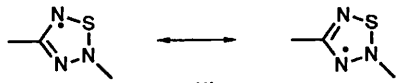
2,5-Dihydro-1,2,3,5-thiatriazole 1-Oxides, 2*H*-1,2,3,5-Thiatriazol-1-ium Salts, and 2,5-Dihydro-1,2,3,5-thiatriazol-5-yl Radicals. X-Ray Molecular Structure of 2,5-Dihydro-2,4-diphenyl-1,2,3,5-thiatriazole 1-Oxide and 2,4-Diphenyl-2*H*-1,2,3,5-thiatriazol-1-ium Bromide

Franz A. Neugebauer,* Hans Fischer, Rowena Crockett,† and Claus Krieger
Abt. Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstr. 29, D6900 Heidelberg, West Germany

N-Substituted amidrazones (**4a–g**) react with thionyl chloride to give 2,5-dihydro-1,2,3,5-thiatriazole 1-oxides (**5a–g**). X-Ray analysis of compound (**5c**) confirmed the 2,5-dihydro structure which is also the predominant tautomer in solution. Reaction of compounds (**5a–g**) with phosphorus pentachloride or pentabromide led to the formation of yellow 2*H*-1,2,3,5-thiatriazol-1-ium salts (**6a–h**), the structure being established by X-ray structure analysis of compound (**6h**). Reduction of compounds (**6a–h**) in 1,2-dimethoxyethane with sodium or potassium metal readily generated 2,5-dihydro-1,2,3,5-thiatriazol-5-yl radicals (**1a–g**) which were studied using ESR, ENDOR, and general triple resonance spectroscopy. The results led to a complete analysis and full assignment of all coupling constants.

2,5-Dihydro-1,2,3,5-thiatriazol-5-yl radicals (**1**) constitute an interesting target molecule, since it combines the basic structural features of 1,2,3,5-dithiadiazolyl (**2**)[1–8] and tetrazolinyl radicals (**3**),[9–12] *i.e.* the thioaminyl and the hydrazyl moiety, in a five-membered seven-π-electron system. The persistent 1,2,3,5-dithiadiazolyl radicals dimerize to give crystalline diamagnetic solids. In these dimers, as shown by X-ray structure analyses,[3,8] the radicals are bonded together through weak S–S bonds. Tetrazolinyl radicals, on the other hand, are monomeric. The stable 5-t-butyl-2,3-bis-(4-nitrophenyl)tetrazolinyl radical has been obtained as green-black needles, m.p. 126–127 °C (decomp.); μ_{eff}/μ_B 1.66 (94%).[12]



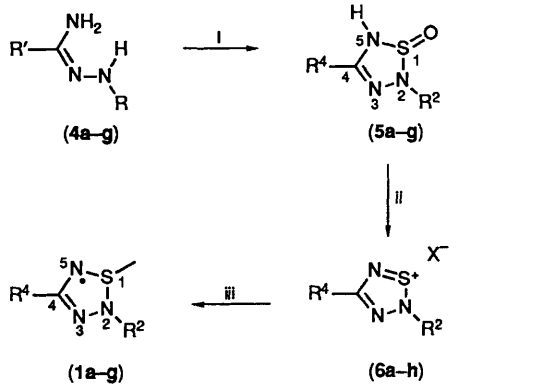
(**1**)

(**2**) (**3**)

We report here the generation and properties of 2,5-dihydro-1,2,3,5-thiatriazol-5-yl radicals (**1**) which were prepared from amidrazones (**4**) *via* 2,5-dihydro-1,2,3,5-thiatriazole 1-oxides (**5**) and 2*H*-1,2,3,5-thiatriazol-1-ium salts (**6**) (Scheme). X-Ray structure determinations of the intermediates (**5c**) and (**6h**) are also presented.

Results and Discussion

2,5-*Dihydro*-1,2,3,5-*thiatriazole* 1-*Oxides* (**5**).—*N,N″*-Disubstituted amidrazones react readily with thionyl chloride to give 2,4,5-trisubstituted-2,5-dihydro-1,2,3,5-thiatriazole 1-oxides.[13–15] This reaction can also be performed with the less substituted amidrazones of type (**4**). In the presence of base (pyridine) corresponding 1,2,3,5-thiatriazole derivatives were



(**4a–g**) (**5a–g**) (**1a–g**) (**6a–h**)

	R^2(R)	R^4(R′)	X	^{15}N
a	Ph	Me	Cl	
b	C_6D_5	Me	Cl	
c	Ph	Ph	Cl	
d	Ph	C_6D_5	Cl	
e	C_6D_5	C_6D_5	Cl	
f	Ph	Ph	Cl	3-^{15}N
g	Ph	Ph	Cl	3,5-$^{15}N_2$
h	Ph	Ph	Br	

Scheme. *Reagents and conditions:* i, $SOCl_2$, base; ii, PX_5; iii, Na(K), DME (dimethoxyethane).

obtained as main products. These compounds can exist in various tautomeric forms, *e.g.* as 2,5-dihydro-(**5**), 2,3-dihydro-1,2,3,5-thiatriazole 1-oxide (**7**), or 2*H*-1,2,3,5-thiatriazol-1-ium hydroxide (**8**).

The tautomeric form in the crystal was established by X-ray structure determination of compound (**5c**) which clearly revealed a 2,5-dihydro structure (Figures 1 and 2; crystallographic data and fractional co-ordinates are given in Tables 2 and 3 respectively). The five-membered ring exhibits a shallow envelope form, the sulphur being displaced by 0.49 Å from the

† On leave from the Chemistry Department, University of Aberdeen, Scotland.

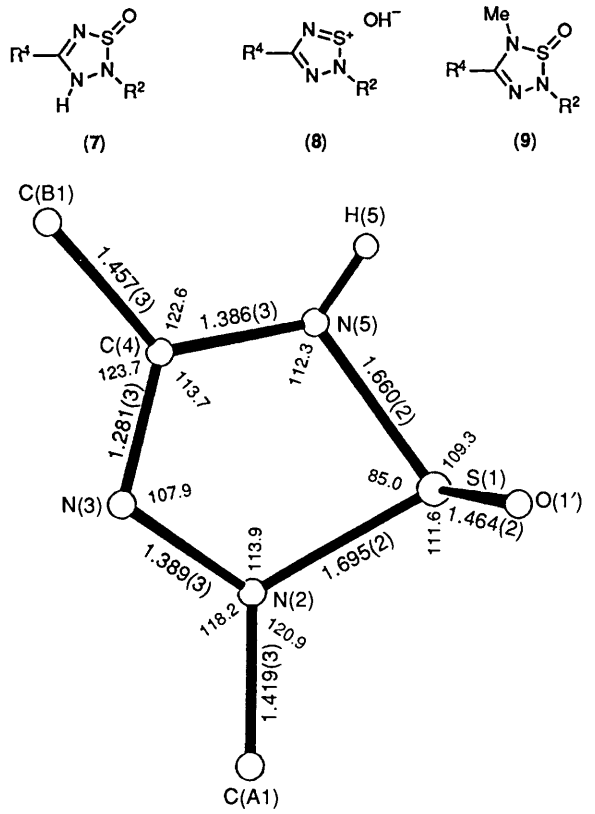


Figure 1. Crystal structure of 2,5-dihydro-2,4-diphenyl-1,2,3,5-thiatriazole 1-oxide (**5c**): Top-view of the central five-membered ring showing bond distances (Å) and angles (°).

