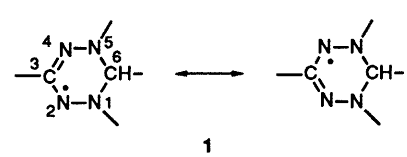
Verdazyls. Part 33.[1] EPR and ENDOR Studies of 6-Oxo- and 6-Thioxoverdazyls. X-Ray Molecular Structure of 1,3,5-Triphenyl-6-oxoverdazyl and 3-*tert*-Butyl-1,5-diphenyl-6-thioxoverdazyl

Franz A. Neugebauer,* Hans Fischer and Claus Krieger
Abt. Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstr. 29, D 6900 Heidelberg, Germany

A range of 6-oxoverdazyls **2b–h** and 6-thioxoverdazyls **3a–c** and **3e–h** has been directly prepared by dehydrogenation of the corresponding 1,4,5,6-tetrahydro-1,2,4,5-tetrazin-3(2*H*)-ones **5b–h** and thiones **7a–c** and **7e–h** with lead dioxide, potassium hexacyanoferrate(III), or bis(4-methylphenyl)-aminyl. X-Ray analyses reveal a nearly planar verdazyl framework for the oxoverdazyl **2a**, whereas the thioxoverdazyl **3f** takes on a flat boat conformation. In the latter, owing to the bulky sulfur the *N*-phenyl groups are considerably twisted out of the plane of the verdazyl ring. Electronic absorption spectra of the deeply coloured radicals exhibit characteristic bands in the visible region with $\lambda_{max,1}$ ranging from 445 to 608 nm. EPR, ENDOR and ^{2}H NMR studies have led to a complete analysis and full assignment of all hyperfine coupling constants. The π-SOMO of 6-oxo- **2** and 6-thioxo-verdazyls **3**, having nodes at C(3) and C(6), is mainly confined to the nitrogens of the verdazyl ring. Spin delocalization into the *N*-phenyl groups is reduced, particularly in the 6-thioxoverdazyls, owing to the large torsion angle about the N–C(phenyl) bond.

In connection with our studies on verdazyl radicals **1**, 6-oxo- **2** and 6-thioxo-verdazyls **3** were of interest, since replacement of the methylene bridge in **1** by carbonyl or thiocarbonyl should clearly affect the properties of the radicals, especially the geometry of the verdazyl ring. Furthermore, in 6-thioxoverdazyls, owing to the bulky thiocarbonyl group, adjacent *N*-aryl substituents would be considerably distorted with regard to the verdazyl ring plane, and hence spin delocalization into the *N*-aryl rings largely reduced. Evidence for such changes can be derived from EPR studies of representative 6-oxo- and 6-thioxo-verdazyls, while X-ray analysis of any of these compounds should reveal the geometry of the particular verdazyl ring system.

Previous work from this laboratory[1] showed that stable 6-oxo- and 6-thioxo-verdazyls are readily obtained by dehydrogenation of corresponding 1,4,5,6-tetrahydro-1,2,4,5-tetrazin-3(2*H*)-ones **5** and -thiones **7**. The synthesis of these precursors, however, turned out to be confined to *N*-alkyl derivatives. Furthermore, none of the prepared radicals provided suitable crystals for X-ray analysis. Recently, R. Milcent *et al.*[2] reported a new synthesis of 1,4,5,6-tetrahydro-2,4,6-triphenyl-1,2,4,5-tetrazin-3(2*H*)-one **5a** (Scheme 1) which was easily dehydrogenated with lead dioxide to give 1,3,5-triphenyl-6-oxoverdazyl **2a**. Using this route we prepared various 6-oxo- **2b–h** and 6-thioxo-verdazyls **3a–c** and **3e–h** and studied their properties. X-Ray analyses of **2a** and **3f** are also presented.



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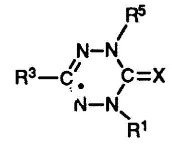


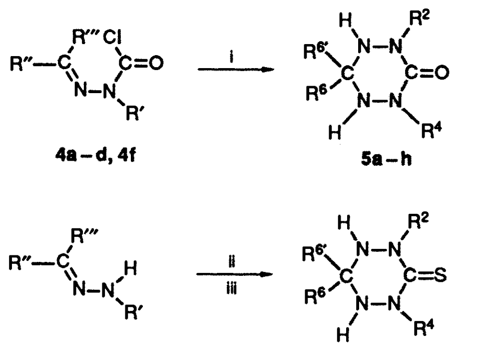
1a; X = H_2
2a–k; X = O
3a–k; X = S

	R^1	R^3	R^5	^{15}N
a	Ph	Ph	Ph	
b	Ph	$[^2H_5]$Ph	Ph	
c	$[^2H_5]$Ph	Ph	$[^2H_5]$Ph	
d	$[^2H_5]$Ph	$[^2H_5]$Ph	$[^2H_5]$Ph	
e	Ph	Ph	Ph	1-^{15}N
f	Ph	$C(CH_3)_3$	Ph	
g	Me	Ph	Ph	
h	Me	$[^2H_5]$Ph	$[^2H_5]$Ph	
i	Me	H	Me	
k	Me	Ph	Me	

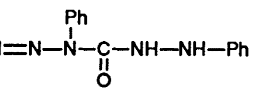
Results and Discussion

Synthesis.—The synthesis of the required 1,4,5,6-tetrahydro-1,2,4,5-tetrazin-3(2*H*)-ones **5** and thiones **7** is summarized in Scheme 1. Similar to the preparation of benzaldehyde 2-chloroformyl-2-phenylhydrazone **4a**[3] the precursor **4f** was obtained from 2,2-dimethylpropanal phenylhydrazone by treatment with phosgene in the presence of triethylamine. Ring closure of the 2-chloroformylhydrazones **4a–d** and **4f** with the appropriate hydrazine by the Milcent procedure[2] readily afforded **5b–h** in *ca.* 60% yield. As a by-product the carbonohydrazides **8a**[4] and **8f** were identified. The hydrazones **6a–c**, **6f** and **6h**, when treated with thiophosgene in the presence of triethylamine, also underwent conversion into 2-chlorothioformylhydrazones. As isolation of these compounds failed owing to decomposition, solutions of the crude product were used in preparing the corresponding 1,4,5,6-tetrahydro-1,2,4,5-tetrazin-3(2*H*)-thiones **7a–c** and **7e–h** (yields *ca.* 20% based on **6**).

Oxidation of **5b–e** with lead dioxide in acetic acid[2] gave the oxoverdazyls **2b–e**. Similar treatment of **5f–h**, however, led to decomposition. We obtained **2f** by dehydrogenation of **5f** with bis(4-methylphenyl)aminyl produced by thermal dissociation of tetrakis(4-methylphenyl)hydrazine. Using this procedure also **2g** and **2h** were generated, but attempts to obtain these radicals in a pure state were unsuccessful. For studies of **2g** and **2h** freshly prepared solutions were employed. Dehydrogenation of **6a–c** and **6e** to the corresponding 6-thioxoverdazyls **3a–c** and **3e** was achieved using potassium hexacyanoferrate(III) as oxidant.[1]



	R^2(R)	R^4(R′)	R^6(R″)	$R^{6'}$(R‴)	^{15}N
a	Ph	Ph	Ph	H	
b	Ph	Ph	[$^2H_5$]Ph	^2H	
c	[$^2H_5$]Ph	[$^2H_5$]Ph	Ph	H	
d	[$^2H_5$]Ph	[$^2H_5$]Ph	[$^2H_5$]Ph	^2H	
e	Ph	Ph	Ph	H	2-^{15}N
f	Ph	Ph	$C(CH_3)_3$	H	
g	Me	Ph	Ph	H	
h	Me	[$^2H_5$]Ph	[$^2H_5$]Ph	^2H	



8a; R = Ph
8f; R = $C(CH_3)_3$

Scheme 1 *Reagents and conditions:* i, Ethanol, $RNHNH_2$, Et_3N; ii, CH_2Cl_2, $CSCl_2$, Et_3N; iii, CH_2Cl_2, $RNHNH_2$, Et_3N.

Attempts to prepare **2f–h** in the same way failed. These thioxoverdazyls were obtained by dehydrogenation of **7f–h** with bis(4-methylphenyl)aminyl.

Crystal Structure of **2a** *and* **3f**.—Owing to their outstanding stability 1,3,5-triarylverdazyls **1** have been the subject of comprehensive X-ray studies. In 1969 D. E. Williams reported the crystal structure of 1,3,5-triphenylverdazyl **1a**.[5] These studies were later extended to a series of derivatives in order to find a relation between crystal structure and observed electron spin–spin interactions, *e.g.* antiferromagnetic and ferromagnetic behaviour at low temperature.[6–12] All these crystal studies, however, only concerned verdazyls of type **1**.

In the radicals **2** and **3** the electronic interaction between the lone pair of electrons at N(1) and the carbonyl or thiocarbonyl bridge may be the major factor determining the molecular structure, particularly the geometry of the verdazyl ring. Fortunately **2a** and **3f** yielded crystals suitable for X-ray analyses. Fig. 1 shows side views of **2a** (*a*) and **3f** (*b*) together with that of **1a** (*c*)[5] as a reference. The crystal structure of **2a**, characterized by a twofold symmetry axis going through C(4″), C(1″), C(3), C(6), and O, reveals a nearly planar, slightly twisted verdazyl skeleton, in which the nitrogens are alternately displaced by ±0.01 Å out of the ring plane. The three-coordinate nitrogens N(1) and N(1ⁱ), which contribute two π-electrons to the π-system, are sp^2-hybridized. The angle of the N–C(phenyl) bond with regard to the N(1), N(2), C(6) plane is 5°. Owing to the spatial requirements of the carbonyl oxygen both *N*-phenyl groups are distorted in a propeller fashion [N(2)–N(1)–C(1′)–C(6′): −34.5(1)°, C(6)–N(1)–C(1′)–C(2′): −41.8(1)°]. The distortion of the C(3)-phenyl group in the same direction is considerably smaller [N(2)–C(3)–C(1″)–C(2″): −12.3(1)°]. Contrary to **2a** the crystal structure of the thioxoverdazyl **3f** shows a mirror plane through C(1″A), C(1″), C(3), C(6) and S (C_s-symmetry). The verdazyl ring of **3f** [Fig. 1(*b*)] takes on a flat boat conformation, with both C(3) and C(6) out of the nitrogen plane (N-plane, ±0.001 Å) on the same side. C(3) is displaced by +0.053 Å, C(6) by +0.100 Å, yielding interplanar angles between the N-plane and the N(2), C(3), N(2ⁱ) plane and between the N-plane and the N(1), C(6), N(1ⁱ) plane of 5.1° and 7.6°, respectively. The boat conformation of **3f** is much less pronounced than that of **1a** [Fig. 1(*c*)],[5] in which C(3) is displaced by 0.099 Å and C(6) by 0.590 Å. Upward displacement of C(6) from the N-plane in **3f** necessarily leads to a downward displacement of C(1′) and C(1′ⁱ) (−0.193 Å), when planarity is retained about N(1). Planarity about N(1) is clearly indicated by the small angle of the N–C(phenyl) bond with regard to the N(1), N(2), C(6) plane being 3°. The C(3) *tert*-butyl group occupies a staggered conformation with C(1″A) lying orthogonal with regard to the N(2), C(3), N(2ⁱ) plane [torsion angles: N(2)–C(3)–C(1″)–C(1″A): +89.0(2)°; N(2)–C(3)–C(1″)–C(1″B): −30.2(3)°]. Owing to the bulky sulfur in **3f** the *N*-phenyl groups are considerably distorted in a mutual anti-propeller fashion. The torsion angles, N(2)–N(1)–C(1′)–C(6′): 80.7(2)° and C(6)–N(1)–C(1′)–C(2′): 87.2(2)°, show an almost orthogonal arrangement of the *N*-phenyl groups with regard to the verdazyl ring.

