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Regioselectivity of Fluoride Ion-Induced Intramolecular Nucleophilic Cyclization of Heptafluoronaphthyl Sulfur Diimides 2-Nf_F-N=S=N-$SiMe_3$ and 2-Nf_FS-N=S=N-$SiMe_3$*

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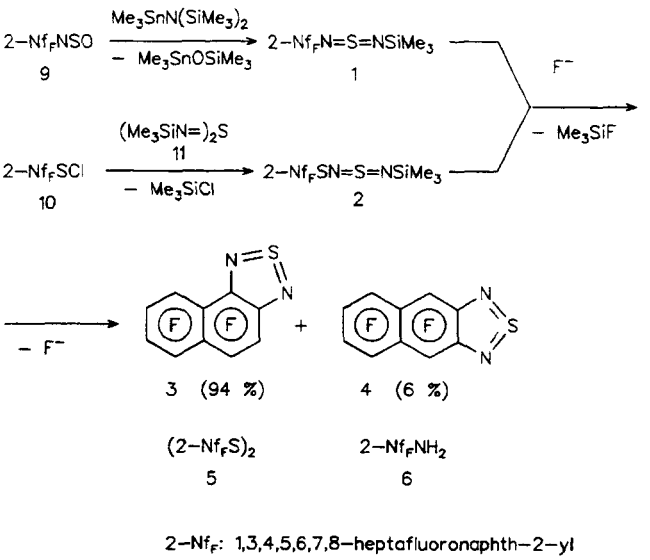
ABSTRACT

The title reaction is highly regioselective, leading in both cases to 4,5,6,7,8,9-hexafluoronaphtho[1,2-c]-[1,2,5]thiadiazole (whose structure is confirmed by X-ray structure analysis) and 4,5,6,7,8,9-hexafluoronaphtho[2,3-c][1,2,5]thiadiazole in ~94:6 ratio. The preferred direction of cyclization is consistent with final product thermodynamics as well as factors of kinetic control for orbital-controlled reactions (calculated by use of frontier MOs theory).

INTRODUCTION

Recently, it has been shown [1,2] that fluoride ion-induced intramolecular nucleophilic ortho-cyclization of 4-$RC_6F_4XN{=}S{=}NSiMe_3$ sulfur diimides makes it possible to obtain, depending on X, previously unknown polyfluorinated 10π-electron 2,1,3-benzothiadiazoles (X = –) [1] or 12π-electron (formally antiaromatic [3]) 1,3,2,4-benzodithiadiazines (X = S) [2]. For the sulfur diimides previously studied, both ortho-positions of the polyfluorinated ring were equivalent, and isomer formation was impossible. In continuation of the this work, the present article deals with the regioselectivity of cyclization of 2-$Nf_FXN{=}S{=}NSiMe_3$ sulfur diimides (**1** and **2**, Scheme 1), which possess nonequivalent ortho-positions.



SCHEME 1

RESULTS AND DISCUSSION

As shown by ^{19}F NMR spectroscopy, compound **1**, when treated with CsF in boiling acetonitrile, was

*Part VIII of the series *Cyclic Aryleneazachalcogenenes*; for Part VII, see Ref. [3].

