenyl diselenide **4** were identified as byproducts from the nucleophilic ring-closure reaction (Figure 2), but this is typical of these types of cyclizations.[15,24]

3.2. Molecular Structure. Selected experimental and calculated geometrical data for the four compounds under investigation are given in Table 1; the atomic numbering is shown in Figure 1. In the crystal, **1** is bent along the Se(1)···N(4) line by 6.0(2)°, and this is very close to the value of 5.5(1)° that was observed for **7**.[4] A comparison of the solid-state data for these two compounds shows the expected elongation of the X(1)−N(2) and C(8a)−X(1) bonds due to the introduction of the selenium atom (X = S and Se); the C(4a)−C(8a) bond in the heterocycle seems to be insensitive to this change. There is a considerable difference between the bond lengths of the two short S═N bonds, N(2)−S(3) and S(3)−N(4), in **7** (about 0.040 Å), which has been reduced to a mere 0.003 Å in **1**; the latter is equal to the difference in **8** and most of its fluorinated derivatives.[15] The large difference for the S═N bonds in **7** is mainly due to the unexpectedly low value for the S(3)−N(4) bond length. In contrast, the N(4)−C(4a) bond is considerably longer in **7** than in **1**. Substitution of sulfur by selenium changes the valence angles in the heterocycle only moderately; the largest difference is found for the C(8a)−X(1)−N(2) angle, as expected, which decreases by about 4° upon going from **7** to **1**. As a result, both the N(2)−S(3)−N(4) and S(3)−N(4)−C(4a) angles become slightly larger in **1** than in **7**. These experimental values can then be compared to the ones calculated for the isolated molecules, which, in contrast to the situation in the crystal, display a coplanar arrangement of the two rings. The elongation of the X(1)−N(2) and C(8a)−X(1) bonds and the insensitivity of the C(4a)−C(8a) bond to the change of X(1) are quite well reproduced. On the other hand, in the gas phase the four S═N bonds are virtually identical in length for the two compounds, as are the two N(4)−C(4a) bonds. Because compounds **1** and **7** are planar in the gas phase, the calculated values of the valence angles, which are much more sensitive to the conformation of the heterocycle than the bond lengths, do not compare as well with the solid-state values. On the other hand, the decrease in the value of the C(8a)−X(1)−N(2) angle by about 4° and the increase in the values of the N(2)−S(3)−N(4) and S(3)−N(4)−C(4a) angles are reproduced by the calculations.

Because **5** is not experimentally accessible, a comparison between it and **8** must be based on the calculated geometries; in contrast to **1** and **7**, the parent compounds **5** and **8** are nonplanar in the gas phase. {**8** and a number of its nonfluorinated substituted derivatives are synthesized by the 1:1 condensation of ArN═S═NSiMe$_3$ (**6**) and SCl$_2$ followed by the electrophilic ortho cyclization of the resulting [ArN═S═NSCl] intermediates.[2,7,10,15,18] The attempt to extend this approach to **6** and SeCl$_2$ failed. Only unidentified acyclic products could be observed in the reaction products using ^{1}H and ^{13}C NMR; neither the target **5** nor any selenium analogues of the Herz salts,[34] which are typical byproducts in the synthesis of 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines,[10,18] could be detected. At ambient temperature, a solution of 1.50 g (0.01 mol) of SeCl$_2$ (prepared from Se and SO$_2$Cl$_2$)[21] and one of 2.10 g (0.01 mol) of **6**,[35] each in 30 mL of THF, were added for 1 h to 300 mL of THF. After an additional 3 h, the dark precipitate was filtered off and the filtrate was evaporated under reduced pressure, yielding a tarry residue.} The elongation of the X(1)−N(2) and C(8a)−X(1) bonds and the insensitivity of the C(4a)−C(8a) bond to the change of X(1) are again clearly visible. The four S═N bonds are again virtually identical in length for the two compounds but, in contrast, there is a larger difference of about 0.01 Å for the N(4)−C(4a) bond. Regarding the valence angles in the heterocycle, trends similar to those for the tetrafluorinated derivatives can be seen. The effect of the fluorine atoms is

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Table 2. Calculated and Experimental ^{13}C, ^{15}N, ^{19}F, and ^{77}Se NMR Chemical Shifts (ppm) for Compounds **1** (Y = F), **5** (Y = H), **7** (Y = F), and **8** (Y = H) Referenced to TMS, Liquid NH$_3$, C$_6$F$_6$, and (CH$_3$)$_2$Se, Respectively

