New tetrahydro-1,2,4,5-tetrazinan-3-ones and oxoverdazyl free radicals

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A series of tetrahydro-1,2,4,5-tetrazinan-3-ones have been prepared by the reaction of carbonic acid bis (1-methylhydrazide) with aromatic aldehydes. These were oxidised to oxoverdazyl free radicals and used immediately for ESR spectroscopy studies that indicate that the unpaired electron is delocalised over the verdazyl ring. The ESR spectra can be very well simulated considering hyperfine couplings with the four nitrogen atoms of the verdazyl ring and the six hydrogen atoms of the two methyl groups bonded to it.

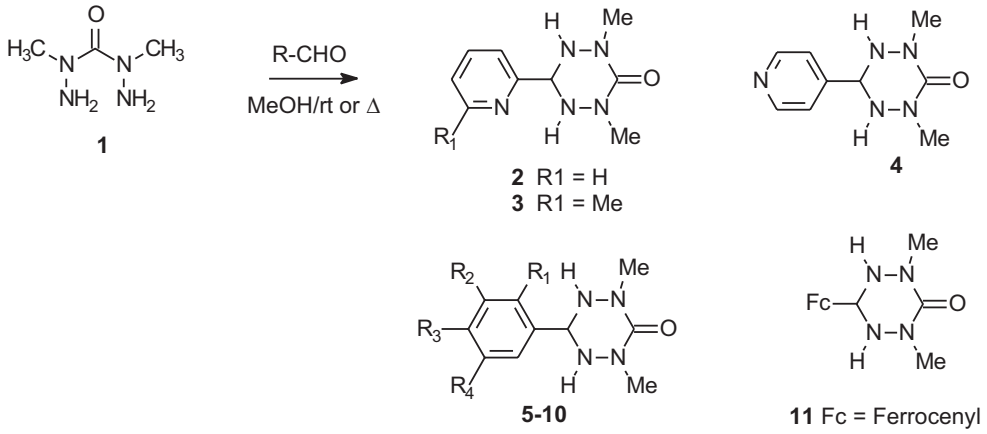
Keywords: verdazyls, ESR, free radicals, 1,2,4,5-tetrazinanones

Stable organic radicals have received much attention in the last few years since they have proved to be very useful building blocks for the preparation of organic magnetic materials, including purely organic ferromagnets.[1] Although there are many well-known families of organic radicals, most of them are very unstable,[2] and among those which are stable enough to be easily studied and characterised, most of them owe their stability to the presence of sterically bulky groups. Nevertheless, these bulky protective groups also prevent the intermolecular magnetic interactions in the solid and render these radicals less useful in the search of magnetically interesting materials. The two conflicting requirements (stability and absence of bulky groups) limit the number of useful known organic radicals to a few examples such as the nitroxide, verdazyl, phenoxyl-based, heterocyclic thiazyl and radical anions derived from TCNE, TCNQ and quinones.[3] Although the most studied organic radicals are the nitroxides,[4] since they provided the first examples of purely organic ferromagnets, in recent years, the verdazyl radicals are becoming more attractive as alternatives to the nitroxide radicals. This increasing interest in the verdazyl radicals is due to their high chemical stability and synthetic versatility.[3] In fact, verdazyl radicals are the only class of organic radicals that are, generally, air- and moisture-stable without bearing bulky substituents.

One of the two main groups of verdazyl radicals are those bearing a carbonyl group between the two three-coordinated N atoms (N2 and N4), the so-called 3-oxoverdazyl† radicals. The only major route to these 3-oxoverdazyl radicals starts with carbonic acid bis-hydrazides that can be condensed with aldehydes, as first reported by Neugebauer and Fischer,[5] to give 6-substituted saturated tetrahydro-1,2,4,5-tetrazin-3-ones (1,2,4,5-tetrazinan-3-ones).[6-13] These tetrazinanone rings can readily be oxidised by different oxidising agents, such as $NaIO_4$, to the corresponding 3-oxoverdazyl radicals. For the synthesis of 2,4-dimethyl-3-oxoverdazyl radicals, the starting carbonic acid bis-(1-methylhydrazide) can conveniently be prepared by reaction of methylhydrazine with triphosgene, following the route developed by Hicks and co-workers.[14]

The spin distribution in 3-oxoverdazyl and verdazyl free radicals has been extensively studied, mainly by ESR,[5,8,14-16] although other techniques such as electron–nuclear double resonance, ENDOR,[17] electron–electron double resonance, ELDOR,[18] and NMR[19] have also been used.

