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A New Thiatriazine Isomer: Synthesis, Tautomerism, and Molecular Structure of 3,6-Diphenyl-4*H*-1,2,4,5-thiatriazine as a Precursor to the 1,2,4,5-Thiatriazinyl Radical

John M. Farrar, Mahesh K. Patel, and Piotr Kaszynski*

Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Victor G. Young, Jr.

X-ray Crystallographic Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The diphenyl derivative of 4*H*-1,2,4,5-thiatriazine (**5**) was prepared by oxidative cyclization of **9**. The molecular structure of **5**, obtained by X-ray diffraction [orthorhombic, $Pna2_1$, $a = 9.7746(13)$ Å, $b = 21.692(2)$ Å, $c = 5.6580(8)$ Å], compares favorably with that predicted with ab initio calculations. The thiatriazine **5** was used as a precursor to the 3,6-diphenyl-1,2,4,5-thiatriazinyl radical (**4**) through either oxidation with PbO_2, or conversion to and reduction of sulfiminyl chloride **6** with Ph_3Sb. The weak ESR quintet ($a_N = 1.03$ mT, $g = 2.0103$) observed in the latter case correlates well with the molecular structure of **4**, but the results of DFT calculations are ambiguous. Ab initio calculations show that 4*H*-1,2,4,5-thiatriazine (**I**-**4*H***) is the most stable tautomer and is the second most stable isomer among the six possible thiatriazines. All isomeric thiatriazinyl radicals exhibit similar spin distribution patterns. 1,2,4,5-Thiatriazinyl radical (**I**-**R**) is calculated to be 23.1 kcal/mol less stable than the most stable 1,2,4,6 isomer **II**-**R**.

Introduction

Liquid crystalline radicals are rare, and those with a π-delocalized neutral spin are still unknown.[1] We have focused on the $-N-S-$ fragment as a spin source and designed new sulfur−nitrogen heterocyclic rings which are potential structural elements for this class of materials.[2] 1,2,4,5-Thiatriazine (**I** in Figure 1) is one such ring whose properly 3,6-disubstituted ("para") derivatives satisfy the geometric requirements of calamitic liquid crystals.[3,4]

A literature search shows that thiatriazines **II**−**VI** are known ring systems and the derivatives of 1,2,4,6-thiatriazine (**II**) are the most abundant.[5,6] The majority of the known thiatriazine derivatives are cyclic sulfon-

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* To whom correspondence should be addressed. Phone/fax: (615) 322-3458. E-mail: PIOTR@ctrvax.vanderbilt.edu.

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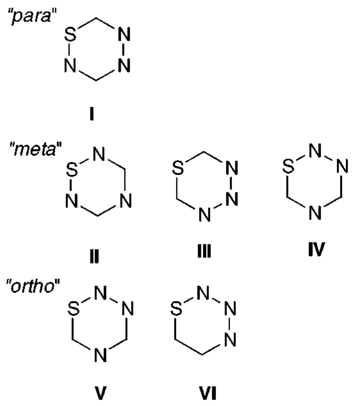
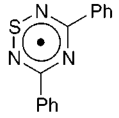


Figure 1. Six thiatriazine ring systems with carbon atoms in the para, meta, and ortho positions.

amides and parts of fused ring systems. Single-ring thiatriazines containing a two-coordinated sulfur atom are rather rare, and those with six, seven, or eight π electrons in the six-atom heterocyclic structure are scarce. For instance, there are only a few examples of such π systems with **II**,[7] **III**,[8,9] and **V**[10] skeletons in addition to our recently reported derivative of **I**.[2]

Although all thiatriazines **I**−**VI** can, in principle, form seven π electron radicals, only derivatives of **II** have been studied in this context.[11] 3,5-Disubstituted 1,2,4,6-thiatriazinyls, and among them the diphenyl derivative **1**,[12] are persistent and thermally stable radicals. They have been obtained by one-electron reduction of the cyclic sulfinimidoyl chlorides such as **2**, which can be prepared from the corresponding sulfenamide **3**.[7]

To assess the usefulness of thiatriazinyl **I** as a structural element for liquid crystals, we set out to study 3,6-diphenyl-1,2,4,5-thiatriazinyl (**4**), the para isomer of **1**, which, in principle, could be accessed from the corresponding 4*H*-1,2,4,5-thiatriazine **5** or chloride **6**.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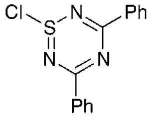
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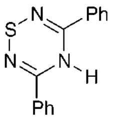
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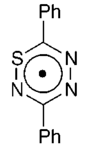
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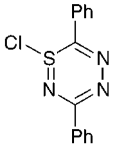
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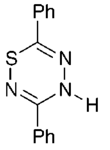
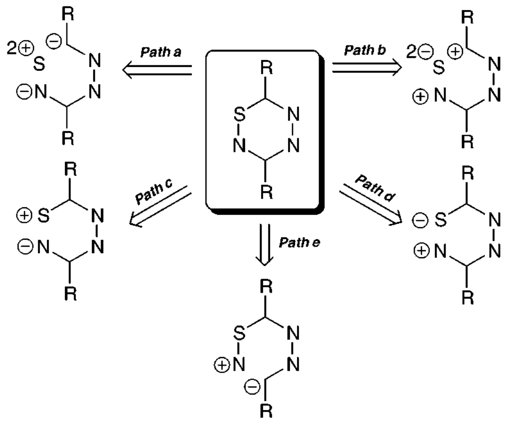

5

Here we describe the methodology for construction of the 1,2,4,5-thiatriazine ring and report the synthesis and molecular and crystal structures of its 3,6-diphenyl derivative **5**. The experimental data are compared with the results of ab initio calculations, which assess the stability of the tautomeric forms for **5** and compare its thermodynamic stability with the five other regioisomers. We also investigate the formation of the chloride **6** and the generation of radical **4**. We compare the experimental ESR spectra with those calculated and discuss the relative stabilities of **1** and **4** in the context of the remaining members of the thiatriazine series.

Scheme 1



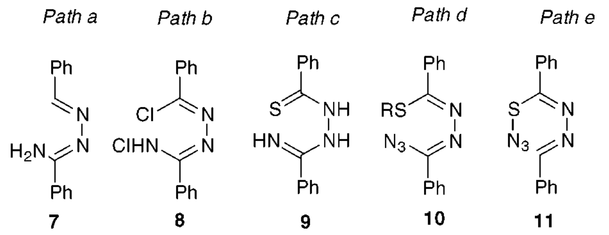


Figure 2. Possible intermediates for routes to **I** shown in Scheme 1.

Results and Discussion

Retrosynthetic Analysis for the 1,2,4,5-Thiatriazine Ring Closure. Scheme 1 shows a retrosynthetic analysis of **I** with five indicated possible routes, and Figure 2 presents likely intermediates for each approach. The critical N−S bond can be formed at different stages of the ring construction, but due to its sensitivity, it is preferably formed at the last step in either a bimolecular reaction (path a and path b) or a intramolecular cyclization reaction (path c and path d).

The formation of the thiatriazine ring in path a follows the preparation of other ring systems,[13,14] the heterocyclic ring of **6** could be formed through a condensation reaction of 1-amino-1,4-diphenyl-2,3-diaza-1,3-butadiene[15] (**7**) with SCl_2, in which the initially formed sulfinimide inserts into the iminyl =C−H bond. Alternatively, the sulfur center may act as a nucleophile and react with 1-chloro-4-(*N*-chloroamino)-1,4-diphenyl-2,3-diaza-1,3-butadiene (**8**) to form **5**, according to path b.