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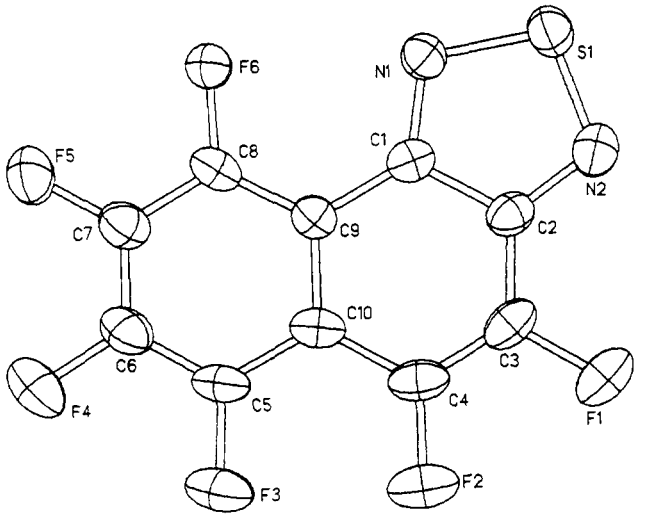
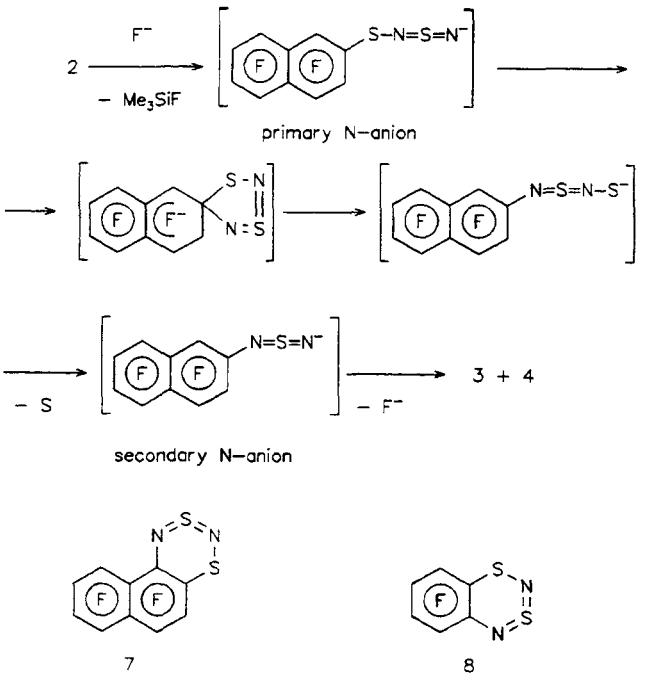


FIGURE 1 Molecule structure of **3**. Selected bond lengths (Å) and bond angles (°): C1–C2 1.421(8), C1–N1 1.345(7), N1–S1 1.619(4), S1–N2 1.614(5), C2–N2 1.346(7), C2–C3 1.395(8), C3–C4 1.342(8), C4–C10 1.441(9), C9–C10 1.411(8), C1–C9 1.430(7), av C–F 1.346; C2–C1–N1 112.3(5), C1–C2–N2 113.7(6), C1–N1–S1 107.5(4), C2–N2–S1 106.8(4), N1–S1–N2 99.7(2). The molecule is planar within ±0.026 Å; the largest deviations from the C_{10} plane are 0.085(7), 0.047(7), and 0.044(7) Å for S1, N1, and N2, respectively. The carbon framework is significantly distorted as compared with naphthalene. In particular, the bond C1–C2 is lengthened, while C3–C4 is shortened as compared with 1.377(2) Å [14] for the same bonds in naphthalene.



SCHEME 2

cyclized to compounds **3** and **4** in ~94:6 ratio (Scheme 1). The structure of **3** was confirmed by X-ray structure analysis (Figure 1). In the case of **2**, the heterocyclic products of reaction were also **3** and **4**, approximately in the same ratio, along with very minor amounts of disulfide **5** and amine **6** (for ^{19}F NMR spectrum of **6**, see Ref. [4]). In both cases, Me_3SiF was also detected in the reaction mixture (for ^{19}F NMR spectrum, see Ref. [5]) (Scheme 1).

Formation of **3** and **4** instead of the desired product **7** (Scheme 2) from **2** is somewhat unexpected. As shown by the model experiments, compound **2**, in the absence of CsF, as well as compound **8** (an analog of **7**, Scheme 2) in the presence of CsF, remain unchanged in boiling acetonitrile. One can suppose that formation of **7** does not take place in the reaction of **2** and that the reaction proceeds according to Scheme 2. The key step is the ipso-cyclization of the primary N-anion, generated from **2** by the action of fluoride ion, with formation of a spirocyclic intermediate. In the synthesis of **8** [2], such complications were not observed.