Here we report the synthesis and characterisation of a series of 1,2,4,5-tetrazinan-3-ones **2–11** by condensation of carbonic acid bis(1-methylhydrazide) with different phenyl- and pyridine-substituted aldehydes (Scheme 1 and Table 1). The crystal structures of compounds **2–4** were acquired to see how the molecules pack in the solid state. Each of the precursors **2–11** was smoothly oxidised with $NaIO_4$ to the corresponding 3-oxoverdazyl radical **12–21** (Scheme 2 and Table 2). Despite all the varied functionality present it was found difficult to obtain crystalline material suitable for



Scheme 1

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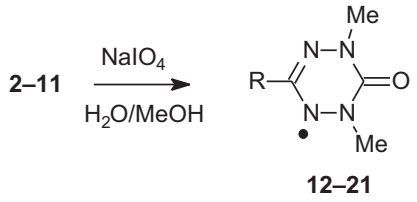
This paper is dedicated to Professor Steven Ley on the occasion of his 60th birthday.

† IUPAC and CAS name: 3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radicals. The primary literature (*e.g.* ref. 5) refers to them as 6-oxoverdazyls. This seems inappropriate, as it places the formal radical centre on N(2).

Table 1 Summary of tetrazinane structures

Compound	R_1	R_2	R_3	R_4	Yield/%
5		^{t}Bu		^{t}Bu	32
6	OH			CO_2H	76
7	OH				17
8		OH			36
9			OH		77
10			Ph_2N		60



Scheme 2

Table 2 Yields for the formation of tetrazinanes and verdazyl free radicals

Tetrazinane	Yield/%)	Verdazyl	Yield/%)
2	22	**12**	93
3	52	**13**	29
4	28	**14**	87
5	32	**15**	66
6	76	**16**	67
7	17	**17**	13
8	36	**18**	49
9	77	**19**	45
10	76	**20**	48
11	60	**21**	20

X-ray diffraction studies. The red radicals were therefore purified briefly and used immediately for ESR studies. These studies indicate, as expected, that the spin distribution is very similar in all the 3-oxoverdazyl radicals, independent of the 6-substituent. 6-(4-Acetamidophenyl)-2,4-dimethyl-3-oxoverdazyl was particularly stable. It formed as a red crystalline solid and was unchanged after five years in a sample vial.[20]

Discussion of crystal structures

In each molecule of structures **2** and **3**, the pyridine substituent adopts the equatorial position with respect to the 1,2,4,5-tetrazinan-3-one ring. In contrast, the pyridine substituent in structure **4** adopts the axial position. The geometry of both independent molecules of **4** is therefore chair-like, and is also reminiscent of the related pyrazole derivative.[21] The molecular structures of **3** and **4** are shown in Figs 1 and 2 respectively. In the structure of **3**, the geometries of N2, C2 and N4 are sp^3-hybridised, while N1, C1 and N3 appear to adopt sp^2-hybridised geometries. The geometry of the 1,2,4,5-tetrazinan-3-one ring of **2** and **4** lead to similar conclusions for these structures. The average planes of the nearly planar N_2C-section of the tetrazinane ring and the pyridine ring form an angle of 86.4(1)° in **2**. The value observed for the same angle in **3** is 78.4(1)°, and it is 75.3(1)° in **4**.

Figure 3 shows the hydrogen-bonded dimer which is formed between two molecules of **2** utilising one N–H donor, N3···N5($-x$, y, $-z$ + 1/2), 3.057(2) Å. In contrast, in **3** the closest intermolecular contacts between any N–H donor and potential N or O acceptors for H-bonds are 3.424 Å and 3.291 Å, respectively. Furthermore, both independent molecules of **4** are linked into chains parallel [10] by intermolecular hydrogen bonding. Three N–H donors and two H-bond acceptors are involved in this arrangement: N12···O20, 2.942(3) Å; N24···O10(x–1/2, y–1/2, z), 3.093(3) Å; N22···O10(x–1/2, y–1/2, z), 2.994(3) Å. This chain is depicted in Fig. 4. Steric and electronic factors can be used to rationalise the ring conformation in the solid state. The formation of hydrogen bond dimers in structure **2** requires the equatorial position of the 2-pyridyl ring. The equatorial position of the 2-methylpyridyl group in structure **3** might be due to the greater bulk of the ring which would favour equatorial