In path c the N−S bond of **5** can be formed from thiobenzoyl derivative **9**[16] via the corresponding sulfenyl halide, which cyclizes to form the thiatriazine. Another

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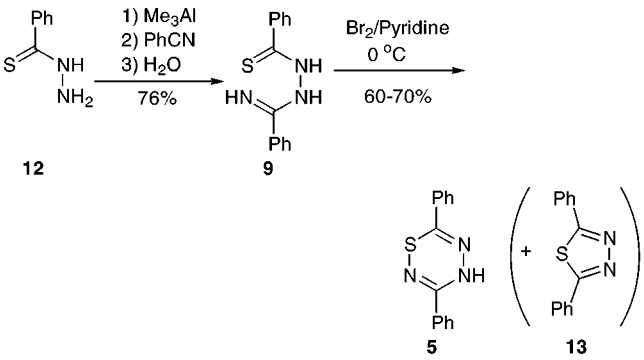
Scheme 2



possibility for thiatriazine ring closure of **I** and preparation of **5** arises from decomposition of azide **10** and the intramolecular nitrene reaction with the sulfur functionality and elimination of an alkene (path d).

Alternatively, the insertion of a nitrogen atom (path e) to form the N−C bond can be envisioned using sulfenyl azide **11** (obtained from the corresponding sulfenyl halide and an azide) in an way analogous to that of a similar ring closure reaction.[17] The intermediate sulfenyl nitrene should insert into the iminyl =C−H bond in the final step.

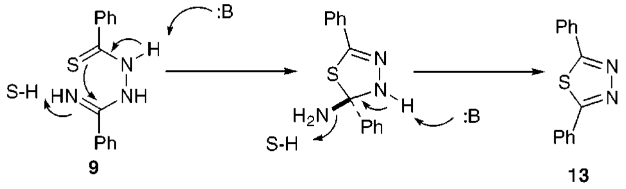
All five approaches were investigated in some detail, but only path c led to the efficient preparation of **I** as 4*H*-1,2,4,5-thiatriazine **5**. Attempts at generation of **I** along path d led to unexpected results described elsewhere.[18]

Synthesis of 5. *N*-Thiobenzoylbenzamidrazone[16] (**9**), an intermediate to **5** in path c, was obtained in 76% yield from thiobenzhydrazide[19] (**12**) and benzonitrile in the presence of 2 equiv of trimethylaluminum. This new preparation of **9** represents a successful extension of the original method[20] developed for benzhydrazide and benzamidrazone to their sulfur analogue thiobenzhydrazide (**12**).

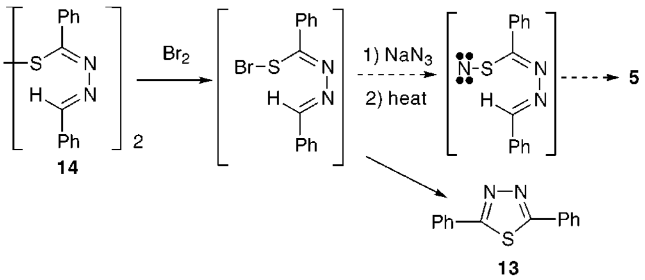
Treatment of benzamidrazone **9** with bromine in the presence of pyridine gave 3,6-diphenyl-4*H*-1,2,4,5-thiatriazine (**5**) along with 2,5-diphenyl-1,3,4-thiadiazole (**13**) as shown in Scheme 2. The ratio of **5**:**13** is sensitive to the reaction conditions. The highest yields of thiatriazine **5** (up to 70%) with less than 10% of the byproduct **13** were obtained at 0 °C and using a large excess of pyridine. However, the most reliable results and yields up to 50% were obtained using 0.5 equiv of bromine. When stoichiometric amounts of pyridine and bromine were used, the yields significantly varied from run to run and ranged from 10% to 45%.

The cyclization reaction is considered to proceed through a sulfenyl halide intermediate. There are numerous examples of such oxidative N−S bond formation reported for the five-membered heterocycles,[21,22] but there are only a few similar examples for the six-membered rings.[23−25]

Scheme 3



Scheme 4



Other oxidants and bases were ineffective in the generation of thiatriazine **5**. In the case of NCS, *t*-BuOCl, and I_2/pyridine as oxidants, the predominant product was thiadiazole **13**, and only traces of the desired **5** were detected at best. An attempt to obtain **5** by initial deprotonation of **9** with NaH followed by treatment with iodine or SO_2Cl_2 as oxidants resulted in the preferential formation of **13** (43% yield), while the desired product was isolated in less than 7% yield. The exclusive formation of **13** was observed when **9** was treated with pyridine or under acidic conditions.[16] We have found that about 80% of **9** was converted into **13** upon storage at room temperature for over a year. Thiatriazine **5** also shows contamination with thiadiazole **13** after prolonged storage.

The formation of the thiadiazole ring of **13** can be rationalized by intramolecular attack of the thiolate anion on the amidinyl carbon atom and loss of ammonia after proton transfer (Scheme 3). Running the reaction under neutral or weakly acidic conditions disfavors the formation of the five-membered ring, and **5** becomes the major product.

Another approach to **5** through disulfide **14** was briefly investigated (path e). The disulfide **14** was envisioned to react with bromine followed by treatment with trimethylsilyl or sodium azide to yield sulfenyl azide **11**, which via a nitrene insertion into the carbon−hydrogen bond would form **5** (Scheme 4).

Treatment of **14** with 0.5 equiv of Br_2 in CCl_4 produced a mixture characterized by a complex NMR spectrum, which was much simplified when 1 equiv of Br_2 was used. In both spectra, the resonance at 8.32 ppm assigned to the N=C−*H* proton was absent and the multiplet corresponding to the ortho hydrogens was shifted downfield from about 7.7 to about 8.1 ppm. Such a shift may indicate that upon bromination an intramolecular cyclization occurs and the thiadiazole ring of **13** is formed. This is not an unexpected result considering a great tendency of divalent sulfur-containing species to close

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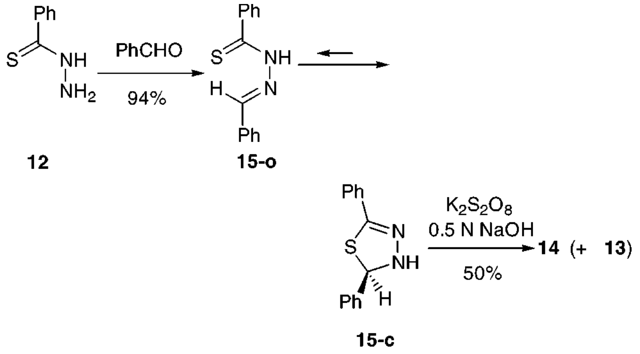
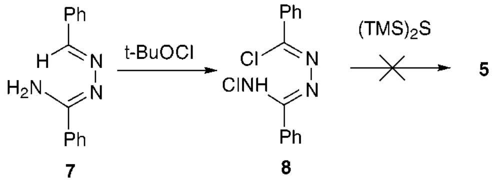
Scheme 5



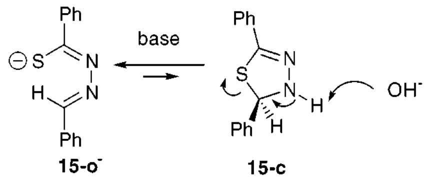
Scheme 6



five-membered rings such as thiadiazole.[26] This attempt was not investigated any further.