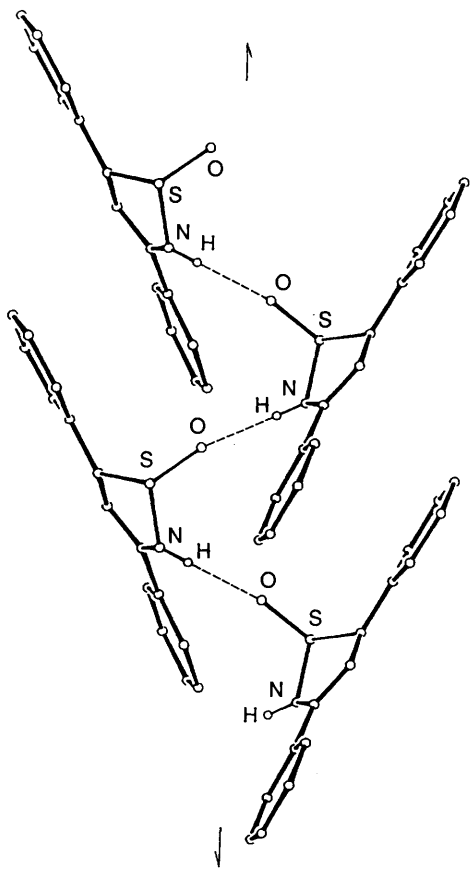


Figure 2. Packing diagram of compound (**5c**), showing the intermolecular hydrogen bridges.

least-squares plane through N(2), N(3), C(4), N(5) which present a perfect planarity. The angle between this plane and the N(5), S(1), N(2) plane is found to be 24°. Bond lengths and angles of the five-membered ring, given in Figure 1, are closely similar to the corresponding data found in 2*H*-[1,2,3,5]thiatriazolo[4,5-a]isoquinoline 3-oxide.[16] The N(3)–C(4) distance [1.281(3) Å] represents a typical C(sp^2)=N(2) double bond as found in oximes.[17] In the phenyl substituents the bond lengths and angles are as expected. The packing diagram in Figure 2 shows nearly linear intermolecular N–H···O hydrogen bridges [N···O distance 2.866(3), H···O distance 2.10(2) Å, N–H···O angle 174(3)°] which lead to a helical arrangement in the crystal.

Intermolecular association is also observed in solution. IR spectra of (**5a–g**) in tetrachloromethane do not show frequences for free NH or OH groups. Furthermore, shifts in the ^{1}H NMR spectra of compounds (**5a–g**) in dichloro[$^2H_2$]methane are concentration dependent, particularly that of the exchangeable proton. 3-^{15}N labelling (**5f**) leaves this singlet resonance unaffected, whereas 3,5-$^{15}N_2$ labelling (**5g**) gives rise to a typical ^{15}N–H doublet (*J* 90.9 Hz). These results agree with the tautomeric structure (**5**). In [$^2H_6$]dimethyl sulphoxide ([$^2H_6$]DMSO) solution, however, compound (**5g**) displays a broad singlet resonance for the exchangeable proton. As compared with the corresponding resonance of the non-labelled analogue (**5c**) (linewidth 5 Hz) only an increase of the linewidth (*ca.* 15 Hz) is found. This observation can be related to a dissociative process of the N–H proton in DMSO. However, there is also the possibility of a tautomeric equilibrium between the tautomeric structures (**5**) and (**8**). Participation of tautomer (**8**) should have an effect on the ^{15}N shifts. Comparison of the ^{15}N resonances of compound (**5g**) [δ(^{15}N) (dichloro-[$^2H_2$]methane) −243.3 (d, *J* 90.6 Hz, N-5), −129.6 (s, N-3); ([$^2H_6$]DMSO) −238.8 (br s, N-5), 131.3 (s, N-3)] with the corresponding data of the 5-methyl derivative (**9g**) [δ(^{15}N) (dichloro[$^2H_2$]methane) −246.0 (s, N-5), −125.5 (s, N-3); ([$^2H_6$]DMSO) −244.7 (s, N-5), 125.7 (s, N-3)] shows no significant shift deviations. In the UV spectra (Figure 3), on the other hand, the maximum of the first absorption band of the methyl derivative (**9c**) [(dioxane) 278 nm (log ε 4.03); (DMSO) 278 nm (log ε 4.05)] is found at considerable shorter wavelength than that of (**5c**) [(dioxane) 301 nm (log ε 4.11); (DMSO) 305 nm (log ε 4.10)]. Attempts to synthesize the *O*-methyl derivative of compound (**8c**) failed. In summary, the experimental results indicate that the obtained dihydro-1,2,3,5-thiatriazole 1-oxides in solution also are present predominantly in the tautomeric form (**5**). In the mass spectra the formation of the cation (**6**) is observed with cleavage of an OH moiety (−17).

2H-1,2,3,5-*Thiatriazol*-1-*ium Salts* (**6**).—The 2,5-dihydro-1,2,3,5-thiatriazole 1-oxides (**5a–g**) and phosphorus pentachloride (or pentabromide) react readily in chloroform to give the yellow 2*H*-1,2,3,5-thiatriazol-1-ium salts (**6a–h**) in high yield. These salts are very sensitive to moisture and hydrolyse back to the starting compounds (**5a–g**). Therefore, the NMR and electronic absorption spectra of salts (**6a–h**) were measured in trifluoroacetic acid (TFA)–trifluoroacetic anhydride (TFAA) (1:3) solution. Chemical shifts and splitting patterns of the proton signals are in full agreement with structure (**6**). The yellow colour of these cations owing to extending conjugation is reflected by a broad band system between 450 and 300 nm, *e.g.* for salt (**6c**) in Figure 3.

In view of the new conjugated five-membered ring system it was desirable to confirm its structure by X-ray crystallography.

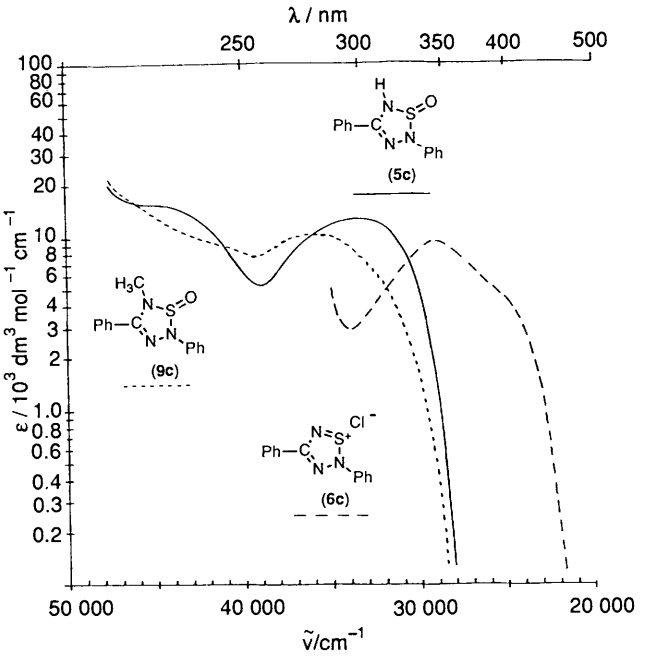


Figure 3. Electronic absorption spectra of compounds (**5c**) and (**9c**) in dioxane, and of compound (**6c**) in [TFA–TFAA (1:3)].