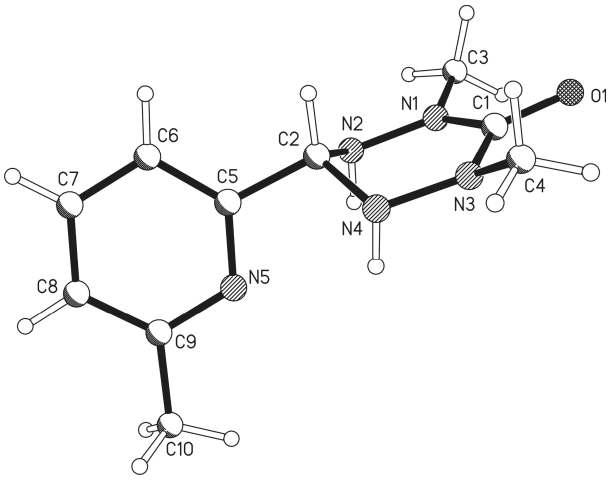


Fig. 1 Molecular structure of **3**.

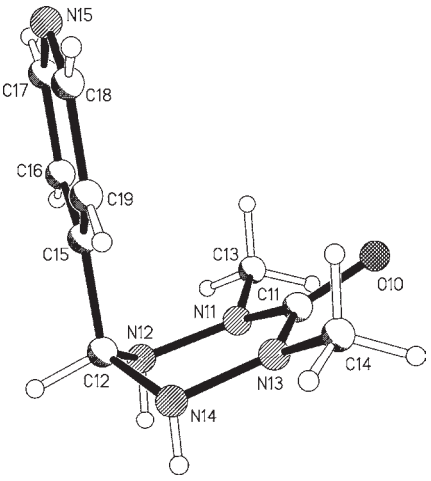


Fig. 2 Molecular structure of **4**.

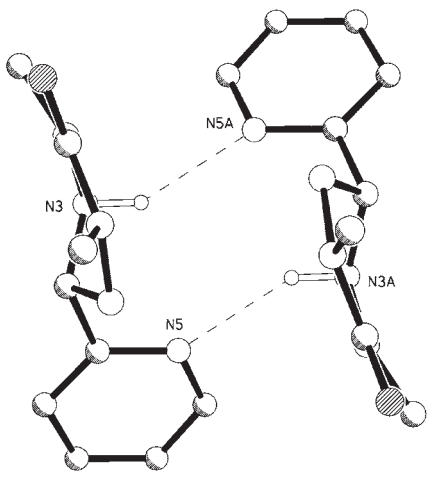


Fig. 3 H-bonded dimer in the structure of **2**.

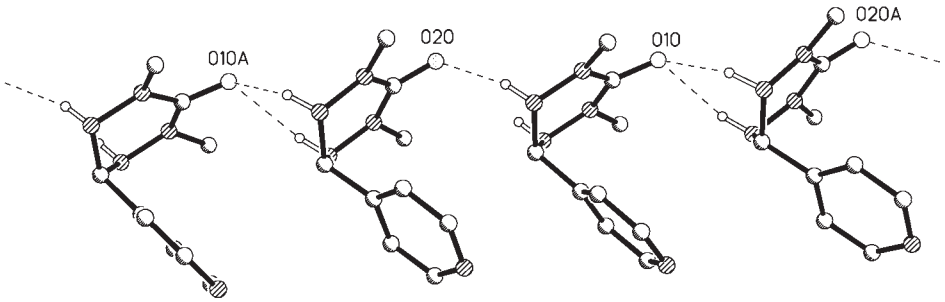


Fig. 4 H-bonded chain in the structure of **4**.

over axial substitution. In structure **4** the axial position of the pyridyl ring allows the formation of the hydrogen bond chains.

Furthermore, a structure comparison study using Xpac[22] reveals a close relationship between **2** and **3** with regard to the packing of molecules. This observation may seem somewhat surprising, given the fundamentally different hydrogen-bonded arrangements in these two structures. Structures **2** and **3** consist of infinite one-dimensional molecular double stacks with inversion symmetry. The geometry of these stacks is similar in **2** and **3**, as can be seen from Fig. 5. They are arranged parallel [010] in both structures. As a consequence, the translation vectors in this direction, 7.607 Å (in **2**) and 7.440 Å (in **3**), have almost the same length. It can be assumed that the assembly of molecules in these stacks is controlled chiefly by efficient space filling of adjacent tetrazane moieties. The crystallographic data are listed in Table 3.

