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Substituted 1,3,2,4-Benzodithiadiazines: Novel Derivatives, By-Products, and Intermediates*

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ABSTRACT: *The synthesis of the title compounds* **1** *by* ***1:1*** *condensation of Ar—N=S=N=SiMe$_3$* **2** *with SCl$_2$ followed by intramolecular ortho-cyclization of each [Ar—N = S = N—S—Cl] intermediate is complicated by further reaction of* **1** *with SCl$_2$ to give Herz salts* **3**. *With the* **2**:*SCl$_2$ ratio of 2:1, the formation of by-products* **3** *is reduced and novel compounds* **1** *are accessible. With ortho-I containing starting material* **2j**, *the parent compound* **1s** *is obtained as the result of an unexpected I, not H, substitution. The rate of the* **1** + *SCl$_2$ reaction depends upon a substituent's position, and the minor 8-R isomers* **1l,p** *(R = Br, I) are isolated for the first time from mixtures with the major 6-R isomers due to reduced reactivity toward SCl$_2$. The synthesized compounds* **1–3** *are characterized by multinuclear (including nitrogen) NMR and X-ray crystallography. According to the X-ray diffraction data,* **1j** *(6-Br) and* **1k** *(7-Br) derivatives are planar, whereas* **1i** *(5-Br) and* **1l** *(8-Br) are bent along the S1···N4 line by ~5° and ~4°, respectively, and the* **1r** *(7-OCH$_3$) derivative is planar in contrast to the known 5-OCH$_3$ isomer, which possesses a significantly folded heterocycle. The distortion of the planar geometry of some compounds* **1** *is interpreted in terms of a pseudo-Jahn-Teller effect as the result of π-highest occupied molecular orbital (HOMO) − σ*-(LUMO) lowest unoccupied molecular orbital + 1 mixing in a planar conformation. The* **2p** *compound is the first structurally defined Ar–N = S = N–SiMe$_3$ azathiene. The compound Ar–N = S = N–S–NH-Ar* **6** *modeling the aforementioned intermediate has been isolated and structurally characterized. We describe the attempts to synthesize compounds* **1** *from 2-aminobenzenethiols and (SN)$_4$ and from salts* **3** *and Me$_3$SiN$_3$, and we discuss the reaction pathways.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:563–576, 2001

INTRODUCTION

Recently, various 5-R, 6-R and 7-R substituted 1,3,2,4-benzodithiadiazines (**1**) (Scheme 1) were synthesized by 1:1 condensation of $RC_6H_4-N=S=N-SiMe_3$ (**2**) with SCl_2 followed by intramolecular electrophilic *ortho*-cyclization [3]. These heterocycles reveal some formal features of antiaromaticity [4] along with high and varied, essentially unpredictable, heteroatom reactivity [1,3,5,6] thus provoking keen interest. However, their chemistry has been only briefly investigated. In particular, it was found that mild thermolysis of **1** in dilute hydrocarbon solutions resulted in practically quantitative yields of stable 1,2,3-benzodithiazolyl π-radicals [1], interesting as potential building blocks in the design and

*Part XV of the series "Cyclic Aryleneazachalcogenenes"; part XIV: Ref. [1], part XIII: Ref. [2].

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synthesis of organic molecules with high-spin ground states (molecular magnets) [7, and references there-in]. On the whole, it is believed that many new reactions will be observed and many new structural types will be found among the reaction products of **1**.

In some cases the preparations of compounds **1** from **2** [3] were unsuccessful, especially with *para*-substituted starting materials (precursors of 7-R isomers of **1**), independent of the character of each substituent R. The 8-R substituted compounds **1**, minor products of regioselective cyclizations of *meta*-substituted starting materials leading predominantly to 6-R isomers, were characterized only spectroscopically without isolation [3].

The present article deals with the improved synthesis of 7-R and some other derivatives of **1** including the first-ever isolation of minor 8-R isomers, as well as with the by-products and intermediates of the cyclization. Attempts to synthesize **1** by different approaches to the ring closure are also described.

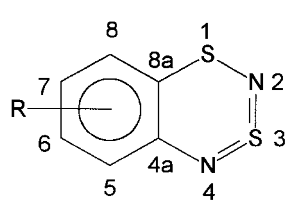
RESULTS AND DISCUSSION

Precursors

The starting materials **2** bearing a strong donor (Me_2N) or a strong acceptor (NO_2) substituent R, as well as an I substituent, were of special interest [8].

The novel compounds **2** were synthesized from $LiN(SiMe_3)_2$ and corresponding $RC_6H_4{-}N=S=O$ (cf. [3,9]) or $RC_6H_4{-}N=SCl_2$ ($R=NO_2$) (Scheme 2). Surprisingly, both approaches were not effectual with R = 3-NO_2 and the first one with R = 2-Me_2N or 4-Me_2N.

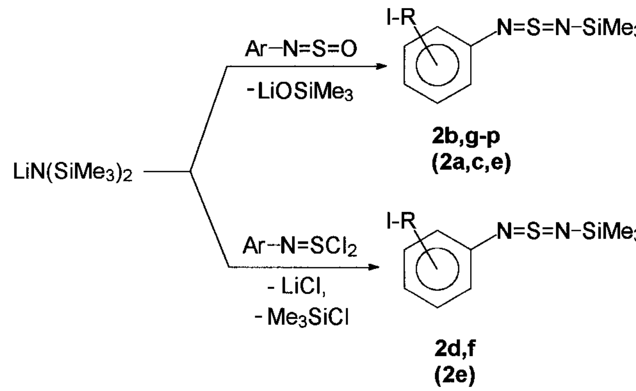
The **2p** compound (Figure 1) is the first structurally defined $Ar{-}N=S=N{-}SiMe_3$ azathiene [**2p**: Ar = 4-(4′-IC_6H_4)C_6H_4]. In the crystal, **2p** adopts the *Z,E* configuration with a dihedral angle between the NSN plane and the adjacent ring of 14.3(2)°, and between the rings of 29.9(1)°. The S^1N^2 bond distance (Figure 1) is rather short but corresponds to those found in the related *(Z,E)*$Ph_3Si{-}N=S=N{-}SiPh_3$ compound (1.506 and 1.508 Å) [10]. Other bond lengths and bond angles are typical [11].



SCHEME 1

Improved Cyclization

The synthesis of **1** by a 1:1 reaction of **2** with SCl_2 is complicated by formation of Herz salts (**3**) (1,2,3-arenodithiazolium chlorides [12]). In some cases they are even the major products. Control experiments (see Cyclic By-Products) indicate that the salts **3** come from further reaction of **1** with SCl_2. It follows that the 2:SCl_2 ratio should be changed in favor of **2** to suppress this side-process while preparing **1**. Indeed, with the 2:SCl_2 ratio of 2:1 it is possible to



SCHEME 2 Compounds **2**:

I/R	Me_2N	NO_2	Br	I	F	OCH_3
2	**(a)**	**d**	**g**	**j**		
3	**b**	**(e)**	**h**	**k**		
4	**(c)**	**f**	**i**	**l**	**m**	**n**

3,5-Br_2: **2o**, 4-(4′-IC_6H_4): **2p**
Parentheses indicate that corresponding compound was not synthesized by this way.

