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A Brave New World: The Heteroatom Chemistry of 1,3,2,4-Benzodithiadiazines and Related Compounds

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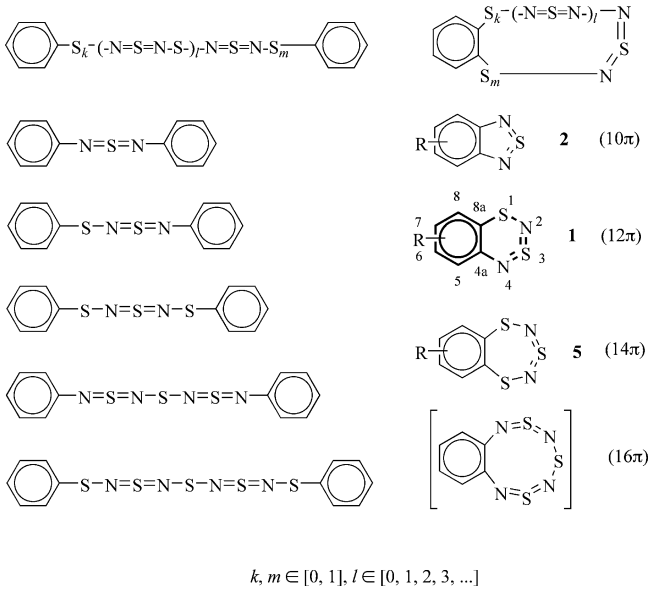
This review highlights the most important advances in the heteroatom chemistry of 1,3,2,4-benzodithiadiazines (π-excessive and formally antiaromatic heterocycles), covering methods for synthesis, nontrivial features of the molecular and π-electronic structure, spectral properties, and reactivity, in particular the transformations into persistent π-radicals. The chemistry of 1,3,2,4-benzodithiadiazines is compared to that of related chalcogen–nitrogen compounds, both cyclic and acyclic.

1. Introduction

In recent years the chemistry of chalcogen–nitrogen compounds has received much attention because of its fundamental and practical significance.[1] It plays an essential role in the design and synthesis of molecular materials, in particular conducting, superconducting, and magnetic materials.[2–8] The molecular structures of chalcogen–nitrogen compounds are extremely diverse and continue to present a serious challenge to chemical theory in general.[1,9] Their chemical reactivity is also far from being well-understood.

Amongst chalcogen–nitrogen compounds, derivatives composed of alternating sulfur and nitrogen atoms connected by multiple bonds (sulfur–nitrogen or SN compounds) are of special interest. With aromatic terminal groups, they form an extensive set of chemical systems containing two topologically nonequivalent subsets – unsaturated chains and unsaturated cycles (Scheme 1). All these SN compounds are π-excessive, since the number of π-electrons exceeds the number of atomic centers of a molecule as a result of the presence of two π-electrons at each S atom. Within a simple MO model, antibonding π*-levels would be occupied in the molecular ground state. Therefore, the resulting thermodynamic destabilization is expected to lead, in particular, to structural diversity and high and varied chemical reactivity.



$k, m \in [0, 1], l \in [0, 1, 2, 3, ...]$

Scheme 1.

The compounds of the first subset (Scheme 1), in particular the extended chains, are analogues of polymeric sulfur nitride $(SN)_x$, a molecular metal and low-temperature superconductor.[7] With planar molecular conformations, they are π-delocalized and have possible applications as molecular wires in the field of molecular electronics.[10] Amongst them are compounds featuring –N=S=N–,[11] –S–N=S=N–,[12] –S–N=S=N–S–,[12c,13] –N=S=N–S–N=S=

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N–,[10c,12a] –S–N=S=N–S–N=S=N–,[14] and –S–N=S=N–S–N=S=N–S–[12c,15] chains, which have been synthesized and structurally characterized by XRD.

In some cases, Se^{II} (–Se–N=S=N–Se–[13ab,16] and –N=S=N–Se–N=S=N–[17]), Se^{IV} (–N=Se=N–),[18] and Te^{IV} (–N=Te=N–)[19] derivatives have also been prepared. Unlike monomeric –N=S=N– and –N=Se=N– compounds, their tellurium congeners are dimeric in the solid state.

In addition to neutral SN chains, positively charged derivatives, e.g. $[ArSNSNSNSAr]^+[X]^-$, have been synthesized and structurally defined by XRD.[12c,20]

The compounds of the second subset (Scheme 1) form a unique consecutive series of alternating $4n+2$ aromatic[21] and $4n$ antiaromatic[21] polyheteroatom π-systems. Known derivatives comprise 2,1,3-benzothiadiazoles with 10 π-electrons,[22] 1,3,2,4-benzodithiadiazines with 12 π-electrons (this review), and 1,3,5,2,4-benzotrithiadiazepines with 14 π-electrons.[23] Higher congeners with 16, 18, 20, etc. π-electrons are still unknown. Their existence under normal conditions is seemingly "allowed", in any case in the context of both the stability and the flexibility of the corresponding –N=S=N–S–N=S=N–, –S–N=S=N–S–N=S=N–, and –S–N=S=N–S–N=S=N–S– fragments (see above).

For 2,1,3-benzothiadiazoles, both Se[24] and Te[19b,25] analogues are known, and their supramolecular chemistry received much attention recently.[25a,25b]

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Amongst the discussed heterocycles, 12-π-electron 1,3,2,4-benzodithiadizines (**1**) (Scheme 1)[26] are the most interesting, since they combine formal features of antiaromaticity with moderate thermal stability. Like their π-excess, their antiaromaticity (even if it is obviously weakened by the first-order heteroatom perturbation in the case of **1**) is a destabilizing factor. Indeed, the heteroatom reactivity of **1** is high and varied, and a number of new reactions are found in which this reactivity takes on different forms. Additionally, a number of new structures are observed amongst the reaction products of **1**.

This review deals with the methods for synthesis, the molecular and π-electronic structure, the spectral properties, and the heteroatom reactivity of compounds **1** in the hydrocarbon (h) and fluorocarbon (f) series. Throughout the review, the notation **1h** and **1f** is used for the parent compound **1** and its tetrafluoro derivative, respectively; this notation is also used for the other classes of compounds that are discussed. Where reasonable, the chemistry of compounds **1** is considered within the broader context of related SN derivatives, both cyclic and acyclic, most importantly 2,1,3-benzothiadiazoles and 1,3,5,2,4-benzotrithiadiazepines.

It should be noted that monocyclic 1,3,2,4-dithiadiazine with 8 π-electrons is still unknown, whereas structure of its 5,6-diphenyl derivative[27] was assigned mistakenly – actually, isomeric 3,5-diphenyl-1,4,2,6-dithiadiazine was obtained.[28]

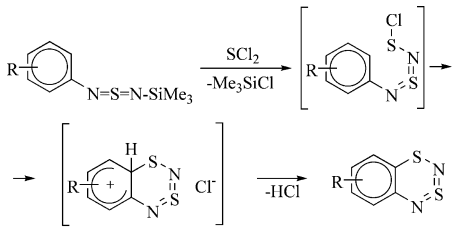
2. Synthesis

There are two preparative approaches to compounds **1**, one for the hydrocarbon and one for the fluorocarbon series, based on electrophilic and nucleophilic ring-closure reactions, respectively. Importantly, these approaches can also be adapted to syntheses of other SN compounds, both cyclic and acyclic.

2.1 Electrophilic Cyclization

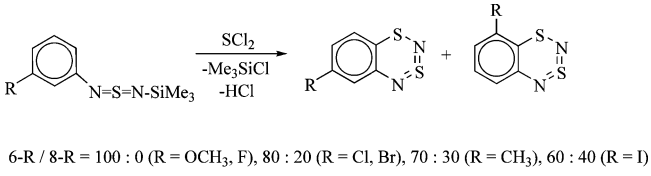
Cyclization

The pioneering preparation of **1h** by Oakley et al. exploited the 1:1 condensation of Ar–N=S=N–$SiMe_3$ with SCl_2, followed by the electrophilic *ortho*-cyclization of the [Ar–N=S=N–S–Cl] intermediates (Ar = Ph).[23c,23d] Later it was found that the method performs well not only for **1h** but also for its 5-R, 6-R, 7-R, and, with some restrictions, 8-R monosubstituted derivatives, as well as for di- and trisubstituted derivatives, in particular fluorine-containing ones (Scheme 2).[29] Isolated yields of the target compounds vary from 56% (for the 6-fluoro derivative) to 1% (for the 7-iodo derivative); for **1h**, the yield is 33%.[23c,29] Interestingly, the introduction of up to three fluorine atoms on the aromatic ring of Ar–N=S=N–$SiMe_3$ does not deactivate the ring towards electrophilic cyclization.[29b] With precursors containing NMe_2 and NO_2 substituents on Ar groups, the products of the ring-closure reaction were not observed.[29c,29d]



Scheme 2.

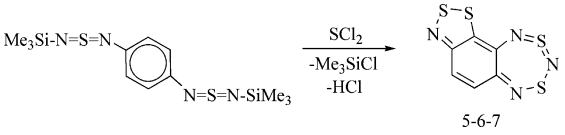
In the case of *meta*-substituted precursors (Ar = 3-RC_6H_4), which possess two nonequivalent positions at which the ring-closure may occur, the electrophilic cyclization proceeds with highly effective regioselectivity (see below) and leads predominantly (in the case of R = CH_3, Cl, Br, I) or even exclusively (in the case of R = OCH_3, F) to 6-R isomers (Scheme 3; the ratios of the major (6-R) to the minor (8-R) isomer are based on ^1H NMR spectroscopic data of the reaction mixtures).[29c,29d] For the disubstituted precursor (with Ar = 3,4-$F_2C_6H_3$), the cyclization is also effectively regioselective, since only one isomer was isolated from the reaction mixture (Scheme 3), and the second possible isomer was not detected.[29b]



Scheme 3.