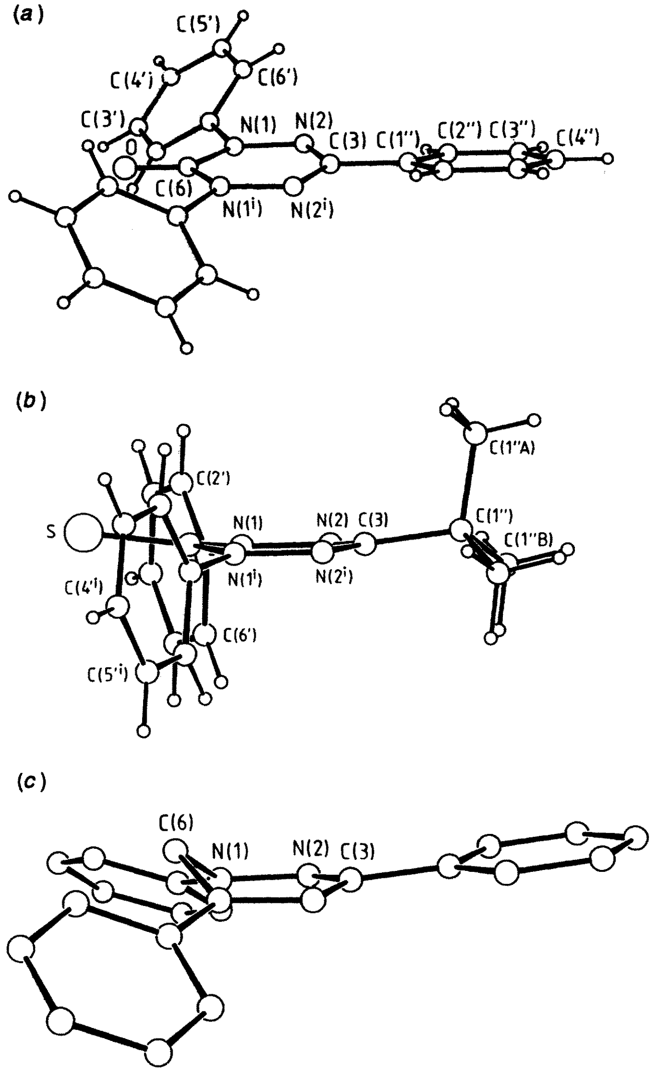


Fig. 1 Molecular structures of **2a** (*a*), **3f** (*b*) and **1a** (*c*)[5] in side views showing the conformational changes of the verdazyl ring

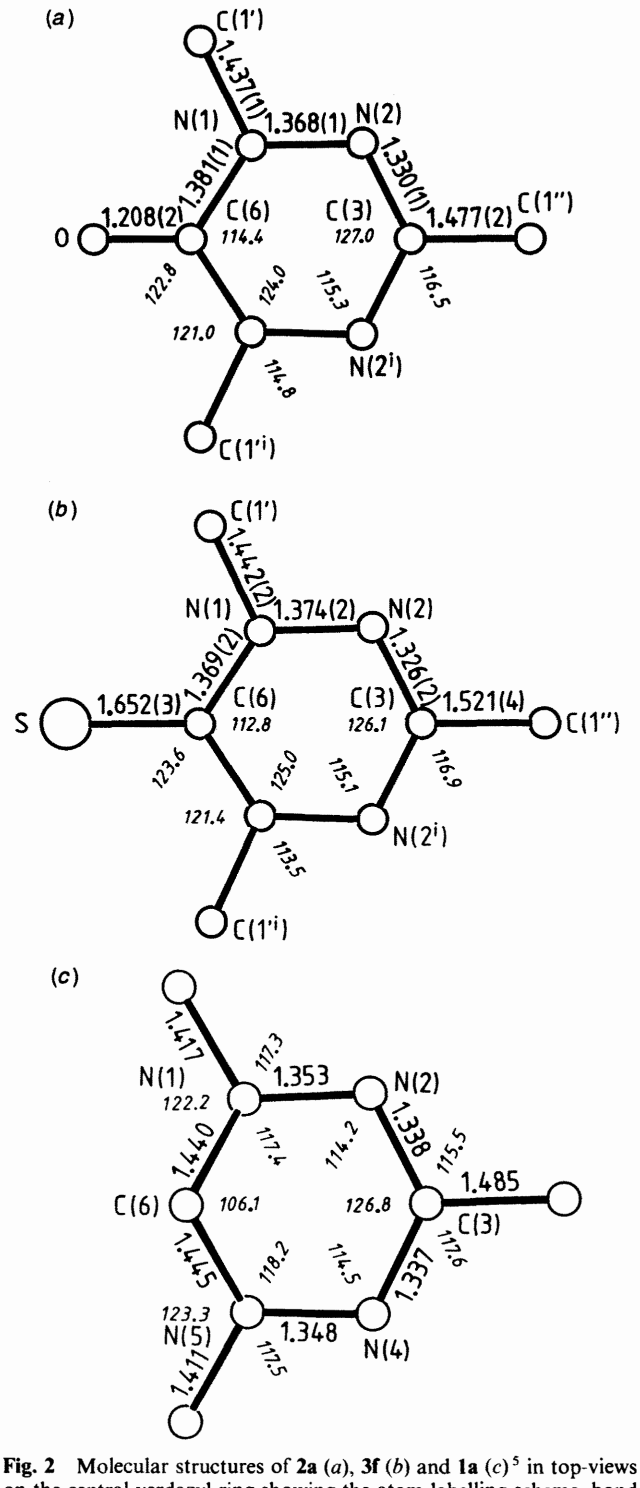


Fig. 2 Molecular structures of **2a** (*a*), **3f** (*b*) and **1a** (*c*)[5] in top-views on the central verdazyl ring showing the atom-labelling scheme, bond distances (Å), and bond angles (°)

Pertinent bond lengths and bond angles of **2a** and **3f** are given in Fig. 2. The data of the hydrazidinyl moiety -N-N-C=N-N- in **2a** and **3f** are very similar to mean data of 1,3,5-triphenylverdazyl **1a**:[5] N(1)-N(2) 1.351(3) Å, N(2)-C(3) 1.338(1) Å; N(1)-N(2)-C(3) 114.4(2)°, N(2)-C(3)-N(4) 126.8°, and to those of other 1,3,5-triarylverdazyls.[6-10] In agreement with strong electronic interaction between the lone pair at N(1) and the attached carbonyl or thiocarbonyl group, the N(1)-C(6) [**2a**: 1.381(1); **3f**: 1.369(2) Å] as well as the C(6)-O [1.208(2) Å] and C(6)-S [1.652(3) Å] bond distances in **2a** and **3f** are of about the same order as corresponding bond lengths

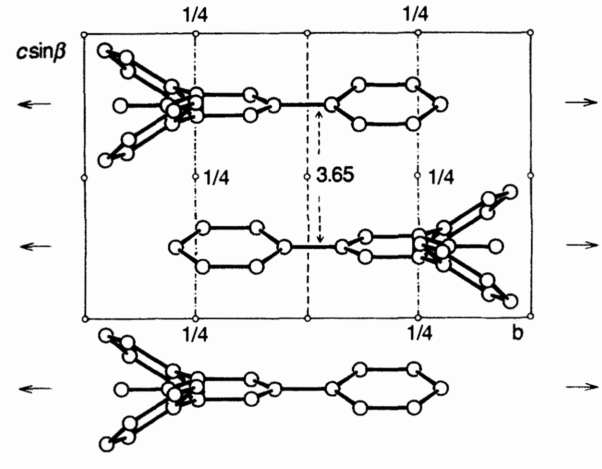


Fig. 3 Packing diagram of **2a** projected down the *a*-axis and showing the intermolecular distance within the column in the *c*-axis. The second layer, not shown in the rear of the Figure, is omitted for clarity.

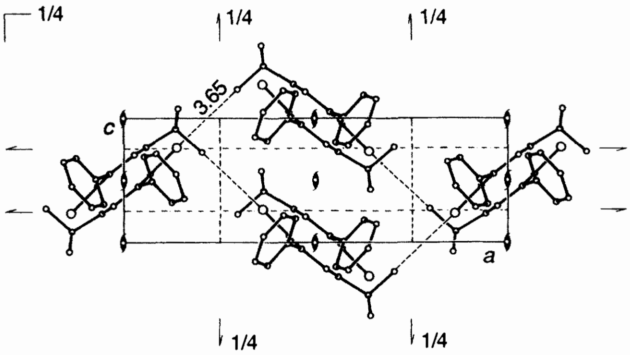


Fig. 4 Packing diagram of **3f** projected down the *b*-axis

found in tetrahydro-1,2,4,5-tetrazine-3,6-dione [mean value N-C = 1.363(12), C=O = 1.224(2) Å] and in the corresponding 3,6-dithione [N-C = 1.349(5), C=S = 1.667(2) Å].[13] As compared to these compounds, the slightly shorter C=O and C=S bonds and, on the other hand, the slightly longer C(6)-N bonds in **2a** and **3f** are probably related to lower electron density at N(1) induced by the phenyl substitution. Furthermore, the N(1)-C(1') bond distance in **2a** [1.437(1) Å] and **3f** [1.442(2) Å] is remarkably longer than the corresponding mean value of **1a** [1.414(3) Å][5] which indicates that, owing to the increased torsion angle of the *N*-phenyl groups in **2a** (mean torsion angle 38°) and **3f** (mean torsion angle 84°), spin delocalization into the *N*-phenyl groups may be significantly reduced as compared to **1a** (mean torsion angle 18°).