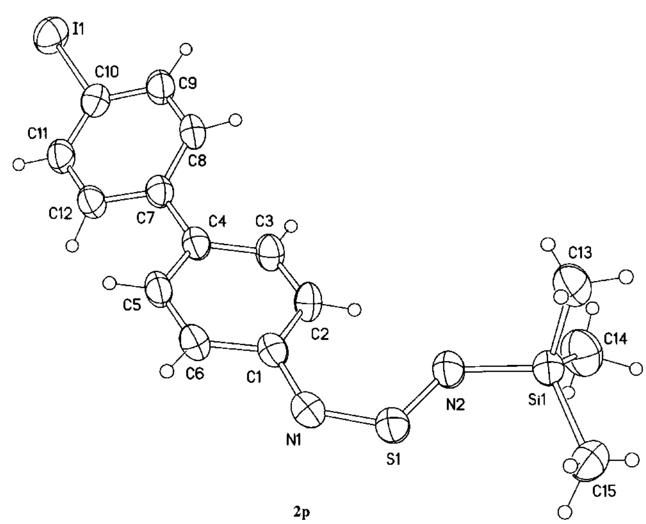


FIGURE 1 Structure of molecule **2p** in the crystal. Selected bond lengths (Å) and bond angles (°): N^1S^1 1,513(3); S^1N^2 1.508(3); N^1C^1 1.417(5); N^2Si^1 1.740(3); I^1C^{10} 2.096(4); $C^1N^1S^1$ 130.3(2); $N^1S^1N^2$ 119.0(2); $S^1N^2Si^1$ 127.7(2).

obtain 7-R derivatives of **1** from the cyclizations previously unsuccessful [3] with the 1:1 ratio (i.e., **1q,r;** R = F, OCH_3) as well as to prepare several novel derivatives (Scheme 3).

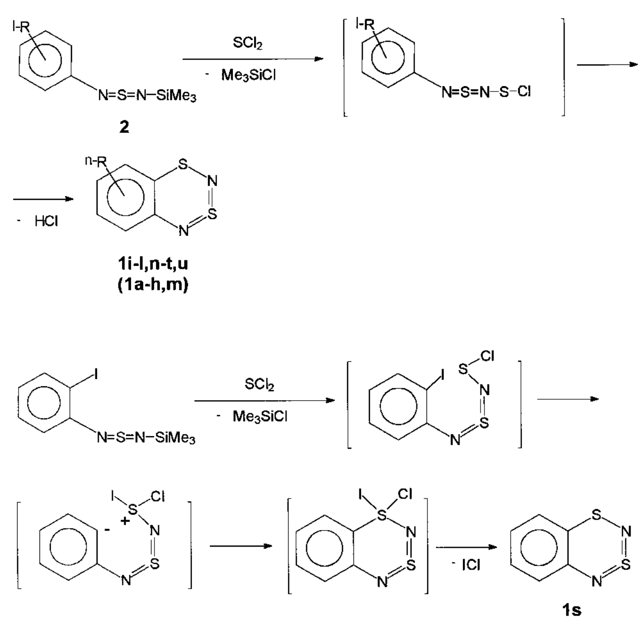
With 4–RC_6H_4–N=S=N–$SiMe_3$, the target heterocycle formation proceeds also with R = Br, I, 4-IC_6H_4. On the other hand, with R = NO_2 or CF_3 the expected compounds are not obtained under the improved reaction conditions (cf. Ref. [3]).

In the case of 2-RC_6H_4–N=S=N–$SiMe_3$ the cyclization readily occurs with R = Br. With starting material **2j** (R = I) the parent 1,3,2,4-benzodithiadiazine **1s** was isolated from the reaction mixture instead of the expected 5-I derivative **1m**. One can think that in this case the ring closure is mediated by the bipolar ion (Scheme 3) [13] originated from initial electrophilic attack on iodine, rather than on carbon [14]. The postulated (Scheme 3) ICl by-product should react further with both **2j** and **1s**. At any rate, control experiments have shown that Cl_2 is highly reactive toward **1** to give a complex mixture of unidentified products. With R = NO_2, the cyclization failed.

Earlier [3], it was discovered that for 3-RC_6H_4–N=S=N–$SiMe_3$ (R = CH_3, OCH_3, F, Cl) the cyclization is highly regioselective, leading predomi-nantly to 6-R substituted compounds **1**, with the preferred direction of ring closure being consistent with the thermodynamics of the corresponding σ-complexes as well as the factors of kinetic control for orbital-controlled El-Nu interaction. In this work, for R = Br, the ratio of the major 6-Br (**1j**) isomer to the minor 8-Br (**1l**) one was found to be 80:20. For R = I, however, the ratio of 6-I (**1n**) and 8-I (**1p**) isomers was only 60:40.

The observed ratio of isomers would be affected by their further reaction with SCl_2 at different rates. Control experiments on available mixtures of 6-R and 8-R isomers (R = Br, I) have shown that the 6-R isomer reacts with SCl_2 much more rapidly than the 8-R isomer, which makes possible the eventual isolation of 8-Br and 8-I derivatives. Thus, the cyclization itself seems to be more regioselective than it appears from the observed ratios of isomers in the reaction mixtures presented in [3] and this work.

With R = Me_2N (**2b**) or CF_3 the cyclization failed.



SCHEME 3 Heterocycles **1**:

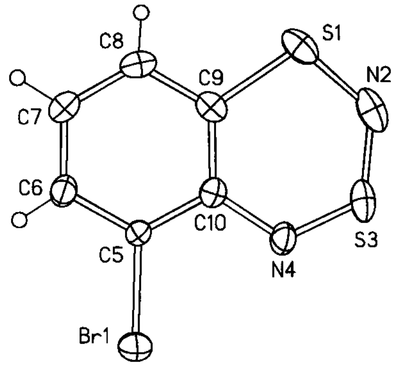
n/R	Me_2N	NO_2	Br	I
5	**(a)**	**(e)**	**i**	**(m)**
6	**(b)**	**(f)**	**j**	**n**
7	**(c)**	**(g)**	**k**	**o**
8	**(d)**	**(h)**	**l**	**p**

R = 7-F, **1q**; 7-OCH_3, **1r**; H, **1s**; 6,8-Br_2, **1t**; 7-(4-IC_6H_4), **1u**
Parentheses indicate that corresponding heterocycle was not synthesized by this way.

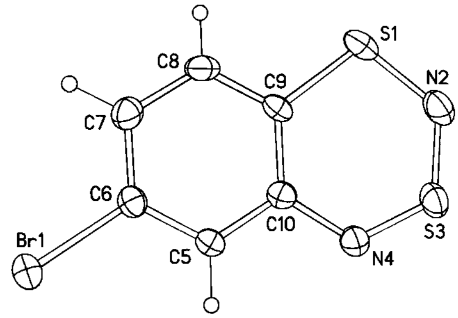
Molecular Structures

According to the previous data of X-ray crystallography, the parent compound **1s** [6] and its 5-CF_3 and 6-F derivatives [3] are planar, whereas 5-OCH_3, 6-CH_3 [3], and 5,6,7,8-F_4 [15] derivatives are bent along the S1···N4 line by ∼11°, ∼7°, and 5.5°, respectively. The MP2/6-31G** calculations do not reproduce this intriguing structural dichotomy with **1s**, its 5-OCH_3 and 5,6,7,8-F_4 derivatives, and the model 1,3,2,4-dithiadiazine (**11**) being found to be bent along the S1···N4 line by ∼38°, ∼39°, ∼34°, and ∼45° respectively. On the other hand, B3LYP/6-31G* calculations [2] predict a bent (26°) conformation for a free molecule of **1s**, but a perfectly planar conformation for its 5,6,7,8-F_4 derivative.