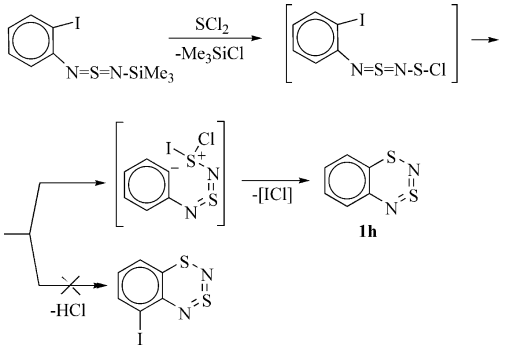
According to PM3 calculations, the preferred direction of cyclization is consistent with the relative stabilities of the corresponding intermediate σ complexes (Scheme 2) as well as with factors of kinetic control for an orbital-controlled reaction between electrophile and nucleophile.[29d]

The attempted synthesis of benzobis(dithiadiazines) resulted in the isolation of low yields of the 5-6-7 tricyclic system (Scheme 4) instead of the expected 6-6-6 systems similar to anthracene and/or phenanthrene. The structure was confirmed by XRD; the reaction route is unclear.[30]



Scheme 4.

Attempts to use a leaving group other than a hydrogen atom, namely a *tert*-butyl group, for the cyclization were unsuccessful.[29d] In the case of the cyclization of Ar–N=S=N–$SiMe_3$ (Ar = 2-IC_6H_4), only **1h** was isolated from the reaction mixture instead of the expected 5-iodo derivative (Scheme 5).[29c] It is believed that this cyclization is mediated by the bipolar ion (Scheme 5) originating from the initial electrophilic attack on the iodine atom, rather than on the carbon atom.[29c]



Scheme 5.

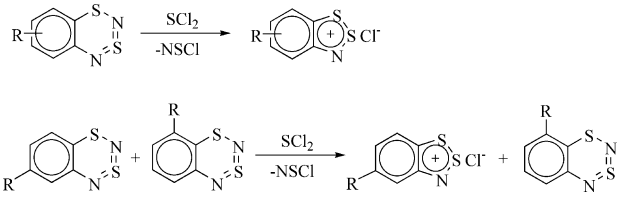
It is of obvious interest to expand the discussed approach to the preparation of Se^{II} analogues of compounds **1**. However, the reaction of Ar–N=S=N–$SiMe_3$ (Ar = Ph) with $SeCl_2$ did not provide any heterocyclic products.[31]

Precursors

The Ar–N=S=N–$SiMe_3$ precursors can easily be prepared from the corresponding $ArNH_2$ via Ar–N=S=O derivatives.[10c,11a,23a,29b–29d,32b,32c] According to XRD analysis, for Ar = Ph (a 1:1 molecular complex with octafluoronaphthalene) and Ar = 4-(4-IC_6H_4)C_6H_4, the precursors adopt the *Z*,*E* configuration (the Ar group is in the *Z* position) in the crystal,[29c,33] which is very similar to the configuration of related Ar–N=S=O compounds.[11a,32b,32c,34]

Side Reactions

In the electrophilic synthesis of compounds **1**, the most important side reaction reducing their yields is further reaction of **1** with SCl_2 to give 1,2,3-arenodithiazolium chlorides (Herz salts) (Scheme 6). The interaction proceeds at different rates dependent on the nature and/or position of the carbocyclic substituent R (see also section 5.4). With R = Cl, Br, I, the 6-R isomer reacts with SCl_2 much more rapidly than the 8-R isomer (Scheme 6). Thus, the electrophilic cyclization itself seems to be even more regioselective than it appears from the ratios of the 6-R and 8-R isomers observed by ^1H NMR spectroscopy in the reaction mixtures (Scheme 3). The rate difference allows the isolation of the minor 8-R isomers from the reaction mixtures containing more of the 6-R isomers (R = Cl, Br, I) by treating the mixtures with an amount of SCl_2 that is equimolar to that of the 6-R isomer.[29c]



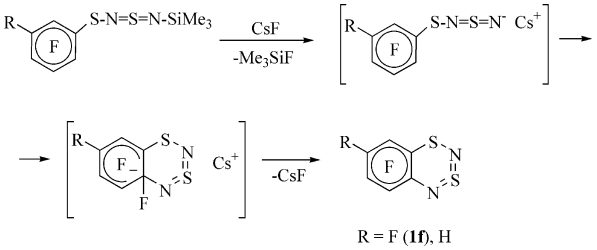
Scheme 6.

In some cases, $(Ar–N=)_2S$ are identified as byproducts. One can explain their formation in terms of the dimerization of the [Ar–N=S=N–S–Cl] intermediates (Scheme 2) through [2π + 2π] cycloaddition reactions, followed by the decomposition of the asymmetric dimers to $(Ar–N=)_2S$ and $[S_3N_2Cl][Cl]$. Dilution of the reaction solutions reduces the yields of these byproducts.[29b]

2.2 Nucleophilic Cyclization

Cyclization

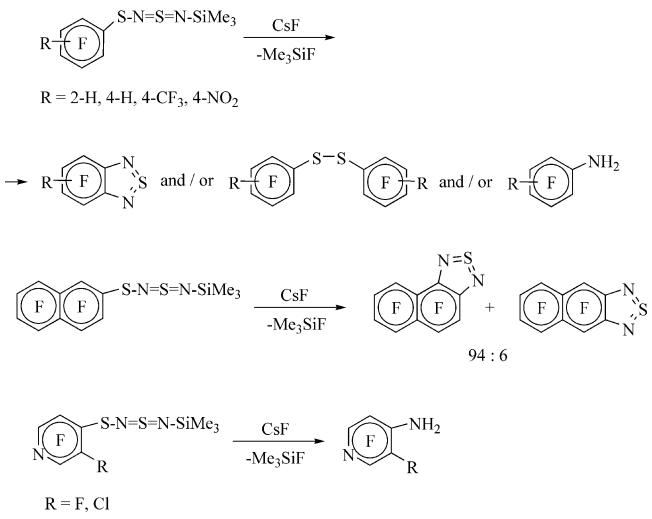
The nucleophilic approach to preparing compounds **1** is based on the intramolecular cyclization of polyfluorinated Ar–S–N=S=N–$SiMe_3$ precursors under the action of CsF in MeCN (Scheme 7).[29b,35] With Ar = C_6F_5, **1f** was obtained in an isolated yield of 54%.[35] With Ar = 3-HC_6F_4, the cyclization proved to be effectively regioselective under the conditions employed, since only one of two possible isomers (Scheme 7) was observed with an isolated yield of 55%. The preferred direction of the ring-closure is seemingly consistent with the same factors as discussed above for the electrophilic cyclization reaction.[29b] The likely intermediates of the nucleophilic cyclization are the corresponding [Ar_FSNSN] anions whose nonfluorinated congeners were recently isolated in the form of stable salts of $[K(18\text{-crown-}6)]^+$ and characterized by XRD.[8b]



Scheme 7.

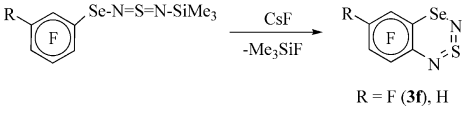
With Ar = *n*-RC_6F_4 (*n* = 2, R = H; *n* = 4, R = H, CF_3, NO_2), only mixtures of corresponding 2,1,3-benzothiadiazoles (**2**), $ArNH_2$, and ArSSAr were observed; the molar ratio of the reaction products depended strongly on both *n* and R.[29b] With Ar = 2-$C_{10}F_7$, the cyclization afforded a 94:6 mixture of angular and linear naphthothiadiazoles. With Ar = 4-C_5F_4N and 4-C_5ClF_3N, the cyclization pro-

duced only the corresponding pyridine amines (Scheme 8).[29d,36] These results can be attributed to both the low nucleophilicity and thermal stability of the intermediate primary $[ArSNSN]^-$ and secondary $[ArNSN]^-$ ions,[8a,32] precursors of compounds **1** and **2**, respectively. The primary $[ArSNSN]^-$ ions can produce the secondary $[ArNSN]^-$ ions by means of *ipso*-cyclization followed by ring-opening to $[ArNSNS]^-$ and elimination of a sulfur atom; the details are given in refs.[29b,29d] and ref.[36]



Scheme 8.

In contrast to the electrophilic cyclization, the nucleophilic cyclization allows for the preparation of the Se^{II} analogues of compounds **1**, i.e. 3,1,2,4-benzothiaselenadiazines (**3**). Starting from Ar–Se–N=S=N–$SiMe_3$ (Ar = C_6F_5, 3-HC_6F_3), the 5,6,7,8-F_4 (**3f**) and 5,6,8-F_3 derivatives of the as yet unknown **3h** were obtained in isolated yields of 7 and 50%, respectively (Scheme 9).[31,37] In the latter case, the cyclization displayed its typical regioselectivity since only one of the two possible isomers was observed.



Scheme 9.

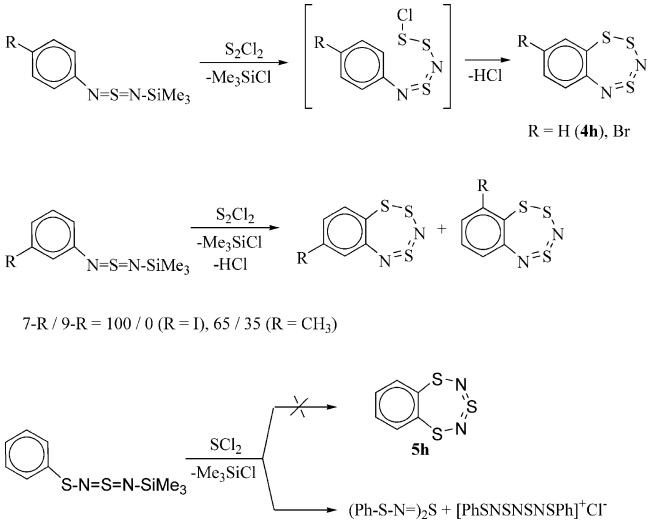
Attempts to adapt the cyclization to the hydrocarbon series by the use of a leaving group other than fluorine, namely NO_2, were unsuccessful. With Ar = 2-$O_2NC_6H_4$, only ArSSAr was obtained.[35]

Precursors

The polyfluorinated Ar–X–N=S=N–$SiMe_3$ precursors are easily accessible from the corresponding thiols and/or disulfides (X = S) or diselenides (X = Se) by a 1:1 condensation of their ArXCl derivatives with $(Me_3SiN=)_2S$.[29b,31,35–37] According to XRD analysis, the precursor with Ar = 2-HC_6F_4 and X = S possesses a planar *Z*,*E* configuration (with the ArX group in the *Z* position) in the crystal,[29b] which is similar to that of Ar–X–N=S=N–$SiMe_3$ (X = S, Se) compounds with hydrocarbon Ar groups.[14,38]

2.3 Related Electrophilic Cyclizations

The electrophilic cyclization of Ar–N=S=N–$SiMe_3$ into compounds **1** under the action of SCl_2 can be adapted to S_2Cl_2 to give 1,2,4,3,5-benzotrithiadiazepines (**4**, Scheme 10).[39a] The isolated yields do not exceed 10%. For Ar = 3-RC_6H_4 (R = CH_3, I), the cyclization is effectively regioselective. For R = CH_3, the 7-R/9-R isomer ratio is 65:35, as shown by ^1H NMR spectroscopy. With R = I, only the 7-I isomer was observed, and its structure was confirmed by XRD.[39a]



Scheme 10.

