New Polysulfur-Nitrogen Heterocycles by Thermolysis of $1,3\lambda^4\delta^2,2,4$ -Benzodithiadiazines in the Hydrocarbon and Fluorocarbon Series

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In contrast to thermolysis of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazine (1) and its 5,6,7,8-tetrafluoro derivative 2 in dilute (10^{-3} M) hydrocarbon solutions, which leads to persistent 1,2,3-benzodithiazolyls in nearly quantitative yields, the thermolysis of 1 and 2 (the 6-6 bicyclic system) in concentrated (0.5 M) solutions at 150–170 °C results in complex mixtures of various polysulfur-nitrogen heterocycles, in particular differently fused 5-5-6, 5-6-7 and 5-6-6-6 polycyclic systems that were previously unknown. The products were isolated by column chromatography, and the structures of the 5-5-6 (11, 12), 5-6-7 (5, 13), and 5-6-6-6 (6, 14, 15) polycyclic systems, as well

Introduction

Hyperelectronic (π - and σ -excessive) 1,3 $\lambda^4 \delta^2$,2,4-benzodithiadiazine^[1] and its carbocyclic substituted derivatives^[2–5] (Scheme 1), including polyfluorinated versions, reveal some features of weak 12 π -electron antiaromaticity^[5–7] combined with moderate thermo- and photostability.^[8–11] Mild thermolysis^[8,9,11] or photolysis^[10,11] of their dilute (10⁻³ M) hydrocarbon solutions results in persistent 1,2,3-benzodithiazolyls (Scheme 1), which are promising building blocks in the design and synthesis of organic molecular magnets and/ or organic molecular conductors.^[12,13] The key intermediates of this transformation are R–S–N: \leftrightarrow R–S \equiv N nitrenoids (R = 1,2,3-benzodithiazol-2-yl), which can be identified under matrix isolation conditions.^[10]



Scheme 1.

The traditional synthetic approach to 1,2,3-benzodithiazolyls is the reduction of 1,2,3-benzodithiazolium chlorides



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as the 6-7 (4) and 5-6 (16) bicyclic derivatives, confirmed by X-ray diffraction. The crystal packing of 6 and 11–16 is discussed with special emphasis on π -stacking interactions. The fluorescent properties of the 5-6-6-6 systems synthesized are reported. An alternative approach to the linear 5-6-6-6 system 15 based on self-condensation of an R–N=PPh₃ precursor (R = 4,5,6,7-tetrafluoro-1,2,3-benzodithiazol-2-yl) is described, and the free-radical character of this new reaction is proved.

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(Herz salts). It should be emphasized that the thermolysis of $1,3\lambda^4\delta^2$,2,4-benzodithiadiazines affords 1,2,3-benzodithiazolyls for which the corresponding 1,2,3-benzodithiazoliums, for example fluoro-containing ones, are unknown.^[8,9]

With dilute solutions of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines, the yields of radicals estimated by means of ESR measurements are nearly quantitative. It is therefore of obvious interest to investigate whether the thermolysis of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines can be a preparative approach to 1,2,3-benzodithiazolyls.

The present article deals with further investigation of the solution thermolysis of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines in both hydrocarbon and fluorocarbon series with special emphasis on concentrated solutions. It will be shown that under thermolysis conditions and in concentrated hydrocarbon solutions all the aforementioned species are seemingly involved in further transformations to give complex mixtures of products including several new and unusual polysulfur-nitrogen heterocyclic systems. Despite very low yields, the latter were isolated and unambiguously characterized by means of X-ray diffraction. Selected spectral properties of the new polysulfur-nitrogen heterocycles synthesized, including fluorescent properties, are also reported.

Results and Discussion

Thermal Transformations

Under argon, the thermolysis of 0.5 M solutions of $1,3\lambda^4\delta^2$,2,4-benzodithiadiazine (1) and its 5,6,7,8-tetra-

fluoro derivative 2 in hydrocarbons (squalane, decane) at 150-170 °C leads to complex mixtures of various polysulfur-nitrogen heterocycles, including previously unknown polycyclic systems (Schemes 2 and 3). In particular, the 6-6 bicyclic system of 1 and 2 transforms into differently fused 5-5-6, 5-6-7, and 5-6-6-6 polycyclic systems. The latter are identified for the first time. Thus, compound 1 affords 2,1,3benzothiadiazole (3), benzopentathiepine (4), [1,2,3]dithi $azolo[5,4-g][2\lambda^4\delta^2,4,1,3,5]$ benzodithiatriazepine (5), and [1,2,3]dithiazolo[4,5-c]phenothiazine (6), which were isolated by column chromatography of the reaction mixtures; 1,2,3-benzothiadiazole (7), benzotrithiol (8), 1,2,4 $\lambda^4\delta^2$,3,5benzotrithiadiazepine (9), and elemental sulfur were also identified in the reaction mixtures by GLC-MS and/or ¹H NMR techniques (Scheme 2), and NH₃ was detected in the gas phase.



Scheme 2.



Scheme 3.