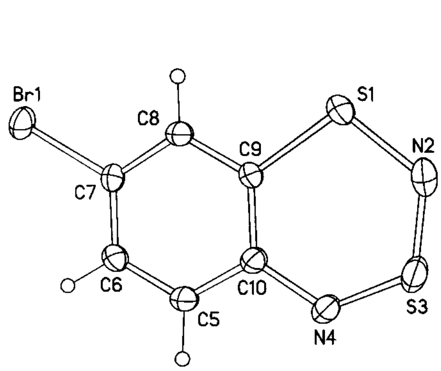
In the present work, both types of molecular geometry were observed again in the crystal (Figure 2, Table 1). For example, among **1i–l** isomers, **1j** (6-Br) and **1k** (7-Br) are planar, whereas **1i** (5-Br) and **1l** (8-Br) are bent along the S1···N4 line by 5.3(3)° and 3.8(3)°, respectively (throughout this work the term *planar* conventionally means that the angle above is smaller than 3°). Furthermore, for two crystallographically independent molecules of **1j**, one is perfectly planar, whereas another is bent by 3.1(2)°, which directly indicates the importance of packing effects. The **1r** (7-OCH_3) derivative (Figure 2, Table 1) is planar, in contrast to the significantly folded 5-OCH_3 isomer (see previous paragraph). Thus, the type of the molecular geometry of the title compound in the crystal, planar or bent, depends



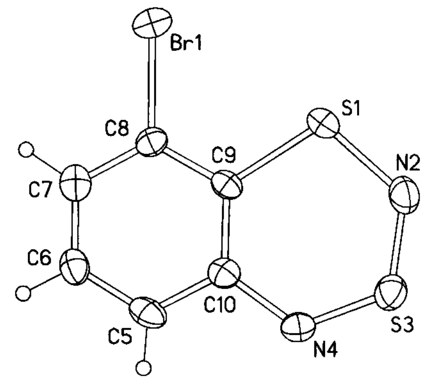
1i



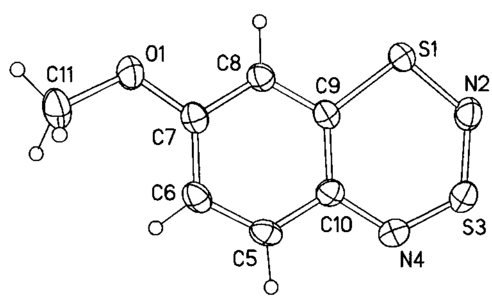
1j



1k



1l



1r

FIGURE 2 Structure of molecules **1i-l,r** in the crystal. For selected bond lengths and bond angles, see Table 1.

not only on the substituent character, but also on its position.

The bond lengths and bond angles of **1i–l,r** are typical [3,11]. Within experimental accuracy they are the same for all molecules (Table 1). In the N=S=N fragment the bond lengths differ except for **1l** (Table 1).

It can be assumed that the distortion of the planar C_s geometry in the calculations reflects the tendency of the molecules to minimize thermodynamic destabilization associated with antiaromaticity via a pseudo-Jahn-Teller effect [16]. With a simplifying molecular orbital (MO) model, one can identify orbital interactions capable of reducing molecular symmetry of the compounds under consideration from C_s to C_1. With C_s symmetry the molecular ground state is $(\cdots\pi^2)$, namely, $^1\mathbf{A}'$. It follows from the calculations (Table 2) that for both **1s** and **11** the C_s structure is the TS of the molecular bending. The transition to C_1 symmetry is possible by vibronic interaction with excited $^1\mathbf{A}''$. states achievable by $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ excitations. For **1s** the lowest-energy excitation of these types is $6a'' \rightarrow 20a'$. The mixing of $6a''$ (π-highest occupied molecular

TABLE 1 Selected Bond Lengths (Å) and Bond Angles (°) in Molecules **1i-1,r**[a]

	1i	**1j** *(two independent molecules)*	**1k**	**1l**	**1r**
S^1N^2	1.674(8)	1.684(5), 1.679(5)	1.664(4)	1.684(5)	1.678(3)
N^2S^3	1.547(8)	1.543(4), 1.548(5)	1.546(4)	1.538(5)	1.538(3)
S^3N^4	1.526(4)	1.527(4), 1.533(4)	1.524(4)	1.533(3)	1.528(3)
N^4C^{10}	1.413(7)	1.425(5), 1.417(5)	1.406(5)	1.426(7)	1.421(4)
S^1C^9	1.779(6)	1.785(4), 1.787(4)	1.787(3)	1.788(4)	1.785(3)
C^9C^{10}	1.413(8)	1.401(6), 1.400(6)	1.408(5)	1.405(6)	1.402(4)
$C^9S^1N^2$	106.5(3)	105.6(2), 106.0(2)	105.8(2)	105.7(2)	106.1(2)
$S^1N^2S^3$	122.9(3)	123.5(2), 123.3(3)	123.8(2)	123.8(3)	123.1(2)
$N^2S^3N^4$	119.2(3)	119.3(2), 119.2(2)	118.8(2)	118.9(2)	119.3(2)
$S^3N^4C^{10}$	123.3(4)	123.0(3), 122.9(3)	123.7(3)	123.3(3)	123.5(2)
$N^4C^{10}C^9$	124.4(5)	124.2(4), 124.9(4)	124.2(3)	124.1(4)	123.8(3)
$C^{10}C^9S^1$	123.2(4)	124.2(3), 123.7(3)	123.7(3)	123.9(4)	124.0(2)

[a]For atom numbering, see Figure 1.

TABLE 2 Quantum Chemical Calculations Data for Molecules **1s** and **11**

Compound (symmetry)	*RHF/6-31G* – E_{tot} (PES point)[a] (a.u.)*	*E_{rel} (kcal mol $^{-1}$)*	*MP2/6-31G*–E_{tot} (PES point)[a] (a.u.)*	*E_{rel} (kcal mol $^{-1}$)*
11 (C_s)	980.664074 (TS)	0.86		
11 (C_1)	980.665451 (min)	0		
1s (C_s)	1133.337707 (TS)	0.28	1134.702832 (TS)	2.43
1s (C_1)	1133.338154 (min)	0	1134.706710 (min)	0

[a]The types of stationary PES points were determined by the Hessian calculations.

orbital (HOMO)) with 20a′ (the lowest virtual σ^*-MO, which is next to the 7a″ π-lowest unoccupied molecular orbital (LUMO), i.e., LUMO + 1) (Figure 3) causes the molecule to fold along the S1···N4 line in accordance with the results of MP2/6-31G** calculations and the data of X-ray crystallography for 5-OCH_3,5-Br, 6-CH_3, 8-Br, and 5,6,7,8-F_4 derivatives. According to the atomic orbital (AO) contributions to the 6a″ and 20a′ MOs (Figure 3), the density of the corresponding one-electron transition is localized mainly on S1. The energy gain on going from C_s to C_1 sym-metry is smaller by 1 kcal mol^{-1} at the RHF level of theory becoming about nine-fold higher (for **1s**) at the MP2 level (Table 2).