Satisfactory crystals were obtained from the bromide (**6h**). The molecular structure of compound (**6h**) in different projections is shown in Figure 4. The bond lengths and angles of the five-membered cation are given in Figure 4(*b*), and crystallographic data and fractional co-ordinates are listed in Tables 2 and 3 respectively. The five-membered ring including the nearest bromide ion is planar within experimental error. The distance between the ring sulphur and the adjacent bromide ion [2.891(1) Å] lies between those of Br–S(3)$^+$ [2.321(4) Å][18] or Br–S(2) [2.208(4) Å][19] and the sum of the corresponding van der Waals radii (3.65 Å,[20a] 3.8 Å[20b]), suggesting that the S–Br bond is partially covalent. The C–N distances of compound (**6h**) [C(4)–N(5) 1.342(4) and C(4)–N(3) 1.356(4) Å] indicate considerable double-bond character and are close to the length of C–N bonds found in 1,2,3,5-dithiadiazolium (1.35–1.49 Å)[21–24] or 2,3,5-trisubstituted 2*H*-tetrazolium ions (1.30 Å),[25] and the S(1)–N(5) distance [1.585(3) Å] is also similar to that of 1,2,3,5-dithiadiazolium ions (1.57–1.59 Å).[21–24] In compound (**6h**) considerable double-bond character is further found for the N(2)–N(3) bond [1.306(4) Å] which exactly corresponds to the N(1)–N(2) and N(3)–N(4) bonds in the 2*H*-tetrazolium ion. The large S(1)–N(2) bond length [1.683(3) Å], however, represents a typical X–S–NX$_2$ (N sp^2) bond (1.707 Å).[17] The crystal structure indicates that the six π-electrons of the five-membered 2*H*-1,2,3,5-thiatriazol-1-ium ion are mainly delocalized within the N(2)···N(3)···C(4)···N(5)···S(1)$^+$ system which is linked at terminal positions by an S–N bond having predominantly single-bond character.

2,5-*Dihydro*-1,2,3,5-*thiatriazol*-5-*yl Radicals* (**1a–g**).—These radicals were conveniently generated by reduction of dilute solutions of the 2*H*-1,2,3,5-thiatriazol-1-ium salts (**6a–g**) in 1,2-dimethoxyethane (DME) with sodium or potassium metal. Their ESR spectra are complex. Representative examples are shown in Figures 5 and 6. In the ENDOR spectrum of compound (**1c**) all ^{14}N and three ^{1}H coupling constants were detected, and, in addition, by performing general triple resonance[26] relative signs were determined. Complete deuteriation in compound (**1e**) confirmed the nitrogen splittings. Derived from

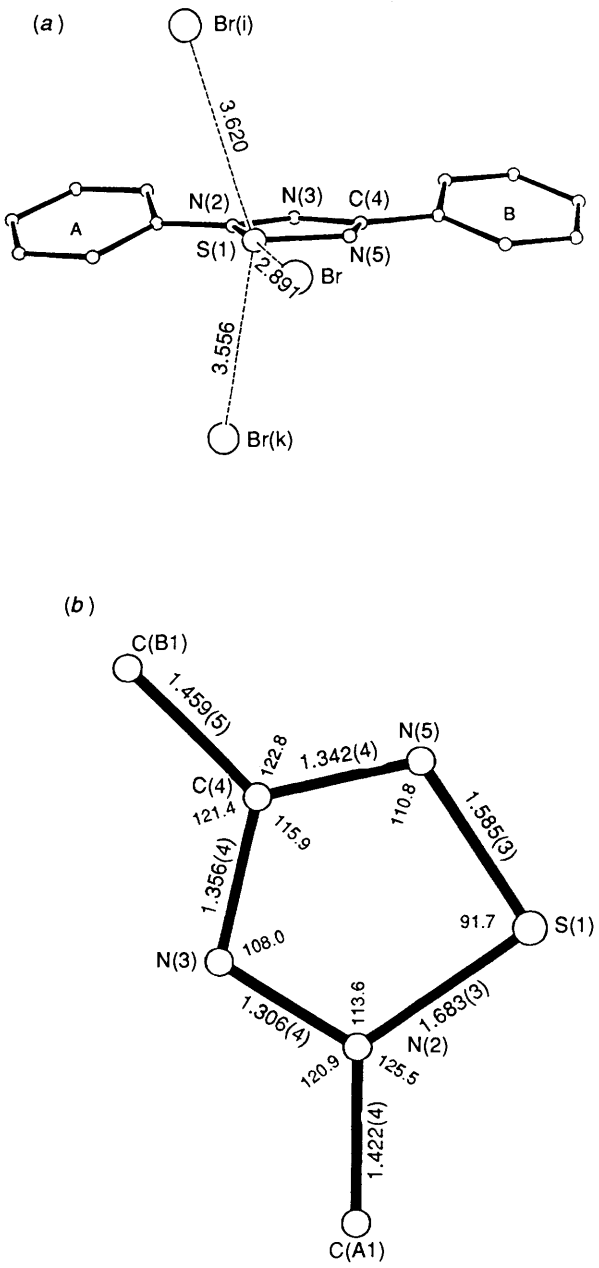


Figure 4. Molecular structure of 2,4-diphenyl-2*H*-1,2,3,5-thiatriazol-1-ium bromide (**6h**): (*a*) Side-view showing the S···Br distances. (*b*) Top-view of the central five-membered ring, showing the atom-labelling scheme, bond distances (Å), and angles (°).

these results, the ESR spectra of compounds (**1a–d**) were analysed and were well simulated with the values given in Table 1. Specific ^{15}N labelling in compounds (**1f**) and (**1g**) clearly assigned the nitrogen coupling constants. As expected, in the *N*-phenyl groups the *ortho* and *para* proton coupling constants are negative [*a*(H) −1.80 G] and that of the *meta* protons positive [*a*(H) +0.60 G]. The further proton splitting of +0.22 G in the ENDOR spectrum of compound (**1c**), not resolved in the ESR spectrum, is tentatively assigned to the *ortho* protons of the *C*-phenyl ring in analogy to ENDOR results obtained for 2,3-dihydro-1*H*-1,2,4-triazol-1-yl radicals.[27]

The 2,5-dihydro-1,2,3,5-triazol-5-yl radicals, which remain monomeric down to 230 K, enclose the basic partial structures of 1,2,3,5-dithiadiazolyl (**2**) and tetrazolinyl radicals (**3**). The nitrogen coupling constants of the hydrazyl moiety, (**1c**): *a*(N^2)

Table 1. Isotropic hyperfine coupling constants and *g*-values of the 2,5-dihydro-1,2,3,5-thiatriazol-5-yl radicals (**1a–g**) in DME.