The thermolysis of compound **2** gives 4,5,6,7-tetrafluoro-2,1,3-benzothiadiazole (**10**), 7,8-difluorobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**11**), 4,5-difluorobenzo[1,2-*d*:4,3-*d'*]bis[1,2,3]dithiazole (**12**), 6,7-difluoro[1,2,3]dithiazolo-[5,4-*g*][$2\lambda^4\delta^2$,4,1,3,5]benzodithiatriazepine (**13**), 4,5,7,8,9,10hexafluoro[1,2,3]dithiazolo[4,5-*c*]phenothiazine (**14**), 4,6,7,8,9,11-hexafluoro[1,2,3]dithiazolo[5,4-*b*]phenothiazine (**15**), and 4,5,7-trifluoro-6-oxo-1,2,3-benzodithiazole (**16**), which were isolated by column chromatography (Scheme 3). Additionally, 4,8-difluorobenzo[1,2-*d*:4,5-*d'*]bis[1,2,3]dithiazole (**17**) was detected in the reaction mixture by ¹⁹F NMR spectroscopy and GLC-MS (Scheme 3; the structure was assigned tentatively by comparison with isomeric 12). In contrast to the thermolysis of 1, evolution of acidic gases was observed.

In both cases the major isolated products are 2,1,3benzothiadiazoles **3** and **10** (Schemes 2 and 3) as transformation of 12π -electron antiaromatic compounds **1** and **2** into 10π -electron aromatic derivatives **3** and **10** is thermodynamically attractive.

The thermal transformations of 1 also proceed in boiling 1-butanol (which does not react nucleophilically with either 1 or 2) at 117 °C, i.e. at much lower temperature than in the hydrocarbons (Scheme 4). In this case only compound 6 was isolated from the reaction mixture, which also contained also small amounts of compounds 3, 4, 7, 9 and elemental S according to the GLC-MS data.



Scheme 4.

In the case of **2**, di-*n*-butyl sulfite and 2,2'-diamino-3,3',4,4',5,5',6,6'-octafluorodiphenyl disulfide (**18**) were isolated as major products along with minor compound **11** (Scheme 4). Formation of $(nBuO)_2S=O$ (not observed in the case of **1**) can be explained by an acid-catalyzed (traces of HF) dehydration of *n*BuOH, 1:1 addition of released H₂O to **2**,^[14] and further reaction of the addition product with *n*BuOH. Compound **18** can also be considered to be a hydrolysis product (see ref.^[3]). Thus, in this case acid-initiated hydrolysis seemingly dominates thermal transformations.

The structures of compounds **4–6** and **11–16** were confirmed by X-ray crystallography (see below).

Thus, the final products of the thermal transformations of $1,3\lambda^4\delta^2$,2,4-benzodithiadiazines appear to depend strongly upon the reaction conditions employed (this work and refs.^[8,9,11]).

Formation of the same 5-6-7 and 5-6-6-6 polycyclic systems in both the hydrocarbon (5, 6) and fluorocarbon (13, 14) series indicates that the required carbocyclic substitution is not electrophilic or nucleophilic in character, as is typical of hydrocarbon and fluorocarbon aromatics, respectively. Rather, we are dealing with radical and nitrenoid processes – a conclusion which is in agreement with previous observations.^[8–11] Thus, tetracyclic compounds 6, 14, and 15 can formally be considered the products of condensation of the corresponding 1,2,3-benzodithiazolyls accompanied by elimination of H₂S or SF₂ in the hydrocarbon and fluorocarbon and fluorocarbon series, respectively (Scheme 5).





The formation of 2,1,3- (3, 10) and 1,2,3-benzothiadiazoles (7) can be explained by oxidative imination of the S atoms of 1 and 2 by R–S–N: nitrenoids followed by splitting of the initial adducts (cf. the ability of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines to undergo oxidative imination with S^{II} and P^{III} derivatives).^[4,15] Compound 7 is known to react with elemental sulfur to give benzopentathiepine 4, which reversibly eliminates S to afford benzotrithiol 8.^[16] Compound 16 could be formed by reaction of 4,5,6,7-tetrafluoro-1,2,3benzodithiazolyl with dioxygen.

Crystal and Molecular Structures

According to the X-ray diffraction data (Tables 2–4 and Figures 1, 2, and 3), the polysulfur-nitrogen heterocyclic molecules 6 and 11–16 are perfectly planar in the crystal. The standard deviations from the mean plane are 0.039, 0.014, 0.011, 0.023, 0.064, 0.064, and 0.018 Å for 6, 11, 12, 13, 14, 15, and 16, respectively.

Generally, the crystal packing of 6 and 11–16 demonstrates numerous shortened contacts^[17,18] between the heteroatoms of neighboring molecules, especially S···S (4, 12, 13, 16), S···N (6, 11–13), S···O (16), S···F (12–16), and F···F (15) contacts.