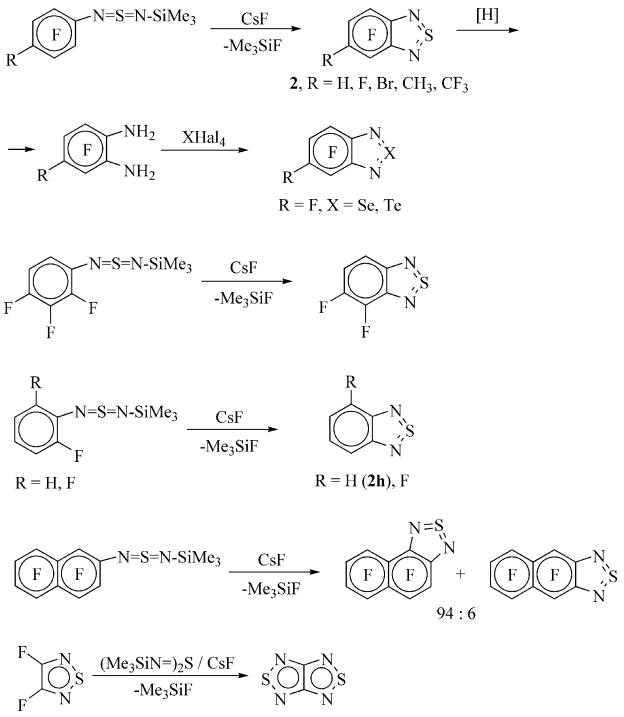
Besides target compounds **4**, smaller-sized heterocycles **1** were also detected in the reaction mixtures in amounts comparable to those of **4**. Since compounds **4** are stable under the cyclization conditions, this implies the elimination of sulfur from the key intermediates [Ar–N=S=N–S–S–Cl] before ring closure.[39b]

Attempts to prepare 1,3,5,2,4-benzotrithiadiazepines (**5**) by the same approach starting from Ar–S–N=S=N–$SiMe_3$ (Ar = Ph) and SCl_2 failed (Scheme 10).[23c,39a] Seemingly, the key intermediates [Ph–S–N=S=N–S–Cl] eliminate $(SN)_2$ to form PhSCl, instead of cyclization into compounds **5**. Then, $(SN)_2$ dimerizes into $(SN)_4$, whereas PhSCl reacts with the starting Ph–S–N=S=N–$SiMe_3$ to give acyclic products (Scheme 10) by known[12c,15,20c] reactions. Spontaneous shortening in solution is typical of extended SN chains. This most likely reflects the π-excessiveness of the chains.[10b,10c,14]

2.4 Related Nucleophilic Cyclizations

The nucleophilic cyclization of *ortho*-fluoro $[ArNSN]^-$ ions generated from Ar–N=S=N–$SiMe_3$ by the action of CsF in MeCN proceeds (except for Ar = 4-NC_5F_4) much

more effectively than the cyclization of $[ArSNSN]^-$ ions. Consequently, this reaction is a convenient method for the synthesis of compounds **2** in both fluorocarbon and hydrocarbon series (Scheme 11).[11a,29b,29d,36,40]



Scheme 11.

The intermediate $[ArNSN]^-$ ions were isolated in the form of stable salts of $[(Me_2N)_3S]^+$ and $[K(18\text{-crown-}6)]^+$.[32] According to the XRD data as well as the results of calculations at the RHF, MP2 and DFT/B3LYP levels of theory, the $[ArNSN]^-$ ions prefer a *Z* configuration similar to that of ArNSO compounds. Since the anions possess a very short terminal SN distance (typical of an SN triple bond) and a relatively long internal SN distance, they are $[Ar–N–S{\equiv}N]^-$ thiazyls rather than $[Ar–N{=}S{=}N]^-$ sulfur diimides.[32]

Polyfluorinated compounds **2** (Scheme 11) are of special preparative interest since they can be easily reduced to polyfluorinated 1,2-diaminobenzenes (or naphthalenes), otherwise hardly accessible.[36,40] The latter, in turn, can be used in the syntheses of the selenium and tellurium congeners of compounds **2**, i.e. 2,1,3-benzoselenadiazoles[40] and 2,1,3-benzotelluradiazoles (Scheme 11).[25c]

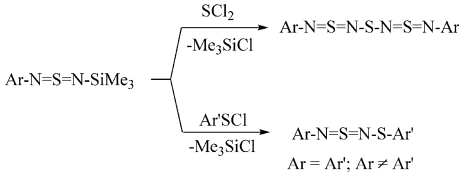
The discussed approach to the ring-closure can also be applied to the synthesis of nonbenzoid SN heterocycles (Scheme 11) as the second step of the nucleophilic double condensation mediated by the [RNSN]-type anions.[8b]

2.5 Related Acyclic Reactions

Most of reactions discussed above in the context of ring-closure can be applied to the synthesis of acyclic SN compounds.

Electrophilic Reactions

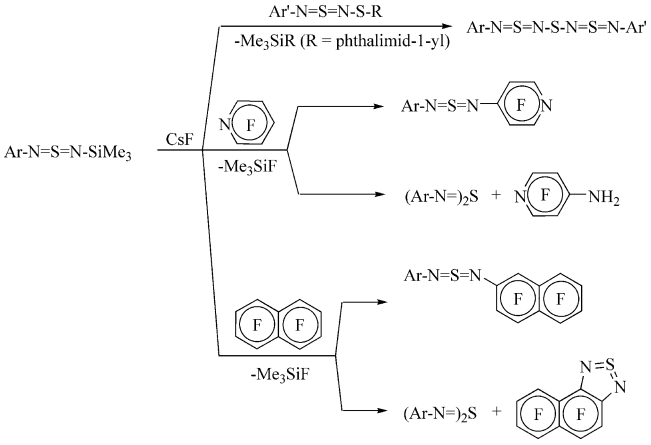
In a 2:1 molar ratio, the reaction between Ar–N=S=N–$SiMe_3$ and SCl_2 leads to $(Ar–N{=}S{=}N–)_2S$ acyclic derivatives (Scheme 12)[10c] via the same [Ar–N=S=N–S–Cl] intermediates as in the synthesis of compounds **1** (Scheme 2). The reaction of Ar–N=S=N–$SiMe_3$ with Ar′SCl affords acyclic analogues of compounds **1** (Scheme 12).[12a,12c]



Scheme 12.

Nucleophilic Reactions

The reaction of $[ArNSN]^-$ ions, generated from Ar–N=S=N–$SiMe_3$ under the action of CsF in MeCN, with various external electrophiles displays a number of interesting features including transfer of an [NSN] fragment. The reactions allow for the preparation of various SN compounds (Scheme 13), including nonsymmetrical derivatives that are otherwise hardly accessible. These reactions also perform well with $[AlkNSN]^-$ ions.[10c,11a,41,42]



Scheme 13.

3. Molecular Structure

3.1 Gas Phase

Compounds **1** reveal an interesting structural dichotomy. According to data recorded with GED and refined with the SARACEN method,[43] free molecules of **1h** and its 5,6,7-trifluoro derivative are bent with respect to the heterocyclic fragment, whereas those of the 6,8-difluoro derivative and **1f** are planar.[44] In particular, the –C–S–N=S– torsion angle for **1h** is ca. 41°. Quantum chemical calculations of the molecular structure of **1h** at various levels of theory (see below for details)[45a] revealed that the DFT/B3LYP method reproduces the experimental data reasonably well. This is,

however, not the case for the MP2 method, which performs well enough for **1h** but predicts an essentially nonplanar heterocycle for a free molecule of **1f**. It follows from the B3LYP calculations and the GED experiments that the precise molecular conformation, with a planar (C_s) or bent (C_1) heterocycle, depends on the presence (C_s) or absence (C_1) of a fluorine atom in the 8-position (Scheme 1) of the carbocycle.[44]

The distortion of **1h** and its 5,6,7-trifluoro derivative away from C_s symmetry seemingly reflects the tendency of the molecules to minimize the thermodynamic destabilization associated with their antiaromaticity by means of a pseudo-Jahn–Teller effect. In the C_s conformation, the molecular ground state is $^1A'$ (π^2). The calculations indicate that the planar structure is a transition state in the molecular bending motion. The transition to C_1 symmetry is possible through a vibronic interaction with excited $^1A''$ states, generated by $\pi\rightarrow\sigma^*$ and $\sigma\rightarrow\pi^*$ excitations. For **1h**, the lowest-energy excitation of this type is $6a''\rightarrow 20a'$. The mixing of $6a''$ (i.e. the π-HOMO) with $20a'$ (i.e. the lowest virtual σ*-MO following the π-LUMO $7a''$) folds the molecule along the S1···N4 line. The density of the one-electron transition is localized mainly on S1 (Figure 1).[29c,44]

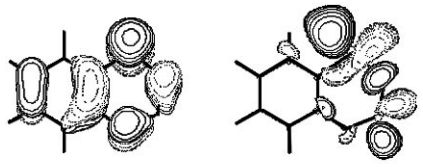


Figure 1. The RHF/6-31G(d) $6a''$ and $20a'$ MOs of C_s-**1h** of which the mixing folds the molecule along the S1···N4 line.