		T/K	$a(N^2)$/G	$a(N^3)$/G	$a(N^5)$/G	$a(H^{2',6'})$/G	$a(H^{3',5'})$/G	$a(H^{4'})$/G	a(H)/G	*g*-value
(**1a**)	ESR	230	7.62	4.19	4.97	1.80	0.60	1.80	1.80[a]	2.0042
(**1b**)	ESR	230	7.60	4.20	5.00				1.80[a]	2.0042
(**1c**)	ESR	300	7.85	4.15[b,c]	5.10[b]	1.80		1.80		2.0042
	ENDOR	220	7.61	4.12	5.08	−1.79	+0.61	−1.79	+0.22[d]	
(**1d**)	ESR	230	7.61	4.08	5.07	1.78	0.60	1.78		2.0042
(**1e**)	ESR	300	7.85	4.15	5.10					2.0042
	ESR	230	7.57	4.10	5.10					2.0042
(**2**)[5]	ESR	229			5.18[e]					2.0037
(**3**)[10]	ESR	300	7.5[f]	5.6[f]						2.0102

[a] $a(H^{Me})$, 3 H. [b] (**1g**): $a(N^2)$ 7.85, $a(^{15}N^3)$ 5.80, $a(^{15}N^5)$ 7.15 G. [c] (**1f**): $a(N^2)$ 7.85, $a(^{15}N^3)$ 5.80, $a(N^5)$ 5.10 G. [d] Probably $a(H^{2'',6''})$, see the text. [e] 4-Phenyl-1,2,3,5-dithiadiazolyl in perdeuteriotoluene, 229 K:[5] $a(N^{3,5})$ 5.18, $a(^{33}S^{1,2})$ 6.18 G. [f] 2,3,5-Triphenyltetrazolinyl in benzene, 300 K:[10] $a(N^{1,4})$ 5.6, $a(N^{2,3})$ 7.5 G.

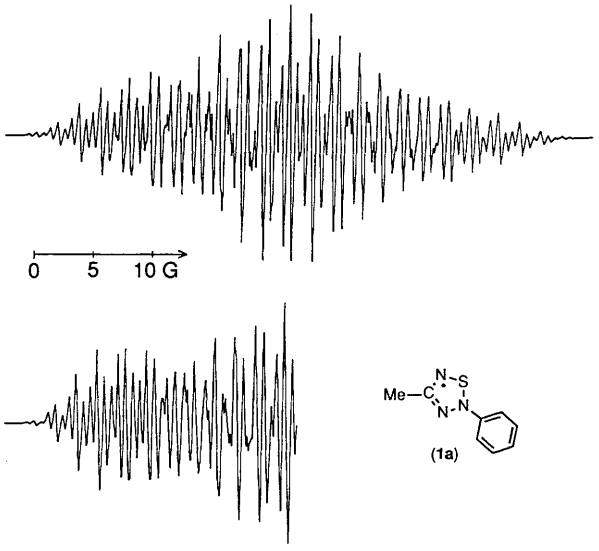


Figure 5. ESR spectrum of compound (**1a**) in DME at 230 K together with a simulation (bottom) using the data in Table 1.

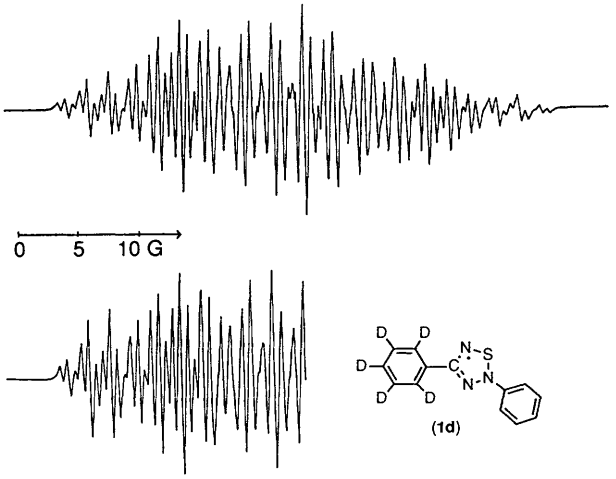


Figure 6. ESR spectrum of compound (**1d**) in DME at 230 K together with a simulation (bottom) using the data in Table 1.

7.85, $a(N^3)$ 4.15 G, are close to the data of the 2,3,5-triphenyltetrazolinyl radical: $a(N^2)$ 7.5, $a(N^1)$ 5.6 G,[10] and the same holds for the N–S moiety, (**1c**): $a(N^5)$ 5.10 G as compared with the *a*(N) 5.18 G splitting of the 4-phenyl-1,2,3,5-dithiadiazolyl radical.[5] Therefore, 2,5-dihydro-1,2,3,5-thiatriazol-5-yl radicals (**1**) can be considered to be a true linking member between radicals (**2**) and (**3**). All these radicals are characterized by a seven-π-electron system with a node at the methine carbon, the latter being indicated by the very small delocalization of the unpaired electron into the *C*-phenyl substituent.

Table 2. Crystallographic data and refinement parameters of 2,5-dihydro-2,4-diphenyl-1,2,3,5-thiatriazole 1-oxide (**5c**) and 2,4-diphenyl-2*H*-1,2,3,5-thiatriazol-1-ium bromide (**6h**).

	(**5c**)	(**6h**)
Formula	$C_{13}H_{11}N_3OS$	$C_{13}H_{10}BrN_3S$
Molecular mass	257.3	320.2
Crystallized from	Methanol	Nitromethane
Crystal size/mm	0.15 × 0.2 × 0.4	0.02 × 0.1 × 0.35
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pbca*
a/Å	25.993(5)	6.945(1)
b/Å	6.958(2)	31.305(5)
c/Å	14.174(4)	11.649(2)
β/°	109.10(2)	
Z	8	8
F(000)	1 072	1 280
D_x/g cm^{-3}	1.412	1.678
μ/cm^{-1} (Mo-K$_\alpha$)	2.46	33.53
Absorption correction	None	Empirical (ψ-scan, τ_{min} 35.52, τ_{max} 99.95%)
Measured reflections	2 910	2 224
$(\sin\theta/\lambda$ Å$^{-1})_{max}$	0.66	0.62
Observed reflections [$I \geqslant 3\sigma(I)$]	1 542	1 502
Refinement R/R_w	0.048/0.050	0.036/0.037
$(\Delta/\sigma)_{max}$	0.2	0.4
$(\Delta\rho$/e Å$^{-3})_{max.}$	0.15	0.18

Experimental

UV–visible spectra were recorded on a Cary 17 spectrophotometer. IR spectra were measured on a Beckman IR 4240 spectrophotometer for samples in KBr. ^{1}H NMR spectra were obtained with a Bruker AM 500 instrument for [$^2H_6$]dimethyl sulphoxide solutions at room temperature unless otherwise stated. Chemical shifts are reported as δ-values with tetramethylsilane as internal standard. ^{15}N NMR spectra were recorded on a Bruker AC 200 spectrometer, with external standard [^{15}N]nitromethane. Mass spectra were taken on a Dupont CEC 21-492 or on a Finnigan MAT 212 mass spectrometer (ionization energy 70 eV). ESR and ENDOR spectra were recorded on a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; *g*-values

Table 3. Fractional atomic co-ordinates for non-hydrogen atoms of compounds (**5c**) and (**6h**) with esds of the least significant figure in parentheses.

