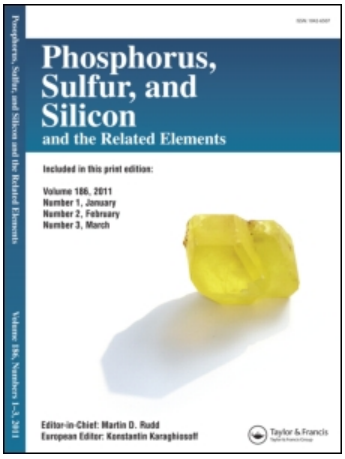

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1,2,4,6-THIATRIAZINYLS: STABLE FREE RADICALS WITH WELL-DEFINED EPR SPECTRA

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The EPR spectra of six 1,2,4,6-thiatriazinyls have been redetermined and simulated using modern computer simulation programs. The hyperfine coupling (hfc) constants determined from the simulations differ in some cases significantly from those reported previously. The presence of unresolved coupling also can be detected in some of the spectra. The hfc values to the two kinds of nitrogen atoms in the ring vary in a systematic fashion with the relative electron-withdrawing character of the substituents attached to the ring carbon atoms at the 3 and 5 positions.

Keywords: EPR spectra; hyperfine coupling constants; simulation; thiatriazine; thiatriazinyl; thiazyl

Stable free radicals of the main group elements are currently the subject of intense investigation.[1] Free radicals have many applications in science, medicine, and technology. Thiazyl compounds—unsaturated compounds with S–N linkages—are a rich field for the production of stable, neutral, free radicals.[2,3] We recently have summarized the known electrochemical data on thiazyl compounds,[4] and extensively have investigated 1,2,3,5-dithiadiazolyl radicals, including their characterization by EPR spectroscopy.[5] Much less is known about the six-membered ring thiatriazinyl system. Kaszinsky has reported recently on a second isomer, but it does not form a stable free radical.[6] Hence the 1,2,4,6-thiatriazinyls, planar ring compounds with substituents in

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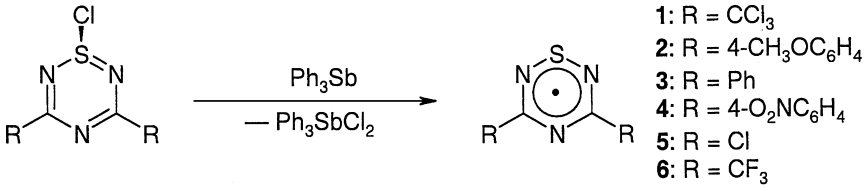
the 3 and 5 position, remain the only isomers for which stable radicals can be generated. Recent detailed computational studies have placed thiazyl radicals, including thiatriazinyls, on a firm theoretical footing.[7,8]

The earliest work involving 1,2,4,6-thiatriazines dates back to 1970 when Geevers reacted sodium dicyanamide with thionyl chloride to give the 1,3,5-trichloro-1,2,4,6-thiatriazine (but incorrectly identified it).[9] Reduction of this compound to the radical was reported much later,[10] while other workers corrected the structural assignment.[11] Kornuta and coworkers reported the formation of several 1-chloro-1,2,4,6-thiatriazine rings by substitution of the chlorine atoms in the above compound, and reported their reduction to radicals.[12,13] More recently the 1-chloro-3,5,-diphenyl-1,2,4,6-thiatriazine was made by Oakley and coworkers,[14] from the reaction of benzamidine with $S_3N_3Cl_3$ to give the 1-chloro thiatriazine precursor in low yields, together with S_4N_4 and the dithiadiazolium chloride $[PhCN_2S_2]^+Cl^-$. Reduction to the thiatriazinyl radical and an EPR spectrum has been reported.[15] This spectrum indicates that the unpaired spin distribution is divided approximately equally over the three nitrogen atoms (with a substantial sulfur contribution as well), with no resolvable coupling to the phenyl-ring protons.[14] Spin delocalization onto the external rings does not occur to any measurable extent due to the electronegative potential exerted by the thiatriazine ring. Molecular orbital coefficients calculated at the Restricted Hartree Fock (RHF) modified neglect of diatomic overlap (MNDO) level correlated well with the observed coupling constants,[14] and indicated a π^* distribution strongly polarized over the —N═S═N— region of the ring. Solid state characterization by x-ray crystallography revealed discrete pairs of thiatriazine rings linked cofacially in a totally eclipsed conformation, with a core that exhibited a shallow boat, or open book, conformation.[14] In the dimer, a net bonding interaction occurs between the two sulfur atoms which arises from overlap of the π^*-SOMOs of the monomeric radicals. An overall diamagnetic ground state for the dimer was predicted. In addition, salts of the cation and a derivative of the anion also were isolated and structurally characterized.[16]