Spectral Properties

In accordance with previous data [3], in ^{15}N NMR spectra of the title compounds, δ^{15}N values lie inside a narrow range, ~280–250 ppm, demonstrating weak dependence upon position and character of a carbocyclic substituent (for details, see Table 6 in Experimental). In the ^{15}N{^{1}H} spectrum of the parent compound **1s**, the signal at 263.1 ppm (Table 3) is a

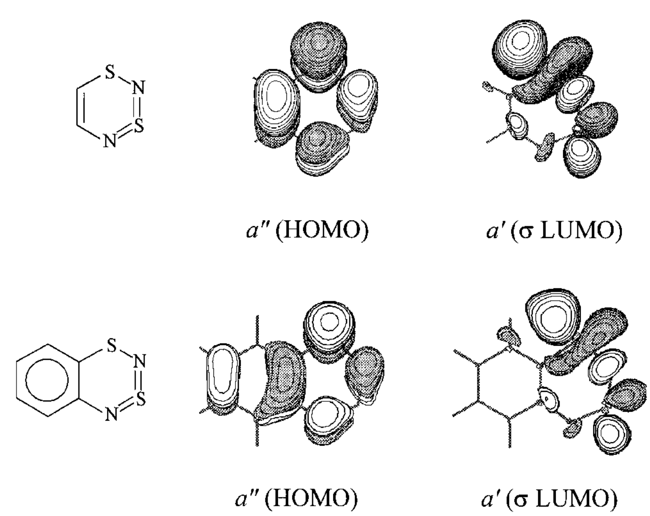


FIGURE 3 The **6a**″ π-HOMO and **20a**′ σ^*-LUMO + 1 (see text) of C_s-**1s** and the corresponding MOs of C_s-11 (RHF/6-31G*).

TABLE 3 Assignment of ^{1}H, ^{13}C, and ^{15}N NMR Spectra of **1s**[a]

δ (J, Hz)	δ (J, Hz)
N^2 269.2 (s)	C^{8a} 115.3 (tdd, 8.5, 1.7, 0.8)
N^4 263.1 (d, 2.3)	C^{4a} 138.5 (tt, 9.3, 2.1)
H^5 5.90 (dd, 7.8, 1.3)	C^5 123.0 (ddt, 163.2, 8.5, 1.3)
H^6 6.63 (tm, 7.8)	C^6 133.2 (ddm, 164.8, 8.5)
H^7 6.79 (tm, 7.6)	C^7 130.5 (ddm, 164.5, 7.2)
H^8 5.79 (dd, 7.5, 1.2)	C^8 124.0 (ddddd, 161.5, 8.9, 2.1, 1.3)

[a]For atom numbering, see Scheme 1.

doublet under selective decoupling with H^8, but a singlet under selective decoupling with H^5, thus proving the empirical assignment given in [3]. Table 3 provides also the complete assignment of the ^{1}H and ^{13}C NMR spectra of **1s** based on double resonance, COLOC, and off-resonance techniques.

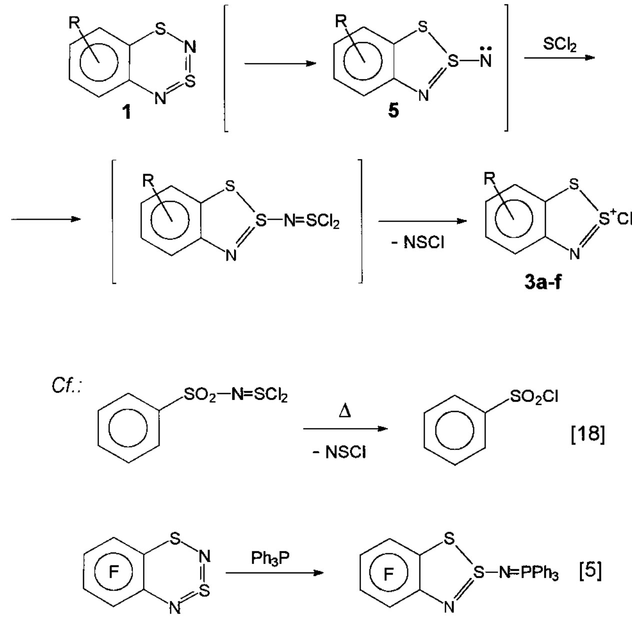
The long-wave absorption maxima in the UV–vis spectra of the title compounds are found in the range of ~610–635 nm (cf. [3]), again with weak dependence upon the position and character of the substituent R (for details, see Table 6).

Cyclic By-Products

The Herz salts **3**, are cyclic by-products. Special preparative experiments as well as ^{14}N NMR identification of thiazyl chloride NSCl in the reaction mixtures suggest that it is possible to explain the formation of **3** by further reaction of **1** with SCl_2 (Scheme 4). One can postulate singlet 1,2,3-benzodithiazol-2-ylnitrene (**5**, an isomer of **1**) to be the key intermediate of the reaction of **1** with SCl_2. Then, the reaction seems to be an oxidative imination of SCl_2 with **5** followed by an elimination of NSCl from the product to give the final salt **3** (Scheme 4) [17]. Previously, similar elimination of NSCl has been observed during thermal decomposition of $PhSO_2N{=}SCl_2$ [18] (Scheme 4). It follows from control experiments that NSCl (taken as its trimer) also reacts with **1** to give Herz salts.

A thermodynamic gain of transformation of an antiaromatic system into an aromatic system seems to be a driving force of the reaction of **1** with SCl_2. With planar geometry [19] and 10π-electrons, the cations of **3** possess aromaticity, although reduced as compared with the symmetric isomer **4** [20,21a].

Previously described 1:1 addition of **1** to PPh_3 that afforded a derivative of (1,2,3-benzodithiazol-2-yl)iminophosphorane (Scheme 4) [5] can also be interpreted as an oxidative imination of the phosphine with nitrene **5**. Thus, the reactions of **1** with formal both an electrophile (SCl_2) and a nucleophile (PPh_3)



SCHEME 4 Salts **3**: R = H **(a)**, 4-OCH_3 **(b)**, 6-OCH_3 **(c)**, 5-Br **(d)**, 5-CH_3 -6-Cl **(e)**, 5-I **(f)**

probably proceed in a similar way. Formation of 1,2,3-benzodithiazolyls by thermolysis of **1** [1] is very likely mediated by **5** as well [17a].

Me_3SiCl is inert toward **1** under conditions of the cyclization, in contrast to its reaction with the related 1,3,5,2,4-benzotrithiadiazepine, leading to 1,3,2-benzodithiazolium chloride (**4**) [23], isomeric with **3a**.

A Model for the Cyclization Intermediate

Compound 4-FC_6H_4–N=S=N–S–NH–C_6H_4F-4 (6), actually isolated from a reaction of 4-FC_6H_4–N=S=N–$SiMe_3$ (**2m**) with salt **3a**, can formally be considered as a [4-FC_6H_4–N=S=N–S–Cl] intermediate in the synthesis of **1q** (Scheme 3), trapped by the parent amine 4-$FC_6H_4NH_2$. According to the data of X-ray crystallography (Figure 4), in the crystal this model compound adopts the *E,Z* configuration (cf. *Z,E* configuration of Ar–N=S=N–$SiMe_3$ **2p**, Figure 1). As the cyclization requires a *Z,Z* configuration, one can conclude that the model belongs to the early stages of the process. The compound **6** features considerable nonplanarity. The molecule consists of three planar fragments: ring C1-C6 (A plane, standard deviation 0.005 Å), chain NSNSN (B plane, standard deviation 0.74 Å), and ring C7-C12 (C plane, standard deviation 0.003 Å) with dihedral angles A-B, B-C, and A-C of 101.4°, 30.7° and 71.6°, respectively. The bond lengths and bond angles of