The synthesis of **14** was accomplished via modification of the procedure described by Holmberg[27] (Scheme 5). The structure of the disulfide was confirmed by NMR analysis, which showed a sharp peak at 8.32 ppm characteristic of the N=C−*H* proton and two carbon resonances at 160.2 and 166.5 ppm, which can be ascribed to the iminyl N=*C*−H and thioimidyl N=*C*−S groups, respectively. These NMR absorptions are absent in **15**, the precursor to **14**, whose spectra are consistent with the 1,3,4-thiadiazoline tautomeric form **15-c** rather than with the hydrazide **15-o**.[28,29]

It has been reported that oxidation of **15** under acidic or neutral conditions leads to the exclusive formation of 1,3,4-thiadiazole (**13**),[27,30] while the conversion to **14** requires the presence of a base.[27] NMR analysis of the crude reaction product obtained under the latter conditions indicated the presence of significant amounts of **13**. As was demonstrated before,[29,30] base shifts the tautomeric equilibrium to the open form anion **15-o**$^-$, which then apparently undergoes a persulfate oxidation to **14**.



Finally, the synthesis of thiatriazine **5** was attempted using dichloride **8** and $(TMS)_2S$ as a source of S^{2-} as shown in Scheme 6 (path b in Figure 1). The sulfide anion was generated in situ by treating a mixture of dichloride **8** and $(TMS)_2S$ with Bu_4NF (1 M in THF) according to a general procedure.[31] Alternatively, a suspension of anhydrous Li_2S in THF was prepared from $(TMS)_2S$ and MeLi[32] and reacted with dichloride **8**. No traces of thiatriazine **5** nor starting **8** were observed in either reaction. A similar negative result was obtained when **8** and $(TMS)_2S$ were refluxed in dry benzene for several hours. These reactions were not investigated further.

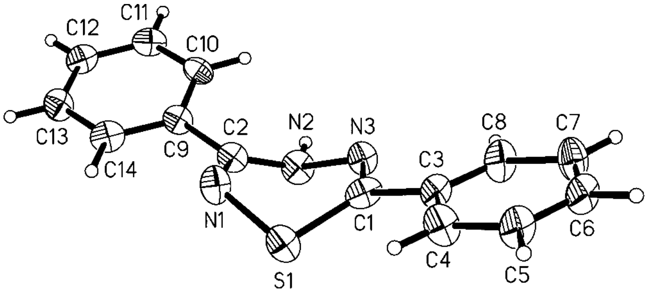


Figure 3. Thermal ellipsoid diagram of **5**. Ellipsoids are drawn at 50% probability, and hydrogen atoms are given arbitrary radii.

Dichloride **8** was obtained in 22% yield by chlorination of amidrazone **7** with *tert*-butyl hypochlorite in methylene chloride (Scheme 6). Although the formation of the *N*,*N*-dichloro isomer is also possible, the spectroscopic data are fully consistent with the structure of **8**. The IR spectrum of **8** exhibits a single peak at 3287 cm^{-1} characteristic of a secondary amine. The N−*H* proton peak appears in the ^{1}H NMR spectrum as a broad singlet at 9.64 ppm, while the imine peak in the starting **7** at 8.57 ppm is absent. The position of the peak of the benzylidene carbon atom in **7** (155 ppm)[33] is substantially shifted upfield in **8** to 132 ppm, while the chemical shift of the amidrazonyl carbon in **7** (159 ppm)[33] is less affected by the chlorination of the nitrogen atom and is shifted downfield by 4 ppm.

N-Benzylidenobenzamidrazone (**7**) was conveniently prepared in 53% yield using an adaptation of a literature procedure in which benzaldehyde was used instead of acylamino α-ketoester.[34] The acyclic structure of **7** was confirmed by NMR analysis.[33]

Molecular and Crystal Structures for 5. X-ray analysis[35] of a single crystal of **5** confirmed its anticipated molecular structure and revealed the 4*H* tautomer of the puckered 1,2,4,5-thiatriazine ring (Figure 3). The experimental details are collected in Table 1, and a summary of the bond lengths and angles for **5** is given in Table 2.

The thiatriazine ring in **5** adopts a boatlike or "open book" conformation characteristic of eight-π-electron six-atom heterocyclic 1,4-dienes.[7,8,36,37] The ring is folded along the S(1)···N(2) axis by about 45°, and the two halves of the open book are nearly coplanar with torsional angle values of 6.2(6)° for the S(1)−N(1)−C(2)−N(2) and 3.2(6)° for the S(1)−C(1)−N(3)−N(2) fragments. The S(1) and the N(2) atoms are displaced from the plane of the remaining ring atoms by about 0.62 and 0.47 Å, respectively.

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Table 1. Crystal Data and Summary of Data Collection for 5

empirical formula	$C_{14}H_{11}N_3S$	θ for data collectn (deg)	$1.88 \leq \theta \leq 25.06$
fw	253.32	index ranges	$0 \leq h \leq 11$, $0 \leq k \leq 25$, $-6 \leq l \leq 6$
cryst habit, color	prism, yellow	total no. of reflns	6251
cryst dimens	0.22 × 0.05 × 0.05 mm	no. of independent reflns	2123 ($R_{int} = 0.0596$)
space group	$Pna2_1$ (no. 33)	refinement method	full-matrix least-squares on F^2
cell dimens (Å)	$a = 9.7746(13)$ $b = 21.692(2)$ $c = 5.6580(8)$	abs correctn max and min transitn abs structure param	SADABS (Sheldrick, 1996) 1.00 and 0.414 0.1(2)
V (Å^3)	1199.7(3)	no. of data/restraints/params	2121/2/167
Z	4	R indices ($I > 2\sigma(I) = 1506$)	R1 = 0.0679, Rw2 = 0.1608
calcd density (g/cm^3)	1.403	R indices (all data)	R1 = 0.0900, Rw2 = 0.1722
abs coeff (mm^{-1})	0.253	goodness-of-fit on F^2	0.952
F(000)	528	max/min peak in final diff map (e$^-$/Å^3)	0.879/−0.619

Table 2. Selected Experimental and Calculated Bond Lengths (Å) and Angles (deg) for 5

distance	exptl	calcd[a]	angle	exptl	calcd[a]
S(1)−N(1)	1.705(5)	1.710	C(1)−S(1)−N(1)	100.0(2)	99.7
N(1)−C(2)	1.308(6)	1.262	S(1)−N(1)−C(2)	114.1(3)	116.7
C(2)−N(2)	1.371(6)	1.384	N(1)−C(2)−N(2)	122.0(4)	123.1
N(2)−N(3)	1.434(6)	1.389	C(2)−N(2)−N(3)	118.2(4)	119.3
N(3)−C(1)	1.282(6)	1.256	S(1)−C(1)−N(3)	120.7(4)	120.8
C(1)−S(1)	1.754(6)	1.775	$\phi(1)$, $\phi(2)$[b]	8, 30	29, 37
C(1)−C_{Ph}	1.480(7)	1.487	α[c]	45	40
C(2)−C_{Ph}	1.496(7)	1.490	S(1): θ[d] (t[e])	146 (0.62)	152 (0.53)
S(1)···N(2)	2.77	2.812	N(2): θ[d] (t[e])	139 (0.47)	144.5 (0.41)

[a] Gas-phase calculation (HF/6-31G*) at the C_1 symmetry. [b] Angles between the planes of three-atom fragments S(1)−C(1)−N(3) and N(1)−C(2)−N(2) and the planes of phenyl rings attached to them. [c] Ring puckering angle defined as an average angle between the S(1)−N(1)−C(2)−N(2) and S(1)−C(1)−N(3)−N(2) planes. [d] The X−*−* angle in which asterisks are the midpoints between the C(1)···N(1) and C(2)···N(3) atoms. [e] Approximate distance of the atom from the C(1)−N(3)−C(2)−N(1) plane.