	1		5	7		8	
	exptl	calcd	calcd	exptl	calcd	exptl	calcd
Se(1)	752.9	818.5	792.7				
N(2)	243.1	334.5	367.0	255.5	332.3	269.2	380.9
N(4)	240.9	291.0	343.2	233.1	275.0	263.1	337.9
C(4a)	121.3	132.2	152.5	122.0	131.8	138.5	153.0
C(5)	139.7	148.8	128.2	139.5	147.7	123.0	127.7
C(6)	141.7	151.5	135.6	141.3	151.8	130.5	135.9
C(7)	142.5	152.9	140.2	143.0	153.5	133.2	140.4
C(8)	141.3	150.6	130.8	140.4	150.5	124.0	128.6
C(8a)	91.9	103.2	122.1	98.9	103.8	115.3	122.3
Y(5)	13.9	18.4	5.91	18.5	16.0	5.90	5.59
Y(6)	6.6	5.9	6.65	6.9	6.3	6.63	6.46
Y(7)	9.8	11.1	6.81	9.9	10.5	6.78	6.64
Y(8)	23.8	20.4	5.72	12.2	14.8	5.79	5.48

most clearly seen in the π-fluoro effect,[12] which increases the symmetry of the isolated molecules from C_1 for the nonfluorinated derivatives **5** and **8** to C_s for the tetrafluoro derivatives **1** and **7**; this will be discussed in greater detail in section 3.4.

3.3. Spectral Properties. For compounds **1** and **7**, the selenium and sulfur atoms can be considered as pseudo-isotopes in the empirical identification of the molecular vibrations, which contain large contributions from the CX and/or XN bonds (X = S and Se) by means of the “selenation” method.[36] Indeed, a comparison of the IR and Raman spectra of **1** and **7**[12] reveals a decrease in a number of vibrational frequencies upon introduction of the selenium atom. For the IR spectrum of **7**, these are the bands at 1635 (9), 1053 (76), 892 (15), 799 (23), 660 (24), 625 (67), and 428 (12) cm^{-1}, and for the Raman spectrum of **7**, these are the bands at 1381 (10), 905 (13), 505 (25), and 283 (15) cm^{-1}; for both spectra, the shifts of the frequencies have been given in parentheses. Apart from these differences, the spectra of **1** and **7** are virtually identical. A comparison of the UV−vis spectra of **1** and **7**[4] shows that substitution of sulfur by selenium leads to a hypsochromic shift of the λ_{max} value for the long-wave absorption from 615 nm in **7** to 584 nm in **1**. This is in accordance with the conclusion that the lowest-energy electronic excitation in 1,$3\lambda^4\delta^2$,2,4-benzodithiadiazines is localized on the heteroatomic fragment.[13] Table 2 compiles the multinuclear experimental and calculated NMR data of the four compounds under consideration. Chemical shifts that could not be unambiguously assigned based on the experimental data alone have now been linked to a specific atom via the calculated chemical shifts, based on the trends in the calculated data rather than on the absolute values. As can be seen in Table 2, the correlation of the values between theory and experiment is far less satisfactory for the nitrogen atoms than for the others. Yet, when these data are compared with previous studies on substituted 1,$3\lambda^4\delta^2$,2,4-benzodithiadiazines,[15] Roesky’s ketone,[37] and a metalladithiadiazole,[38] it is clear that the unsatisfactory numerical agreement obtained here is not unusual. Fadda et al. recently suggested that density functional theory tends to perform quite poorly for azines;[39] this, in combination with the sensitive solvent dependence of nitrogen chemical shifts, makes predicting nitrogen chemical-shift values difficult.

The differences between the chemical shifts of the bands in the ^{15}N NMR spectra of **1** and **7** may, at least in part, be attributed to the above-mentioned differences in the energies of electronic excitation via the ΔE factor in the chemical-shift equation:[40] the δ^{15}N values at 255.5 and 233.1 ppm for **7**[15] decrease to 243.1 and 240.9 ppm for **1**, and this can be related to the lower λ_{max} value for **1**.