The molecules of **2a** (C_2) are packed in columns along the *c*-axis (Fig. 3). The verdazyl ring and C(3)-phenyl ring are lying alternately on top of each other. Within the array the mean intermolecular distance is 3.65 Å, which can be considered to be a mean distance between adjacent π-systems. The centres of the verdazyl rings, however, are 5.63 Å apart. There are no intermolecular contacts shorter than normal van der Waals distances. The molecules of **3f** lie on mirror planes in (010) and are stacked along the short *c*-axis, forming an angle of 38.4° between stacking axis and verdazyl ring plane (Fig. 4). This leads to an interplanar distance of 4.28 Å between adjacent verdazyl rings. The shortest distances observed within the stack are N(2)···C(1'') (x, y, $1 + z$) 4.847(3) Å and between stacks C(2')···C(3') ($1 - x$, $1 - y$, $1 - z$) 3.565(4), C(2')···C(4') ($1 - x$, $1 - y$, $1 - z$) 3.580(4), and S···C(1''A) ($-\frac{1}{2} + x, y, \frac{3}{2} - z$) 3.645(4) Å, but as with **2a** there are no intermolecular contacts shorter than normal van der Waals distances.

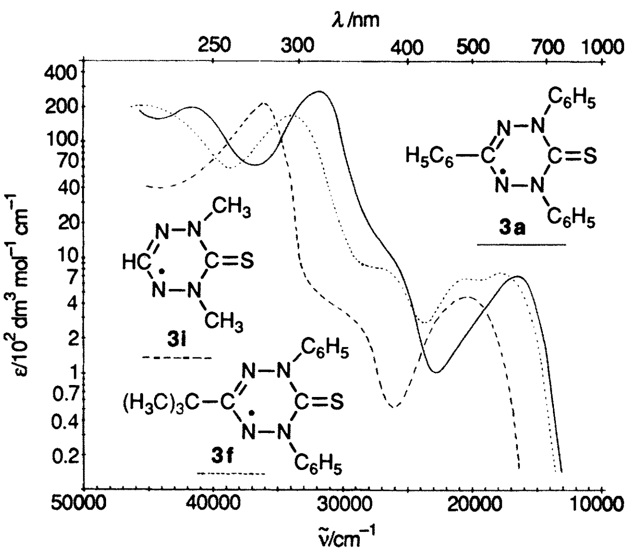


Fig. 5 Electronic absorption spectra of compounds **3a**, **3f** and **3i** in dioxane

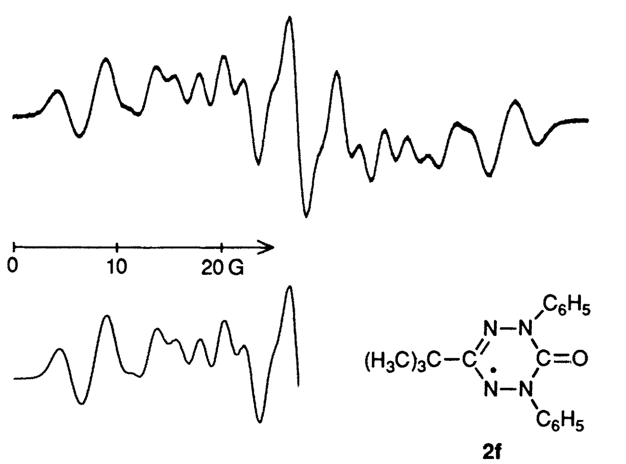


Fig. 6 First derivative X-band EPR spectrum of 3-*tert*-butyl-1,5-diphenyl-6-oxoverdazyl (**2f**) in toluene at 300 K together with a simulation using the data in Table 1

Electronic Absorption Spectra.—6-Oxo- **2** and 6-thioxoverdazyls **3** are deeply coloured compounds ranging from yellow through red to blue. In the visible region one observes a broad band system (see Fig. 5) which is probably related to $\Phi_h(\mathrm{SOMO}) \longrightarrow \Phi_l(\mathrm{LUMO})$ and $\Phi_{h-1} \longrightarrow \Phi_h(\mathrm{SOMO})$ excitations.[14] The position of this longwave band system depends mainly on the nature of the substituents at N(1), C(3), N(5) and C(6). The first band of the least substituted 6-oxoverdazyl **2i** is found at 445 nm.[1] Extension of the conjugated system either by substitution in the 1,5-positions (**2f**: $\lambda_{max,1}$ 499 nm) or in the 3-position (**2k**: $\lambda_{max,1}$ 492 nm,[1] **2a**: $\lambda_{max,1}$ 563 nm) leads to pronounced bathochromic shifts of the longwave band. The corresponding 6-thioxoverdazyl series gives similar results (Fig. 5, **3i**: $\lambda_{max,1}$ 495 nm;[1] **3f**: $\lambda_{max,1}$ 565 nm; **3k**: $\lambda_{max,1}$ 526 nm;[1] **3a**: $\lambda_{max,1}$ 608 nm). Finally, replacement of the carbonyl oxygen by sulfur results in an additional bathochromic shift of *ca.* 50 nm (**2a**: $\lambda_{max,1}$ 563 nm; **3a**: $\lambda_{max,1}$ 608 nm). It is noteworthy, that corresponding verdazyls of type **1** show an even greater redshift, **1a**: $\lambda_{max,1}$ 720 nm.[15] These verdazyls no longer represent a cyclic conjugated system but have to be considered as *cis,cis*-arranged polymethine dyes, since C(6) does not take part in the conjugation.

EPR, ENDOR and ^{2}H *NMR Studies.*—Table 1 summarizes

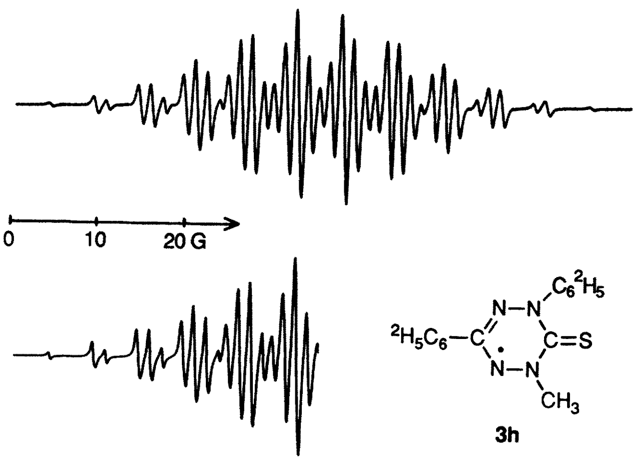


Fig. 7 First derivative X-band EPR spectrum of 1-methyl-3,5-di-[$^2H_5$]phenyl-6-thioxoverdazyl (**3h**) in toluene at 300 K together with a simulation using the data in Table 1

the experimental results, the isotropic hyperfine coupling (HFC) constants of **2a–h**, **3a–c**, **3f** and **3h**. The EPR spectra of **2a**, **2f**, **2g**, **3a**, **3f** and **3g** are poorly resolved, and their simulations yield only data of dominant splittings. A typical example is shown in Fig. 6. In order to obtain better resolution some of these compounds were partially or completely deuteriated. Analyses of the EPR spectra of **2a–d**, **3b** and **3c** clearly gave the magnitude of the nitrogen HFC constants, **2a–d**: a(N) = 6.44 (2 N), a(N) = 4.49 G (2 N); **3a–c**: a(N) = 6.57 (2 N), a(N) = 4.95 G (2 N). ^{15}N Labelling in the 1-position provided an unambiguous assignment. Simulations of the EPR spectra of **2e** and **3e** fit with $a(1-{}^{15}\mathrm{N}) = 6.35$ and $a(1-{}^{15}\mathrm{N}) = 6.90$ G, respectively. Consequently, the smaller ^{14}N splitting of **2a** and **3a** was assigned to the 1,5-nitrogens. ENDOR studies of **2a–d** and **3a–c** not only confirmed the nitrogen splittings but also revealed ^{1}H HFC constants, and, in addition, general triple resonance experiments[16] provided their relative signs. Multiplicities of different sets of equivalent hydrogens were derived in part from sufficiently resolved EPR spectra, *e.g.* of **2b** and **3b**, which are well simulated using the data given in Table 1. By these methods all ^{1}H HFC constants of **2a–c**, **2f**, **3b**, **3c** and **3f** were determined and assigned. Only in the case of **2f** was it not possible to resolve the superimposed a(2,6-H) and a(4-H) ENDOR lines. As expected, replacement of the phenyl group in the 3-position by *tert*-butyl has no significant effect on the nitrogen splittings.

Analyses of the EPR and ENDOR spectra of **2g** and **3g** are more complicated, since the methyl substitution at the nitrogen suspends the symmetry of the molecule. The ENDOR spectrum of **2g** shows as expected four different nitrogen line pairs. Additionally, all ^{1}H HFC constants are observable, but as with **2f** the a(2,6-H) and a(4-H) lines are superimposed. The resolved EPR spectra of the deuteriated derivatives **2g** and **3h** (Fig. 7) are well simulated with the data given in Table 1. When one assumes that relationships of **2k**, $a(\mathrm{H{-}CH_3})/a(1\text{-N}) = 1.06$ and $a(\mathrm{H{-}CH_3})/a(2\text{-N}) = 0.84$, also hold for **2g**, then a tentative assignment of the nitrogen splittings in **2g** and **2h** can be made: $a(\mathrm{H{-}CH_3})/a(1\text{-N}) = 5.20/4.86 = 1.07$; $a(\mathrm{H{-}CH_3})/a(2\text{-N}) = 5.20/6.33 = 0.82$; a(4-N) = 6.60; a(5-N) = 4.67 G. The influence of unsymmetric methyl substitution in **3g** is less pronounced. In the ENDOR spectra of **3g** and **3h** three nitrogen splittings show up: a(N) = 6.49 (2 N), a(N) = 5.24, and a(N) = 5.09 G. Based on the arguments used for **2g**, we tentatively assign a(N) = 6.45 (2,4-N), a(N) = 5.25 (5-N), and a(N) = 5.10 G (1-N) [**3k**: $a(\mathrm{H{-}CH_3})/a(1\text{-N})$ *ca.* 1.0].[1] In the ENDOR spectrum of **3g**, besides the nitrogen line pairs only the H(CH$_3$) lines are clearly detectable. All further ^{1}H HFC constants are represented by an unresolved broad line pair.