The intraring bond lengths correspond to S−C, S−N, C−N, and N−N single bonds and C=N double bonds and are consistent with the structure of the 4*H* tautomer. For instance, the S(1)−C(1) and S(1)−N(1) distances (1.754(6) and 1.705(5) Å) in **5** are close to the values of 1.770(3) and 1.689(2) Å observed for the analogous S−C$^{(sp^2)}$ and S−N$^{(sp^2)}$ bonds in an acyclic *N*-sulfenyl ketimine.[38] Similarly, the imine C=N bond length of the *N*-sulfenyl ketimine[38] is consistent with those for C=N double bonds found in **5**.

The ring internal angles are within expectation. The angle centered on the sulfur atom (100.0(2)°) is typical for organic sulfides and consistent with that of 98.2(1)° found for the analogous acyclic fragment C$^{(sp^2)}$−S−N$^{(sp^2)}$ in acyclic *N*-sulfenyl ketimine.[38] The ring carbon atoms and their three substituents are coplanar within experimental error, confirming their sp^2 hybridization.

The proton of the N(2) atom was refined positionally, but it refined to about 0.75 Å instead of the usual 0.90 Å length. This was fixed at 0.90(2) Å, still allowing the proton to find its best position.

The phenyl rings are rotated relative to the planes defined by the adjacent thioiminyl and amidinyl fragments by 8° and 30°, respectively. The higher torsional angle observed for the ring attached to the C(2) carbon may reflect the steric interactions of the phenyl ring with the N(2) hydrogen atom.

The crystal structure appears to be composed of infinite chains of hydrogen-bonded groups through the ring nitrogen atom, N(2). The proton points close to the midpoint between the S(1) and N(2) atoms weighted for the van der Waals radii, forming 80° and 100° angles, respectively. The distances from the proton to the neighboring N(2) and S(1) atoms are 2.45 and 2.98 Å, respectively, which corresponds to 89% and 102% of the van der Waals separation.[39]

The gas-phase ab initio geometry for **5** matches the experimental solid-state results well, and the comparison is shown in Table 2. The calculations predict a boatlike conformation for the heterocycle with similar puckering angles α and θ. The calculated distances are generally larger on average by 0.010 Å. The noticeable differences are observed for the N(1)−C(2) and N(2)−N(3) distances. The smaller experimental dihedral angles ϕ are presumably due to their compression in the crystal as compared to the gas-phase environment used in the calculations. In both cases, however, the angle between the phenyl ring and the three-atom fragment centered on C(2), ϕ_2, is large and reflects the H(12)···Ph steric interactions.

A comparison of the calculated geometries for the parent ring with its diphenyl derivative **5** shows that the introduction of the phenyl substituents has relatively little effect on the ring geometry. The most affected are the two carbon atoms, C(1) and C(2), whose bonding distances to the neighboring atoms are slightly expanded by about 0.01 Å, and the intraring angles centered on the carbon atoms are contracted by about 3°. The dihedral angle between the two halves of the open book conformation is expanded by about 4°.

Attempted Generation of Radical 4 from 5 and 7. Treatment of the 4*H*-thiatriazine **5** with lead dioxide/potassium carbonate[40,41] or thianthrenium perchlorate/pyridine[2] failed to generate radical **4** (Scheme 7), and the starting material was recovered. Negative results were also obtained by initial deprotonation of **5** with NaH followed by reaction of the resulting anion with iodine or silver triflate. No ESR signal was observed.

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(38) Pirozhenko, V. V.; Chernega, A. N.; Boldeskul, I. E.; Yufit, D. S.; Antipin, M. Y.; Struchkov, Y. T.; Talanov, V. S.; Shermovich, Y. G. *J. Gen. Chem. USSR* **1983**, *53*, 325.

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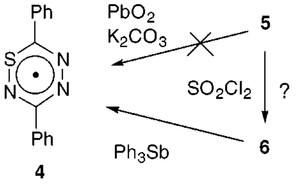
(40) Miura, Y.; Yamano, E.; Tanaka, A.; Yamauchi, J. *J. Org. Chem.* **1994**, *59*, 3294.

(41) Markovskii, L. N.; Talanov, V. S.; Polumbrik, O. M.; Shermolovich, Y. G. *J. Org. Chem. USSR* **1981**, *17*, 2338.

Scheme 7



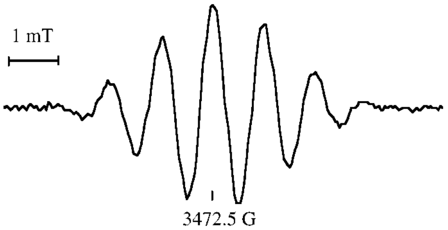
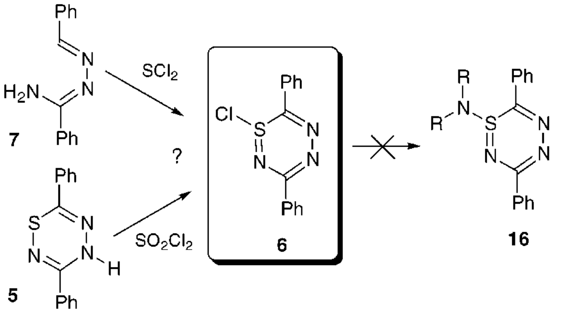


Figure 4. ESR spectrum of a radical obtained from **5** (see the text).

Scheme 8



Since the direct oxidation of **5** was unsuccessful, it was hoped that radical **4** could be generated by reduction of the chloride **6** with triphenylantimony, according to a general procedure.[12] The synthesis of chloride **6** was envisioned from 4*H*-thiatriazine **5** by treatment with sulfuryl chloride, conditions described for preparation of the analogous chloride **2** from **3**,[7] or amidrazone **7** in reaction with sulfur dichloride (path a in Figure 1) under general conditions.[13,14]

Addition of SO_2Cl_2 to a solution of **5** in acetonitrile resulted in the immediate appearance of an orange color, presumably **6**, which bleached within a few seconds at ambient temperature. The orange color is characteristic of cyclic sulfinimidoyl chlorides, which are thermally unstable species that readily decompose in solution unless excess chlorine or SCl_2 is present.[13,14] The bleaching was slower at −40 °C and still slower in methylene chloride at −78 °C. Treatment of the latter reaction mixture with triphenylantimony caused a color change to dark green and the appearance of a weak ESR signal (Figure 4).