ESR spectra

All the radicals present very similar ESR spectra in $CHCl_3$ solution, regardless of the kind of ring (phenyl or pyridine) bonded in the 6-position. Thus, in all cases, a total of 11 lines (plus two very weak extreme lines) can be observed (Fig. 6). These structures arise from the hyperfine coupling of the unpaired electron with the four nitrogen atoms of the verdazyl ring (^{14}N, I = 1, natural abundance = 99.6%) and

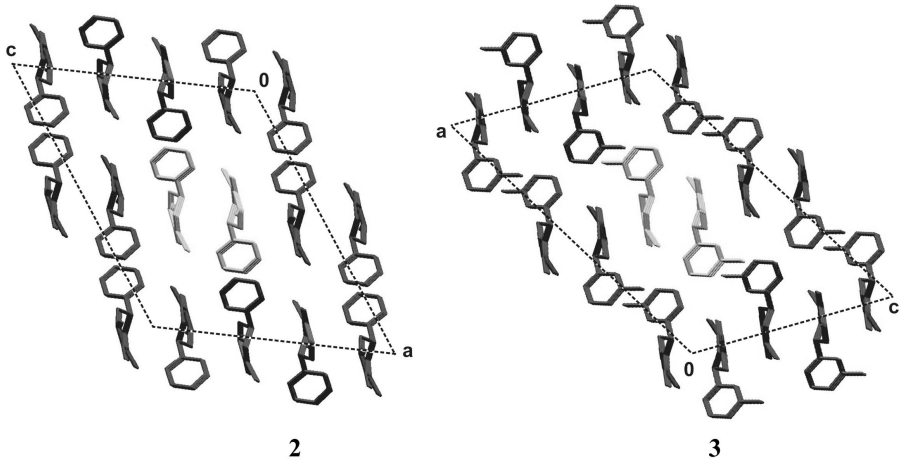


Fig. 5 Crystal structures of **2** and **3**, viewed in direction of the respective *b*-axis.

Table 3 Crystallographic data for **2**, **3** and **4**

	2	**3**	**4**
Empirical formula	$C_9H_{13}N_5O$	$C_{10}H_{15}N_5O$	$C_9H_{13}N_5O$
Formula weight	207.24	221.27	207.24
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	19.7796(5)	23.4912(9)	19.3331(9)
b (Å)	7.6072(2)	7.4400(4)	8.9169(4)
c (Å)	16.1836(4)	14.8094(6)	23.3012(11)
β (°)	124.535(1)	120.708(3)	98.719(3)
V (Å^3)	2005.99(9)	2225.38(17)	3970.5(3)
Z	8	8	16
D_{calc} (g cm^{-3})	1.372	1.321	1.387
Crystal	Colourless plate	Colourless block	Colourless plate
Crystal size (mm)	1.20 × 1.00 × 0.15	0.20 × 0.20 × 0.15	0.20 × 0.10 × 0.05
Reflections collcd.	9676	5359	9782
Independent refls.	1954	2111	3558
R_{int}	0.0690	0.0547	0.1078
R ind's [$F^2>2\sigma(F^2)$]	*R1* = 0.0408	*R1* = 0.0463	*R1* = 0.0601
R indices (all data)	*R1* = 0.0517	*R1* = 0.0570	*R1* = 0.1242
	WR2 = 0.1157	*wR2* = 0.1353	*wR2* = 0.1238

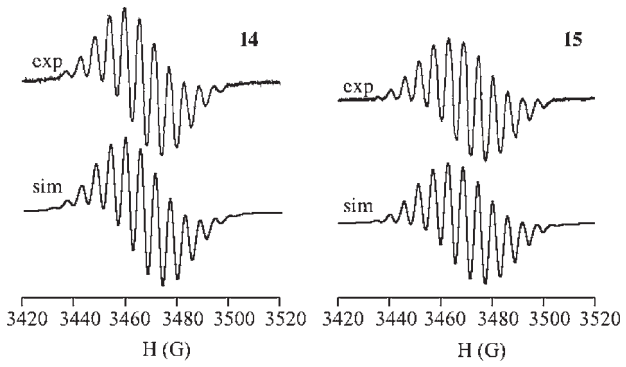


Fig. 6 Experimental (top) and simulated (bottom) ESR spectra of **14** (a radical with a pyridine ring) (left) and **15** (a radical with a phenyl ring) (right).

with the six hydrogen atoms (^{1}H, I = 1/2, natural abundance = 99.98%) of the two methyl groups bonded to N2 and N4 of the verdazyl ring. In all the cases a very satisfactory simulation of the shape, intensity and position of all the lines in these spectra (Fig. 6) can be obtained by taking into account a hyperfine coupling with the two groups of two equivalent nitrogen atoms (N1–N5 and N2–N4) plus an additional coupling with the six hydrogen atoms of the two methyl groups bonded to the N2 and N4 atoms in the verdazyl ring.