We recently have returned to the study of the thiatriazinyl ring system. In the course of this work we have reassessed the isotropic EPR spectra of this class of radicals, which can be characterized unambiguously by their well-defined hyperfine coupling constants. A direct correlation has been established between the observed a_N values and the substituents attached to the ring carbon atoms. We report here the results of this EPR investigation.

RESULTS AND DISCUSSION

Synthesis of the *S*-chloro and radical thiatriazinyls followed literature procedures: **1**,[12] **2**,[10] **3**,[14] **4**,[10] **5**,[9] and **6**.[10] Only **3** has been structurally characterized in the solid state, as a face-to-face dimer with a relatively short interanular S···S contact of 2.666(3) Å. Thiatriazinyls were generated by reduction of the corresponding *S*-chlorothiatriazines using triphenylantimony. In the case of **2**, **3**, and **4**, the thiatriazinyl radicals were isolated as their solid dimers and purified by vacuum sublimation in a three-zone tube furnace. For **1** and **5** the radicals were generated in solution from the *S*-chloro compound in a vacuum-sealed cylindrical EPR tube, whereas **6** was generated by passing the *S*-chloro compound in the vapor phase over solid Ph_3Sb and trapping the radical at low temperature, as described in the literature.[10]



SCHEME 1

EPR Spectra

To illustrate the well-defined EPR spectra of the title compounds, we will consider compound **1** in detail. Thiatriazinyls **1–6** each have two kinds of N atom, the two in the formal —N=S=N— linkage (identified as N_2 and N_6) and the single atom of the —C=N=C— unit (N_4). The major isotopes of sulfur and carbon are EPR silent. Hence the dominant hyperfine coupling (hfc) is likely to come from the ^{14}N ($I = 1$) and ^{37}Cl ($I = 3/2$) nuclei. The EPR spectrum of **1** is shown in Figure 1a. Consideration of the SOMO, generated from an AM1 calculation on a geometry optimized model of **1**, suggests that most of the unpaired spin density resides in the π-system of the three nitrogen and the sulfur atoms (Figure 1c). The SOMO coefficient for N_4 is also slightly larger than that for $N_{2,6}$, but they are of the same order of magnitude. From these considerations it was possible to simulate the spectrum based on one larger and two equivalent smaller hfc's to ^{14}N. EPR simulations were performed with WinEPR SimFonia 1.25 supplied by Bruker

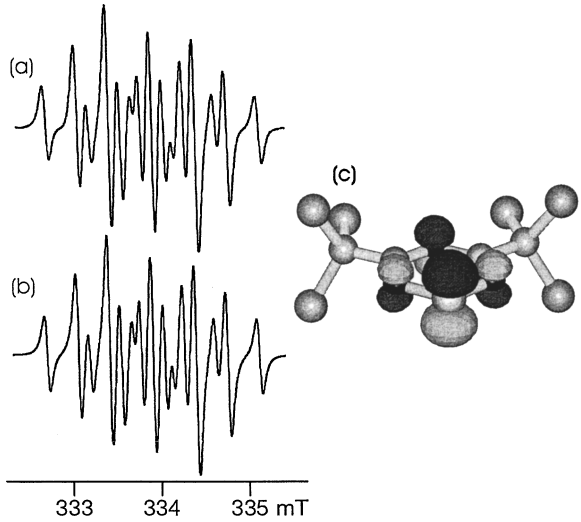


FIGURE 1 (a) Experimental and (b) simulated EPR spectrum of 3,5-*bis*-(trichloromethyl)-1,2,4,6-thiatriazinyl (RT in CH_2Cl_2 solution). (c) 3D surface plot of the SOMO of the radical.