Amidrazone **7** was treated with 2 equiv of sulfur dichloride in methylene chloride containing a stoichiometric amount of pyridine at −78 °C. Upon addition of SCl_2 the solution became dark orange and changed to pale yellow when treated with Ph_3Sb. No ESR signal was obtained.

In an attempt to demonstrate the presence of chloride **6** in the reaction mixture obtained from **5**, the orange solution was treated with either *N*-trimethylsilylmorpholine or *N*,*N*-dimethyl-*N*-trimethylsilylamine (Scheme 8). In both cases a complex mixture of products was formed, and the expected[7,14,42] adduct **16** could not be isolated.

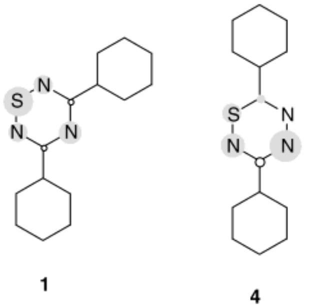


Figure 5. Calculated (B3LYP/6-31G*) total spin density maps for **1** and **4**.

The radical generated from thiatriazine **5** was obtained in about 1% yield based on ESR signal integration. It persists for several hours in solution and shows little sensitivity to oxygen but is immediately quenched upon filtration through a silica gel, alumina, or Florisil plug under a nitrogen atmosphere.

The ESR signal of the radical consists of five well-defined lines[43] with a hyperfine coupling (hfc) of a_N = 1.03 mT and a relatively large g = 2.0103 (Figure 4) and is consistent with the structure of **4**. The latter value compares to g = 2.0059 measured for radical **1**,[12] an isomer of **4**. The two g values, however, do not correlate well with the calculated spin concentrations on the sulfur atom in **4** and **1**, which are 0.27 and 0.37, respectively.

The assignment of the ESR spectrum to the cyclic structure of **4** was aided with DFT calculations, which were found to be well suited for analysis of cyclic thioaminyl radicals such as **1** and **4**.[44] The distributions of spin densities in heterocyclic rings **1** and **4** are similar. Atoms 3 and 5 (positions meta to sulfur) are at nodal positions and have only small negative values (Figure 5). This results in only two nitrogen atoms with significant spin densities in **4**, and a quintet pattern for the ESR spectrum is expected.

The results of the hfc calculation for **4** turned out to be rather ambiguous. Analysis of scaled Fermi contact values for **1** at the planar C_{2v} ground state shows that the two types of nitrogen atoms, N(2,6) and N(4), exhibit close hfc's of 12.75 and 13.16 MHz, which yield an average value of 12.96 MHz.[44] This compares reasonably well with the experimental hfc value of 11.15 MHz for the septet, and the geometry is in agreement with the planar molecular structure of the radical **1** in its dimer.[12] The calculations show low sensitivity to conformational changes, and the hfc values obtained for the staggered orientation of the phenyl rings are slightly higher by 0.6 MHz. Similar values were obtained for the radical when the UHF/6-31G* geometry was used in the Fermi constant calculations (B3LYP/6-31G*//UHF/6-31G* level of theory).

In contrast to **1**, hfc values calculated for radical **4** are sensitive to changes in the molecular geometry. Geometry optimization performed at the UHF/6-31G* level yields a planar structure of 3,6-diphenyl-1,2,4,5-thiatriazinyl

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[42] Kornuta, P. P.; Derii, L. I.; Markovskii, L. N. *J. Org. Chem. USSR* **1980**, *16*, 1130.

[43] Alternatively, the spectrum may be interpreted as a septet if the weak features on the edges of the spectrum are included. This would require three nitrogen atoms with similar hfc's.

[44] Kaszynski, P. Submitted for publication.

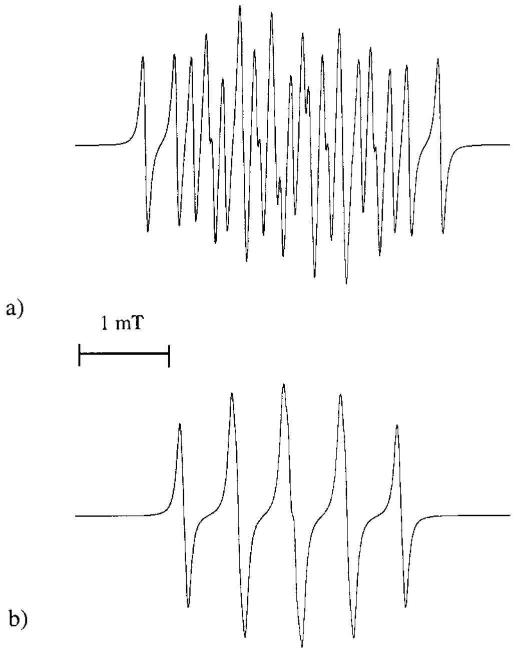

Figure 6. Simulated ESR spectra for **4** based on hfc values obtained from (a) B3LYP/6-31G* (a_N = 15.58, 22.03, 10.17 MHz), and (b) B3LYP/6-31G*//UHF/6-31G* (a_N = 16.69, 18.49, 0.8 MHz) calculations. Line width 0.5 G, $g = 2.0059$.

(**4**), while the same optimization on the B3LYP/6-31G* level of theory predicts a puckered thiatriazinyl ring along the S(1)···N(4) line (24°) and the C(6)−Ph dihedral angle of 17°. Spin densities (Figure 5) calculated for both geometries at the B3LYP/6-31G* method are similar and within 10%, while the Fermi constants differ significantly. The largest difference is observed for the N(5) atom, which has a low Fermi contact value (0.84 MHz) for the planar UHF geometry, while in the puckered B3LYP geometry this value is an order of magnitude larger (10.17 MHz). The average hfc values for the N(2) and N(4) atoms are 0.67 and 0.62 mT for the two geometries. This large difference in the hfc values for the N(5) atom results in two significantly different ESR spectra as is shown in Figure 6.

The pattern of the weak ESR signal generated from **5** is similar to the quintet shown in Figure 6b, but the hfc's are significantly different. While the experimental spectrum shows a_N = 1.03 mT, the predicted value is a_N = 0.67 mT, which is in line with the hfc observed in **1** (a_N = 0.397 mT). Thus, considering the concentration of the radical and the hfc, the evidence for the assignment of the spectrum to radical **4** is weak at best.

Hydrogen atoms of the phenyl rings in **1** and **4** show only small spin concentrations, and the largest hfc values ($a_H > 0.07$ mT) are predicted for the ortho and para hydrogens. No hydrogen splitting is observed in the spectrum of **1**.[12]

Comparison of 4 and 5 with Other Thiatriazines. A comparison of isomeric thiatriazines provides useful information and serves as a predictive tool for future exploration of this class of compounds.

Tautomers. The thermodynamic stability of the **I-4*H*** tautomer was compared with those for the remaining 2*H* and 6*H* tautomers, and their optimized geometries and relative energies are shown in Figure 7. The 4*H* tautomer appears to be most stable, presumably by allowing for the low-energy distortion from planarity and forming the boat conformation. This is certainly consistent with tautomeric preferences for other eight-π-electron six-membered heterocyclic 1,4-dienes, which all form boatlike conformations, avoiding the ring planarity and the unfavorable electronic conjugation of eight π electrons. The planarization energies for the thiatriazine tautomers are not high, and the ΔSCF for the planar and boat **I-4*H*** is 3.1 kcal/mol, while the same energy difference calculated for the 2*H* tautomer is 4.1 kcal/mol.