Table 1 Isotropic hyperfine coupling constants and g-values of oxoverdazyls **2a–h**, thioxoverdazyls **3a–c**, **3f**, **3h**, and reference radicals **1a**, **2k**, **3k** in toluene unless otherwise stated

	Method	T/K	a(N)/G	a(H)[R^1]/G	a(H)[R^3]/G	a(H)[R^5]/G	g
1a	NMR[a]	295		−1.05 (2,6-H) +0.39 (3,5-H) −1.11 (4-H)	+0.39 (2,6-H) +0.27 (4-H)	−1.05 (2,6-H) +0.39 (3,5-H) −1.11 (4-H)	
2a	EPR	300	6.45 (2,4-N) 4.50 (1,5-N)[b]				2.0037
	ENDOR	230	6.45 (2,4-N)[c] 4.49 (1,5-N)[c]	−0.70 (2,6-H) +0.37 (3,5-H) −0.65 (4-H)	+0.37 (2,6-H) −0.18 (3,5-H) +0.32 (4-H)	−0.70 (2,6-H) −0.37 (3,5-H) −0.65 (4-H)	
2b	EPR	300	6.43 (2,4-N) 4.50 (1,5-N)	0.70 (2,6-H) 0.33 (3,5-H) 0.64 (4-H)		0.70 (2,6-H) 0.33 (3,5-H) 0.64 (4-H)	2.0037
	ENDOR	230		−0.69 (2,6-H) +0.36 (3,5-H) −0.66 (4-H)		−0.69 (2,6-H) +0.36 (3,5-H) −0.66 (4-H)	
2c	EPR	300	6.46 (2,4-N) 4.47 (1,5-N)				2.0037
	ENDOR	230	6.44 (2,4-N)[c] 4.48 (1,5-N)[c]		+0.39 (2,6-H) −0.18 (3,5-H) +0.31 (4-H)		
2d	EPR	300	6.42 (2,4-N) 4.49 (1,5-N)				
	NMR[d]	300		−0.102 (2,6-^{2}H) +0.054 (3,5-^{2}H) −0.093 (4-^{2}H)	+0.062 (2,6-^{2}H) −0.026 (3,5-^{2}H) +0.049 (4-^{2}H)	−0.102 (2,6-^{2}H) +0.054 (3,5-^{2}H) −0.093 (4-^{2}H)	
2f	EPR	300	6.49 (2,4-N) 4.42 (1,5-N)				2.0037
	ENDOR	230	6.49 (2,4-N)[c] 4.42 (1,5-N)[c]	−0.68 (2,4,6-H) +0.36 (3,5-H)	+0.10 [$C(CH_3)_3$]	−0.68 (2,4,6-H) +0.36 (3,5-H)	
2g	ENDOR	230	6.60[c,e] 6.33[c,e] 4.86[c,e] 4.67[c,e]	+5.20 (CH_3)	+0.37 (2,4,6-H) −0.17 (3,5-H)	−0.76 (2,4,6-H) +0.37 (3,5-H)	2.0037
2h	EPR	300	6.56[e] 6.32[e] 4.90[e] 4.67[e]	5.09 (CH_3)			
	ENDOR	260	6.57[e] 6.33[e] 4.88[e] 4.64[e]	5.16 (CH_3)			
2k[f]	ENDOR	260	6.49 (2,4-N) 5.13 (1,5-N)	5.46 (CH_3)	0.36 (2,4,5-H) 0.17 (3,5-H)	5.46 (CH_3)	2.0036
3a	EPR	300	6.55 (2,4-N) 4.95 (1,5-N)[g]				2.0035
	ENDOR	260	6.55 (2,4-N) 4.96 (1,5-N)	*h*	*h*	*h*	
3b	EPR	300	6.57 (2,4-N) 4.95 (1,5-N)	0.40 (2,6-H) 0.28 (3,4,5-H)		0.40 (2,6-H) 0.28 (3,4,5-H)	2.0035
	ENDOR	230	6.55 (2,4-N)[c] 4.96 (1,5-N)[c]	−0.38 (2,6-H) +0.32 (3,5-H) −0.24 (4-H)		−0.38 (2,6-H) +0.32 (3,5-H) −0.24 (4-H)	
	NMR[d]	300			+0.059 (2,6-^{2}H) −0.025 (3,5-^{2}H) +0.046 (4-^{2}H)		
3c	EPR	300	6.58 (2,4-N) 4.95 (1,5-N)				2.0035
	ENDOR	230			+0.37 (2,6-H) −0.17 (3,5-H) +0.30 (4-H)		
	NMR[d]	300		−0.057 (2,6-^{2}H) +0.048 (3,5-^{2}H) −0.035 (4-^{2}H)		−0.057 (2,6-^{2}H) +0.048 (3,5-^{2}H) −0.035 (4-^{2}H)	

Table 1 (*continued*)

	Method	T/K	a(N)/G	a(H)[R^1]/G	a(H)[R^3]/G	a(H)[R^5]/G	g
3f	EPR	300	6.66 (2,4-N) 4.90 (1,5-N)				2.0036
	ENDOR	230	6.66 (2,4-N)[c] 4.91 (1,5-N)[c]	−0.39 (2,6-H) +0.31 (3,5-H) −0.26 (4-H)	+0.11 [$C(CH_3)_3$]	−0.39 (2,6-H) +0.31 (3,5-H) −0.26 (4-H)	
3g	EPR	300	6.45 (2 N)[e] 5.25 (2 N)[e]	4.8 (CH_3)			2.0036
	ENDOR	260	6.49 (2 N)[e] 5.24[c] 5.09[c]	5.04 (CH_3)	*h*	*h*	
3h	EPR	300	6.45 (2 N)[e] 5.25[e] 5.11[e]	4.99 (CH_3)			2.0036
	ENDOR	260	6.48 (2 N)[e] 5.24[e] 5.10[e]	5.05 (CH_3)			
	NMR[d]	295			+0.058 (2,6-^{2}H) −0.025 (3,5-^{2}H) +0.046 (4-^{2}H)	−0.061 (2,6-^{2}H) +0.050 (3,5-^{2}H) −0.037 (4-^{2}H)	
3k[f]	EPR	300	6.35 (2,4-N) 5.40 (1,5-N)	5.40 (CH_3)		5.40 (CH_3)	2.0037

[a] Ref. 20; solvent di-*tert*-butyl nitroxide (DBNO). [b] **2e**: $a(1\text{-}^{15}N)$ = 6.35 G. [c] 260 K. [d] DBNO; a(H) = 6.51 $a(^2H)$; **2d**: R^1 = R^5: −0.66 (2,6-H), + 0.35 (3,5-H), −0.61 G (4-H); R^3: +0.40 (2,6-H), −0.17 (3,5-H), +0.32 G (4-H); **3b**: R^3: +0.38 (2,6-H), −0.16 (3,5-H), +0.30 G (4-H); **3c**: R^1 = R^5: −0.37 (2,6-H), +0.31 (3,5-H), −0.23 G (4-H); **3h**: R^3: +0.38 (2,6-H), −0.16 (3,5-H), +0.30 G (4-H); R^5: −0.39 (2,6-H), +0.32 (3,5-H), − 0.24 G (4-H). [e] No unequivocal assignment; for a tentative assignment see text. [f] Ref. 1. [g] **3e**: $a(1\text{-}^{15}N)$ = 6.90 G. [h] Broad line pair (0.2–0.4 G) not resolved.

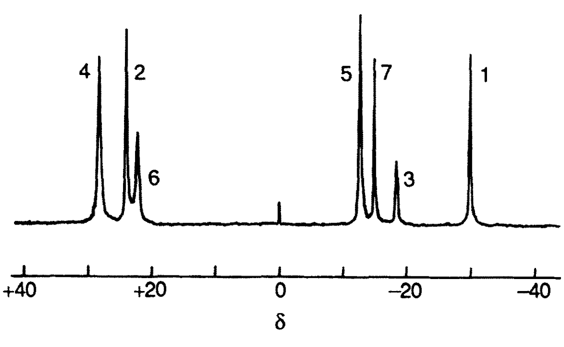


Fig. 8 ^{2}H NMR spectrum of **3h** in di-*tert*-butyl nitroxide (DBNO) at 295 K (internal standard [$^2H_6$]benzene); R^1 = R^5: 1 (2,6-^{2}H), 2 (3,5-^{2}H), 3 (4-^{2}H); R^3: 4 (2,6-^{2}H), 5 (3,5-^{2}H), 6 (4-^{2}H); 7 [^{2}H]DBNO (natural abundance)

The stability of the 6-oxo- and 6-thioxo-verdazyls makes NMR studies possible, *i.e.* investigations of paramagnetic shifts.[17,18] Measurements of ^{2}H paramagnetic shifts of **2d**, **3b** and **3c** in di-*tert*-butyl nitroxide[19] (Table 1) confirm the ^{1}H ENDOR and general triple resonance results, and, beyond that, they provide absolute signs of these splittings. The NMR method is particularly useful for determinations of small splittings. In the ENDOR spectrum of **3g** the small ^{1}H splittings are not resolved. The ^{2}H NMR spectrum of **3h** (Fig. 8), on the other hand, exhibits clearly separated ^{2}H paramagnetic shifts, and the corresponding ^{2}H HFC constants can be readily determined.