	x	*y*	*z*
Molecule (**5c**)			
S(1)	0.221 43(3)	0.196 1(1)	0.107 44(6)
N(2)	0.159 36(8)	0.167 4(3)	0.019 8(2)
N(3)	0.118 57(8)	0.276 5(3)	0.037 0(2)
C(4)	0.141 3(1)	0.411 9(4)	0.097 5(2)
N(5)	0.197 70(8)	0.408 2(4)	0.127 5(2)
O(1′)	0.228 26(7)	0.070 8(3)	0.193 7(1)
C(A1)	0.144 6(1)	−0.009 0(4)	−0.032 4(2)
C(A2)	0.092 0(1)	−0.073 9(5)	−0.061 3(2)
C(A3)	0.078 5(1)	−0.243 1(5)	−0.113 6(2)
C(A4)	0.117 2(1)	−0.349 1(5)	−0.136 5(2)
C(A5)	0.169 3(1)	−0.284 3(5)	−0.108 7(2)
C(A6)	0.183 0(1)	−0.113 9(5)	−0.057 3(2)
C(B1)	0.111 3(1)	0.562 5(4)	0.128 3(2)
C(B2)	0.136 6(1)	0.729 0(5)	0.173 9(2)
C(B3)	0.107 6(1)	0.870 7(5)	0.200 7(2)
C(B4)	0.052 7(1)	0.848 9(5)	0.181 5(2)
C(B5)	0.027 1(1)	0.685 1(5)	0.136 4(2)
C(B6)	0.056 1(1)	0.542 6(5)	0.110 2(2)
Molecule (**6h**)			
Br	0.091 56(8)	0.089 31(2)	0.099 16(4)
S(1)	0.596 3(2)	0.108 06(4)	0.157 88(9)
N(2)	0.611 5(5)	0.118 8(1)	0.016 6(3)
N(3)	0.630 4(5)	0.159 4(1)	−0.006 3(3)
C(4)	0.632 5(6)	0.181 0(1)	0.094 7(3)
N(5)	0.616 8(6)	0.157 1(1)	0.189 8(3)
C(A1)	0.606 4(6)	0.088 0(1)	−0.073 1(3)
C(A2)	0.650 8(7)	0.045 8(2)	−0.047 4(4)
C(A3)	0.643 2(7)	0.015 8(2)	−0.134 0(4)
C(A4)	0.599 1(7)	0.027 2(1)	−0.243 6(4)
C(A5)	0.557 9(7)	0.069 7(2)	−0.268 7(4)
C(A6)	0.563 4(7)	0.100 2(1)	−0.183 6(4)
C(B1)	0.650 8(6)	0.227 4(1)	0.098 1(3)
C(B2)	0.607 1(7)	0.251 7(2)	0.002 9(4)
C(B3)	0.624 6(7)	0.295 1(2)	0.006 4(4)
C(B4)	0.685 1(7)	0.315 1(2)	0.104 9(4)
C(B5)	0.730 5(7)	0.290 8(2)	0.200 4(3)
C(B6)	0.711 7(7)	0.247 4(1)	0.196 7(3)

were determined by using an NMR gaussmeter and a Hewlett-Packard 5246 L frequency converter. This was calibrated with the perylene radical cation.

X-Ray Analyses of Compounds (**5c**) *and* (**6h**).—All measurements were made on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.710 69 Å, θ/2θ scanning technique). Lattice parameters were determined from least-squares fit using 30 reflections (θ range: 10–14°). The structures were solved by direct methods (MULTAN) and were refined by full-matrix least-squares minimizing $\Sigma w(\Delta F)^2$ with the weighting scheme $w = [\sigma(F)^2 + (0.01 F_0)^2]^{-1}$. Hydrogen atoms were refined with isotropic and all other atoms with anisotropic temperature factors.[28] Atomic scattering factors and anomalous-dispersion corrections were taken from International Tables for X-ray Crystallography.[29] The crystallographic data and the parameters of structure refinement are given in Table 2, with final fractional atomic co-ordinates for non-hydrogen atoms in Table 3.*

* *Supplementary material* (see section 5.6.3 of Instructions for Authors, in the January issue). Atomic co-ordinates, bond lengths and angles, torsional angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

N^2-[$^2H_5$]Phenylacetamidrazone hydrochloride {(**4b**), labelled starting material [2,3,4,5,6-$^2H_5$]aniline}, N^2-phenyl[$^2H_5$]-benzamidrazone {(**4d**), [2,3,4,5,6-$^2H_5$]benzaldehyde}, N^2-[$^2H_5$]phenyl[$^2H_5$]benzamidrazone {(**4e**), [2,3,4,5,6-$^2H_5$]aniline}, N^2-phenyl[$^{15}N^1$]benzamidrazone [(**4f**), $Na^{15}NO_2$], N^2-phenyl[$^{15}N^1$,$^{15}N^3$]benzamidrazone [(**4g**), $Na^{15}NO_2$], and their precursors were prepared following literature procedures for the corresponding non-labelled compounds.

1-*Nitroacetaldehyde* [$^2H_5$]*Phenylhydrazone*.[30,31]—This had m.p. 144 °C (decomp.); δ_H 2.47 (3 H, s, Me) and 10.38 (1 H, s).

N^2-[$^2H_5$]*Phenylacetamidrazone Hydrochloride* (**4b**·HCl).[32,33]—This had m.p. 200–201 °C (decomp.) (Found: C, 50.1; H + ^{2}H, 9.6; Cl, 18.6; N, 22.0. Calc. for $C_8H_7{}^2H_5ClN_3$: C, 50.39; H + ^{2}H, 8.98; Cl, 18.59; N, 22.04%); δ_H 2.31 (3 H, s, Me), 8.56 (1 H, s), 8.95 (1 H, s), 9.57 (1 H, s), and 11.47 (1 H, s).

N^2-*Phenyl*[$^2H_5$]*benzamidrazone* (**4d**).[34]—1,5-Diphenyl-3-[$^2H_5$]phenylformazan[35] (6.10 g, 20 mmol) in ethanol (100 cm^3) was hydrogenated (40 mmol H_2) in the presence of 5% Pd/C (2.5 g) as catalyst. After filtration, the solution was evaporated under reduced pressure. The residue was crystallized from diethyl ether–pentane to give compound (**4d**) (2.80 g, 65%) as reddish crystals, m.p. 85–86 °C (decomp.).

N^2-[$^2H_5$]*Phenyl*[$^2H_5$]*benzamidrazone* (**4e**).[34]—Prepared from 1,3,5-tri[$^2H_5$]phenylformazan[36] (6.20 g, 20 mmol) as described above: reddish crystals (2.50 g, 57%), m.p. 85–87 °C (decomp.).

α-*Nitrobenzaldehyde* [2-^{15}N]*Phenylhydrazone*.[37]—This had m.p. 102–103 °C.

N^2-*Phenyl*[$^{15}H^1$]*benzamidrazone* (**4f**).[34]—Prepared by hydrogenation (45 mmol H_2) of α-nitrobenzaldehyde [2-^{15}N]-phenylhydrazone (3.63 g, 15 mmol) in the presence of 5% Pd/C (2.0 g) as described for compound (**4d**): reddish crystals (2.30 g, 72%), m.p. 85–86 °C (decomp.).

N^2-*Phenyl*[$^{15}N^1$,$^{15}N^3$]*benzamidrazone* (**4g**).[34]—Prepared from 1,3,5-triphenyl[2,4-$^{15}N_2$]formazan[38] (1.51 g, 5 mmol) as described for compound (**4e**): reddish crystals (600 mg, 60%), m.p. 85–86 °C (decomp.).