The hyperfine coupling constants so obtained are listed in Table 4. As expected, the hyperfine coupling constants are very similar for all the radicals, regardless of the substituent in the 6-position, confirming the presence of a very similar spin distribution in all the radicals. In fact, previous ESR and theoretical studies on verdazyl and 3-oxoverdazyl radicals indicate that the odd electron resides in a π* singly occupied molecular orbital (SOMO) spanning the four nitrogen atoms of the ring, with a nodal plane at the 6-position that precludes any strong coupling with the substituent groups in this position.[3] These previous ESR studies also show that the hyperfine coupling constants (a) of the two pairs of chemically equivalent nitrogen atoms (N1/N5 and N2/N4) are very similar, with $a(N_{1,5}) \approx 6.3–6.5$ G and $a(N_{2,4}) \approx 5.3$ G when N2 and N4 bear alkyl groups. In this last case, the protons hyperfine coupling constants of the alkyl groups, $a(H_{2,4})$, are usually identical to those of the N2 and N4 atoms to which they are bonded (≈ 5.3 G).[3]

As can be seen in Table 4, the 3-oxoverdazyl radicals **12–21** also present similar hyperfine couplings with the two pairs of chemically equivalent N atoms, although the coupling constants with one pair of equivalent nitrogen atoms (in the range 6.2–6.6 G) are somewhat higher those of the other pair of equivalent nitrogen atoms (in the range 5.2–5.7 G). In fact, although from the fitting procedure it is not possible to assign these a(N) values, by comparison with the published values for other oxoverdazyl radicals (see above),[15-16] we can certainly assign these a(N) values as shown in Table 4. This assignment is also in agreement with the values recently reported for other 2,4-dimethyl-3-oxoverdazyl radicals bearing different substituents in the 6-position, such as 1,6-dithiapyrene (DTPY)[15] and corannulene[16], where values of $a(N_{1,5}) = 6.55$ and 6.50 G, $a(N_{2,4}) = 5.18$ and 5.19 G and $a(H_{2,4}) = 5.45$ and 5.46 G, respectively, have been found.

Given the relatively broad linewidths of the ESR spectra (between 2.2 and 3.0 G), that reduces the sensitivity of the simulated spectra, and in order to reduce the number of adjustable parameters, we have fixed the $a(H_{2,4})$ values identical to those of the $a(N_{2,4})$.

As has been shown for other 2,4-dimethyl-3-oxoverdazyls with aryl groups in the 6-position,[15,16] no hyperfine coupling (or one too small to be detected) is observed to the aryl ring atoms, in agreement with the very similar aspect of all the ESR spectra, regardless of the type of ring bonded to the verdazyl radical. This idea is further supported by NMR, TRIPLE and ENDOR spectroscopies that have shown that these coupling constants are small and well below 1 G.[3,19] The g value of all the radicals was very similar, around 2.0050.

Table 4 Hyperfine coupling constants (gauss) of verdazyls **12–21**, ESR at 298 K, $CHCl_3$ as solvent, under argon

Verdazyl	$a(N_{1,5})$	$a(N_{2,4})$	$a(H_{2,4})$
12	6.2	5.5	5.5
13	6.4	5.7	5.7
14	6.5	5.3	5.3
15	6.3	5.4	5.4
16	6.6	5.7	5.7
17	6.5	5.6	5.6
18	6.6	5.2	5.2
19	6.6	5.3	5.3
20	6.6	5.2	5.2
21	6.6	5.3	5.3

Conclusions

A series of 1,2,4,5-tetrazinan-3-one precursors to oxoverdazyls have been prepared and characterised. The crystal structures of three of these precursors show the presence of intermolecular hydrogen bonds in the three structures and the equatorial or axial position of the pyridine substituent. Oxidation by $NaIO_4$ of the 1,2,4,5-tetrazinan-3-one precursors **2–11** gives rise to the corresponding oxoverdazyl radicals **12–21** that present, in all cases, in $CHCl_3$ solution very similar ESR spectra with eleven lines, confirming the similar spin distribution in all the radicals. All the ESR spectra could be very well simulated with hyperfine coupling constants in the range 6.2–6.6 G, 5.2–5.7 G and 5.2–5.7 G for the $N_{1,5}$, $N_{2,4}$ and $H_{2,4}$ atoms, respectively. These values agree with previous results obtained for other similar 2,4-dimethyl-3-oxoverdazyl radicals.[14]

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 253860 (**2**), 253861 (**3**), 253862 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http: //www.ccdc.cam.ac.uk/conts/retrieving.html).