The crystal structures of **6**, **13**, and **15** reveal π -stacks with a slipped-parallel arrangement of the neighboring molecules. The molecules of **6** and **13** are arranged in a head-to-tail fashion, whilst those of **15** are packed in a head-to-head mode. The separation between the planes of π -stacked molecules is 3.67, 3.33–3.37, and 3.44 Å for **6**, **13**, and **15**, respectively (see Figures 4, 5, and 6, respectively), whereas their inclination varies from 0° for **15** to 2.8° for **6**. The crystal packing of **15** reveals shortened intermolecular F…F contacts of 2.74–2.79 Å.

In the crystal lattice of **12** (Figure 7), one of two crystallographically independent molecules is involved in $S \cdots \pi$ interactions (S…ring centroid distance: 3.46 Å) leading to columnar stacks, whilst another one is involved in $\pi - \pi$ interactions that form dimeric pairs (interplanar separation: 3.51 Å). Both stacks and pairs are arranged in a head-totail fashion. For the hydrocarbon analog of **12**, a slipped π stack structure with a head-to-head orientation of neighboring molecules is observed.^[19]



Figure 1. Molecular structures of **6**, **14**, and **15**. Selected bond lengths [Å] and bond angles [°]: **6**: C3a–N3 1.308(3), N3–S2 1.644(2), S2–S1 2.0934(9), S1–C11b 1.747(2), S11–C10a 1.752(2), S11–C11a 1.740(2), N6–C5a 1.312(3), C4–C5 1.342(3), C11a–C11b 1.365(3); C3a–N3–S2 116.0(2); N3–S2–S1 98.56(8), S2–S1–C11b 91.39(8). **14**: C3a–N3 1.303(4), N3–S2 1.627(3), S2–S1 2.0998(19), S1–C11b 1.747(3), S11–C10a 1.749(3), S11–C11a 1.749(3), N6–C5a 1.308(4), C4–C5 1.328(4), C11a–C11b 1.366(4); C3a–N3–S2 115.9(2), N3–S2–S1 98.57(11), S2–S1–C11b 91.50(11). **15** (averaged over four crystallographically independent molecules): C17–S1 1.73(2), S1–S2 2.114(7), S2–N3 1.66(2), N3–C4 1.32(2), N14–C13 1.42(2), N14–C15 1.27(2), S7–C8 1.766(7), S7–C6 1.73(2); C17–S1–S2 91.3(6), S1–S2–N3 97.9(6), S2–N3–C4 115.5(12), C13–N14–C15 119.4(12), C6–S7–C8 101.5(6).

The structure of **5**, a non-fluorinated analog of **13**, was reported earlier.^[20] Previously, compound **5** was obtained in ca. 1% yield from an unsuccessful attempt to prepare the benzobis($1,3\lambda^4\delta^2,2,4$ -dithiadiazine) system.^[20] The crystal packing, with a π -stacked head-to-tail arrangement of neighboring molecules, features an interplanar separation of 3.39 Å that is closely reminiscent of that of **13** (Figure 5).

In contrast to **6**, the neighboring molecules in its fluorinated analog **14** are oriented in a head-to-head manner, whilst their enlarged offset leads to F··· π interactions rather than normal π -stacking interactions (Figure 8). The dihedral angle between molecular planes is 6° and the F··· π separation is 3.44–3.53 Å (Figure 8). As above, the different orientation of the molecules for **6** and **14** can be attributed to S···N interactions in the lattice of **6** (S···N contacts: 3.10 and 3.06 Å) and to S···F interactions in that of **14** (S···F contacts: 3.07 and 2.90 Å).



Figure 2. Molecular structures of 11-13 and 16. Selected bond lengths [Å] and bond angles [°]: 11: C3a-N3 1.330(2), N3-S2 1.628(2), S2-N1 1.625(2); C3a-N3-S2 106.0(1), N3-S2-N1 100.10(8), S2-N1-C8b 106.5(1). 12 (two crystallographically independent parts of molecule): C1-S1 1.743(2), 1.741(2), S1-S2 2.0944(9), 2.083(1), S2-N3 1.643(2), 1.645(2), C3-N3 1.310(3), 1.307(3); C1-S1-S2 91.04(8), 90.81(8), S1-S2-N3 99.10(8), 99.46(8), S2-N3-C3 115.2(2), 114.8(2). 13: C6-N6 1.308(4), N6-S7 1.576(3), S7-N8 1.621(3), S9-N8 1.568(3), S9-N10 1.539(3), C10-N10 1.350(4), C1-S1 1.700(3), S1-S2 2.055(1), S2-N3 1.614(3), C3-N3 1.304(4); C6-N6-S7 137.0(2), N6-S7-N8 117.6(1), S7-N8-S9 130.3(2), N8-S9-N10 120.8(2), C10-N10-S9 135.6(2), C1-S1-S2 91.8(1), S1-S2-N3 99.0(1), S2-N3-C3 115.3(2). 16: S1-S2 2.064(1), S2-N3 1.617(2), N3-C3a 1.314(3), S1-C7a 1.723(2), C6-O1 1.234(3); S1-S2-N3 99.19(8), S2-N3-C3a 115.7(2), S2-S1-C7a 92.07(9), S1-C7a-C3a 113.5(2), N3-C3a-C7a 119.6(2).