3.4. Bonding and Aromaticity. One of the most complicated and debated issues in the field of chemistry is aromaticity. It is known that aromaticity involves cyclic electron delocalization coupled with an energetic stabilization, but the underlying physical nature of this aromatic stabilization is not known. An extensive set of criteria, which can be grouped into structural, energetic, and magnetic criteria, can be found in the literature (see, for example, refs 41 and 42), but it is believed that not one of them alone can lead to the unambiguous definition of aromaticity. We recently showed that the combination of a set of these criteria allows one to formulate a multidimensional description of the trends in the aromaticity of planar five-membered NSNS ring systems.[43] We will now apply this method to the six-membered rings under investigation in this paper, and we will focus on structural (geometrical parameters and bond orders) and magnetic (values of the NICS) criteria. The geometrical parameters are listed in Table 1, and the calculated bond orders have been given in Table 3. Table 4 compiles the NICS values in the center of the rings, NICS(0), and those above and below the planes of the rings, NICS(1) and NICS(−1).

The electron and bond-length distribution in the XNSN fragment (X = S and Se) is most pertinent to the discussion of (anti)aromaticity, and the latter will be based on the calculated geometries. As mentioned in section 3.2, compounds **7** and **8** display two short S=N bonds, N(2)−S(3) and S(3)−N(4), with bond lengths of about 1.57 Å, and one long S−N bond, S(1)−N(2), with a length of about 1.71 Å. This trend is also found in the Hirshfeld bond orders: the short SN bonds have values of about 1.8 and are virtually double, while the long one has a value of about 1.2 and is

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Table 3. Hirshfeld Bond Orders Calculated for Compounds **1** (X = Se; Y = F), **5** (X = Se; Y = H), **7** (X = S; Y = F), and **8** (X = S; Y = H)

	1	**5**	**7**	**8**
X(1)−N(2)	1.04	0.99	1.26	1.19
N(2)−S(3)	1.84	1.83	1.81	1.79
S(3)−N(4)	1.81	1.81	1.80	1.79
N(4)−C(4a)	1.33	1.28	1.31	1.27
C(4a)−C(8a)	1.41	1.42	1.39	1.41
C(8a)−X(1)	0.86	0.89	0.98	1.00
C(4a)−C(5)	1.44	1.45	1.46	1.46
C(5)−C(6)	1.45	1.51	1.44	1.50
C(6)−C(7)	1.52	1.53	1.54	1.55
C(7)−C(8)	1.44	1.48	1.43	1.48
C(8)−C(8a)	1.57	1.54	1.56	1.53

Table 4. NICS Values (in ppm) in the Plane of the Molecule at the Ring Center [NICS(0)] and at 1 Å above [NICS(1)] and 1 Å below [NICS(−1)] the Ring Centers of the Four Compounds under Consideration

	heterocycle			carbocycle		
	NICS(0)	NICS(1)	NICS(−1)	NICS(0)	NICS(1)	NICS(−1)
1	15.16	12.45	12.45	−7.14	−4.20	−4.20
5	11.72	8.98	7.93	−2.19	−5.19	−4.21
7	19.71	15.95	15.95	−5.60	−2.82	−2.82
8	14.48	9.99	12.31	−1.65	−3.62	−5.95

clearly closer to single. In the selena analogues **1** and **5**, a similar situation can be found because there are also two short S═N bonds with bond lengths of about 1.56 Å. The values of the bond orders confirm that these are quite similar to the corresponding bonds in **7** and **8** because these values are also about 1.8. The nature of the SeN bonds, with a bond length of about 1.87 Å, is more difficult to ascertain, but by comparison of the bond lengths with those in related systems[32] and considering the values of the bond orders, which are very close to 1, we conclude that both SeN bonds are single. This leads to the general conslusion that the four considered compounds display a XN═S═N fragment, which is characterized by the localization of four of the six π electrons of the heterocycle in two S═N double bonds; this is typical for antiaromaticity. In contrast, for all four compounds, the six carbon−carbon bonds making up the carbocycle all have bond orders of around 1.5, which is a clear indication of π-electron delocalization and aromaticity.

Regarding the magnetic criterion, the results of the calculation of the NICS(0) values are given in Table 4: these are positive for the heterocycles of the four compounds, and this points to antiaromaticity for these rings. It was pointed out by von Ragué Schleyer et al.[31] that there are some artifacts in the NICS(0) values, calculated in the plane of the molecule, due to the σ framework of the molecule. To circumvent this, they proposed to calculate so-called NICS(1) values at 1 Å above the ring center because aromaticity involves the delocalization of the π electrons; for nonplanar systems, this concept can be extended to include a NICS(−1) value calculated below the ring center. For the planar compounds **1** and **7**, NICS(1) values of 12.45 and 15.95 ppm are found, respectively, and it is clear that the heterocycles in these two compounds are indeed antiaromatic. For the nonplanar analogues **5** and **8**, the NICS(1) values of 8.98 and 9.99 ppm, respectively, and the NICS(−1) values of 7.93 and 12.31 ppm, respectively, also confirm the antiaromaticity of the heterocycle. All of the corresponding values for the carbocycles are negative, and this suggests aromaticity.