Experimental

Melting points were carried out using a Kofler hot-stage microscope. Elemental analyses were carried out by Butterworth Laboratories using a PE 2400 CHN analyser. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda UV-VIS spectrometer. Infrared spectra were recorded on an ATI Mattson FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained at 250 MHz and 62.9 MHz respectively on a Bruker AC 250 spectrometer and at 400 MHz and 100.5 MHz respectively on a Varian 400 spectrometer. Chemical shifts (δ) are given in ppm relative to the residual solvent. X-band ESR spectra were obtained on a Bruker ECS106 electron spin resonance spectrometer. All the ESR spectra were measured on $CHCl_3$ solutions of the radicals with typical concentrations in the mM range, at room temperature. The simulations of the ESR spectra were done with the Win-EPR SimFonia software from Bruker. Since the simulated spectra are very sensitive to the N-hyperfine coupling constants, a(N), and much less sensitive to the H-hyperfine coupling constants, a(H), the estimated errors are about 0.1 G for the a(N) and about 1 G for the a(H) constants. The relative insensitivity of the simulated spectra to a(H) precludes a precise determination of their values and, in fact, these H-hyperfine coupling constants were set to be equal to the $N_{2,4}$ constants (see Table 4).

Intensity data for single crystals were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer with a rotating anode at 120 K. The structures were solved by direct methods using SHELXS, and they were refined on F^2 by least-squares procedures using SHELXL.[23] All non-hydrogen atoms were refined freely using anisotropic displacement parameters. All hydrogen atoms were identified in a difference map. The positions of hydrogen atoms attached to nitrogen were refined freely, and the positions of hydrogen atoms bonded to carbon were constrained to idealised geometries. The relevant crystal data parameters are displayed in Table 3.

2,4-Dimethylcarbonohydrazide (**1**): To a stirred solution of methyl hydrazine (6.0 g, 0.13 mol) in anhydrous CH_2Cl_2 (50 ml) cooled to below –10°C was added triphosgene (3.2 g, 10.83 mmol) in anhydrous CH_2Cl_2 (40 ml) over 1 h. The reaction mixture was left to rise to rt and stirred for 2 h. The reaction mixture was filtered to remove the hydrochloride salt (5.1 g), and the filtrate was concentrated to an off-white oil which was dried on a high vacuum line to give the title compound (3.6 g, 94%) as a colourless solid, m.p. 54–57°C (from dichloromethane) (lit.[1,4] 58–59°C). IR: ν_{max}/cm^{-1} (KBr) 3463br s, 3390 s, 3300vs, 2964 s, 1650br s, 1495br s. NMR: δ_H(400 MHz; $CDCl_3$) 2.97 (6H, s, 2 × CH_3), 3.95 (4H, br s, 2 × NH_2); δ_C(100.5 MHz; $CDCl_3$) 43.0, 167.0. MS: *m/z* (ES^+) 119.1 ($[M + H]^+$, 100%).

Synthesis of tetrazinanones **2-6**, *typical procedure. 2,4-dimethyl-6-(2-pyridyl)-1,2,4,5-tetrazinan-3-one* (**2**):[14] 2,4-Dimethylcarbonohydrazide (0.5 g, 4.72 mmol) in anhydrous MeOH (25 ml) was stirred and pyridine-2-carbaldehyde (0.51 g, 4.72 mmol) in anhydrous MeOH (20 ml) was slowly added. The reaction mixture was refluxed for 24 h, then cooled, and the solvent was removed *in vacuo* to yield the title compound (0.21 g, 22%) as colourless crystals, m.p. 157–159°C from ethanol/ethyl acetate 1: 1 in the cold over 2 weeks (lit.[14] 148–149°C). IR: ν_{max}(KBr)/cm^{-1} 3186 s, 3052 m, 2925 m, 1630vs, 1470 s, 1431 m, 1383 m, 1127 m, 947 m, 870 m, 781 m. NMR: δ_H (250 MHz; $CDCl_3$) 3.14 (6H, s, 2 × CH_3), 4.94 (3H, m, 2 × NH and CH), 7.30 (1H, d *J* = 4.7, Ar), 7.43 (1H, d, *J* = 7.6, Ar), 7.72 (1H, d *J* = 7.6, Ar) and 8.53 (1H, d, *J* = 4.7, Ar); δ_C (62.9 MHz; $CDCl_3$) 38.1, 69.5, 123.6, 124.3, 137.3, 149.6, 153.6, 154.5. MS: *m/z* 207 (M^+, 100%), 205 (20), 162 (55). Found: C, 52.1; H, 6.2; N, 33.6. $C_9H_{13}N_5$ requires C, 52.2; H, 6.3; N, 33.8%.