Figure 3. Molecular structure of **4**. Selected bond lengths [Å] and bond angles [°] (averaged over two crystallographically independent molecules): C10–S1 1.806(9), S1–S2 2.044(4), S2–S3 2.050(4), S3–S4 2.043(4), S4–S5 2.041(4), S5–C11 1.808(10); C11–C10–S1 123.2(8), C10–S1–S2 103.6(3), S1–S2–S3 104.1(1), S2–S3–S4 102.5(1), S3–S4–S5 104.3(2), S4–S5–C11 103.5(3), S5–C11–C10 122.7(7).

The crystal packing of **11** and **16** reveals a typical herringbone pattern. In contrast to **11**, columnar π -stacks and molecular layers are formed in the crystal structure of its non-fluorinated analog. Additionally, shortened S…N contacts give rise to a ribbon-like quasi-polymeric structure.^[21]

For compound **4**, which was structurally defined previously^[22] (see ref.^[16] for derivatives), a new polymorph is observed. The hetero rings of two crystallographically independent molecules have the chair-twist-chair (TC) confor-



Figure 4. Orientation of neighboring molecules in the crystal lattice of **6**.



Figure 5. Orientation of neighboring molecules in the crystal lattice of **13**.



Figure 6. Orientation of neighboring molecules in the crystal lattice of **15**.



Figure 8. Orientation of neighboring molecules in the crystal lattice of **14**.

mation with C_2 symmetry. The molecules are involved in π -stacking interactions with a separation of 3.52–3.57 Å between neighboring benzene rings (Figure 9). Overall, the stacks form a layered structure.



Figure 7. Orientation of neighboring molecules in the crystal lattice of **12**.



Figure 9. Orientation of neighboring molecules in the crystal lattice of **4**.

In the previously observed crystal lattice,^[22] π -stacked dimers can be identified (separation of benzene rings: 3.41 Å) that are combined into stacks by S··· π interactions (ring centroid···S atom distance: 3.48 Å). Overall, the stacks form a herringbone structure.^[22]

Selected Spectral Properties

For 1 and its carbocyclic substituted derivatives, the maxima of the weak (log $\varepsilon \approx 2.4$ –2.8) long-wavelength absorptions in the UV/Vis spectra are in the range of ca. 610- $635 \text{ nm}.^{[1-5]}$ The 5-5-6 (12 and its hydrocarbon analog^[19]), 5-6-7 (5, 13), and angular 5-6-6-6 (6, 14) systems reveal strong (log $\varepsilon \approx 3.9$ –4.2) absorptions in about the same range of ca. 570-635 nm, whereas the linear 5-6-6-6 system 15 absorbs at shorter wavelengths (Table 1), with only a weak dependence of the corresponding $\pi \rightarrow \pi^*$ transitions in extended polyheteroatom π -systems upon substitution of fluorine for hydrogen. Additionally, the 5-6-6-6 systems (6, 14, 15) demonstrate strong fluorescence in the range of ca. 660-680 nm (Table 1). The Stokes shifts are very different for angular (ca. 40-60 nm for 6, 14) and linear (ca. 140 nm for 15) derivatives (Table 1). Taking into account the solubility of the discussed compounds in organic solvents, their thermal stability, and their stability towards moisture (in sharp contrast to starting $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines),^[3,14] it is possible to believe that the polysulfur-nitrogen heterocycles synthesized here can be considered as potential fluorescent dyes. Furthermore, the spectral properties of compound 15 are very similar to those of novel nondoping organic light-emitting diodes (OLEDs).^[23]

Table 1. Spectroscopic data for compounds 5, 6, and 11-16.

Alternative Approaches to 5-6-6-6 Systems

Due to the potential of the 5-6-6-6 systems as fluorescent dyes, rational approaches to their preparation are of interest. These can probably be designed based on phenothiazine systems in both the hydrocarbon and fluorocarbon series.

Meanwhile, it was found that compound **15**, the most interesting in the context of OLEDs, can be obtained in moderate yield as the final product of a spontaneous transformation of R–N=PPh₃ (**19**; R = 4,5,6,7-tetrafluoro-1,2,3-benzodithiazol-2-yl) in CHCl₃ solution (Scheme 6). The ¹⁹F and ³¹P NMR spectra of the reaction mixture reveal formation of Ph₃PF₂ [$\delta_{^{19}F}$ = 121.9 ppm (d, $J_{F,P}$ = 660 Hz); $\delta_{^{31}P}$ = -54.5 ppm (t, $J_{P,F}$ = 660 Hz); cf. ref.^[24]] and, tentatively, Ph₃P=N–H [$\delta_{^{31}P}$ = 22.0 (s); cf. ref.^[25]] as by-products. At the same time, Ph₃P=S^[26] and (SN)₄^[27] are not observed in the ³¹P and ¹⁴N NMR spectra, respectively. The reaction is solvent-dependent and does not proceed, for example, in toluene.



Scheme 6.