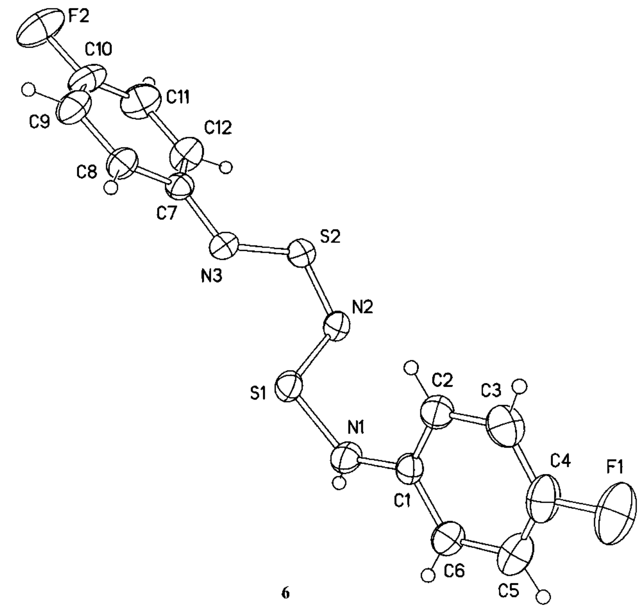


FIGURE 4 Structure of molecule **6** in the crystal. Selected bond lengths (Å) and bond bond angles (°): N^1S^1 1.639(4); S^1N^2 1.690(3); N^2S^2 1.549(3); S^2N^3 1.551(3); C^1N^1 1.402(5); C^7N^3 1.415(4); $C^1N^1S^1$ 125.2(3); $N^1S^1N^2$ 101.2(2); $S^1N^2S^2$ 118.5(2); $N^2S^2N^3$ 110.0(2); $S^2N^3C^7$ 119.4(3).

the sulfur-nitrogen fragment of **6** are typical (cf. the nearest analog Ph—N=S=N—S—Ph [24]).

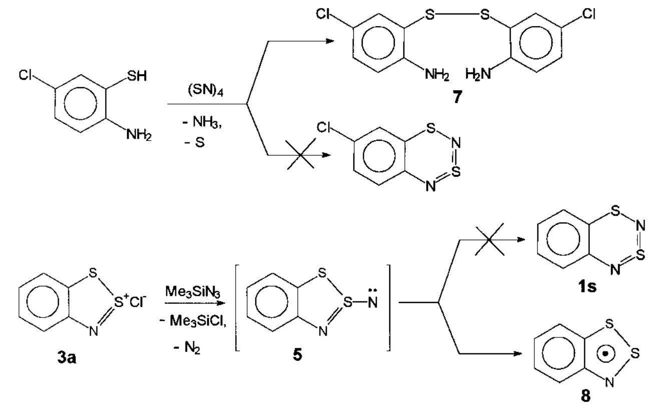
Attempted Approaches to the Ring Closure

An attempt was made to synthesize **1** by reaction of 2-aminobenzenethiols with $(SN)_4$ as a source of the sulfur-nitrogen fragment necessary to the ring closure. However, the reaction proceeded only as oxidation of the thiol to the corresponding disulfide (Scheme 5).

Another approach tried was based on the reaction of a Herz salt **3** with Me_3SiN_3. It was believed that the reaction will lead via the corresponding covalent azide to a singlet nitrene **5** capable of isomerization into a compound **1** (cf. singlet nitrenes Ar—N: [25] and Ar—S—N: [26,27]). However, only persistent 1,2,3-benzodithiazolyl radicals **8** [1] were identified as reaction products (Scheme 5; cf. [27]). It should be noted that formation of a Herz-type ionic azide is also possible in this system followed by a redox process directly leading to an **8** radical [21b].

EXPERIMENTAL

The ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were measured on a Bruker DRX-500 spectrometer at frequencies of 500.13, 125.76, 36.13, and 50.68 MHz,



SCHEME 5

respectively, with standards tetramethylsilane (TMS) and NH_3 (liq.); the ^{19}F NMR spectra were taken on a Bruker AC-200 machine at a frequency of 188.28 MHz with C_6F_6 as the standard. The mass spectra (EI, 70 eV) were collected on a Finnigan MAT MS-8200 instrument, and the UV–vis spectra were recorded on Specord M40 and HP 8453 spectrophotometers.

The X-ray structure determinations (Table 4) were carried out on a Syntex $P2_1$ diffractometer using Cu Kα radiation (compounds **1k,r, 6**) and on a Bruker P4 diffractometer using Mo Kα radiation (compounds **1i,j,l, 2p**), with a graphite monochromator. Corrections for absorption by crystal habit were used for **1i-l** and **6**. The structures were solved by direct methods using the SHELX-86 (**1j,k,r, 6**), SHELXS-97 (**2p**), and XS-SHELXTL (**1i,l**) programs and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation using the SHELXL-93 and SHELXL-97 (**1j,k,l,r,2p, 6**) and XL-SHELXTL (**1i**) programs. Hydrogen atoms were located on difference Fourier maps (**1j,l,r, 2p**) or geometrically (**1i,k, 6**).

The ESR spectra were recorded on a Bruker EMX spectrometer (MW power, 0.64 mW; modulation frequency, 100 KHz; modulation amplitude, 0.1 G).

The RHF/6-31G*, MP2/6-31G*, MP2/6-31G**, and the PM3 calculations were performed using the GAMESS program [28] and the MNDO-92 program [29], respectively.

Compounds **1s** [6], **2f,m,n** [3,9], **3a–c** [12], and 7 [30] were known previously.

The syntheses described subsequently were performed in an argon atmosphere in absolute solvents with stirring. The reagents were added dropwise, and the solvents were distilled off at reduced pressure. Tables 5 and 6 list the physical and analytical data for the compounds synthesized.

TABLE 4 Crystal and Refinement Data of Compounds **1i–1r**, **2p**, and **6**[a]

	1i	**1j**	**1k**	
Formula	$C_6H_3BrN_2S_2$	$C_6H_3BrN_2S_2$	$C_6H_3BrN_2S_2$	
M	247.13	247.13	247.13	
Crystal system	Orthorhombic	Triclinic	Triclinic	
Space group	*Fdd*2	P-1	P-1	
a (Å)	13.094(2)	3.9933(5)	6.067(2)	
b (Å)	31.286(5)	10.903(1)	7.444(2)	
c (Å)	7.741(1)	18.428(2)	8.784(2)	
α (°)		97.532(7)	85.00(2)	
β (°)		91.743(9)	84.42(2)	
γ (°)		95.351(8)	86.84(2)	
V (A^3)	3171.1(8)	791.21(15)	392.9(2)	
Z	16	4	2	
D_c (g cm^{-3})	2.071	2.075	2.089	
μ (mm^{-1})	5.638	5.649	11.518	
F (000)	1920	480	240	
Crystal size (mm)	0.09 × 0.50 × 0.90	0.01 × 0.14 × 1.7	0.09 × 0.40 × 1.20	
Scan mode	θ–2θ	θ–2θ	θ–2θ	
2θ range (°)	<55	<50	<140	
Reflections measured	1103	2587	1490	
Observed $F_0 > 4\sigma_F$	1016	2075	1381	
Transmission	0.13–0.60	0.47–0.84	0.04–0.38	
R (observed)	0.0346	0.0340	0.0405	
wR_2 (all data)	0.0957	0.0884	0.1134	
Goodness of fit	1.064	1.038	1.093	
	1l	**1r**	**2p**	**6**
Formula	$C_6H_3BrN_2S_2$	$C_7H_6N_2OS_2$	$C_{15}H_{17}IN_2SSi$	$C_{12}H_9F_2N_3S_2$
M	247.13	198.26	412.36	297.34
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$
a (Å)	13.6916(17)	6.052(1)	6.2520(4)	12.463(3)
b (Å)	3.9952(4)	10.554(2)	11.8804(8)	4.652(1)
c (Å)	14.393(2)	12.938(2)	12.2049(7)	23.276(6)
α (°)			96.821(5)	
β (°)	95.79(1)	97.49(2)	101.336(5)	102.86(2)
γ (°)			93.620(5)	
V (A^3)	783.28(16)	819.3(2)	879.1(1)	1315.6(5)
Z	4	4	2	4
D_c (g cm^{-3})	2.096	1.607	1.558	1.501
μ (mm^{-1})	5.709	5.479	2.001	3.812
F (000)	480	408	402	608
Crystal size (mm)	0.025 × 0.4× 0.84	0.12 × 0.17 × 1.40	0.06 × 0.47 × 1.30	0.12 × 0.16 × 1.60
Scan mode	θ–2θ	θ–2θ	θ–2θ	
2θ range (°)	<50	<130	<50	<140
Reflections measured	1340	1390	3079	2328
Observed $F_0 > 4\sigma_F$	1101	1086	2595	1436
Transmission	0.19–0.89		0.39–0.85	0.38–0.70
R (observed)	0.0391	0.0476	0.0334	0.0542
wR_2 (all data)	0.1045	0.1277	0.0957	0.1395
Goodness of fit	1.084	1.110	1.057	1.020