This orbital interaction is sensitive to the energy difference between the contributing MOs. In **1h**, the substitution of any hydrogen atom by a fluorine atom does not affect the energy of the $20a'$ σ*-MO, which is localized on the SN bonds. In contrast, replacing the hydrogen atom at C8 by a fluorine atom leads to an inductive stabilization of the $6a''$ π-HOMO, since C8 does not contribute to this MO. In all other cases, that is at C5, C6, and C7, this effect will be compensated for to a great extent by the mesomeric destabilization due to the nonzero contributions of these carbons atoms to the $6a''$ π-MO (Figure 1). Thus, the fluorine atom at C8 enlarges the energy difference mentioned above (and fluorine atoms at C5, C6, and C7 do not) and counteracts the pseudo-Jahn–Teller distortion of the molecule. This explains why free molecules of **1h** and its 5,6,7-trifluoro derivative are bent whereas those of the 6,8-difluoro derivative and **1f** are planar.[29c,44]

Thus, there is an interesting stereoelectronic effect inherent in free molecules of these compounds **1**, namely, that the conformation of the heterocyclic ring can be controlled by the substitution of the carbocyclic ring.

According to DFT/B3LYP calculations, molecules of the 5-F, 5-OCH_3, 5-CF_3, 6-CH_3, 6-Cl, and 7-CH_3 derivatives of **1h** are bent along the S1···N4 line to ca. 26°.[46a,56a]

A comprehensive theoretical study on the molecular geometry of **1h** by a large number of DFT and post-HF techniques with various basis sets revealed that with post-HF methods such as MP4(SDQ), QCISD, and CCSD, convergence of the geometrical parameters is already obtained for the relatively small 6-311+G(d) basis set. Taking the MP4(SDQ)/cc-pVTZ geometry as a reference, the DFT/B1B95 functional appears to provide the most satisfactory description of all the examined functionals.[45a]

According to MW spectroscopy, compound **2h** is planar in the gas phase.[47a] Experimental gas-phase data for compounds **4** and **5** are unknown. According to MP2/6-31G(d) calculations,[39a] a free molecule of **4h** possesses a significantly bent heterocycle with a conformation resembling that of benzopentathiepine,[48] whereas a free molecule of **5h** is planar.

3.2 Solid State

The two types of molecular conformation mentioned above, planar and bent, are also typical of compounds **1** in the solid state. According to XRD analysis, **1h** and its 5-CF_3, 6-F, 7-Br, 7-OCH_3, 5,6,7-F_3, and 5,6,8-F_3 derivatives are planar in the crystals, whereas 5-Br, 5-OCH_3, 6-CH_3, 8-Br, 5,7-tBu$_2$, 6,8-F_2, and **1f** are bent along the S1···N4 line to various angles varying from 3.8° for 8-Br to 24.1° and 26.2° for 5,7-tBu$_2$ (two crystallographically independent molecules).[23c,29,35] Of the two crystallographically independent molecules of the 6-Br derivative, one is perfectly planar, whereas the other is bent to 3.1°.[29c] All these data clearly indicate the influence of packing effects on the conformation of the heterocycle in the solid state. Comparison of the XRD data with those of the GED and quantum chemical calculations reveals that in most cases packing forces flatten the heterocycle. Two known exceptions are **1f** and the 6,8-F_2 derivative, for which the situation is the other way around. Thus, compounds **1** are structurally nonrigid as a result of a low-energy vibration mode that allows them to change shape on going from one phase to another.

Currently, there is considerable interest in theoretical methods for the reliable prediction of the crystal packing of organic solids (for selected publications, see ref.[13a] and the references cited therein). Compound **1h**, chosen at random from the Cambridge Structural Database, was used in an evaluation of one of those methods. The possibility of molecular deformation upon packing was not, however, taken into account.[49]

The bond lengths and bond angles in **1h** and its derivatives are rather typical for SN compounds[50a] and correspond to Cambridge Structural Database statistics.[50b,50c] For **1h** and its 5-CF_3, 6-F, 7-OCH_3, 8-Br, and 5,6,7-F_3 derivatives, the lengths of the two SN bonds of the –N=S=N– fragment are practically identical, whereas for the 5-OCH_3, 5-Br, 6-CH_3, 6-Br, 7-Br, 5,7-tBu$_2$, 6,8-F_2, 5,6,8-F_3 derivatives and **1f**, they are markedly different, and these situations do not correlate with the type of molecular conformation, C_s or C_1.[23c,29,35]

On going from the solid state to the gas phase, the bond lengths of **1h** do not change significantly except for the CN and CS bonds, which shorten slightly. For **1f** the situation is different: the CN bond shortens, while the CS, S1N2, and S3N4 bonds lengthen, and the N2S3 bond does not change.[23c,35,44b]

According to XRD analysis, compound **3f** is bent along the Se1···N4 line by 6.0°, whereas the four crystallographically independent molecules of its 5,6,8-F_3 derivative are bent by 1.3, 1.6, 5.4, and 10.2°, i.e., two molecules are planar and two are folded.[31,37] Despite the similarities between **1f** and **3f** with respect to molecular composition and shape, their crystal packing is substantially different. In particular, the crystal lattice of **3f** features channel-like cavities along the C_3 axes, with a radius of ca. 2.47–2.79 Å and a volume of ca. 306 Å^3 per unit cell. The inner walls of the cavities are lined with fluorine atoms, and one might consider them as "fluorine nanotubes". The tube contains disordered N_2 molecules seemingly adsorbed from the atmosphere; the space filling is partial. The crystal structure of the 5,6,8-F_3 derivative of **3h** reveals a completely different pattern, not featuring any channels.[31,37]

According to XRD analysis, molecules of **2h** and its selenium and tellurium congeners are planar in the crystal.[25a,47b,47c] The same is true for **5h** and **5f**.[23] The 7-I derivative of compound **4h** possesses the same bent conformation in the solid state as is calculated for a free molecule of **4h**.[39a] This is in striking contrast to the situation with compounds **1**, where the molecular conformation significantly changes on going from the gas phase to the solid state (see above).

4. Spectral Properties and Electronic Structure

4.1 Ultraviolet Photoelectron Spectroscopy

According to calculations at the RHF/6-31G(d) and DFT/B3LYP/6-31G(d) levels of theory, the planar (C_s) conformation of **1h** is less stable than the bent (C_1) conformation only by ca. 0.3 kcal mol^{-1}, the eigenvalues of the uppermost occupied MOs being affected only to a negligible extent. This makes it possible to use the terms π-MOs and σ-MOs in the discussion of the UPS spectra, taking into account that there is obviously no clear-cut σ,π-separation in the bent molecular conformations.[46a]

In HeI spectra, the vertical IE_1 of **1h** (7.75 eV)[46b] is essentially lower than the IE_1 of **2h** (8.95 eV)[46d] and practically equal to the $IE_1$of **5h** (7.88 eV).[46c] This feature is due to the large contribution of the 3p-AO of sulfur to the π-HOMO of **1h** and **5h**.[46]

The carbocyclic F, Cl, Br, CH_3, CF_3, and OCH_3 substituents in **1h** either slightly stabilize the π-HOMO (π_1) or do not change its energy at all (7-CH_3, 5-OCH_3). The most effective π_1-stabilizing substituents are 5-CF_3 and 5-F, for which ΔIE_1 is equal to 0.48 and 0.36 eV, respectively. These results indicate that the substituents provide mainly an inductive influence on π_1, i.e., π_1 is significantly localized on the heterocycle with a relatively small contribution from the carbocycle.[46a] The IE_2 of **1h** (9.22 eV)[46b] is virtually equal to the IE_1 of benzene. Contrary to π_1, the next occupied MO, π_2, displays both stabilization and destabilization, which indicates the complex inductive and mesomeric influence of the substituents. The most stabilizing substituent is again 5-CF_3 (ΔIE_2 = 0.60 eV), whereas the most destabilizing one is 5-OCH_3 (ΔIE_2 = –0.58 eV). These results suggest a large contribution from the carbocycle to π_2 and a small contribution from the heterocycle. Empirical analysis of the substitution effects on IE_3 and IE_4 is complicated by the overlap of spectral bands.[46a]

On going from **1h** to **1f**, IE_1 and IE_2 increase by 0.55 and 0.42 eV, respectively,[46b] which is a typical manifestation of the π-fluoro or perfluoro effect[51] observed in chalcogen–nitrogen heterocycles.[23a,46b,46d] The IE_2 of **1f** is very similar to the IE_1 of 1,2,3,4-tetrafluorobenzene (9.8 eV in the HeII spectrum). The IE_2 band vibrational structure with a frequency of 1130 cm^{-1}, typical of CF bond-stretching vibrations, confirms the π_2 localization on the carbocycle and suggests its similarity to the π-HOMO of the fluoroarene.

RHF/6-31G(d) calculations reproduce the IEs very well and predict the π,π,π,σ_N,π sequence for the uppermost occupied MOs of **1h** and its derivatives. They also allow a further specification of the structures of these MOs. According to the calculations, the π_1 is indeed considerably localized (within the united molecular π-system) on the heterocycle, whereas π_2 and π_3 are located on the carbocycle. The π_2 and π_3 of **1h** are reminiscent of the $1e_{1g}$S and $1e_{1g}$A MOs of benzene, respectively.[46a]

4.2 Electronic Absorption (UV/Vis) Spectroscopy

Compounds **1** possess low-lying excited states. In the UV/Vis spectra, the long-wavelength band lies in the range of ca. 605–635 nm ($\log\varepsilon \approx 2.3$–$2.8$), revealing a weak dependence on the positions and types of the carbocyclic substituents.[23c,29,35] Both time-dependent DFT/B3LYP/6-31+G(d) calculations[52c] and higher-level CASSCF/CASPT2 calculations[52a] reproduce the experimental UV/Vis spectrum of **1h** well (Figure 2). The long-wavelength band with a maximum at 616 nm and the next band at 371 nm correspond to π→π* transitions. The unresolved band at 314 nm can be assigned to a π→σ* transition.[52c] In going from **1h** to **1f**, the positions of the long-wavelength maxima (at 616 and 371 nm) are virtually unaffected, whereas the short-wavelength bands (at 291 and 283 nm) show an appreciable hypsochromic shift. This independently indicates that the electronic transition responsible for the deep blue color of compounds **1** is localized on the heterocycle.[35]

A comparison of the UV/Vis spectra of **1f** and **3f** shows that substitution of sulfur by selenium leads to a hypsochromic shift of the λ_{max} value of the long-wavelength absorption from 616 nm in **1f** to 584 nm in **3f**.[37] In accordance with the effects of hydrogen substitution by fluorine in the carbocycle, this indicates that the lowest-energy electronic transition is localized on the heterocycle.