and optimized using PEST WinSim 1.0 from the National Institutes of Health, USA. The simulated spectrum is shown in Figure 1b, and the excellent match to the experimental trace is evident. The original analysis gave $a_{N2,6} = 0.3580$ mT and $a_{N4} = 0.4919$ mT. There is no resolvable hfc to ^{37}Cl, but the rather large linewidth of 0.060 mT in this simulation suggested the presence to further unresolved hfc. Indeed, the trifluoromethyl analogue **6** has well-resolved septets from coupling to six equivalent ^{19}F nuclei in rotationally averaged CF_3 groups. Comparison to **5** for which the directly-bound ^{37}Cl hfc is 0.068 suggests an upper limit for ^{37}Cl hfc in **1** of about 0.007 mT. Consequently, the final optimization was performed with the inclusion of six equivalent ^{37}Cl nuclei. The refinement converged to a ^{37}Cl hfc value of 0.0071 mT with a greatly reduced linewidth of 0.046 mT, the latter more in line with those of the other thiatriazinyls in Table I.

By far the best-resolved spectrum is that of **2**, which simulates well using a linewidth of only 0.020 mT. Small satellites from hfc to the ^{15}N nuclei, which are obscured in the spectra of the other five compounds, are clearly visible in the baseline. An EPR spectrum of **2** obtained at high gain, along with a simulation, are shown in Figure 2. Note that the peaks are clipped so that only the basal regions are displayed. Observations of ^{15}N satellites in EPR spectra of thiazyl radicals are extremely rare. Finally, it seems likely that the hfc to the two kinds of

TABLE I EPR Data on Thiatriazinyls[a]

Compd.	R =	$a_{N2,6}$ mT	a_{N4} mT	Additional hfc	*g*-value	Lineshape[b] (%)	Linewidth
1	CCl_3	0.3587	0.4921	^{37}Cl: 0.071	2.0077	100	0.046
	Lit.[13]	0.36	0.53				
2	4-$CH_3OC_6H_4$	0.3927	0.3927	^{15}N: 0.523	2.0064	16	0.020
	Lit.[10]	0.365	0.365				
3	C_6H_5	0.3891	0.4116	—	2.0059	85	0.039
	Lit.[14]	0.397	0.397				
4	4-$O_2NC_6H_4$	0.3729	0.4319	—	2.0055	100	0.044
	Lit.[10]	0.372	0.427				
5	Cl	0.3772	0.4358	^{37}Cl: 0.068	2.0055	94	0.041
	Lit.[10]	0.345	0.415	^{37}Cl: 0.062			
6	CF_3	0.3350	0.4590	^{19}F: 0.042	2.0065	100	0.025

[a]Hyperfine coupling constants and linewidths expressed in units of *milli*Tesla (mT).
[b]Expressed as the % Lorentzian character; balance is Gaussian. Lorentzian lineshape is expected where relaxation effects dominate, whereas Gaussian lineshape is associated with unresolved hfc.

symmetry-inequivalent N nuclei, $N_{2,6}$ and N_4, are *accidentally* equivalent in **2**, but only *apparently* equivalent in **3**. Indeed, it was possible to simulate the spectrum of **3** using a narrower linewidth but with hfc to $N_{2,6}$ and N_4 of, respectively, 0.3891 and 0.4116 mT.