The sign pattern of the ^{1}H HFC constants in **2a** and **3b** (**3c**) matches exactly with that of **1a**.[20] Furthermore, the ratio a(2,6-H)/a(4-H) of the *C*-phenyl hydrogens in **2a** and **3c** is > 1 as in **1a**. The corresponding ratio of the *N*-phenyl hydrogens, however, shows a dissimilarity; a(2,6-H)/a(4-H) for **1a** is < 1, for **2a** and **3b** > 1. This reverse ratio and the small magnitude of the *N*-phenyl ^{1}H HFC constants in **2a** and **3b** are due to considerably large distortion angles about the N–C(phenyl) bonds (see crystal structure, **2a**: 38°; **3f**: 84°). In the thioxo-verdazyls **3**, *e.g.* **3b** and **3f**, a(3,5-H) is even comparable in magnitude with a(2,6-H) and a(4-H). This result can be rationalized by taking π–σ delocalization (*N*-phenyl hyperconjugation)[21,22] into account, in agreement with a very large distortion angle about the N–C(phenyl) bond in thioxoverdazyls. The π-SOMO of 6-oxo- **2** and 6-thioxo-verdazyls **3**, having nodes at C(3) and C(6), is mainly confined to the nitrogens of the verdazyl ring. The stability of these radicals, comparable with that of verdazyls of type **1**, also has its roots in the optimal delocalization of the unpaired electron in the *cis,cis*-arranged hydrazidinyl system.

Experimental

UV–VIS spectra were recorded on a Cary 17 spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker AM 500 instrument for [$^2H_6$]dimethyl sulfoxide solutions at 305 K. Chemical shifts are reported as δ values with tetramethylsilane as internal standard. J values are in Hz. ^{2}H NMR paramagnetic shift measurements[20] were carried out on a Bruker MSL 400 MHz spectrometer. Mass spectra were taken on a Finnigan MAT 212 mass spectrometer (ionization energy 70 eV). To monitor the progress of reactions and the separation of the products, TLC on silica gel (Macherey-Nagel G/UV_{254} plates) was used. EPR and ENDOR spectra were recorded on a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; g-values were determined by using a NMR gaussmeter and the Hewlett-Packard 5246 L frequency converter. This was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = (0.7145/g) G.

X-Ray Structure Analysis of Radicals **2a** *and* **3f**.—All measurements were made on an Enraf–Nonius CAD-4 circle diffractometer with graphite-monochromated Mo-Kα radiation

Table 2 Crystallographic data and refinement parameters of 1,3,5-triphenyl-6-oxoverdazyl **2a** and 3-*tert*-butyl-1,5-diphenyl-6-thioxoverdazyl **3f**

	2a	**3f**
Formula	$C_{20}H_{15}N_4O$	$C_{18}H_{19}N_4S$
Molecular mass	327.4	323.4
Crystallized from	Ethyl acetate	Pentane
Crystal size/mm	0.08 × 0.15 × 0.2	0.05 × 0.08 × 0.2
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pnma*
a/Å	19.263(3)	16.635(2)
b/Å	11.392(2)	18.434(3)
c/Å	7.304(1)	5.460(1)
β/°	90.72(2)	
Z	4	4
Symmetry of the molecule in crystal	C_2	C_s
$F_{000/e}$	684	684
D_x/g cm^{-3}	1.358	1.283
μ/cm^{-1} (Mo-Kα)	0.816	1.887
Measured reflections	1667	1646
$(\sin\theta/\lambda$ Å$^{-1})_{max}$	0.63	0.62
Observed reflections [$I \geq 3.0\sigma(I)$]	1107	888
Refinement R/R_w	0.034/0.038	0.034/0.036
$(\Delta/\sigma)_{max}$	0.01	0.01
$(\Delta\rho/e$ Å$^{-3})_{max}$	0.06	0.13

Table 3 Atomic co-ordinates for non-hydrogen atoms of compounds **2a** and **3f** with esds of the least significant figure in parentheses

	x	*y*	*z*
Molecule **2a**			
N(1)	0.558 44(5)	0.248 02(9)	0.213 2(2)
N(2)	0.560 18(6)	0.127 99(9)	0.214 9(2)
C(3)	0.500	0.075 8(2)	0.250
C(6)	0.500	0.313 7(2)	0.250
O	0.500	0.419 7(1)	0.250
C(1′)	0.624 49(7)	0.303 4(1)	0.185 6(2)
C(2′)	0.630 34(8)	0.405 4(1)	0.083 1(2)
C(3′)	0.695 49(9)	0.453 4(1)	0.057 9(2)
C(4′)	0.753 67(8)	0.401 3(2)	0.130 8(2)
C(5′)	0.747 37(8)	0.300 0(2)	0.231 0(2)
C(6′)	0.683 09(8)	0.250 5(1)	0.258 8(2)
C(1″)	0.500	−0.053 8(2)	0.250
C(2″)	0.556 01(7)	−0.115 8(1)	0.181 6(2)
C(3″)	0.555 59(8)	−0.236 6(1)	0.181 8(2)
C(4″)	0.500	−0.297 2(2)	0.250
Molecule **3f**			
N(1)	0.462 7(1)	0.311 9(1)	0.448 3(3)
N(2)	0.527 4(1)	0.314 16(9)	0.292 1(3)
C(3)	0.557 5(2)	0.250	0.231 7(6)
C(6)	0.431 1(2)	0.250	0.548 2(6)
S	0.361 93(5)	0.250	0.765 3(2)
C(1″)	0.635 7(2)	0.250	0.087 2(6)
C(1″A)	0.703 7(2)	0.250	0.272 9(7)
C(1″B)	0.642 0(2)	0.317 5(1)	−0.073 4(5)
C(1′)	0.426 5(1)	0.381 9(1)	0.490 5(5)
C(2′)	0.447 3(2)	0.422 2(1)	0.691 9(5)
C(3′)	0.415 9(2)	0.491 1(1)	0.716 6(5)
C(4′)	0.363 8(2)	0.517 9(1)	0.548 3(6)
C(5′)	0.342 7(2)	0.476 9(2)	0.350 0(6)
C(6′)	0.374 7(2)	0.408 1(1)	0.318 9(5)

(λ 0.710 69 Å, $\theta/2\theta$ 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. Atomic scattering factors and anomalous-dispersion corrections were taken from International Tables for X-Ray Crystallography.[23] The crystallographic data and the parameters of structure refinement are given in Table 2, the final fractional atomic co-ordinates for non-hydrogen atoms in Table 3.*

[$^2H_5$]Phenylhydrazine (labelled starting material [2,3,4,5,6-$^2H_5$]aniline),[24] [1-^{15}N]phenylhydrazine ([^{15}N]aniline), [$^2H_6$]-benzaldehyde phenylhydrazone ([$^2H_6$]benzaldehyde), benzaldehyde [$^2H_5$]phenylhydrazone, [$^2H_6$]benzaldehyde [$^2H_5$]-phenylhydrazone, [$^2H_6$]benzaldehyde 2-chloroformyl-2-phenylhydrazone **4b**, benzaldehyde 2-chloroformyl-2-[$^2H_5$]-phenylhydrazone **4c**, and [$^2H_6$]benzaldehyde 2-chloroformyl-2-[$^2H_5$]phenylhydrazone **4d** were prepared following literature procedures for the corresponding non-labelled compounds.[3]

2,2-Dimethylpropanal 2-Chloroformyl-2-phenylhydrazone **4f**.—A solution of phosgene (4.5 g, 45 mmol) in toluene (50 cm^3) was slowly added to a stirred solution of 2,2-dimethylpropanal phenylhydrazone (7.04 g, 40 mmol) and triethylamine (5.05 g, 50 mmol) in toluene (200 cm^3), and stirring was continued for 30 min. The reaction mixture was filtered through a short (15 cm) silica gel column (diameter 10 cm) using toluene (*ca.* 500 cm^3) as eluent. The filtrate was evaporated under reduced pressure. Recyrstallization of the residue from hexane afforded the product as colourless crystals (5.62 g, 59%), m.p. 77–78 °C (Found: C, 60.2; H, 6.4; N, 11.6. $C_{12}H_{15}ClN_2O$ requires C, 60.37; H, 6.33; N, 11.74%); δ_H 1.04 [9 H, s, C(CH$_3$)$_3$], 6.67 (1 H, s, CH=N), 7.17 (2 H, d, *J* 7.7, 2-, 6-H in NPh), 7.47–7.53 (3 H, 3-, 4-, 5-H in NPh); *m*/*z* 240 ($M^{•+}$, 1%), 238 ($M^{•+}$, 4%), 183 (21), 181 (100), 120 (10), 119 (11), 77 (62).

1,4,5,6-Tetrahydro-2,4,6-triphenyl-1,2,4,5-tetrazin-2(2H)-one **5a**.[2]—To a stirred suspension of benzaldehyde 2-chloroformyl-2-phenylhydrazone **4a**[3] (2.59 g, 10 mmol) in ethanol (20 cm^3) a solution of phenylhydrazine (1.08 g, 10 mmol) and triethylamine (1.06 g, 10.5 mmol) in ethanol (20 cm^3) was added, and stirring was continued for 2 h. After standing at 5 °C for 12 h the precipitated product was collected and chromatographed (silica gel, dichloromethane) to give compound **5a** (R_f = 0.13; 2.15 g, 65%) as colourless needles from ethyl acetate/hexane, m.p. 212–213 °C (Found: C, 73.0; H, 5.65; N, 16.8. $C_{20}H_{18}N_4O$ requires C, 72.7; H, 5.49; N, 16.96%); δ_H 5.39 (1 H, t, *J* 9.1, 6-H), 6.38 (2 H, d, 1-, 5-H), 7.08 (2 H, t, *J* 7.4, 4-H in NPh), 7.3–7.4 (7 H, 3-, 5-H in NPh, 3-, 4-, 5-H in CPh), 7.54 (2 H, d, *J* 6.9, 2-, 6-H in CPh), 7.63 (4 H, d, *J* 8.0, 2-, 6-H in NPh); *m*/*z* 331 (11%), 330 ($M^{•+}$, 75), 223 (17), 196 (10), 195 (10), 107 (21), 104 (100), 91 (11), 77 (99). Further elution yielded 1-benzylidene-2,5-diphenylcarbonohydrazide **8a**[4] (R_f = 0.09; 410 mg, 12%) as colourless prisms from ethanol, m.p. 178–179 °C (Found: C, 73.0; H, 5.55; N, 17.1. $C_{20}H_{18}N_4O$ requires C, 72.71; H, 5.49; N, 16.96%); δ_H(assignment based on H,H-COSY) 6.70 (1 H, t, *J* 7.3, 4-H in 5-Ph), 6.83 (2 H, d, *J* 8.4, 2-, 6-H in 5-Ph), 7.16 (2 H, dd, 3-, 5-H in 5-Ph), 7.20 (1 H, s, CH=N), 7.25 (2 H, d, *J* 7.7, 2-, 6-H in 2-Ph), 7.34–7.39 (3 H, 2-, 4-, 6-H in PhCH), 7.49 (1 H, t, *J* 7.4, 4-H in 2-Ph), 7.58 (2 H, dd, 3-, 5-H in 2-Ph), 7.67 (1 H, d, *J* 2.0, 5-NH), 7.84–7.89 (2 H, 3-, 5-H in PhCH), 9.54 (1 H, d, 4-NH); *m*/*z* 331 (19%), 330 ($M^{•+}$, 92), 223 (18), 197 (20), 196 (42), 195 (36), 120 (20), 107 (22), 106 (19), 93 (29), 92 (23), 78 (12), 77 (100).