2,5-*Dihydro*-4-*methyl*-2-*phenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**5a**).—Solutions of N^2-phenylacetamidrazone hydrochloride (5.57 g, 30 mmol) in pyridine (50 cm^3), and thionyl chloride (10.7 g, 90 mmol) in anhydrous chloroform (100 cm^3), were added dropwise, separately at the same time, to stirred, anhydrous chloroform (300 cm^3) at *ca.* 5 °C. The solution was stirred for 2 h at 5 °C after the addition was complete. The reaction mixture was then washed repeatedly with water, dried ($MgSO_4$), and evaporated to provide the crude reaction product, which was crystallized from ethanol–water to give *compound* (**5a**) (4.03 g, 69%) as plates, m.p. 139–140 °C (Found: C, 49.4; H, 4.6; N, 21.5; S, 16.6. $C_8H_9N_3OS$ requires C, 49.21; H, 4.65; N, 21.52; S, 16.42%); ν_{max} 3 170 cm^{-1}; δ_H 2.24 (3 H, s, Me), 7.08 (1 H, tt, *J* 6.5, 1.8 Hz, 4-H in NPh), 7.34–7.41 (4 H, m, ArH), and 11.26 (1 H, s, NH); irradiation of NH (δ 11.26) yielded an NOE response for the methyl protons (δ 2.24); *m/z* 195 ($M^{+\cdot}$, 66%), 178 (23), 109 (16), 105 (48), 91 (60), and 77 (100).

2,5-*Dihydro*-4-*methyl*-2-[$^2H_5$]*phenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**5b**).—Solutions of N^2-[$^2H_5$]phenylacetamidrazone hydrochloride (5.72 g, 30 mmol) in pyridine (100 cm^3), and

thionyl chloride (10.7 g, 90 mmol) in anhydrous chloroform (100 cm^3), were treated in anhydrous chloroform (300 cm^3) as described for compound (**5a**): the labelled product (**5b**) (4.31 g, 72%) was obtained as *plates*, m.p. 142 °C (Found: C, 48.0; H + ^2H, 7.1; N, 20.9; S, 15.9. $C_8H_4{}^2H_5N_3OS$ requires C, 47.98; H + ^2H, 7.04; N, 20.98; S, 16.01%); ν_{max} 3 140 cm^{-1}; δ_H 2.24 (3 H, s, Me) and 11.26 (1 H, s, NH), deuteriation >96%; *m/z* 200 ($M^{+\bullet}$, 55%), 183 (19), 114 (13), 110 (36), 96 (40), and 82 (100).

2,5-*Dihydro*-2,4-*diphenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**5c**).—To a stirred solution of N^2-phenylbenzamidrazone (4.22 g, 20 mmol) in anhydrous chloroform (20 cm^3) and pyridine (8 cm^3), cooled to *ca.* 5 °C, was added dropwise thionyl chloride (4.76 g, 40 mmol) in anhydrous chloroform (20 cm^3). The solution was stirred for 2 h at 5 °C after the addition was complete. The reaction mixture was then diluted with chloroform (200 cm^3), washed repeatedly with water, dried ($MgSO_4$), and evaporated to provide the crude reaction product, which was crystallized from ethanol–water to give *compound* (**5c**) as crystals (2.85 g, 55%), m.p. 162–163 °C (decomp.) (Found: C, 60.7; H, 4.5; N, 16.05; S, 12.4. $C_{13}H_{11}N_3OS$ requires C, 60.68; H, 4.31; N, 16.33; S, 12.46%); λ_{max}(dioxane) 220sh (log ε 4.19) and 301 nm (4.11); (DMSO) 305 nm (4.10); ν_{max} 3 185 cm^{-1}; δ_H 7.16 (1 H, tt, *J* 7.3, 1.1 Hz, 4-H in NPh), 7.44 (2 H, dd, 3-, 5-H in NPh), 7.52–7.60 (5 H, m, 2-, 6-H in NPh and 3-, 4-, 5-H in CPh), 7.96 (2 H, dd, *J* 7.5, 1.6 Hz, 2-, 6-H in CPh), and 11.99 (1 H, s, NH); irradiation of NH (δ 11.99) yielded a strong NOE response for 2-, 6-H in CPh (δ 7.96); *m/z* 257 ($M^{+\bullet}$, 17%), 240 (26), 152 (12), 135 (18), 109 (29), 105 (61), 104 (37), 103 (20), 91 (14), 78 (10), and 77 (100).

2,5-*Dihydro*-2-*phenyl*-4-[$^2H_5$]*phenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**5d**).—Prepared as described above, using N^2-phenyl-[$^2H_5$]benzamidrazone (2.16 g, 10 mmol) and obtained from ethanol–water as *crystals* (1.40 g, 53%), m.p. 165–166 °C (decomp.) (Found: C, 59.7; H + ^2H, 6.1; N, 16.0; S, 12.1. $C_{13}H_6{}^2H_5N_3OS$ requires C, 59.52; H + ^2H, 6.15; N, 16.02; S, 12.22%); ν_{max} 3 185 cm^{-1}; δ_H 7.15 (1 H, t, *J* 7.3 Hz, 4-H in NPh), 7.44 (2 H, dd, 3-, 5-H in NPh), 7.54 (2 H, d, *J* 7.7 Hz, 2-, 6-H in NPh), and 11.98 (1 H, s, NH); deuteriation in CPh >98%; *m/z* 262 ($M^{+\bullet}$, 18%), 245 (23), 157 (9), 152 (13), 140 (17), 109 (51), 108 (56), 105 (53), 91 (22), 82 (17), and 77 (100).

2,5-*Dihydro*-2,4-*di*[$^2H_5$]*phenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**5e**).—Prepared as described above, using N^2-[$^2H_5$]phenyl-[$^2H_5$]benzamidrazone (2.21 g, 10 mmol) and obtained from ethanol–water as *crystals* (1.33 g, 50%), m.p. 159–160 °C (decomp.) (Found: C, 58.5; H + ^2H, 7.9; N, 15.6; S, 11.9. $C_{13}H^2H_{10}N_3OS$ requires C, 58.40; H + ^2H, 7.95; N, 15.72; S, 11.99%); ν_{max} 3 185 cm^{-1}; δ_H 11.98 (1 H, s, NH); deuteriation in NPh >98%; in CPh, however, *ca.* 95% with a random distribution of H; *m/z* 267 ($M^{+\bullet}$, 2%), 250 (12), 140 (13), 114 (24), 110 (50), 109 (42), 108 (18), 96 (8), and 82 (100).