We found by ESR spectroscopy that in CHCl₃ solution (but not in toluene) and at ambient temperature, compound **19** spontaneously produces 1,2,3-benzodithiazolyl (**20**; Scheme 7; see refs.^[8,9] for the ESR spectrum), seemingly by reversible homolytic splitting of the exocyclic S–N bond. At the same time, the second product of such splitting – the

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	NMR, δ [ppm] ¹ H	¹⁹ F ^[a]	¹³ C	¹⁴ N	UV/Vis $\lambda_{\max} [nm] (\log \varepsilon)$	Fluorescence $\lambda_{max}/\lambda_{exit.}$ [nm]
5	7.60 (d) ^[b] , 7.11 (d) ^[b]				625 (4.0), 582 (4.0) ^[20]	
6	7.48 (d, 1 H), 7.41 (d, 1 H), 7.23 (m, 2 H), 7.18 (td, 1 H), 7.14 (ddd, 1 H)				610 (4.02), 579 (4.02), 337 (4.15), 253 (4.23)	667/330
11		15.8	148.2, 144.6, 142.3	334	315 (3.89; sh.), 286 (4.44)	
12		17.9	149.6, 142.8, 123.7	295	589 (4.23), 340 (4.17), 234 (3.84) ^[c]	
13		31.3, 0.8 ^[d]			635 (3.95), 587 (4.02), 363 (4.09)	
14		23.9, 20.7, 19.4, 17.3, 8.7, 4.8	148.8, 145.2, 144.9, 143.8, 143.5, 141.9, 140.1, 132.5, 126.3, 105.7, 103.4		615 (3.88; sh.), 585 (3.90), 394 (3.70), 349 (3.92), 255 (4.10)	657/340
15		42.0, 40.9, 18.8, 16.5, 7.4, 4.5			533 (4.68), 268 (4.70), 235 (4.49)	675/335
16		32.8, 20.6, 17.8 ^[d]			482 (3.97), 348 (3.80), 253 (3.47)	

[a] C_6F_6 as standard; the chemical shift of C_6F_6 with respect to CFCl₃ is -162.2 ppm. [b] J = 10 Hz. [c] Cf. Hydrocarbon analog (in CH₂Cl₂): 572 (4.2), 329 (4.0).^[19] [d] In [D₈]toluene.

 $Ph_3P=N$ radical – was not observed, very likely due to fast decay by hydrogen abstraction from the CHCl₃ solvent. Thus, the equilibrium shown in Scheme 7 might be shifted towards radical **20** and an explanation of the self-condensation of **19** into **15** can be suggested, including the role of the CHCl₃ solvent (Scheme 7).





A postulated SN[•] by-product (Scheme 7) is very unstable and undetectable by ESR spectroscopy in the condensed phase due to strong *g*-anisotropy (see ref.^[28] and references therein).

Conclusions

In contrast to thermolysis in dilute solutions, which leads to persistent 1,2,3-benzodithiazolyls (which are promising building blocks in the design and synthesis of organic molecular magnets and/or organic molecular conductors) in nearly quantitative yields, the thermal transformations of $1,3\lambda^4\delta^2,2,4$ -benzodithiadiazines 1 and 2 (the 6-6 bicyclic system) in concentrated solutions results in complex mixtures of various polysulfur-nitrogen heterocycles, in particular differently fused 5-5-6, 5-6-7, and 5-6-6-6 polycyclic systems that were previously unknown. Despite very low yields, the products were isolated and unambiguously identified by X-ray diffraction. The polycyclic π -functional molecules prepared engage in anisotropic intermolecular interactions in the solid state and are therefore of interest for materials science.^[29] In both hydrocarbon and fluorocarbon series, the polycyclic systems synthesized demonstrate strong long-wavelength absorption and fluorescence and can be considered as potential fluorescent dyes. All the aforementioned properties motivate the elaboration of rational approaches to the discussed compounds, and this can be a direction for further investigations in this field. The transformation of the $R-N=PPh_3$ derivative 19 (R = 4,5,6,7-tetrafluoro-1,2,3-benzodithiazol-2-yl) into the 5-6-6-6 system 15, which was discovered and explained in the present work, can be considered promising in this context.

Experimental Section

General: Compounds 1^[1] and 2^[2] were prepared by known methods. Their thermolysis was carried out under argon in absolute solvents, with stirring. The concentration of residual water in *n*BuOH was controlled by gas chromatography to be 0.02 M. The chromatographic separations of the products were performed with silica columns. The physical and analytical data for the compounds synthesized are listed in Tables 4 and 5. Compound 19^[15] was prepared in 60% yield by an improved procedure, the details of which will be given elsewhere.^[30]

The ¹H, ¹³C, ¹⁴N, and ³¹P NMR spectra were measured with a Bruker DRX-500 spectrometer at frequencies of 500.13, 125.76, 36.13, and 202.46 MHz, respectively, with TMS, NH₃ (liq.) and 85% H₃PO₄ 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; solutions in CDCl₃ were used unless otherwise indicated.

The high-resolution mass spectra (EI, 70 eV) were recorded with a Finnigan MAT MS-8200 instrument.