Thus, the cyclization of the N-anion generated by fluoride ion from **1** and **2** (secondary N-anion in the case of **2**, Scheme 2) is highly regio selective, occurring predominantly with the displacement of the fluoride from the 1-position of the heptafluoronaphthalene ring (Schemes 1 and 2). Analogous cyclizations of C- [6] and S- [7] anions, derivatives of 2–Nf_F, are also regio selective with the ratio of 92:8 [6] and 78:22 [7] for the fluoride replacement at the 1- and 3-positions of the naphthalene ring, respectively.

The preferred direction of the cyclization of **1** and **2** is consistent with final product thermodynamics as well as factors of kinetic control for orbital-controlled reactions (calculated by use of frontier MOs theory [8]). Thus, according to the PM 3 data, ΔH_f^0 values are equal to −181.8 and −170.3 kcal mol^{-1} for **3** and **4**, respectively. Under the orbital control with the main contribution to the interaction energy being produced by the overlapping of the nucleophile's HOMO (in this case, nitrogen 2p-AO, which bears the anionic charge and lies within the σ-framework in the anion ground state) and the electrophile's LUMO (in this case, 2-Nf_F's lowest virtual π^*-orbital), the site of cyclization is determined by the largest coefficient at 2-Nf_F's carbon 2p-AOs in the LUMO. According to the PM 3 data for octafluoronaphthalene, the contribution to the LUMO from the carbon atom in the 1-position exceeds greatly the contribution from that in the 3-position, being equal to 17 and 7%, respectively.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer at frequencies of 200 and 188.28 MHz, respectively, with internal stan-

TABLE 1 Crystal and Refinement Data of **3**[a]

Formula	$C_{10}F_6N_2S$
M	294.18
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.756(3)
b (Å)	4.829(1)
c (Å)	13.681(3)
β (°)	92.05(3)
V (Å^3)	974.2(4)
Z	4
D_c (g cm^{-3})	2.006
μ(cm^{-1})	37.8
Crystal size (mm)	0.2 × 0.3 × 0.9
Scan mode	θ–2θ
θ range (°)	3–57
Measured reflections	1319
Observed unique reflections [$I > 2\sigma(I)$]	712
F(000)	576
Final wR_2 (*R*)	0.1190(0.0532)
Transmission factors, max	0.60
min	0.125

[a]Atomic coordinates, thermal parameters, bond lengths, and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

dards being TMS and C_6F_6; the natural abundance ^{15}N NMR spectrum was taken on a Bruker AM-400 spectrometer at frequency 40.55 MHz with external standard NH_3 (liq.); the mass spectra were taken on a Finnigan MAT MS-8200 mass spectrometer (EI, 70 eV); and the UV-vis spectra were taken on a Specord UV-Vis spectrophotometer.

The X-ray structure determination (Table 1) was carried out on a Syntex $P2_1$ diffractometer using Cu K_α radiation with a graphite monochromator. An analytical correction for absorption was made using the DIFABS program. The structure was solved by direct methods using the SHELX-86 program and refined by the least-squares method in the full-matrix anisotropic approximation using the SHELXL-93 program.

The PM 3 calculations with full geometry optimization were carried out using the MNDO-89 program (which is a development of the MNDO-85 program [9]).

Cesium fluoride was calcinated directly before use. The syntheses described subsequently, except for **9** and **10**, were carried out in an argon atmosphere, in absolute solvents. The reagents were added dropwise, and the solvents were distilled off under reduced pressure. Tables 2 and 3 list the physical and analytical data for the compounds synthesized.