A comparison of the relative SCF energies of the 4*H*-1,2,4,5-thiatriazine with other isomeric 4*H* tautomers[45] shown in Figure 8 indicates that the 4*H*-1,2,4,6-thiatriazine **II-4*H*** is the most stable and the 1,2,4,5 isomer **I-4*H*** is the next most stable in the series. In general, the relative stability of the thiatriazines roughly correlates with the ring folding angle α (Figure 8) and also decreases as the S−N bond length increases. Among the thiatriazines the least stable is 4*H*-1,2,3,4-thiatriazine (**VI-4*H***).

Radicals. Calculations at the B3LYP/6-31G* level of theory predict that the 1,2,4,5-thiatriazinyl (**I-R**) is less stable by 23 kcal/mol than the most thermodynamically stable thiatriazinyl radicals **II-R** (Figure 9). Other radicals, except for **VI-R**, show similar low stability relative to that of **II-R**, and the 1,2,3,5-thiatriazinyl (**IV-R**) appears to be the second most stable among the thiatriazinyls. No minimum on the potential energy surface corresponding to the 1,2,3,4-thiatriazinyl (**VI-R**) was found, and instead the radical undergoes loss of an N_2 molecule. Radical **IV-R** shows a significantly elongated S−N bond (2.03 Å), and it can be considered to be an intramolecular adduct of a thiyl radical to the diazo group. Similarly, the S(1)−N(2) bond in **V-R** is longer by about 0.1 Å as compared to the typical value of 1.69 Å.

Radicals **II-R** and **V-R** are planar according to normal-mode analysis, while the remaining radicals are significantly puckered. The planar structure of **I-R** represents a conformational maximum between two puckered minima with the calculated interconversion energy barrier Δ*G* of 1.93 kcal/mol.

The results of geometry optimization obtained with the DFT methods differ for some radicals from those obtained at the UHF/6-31G* level of theory. Radicals **IV-R**−**VI-R** show much less tendency toward ring opening, and the largest elongation of the S−N bond by 0.1 Å is calculated for **VI-R**, which now represents an intramolecular adduct of a thiyl radical to the azido group. The UHF calculations predict that only **III-R** and **VI-R** adopt a boat conformation while the remaining radicals, including **I-R**, are planar.

The distributions of spin densities in the radicals are similar in all five isomers, showing positive spin populations on the sulfur and in the 2,4,6 position and small negative spin densities on the atoms meta to sulfur. Except for **II-R**, all radicals have one or two carbon atoms bearing positive spin densities. This is expected to be energetically unfavorable and may be one of the reasons

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(45) For the purpose of this comparison it has been assumed that the 4*H* tautomer is the most stable for all isomeric heterocycles. The actual solid-state experimental evidence is available for only three of them.

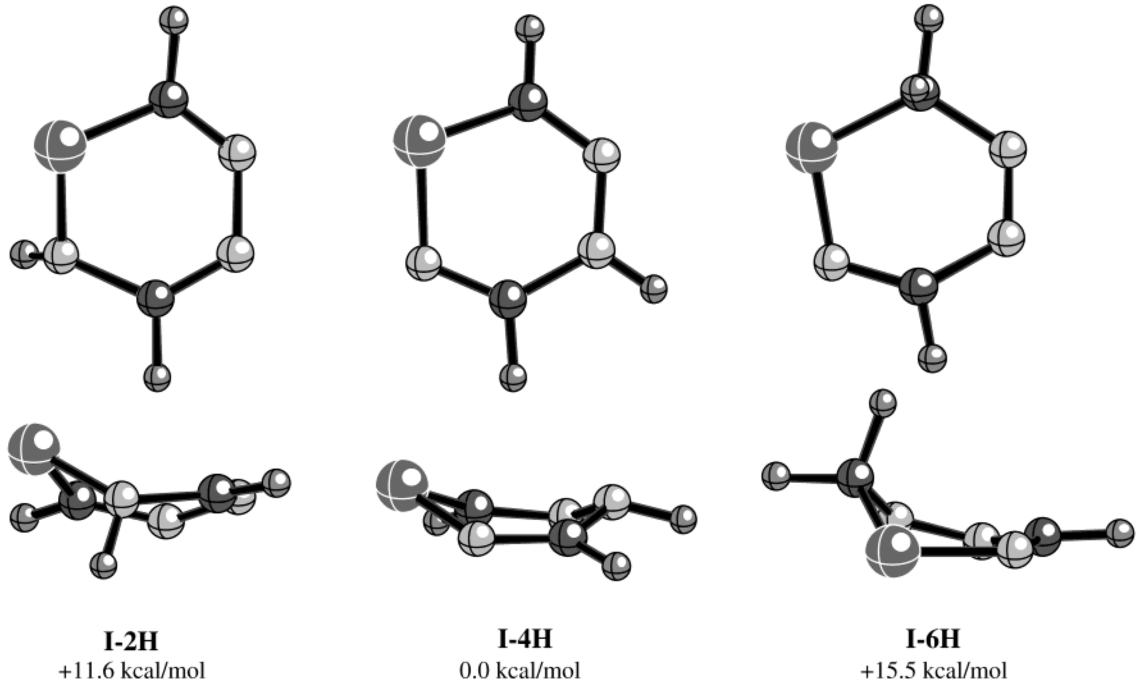

Figure 7. Ab initio (HF/6-31G*) optimized geometries and the relative SCF energies for three tautomers of 1,2,4,5-thiatriazine.

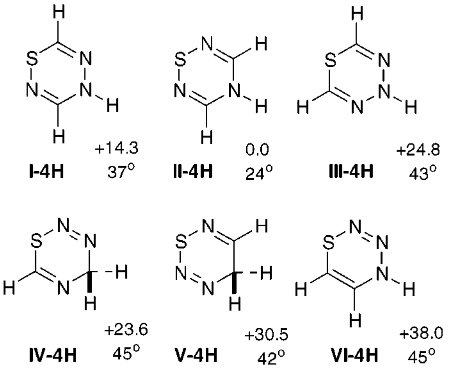

Figure 8. Relative SCF (HF/6-31G*) energies and dihedral angles α for isomeric thiatriazine 4*H* tautomers.

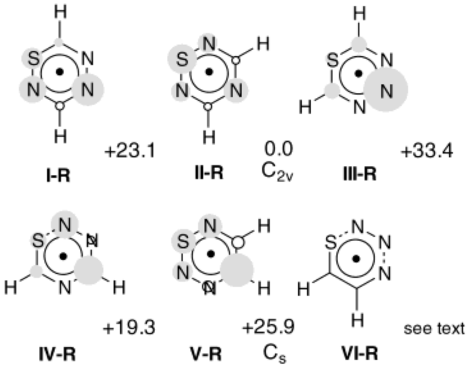

Figure 9. Calculated (B3LYP/6-31G*) spin distribution maps in isomeric thiatriazinyls with indicated relative SCF energies and molecular symmetries other than C_1. Circles represent relative total positive (full circles) and negative (open circles) spin densities.

for their calculated lower thermodynamic stabilities relative to that of the **II**-**R** isomer.

The stability order for the radicals, excluding **III**, roughly parallels that of the stabilities of the 4*H*-thiatriazines.