2,5-*Dihydro*-2,4-*diphenyl*-[3-^{15}N]-1,2,3,5-*thiatriazole* 1-*Oxide* (**5f**).—Prepared as described above, using N^2-phenyl[$^{15}N^1$]-benzamidrazone (2.12 g, 10 mmol) and obtained from ethanol–water as *crystals* (1.50 g, 58%), m.p. 160–161 °C (decomp.) (Found: C, 60.6; H, 4.4; N + ^{15}N, 16.6; S, 12.7. $C_{13}H_{11}N_2{}^{15}NOS$ requires C, 60.45; H, 4.29; N + ^{15}N, 16.66; S, 12.41%); ν_{max} 3 185 cm^{-1}; δ_H 7.16 (1 H, tt, *J* 7.3, 1.1 Hz, 4-H in NPh), 7.45 (2 H, dd, 3-, 5-H in NPh), 7.52–7.59 (5 H, m, 2-, 6-H in NPh and 3-, 4-, 5-H in CPh), 7.95 (2 H, dd, *J* 7.5, 1.8 Hz, 2-, 6-H in CPh), and 11.98 (1 H, s, NH); δ_H(dichloro[$^2H_2$]methane) 7.19 (1 H, t, *J* 7.3 Hz, 4-H in NPh), 7.41–7.51 (5 H, m, 3-, 5-H in NPh and 3-, 4-, 5-H in CPh), 7.55–7.60 (2 H, m, 2-, 6-H in NPh), 7.74–7.79 (2 H, m, 2-, 6-H in CPh), and 8.35 (1 H, s, NH); δ_H(dichloro[$^2H_2$]methane; high dilution) 7.19 (1 H, tt, *J* 7.4, 0.9 Hz, 4-H in NPh), 7.41–7.46 (2 H, m, 3-, 5-H in NPh), 7.50–7.54 (3 H, m, 3-, 4-, 5-H in CPh), 7.59 (2 H, dt, *J* 7.7, 1.0 Hz, 2-, 6-H in NPh), 7.82–7.88 (2 H, m, 2-, 6-H in CPh), and 7.88 (1 H, s, NH); *m/z* 258 ($M^{+\bullet}$, 6%), 241 (19), 152 (8), 135 (14), 109 (28), 106 (49), 104 (52), 103 (25), 91 (11), and 77 (100).

2,5-*Dihydro*-2,4-*diphenyl*-[3,5-$^{15}N_2$]-1,2,3,5-*thiatriazole* 1-*Oxide* (**5g**).—Prepared as described above, using N^2-phenyl-[$^{15}N^1$,$^{15}N^3$]benzamidrazone (530 mg, 2.5 mmol) and obtained from ethanol–water as *crystals* (350 mg, 53%), m.p. 160–161 °C (decomp.) (Found: C, 60.5; H, 4.2; N + ^{15}N, 17.2. $C_{13}H_{11}N{}^{15}N_2OS$ requires C, 60.21; H, 4.28; N + ^{15}N, 16.97%); ν_{max} 3 180 cm^{-1}; δ_H 7.16 (1 H, t, *J* 7.3 Hz, 4-H in NPh), 7.44 (2 H, dd, 3-, 5-H in NPh), 7.51–7.61 (5 H, m, 2-, 6-H in NPh and 3-, 4-, 5-H in CPh), 7.95 (2 H, dd, *J* 7.7, 1.5 Hz, 2-, 6-H in CPh), and 11.98 (1 H, s, NH); irradiation of NH (δ 11.98) yielded a strong NOE response for 2-, 6-H in CPh (δ 7.95); δ_H(dichloro[$^2H_2$]methane) 7.19 (1 H, t, *J* 7.2 Hz, 4-H in NPh), 7.38–7.50 (5 H, m, 3-, 5-H in NPh, 3-, 4-, 5-H in CPh), 7.55–7.60 (2 H, m, 2-, 6-H in NPh), 7.66 (2 H, dd, *J* 8.2, 1.4 Hz, 2-, 6-H in CPh) 8.40 (d, *J* 90.9 Hz, ^{15}NH); irradiation of NH (δ 8.40) yielded a strong NOE response for 2-, 6-H in CPh (δ 7.76) and *vice versa*; δ(^{15}N) −238.8 (br s, N-5) and −131.3 (s, N-3); (dichloro[$^2H_2$]methane) −243.3 (d, *J* 90.6 Hz, 5-N) and −129.6 (s, N-3); *m/z* 259 ($M^{+\bullet}$, 1%), 242 (9), 136 (11), 109 (21), 106 (43), 105 (36), 104 (14), 91 (7), and 77 (100).

4-*Methyl*-2-*phenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6a**).—A solution of phosphorus pentachloride (420 mg, 2 mmol) in anhydrous chloroform (10 cm^3) was added to a solution of compound (**5a**) (390 mg, 2 mmol) in anhydrous chloroform (25 cm^3). The reaction mixture was heated to boiling for *ca.* 5 min and then cooled in an ice-bath. The product, as yellow crystals, precipitated from the solution on addition of anhydrous diethyl ether. Filtration yielded the *salt* (**6a**) (270 mg, 62%), m.p. 175–176 °C (decomp.) (Found: C, 44.8; H, 4.0; Cl, 16.9; N, 19.5. $C_8H_8ClN_3S$ requires C, 44.97; H, 3.77; Cl, 16.59; N, 19.66%); δ_H[TFA–TFAA (1:3)] 3.27 (3 H, s, Me), 7.82 (2 H, dd, 3-, 5-H in Ph), 7.94 (1 H, t, *J* 7.6 Hz, 4-H in Ph), and 8.25 (2 H, d, *J* 8.1 Hz, 2-, 6-H in Ph); *m/z* 178 ($M - Cl^-$, 49%), 109 (12), 108 (13), 105 (51), 91 (7), and 77 (100).

The following compounds were prepared analogously.

4-*Methyl*-2-[$^2H_5$]*phenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6b**). From compound (**5b**) (400 mg, 2 mmol): *compound* (**6b**) (320 mg, 73%) had m.p. 177–178 °C (decomp.) (Found: C, 43.7; H + ^2H, 6.2; N, 18.9. $C_8H_3{}^2H_5ClN_3S$ requires C, 43.93; H + ^2H, 5.99; N, 19.21%); δ_H[TFA–TFAA (1:3)] 3.26 (3 H, s, Me), deuteriation >96%; *m/z* 183 ($M - Cl^-$, 25%), 114 (15), 110 (37), 96 (26), and 82 (100).

2,4-*Diphenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6c**). From compound (**5c**) (514 mg, 2 mmol): *compound* (**6c**) (400 mg, 73%) was obtained as yellow crystals, m.p. 207–208 °C (decomp.) (Found: C, 56.8; H, 3.7; Cl, 12.8; N, 15.0; S, 12.3. $C_{13}H_{10}ClN_3S$ requires C, 56.62; H, 3.66; Cl, 12.86; N, 15.24; S, 11.63%); λ_{max}[TFA–TFAA (1:3)] 345 nm (log ε 3.93); δ_H[TFA–TFAA (1 : 3)] 7.72 (2 H, dd, 3-, 5-H in CPh), 7.80 (1 H, t, *J* 7.4 Hz, 4-H in CPh), 7.86 (2 H, dd, 3-, 5-H in NPh), 7.97 (1 H, t, *J* 7.5 Hz, 4-H in NPh), 8.35 (2 H, d, *J* 8.2 Hz, 2-, 6-H in NPh), and 8.52 (2 H, d, *J* 7.5 Hz, 2-, 6-H in CPh); the COSY spectrum shows that the resonances at δ_H 7.72, 7.80, and 8.52 are coupled with each other, as are those at δ_H 7.86, 7.97, and 8.35; *m/z* 240 ($M - Cl^-$, 32%), 135 (16), 109 (22), 105 (48), 103 (22), 91 (5), and 77 (100).