The UV/Vis spectra were recorded on Specord M40 and Hewlett– Packard 8453 spectrophotometers for solutions in CHCl₃. The fluorescent spectra were measured with a Kontron SFM-25 spectrofluorimeter for MeCN solutions.

The GLC-MS determinations were performed with a Hewlett– Packard G1800A GDC apparatus. The GC measurements were carried out with a Hewlett–Packard 5890 instrument.

The ESR measurements were carried out on a Bruker ESP-300 spectrometer (MW power: 265 mW; modulation frequency: 100 kHz; modulation amplitude: 0.005 mT) for a CHCl₃ solution of **19**. The spectral integration and simulation were performed with the Winsim 32 program.

Crystallographic Analysis: The single-crystal structure determinations (Tables 2, 3, and 4) were carried out on Bruker P4 (**4–6**, **11–14**, **16**) and Syntex P2₁ (**15**) diffractometers with graphite-monochromated Mo- K_{α} ($\lambda = 0.71073$ Å) and Cu- K_{α} ($\lambda = 1.54178$ Å) radiation, respectively. The structures were solved by direct methods by use of the SHELXS-97 program^[31] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation by use of the SHELXL-97 program.^[31] Hydrogen atoms were located geometrically. The structures obtained were analyzed for shortened contacts between non-bonded atoms with the PLATON program.^[32,33]

For compounds 4 and 15, available single crystals were very small (Tables 2 and 4) and reflections could only be measured to $\theta = 22.5^{\circ}$ and $\theta = 57^{\circ}$, respectively. The structure of 15 was refined with AFIX and EADP restraints applied to selected geometrical and anisotropic parameters, respectively: the C₆F₄ moiety was restrained to be a right hexagon with all C–F bond distances of 1.35 Å, for each C–F bond of the molecule thermal parameters of the F atom were fixed at corresponding values of the C atom.

CCDC-268796 (for 4), -268797 (for 6), -268798 (for 11), -268799 (for 12), -268800 (for 13), -268801 (for 14), -268802 (for 15), and -268803 (for 16) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. For 5, the data obtained in this work are in full agreement with those published previously.^[20]

Identification of Known Compounds: The isolated compounds **3**,^[34] **5**,^[20] **10**,^[35] and **18**,^[3] described previously, were identified by comparison of reported m.p.'s, unit cell (XRD) and spectral (¹H and

Table 2. Crystal data and structure refinement for compounds 4, 6, and 11.

Compound	4	6	11
Empirical formula	C ₆ H ₄ S ₅	C ₁₂ H ₆ N ₂ S ₃	$C_6F_2N_4S_2$
Formula mass	236.39	274.37	230.22
Temperature [K]	298(2)	296(2)	296(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	C2/c	Pnma
<i>a</i> [Å]	7.729(1)	12.9236(7)	9.2356(6)
<i>b</i> [Å]	9.457(1)	12.8240(8)	16.856(1)
c [Å]	25.453(3)	15.214(1)	5.1668(4)
β[°]	95.06(1)	114.964(5)	90
Volume [Å ³]	1853.3(4)	2285.9(3)	804.33(9)
Z	8	8	4
$D_{\text{calcd.}} [\text{Mgm}^{-3}]$	1.694	1.594	1.901
Absorption coefficient [mm ⁻¹]	1.179	0.622	0.654
Crystal size [mm ³]	$0.20 \times 0.15 \times 0.05$	$0.70 \times 0.20 \times 0.15$	$0.80 \times 0.34 \times 0.05$
θ range for data collection [°]	2.30-22.50	2.35-25.00	2.42-30.00
Index ranges	$-8 \le h \le 0$	$0 \le h \le 15$	$-12 \le h \le 0$
-	$0 \le k \le 10$	$-15 \le k \le 0$	$0 \le k \le 23$
	$-27 \le l \le 27$	$-18 \le l \le 16$	$-7 \le l \le 0$
Reflections collected	2627	2096	1212
Independent reflections	2417 $[R_{(int)} = 0.0466]$	$2017 [R_{(int)} = 0.0205]$	$1212 [R_{(int)} = 0.0]$
Completeness to θ [%]	99.8	100.0	100.0
Absorption correction	empirical	empirical	integration
Min. and max. transmission	0.73 and 0.88	0.96 and 0.99	0.78 and 0.97
Data/restraints/parameters	2417/0/199	2017/0/154	1212/0/64
Goodness-of-fit on F^2	0.885	1.062	1.044
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0572, wR_2 = 0.1319$	$R_1 = 0.0329, wR_2 = 0.0843$	$R_1 = 0.0381, wR_2 = 0.0923$
R indices (all data)	$R_1 = 0.1163, wR_2 = 0.1487$	$R_1 = 0.0420, \ \mathrm{w}R_2 = 0.0894$	$R_1 = 0.0616, wR_2 = 0.1033$

Table 3. Crystal data and structure refinement for compounds 12-14.