2,4-Dimethyl-6-(6-methyl-2-pyridyl)-1,2,4,5-tetrazinan-3-one (**3**): From 6-methylpyridine-2-carbaldehyde (0.95 g), as prisms (52%), m.p. 133–135°C from methanol/ethyl acetate 1: 5 in the cold over 2 weeks. IR: ν_{max} (KBr)/cm^{-1} 3239 s, 3152 s, 2926brs, 2786 s, 2200 m, 2082 m, 1663vs, 1630vs, 1494vs, 1403vs, 1239 s, 1142 s, 1091 s, 896 m, 736 s. NMR: δ_H (400 MHz; $CDCl_3$) 2.45 (3H, s, CH_3), 3.10 (6H, s, 2 × CH_3), 4.75 (1H, t, *J* = 11.6 Hz, CH), 4.94 (2H, d, *J* = 11.6 Hz, 2 × NH), 7.09 (1H, d, *J* = 7.6 Hz, Ar), 7.17 (1H, d, *J* = 7.6 Hz, Ar) and 7.55 (1H, t, *J* = 7.6 Hz, Ar); δ_C (100.5 MHz; $CDCl_3$) 25.3, 39.1, 70.4, 121.5, 124.9, 138.4, 153.8, 155.5, 159.8. MS: *m/z* 222 (M^+ + 1, 100%), 207 (35). Found: C, 54.3; H, 6.8; N, 31.4. $C_{10}H_{15}N_5O$ requires C, 54.3; H, 6.8; N, 31.8%.

2,4-Dimethyl-6-(4-pyridyl)-1,2,4,5-tetrazinan-3-one (**4**): From pyridine-4-carbaldehyde (0.54 g) as colourless prisms (28%), m.p. 132–133°C (decomp.) from dichloromethane: petroleum ether 40–60ºC 1: 1 layered in the cold. IR: ν_{max}(KBr)/cm^{-1} 3622 m, 3242 s, 3185vs, 3122 s, 3065 m, 3025 s, 2973vs, 2878br s, 1958 m, 1665 s, 1615vs, 1561 s, 1522 s, 1481 s, 1433 s, 1406 s, 1325vs, 1300vs, 1102vs, 981 m, 863 s, 813 s, 729 m. NMR: δ_H (400 MHz; $CDCl_3$) 3.05 (6H, s, 2 × CH_3), 4.74 (2H, d, *J* = 7.5 Hz, 2 × NH), 4.97 (1H, br t, CH), 7.46 (2H, d, *J* = 6.0 Hz, Ar) and 8.56 (2H, d, *J* = 6.0 Hz, Ar); δ_C (100.5 MHz; $CDCl_3$) 39.2, 69.2, 123.0, 1546, 151.2, 156.1. MS: *m/z* 207 (M^+, 23%), 105(100); HRMS: *m/z* (ES^+) 208.1192 $[M + H]^+$, $C_9H_{13}N_5O$ requires 208.1193.

6-(3,5-Di-t-butylphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**5**): From 3,5-di-*t*-butylbenzaldehyde (0.7 g) as a colourless solid (32%), m.p. 181–184°C from ethanol. IR: ν_{max} (KBr)/cm^{-1} 3258 m, 3221 m, 2961br s, 1601 s, 1509 s, 1480 s, 1361 s, 1247 m, 1188 m, 1123 m, 1091 m, 973 s, 864 s, 729 s, 717 s, 642 m. NMR: δ_H (400 MHz; $CDCl_3$) 1.29 (18H, s, 2 × $C(CH_3)_3$), 3.13 (6H, s, 2 × CH_3), 4.41 (2H, d, *J* = 9.4 Hz, 2 × NH), 4.97 (1H, t, 9.4, CH), 7.31 (2H, m, Ar), 7.37 (1H, m, Ar); δ_C (100.5 MHz; $CDCl_3$) 32.5, 36.0, 39.2, 71.1, 121.6, 124.0, 135.3, 152.4, 156.6. MS: *m/z* (CI^+) 319.3 ($[M + H]^+$, 100%); HRMS: *m/z* (ES^+) 319.2500 $[M + H]^+$, $C_{18}H_{31}N_4O$ requires 319.2498.