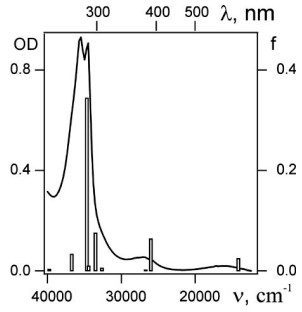


Figure 2. The UV/Vis spectrum of **1h** in hexane at 295 K. The vertical bars indicate the positions and oscillator strengths of the electronic transitions calculated at the CASSCF(16,12)/CASPT2/ANO-S level on the basis of the B3LYP/6-311G(df,p) geometry.

In the series of 10-, 12-, and 14-π-electron heterocycles (**2h**, **1h**, and **5h**, respectively), the λ_{max} of the long-wavelength band of **1h** sharply violates the monotonous correlation (310, 616, and 379 nm, respectively).[22c,23c] However, the low-lying first excited state of **1h** cannot be immediately attributed to its antiaromaticity, since, for example, the related 14-π-electron aromatic naphtho[1,8-*c*][1,2,6]thiadiazine has a maximum of the long-wavelength band at 642 nm, i.e., in the same range.

On going to **2h** and **5h** from their acyclic analogues, Ph–N=S=N–Ph (λ_{max} = 420 nm)[53a] and Ph–S–N=S=N–S–Ph (λ_{max} = 460 nm),[53b] respectively, the energy of the transition to the lowest excited state increases, whereas on going to **1h** from its acyclic analogue, Ph–S–N=S=N–Ph (λ_{max} = 434 nm),[12a] the energy decreases significantly. However, it is necessary to take into account that the acyclic derivatives normally exist in solution as equilibria of isomers (mainly *Z*,*E* and *Z*,*Z*) with slightly different λ_{max} values.[11–13]

4.3 Multinuclear NMR Spectroscopy

The most interesting feature of the NMR spectra of compounds **1** is the enhanced shielding of the ^{1}H, ^{13}C, and ^{19}F nuclei (for the monofluoro derivatives) attached to C5 and C8 – i.e., those closest to the heterocycle – as compared to those attached to C6 and C7.[23c,29] For **1h**, $\delta(^1H)$ is 5.90 and 5.79 for H5 and H8, and 6.63 and 6.79 for H6 and H7, respectively. This may indicate a contribution to the magnetic shielding from low-lying excited states (e.g., with respect to magnetically-active π→σ* and/or *n*→π* excitations localized on the heterocycle), and/or from paratropic ring currents associated with antiaromaticity.[21c] The GIAO calculations at the RHF and DFT/B3LYP levels of theory reproduce these shielding patterns.[29b] However, the results of these calculations cannot be interpreted in chemical terms. In any case, the cycloaddition of **1h** to norbornadiene (section 5.5), destroying the heterocyclic π-conjugation, returns the $\delta(^1H)$ values of H5 and H8 to values typical of the usual benzene derivatives (6.85 and 6.67).[23c] Similar changes in the ^{1}H NMR spectra are observed on going from **1h** to its 1,1-dioxide, and on substitution of the S1 atom by a C=O group.[54]

In the ^{19}F NMR spectra of the di-, tri-, and tetrafluorinated derivatives of **1h** no regularities are observed. Seemingly, the mutual effects of the fluorine atoms dominate all other effects on $\delta(^{19}F)$.[29b,35]

In the ^{15}N NMR spectra of **1h** and its monosubstituted derivatives, $\delta(^{15}N)$ lie in a narrow range of ca. 280–250 ppm with only a weak dependence on the nature of the carbocyclic substituent.[29] According to $^{15}N\{^1H\}$ experiments and GIAO B3LYP calculations, the high-field signal can be assigned to the N4 nucleus and the low-field signal to the N2 nucleus.[29b]

Compound **1f** and the di- and trifluorinated derivatives of **1h** reveal an enhanced shielding of the N4 nucleus [$\delta(^{15}N) \approx$ 240–230 ppm] and an unaffected shielding of the N2 nucleus.[29,55b] It is known that, in (hetero)aromatic compounds, substitution of hydrogen by fluorine normally leads to an enhanced shielding of the heavier nuclei in positions α to the substitution site.[55] In particular, while on going from **2h** to **2f** the ^{15}N shielding sufficiently increases, $\delta(^{15}N)$ is not affected on going from **5h** to **5f**.[23a,55b]

In the hydrocarbon series, the series **2h** (10π), **1h** (12π), and **5h** (14π) reveals an enhancement of the magnetic shielding of ^{15}N nuclei (by ca. 85 ppm on going from **2h** to **5h**). In the fluorocarbon series this effect is less prominent.[23a,55b] A likely reason is the drain of electron density from the sulfur atoms to the nitrogen atoms.[55b] A similar effect is also observed for the acyclic derivatives Ph–N=S=N–Ph, Ph–S–N=S=N–Ph, and Ph–S–N=S=N–S–Ph, but on smaller scale and in a less clear form. The latter may be due to the complex isomeric equilibria of these acyclic derivatives in solution.[11d,11e,13c]

4.4 IR and Raman Spectroscopy

According to calculations at the DFT/B3LYP level of theory with the 6-31+G(d)[56a] and 6-311(df,p)[52a] basis sets, which agree well with the experimental IR and Raman spectroscopic results (Figure 3),[52a] the ν_{as}(NSN) and ν_s(NSN) stretching modes of **1h** and its derivatives lie in the ranges 1230–1220 and 975–965 cm^{-1}, respectively. In the Raman spectra obtained with an excitation line at 1064 nm these bands are the most intense.[56a]

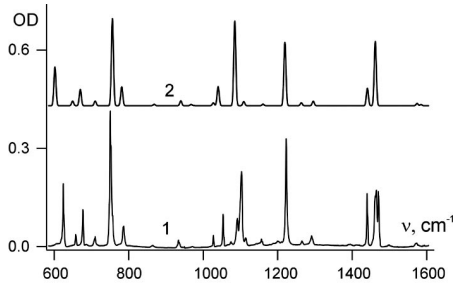


Figure 3. The IR spectra of **1h**: (1) experimental spectrum in an argon matrix at 12 K, and (2) theoretical spectrum calculated at the DFT/B3LYP/6-311G(df,p) level of theory.

The ν_{as}(NSN) and ν_s(NSN) values of compounds **1** are similar to those of the acyclic Ar–N=S=N–Ar derivatives observed in the ranges 1300–1250 and 985–960 cm^{-1}, respectively.[56b]

For compounds **1f** and **3f**, the sulfur and selenium atoms can be considered as pseudo-isotopes in the empirical identification of the molecular vibrations which contain a large contribution from the CX and/or XN bonds (X = S, Se) by means of the "selenation" method.[55a] A comparison of the IR and Raman spectra of **1f** and **3f** reveals a decrease in a number of vibrational frequencies upon introduction of the selenium atom. For the IR spectrum of **1f** 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 **1f**, 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 **1f** and **3f** are virtually identical.[37]

The Raman spectra of **1h** and its derivatives, measured with excitation lines at 458, 477, 488, 497, and 515 nm, gradually approaching the λ_{max} of the long-wavelength band in the electron absorption spectra at 605–635 nm, reveal resonance intensity enhancement of the ν_{as}(NSN) and ν_s(NSN) bands. The bands in the range 1580–1380 cm^{-1} related to the ν(CC) stretching modes of the carbocycle are only slightly influenced by the excitation energy. These results indicate that in compounds **1** the π→π* electronic transition at 605–635 nm is localized mainly on the SN part of the molecules, whereas the carbocyclic part participates to a lesser extent. Overall, the results confirm a weak but definite mixing of the fragment π-orbitals associated with the carbocyclic and heterocyclic parts of the molecules of compounds **1**.[56a]

4.5 Other Spectral Techniques

The C1s, N1s, S2s, and S2p ISEELS and S1s XAS spectra of **1h** characterize its excited states. The C1s ISEELS spectrum with the only C1s→π* transition of high intensity suggests a benzene-like character of the corresponding π*-states.[46c]

4.6 Aromaticity/Antiaromaticity

The physical origin of the aromaticity (stabilization) and antiaromaticity (destabilization) of π-systems is still under discussion.[21] One can think that two very different fundamental laws stand behind them, namely, Coulomb's law (aromaticity) and the Pauli antisymmetry principle (antiaromaticity).[21b] According to another point of view, however, the instability of antiaromatic compounds is of kinetic origin and relates to low-lying triplet states.[21] Generally, aromaticity and antiaromaticity of π-systems is characterized by a combination of various energetic, geometric, and magnetic criteria. Each category of criteria has its limitations and ambiguities. Application of these criteria usually yields different, and very frequently contradictory results, especially in the case of polyheteroatom π-systems.[21]

As mentioned above, the energy gain on going from the planar (C_s) to the bent (C_1) conformation in the case of **1h** is ca. 0.3 kcal mol^{-1} at the RHF/6-31G(d) and DFT/B3LYP/6-31G(d) levels of theory, and ca. 2.7 kcal mol^{-1} at the MP2/6-31G(d) level.[29c] The eigenvalues of the uppermost occupied MOs are practically insensitive to the type of conformation.[29c,46a] This makes it possible to use terms such as π-MOs in the following discussion.

The quantum chemical calculations on compounds **1** performed at various levels of theory show that in the planar conformation the carbocycle and the SN chain form a united π-system of the molecule containing 12 electrons.[29b,29c,44,46a–46c] This system features a notably low IE_1, low-lying π*-excited states, and enhanced magnetic shielding of the ^1H, ^{13}C, and ^{19}F nuclei attached to C5 and C8, i.e., those closest to the heterocycle, probably due to paratropic ring currents in the latter. All these peculiarities can be associated with antiaromaticity.[21]

At the same time, the calculations reveal a heteroatom-induced tendency of the π-MOs towards localization on separate molecular fragments. Thus, the π-HOMO of **1h** (6*a''*) can roughly be considered as localized (73%) on the SN chain, whereas the next two occupied π-MOs (5*a''* and 4*a''*) can be seen as localized (76 and 78%, respectively) on the carbocycle.[29b,29c,44,46a–46c] Consequently, one cannot expect a uniform perimeter of the π-delocalization. The Hirshfeld bond orders (overlap populations) in **1h** and its selenium analogues confirm this.[37,45b] Overall, one can expect that the antiaromaticity of compounds **1** should be weakened by heteroatom first-order perturbation, which reduces the cyclic π-delocalization.