Compound	12	13	14
Empirical formula	$C_6F_2N_2S_4$	$C_6F_2N_4S_4$	$C_{12}F_6N_2S_3$
Formula mass	266.32	294.34	382.32
Temperature [K]	296(2)	296(2)	296(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/m	$P2_1/c$	$P2_1/n$
a [Å]	7.818(2)	8.513(3)	7.292(6)
<i>b</i> [Å]	23.204(5)	16.677(6)	4.700(4)
c [Å]	10.124(2)	6.690(2)	37.29(3)
β [°]	102.45(1)	97.71(1)	94.27(5)
Volume [Å ³]	1793.4(6)	941.2(6)	1274.7(19)
Ζ	8	4	4
$D_{\text{calcd.}} [\text{Mgm}^{-3}]$	1.973	2.077	1.992
Absorption coefficient [mm ⁻¹]	1.043	1.011	0.653
Crystal size [mm ³]	$0.80 \times 0.28 \times 0.20$	$0.70 \times 0.34 \times 0.10$	$0.90 \times 0.44 \times 0.02$
θ range for data collection [°]	2.06-27.50	2.41-27.51	2.19-25.00
Index ranges	$0 \le h \le 9$	$-10 \le h \le 11$	$0 \le h \le 8$
	$0 \le k \le 30$	$-21 \le k \le 0$	$0 \le k \le 5$
	$-13 \le l \le 12$	$-8 \le l \le 0$	$-44 \le l \le 44$
Reflections collected	2243	2337	2421
Independent reflections	$2094 [R_{(int)} = 0.0323]$	2158 $[R_{(int)} = 0.0822]$	2229 $[R_{(int)} = 0.0348]$
Completeness to θ [%]	98.7	99.9	98.8
Absorption correction	integration	integration	integration
Min. and max. transmission	0.77 and 0.84	0.72 and 0.91	0.84 and 0.99
Data/restraints/parameters	2094/0/128	2158/0/145	2229/0/208
Goodness-of-fit on F^2	1.036	1.049	1.038
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0383, wR_2 = 0.1039$	$R_1 = 0.0546, wR_2 = 0.1451$	$R_1 = 0.0383, wR_2 = 0.0974$
R indices (all data)	$R_1 = 0.0412, \ \mathrm{w}R_2 = 0.1061$	$R_1 = 0.0653, wR_2 = 0.1551$	$R_1 = 0.0563, wR_2 = 0.1068$

¹⁹F NMR, UV/Vis, MS) parameters with those obtained in this work. Di-*n*-butyl sulfite was identified by GLC-MS. Compounds 7,^[34] **8**,^[16] and **9**^[36] were identified without isolation by means of GLC-MS and ¹H NMR techniques by comparison with the authentic samples.

See Table 5 for spectroscopic data for compounds 5, 6, and 11–16.

Thermolysis of $1,3\lambda^4\delta^2$,2,4-Benzodithiadiazine (1) in Squalane. Formation of Compounds 3–6: A solution of 0.34 g (2 mmol) of 1 in 3 mL of squalane was stirred at 150–160 °C for 3 h, cooled to

Table 4. Crystal data and	structure refinement for	compounds 15 and 16.
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Compound	15	16
Empirical formula	$C_{12}F_6N_2S_3$	C ₆ F ₃ NOS ₂
Formula mass	382.32	223.19
Temperature [K]	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	Cc	$P2_1/n$
<i>a</i> [Å]	11.310(2)	5.1828(7)
b [Å]	11.311(2)	9.706(1)
<i>c</i> [Å]	39.884(8)	14.298(2)
β [°]	97.97(2)	95.85(1)
Volume [Å ³]	5052.7(18)	715.5(2)
Ζ	16	4
$D_{\text{calcd.}} [\text{Mg}\text{m}^{-3}]$	2.010	2.072
Absorption coefficient [mm ⁻¹]	6.119	0.749
Crystal size [mm ³]	$0.13 \times 0.13 \times 0.03$	$0.80 \times 0.20 \times 0.08$
θ range for data collection [°]	2.24-57.43	2.54-24.99
Index ranges	$0 \le h \le 12$	$-6 \le h \le 0$
	$0 \le k \le 12$	$0 \le k \le 11$
	$-43 \le l \le 43$	$-16 \le l \le 16$
Reflections collected	4151	1398
Independent reflections	$3688 [R_{(int)} = 0.1374]$	$1250 [R_{(int)} = 0.0186]$
Completeness to θ [%]	100.0	99.9
Absorption correction	empirical	empirical
Min. and max. transmission	0.46 and 0.82	0.87 and 0.98
Data/restraints/parameters	3688/38/544	1250/0/118
Goodness-of-fit on F^2	1.051	1.065
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0739, wR_2 = 0.1679$	$R_1 = 0.0329, wR_2 = 0.0939$
R indices (all data)	$R_1 = 0.1311, wR_2 = 0.2071$	$R_1 = 0.0387, wR_2 = 0.0980$

Table 5. Characterization of compounds 5, 6, and 11-16.