The following compounds were prepared analogously.

6-Deuterio-1,4,5-trihydro-2,4-diphenyl-6-[$^2H_5$]phenyl-1,2,4,-

* *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.

5-*tetrazin*-3(2H)-*one* **5b**. From [$^2H_6$]benzaldehyde 2-chloroformyl-2-phenylhydrazone **4b** (1.06 g, 4 mmol): compound **5b** (830 mg, 62%) had m.p. 211–213 °C (Found: C, 71.65; H + ^{2}H, 7.25; N, 16.65. $C_{20}H_{12}{}^2H_6N_4O$ requires C, 71.40; H + ^{2}H, 7.19; N, 16.65%); δ_H 6.38 (2 H, s, 1-, 5-H), 7.08 (2 H, t, *J* 7.3, 4-H in NPh), 7.34 (4 H, dd, 3-, 5-H in NPh), 7.63 (4 H, d, *J* 8.0, 2-, 6-H in NPh); *m/z* 337 (16%), 336 ($M^{\cdot+}$, 100), 229 (21), 202 (13), 201 (11), 110 (94), 109 (23), 107 (27), 93 (14), 91 (10), 82 (59), 77 (80).

1,4,5,6-*Tetrahydro*-2,4-*di*[$^2H_5$]*phenyl*-6-*phenyl*-1,2,4,5-*tetrazin*-3(2H)-*one* **5c**. From benzaldehyde 2-chloroformyl-2-[$^2H_5$]-phenylhydrazone **4c** (530 mg, 2 mmol) and [$^2H_5$]phenylhydrazine (226 mg, 2 mmol): compound **5c** (390 mg, 57%) had m.p. 210–211 °C (Found: C, 70.55; H + ^{2}H, 8.35; N, 16.5. $C_{20}H_8{}^2H_{10}N_4O$ requires C, 70.55; H + ^{2}H, 8.29; N, 16.46%); δ_H 5.38 (1 H, t, *J* 9.1, 6-H), 6.37 (2 H, d, 1-, 5-H), 7.3–7.4 (3 H, 3-, 4-, 5-H in CPh), 7.54 (2 H, d, *J* 6.9, 2-, 6-H in CPh); *m/z* 341 (13%), 340 ($M^{\cdot+}$, 86), 228 (19), 201 (12), 200 (11), 125 (11), 112 (22), 105 (10), 104 (100), 96 (10), 82 (23), 77 (40).

6-*Deuterio*-1,4,5-*trihydro*-2,4,6-*tri*[$^2H_5$]*phenyl*-1,2,4,5-*tetrazin*-3(2H)-*one* **5d**. From [$^2H_6$]benzaldehyde 2-chloroformyl-2-[$^2H_5$]phenylhydrazone **4d** (540 mg, 2 mmol) and [$^2H_5$]phenylhydrazine (226 mg, 2 mmol): compound **5d** (420 mg, 61%) had m.p. 212–213 °C (Found: C, 69.25; H + ^{2}H, 9.8; N, 16.3. $C_{20}H_2{}^2H_{16}N_4O$ requires C, 69.33; H + ^{2}H, 9.88; N, 16.17%); δ_H 6.38 (s, 1-, 5-H); *m/z* 346 ($M^{\cdot+}$, 57%), 234 (11), 112 (41), 110 (100), 109 (11), 96 (12), 82 (96), 81 (12).

1,4,5,6-*Tetrahydro*-2,4,6-*triphenyl*-[2-^{15}N]1,2,4,5-*tetrazin*-3-(2H)-*one* **5e**. From benzaldehyde 2-chloroformyl-2-phenylhydrazone **4a** (260 mg, 1 mmol) and [1-^{15}N]phenylhydrazine (110 mg, 1 mmol): compound **5e** (170 mg, 51%) had m.p. 210–211 °C (Found: C, 72.65; H, 5.6; N + ^{15}N, 17.15. $C_{20}H_{18}N_3{}^{15}NO$ requires C, 72.49; H, 5.48; N + ^{15}N, 17.21%); δ_H 5.38 (1 H, t, *J* 8.9, 6-H), 6.36 (2 H, d, 1-, 5-H), 7.07 (2 H, t, *J* 7.4, 4-H in NPh), 7.28–7.40 (7 H, 3-, 5-H in NPh, 3-, 4-, 5-H in CPh), 7.54 (2 H, d, *J* 7.0, 2-, 6-H in CPh), 7.62 (4 H, d, *J* 8.1, 2-, 6-H in NPh); *m/z* 332 (14%), 331 ($M^{\cdot+}$, 92), 104 (83), 77 (100).

6-tert-*Butyl*-1,4,5,6-*tetrahydro*-2,4-*diphenyl*-1,2,4,5-*tetrazin*-3(2H)-*one* **5f**.—To a stirred solution of phenylhydrazine (2.38 g, 22 mmol) and triethylamine (2.53 g, 25 mmol) in ethanol (50 cm^3) 2,2-dimethylpropanal 2-chloroformyl-2-phenylhydrazone **4f** (4.77 g, 20 mmol) was added, and the mixture was heated to boiling point for 1 min. Addition of water precipitated the product which was collected and chromatographed (silica gel, dichloromethane) to give compound **5f** (R_f = 0.17; 4.07 g, 66%) as colourless crystals from methanol, m.p. 158–159 °C (Found: C, 69.85; H, 7.0; N, 18.0. $C_{18}H_{22}N_4O$ requires C, 69.65; H, 7.14; N, 18.05%); δ_H 0.96 [9 H, s, $C(CH_3)_3$], 3.91 (1 H, t, *J* 9.8, 6-H), 5.92 (2 H, d, 1-, 5-H), 7.02 (2 H, t, *J* 7.3, 4-H in NPh), 7.31 (4 H, dd, 3-, 5-H in NPh), 7.59 (4 H, d, *J* 8.2, 2-, 6-H in NPh); *m/z* 311 (10%), 310 ($M^{\cdot+}$, 72), 253 (78), 120 (12), 108 (21), 107 (100), 84 (12), 77 (78). Further elution yielded 1-(2,2-dimethylpropylidene)-2,5-diphenylcarbonohydrazide **8f** (R_f = 0.06; 940 mg, 15%) as colourless crystals from methanol, m.p. 184–185 °C (Found: C, 69.5; H, 7.3; N, 18.1. $C_{18}H_{22}N_4O$ requires C, 69.65; H, 7.14; N, 18.05%); δ_H 1.05 [9 H, s $C(CH_3)_3$], 6.50 (1 H, s, CH=N), 6.70 (1 H, t, *J* 7.3, 4-H in 5-Ph), 6.78 (2 H, d, *J* 8, 2-, 6-H in 5-Ph), 7.13 (2 H, d, *J* 7.7, 2-, 6-H in 2-Ph), 7.16 (2 H, dd, 3-, 5-H in 5-Ph), 7.43 (1 H, t, *J* 7.4, 4-H in 2-Ph), 7.52 (2 H, dd, 3-, 5-H in 2-Ph), 7.62 (1 H, d, *J* 2.2, 5-NH), 8.77 (1 H, d, 4-NH); *m/z* 311 (18%), 310 ($M^{\cdot+}$, 100), 253 (78), 226 (14), 120 (42), 119 (43), 108 (15), 107 (87), 105 (13), 93 (21), 92 (19), 77 (83).

1,4,5,6-*Tetrahydro*-2-*methyl*-4,6-*diphenyl*-1,2,4,5-*tetrazin*-3-(2H)-*one* **5g**.—To a stirred suspension of benzaldehyde 2-chloroformyl-2-phenylhydrazone **4a**[3] (2.59 g, 10 mmol) in ethanol (20 cm^3) a solution of methylhydrazine (0.46 g, 10 mmol) and triethylamine (1.06 g, 10.5 mmol) in ethanol (20 cm^3) was added. After stirring at room temperature for 2 h, water was added to the reaction mixture and the whole was extracted with dichloromethane. The organic layer was washed, dried ($MgSO_4$) and evaporated to provide the crude product, which was crystallized from ethanol to give compound **5g** as colourless crystals (2.31 g, 86%), m.p. 119–120 °C (Found: C, 67.3; H, 6.05; N, 20.7. $C_{15}H_{16}N_4O$ requires C, 67.15; H, 6.01; N, 20.88%); δ_H 3.10 (3 H, s, CH_3), 5.15 (1 H, dd, 6-H), 5.89 (1 H, d, *J* 9.1, 1-H), 6.16 (1 H, d, *J* 8.6, 5-H), 7.02 (1 H, t, *J* 7.3, 4-H in NPh), 7.27 (2 H, dd, 3-, 5-H in NPh), 7.32–7.42 (3 H, 3-, 4-, 5-H in CPh), 7.57 (2 H, d, *J* 7.4, 2-, 6-H in CPh), 7.60 (2 H, d, *J* 7.9, 2-, 6-H in NPh); irradiation of the methyl group (δ_H 3.10) yielded a strong NOE response for 1-H (δ_H 5.89); *m/z* 269 (10%), 268 ($M^{\cdot+}$, 77), 122 (11), 107 (15), 104 (100), 77 (77).

6-*Deuterio*-1,4,5-*trihydro*-2-*methyl*-4,6-*di*[$^2H_5$]*phenyl*-1,2,4,-5-*tetrazin*-3(2H)-*one* **5h**.—Prepared from [$^2H_6$]benzaldehyde 2-chloroformyl-2-[$^2H_5$]phenylhydrazone **4d** (540 mg, 2 mmol) as described for compound **5g**: compound **5h** was obtained from ethanol as colourless crystals (390 mg, 70%), m.p. 118–119 °C (Found: C, 64.65; H + ^{2}H, 9.8; N, 20.05. $C_{15}H_5{}^2H_{11}N_4O$ requires C, 64.48; H + ^{2}H, 9.74; N, 20.05%); δ_H 3.09 (3 H, s, CH_3), 5.88 (1 H, s, 1-H), 6.14 (1 H, s, 5-H); *m/z* 280 (11%), 279 ($M^{\cdot+}$, 100), 127 (16), 112 (25), 110 (99), 109 (17), 96 (12), 82 (82), 81 (10).