Conclusions

Oxidative cyclization of thiohydrazide **9** proved to be an effective way to prepare 3,6-diphenyl-4*H*-1,2,4,5-thiatriazine (**5**), an example of the last unknown isomer of thiatriazine. Other methods for construction of the 1,2,4,5-thiatriazine ring have been investigated with less success.

The attempts at generation of the 1,2,4,5-thiatriazinyl radical **4** from **5** or from acyclic precursor **7** are mostly discouraging, although a weak ESR signal was observed in the former experiment. Correlation of the signal with the structure of **4** was attempted with the aid of DFT calculations, but the results were inconclusive. The calculated hfc's show significant sensitivity to conformational changes, which results in qualitatively different ESR spectral patterns. It is possible that the radical **4** and the intermediate chloride **6** are much less stable than the analogous **1** and **2**, which are the only known radicals and chlorides among the thiatriazines.

On the basis of quantum-mechanical calculations, it appears that the 1,2,4,6-thiatriazine is unique among the isomeric thiatriazines. Both the radical **II**-**R** and the thiatriazine **II**-**4*H*** are at least 14 kcal/mol more stable than the next member of the family of isomers, radical **IV**-**R** and thiatriazine **I**-**4*H***. The 1,2,4,5-thiatriazinyl (**I**-**R**) is predicted to be less stable than the known 1,2,4,6-thiatriazinyl by about 23 kcal/mol, which may explain the difficulty with experimental observation of **4**.

The lack of a convenient method for generation of the radical **4** and its seemingly low stability cast serious doubt on 1,2,4,5-thiatriazinyl being used as a structural element for liquid crystals. Fortunately, other heterocyclic radicals were found to be suitable for this purpose. For instance a liquid-crystal-like molecule containing the benzothiadiazenyl has been demonstrated to easily form highly stable radicals.[46]

Computational Methods

Quantum mechanical calculations were carried out at the HF/6-31G* and B3LYP/6-31G* levels of theory using the Gaussian 94 package[47] on an SGI R8000 workstation. Geometry constraints were used in geometry optimizations as specified. The ground-state conformations and transition states were verified by analysis of normal modes. Thermodynamic parameters were calculated using scaling factors of 0.9135 and 0.9804 for HF and B3LYP methods, respectively.[48] The calculated Fermi contact values were expressed in megahertz and scaled by 1.046.[44] Simulation of ESR spectra was done using the Calleo ESR 1.2 program.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. NMR spectra were measured at 300 MHz (^{1}H spectra) and 100 MHz (^{13}C) in $CDCl_3$ and referenced to TMS (^{1}H) or the solvent (^{13}C), unless specified otherwise. Coupling constants were calculated from chemical shifts. IR spectra were recorded in KBr. Mass spectrometry was performed using a GC−MS instrument. Elemental analysis was provided by Atlantic Microlab, Norcross, GA.

X-band ESR spectra were taken on a Bruker 300E in distilled dichloromethane or benzene. Solvents were degassed by the freeze/pump/thaw method repeated three times. Spin concentration was calculated by integration of the signal intensity of the sample versus a measured amount of 2,2-diphenyl-1-picrylhydrazyl hydrate radical purchased from Aldrich and assumed to be 100%. Samples were referenced using strong pitch with $g = 2.0028$.

All reagents were used as received except as noted. Tetrahydrofuran was distilled from Na/benzophenone ketyl. Benzene, dichloromethane, and pyridine were distilled from CaH_2. Acetonitrile was distilled from phosphorus pentoxide. Benzene-d_6 was kept over Na.

X-ray Crystallography for 3,6-Diphenyl-4*H*-1,2,4,5-thiatriazine (5). A crystal of the compound grown from a methylene chloride/pentane mixture was attached to a glass fiber and mounted onto the Siemens SMART Platform CCD system for data collection at 173(2) K and a wavelength of $\lambda = 0.710\ 73$ Å. An initial set of cell constants was calculated from reflections harvested from 3 sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrixes determined from 42 reflections. Final cell constants are calculated from a set of 1983 strong reflections from the actual data collection. Please refer to Table 1 for additional crystal and refinement information.

All crystals appeared to twin in a manner similar to that of branching in trees. The specimen used for data collection was freed from most, but not all, twins. The specimen appears to be enantiomerically pure in the solid state. Some methods for modeling twins were attempted, but none improved the model significantly.

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. For the amine proton, see the text.

Attempted Generation of 3,6-Diphenyl-1,2,4,5-thiatriazinyl (4). Method A. Thiatriazine **5** (5 mg, 0.02 mmol) was dissolved in degassed benzene (1 mL) and stirred over PbO_2 (4.7 mg, 0.02 mmol) and K_2CO_3 (2.7 mg, 0.02 mmol) for 0.5 h. The solution changed to a darker yellow.

Method B. Thiatriazine **5** (5 mg, 0.0198 mmol) and pyridine (3 mg) were dissolved in dry CH_2Cl_2 (5 mL), degassed, and cooled to −77 °C. Distilled sulfuryl chloride (3 μL) was added, and the solution immediately became orange. The solution was filtered through a coarse frit onto solid Ph_3Sb (8 mg, 0.023 mmol). The solution became green-black and was transferred to a flame-dried ESR tube. The solution was degassed twice more before the ESR spectrum was taken.

Method C. Thiatriazine **5** (1 mg, 0.004 mmol) was dissolved in CH_2Cl_2 (1 mL). Chlorine (18 μL, 0.215 M in CCl_4) was added via syringe. After overnight stirring, the starting material was recovered.

Method D. Amidrazone **7** (5.64 mg, 0.025 mmol) was dissolved in CH_2Cl_2 (2 mL) containing pyridine (3 mg) and cooled to −77 °C. SCl_2 in CH_2Cl_2 (0.90 mL, 0.06 M) was added dropwise. The resulting orange solution was placed over Ph_3Sb (0.1 g). The reaction time with SCl_2 was varied from 10 min to 1 h before reaction with Ph_3Sb and measurement of ESR signal.

3,6-Diphenyl-4*H*-1,2,4,5-thiatriazine (5). A solution of bromine (0.10 mL, 2.0 mmol) and dry pyridine (2 mL) was added dropwise to **9** (1.00 g, 3.9 mmol) dissolved in dry THF (20 mL) over 2 min at 0 °C under nitrogen. The reaction mixture was gradually warmed to room temperature with stirring over 2 h and passed through a silica gel plug using methylene chloride. The orange filtrate was evaporated, and the resulting red solid was purified on Chromatotron (silica, CH_2Cl_2/hexanes, 1:1). Collecting the red lead band with CH_2Cl_2 elution gives the desired product of 0.530 g (54% yield) as a red solid which can be further purified by recrystallization from a CH_2Cl_2/pentane mixture to give golden needles or by sublimation: mp 126.5−127 °C; ^{1}H NMR (CD_2Cl_2) δ 7.39−7.57 (m, 6H), 7.76 (d, $J = 7.28$ Hz, 2H), 7.82 (d, $J = 7.03$ Hz, 2H), 8.76 (s, 1H); ^{13}C NMR δ 126.98, 127.12, 128.68, 128.89, 130.88, 131.57, 131.71, 132.52, 148.90, 160.22; IR 3326, 3311, 1298, 693 cm^{-1}. Anal. Calcd for $C_{14}H_{11}N_3S$: C, 66.40; H, 4.35; N, 16.60; S, 12.65. Found: C, 66.43; H, 4.41; N, 16.65; S, 12.58.