On the basis of the dissociation constants of the norbornadiene adducts (section 5.5), the difference in resonance energy between the 12-π-electron **1h** and the 14-π-electron **5h** was estimated to be 5 kcal mol^{-1}.[23c] The values of the absolute hardness, η, indicate that planar **1h** is significantly destabilized with respect to the 10- and 14-π-electron analogues **2h** and **5h**: the values of η_{MNDO} are 2.797, 4.089, and 3.408 eV, respectively.[57a] Despite the possibility of a useful comparison with acenes,[57b] η does not allow the estimation of the antiaromaticity of compounds **1**.

In this situation, the NICS concept[21a,58] appears to be a useful criterion for the quantification of the antiaromaticity of compounds **1**. According to calculations at the GIAO/RHF/6-31G(d)//B3LYP/6-311+G(d) level of theory, the heterocyclic ring of **1h** has a positive NICS value of 10.7 ppm and is antiaromatic, whilst the carbocyclic ring has a negative value of –6.7 ppm and is aromatic [throughout the text, the NICS(0) values are presented; note that NICS values are somewhat method- and basis-set-dependent and that NICS(0) and NICS(1) values are different].[29b] In comparison, at the same level of theory, but on the basis of B3LYP/6-31G(d) geometries, the NICS values for benzene, naphthalene, and D_{4h}-cyclooctatetraene are –9.7, –9.9, and 30.1 ppm, respectively.[58b]

Fluorination of the carbocycle affects the NICS values of both the carbocycle and heterocycle, and for **1f** these values are –11.8 and 14.9 ppm, respectively.[29b] For **3f**, the NICS values for the carbocycle and heterocycle are –7.1 and 15.2 ppm, respectively.[37] An increase in the aromaticity of arenes upon fluorination according to NICS is typical,[21a] and can be explained by the donation of the π-electron density of the fluorine atoms to the ring system.

Thus, on the NICS scale the antiaromaticity of the heterocyclic moiety of **1h** is about 1/3 the antiaromaticity of D_{4h}-cyclooctatetraene. According to recent estimations of the resonance energy, however, the destabilization of the latter due to the cyclic interaction of the π-bonds (i.e., the antiaromaticity) is negligible.[60] Taking these findings into account, along with the fact that only the heterocyclic moieties of compounds **1** are antiaromatic, within the NICS context, whereas the carbocyclic moieties are aromatic (and the C4a–C8a bond belongs to both moieties at the same time), as well as data on their thermal stability (section 5.1), one can speculate that, in terms of the aromaticity/antiaromaticity concept,[21] compounds **1** could reasonably be classified on the whole as conjugated nonaromatic substances.[29b]

According to the data from a large number of experimental and theoretical methods, planar compounds **2** and **5** possess united cyclic π-systems with 10 and 14 electrons, respectively.[23a,46c,46d,55a,61] Hence, they are heteroaromatic. Indeed, for the nonfused archetypes of **2h** and its selenium congener, the NICS values are –13.6 and –12.5 ppm, respectively.[21a] For the nonfused archetype of **5h** this value is –9.3 ppm.[59]

The nonsymmetric isomer of **5h**, compound **4h**, has no united cyclic π-system since its heterocyclic part is bent.[39a]

The π-systems of compounds **2** and their selenium congeners reveal an interesting topological peculiarity. The X (X = S, Se) and nitrogen atoms make a predominant contribution to the π-MOs transformed by different irreducible representations of the C_{2v} group, a_2 and b_1, respectively. As a result, even though both X and the nitrogen atoms participate in a united molecular 10-π-electron system, there is practically no π-bond between them. This explains, in particular, the long NX (X = S, Se) bonds in these compounds.[55a]

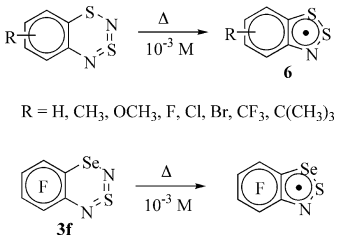
5. Heteroatom Reactivity

For compounds **1**, the available data on reactivity are mostly related to transformations of the heterocycle. The carbocycle is involved only in a few known reactions.

5.1 Thermolysis and Photolysis

Thermolysis

The parent **1h** is stable in boiling toluene.[23c] According to ESR spectroscopic data, mild thermolysis of compounds **1** in dilute (10^{-3} M) hydrocarbon solutions at ca. 150 °C yields nearly quantitatively persistent 1,2,3-benzodithiazolyl radicals (Herz radicals, **6**) including previously unknown derivatives (Scheme 14).[29a,52c,52e] The reaction kinetics can be described as first-order.

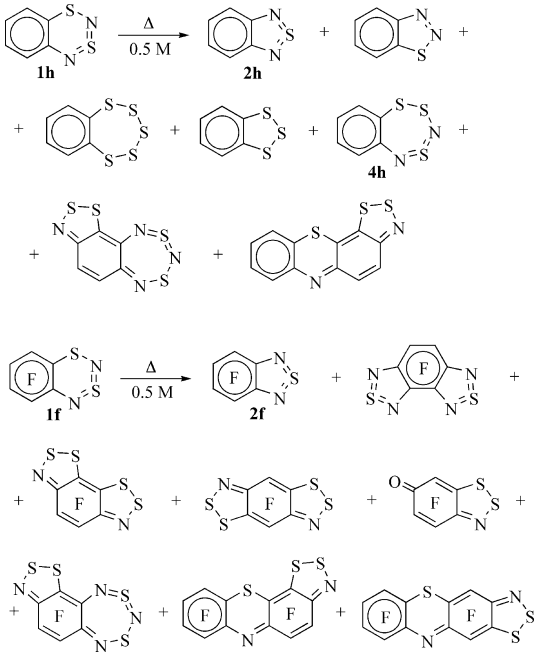


Scheme 14.

The traditional approach to radicals **6** is based on the reduction of 1,2,3-benzodithiazolium salts (Herz salts).[62] The thermolysis of compounds **1** allows the preparation of radicals **6** for which the corresponding Herz salts are still unknown.[29a,52c,52e]

Similarly, the thermolysis of **3f** gives the first representative of polyfluorinated 2,1,3-benzothiaselenazolyls (Scheme 14) identified by ESR spectroscopy.[31]

The thermolysis of **1h** and **1f** (the 6-6 bicyclic systems) in concentrated (0.5 M) hydrocarbon solution at 150–170 °C results in complex mixtures of various SN heterocycles containing previously unknown derivatives, such as differently fused 5-5-6, 5-6-7, and 5-6-6-6 polycyclic systems, together with 5-6 and 6-7 bicyclic systems (Scheme 15). The structures of the reaction products were confirmed by XRD.[48a]



Scheme 15.

Formation of the same 5-6-7 and 5-6-6-6 polycyclic systems in both the hydrocarbon and fluorocarbon series indicates that the required carbocyclic substitution is not electrophilic or nucleophilic in character, as is typical of hydro-

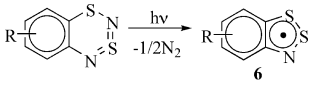
carbon and fluorocarbon aromatics, respectively. Rather, the chemistry is of radical (see above) and nitrenoid (see below) character.[48a]

Thus, under conditions of thermolysis, compounds **1** can be seen as precursors of new and unusual polycyclic SN derivatives of which the conventional methods for synthesis are not evident. The 5-6-6-6 derivatives have potential applications as fluorescent dyes. They are thermally and hydrolytically stable, soluble in organic solvents, and strongly absorb and emit light at 530–615 and 660–675 nm, respectively. For the linear 5-6-6-6 system, the fluorescence features an abnormally large Stokes shift of 140 nm.[48a]

Photolysis

Although photochemical methods are used for synthetic purposes rather rarely, they provide ample opportunities for studying the mechanisms of the processes. In the case where both thermolysis and photolysis result in identical products, it can be assumed that the reaction intermediates in these processes are the same.

At ambient temperature, prolonged irradiation of hydrocarbon solutions of **1h**, its 5,7-tBu$_2$ derivative, and **1f** by visible light ($\lambda > 450$ nm) does not cause any noticeable photochemical transformations. With UV irradiation of 365 or 313 nm, the compounds transform nearly quantitatively into the corresponding radicals **6** and dinitrogen (Scheme 16).[52b] The quantum yield of photolysis of **1h** at 313 nm is 0.08 in benzene and 0.15 in hexane. For the photolysis at 365 nm, the quantum yields decrease by more than 20 times. This indicates that a highly excited electronic state of compounds **1**, related likely to $\pi\rightarrow\sigma^*$ excitations localized on the SN bonds, is responsible for their photolytic transformation into radicals **6**.[52c] At the same time, low-lying excited states related to $\pi\rightarrow\pi^*$ transitions, which are also localized on the SN fragment according to the resonance Raman spectroscopic and computational data, seemingly do not participate in the photochemical transformation under discussion.[52]



R = H (**6h**), F_4 (**6f**), 4,6-t-Bu$_2$

Scheme 16.

The photolysis of **1h** and **1f** in frozen solution at 77 K leads to ESR-silent species detected by UV/Vis spectroscopy. Warming of the glassy matrices to room temperature results in the disappearance of these species and the formation of radicals **6** observed by ESR and UV/Vis techniques.[52a,52d]

According to the data from UV/Vis spectroscopy, photolysis of **1h** and **1f** in an argon matrix at 14 K leads to the same species as the photolysis in the frozen solutions.[52d] Moreover, ambient-temperature laser flash photolysis of **1h** solutions at 266 nm produces primary intermediates with a spectrum identical to that of the low-temperature products (Figure 4).[52a]

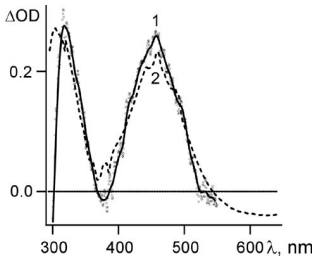
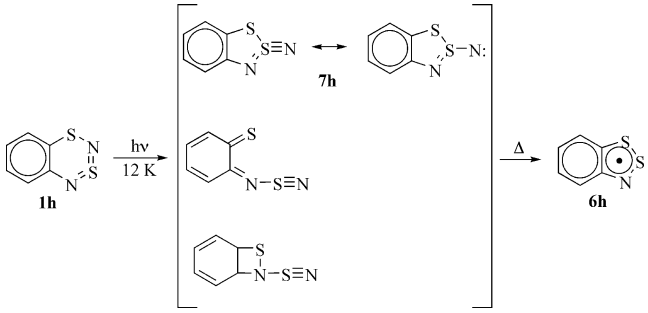


Figure 4. (1) Transient absorption spectrum detected 20 ns after the laser excitation of **1h** at 295 K (multiplied by 9) and (2) differential absorption spectrum recorded in an argon matrix at 14 K upon irradiation at 313 nm for 5 min.