1,4,5,6-*Tetrahydro*-2,4,6-*triphenyl*-1,2,4,5-*tetrazin*-3(2H)-*thione* **7a**.—A solution of thiophosgene (6.90 g, 60 mmol) in dichloromethane (50 cm^3) was slowly added to a stirred solution of benzaldehyde phenylhydrazone (9.80 g, 50 mmol) in dichloromethane (100 cm^3) at 25 °C, and stirring was continued for 30 min. Then a solution of triethylamine (6.57 g, 65 mmol) in dichloromethane (20 cm^3) was added, and the mixture was stirred for 1 h. The black reaction mixture was filtered through a short (15 cm) silica gel column (diameter 10 cm) using dichloromethane (*ca.* 1 dm^3) as eluent. The brown eluate was concentrated at 20 °C under reduced pressure. To the stirred solution of the residue in dichloromethane (150 cm^3) were added a solution of phenylhydrazine (4.32 g, 40 mmol) in dichloromethane (50 cm^3) followed by a solution of triethylamine (5.05 g, 50 mmol) in dichloromethane (50 cm^3). Stirring at room temperature was continued for 2 h. After addition of water the organic layer was separated, washed with water, dried ($MgSO_4$), and subjected directly to chromatography (silica gel, dichloromethane) to give compound **7a** (R_f = 0.05; 3.73 g, 22%) as colourless crystals from acetic acid, m.p. 232–233 °C (Found: C, 69.25; H, 5.2; N, 16.15; S, 9.05. $C_{20}H_{18}N_4S$ requires C, 69.34; H, 5.24; N, 16.17; S, 9.25%); δ_H 5.54 (1 H, t, *J* 9.2, 6-H), 6.51 (2 H, d, 1-, 5-H), 7.22 (2 H, t, *J* 7.3, 4-H in NPh), 7.32–7.40 (7 H, 3-, 5-H in NPh, 3-, 4-, 5-H in CPh), 7.46 (4 H, d, *J* 7.9, 2-, 6-H in NPh), 7.53 (2 H, d, *J* 7.7, 2-, 6-H in CPh); *m/z* 346 ($M^{\cdot+}$, 39%), 136 (19), 135 (12), 107 (11), 104 (58), 77 (100).

The following compounds were prepared analogously.

6-Deuterio-1,4,5-*trihydro*-2,4-*diphenyl*-6-[$^2H_5$]*phenyl*-1,2,4,-5-*tetrazin*-3(2H)-*thione* **7b**. From thiophosgene (1.38 g, 12 mmol), [$^2H_6$]benzaldehyde phenylhydrazone (2.02 g, 10 mmol), and phenylhydrazine (864 mg, 8 mmol): compound **7b** (670 mg, 19%) had m.p. 229–230 °C (Found: C, 68.35; H + ^{2}H, 6.75; N, 15.7; S, 8.9. $C_{20}H_{12}{}^2H_6N_4S$ requires C, 68.15; H + ^{2}H, 6.86; N, 15.90; S, 9.10%); δ_H 6.48 (2 H, s, 1-, 5-H), 7.22 (2 H, t, *J* 7.4, 4-H in NPh), 7.35 (4 H, dd, 3-, 5-H in NPh), 7.46 (4 H, d, *J* 8.2, 2-, 6-H in NPh); *m/z* 353 (15%), 352 ($M^{\cdot+}$, 76), 245 (16), 151 (13), 137 (23), 135 (19), 110 (43), 109 (27), 107 (16), 82 (24), 78 (10), 77 (100).

1,4,5,6-*Tetrahydro*-2,4-*di*[$^2H_5$]*phenyl*-6-*phenyl*-1,2,4,5-*tetra*-

zin-3(2H)-*thione* **7c**. From thiophosgene (1.38 g, 12 mmol), benzaldehyde [$^2H_5$]phenylhydrazone (2.01 g, 10 mmol), and [$^2H_5$]phenylhydrazine (904 mg, 8 mmol): compound **7c** (675 mg, 19%) had m.p. 230–231 °C (Found: C, 67.7; H + ^{2}H, 8.0; N, 15.9; S, 8.95. $C_{20}H_8{}^2H_{10}N_4S$ requires C, 67.38; H + ^{2}H, 7.91; N, 15.72; S, 8.99%); δ_H 5.55 (1 H, t, *J* 9.1, 6-H), 6.53 (2 H, d, 1-, 5-H), 7.3–7.4 (3 H, 3-, 4-, 5-H in CPh), 7.54 (2 H, d, *J* 7.7, 2-, 6-H in CPh); *m/z* 357 (12%), 356 ($M^{\cdot+}$, 50), 355 (30), 354 (11), 244 (21), 204 (22), 203 (13), 201 (15), 200 (12), 156 (15), 141 (38), 140 (41), 139 (11), 113 (17), 112 (23), 111 (11), 106 (10), 105 (31), 104 (100), 98 (19), 97 (13), 96 (20), 83 (10), 82 (84), 81 (26), 80 (14), 78 (13), 77 (36).

1,4,5,6-*Tetrahydro*-2,4,6-*triphenyl*-[2-^{15}N]1,2,4,5-*tetrazin*-3(2H)-*thione* **7e**. From thiophosgene (690 mg, 6 mmol), benzaldehyde phenylhydrazone (980 mg, 5 mmol), and [1-^{15}N]-phenylhydrazine (436 mg, 4 mmol): compound **7e** (320 mg, 18%) had m.p. 228–229 °C (Found: C, 69.55; H, 5.3; N + ^{15}N, 16.75; S, 9.25. $C_{20}H_{18}N_3{}^{15}NS$ requires C, 69.14; H, 5.22; N + ^{15}N, 16.41; S, 9.23%); δ_H 5.53 (1 H, t, *J* 9.2, 6-H), 6.50 (2 H, d, 1-, 5-H), 7.22 (2 H, t, *J* 7.4, 4-H in NPh), 7.32–7.40 (7 H, 3-, 5-H in NPh, 3-, 4-, 5-H in CPh), 7.46 (4 H, d, *J* 7.7, 2-, 6-H in NPh), 7.53 (2 H, d, *J* 7.9, 2-, 6-H in CPh); *m/z* 347 ($M^{\cdot+}$, 58%), 104 (56), 77 (100).

6-tert-*Butyl*-1,4,5,6-*tetrahydro*-2,4-*diphenyl*-1,2,4,5-*tetrazin*-3(2H)-*thione* **7f**.—Prepared from 2,2-dimethylpropanal phenylhydrazone (8.80 g, 50 mmol) as described for compound **7a**: compound **7f** (R_f = 0.05, dichloromethane; 2.70 g, 17%) was obtained from ethanol as colourless crystals, m.p. 213–214 °C (Found: C, 66.25; H, 6.8; N, 17.25; S, 9.75. $C_{18}H_{22}N_4S$ requires C, 66.22; H, 6.79; N, 17.16; S, 9.82%); δ_H 0.92 [9 H, s, $C(CH_3)_3$], 4.07 (1 H, t, *J* 10.6, 6-H), 6.01 (2 H, d, 1-, 5-H), 7.17 (2 H, t, *J* 7.5, 4-H in NPh), 7.34 (4 H, dd, 3-, 5-H in NPh), 7.50 (4 H, d, *J* 7.6, 2-, 6-H in NPh); *m/z* 326 ($M^{\cdot+}$, 4%), 270 (10), 269 (100), 253 (13), 77 (28).

1,4,5,6-*Tetrahydro*-2-*methyl*-4,6-*diphenyl*-1,2,4,5-*tetrazin*-3-(2H)-*thione* **7g**.—Prepared from thiophosgene (6.90 g, 60 mmol), benzaldehyde phenylhydrazone (9.80 g, 50 mmol), and methylhydrazine (2.30 g, 50 mmol) as described for compound **7a**: compound **7g** (R_f = 0.1, dichloromethane) was obtained from ethanol as colourless crystals (4.45 g, 31%), m.p. 181–182 °C (Found: C, 63.55; H, 5.65; N, 19.85; S, 10.85. $C_{15}H_{16}N_4S$ requires C, 63.35; H, 5.67; N, 19.70; S, 11.28%); δ_H 3.58 (3 H, s, CH_3), 5.27 (1 H, dd, 6-H), 6.18 (1 H, d, *J* 8.9, 1-H), 6.33 (1 H, d, *J* 8.7, 5-H), 7.18 (1 H, t, *J* 7.2, 4-H in NPh), 7.27–7.35 (4 H, 2-, 3-, 5-, 6-H in NPh), 7.35–7.44 (3 H, 3-, 4-, 5-H in CPh), 7.52 (2 H, d, *J* 7.5, 2-, 6-H in CPh); irradiation of the methyl group (δ_H 3.58) yielded a strong NOE response for 1-H (δ_H 6.18): *m/z* 285 (17%), 284 ($M^{\cdot+}$, 89), 207 (16), 195 (10), 177 (17), 136 (17), 135 (29), 133 (11), 132 (16), 108 (12), 107 (20), 106 (15), 105 (29), 104 (94), 93 (22), 89 (28), 78 (18), 77 (100), 74 (35).

6-*Deuterio*-1,4,5-*trihydro*-2-*methyl*-4,6-*di*[$^2H_5$]*phenyl*-1,2,4,-5-*tetrazin*-3(2H)-*thione* **7h**.—Prepared from thiophosgene (4.14 g, 36 mmol), [$^2H_6$]benzaldehyde [$^2H_5$]phenylhydrazone (6.21 g, 30 mmol), and methylhydrazine (1.38 g, 30 mmol) as described above: compound **7h** (2.46 g, 28%) was obtained from ethanol as colourless crystals, m.p. 181–182 °C (Found: C, 61.15; H + ^{2}H, 9.35; N, 18.9; S, 10.55. $C_{15}H_5{}^2H_{11}N_4S$ requires C, 60.98; H + ^{2}H, 9.21; N, 18.96; S, 10.85%); δ_H 3.56 (3 H, s, CH_3), 6.15 (1 H, s, 1-H), 6.30 (1 H, s, 5-H); *m/z* 295 ($M^{\cdot+}$, 46%), 294 (21), 183 (11), 140 (16), 112 (20), 111 (18), 110 (91), 109 (24), 89 (30), 84 (10), 82 (100), 81 (22), 80 (11), 75 (24).