	M.p. [°C]	Formula	MS: M^+ (<i>m</i> / <i>z</i>) measured (calculated)
5	269-271	$C_6H_4N_4S_4$	257.9154 (257.9162)
6	206-208	$C_{12}H_6N_2S_3$	273.9724 (273.9693)
11	175–176 ^[a]	$C_6F_2N_4S_2$	229.9542 (229.9533)
12	230-232 ^[a]	$C_6F_2N_2S_4$	265.8918 (265.8912)
13	280-282 ^[a]	$C_6F_2N_4S_4$	293.8972 (293.8974)
14	216-217	$C_{12}F_6N_2S_3$	381.9133 (381.9128)
15 ^[b]	234–236	$C_{12}F_6N_2S_3$	381.9152 (381.9128)
16	210-212	$C_6F_3NOS_2$	222.9371 (222.9374)

[[]a] In a sealed capillary. [b] Correct elemental analyses for C, F, N, S.

20 °C, filtered and chromatographed. Elution with hexane gave 50 mg of a red oil consisting (GLC-MS, ¹H NMR) of compounds **9** (33%), **4** (31%), **8** (13%), **3** (3%), **7** (1.5%), elemental S (0.6%), and squalane (5%). Compound **4** (5 mg) was isolated by low-temperature crystallization from hexane as pale-yellow crystals (m.p. 55-56 °C). Elution with toluene gave 30 mg (10% yield) of compound **3**^[34] as colorless crystals. Elution with 1:1 CH₂Cl₂/ethyl acetate followed by crystallization of the product from 10:1 hexane/ toluene gave compound **6** (4 mg) as black crystals. The reaction precipitate was refluxed in toluene and the solution formed was chromatographed. Elution with toluene followed by recrystallization of the product from the same solvent gave compound **5** (2 mg) as black crystals. The gases evolved during the thermolysis were absorbed by dilute HCl. Photometrical analysis with Nessler's reagent revealed NH₃ in 3% yield.

Thermolysis of 5,6,7,8-Tetrafluoro-1, $3\lambda^4\delta^2$,2,4-benzodithiadiazine (2) in Decane. Formation of Compounds 10–16: A solution of 0.96 g (4 mmol) of 2 in 8 mL of decane was stirred at 160–170 °C for 6 h, cooled to 20 °C, filtered and chromatographed (hexane). Com-

pound 10^[35] (36 mg; 5%) was obtained as colorless crystals. The reaction precipitate was sublimed at 170 °C/2 mm and the sublimate chromatographed. Elution with toluene gave blue and red zones. Sublimation of the product from the blue zone at 110 °C/ 2 mm gave a mixture of 12, 14, and 17. Compound 14 (6 mg) was obtained as black crystals by further chromatography of this mixture (1:1 hexane/toluene) followed by crystallization from hexane. Compound 12 (3 mg) was obtained as black crystals by crystallization of its mixture with isomeric 17 from 4:1 hexane/toluene. The mother liquor contained residual 12 (GLC-MS: $m/z = 226 [M^+]$; ¹⁹F NMR: δ = 17.9 ppm) and **17** (GLC-MS: m/z = 226 [M⁺]; ¹⁹F NMR: $\delta = 40.7$ ppm; the structure was assigned tentatively). Crystallization (toluene) of the non-volatile residue from sublimation gave 13 (3 mg) as black crystals. Sublimation of the product from the red zone at 120 °C/2 mm gave 15 (1 mg) as black crystals. Elution with 10:1 toluene/ethyl acetate gave 11 and 16, which were purified by sublimation at 120 °C/2 mm. Compound 11 (12 mg) was obtained as colorless crystals and compound 16 (6 mg) as black crystals.

Thermolysis of Compound 1 in 1-Butanol. Formation of Compound 6: A solution of 0.17 g (1 mmol) of 1 in 1 mL of *n*BuOH was refluxed for 3.5 h, cooled to 20 °C and chromatographed. Elution with CH₂Cl₂ gave ca. 4 mg of a mixture (GLC-MS data) of compounds 3 (20%), 4 (traces), 7 (40%), 9 (20%), and elemental S (20%). Elution with 10:1 CH₂Cl₂/ethyl acetate gave compound 6. The latter was repeatedly chromatographed under the same conditions and recrystallized from 10:1 hexane/toluene to give black crystals (1 mg).

Thermolysis of Compound 2 in 1-Butanol. Formation of Compounds 11 and 18: A solution of 0.48 g (2 mmol) of 2 in 2 mL of *n*BuOH was refluxed for 4 h, cooled to 20 °C, and chromatographed (hexane) to give ca. 0.17 g of di-*n*-butyl sulfite, compound 11, and compound 18. Compound 11 (4 mg) was obtained as colorless crystals

Spontaneous Transformation of Compound 19 in Chloroform Solution. Formation of Compound 15: A solution of 0.10 g (0.2 mmol) of 19 in 0.5 mL of CHCl₃ was kept for 7 d at ambient temperature and then evaporated. The residue was chromatographed (benzene) to give compound 15 (12 mg, 30%) as black crystals.

According to the ESR measurements, the radical **20** appeared immediately upon dissolving precursor **19** and was detectable for a few days. For the ¹⁹F and ³¹P NMR measurements, the preparation was performed in CDCl₃ solution.

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