1-(1,3,4,5,6,7,8-Heptafluoronaphth-2-yl)-3-trimethylsilyl-1, 3-diaza-2-thiaallene (**1**)

(a) A mixture of 5.38 g (0.02 mol) of 2-Nf_FNH_2 [10], 10 mL of benzene, and 11.9 g (0.1 mol) of $SOCl_2$ was boiled until HCl evolution ceased. The solvent was distilled off, and the residue was sublimed in vacuum and then recrystallized from hexane/$CHCl_3$ (5:1). N-Sulfinyl-2-amino-1,3,4,5,6,7,8-heptafluoronaphthalene (**9**) was obtained as bright yellow crystals.

(b) To a stirred solution of 3.24 g (0.01 mol) of $Me_3SnN(SiMe_3)_2$ [11] in 40 mL of MeCN maintained at 0 °C was added a solution of 3.15 g (0.01 mol) of **9** in 10 mL of MeCN. During 1 hour, the temperature was raised to 20 °C. After 1 hour, the solvent was distilled off, and the residue was recrystallized from hexane. Compound **1** was obtained as yellow crystals.

1-(1,3,4,5,6,7,8-Heptafluoronaphth-2-yl)-4-trimethylsilyl-2,4-diaza-1,3-dithia-2,3-butadiene (**2**)

(a) An excess of Cl_2 was passed through a solution of 5.72 g (0.02 mol) of 2-Nf_FSH [6] in 50 mL of CCl_4 at 20 °C. The solvent was distilled off, and the residue was distilled in vacuum. 1,3,4,5,6,7,8-Heptafluoronaphth-2-ylsulfenyl chloride (**10**) was obtained as an orange oil.

(b) To a stirred solution of 132 g (0.5 mol) of $(Me_3Si)_2NMgBr$ [12] in 200 mL of THF maintained at −30 °C was added 150 mL of Et_2O followed by a solution of 29.74 g (0.25 mol) of $SOCl_2$ in 50 mL of Et_2O. The mixture was stirred for 2 hours at 20 °C. After the usual workup, 1,3-bis-(trimethylsilyl)-1, 3-diaza-2-thiaallene (**11**) [13] was obtained in 60% (31.0 g) yield, bp 66–67 °C/18 mm.

(c) To a stirred solution of 2.32 g (0.011 mol) of **11** in 10 mL of Et_2O maintained at 0 °C was added a solution of 3.21 g (0.01 mol) of **10** in 10 mL of Et_2O. After a reaction period of 1 hour at 20 °C, the solvent was distilled off, and the residue was recrystallized from hexane. Compound **2** was obtained as pale yellow crystals.

4,5,6,7,8,9-Hexafluoronaphtho[1,2-c][1,2,5]thiadiazole (**3**), *4,5,6,7,8,9-hexafluoronaphtho[2,3-c][1,2,5]thiadiazole* (**4**), *and 1,1',3,3',4,4',5,5',6,6',7,7',8,8'-tetradecafluorodinaphth-2-yl disulfide* (**5**)

(a) To a stirred suspension of 1.52 g (0.01 mol) of CsF in 200 mL of MeCN was added during 2 hours, with boiling, a solution of 3.86 g (0.01 mol) of **1** in 30 mL of MeCN. The mixture was boiled for 0.5 hours, cooled to 20 °C, and filtered, and the solvent was distilled off. The residue (which consisted of a mixture of **3** and **4** in ~15.7:1 ratio, according to the ^{19}F NMR data) was sublimed in vacuum and then recrystallized from heptane. Compound **3** was obtained as transparent pale yellow crystals.

(b) To a stirred suspension of 0.31 g (0.002 mol) of CsF in 50 mL of MeCN was added during 0.5 hours, with boiling, a solution of 0.84 g (0.002 mol)