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

TABLE 5 Characterization of the Compounds

Compound	*m.p. (°C), b.p. (°C/mm)*	*Yield (%)*	*Formula*	*MS M⁺ (m/z) Measured (calculated, ³⁵Cl, ⁷⁹Br)*
1i	103–105	18	$C_6H_3BrN_2S_2$	245.8925 (245.8922)
1j	92–93	15	$C_6H_3BrN_2S_2$	245.8925 (245.8922)
1k	118–120	3	$C_6H_3BrN_2S_2$	245.8932 (245.8922)
1l	95–97	3	$C_6H_3BrN_2S_2$	245.8922 (245.8922)
1n	130–130.5	1	$C_6H_3IN_2S_2$	293.8780 (293.8784)
1o	137–138	1	$C_6H_3IN_2S_2$	293.8786 (293.8784)
1p	124–126	8	$C_6H_3IN_2S_2$	293.8771 (293.8784)
1q	88–89	3	$C_6H_3FN_2S_2$	185.9720 (185.9722)
1r	109–110	18	$C_7H_6N_2OS_2$	197.9920 (197.9922)
1t	152–153	10	$C_6H_2Br_2N_2S_2^a$	323.8032 (323.8027)
1u	108–110	2	$C_{12}H_7IN_2S_2$	369.9096 (369.9097)
2b	105–107/1	37	$C_{11}H_{19}N_3SSi$	253.1077 (253.1069)
2d	105–107/1	67	$C_9H_{13}N_3O_2SSi$	255.0494 (255.0498)
2f	144–145/1, 52-53	54	$C_9H_{13}N_3O_2SSi$	255.0507 (255.0498)
2g	126–128/1	62	$C_9H_{13}BrN_2SSi$	287.9723 (287.9753)
2h	124–126/1	60	$C_9H_{13}BrN_2SSi$	287.9761 (287.9753)
2i	28–29,125–126/3	48	$C_9H_{13}BrN_2SSi$	287.9731 (287.9753)
2j	141–143/1	30	$C_9H_{13}IN_2SSi$	335.9618 (335.9615)
2k	134–135/1	65	$C_9H_{13}IN_2SSi$	335.9618 (335.9615)
2l	121–123/0.4	20	$C_9H_{13}IN_2SSi$	335.9621 (335.9615)
2o	125–126/1	60	$C_9H_{12}Br_2N_2SSi$	366 (366)
2p	75–76	17	$C_{15}H_{17}IN_2SSi$	411.9926 (411.9928)
3a	194–196 (dec.)	54	$C_6H_4ClNS_2$	153.9775 (153.9785)[b]
3b	154–158 (dec.)	74	$C_7H_6ClNOS_2$	183.9887 (183.9891)[b]
3c	170–174 (dec.)	79	$C_7H_6ClNOS_2$	183.9896 (183.9891)[b]
3d	193–197 (dec.)	60	$C_6H_3BrClNS_2$	231.8874 (231.8891)[b]
3e	185–190 (dec.)	58	$C_7H_3Cl_2NS_2$	201.9512 (201.9552)[b]
3f	180–185 (dec.)	54	$C_6H_3ClIN_2S$	279.8750 (279.8754)[b]
6	126–127		$C_{12}H_9F_2N_3S_2$	297.0221 (297.0221)

TABLE 5 (***Continued***) Characterization of the Compounds

Compound	*m.p. (°C), b.p. (°C/mm)*	*Yield (%)*	*Formula*	*MS M⁺ (m/z) Measured (calculated, ³⁵Cl, ⁷⁹Br)*
7	109–110[c]	82	$C_{12}H_{10}Cl_2N_2S_2$	315.9665 (315.9662)
10a	107–108/1	47	$C_8H_{10}N_2OS$	182.0510 (182.0514)
10b	55–56	95	$C_6H_3Br_2NOS$	294.8303 (294.8308)
10c	131–132	90	$C_{12}H_8INSO$	340.9372 (340.9373)
10d	120–122/4	92	$C_8H_{10}N_2OS$	182.0514 (182.0514)

[a]Elemental analysis, found (calculated), %: **1t:** C, 22.21 (22.09); H, 0.51 (0.61); Br, 48.90 (49.08); N, 8.47 (8.59); S, 19.86 (19.63).
[b]($M^+ -$ Cl) peak.
[c]Corresponds to Ref. [30].

*1-Aryl-3-trimethylsilyl-1,3-diaza-2-thiaallenes (**2b,d,f,g–k,o,p**)*

A solution of 0.06 mol of the corresponding ArNSO in 25 mL of hexane was added to a suspension of 10.0 g (0.06 mol) of $LiN(SiMe_3)_2$ in 50 mL of hexane at −30°C. During 2 hours, the temperature was raised to 20°C, and 6.6 g (0.06 mol) of Me_3SiCl in 10 mL of hexane was added. The precipitate was filtered off, the solvent was distilled off, and the residue (except for **2p**) was distilled in vacuum. Compounds **2b,g–k,o** were obtained as orange oils (2i solidified to orange-yellow crystals upon standing), and 2p was obtained as yellow crystals (from hexane). With Ar $=$ 2-$Me_2NC_6H_4$, 4-$Me_2NC_6H_4$, only $ArNHSiMe_3$ (45 and 60%, respectively) and $(ArN=)_2S$ were isolated. With Ar = 3-$O_2NC_6H_4$, in both hexane and Et_2O (see [3,9]) only the corresponding $(ArN=)_2S$ [31] was obtained in high yield. For previously described 3-$CF_3C_6H_4NSNSiMe_3$, the yield in hexane was 82% compared to 30% in Et_2O [3].

To a suspension of 4.01 g (0.024 mol) of $LiN(SiMe_3)_2$ in 50 mL of Et_2O at −60°C, 5.73 g (0.024 mol) of n-$O_2NC_6H_4N{=}SCl_2$ (n = 2–4) [32] was added in small portions during 15 minutes. During 2 hours, the temperature was raised to 20°C, the precipitate was filtered off, and the residue distilled in vacuum. With n = 2, 4, compounds **2d,f** were isolated as yellow oils (**2f** solidified upon standing). With n = 3, a mixture of $ArNSNSiMe_3$ (**2e**) and $ArNHSiMe_3$ along with $(ArN=)_2S$ was obtained.