1,3,5-*Triphenyl*-6-*oxoverdazyl* **2a**.[2]—Compound **5a** (660 mg, 2 mmol) was dissolved in hot acetic acid (40 cm^3). To the stirred mixture at room temperature lead dioxide (720 mg, 3 mmol) was added, and stirring was continued for 1 h. The precipitated product was collected and recrystallized from ethyl acetate to afford compound **2a** as violet needles (480 mg, 74%), m.p. 210–211 °C (Found: C, 73.6; H, 4.7; N, 17.4. $C_{20}H_{15}N_4O$ requires C, 73.38; H, 4.62; N, 17.12%); λ_{max}(dioxane)/nm 563 (log ε 3.40), 5.40 (3.36), 315 (4.11), 254 (4.30) and 234 (4.26); *m/z* 328 (16%), 327 (M^+, 100), 105 (15), 91 (21), 77 (90).

The following compounds were prepared analogously.

1,5-*Diphenyl*-3-[$^2H_5$]*phenyl*-6-*oxoverdazyl* **2b**. From compound **5b** (672 mg, 2 mmol) and lead dioxide (720 mg, 3 mmol): compound **2b** (470 mg, 71%) had m.p. 211–212 °C (Found: C, 72.65; H + ^{2}H, 6.05; N, 16.9. $C_{20}H_{10}{}^2H_5N_4O$ requires C, 72.27; H + ^{2}H, 6.06; N, 16.86%); *m/z* 333 (11%), 332 (M^+, 71), 105 (31), 91 (22), 77 (100).

3-*Phenyl*-1,5-*di*[$^2H_5$]*phenyl*-6-*oxoverdazyl* **2c**. From compound **5c** (340 mg, 1 mmol) and lead dioxide (360 mg, 1.5 mmol): compound **2c** (260 mg, 77%) had m.p. 211–212 °C (Found: C, 71.45; H + ^{2}H, 7.45; N, 16.65. $C_{20}H_5{}^2H_{10}N_4O$ requires C, 71.19; H + ^{2}H, 7.46; N, 16.61%); *m/z* 338 (10%), 337 (M^+, 63), 110 (11), 96 (19), 82 (100).

1,3,5-*Tri*[$^2H_5$]*phenyl*-6-*oxoverdazyl* **2d**. From compound **5d** (346 mg, 1 mmol) and lead dioxide (360 mg, 1.5 mmol): compound **2d** (255 mg, 75%) had m.p. 210–211 °C (Found: C, 70.1; ^{2}H, 8.75; N, 16.3. $C_{20}{}^2H_{15}N_4O$ requires C, 70.14; ^{2}H, 8.82; N, 16.36%); *m/z* 343 (10%), 342 (M^+, 68), 110 (12), 96 (21), 82 (100).

1,3,5-*Triphenyl*-6-*oxo*-[1-^{15}N]*verdazyl* **2e**. From compound **5e** (132 mg, 0.4 mmol) and lead dioxide (144 mg, 0.6 mmol): compound **2e** (80 mg, 61%) had m.p. 209–210 °C (Found: C, 73.55; H, 4.6; N + ^{15}N, 17.5. $C_{20}H_{15}N_3{}^{15}NO$ requires C, 73.16; H, 4.60; N + ^{15}N, 17.37%); *m/z* 329 (22%), 328 (M^+, 100), 92 (35), 91 (30), 77 (100).

3-tert-*Butyl*-1,5-*diphenyl*-6-*oxoverdazyl* **2f**.—A solution of compound **5f** (155 mg, 0.5 mmol) and tetrakis(4-methylphenyl)-hydrazine (294 mg, 0.75 mmol) in toluene (30 cm^3) was sealed in an ampoule and heated at 70 °C for 2 h. After cooling, the red solution was evaporated under reduced pressure below 40 °C, and the residue was chromatographed on deactivated silica gel using benzene as eluent to give **2f** (43 mg, 28%) as red needles from pentane, m.p. 117–118 °C (Found: C, 70.6; H, 6.4; N, 18.0. $C_{18}H_{19}N_4O$ requires C, 70.34; H, 6.23; N, 18.23%); λ_{max}(dioxane)/nm 499 (log ε 3.54), 390 (3.14) and 305 (4.13); *m/z* 307 (M^+, 51%), 107 (13), 105 (15), 91 (18), 77 (100).

1-*Methyl*-3,5-*diphenyl*-6-*oxoverdazyl* **2g** *and* 1-*methyl*-3,5-*di*[$^2H_5$]*phenyl*-6-*oxoverdazyl* **2h** were generated by heating a de-gassed mixture of **5g** (2 mg) (or **5h**) and tetrakis(4-methylphenyl)hydrazine (2 mg) in toluene (1 cm^3) to 60 °C for 1 min (or the solution was allowed to stand for 30 min at room temperature).

1,3,5-*Triphenyl*-6-*thioxoverdazyl* **3a**.—To a stirred solution of **7a** (692 mg, 2 mmol) in *N,N*-dimethylformamide (150 cm^3) a solution of potassium hexacyanoferrate(III) (2.17 g, 6.6 mmol) and sodium carbonate (350 mg, 3.3 mmol) in water (120 cm^3) was added within 5 min. Immediately thereafter the reaction mixture was rapidly heated to boiling point for 1 min. On cooling, the mixture was diluted with water and the product extracted with diethyl ether. After washing with water (three times) the ethereal solution was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel using toluene as eluent to give **3a** (132 mg, 19%) as blue needles from dioxane, m.p. 197–198 °C (decomp.) (Found: C, 70.2; H, 4.55; N, 16.05; S, 9.05. $C_{20}H_{15}N_4S$ requires C, 69.94; H, 4.40; N, 16.32; S, 9.34%); λ_{max}(dioxane)/nm 608 (log ε 2.85), 313 (4.48) and 241 (4.34); *m/z* 343 (M^+, 33%), 312 (10), 91 (15), 77 (100).

The following compounds were prepared analogously.

1,5-Diphenyl-3-[$^2H_5$]phenyl-6-thioxoverdazyl **3b**. From compound **7b** (352 mg, 1 mmol): compound **3b** (60 mg, 17%) had m.p. 198–199 °C (decomp.) (Found: C, 68.6; H + ^{2}H, 5.8; N, 16.2; S, 9.0. $C_{20}H_{10}{}^2H_5N_4S$ requires C, 68.94; H + ^{2}H, 5.78; N, 16.08; S, 9.20%); *m/z* 349 (12%), 348 (M^+, 69), 135 (10), 91 (10), 77 (100).

3-Phenyl-1,5-di[$^2H_5$]phenyl-6-thioxoverdazyl **3c**. From compound **7c** (356 mg, 1 mmol): compound **3c** (72 mg, 20%) had m.p. 195–197 °C (decomp.) (Found: C, 67.8; H + ^{2}H, 7.3; N, 15.6; S, 9.05. $C_{20}H_5{}^2H_{10}N_4S$ requires C, 67.95; H + ^{2}H, 7.13; N, 15.85; S, 9.07%); *m/z* 353 (M^+, 17%), 323 (35), 322 (48), 321 (30), 320 (16), 305 (12), 199 (12), 140 (10), 105 (17), 96 (100), 95 (30), 82 (60), 81 (15), 77 (11).

1,3,5-Triphenyl-6-thioxo-[1-^{15}N]verdazyl **3e**. From compound **7e** (174 mg, 0.5 mmol): compound **3e** (30 mg, 17%) had m.p. 196–197 °C (decomp) (Found: C, 69.9; H, 4.55; N + ^{15}N, 16.0; S, 9.1. $C_{20}H_{15}N_3{}^{15}NS$ requires C, 69.74; H, 4.39; N, 16.56; S, 9.31%); *m/z* 344 (M^+, 57%), 92 (8), 91 (10), 77 (100).

*3-*tert*-Butyl-1,5-diphenyl-6-thioxoverdazyl* **3f**.—A sealed solution of compound **7f** (163 mg, 0.5 mmol) and tetrakis(4-methylphenyl)hydrazine (294 mg, 0.75 mmol) in toluene (30 cm^3) was heated at 70 °C for 2 h. After cooling the violet solution was evaporated under reduced pressure below 40 °C, and the residue was chromatographed on deactivated silica gel using benzene as eluent to give **3f** (48 mg, 30%) as violet needles from pentane, m.p. 156–157 °C (decomp.) (Found: C, 67.2; H, 5.95; N, 17.15; S, 9.9. $C_{18}H_{19}N_4S$ requires C, 66.84; H, 5.92; N, 17.32; S, 9.91%); λ_{max}(dioxane)/nm 565 (log ε 2.88), 481 (2.82) and 293 (4.24); *m/z* 328 (M^+, 38%), 135 (14), 77 (100).

The following compounds were prepared analogously.

1-Methyl-3,5-diphenyl-6-thioxoverdazyl **3g**. From compound **7g** (142 mg, 0.5 mmol): compound **3g** (37 mg, 26%), violet needles from ethyl acetate, had m.p. 153–154 °C (decomp.) (Found: C, 64.3; H, 4.55; N, 20.05; S, 11.1. $C_{15}H_{13}N_4S$ requires C, 64.03; H, 4.66; N, 19.91; S, 11.40%); λ_{max}(dioxane)/nm 576 (log ε 2.73), 307 (4.53) and 240 (4.20); *m/z* 282 (12%), 281 (M^+, 50), 135 (16), 77 (100).

1-Methyl-3,5-di[$^2H_5$]phenyl-6-thioxoverdazyl **3h**. From compound **7h** (148 mg, 0.5 mmol): compound **3h** (28 mg, 19%), violet needles from ethyl acetate, had m.p. 152–153 °C (decomp.) (Found: C, 62.0; H + ^{2}H, 8.0; N, 19.2; S, 10.8. $C_{15}H_3{}^2H_{10}N_4S$ requires C, 61.82; H + ^{2}H, 7.95; N, 19.23; S, 11.00%); *m/z* 292 (21%), 291 (M^+, 100), 290 (65), 140 (28), 109 (11), 82 (94), 81 (46).

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