According to the results of matrix isolation spectroscopy and computational data including those obtained at the CASSCF/CASPT2 level of theory, the intermediates under discussion are four- and five-membered heterocyclic and *ortho*-quinoid acyclic species (Scheme 17). With selective irradiation, these isomeric intermediates can be mutually interconverted as well as converted back to the starting **1h**.[52a] According to the calculations, the intermediates lie significantly higher (33–40 kcal mol^{-1}) in energy than the starting compound **1h**, but they are close in energy among themselves. The calculations predict that the four- and five-membered (**7h**) heterocyclic species have a somewhat lower energy than the *ortho*-quinoid species.[52a]



Scheme 17.

For intermediates **7**, nitrenoid structures composed of RS–N: singlet nitrene and RS≡N thiazyl structures can be assumed. This makes **7** of especial interest since they may be responsible for the ability of compounds **1** to oxidatively iminate P^{III} and S^{II} derivatives (sections 5.3 and 5.4). At the DFT/B3LYP/6-31G(d) level of theory, the triplet state of **7h** is higher than the singlet state by 1.8 kcal mol^{-1} in the gas phase and by 4.5 kcal mol^{-1} in hexane (with the polarized continuum solvent model).[52d] This is in agreement with computational data for singlet and triplet HSN.[63d]

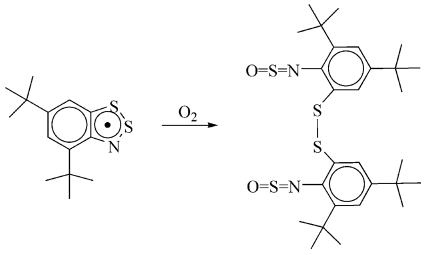
According to the DFT/B3LYP/6-31G(d) calculations, molecules of **7h** are planar.[52a,52d] The length of the exocyclic SN bond (1.47 Å) is much closer to the value of a triple (1.42–1.49 Å in RS≡N and R_3S≡N) than to that of a single (1.72 Å) SN bond.[32b,32c,63] It should be noted that nitrenes,[64] in which the nitrogen atom is bound to a non-carbon atom, are poorly studied. The participation of RS–N: singlet nitrenes was postulated for a number of reactions

but they were never detected.[65] Data on reactivity of RS≡N thiazyls are scanty and can hardly be systematized.[66] The $R_3S{\equiv}N$ thiazyls with R = Ar are stable towards heat and water and display a relatively high basicity and nucleophilicity.[63d]

Compounds **2** are thermally stable up to at least 300 °C.[22] Thermolysis of dilute hydrocarbon solutions of compounds **4** and **5** affords radicals **6** and their 1,3,2-isomers, respectively.[67a] Preparative thermolysis of a number of compounds **5** produces the corresponding benzotrithioles.[67b] Preparative photolysis (at 300 nm) of **2h**[22] and **5h**[67c] features the elimination of the sulfur atom (for **2h**, in combination with the opening of the carbocycle), leading to 2,4-hexadiene dinitrile[22] and unidentified products, respectively. Intermediates were not detected.[67c] Photolysis (at 436, 365, or 313 nm) of diluted hydrocarbon solutions of **4h** and **5h** gives radicals **6** and their 1,3,2-isomers, respectively.[67a]

Overall, the previously unmentioned propensity of neutral SN heterocycles such as **1**, **4**, **5**, and a number of others[67d] to form stable thiazyl radicals under relatively mild conditions is recognized.[52,67a,67d]

In solution, the radicals **6**, the photolytic and thermolytic products of compounds **1** and **4**, interact with dioxygen to give diphenyl disulfide derivatives bearing –N=S=O functions in the 2- and 2′-positions (Scheme 18). The kinetics of the decay of radicals **6** can be described by a self termination-like process with an effective second-order rate constant depending linearly on the concentration of dissolved O_2.[29a,52b]

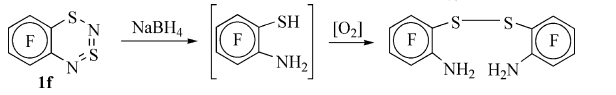


Scheme 18.

5.2 Reduction and Oxidation

Electrochemical reduction and oxidation of compounds **1**[23c,68] in the hydrocarbon and fluorocarbon series proceed at relatively low potentials (E_p^{1Red} = –0.87, –0.55 V; E_p^{1Ox} = 1.15, 1.44 V for **1h** and **1f**, respectively)[68] and lead to the corresponding radical ions. The radical anions are highly unstable, whereas the radical cations in the hydrocarbon series are rather long-lived and were characterized by ESR.[68] The redox properties of **1h** are similar to those of **5h** but very different from those of **2h**.[6,23c]

Chemical reduction of compounds **1** with $NaBH_4$ affords the corresponding 2-aminobenzenethiols isolated after oxidation in the form of 2,2′-diaminodiphenyl disulfides (Scheme 19).[29d]



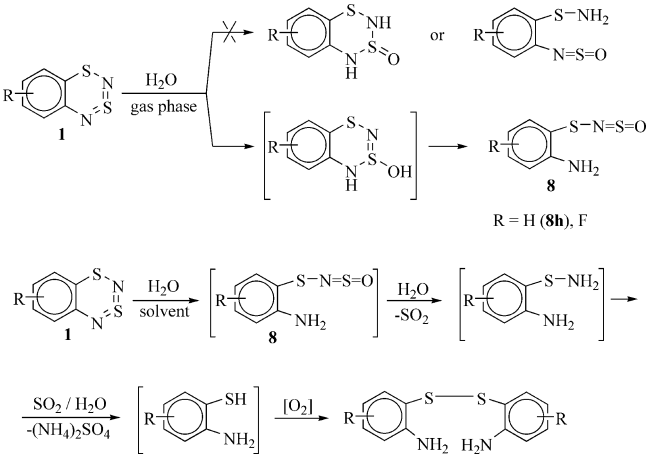
Scheme 19.

5.3 Reactions with Nucleophiles

For compounds **1**, only reactions with O- and P-nucleophiles are known.

O-Nucleophiles

Compounds **1**, which are solids under normal conditions, slowly add H_2O from the atmosphere to give 2-amino-*N*-sulfinylbenzenesulfenamides (**8**, Scheme 20), the first derivatives of the still unknown 2-aminobenzenesulfenamide.[69a,69b] The structures of the compounds have been confirmed by XRD.[69a,69b] Taking into account the high volatility of compounds **1**,[44,46a–46c] it is believed that, under macroscopically heterogeneous conditions, the addition of H_2O actually proceeds in the gas phase followed by the precipitation of solid products.[69] Seemingly, the kinetically unfavorable reaction conditions prevent compounds **1** from further hydrolysis (see below).



Scheme 20.

Traces of Ph_3Sb significantly facilitate the reaction and are critically important in the preparation of the parent **8h**.[69a,69b] In this case, the reaction seemingly proceeds on the solid phase surface.

The nonempirical Car–Parrinello molecular dynamics simulations performed for **1h** revealed a two-step process for the addition of H_2O. In a first step, a hydroxylated intermediate is formed, essentially by the addition of a water molecule to the S3=N4 bond. The second step involves the transfer of the proton of the OH group in the intermediate to N4, at which point the S3–N4 single bond is broken and **8h** is formed (Scheme 20). Other possible reaction products (Scheme 20) could be excluded on the basis of the energetic criteria.[69c]

It should be noted that neither 2-aminobenzenesulfenamide (an a priori useful synthon) nor its derivatives can be prepared in an obvious way, e.g. by the reduction of 2-

nitrobenzenesulfenamides or 1,2,3-benzothiadiazoles, because of the well-known instability of the sulfenamide S–N linkage even under the mildest reductive conditions.

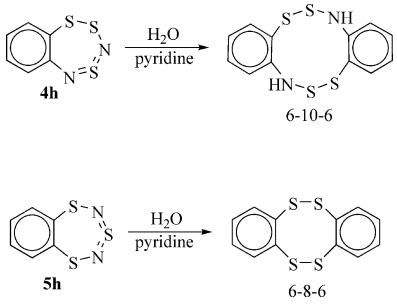
Prolonged (a few months) exposure of compounds **1** to air leads to 2,2′-diaminodiphenyl disulfides. In sealed glass tubes compounds **1** are practically infinitely stable.[57a]

The homogeneous hydrolysis of compounds **1** in organic solvents affords the corresponding 2,2′-diaminodiphenyl disulfides, including some previously unknown, as final products (Scheme 20).[29d] The most likely key intermediates are 2-aminobenzenesulfenamides and SO_2. The latter reduces the former to the corresponding thiols.

Overall, the formation of the dithiadiazine ring (sections 2.1 and 2.2) followed by its hydrolysis (or reduction, section 5.2) can be considered to be a useful method for both the *ortho*-thiolation of benzeneamines in the hydrocarbon series and the *ortho*-amination of benzenethiols in the fluorocarbon series[29d] (cf. also the related approach to the *ortho*-amination of polyfluoroaromatic amines via polyfluorinated compounds **2** and their naphtho congeners, Scheme 11).[29d,40] 2,2′-Diaminodiphenyl disulfides are suitable starting materials in the preparation of 1,5-benzothiadiazepines with antianginal and antihypertensive activities.[70] One can believe that their fluorinated derivatives have some prospects in the synthesis of currently unknown fluorinated 1,5-benzothiadiazepines with potentially useful pharmacological properties.