TABLE 6 Spectral Data of the Compounds

	NMR[a] δ			
Compound	^{1}H	^{13}C	^{15}N (J, Hz)	UV/Vis[b] λ_{max} (nm) (log ε)
1i	6.85, 6.59, 5.69	137.1, 134.8, 133.3, 122.9, 119.5, 117.6	276.9 (s), 256.4 (s)	635 (2.67), 391 (3.18), 303 (4.18), 296 (4.18)
1j	6.92, 6.06, 5.66	139.4, 135.3, 125.9, 125.0, 123.4, 114.4	273.0 (s), 259.4 (d, 2.3)	633 (2.57), 377 (3.02), 290 (4.33)
1k	6.73, 5.92, 5.75	137.5, 133.0, 126.7, 125.7, 124.1, 117.2	266.2 (s), 260.3 (d, 2.4)	629 (2.52), 376 (2.92), 365 (2.93), 298 (4.06), 290 (4.66)
1l	6.78, 6.39, 5.69	139.6, 136.1, 130.9, 122.0, 119.6, 116.9	264.7 (s), 252.3 (d, 2.8)	624 (2.65), 386 (3.16), 298 (4.20)
1n	7.14, 6.24, 5.53	141.5, 139.0, 131.2, 125.2, 115.4, 94.2	272.3 (s), 259.2 (d)	629 (2.37), 379 (3.01), 289 (4.25)
1o	6.98, 6.10, 5.61	139.5, 138.3, 132.2, 124.3, 117.0, 96.7	264[d]	626 (2.66), 402 (3.09, sh), 379 (3.23), 291 (4.20)
1p	7.02, 6.27, 5.72	142.1, 140.6, 131.6, 122.9, 120.0, 95.2	269.2 (s), 254.7 (d)	624 (2.61), 393 (3.11), 288 (3.99)
1q[c]	6.25, 5.90, 5.59	165.2, 134.5, 124.6, 117.5, 115.4, 112.3	260.7 (s), 256.5 (s)	608 (2.63), 296 (4.24), 288 (4.23)
1r	6.06, 5.89, 5.41, 3.63	163.4, 131.8, 124.6, 116.5, 112.0, 111.5, 55.3	263.4 (d, 2.5), 249.1 (s)	626 (2.84), 378 (3.39), 357 (3.09), 303 (4.23)
1t	6.90, 5.77	140.7, 137.6, 125.2, 123.4, 119.7, 116.7	270[d], 251[d]	632 (2.38), 390 (2.82), 303 (4.01), 294 (4.00)
1u	7.60, 7.00, 6.68, 5.86, 5.83			626 (2.77), ∼380 (3.38, sh), 311 (4.35)
2b	7.07, 6.91, 6.48, 2.90, 0.21			401 (3.40, sh), 342 (3.97), 281 (3.97), 248 (4.12)
2d	7.91, 7.55, 7.36, 7.23, 0.16			344 (3.75), 266 (4.05)
2g	7.69, 7.63, 7.34, 6.88, 0.27			351 (3.47), 270 (3.53), 267 (3.56)
2h	7.80, 7.48, 7.23, 7.12, 0.22			342 (3.67), 245 (3.59)
2i	7.85, 7.34, 0.37			352 (3.94)
2j	7.84, 7.34, 7.23, 6.79, 0.16			350 (3.15), 263 (3.54), 257 (3.56)
2k	7.98, 7.51, 7.44, 6.99, 0.22			342 (3.74), 255 (3.51), 225 (3.82)
2l	7.58, 7.42, 0.24			358 (3.57), 245 (3.44)
2o	7.78, 7.51, 0.30			340 (3.78)
2p	7.84, 7.77, 7.54, 7.35, 0.34			367 (4.28), 270 (4.22)
3a[c]	9.09, 9.00, 8.65, 8.46[f]	164.0, 156.2, 139.1, 133.9, 128.1, 123.4	406[d]	426 (3.25), 347 (4.38)[g]
3b	8.60, 8.39, 7.62, 4.42	159.8, 158.1, 157.8, 145.6, 115.7, 111.8, 58.1	378[d]	551 (3.54), 344 (4.05)
3c	8.79, 8.29, 7.76, 4.39[f]	173.5, 163.9, 161.8, 131.9, 130.8, 105.2, 59.7	389[d]	439 (3.87), 368 (3.77)
3d	9.22, 8.84, 8.61	166.3, 156.7, 143.6, 131.7, 131.3, 125.0	406[d]	
3e	8.99, 8.90, 2.95	165.5, 157.2, 154.9, 148.6, 129.8, 125.3, 21.6	400[d]	440 (3.43, sh), 378 (4.21)
3f	9.49, 8.77, 8.72	167.2, 158.3, 149.7, 139.2, 125.9, 103.1	401.7 (d, 1.4)	
6[c]	7.04–6.98, 5.79	160.6, 158.7, 142.0, 140.6, 116.0, 115.8	298[d,h]	414 (4.00)

TABLE 6 (***Continued***) Spectral Data of the Compounds

Compound	NMR[a] δ ^1H	^{13}C	^{15}N (J, Hz)	UV/Vis[b] λ_{max} (nm) (log ε)
7	7.12–7.04, 6.55, 4.21			
10a	7.14–7.09, 6.62, 2.90			436 (3.20)
10b	7.90, 7.68			313 (3.70)
10c	7.93, 7.78, 7.59, 7.33			354 (4.32)
10d	8.35, 7.10, 6.75, 6.70, 2.87			392 (2.00)

[a]In $CDCl_3$; **7, 10a, b**, CCl_4; **3a–d**, CF_3COOH; **2d**, neat liquid.
[b]In $CHCl_3$; **2b,d,g–i, o, 6, 10c**, heptane; **3a–f,** CF_3COOH.
[c]δ^{19}F: **1q,** 55.5; **6,** 45.1, 39.9.
[d]^{14}N
[e]cf. 1,3,2-benzodithiazolium chloride (**4**) [23]: δ^1H: 9.09, 8.22; δ^{13}C: 163.3, 132.6, 122.8; δ^{14}N: 378; λ_{max} (log ε) 398 (3.38).
[f]cf. Ref. [45]
[g]cf. Ref. [46]
[h]Unresolved asymmetric broad line.

*Substituted 1,3,2,4-Benzodithiadiazines (**1i-l,n–r,t,u**)*

Solutions of 0.01 mol of Ar—N=S=N—$SiMe_3$ (**2**, this work and [3]) and 0.51 g (0.5 mol) of SCl_2 (0.0075 mol in the case of **2g,h,k**), each in 30 mL of CH_2Cl_2, were mixed by adding them to 300 mL of CH_2Cl_2 at 20°C, over a period of 1 hour. After an additional 1 hour, the reaction mixture was filtered, the solvent was distilled off, and the residue was sublimed in vacuum and recrystallized from hexane. Compounds **1j,l,o,q,r,u** were obtained as black crystals, **1i,k** were obtained as shiny black-green prisms, and **1t** was obtained as lustrous dark-green crystals.

A mother liquor from recrystallization of **1j** was evaporated to dryness. The residue (which consisted of a mixture of ~60% of **1l** and ~40% of **1j** according to the ^{1}H NMR data) was treated with an amount of SCl_2 equimolar to **1j** under conditions described below (Reactions of compounds **1** with SCl_2). Compound **1l** was isolated as black crystals.