2-*Phenyl*-4-[$^2H_5$]*phenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6d**). From compound (**5d**) (131 mg, 0.5 mmol): *compound* (**6d**) (105 mg, 75%) was obtained as yellow crystals, m.p. 204–205 °C (decomp.) (Found: C, 55.6; H + ^2H, 5.4; N, 14.6; S, 11.05. $C_{13}H_5{}^2H_5ClN_3S$ requires C, 55.61; H + ^2H, 5.38; N, 14.97; S, 11.24%); δ_H[TFA–TFAA (1:3)] 7.85 (2 H, dd, 3-, 5-H in NPh), 7.96 (1 H, t *J* 7.4 Hz, 4-H in NPh), and 8.35 (2

H, d, *J* 8.1 Hz, 2-, 6-H in NPh); *m/z* 245 (*M* − Cl^-, 24%), 140 (19), 109 (40), 108 (46), 105 (69), 91 (7), 82 (11), and 77 (100).

2,4-*Di*[$^2H_5$]*phenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6e**). From compound (**5e**) (534 mg, 2 mmol): *compound* (**6e**) (430 mg, 75%) was obtained as yellow crystals, m.p. 208–209 °C (decomp.) (Found: C, 54.9; ^2H, 7.3; Cl, 12.4; N, 14.6; S, 11.4. $C_{13}{}^2H_{10}ClN_3S$ requires C, 54.63; ^2H, 7.05; Cl, 12.40; N, 14.70; S, 11.22%); *m/z* 250 (*M* − Cl^-, 12%), 140 (12), 114 (20), 110 (40), 108 (16), 96 (6), and 82 (100).

2,4-*Diphenyl*-[3-^{15}N]-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6f**). From compound (**5f**) (516 mg, 2 mmol): *compound* (**6f**) (390 mg, 71%) was obtained as yellow crystals, m.p. 209–210 °C (decomp.) (Found: C, 56.6; H, 3.7; Cl, 13.0; N + ^{15}N, 15.7; S, 11.3. $C_{13}H_{10}ClN_2{}^{15}NS$ requires C, 56.42; H, 3.64; Cl, 12.81; N + ^{15}N, 15.54; S, 11.59%); *m/z* 241 (*M* − Cl^-, 22%), 135 (15), 109 (30), 106 (55), 103 (30), 91 (10), and 77 (100).

2,4-*Diphenyl*-[3,5-$^{15}N_2$]-2H-1,2,3,5-*thiatriazol*-1-*ium Chloride* (**6g**). From compound (**5g**) (259 mg, 1 mmol): *compound* (**6g**) (190 mg, 68%) was obtained as yellow crystals, m.p. 210–211 °C (decomp.) (Found: C, 56.1; H, 3.6; N + ^{15}N, 15.8. $C_{13}H_{10}ClN^{15}N_2S$ requires C, 56.21; H, 3.63; N + ^{15}N, 15.84%); *m/z* 242 (*M* − Cl^-, 28%), 136 (10), 109 (18), 106 (49), 104 (14), 91 (4), and 77 (100).

2,4-*Diphenyl*-2H-1,2,3,5-*thiatriazol*-1-*ium Bromide* (**6h**). From phosphorus pentabromide (862 mg, 2 mmol) and compound (**5c**) (514 mg, 2 mmol); *compound* (**6h**) (460 mg, 72%) was obtained as orange crystals, m.p. 222–223 °C (decomp.) or as orange plates, m.p. 224–225 °C (decomp.) (from $MeNO_2$) (Found: C, 48.5; H, 3.1; Br, 25.55; N, 13.0; S, 9.9. $C_{13}H_{10}BrN_3S$ requires C, 48.76; H, 3.15; Br, 24.96; N, 13.12; S, 10.01%); λ_{max}[TFA–TFAA (1:3)] 344 nm (log ε 3.96); δ_H[TFA–TFAA (1:3)] 7.72 (2 H, dd, 3-, 5-H in CPh), 7.79 (1 H, t, *J* 7.4 Hz, 4-H in CPh), 7.86 (2 H, dd, 3-, 5-H in NPh), 7.97 (1 H, t, *J* 7.5 Hz, 4-H in NPh), 8.36 (2 H, d, *J* 8.2 Hz, 2-, 6-H in NPh), and 8.52 (2 H, d, *J* 7.7 Hz, 2-, 6-H in CPh); *m/z* 240 (*M* − Br^-, 43%), 135 (14), 109 (30), 105 (69), 103 (14), 91 (6), 78 (7), 77 (100), and 76 (8).

2,5-*Dihydro*-5-*methyl*-2,4-*diphenyl*-1,2,3,5-*thiatriazole* 1-*Oxide* (**9c**).—To a stirred mixture of (**5c**) (514 mg, 2 mmol) and iodomethane (0.5 cm^3, 8 mmol) in dimethylformamide (DMF) (10 cm^3) was added dropwise a solution of KOH (500 mg, 8 mmol) in methanol (4 cm^3). The reaction mixture was stirred for 1 h and then diluted with diethyl ether (100 cm^3), washed repeatedly with water, dried ($MgSO_4$), and evaporated. The crude product remaining was chromatographed over silica gel (eluant dichloromethane) to give *compound* (**9c**) (350 mg, 65%) as crystals from cyclohexane, m.p. 74–75 °C (Found: C, 62.0; H, 4.8; N, 15.4. $C_{14}H_{13}N_3OS$ requires C, 61.97; H, 4.83; N, 15.49%); λ_{max}(dioxane) 278 nm (log ε 4.03); (DMSO) 278 nm (log ε 4.05); δ_H 3.44 (3 H, s, Me), 7.17 (1 H, t, *J* 7.3 Hz, 4-H in NPh), 7.44 (2 H, dd, 3-, 5-H in NPh), 7.50 (2 H, d, *J* 7.9 Hz, 2-, 6-H in NPh), 7.55–7.62 (3 H, m, 3-, 4-, 5-H in CPh), and 7.72–7.77 (2 H, m, 2-, 6-H in CPh); irradiation of the methyl group (δ_H 3.44) yielded a strong NOE response for 2-, 6-H in CPh (δ_H 7.75); *m/z* 271 ($M^{+\cdot}$, 88%), 194 (85), 118 (100), 91 (93), and 77 (70).

2,5-*Dihydro*-5-*methyl*-2,4-*diphenyl*-[3,5-$^{15}N_2$]-1,2,3,5-*thiatriazole* 1-*Oxide* (**9g**).—A mixture of compound (**5g**) (200 mg, 0.77 mmol), iodomethane (0.5 cm^3, 8 mmol), and K_2CO_3 (1.5 g) in DMF (10 cm^3) was stirred for 2 h. The reaction mixture was then worked up as described above to give *compound* (**9g**) (135 mg, 64%) as crystals from cyclohexane, m.p. 74–75 °C (Found: C, 61.7; H, 4.6; N, 16.0. $C_{14}H_{13}N^{15}N_2OS$ requires C, 61.52; H, 4.79; N, 16.10%); δ_H 3.44 (3 H, s, Me), 7.17 (1 H, t, *J* 7.3 Hz, 4-H in NPh), 7.44 (2 H, dd, 3-, 5-H in NPh), 7.50 (2 H, d, *J* 7.7 Hz, 2-, 6-H in NPh), 7.54–7.62 (3 H, m, 3-, 4-, 5-H in CPh), and 7.72–7.77 (2 H, m, 2-, 6-H in CPh); $\delta(^{15}N)$ −244.7 (s, N-5) and −125.7 (s, N-3); (dichloro[$^2H_2$]methane) −246.0 (s, N-5) and −125.5 (s, N-3).

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