TABLE 2 Characterization of the Compounds

	Mp (°C), Bp (°C/mm)	Yield (%)	Formula[a]	Found (%) (Calculated) C	H	N	S	F
1	50–51	77	$C_{13}H_9F_7N_2SSi$	40.47	2.14	7.07	8.08	34.80
				(40.41	2.35	7.25	8.30	34.42)
2	61–62	80	$C_{13}H_9F_7N_2S_2Si$	36.97	2.20	6.75	15.04	31.56
				(37.32	2.15	6.70	15.31	31.82)
3	132–134	68[b]	$C_{10}F_6N_2S$	41.07	—	9.60	10.82	38.72
				(40.83	—	9.52	10.90	38.75)
5	119–120		$C_{20}F_{14}S_2$	41.84	—	—	11.55	46.70
				(42.11	—	—	11.23	46.67)
9	61–62	92	$C_{10}F_7NOS$	37.86	—	4.37	10.32	42.06
				(38.11	—	4.44	10.17	42.20)
10[c]	107–108/1	95	$C_{10}ClF_7S$	37.19	—	—	10.16	41.32
				(37.44	—	—	9.98	41.50)

[a] M^-, *m/z*, measured (calculated): **2**, 418 (418); **3** (experimental mixture of **3** and **4** as well), 293.9691 (293.9686); **5**, 569.9226 (569.9218).
[b] From compound **1**.
[c] Cl (%), measured (calculated): 11.18 (11.08).

TABLE 3 Spectral Data of the Compounds

	^{19}F NMR[a], δ (relative intensity)	UV-Vis[b], λ_{max} (nm) (log ε)
1[c]	39.1 (1), 23.3 (1), 17.9–12.4 (3), 7.3–5.7 (2)	406 (3.58) sh, 336 (3.66)
2[c]	53.4 (1), 32.6 (1), 19.4 (1), 16.5 (1), 14.8 (1), 10.4 (1), 7.1 (1)	357 (4.28)
3[d]	24.9 (1), 19.5 (1), 19.2 (1), 15.6 (1), 11.6 (1), 10.0 (1)	368 (4.02), 352 (4.04)
4	38.6 (2)[e], 16.4 (2)[e], 8.3 (2)	
5	54.3 (1), 32.3 (1), 19.8 (1), 16.9 (1), 15.8 (1), 11.9 (1), 8.0 (1)	
9	44.1 (1), 23.8 (1), 19.7–13.8 (3), 10.1 (1), 7.9 (1)	398 (3.31)
10	59.2 (1), 34.4 (1), 20.5 (1), 17.2 (1), 16.1 (1), 13.3 (1), 8.3 (1)	

[a] Solvents: **1**, **5**: $CDCl_3$; **2**, **9**, **10**: CCl_4; **4**: C_6H_6.
[b] Solvents: **1**, **2**: heptane; **3**: EtOH; **9**: $CHCl_3$.
[c] δ ^1H (the same solvents as for ^{19}F NMR): **1**: 0.22; **2**: 0.35.
[d] δ ^{15}N ($CDCl_3$): 338.3 (d, J = 15.5 Hz), 325.0 (m). Tentative assignment to N1 and N2 (numbering of Figure 1), respectively, is based on known strong shielding of heavy nuclei, which are *ortho* to *F* in heteroaromatics ([15] and references therein) as well as signal multiplicities.
[e] $J_{peri} \sim 64$ Hz.

of **2** in 10 mL of MeCN. The mixture was cooled to 20 °C and filtered, and the solvent was distilled off. The residue (which consisted of a mixture of **3–6**, according to the ^{19}F NMR data) was sublimed in vacuum at 1 mm: at 100 °C, compound **3** was obtained, and at 120 °C, compound **5** was obtained. Both compounds were recrystallized from heptane (**3**, 67%; **5**, as white cottonlike crystals, 10 mg).

Control Experiments

(a) A solution of 0.42 g (0.001 mol) of **2** in 30 mL of MeCN was boiled for 1 hour. After the usual workup, **2** was recovered unchanged in quantitative yield.

(b) To a stirred suspension of 0.30 g (0.002 mol) of CsF in 20 mL of MeCN was added, with boiling, a solution of 0.48 g (0.002 mol) of **8** [2]. The mixture was boiled for 1 hour, cooled to 20 °C, and filtered, and the solvent was distilled off. Compound **8** was recovered unchanged in 95% yield by sublimation of the residue in vacuum.

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