The combination of geometrical and magnetic criteria unequivocally leads to the conclusion that the heterocycles of the four compounds under investigation are antiaromatic while the carbocycles are aromatic. The distortion of the heterocycle of **8** from C_s to C_1 symmetry, observed in the gas phase, reflects the tendency of the molecule to minimize the thermodynamic destabilization associated with antiaromaticity by means of a pseudo-Jahn−Teller effect.[12] The planar geometry of **7** was thought to be due to a conflict between the pseudo-Jahn−Teller effect and the π-fluoro effect, caused by the presence of a fluorine atom in the 8 position, resolved in favor of the latter.[12,17] It is clear that the planarity of **1** and the nonplanarity of **5** in the gas phase strengthen these ideas and suggest that the influence of the selenium atom on these effects is very small.

3.5. Crystal Structures. Despite the close similarity between **1** and **7** with respect to molecular composition, shape, and volume, their crystal packings are very different. In **7**,[4] the S(1)···F(8) short contacts of 3.172(3) Å lead to centrosymmetric dimers, which are themselves combined into layers by the S(3)···F(6) short contacts of 3.152(3) Å (the sum of the van der Waals radii is 3.20 Å).[44] The interlayer separations of the sulfur atoms, which are 3.571(2) and 3.601(2) Å, are close to their normal contact value of 3.68 Å.[45] The layers feature π interactions of the type C−F···Ar_F with a F···$Cg(Ar_F)$ distance of 3.385(3) Å and the C−F bond inclined at 36.0(2)° [$Cg(Ar_F)$ designates the centroid of the Ar_F ring]. In contrast, the crystal structure of the parent **8** displays π stacks with a uniform interplanar separation of 3.29 Å.[2]

In the crystal structure of **1**, which is represented in Figure 3, the Se···Se contacts of 3.6124(8) Å (the sum of the van der Waals radii is 3.80 Å)[46] combine molecules into spirals along the S_3 screw axes. In addition, the molecules in the spirals are connected by Se···S contacts of 3.568(1) Å (the sum of the van der Waals radii is 3.70 Å),[46] S···F contacts of 3.169(3) Å, and π interactions of the type C−F···Ar_F with F···$Cg(Ar_F)$ distances of 3.430(4) and 3.375(4) Å and noninclined C−F bonds. The overall three-dimensional architecture of the crystal results from S(3)···N(4) interactions of 3.221(3) Å (the sum of the van der Waals radii is 3.27 Å)[46] and F···F interactions of 2.894(4) and 2.849(4) Å (the sum of the van der Waals radii is 2.94 Å)[46] between the spirals.

As a result, the crystal structure of **1** features channel-like cavities along the C_3 axes, with a radius varying between about 2.47 and 2.79 Å and a volume of about 306 Å^3 per unit cell. The inner walls of the cavities are lined with fluorine atoms, and one might consider them as “fluorine