The second fraction from chromatographic separation (CH_2Cl_2) was identified as 2,5-diphenyl-1,3,4-thiadiazole (**13**): mp 140−141 °C (lit.[26] mp 141−142 °C); ^{1}H NMR (CD_2Cl_2) δ 7.51−7.54 (m, 6H), 8.00−8.03 (m, 4H); ^{13}C NMR (CD_2Cl_2) δ 128.18, 129.53, 130.63, 131.42, 168.45. Anal. Calcd for $C_{14}H_{10}N_2S$: C, 70.59; H, 4.20; N, 11.77; S, 13.45. Found: C, 70.44; H, 4.17; N, 11.70; S, 13.40.

1-Amino-1,4-diphenyl-2,3-diaza-1,3-butadiene[15] (7). Benzamidine hydrochloride hydrate (8.73 g, 50 mmol) was dissolved in ethanol (50 mL), and a solution of hydrazine hydrate (2.50 g, 50 mmol) in ethanol (10 mL) was added. The mixture was stirred at ambient temperature for 30 min (while a precipitate formed), and benzaldehyde (5.30 g, 50 mmol) in ethanol (10 mL) was added. The resulting yellow mixture was stirred for 3 h, the precipitate was filtered off, and the solution was evaporated to leave a yellow crystalline product. The crude product was dissolved in benzene and passed through an alumina plug and the solvent removed. The remaining solid (7.66 g) was recrystallized twice from a toluene/isooctane mixture to give 6.47 g (53% yield) of yellow crystals: mp 133−134 °C (lit.[33] 133−134 °C); ^{1}H NMR (400 MHz) δ 5.75 (br, 2H), 7.41−7.49 (m, 6H), 7.79−7.82 (m, 2H), 7.84−7.87 (m, 2H), 8.57 (s, 1H).

1-Chloro-4-(*N*-chloroamino)-1,4-diphenyl-2,3-diaza-1,3-butadiene (8). A solution of *tert*-butyl hypochlorite (2.30 g, 21 mmol) in dry methylene chloride (20 mL) was added dropwise to amidrazone **7** (2.23 g, 10 mmol) dissolved in dry CH_2Cl_2 (25 mL) at 0 °C. The mixture was stirred for 1.5 h, and the solvents were evaporated. The resulting crude product was dissolved in a small amount of CH_2Cl_2 deposited on a silica

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[46] Farrar, J. M.; Huang, J.; Kaszynski, P. Submitted for publication.

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gel plug and eluted with CH_2Cl_2, keeping the yellow band on the gel. The filtrate was evaporated, yielding 1.38 g of yellow oil which was recrystallized twice from hexanes to give 0.65 g (22% yield) of the dichloride as long colorless needles: mp 118−124 °C dec; ^{1}H NMR (400 MHz) δ 7.34−7.43 (m, 3H), 7.45−7.53 (m, 3H), 7.66−7.73 (m, 4H), 9.65 (br s, 1H); ^{13}C NMR δ 127.09, 127.99, 128.52, 129.38, 130.71, 130.83, 130.96, 131.25, 132.92, 162.98; IR 3287, 3065, 1588, 1565, 1385, 1257, 933, 708 cm^{-1}. Anal. Calcd for $C_{14}H_{11}N_3Cl_2$: C, 57.55; H, 3.79; N, 14.38; Cl, 24.27. Found: C, 57.62; H, 3.86; N, 14.39; Cl, 24.17.

Benzenecarbothioic Acid 2-(Iminophenylmethyl)hydrazide (9).[16] To thiobenzoic hydrazide[19,49] (**12**; 2.50 g, 16.45 mmol) partially dissolved in dry benzene (20 mL) was added dropwise 2 M Me_3Al in toluene (17.3 mL, 34.55 mmol) over 10 min. To the resulting green, homogeneous solution was added benzonitrile (2.03 g, 19.74 mmol) dissolved in benzene (2.5 mL). The mixture was heated to reflux under nitrogen for 6 h. Water (11 mL) was then very slowly added to the mixture, and the resulting yellow-green product was filtered and quickly washed with MeOH. Evaporation of the solvent gave 2.54 g (76% yield) of bright yellow needles: mp 151.5−152.5 °C (lit.[16] mp 154−156 °C); ^{1}H NMR (acetone-d_6) δ 2.88 (s, 1H), 2.92 (s, 2H), 7.29−7.33 (m, 3H), 7.67−7.80 (m, 3H), 7.97 (m, 2H), 8.32 (m, 2H); ^{13}C NMR (acetone-d_6) δ 127.93, 128.02, 128.48, 128.84, 129.73, 130.59, 134.27, 142.62, 155.99, 183.99. Anal. Calcd for $C_{14}H_{13}N_3S$: C, 65.88; H, 5.10; N, 16.47; S, 12.55. Found: C, 65.95; H, 5.11; N, 16.42; S, 12.47.

***N*-Phenylmethylenebenzenecarbohydrazonyl Disulfide (14).**[27] To **15** (1.50 g, 6.25 mmol) suspended in 1 N NaOH (12.5 mL, 12.5 mmol) was added dropwise $K_2S_2O_8$ (1.69 g, 6.25 mmol) dissolved in water (38 mL) at 0 °C. A yellow solid gradually began to accumulate. Stirring was continued for 2 days at room temperature, and then the solid was collected by filtration, washed with water, dried, and recrystallized from ethanol (65 mL) to afford 0.74 g (50% yield) of yellow needles: mp 133.5−134.5 °C (lit.[27] mp 134−136 °C); ^{1}H NMR δ 7.30−7.48 (m, 16H), 7.72 (dd, $J_1 = 7.7$ Hz, $J_2 = 1.4$ Hz, 4H), 8.32 (s, 2H); ^{13}C NMR δ 127.89, 128.25, 128.66 (2C), 129.30, 130.09, 131.54, 133.77, 160.17, 166.52. Anal. Calcd for $C_{28}H_{22}N_4S_2$: C, 70.29; H, 4.60; N, 11.72; S, 13.39. Found: C, 70.17; H, 4.54; N, 11.77; S, 13.32.

2,5-Diphenyl-Δ²-1,3,4-thiadiazoline (15)[50] was obtained in 94% yield according to the literature procedure:[29] mp 76−78 °C (lit.[29] mp 78−80 °C); ^{1}H NMR δ 6.37 (s, 1H), 7.35−7.40 (m, 4H), 7.47−7.51 (m, 4H), 7.67−7.70 (m, 1H), 8.00−8.03 (m, 2H); (C_6D_6) δ 5.81 (br s, 1H), 5.87 (s, 1H), 6.99−7.07 (m, 6H), 7.18−7.22 (m, 2H), 7.80−7.82 (m, 2H); ^{13}C NMR δ 74.64 (br), 126.48, 127.02, 127.05, 128.53, 128.95, 129.09, 129.66, 131.17, 140.68.

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Supporting Information Available: Text describing data collection and structure solution and refinement and tables giving crystal data, atomic coordinates, isotropic and anisotropic displacement parameters, bond distances and angles, and torsion angles for **5** and spin distribution in isomeric thiatriazinyls. This material is available free of charge via the Internet at http://pubs.acs.org.

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