1-Butanol, even at its boiling point, does not react nucleophilically with either **1h** or **1f**.[48a]

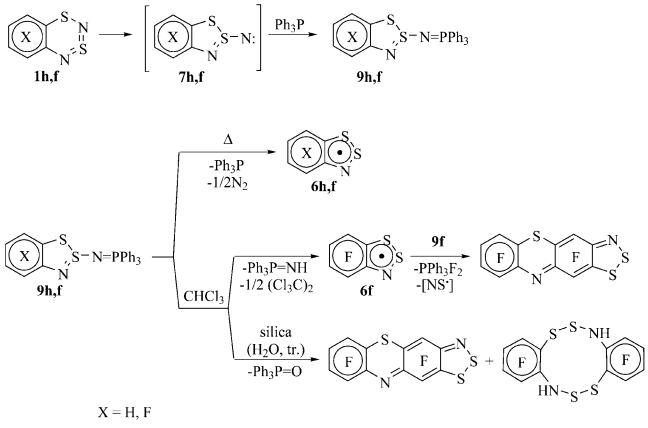
Compounds **2** are stable towards H_2O. They can even be prepared in aqueous media and redistilled with steam.[22] Compounds **5** are stable towards hydrolysis in neutral, weakly acidic, and weakly basic media, conditions under which the hydrolysis of compounds **4** proceeds very slowly.[39a,67b] However, in aqueous pyridine, the 6-7 bicyclic systems of **4h** and **5h** unexpectedly transform into 6-10-6 and 6-8-6 tricyclic systems, respectively (Scheme 21).[39] The structure of the 6-10-6 system is confirmed by XRD.[39a]



Scheme 21.

P-Nucleophiles

In both the hydrocarbon and fluorocarbon series, compounds **1** add Ph_3P in a 1:1 molar ratio to give Ph_3P=N–R iminophosphoranes (**9**, R = 1,2,3-benzodithiazol-2-yl; Scheme 22). The reaction can be explained by the oxidative imination of Ph_3P by the nitrenoids **7**. The structures of **9h**,**f** are confirmed by XRD. In both series they reveal π-stacking interactions between the R group and one of the Ph groups.[69b,71]



Scheme 22.

Seemingly, this unusual addition is kinetically driven. Thermodynamically, one could rather expect the aromatization of compounds **1** to the corresponding 10-π-electron 1,2,3-benzothiadiazoles by elimination of sulfur in the form of Ph_3P=S.

Reaction of **5h** with Ph_3P gives a mixture of unidentified products.[67c]

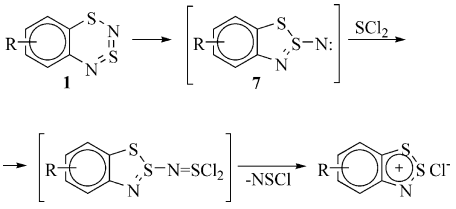
Generally, the addition of P-nucleophiles to SN compounds is very rare.[1,71] Reactions of cyclic and acyclic SN compounds with tertiary phosphanes and phosphites which lead to P=N derivatives are normally accompanied by partial or complete elimination of sulfur from the SN system, as a rule in the form of P=S derivatives.[11f,11g]

The derivatives **9** prepared by the addition of Ph_3P to compounds **1** display interesting properties. They form radicals **6** upon heating at 120 °C in dilute hydrocarbon solutions (Scheme 22), i.e., at lower temperatures than compounds **1**. Furthermore, in the fluorocarbon series they generate radicals **6**, detected by ESR, just upon being dissolved in $CHCl_3$ at ambient temperature. Further reactions in this solution lead to a 5-6-6-6 tetracyclic system isolated in 30% yield (Scheme 22; cf. Scheme 15). Chromatography of the $CHCl_3$ solution of **9f** on silica allows for the isolation of polyfluorinated 5-6-6-6 (cf. Scheme 15) and 6-10-6 (cf. Scheme 21) heterocyclic systems (Scheme 22). Their structures are confirmed by XRD.[48a,69b]

5.4 Reactions with Electrophiles

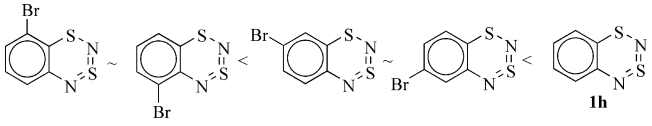
For compounds **1**, only reactions with S-electrophiles are known.

Reaction of compounds **1** with SCl_2 leads to Herz salts and NSCl (Scheme 23). The reaction can be explained by the oxidative imination of SCl_2 by nitrenoids **7** to give intermediate R–N=SCl_2 (R = 1,2,3-benzodithiazol-2-yl) derivatives. The latter eliminate NSCl to give the Herz salts[29c] (cf. the similar decomposition of $PhSO_2N$=SCl_2).[72]



Scheme 23.

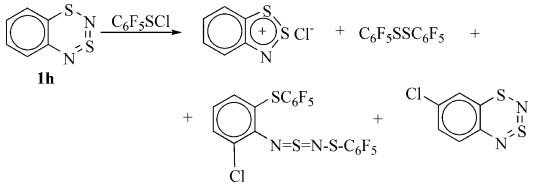
The reaction rate depends strongly on the nature and position of the substituent R in the carbocycle. For example, the 8-R isomers are systematically less active towards SCl_2 than the 6-R ones (R = Cl, Br, I). For R = Br, the relative rates estimated by competitive reactions are shown in Scheme 24. The discussed rate difference has preparative significance, as it allows for the separation of the minor 8-R isomers from the major 6-R ones from the reaction mixtures (section 2.1), which is accomplished by treating these with SCl_2 in an amount equimolar to that of the 6-R isomers.[29c,57a]



Scheme 24.

The reaction of compounds **1** with SCl_2 is a new preparative approach to Herz salts, which leads to much more pure samples of the target salts[29c,57a] than the classical Herz reaction.[3e,62,73]

Reaction of **1h** with C_6F_5SCl also leads to the corresponding Herz salt. In this case, however, several byproducts, including an acyclic SN derivative identified by XRD, are observed (Scheme 25).[57a] This SN derivative probably presents an interesting example of the additive ring-opening reaction of the compounds **1**.

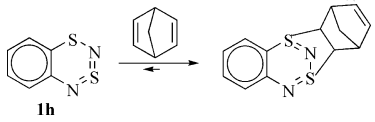


Scheme 25.

Compounds **1** do not react with electrophiles such as Me_3SiCl, which is a byproduct of their synthesis by the electrophilic ring-closure reaction (section 2.1).[29c] The same is also true for most of the cyclic and acyclic SN derivatives, including compounds **2**. In contrast, compounds **4** and **5** react with Me_3SiCl (**4**, slow; **5**, fast) to give Herz salts or their 1,3,2-isomers, respectively.[23b,39a,74]

5.5 Cycloaddition Reactions

Compound **1h** undergoes a reversible cycloaddition to norbornadiene (Scheme 26), $K_{diss.} = 5 \times 10^{-6}$ M ($CHCl_3$). The structure of the adduct is confirmed by XRD.[23c]



Scheme 26.

Compound **5h** adds norbornadiene in the same way.[23c] However, it is inactive towards various unsaturated compounds with a broadly varied stereoelectronic demand.[67c]

Compound **2h** reacts with 1,2-dimethylacetylenedicarboxylate to give a quinoxaline derivative, seemingly by means of a 1,3-cycloaddidion followed by elimination of sulfur. Reaction with dehydrobenzene gives a 1,2-benzisothiazole derivative. In both cases the yields are low.[22b]

The available data are obviously not enough for a reliable estimation of the synthetic potential of compounds **1** and **5** in cycloaddition reactions. As a preliminary guess, however, this potential can be estimated as rather moderate.

On the other hand, various cycloaddition reactions are strongly inherent of acyclic N=S=N derivatives which can serve as 2π (N=S) or 4π (N=S=N) components.[11f,75] In this context, compounds **4** lacking cyclic π-conjugation might be of special interest.

5.6 Other Chemical Properties

In contrast to acyclic N=S=N derivatives,[11f,11g] compounds **1** cannot be desulfurized by Zn in boiling toluene, i.e., their aromatization to 10-π-electron 1,2,3-benzothiadiazoles does not proceed under these conditions.[71]

Despite favorable values of IE_1 and EA_1,[46a–46c,68] nothing is known about the charge-transfer complexes and/or the radical ion salts of compounds **1**.

Compound **1h**, the hetero analogue of naphthalene, does not form π-stacked molecular complexes with octafluoronaphthalene, whereas the complex between $C_{10}H_8$ and $C_{10}F_8$ forms very readily.[33]

Compound **5h** does not produce charge-transfer complexes with either electron acceptors or electron donors.[23c]

6. Conclusions

One can conclude that the heteroatom chemistry of 1,3,2,4-benzodithiadiazines is very promising despite its infancy. The heteroatom reactivity of these compounds is high and varied, and the structurally diversified reaction products can hardly be predicted. Therefore, the heuristic aspects of this chemistry are especially exciting.

Overall, the combination of sulfur and nitrogen atoms allows for the design of various acyclic and cyclic π-systems (both aromatic and antiaromatic), including extended ones, by the substitution of the carbon atoms of unsaturated organic compounds. For example, $H_2C=C=CH_2$ and naphthalene can be transformed into HN=S=NH[76] and 1,3,2,4-benzodithiadiazine, respectively. With benzene, complete substitution yields the S_3N_3 ring system, which is known in

the cationic (8π),[77] radical (9π),[77] and anionic (10π)[9,78] states, whereas incomplete substitution provides 8-π-electron 1,3,2,4,6-dithiatriazines.[79] Particularly interesting 16-π-electron 5-6-5 tricyclic systems of the 1,3,2- and 1,2,3-dithiazole-types can be derived from anthracene with the contraction of two rings, and they exhibit a biradical, quinoidal, or zwitterionic ground state.[80] As one can see, the currently designed and synthesized species are extremely diverse. They are represented by neutral molecules, cations, anions, neutral radicals, radical cations, radical anions, nitrenoids, molecular complexes, etc. The resulting SN chemistry, including the part involving the title compounds, is very rich. The carbon-substitution approach can ultimately lead to the complete exclusion of carbon from organic chemistry without substantially affecting its conceptual and methodological basis. The resulting "carbon-less organic chemistry" (frequently, a paradox explains things much more clearly than any definition) or "metal-less inorganic chemistry" will no doubt bring a substantial amount of new fundamental results in the nearest future.

Acknowledgments

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