The spectrum of **4**, which has the more electron-withdrawing *para*-nitro group on the phenyl ring, displays resolved splitting to the two kinds of nitrogen nuclei.[10] The hfc values for **5** are extremely similar to

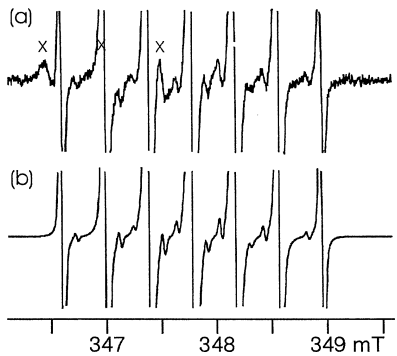


FIGURE 2 (a) Experimental and (b) simulated EPR spectrum of 3,5-di(4-methoxyphenyl)-1,2,4,6-thiatriazinyl (RT in CH_2Cl_2 solution) at high gain. The small satellites are from coupling to the ^{15}N isotope. Peaks marked with X are from a trace amount of the corresponding 1,2,3,5-dithiadiazolyl ($g = 2.011$, ref. 5) present as an impurity.

those of **4**, but the directly-bound chlorine atoms lead to further splitting attributable to two equivalent ^{37}Cl nuclei. This complex-looking spectrum easily is simulated and optimized using the computer simulation tools. The values we obtain are significantly different from the previously-reported values obtained from a less well-resolved EPR spectrum. On the other hand, our simulations of the spectrum of **6** fit well with the original report.[10]

The substituent influence in **1–6** is clearly seen in the relative size of the coupling to $N_{2,6}$ and N_4. The ratio of the latter to the former is 1:1 for **2** and 1:1.06 for **3**, whereas it increases to 1:1.16 in **4** and **5** and is 1:1.37 in **1** and **6**. Hence, as the substituents becomes more strongly electron-withdrawing, the hfc to N_4 increases due to polarization of the unpaired spin density away from the dominant —N=S=N— region of the molecule.

Electronic Structure Calculations

Both the hfc and the redox potentials[4] are significantly influenced by the change in substituents in **1–6**. This behaviour is distinct from that of a similar series of 1,2,3,5-dithiadiazoles;[5] the *insensitivity* of the latter has been attributed to a SOMO with a node at C that limits the influence of the substituents to a purely inductive effect.[2,3] In thiatriazinyls, by contrast, the ring carbon atoms have distinct (though small) contributions to the π-SOMO, so that substituent influence should be weakly communicated *via* the π-system. We find that this provides an adequate explanation for the greater substituent influence on both the redox potentials and the hfc constants in the latter ring system.[4]

CONCLUSIONS AND FURTHER WORK

The electronic structure of thiatriazinyl radicals are directly reflected in their well-defined EPR spectra through the relative size of the hfc to the two kinds of symmetry-inequivalent nitrogen atoms in the six-membered ring. The electrochemistry of this ring system has been investigated in a preliminary fashion, but is pursuing the development of a more general synthetic route to thiatriazinyls that will allow the preparation of a series of derivatives in which the influence of changing the *para* substituent on a *single* phenyl ring can be systematically investigated. In this way we will be able to compare thiatriazinyls directly with the 1,2,3,5-dithiadiazolyls that we have previously investigated with a range of donor and acceptor substituents. Such “fine

tuning" of the thiatriazinyl series should allow a definitive comparison of the two ring systems in terms of the intrinsic tunability of their redox behaviour. The influence of such remote substituents also may be observable in their EPR spectra. The results of these investigations will be reported in a future publication.

EXPERIMENTAL

EPR Spectroscopy

EPR spectra were determined on a Bruker EMX 113/10 spectrometer at RT in 4 mm pyrex cylindrical tubes sealed under vacuum after freeze-thaw degassing. Solutions were diluted by internal distillation of the solvent in the sealed tube system until line-widths became constant. Line broadening from radical-radical interactions was commonly observed at higher concentrations.

Electronic Structure Calculations

The computational studies were performed with full geometry optimization using HyperChem Pro 5.1 running under Windows XP. Geometry optimization of open-shell species employed UHF functions, but the SOMO coefficients were determined in RHF calculations using the half-electron approximation.

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