The compounds **1n,p** (38%) were obtained by sublimation of reaction residue as a 3:2 mixture (^{1}H NMR). Fractional crystallization from hexane afforded pure **1n** as black needles. A sample of pure **1p** was prepared by reaction of the **1n,p** mixture with SCl_2 (see below Reactions of compounds **1** with SCl_2).

*1,3,2,4-Benzodithiadiazine (**1s**)*

Under the conditions described previously, compound **1s** [6] was obtained from **2j** in 9% yield.

*Reactions of Compounds **1** with SCl_2. 1,2,3-Benzodithiazolium Chloride (**3a**) and Its 4-Methoxy- (**3b**), 6-Methoxy- (**3c**), 5-Bromo- (**3d**), 5-Methyl-6-chloro- (**3e**), and 5-Iodo (**3f**) Derivatives, and ^{14}N NMR Detection of Thiazyl Chloride NSCl*

At 20°C, a solution of 0.003 mol of the corresponding **1** (this work and [3]) in 10 mL of CH_2Cl_2 was added during 45 minutes to a solution of 0.31 g (0.003 mol) of SCl_2 in 10 mL of the same solvent. After 15 minutes, the precipitate was filtered off, dried in vacuum, and, in the case of **3a–c**, recrystallized from $SOCl_2$:CCl_4 (3:1). Salts **3a–e** [12] were obtained as crystalline solids (in the case of **3e,d** chlorination of a carbocycle occurred during reaction or recrystallization, respectively).

To detect NSCl, the interaction was performed in CCl_4 with more concentrated (~0.6 M) solutions, and the ^{14}N NMR spectrum of the reaction mixture was measured periodically during the reaction. The ^{14}N NMR identification of NSCl (δ^{14}N: 730) was based on previously reported data [33] and on control measurements with an authentic sample prepared [33] by heating a solution of $(NSCl)_3$ [34] in CCl_4. At the same time, $(NSCl)_3$ [33,35] was not found in the reaction mixtures in accordance with the conclusion that trimerization of NSCl is very ki-netically hindered [33].

At 20°C, to a solution of 0.247 g (0.001 mol) of a 1:1 mixture of 6-Br (**1j**) and 8-Br (**1l**) derivatives of **1** in 5 mL of CH_2Cl_2 was added during 15 minutes to a solution of 0.051 g (0.0005 mol) of SCl_2 in 5 mL of the same solvent. The precipitate was filtered off. Salt **3d** (0.081 g; 60%) was obtained as a yellow powder. Its purity was checked by ^{1}H NMR spectroscopy. No traces of the 7-Br isomer have been found. The filtered solution was evaporated to dryness, and the residue was sublimed in vacuum. A 10:1 (^{1}H NMR) mixture (0.121 g) of **1l** and **1j** was obtained. Recrystallization from hexane gave pure **1l** (0.060 g).

In a similar way, **3f** (light brown powder) and **1p** (black crystals) were prepared from the 3:2 mixture of **1n** and **1p**.

Reaction of 5,6,7,8-tetrafluoro-1,3,2,4-benzodithiadiazine [15] with SCl_2 provided only unidentified products without any evidence of the formation of the polyfluorinated analog of **3a**.

*Reaction of 1,3,2,4-Benzodithiadiazine (**1s**) with $(NSCl)_3$ and Cl_2*

At 20°C, to a solution of 0.17 g (0.0007 mol) of $(NSCl)_3$ [34] in 2 mL of CCl_4 was added a solution of 0.34 g (0.002 mol) of **1s** [6] in 2 mL of the same solvent. The crude salt **3a** (0.38 g; 80%) was obtained as a brown precipitate.

At 20°C, an excess of Cl_2 was passed through a solution of 0.34 g (0.002 mol) of **1s** in 10 mL of CCl_4. A slightly exothermic fast reaction afforded a complex mixture (^{1}H NMR, MS) of unidentified products.

*Attempted Preparation of **1** from 2-Aminobenzenethiols*

*Reaction of 5-Chloro-2-aminobenzenethiol (**9**) with $(SN)_4$* A mixture of 0.80 g (0.005 mol) of **9** [30], 0.46 g (0.0025 mol) of $(SN)_4$ (see below), and 50 mL of MeCN was boiled until NH_3 evolution ceased (~1 hour). The mixture was filtered, the solvent was distilled off, and the residue was recrystallized from toluene. Compound **7** was obtained as yellow crystals.

*Attempted Preparation of **1** from Herz Salts*

*Reaction of 1,2,3-Benzodithiazolium Chloride (**3a**) with Trimethylsilyl Azide, and ESR Detection of 1,2,3-benzodithiazolyl (**8**)* A mixture of 0.115 mg (10^{-6} mol) of Me_3SiN_3 [36], 0.190 mg (10^{-6} mol) of **3a**, and 1 mL of hexane, outgassed by three freeze-pump-thaw cycles, was heated in an ESR valve-equipped quartz capillary tube to 50°C. The ESR spectrum of the solution was identical to that of **8** [1]. Experiments on a preparative scale (in both hexane and MeCN) were accompanied by gas evolution and, after usual work-up, gave unidentified red tar. Similar results were obtained with salts **3b,c**.

Cyclotetra(azathiene) $(SN)_4$

At 20°C, solutions of 4.12 g (0.02 mol) of $(Me_3SiN{=})_2S$ [37] and 2.06 g (0.02 mol) of SCl_2, each in 30 mL of CH_2Cl_2, were mixed by adding them to 100 mL of CH_2Cl_2 over a period of 1 hour. After an additional 2 hours, the mixture was filtered, the solvent was distilled off, and the residue was recrystallized from toluene. $(SN)_4$ [38] (1.57 g; 85%) was obtained as orange-yellow needles, m.p. (decomposition) 185–186°C (cf. [38]).

*Reaction of 1-(4-fluorophenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallene (**2m**) with 1,2,3-benzodithiazolium chloride (**3a**)*

At 20°C, to a suspension of 0.40 g (0.0021 mol) of **3a** (this work and Ref. [12]) in 5 mL of CH_2Cl_2 was added, during 20 minutes, a solution of 0.48 g (0.0021 mol) of **2m** [3] in 5 mL of the same solvent. The mixture was stirred overnight, the solution was filtered off, the solvent was distilled off, and the residue was recrystallized twice from hexane. Compound **6** was obtained in 0.01 g yield as small orange needles.

N-Sulfinylanilines. RC_6H_4NSO (**10**) was prepared by the Michaelis reaction [39] from the corresponding amines and $SOCl_2$ [40] except for the Me_2N-substituted derivatives synthesized from $ArNH_2$ and $PhSO_2$ NSO [40] or $ArNH_2$ and dipyrid-2-yl sulfite [47]. Most compounds were known earlier [40], except for those in which R = 3-Me_2N (**10a**, dark red oil), 3,5-Br_2 (**10b**, pale yellow crystals), 4-(4′-IC_6H_4) (**10c**, bright yellow crystals) and 2-Me_2N (**10d**, dark red oil) derivatives.

4-Iodo-4′-aminobiphenyl [41]. 70%, Colorless plates, m.p. 165–165.5°C (hexane/toluene) for preparation of **10c** was obtained by $SnCl_2$/HCl reduction of 4-iodo-4′-nitrobiphenyl synthesized in one step from biphenyl under the Tronov–Novikov conditions [42] by a known procedure [43] [37%, colorless crystals, m.p. 217–218°C (toluene) (212°C [43])]. Both compounds were purified by column chromatography on silica followed by recrystallization. Warning: the compounds needed to be treated with caution because they are potential carcinogens [44].

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