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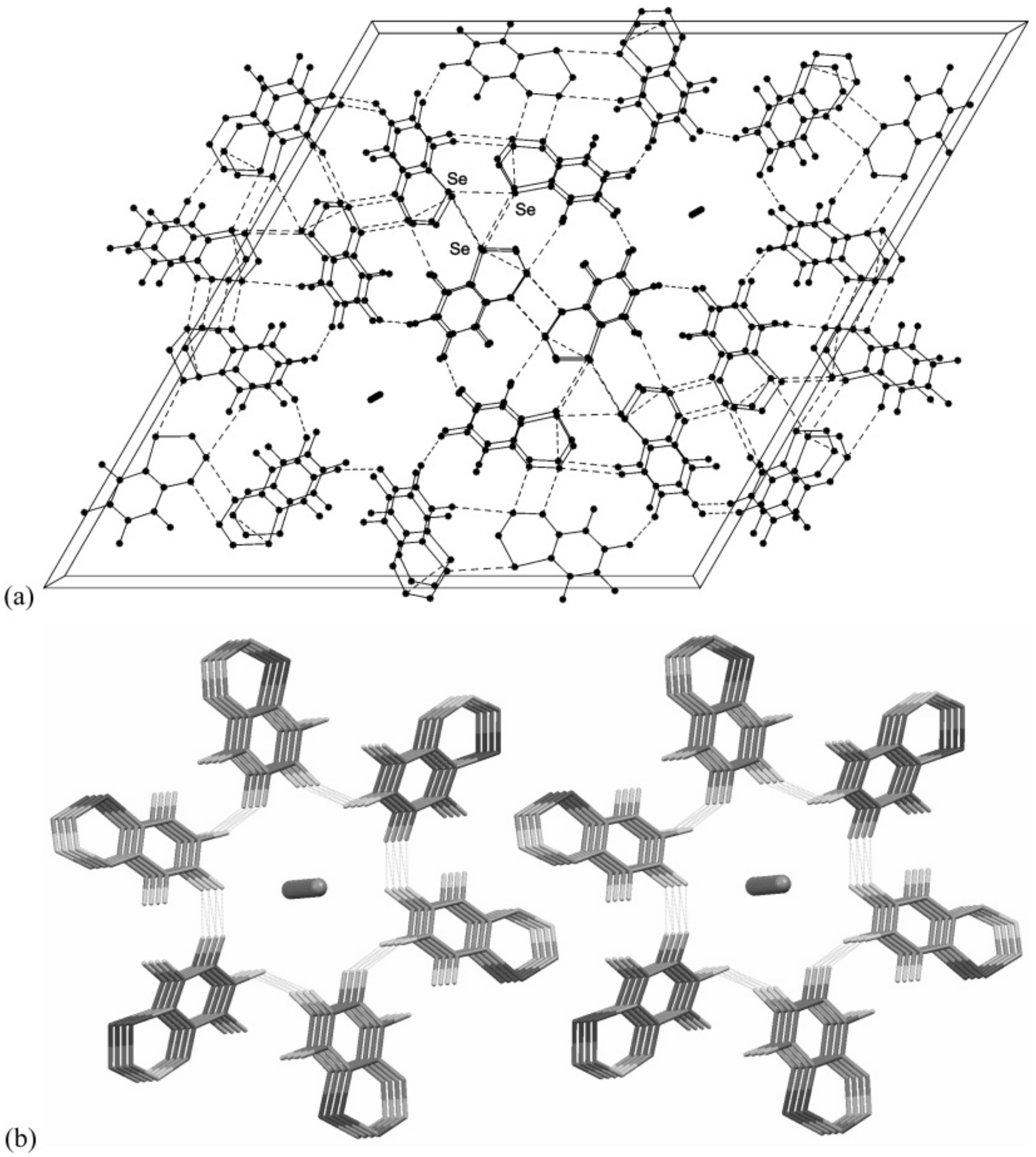

Figure 3. Crystal packing of compound **1**: (a) overview of the packing in which dashed lines indicate short contacts between nonbonded atoms and dotted lines in the lattice channels indicate the disordered N_2 molecules; (b) detailed view of the channels.

nanotubes”. In the crystal that was used to obtain the data presented in this paper, the cavities contained diffuse residual electron density. The latter was modeled as disordered N_2 molecules, and this led to better refinement. The space filling is only partial, and N_2 is assumed to be adsorbed from the atmosphere during the lower-temperature XRD measurements. In the recent past, inclusion structures containing small molecules such as N_2, CO_2, SO_2, and Ar have been observed for fluoro-substituted 1,2,3,5-dithiadiazolyls.[47]

In the context of these fluorine nanotubes, we note that there is increasing interest in the use of secondary bonding interactions, in particular those involving (heavier) chalcogen atoms,[46,48−50] supramolecular chemistry, and the engineering of crystals toward advanced materials applications. However, it is clear that these interactions cannot easily be controlled in the solid state: e.g., the crystal structure of 5,6,8-trifluoro-$3\lambda^4\delta^2$,1,2,4-benzothiaselenadiazine, one of the closest analogues of **1**, reveals a completely different pattern, not featuring any channels.[20]

4. Conclusions

Even though the differences between **1** and its 1,3-dithia analogue **7** are small from a molecular point of view, the substitution of a sulfur atom in **7** by a selenium atom in **1** has considerable repercussions on the supramolecular structure, i.e., the crystal packing. As a result of an increased number of intermolecular short contacts, **1** displays channel-like cavities, which can be described as “fluorine nanotubes” and which contain atmospheric N_2.

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Acknowledgment. The Novosibirsk authors are grateful to the Deutsche Forschungsgemeinschaft, Germany (Project 436 RUS 113/486/0-2 R), and the Russian Foundation for Basic Research, Russia (Project 02-03-04001), for joint financial support of their work.

IC051534+