6-(5-Carboxy-2-hydroxyphenyl)-1,5-dimethyl-1,2,4,5-tetrazinan-3-one‡ (**6**): From 5-carboxy-2-hydroxybenzaldehyde (3.1 g, 76%) as colourless needles, m.p. >250°C (from methanol/water). IR: ν_{max}/cm^{-1} 3405 m, 3260 s, 3229 s, 1698 s, 1582 s, 1280 s, 1222 s. NMR: δ_H (250 MHz; DMSO-d_6) 2.95 (6 H, s, 2 × CH_3), 5.08 (1 H, br s, H-6), 5.77–6.02 (2 H, br s, 2 × NH), 6.90 (1 H, d, *J* 8.2, Ar), 7.78 (1 H, d, *J* 8.2, Ar), 7.98 (1 H, s, Ar) and 10.40-11.62 (1 H, br s, OH); δ_C (62.9 MHz; DMSO-d_6) 37.3, 65.5, 115.6, 121.5, 121.7, 129.7, 131.2, 154.3 and 159.50, 167.0. MS: *m/z* (ESI +) 555 ($2M^+$ + Na, 43%), 289 (M^+ + Na, 100%), 267 (M^+ + 1, 43%), 119 (28). Found: C, 49.5; H, 5.3; N, 20.75. $C_{11}H_{14}N_4O_4$ requires C, 49.6; H, 5.3; N, 21.05%.

Synthesis of tetrazinanones **7–10**, *typical procedure. 6-(2-hydroxyphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one* (**7**): To a stirred solution of **1** (1.0 g, 8.5 mmol) in MeOH (20 ml) was added a solution of 2-hydroxybenzaldehyde (1.0 g, 8.5 mmol) in MeOH (10 ml). After 18 h at room temperature the solvent was removed under reduced pressure to give a sticky solid which was triturated with EtOAc to give a colourless solid. This was purified by flash chromatography (EtOAc) to give a colourless solid which was recrystallised from ethyl acetate/methanol to give the title compound as colourless needles(0.32 g, 17%), m.p. 143–145°C. ν_{max}/cm^{-1} 3412 m, 3234 s, 1600 s, 1581 s. NMR: δ_H (250 MHz; DMSO-d_6) 2.96 (6 H, s, 2 × CH_3), 5.02 (1 H, m, H-6), 5.74 (2 H, d, *J* = 9.8, 2 × NH), 6.77–6.85 (2 H, m), 7.13–7.19 (1 H, m), 7.29–7.32 (1 H, m), 9.87 (1 H, bs, OH); δ_C (62.9 MHz, DMSO-d_6) 37.4, 65.9, 115.6, 119.1, 121.7, 127.7, 129.4, 154.3, 155.1. MS: *m/z* (ESI +) 245 (M^+ + Na, 100%), 223 (M^+ + 1, 48%). Found: C, 54.1; H, 6.0; N, 25.1. $C_{10}H_{14}N_4O_2$ requires C, 54.05; H, 6.3; N, 25.2%.

6-(3-Hydroxyphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**8**): From 3-hydroxybenzaldehyde, colourless prisms (0.65 g, 36%) from ethyl acetate/methanol, m.p. 180–182°C. IR: ν_{max}/cm^{-1} 3380 m, 3280 s, 1611 s, 1592 s. NMR: δ_H (250 MHz; DMSO-d_6) 2.93 (6 H, s, 2 × CH_3), 4.80 (1 H, t, *J* = 7.9 Hz, H-6), 5.59 (2 H, d, *J* = 7.9 Hz, 2 × NH), 6.67–6.705 (1 H, m), 6.92–6.95 (2 H, m), 7.11–7.17 (1 H, m), 9.38 (1 H, d, *J* = 1.5 Hz, OH); δ_C (67.8 MHz; DMSO-d_6) 37.6, 68.5, 114.1, 114.7, 117.5, 129.2, 138.2, 154.6, 157.3. MS: *m/z* (ESI +) 245 (M^+ + Na, 12%), 223 (M^+ + 1, 100%). Found: C, 53.9; H, 6.1; N, 25.1. $C_{10}H_{14}N_4O_2$ requires C, 54.05; H, 6.3; N, 25.2%.

6-(4-Hydroxyphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**9**): From 4-hydroxybenzaldehyde, colourless crystals (1.46 g, 77%) from ethyl acetate/methanol, m.p. 190°C. IR: ν_{max}/cm^{-1} 3245 m, 3208 m, 1605 s, 1592 s. NMR: δ_H (250 MHz; DMSO-d_6) 2.98 (6 H, s, 2 × CH_3), 4.81 (1 H, t, *J* = 8.2 Hz, H-6), 5.57 (2 H, d, *J* = 8.2 Hz, 2 × NH), 6.78 (2 H, d, *J* = 8.5 Hz, Ar), 7.35(2 H, d, *J* = 8.5 Hz, Ar), 9.50 (1 H, s, OH); δ_C(62.9 MHz; DMSO-d_6) 37.7, 68.5, 114.9, 126.9, 128.2, 154.6, 157.1. MS: *m/z* (ESI +) 467 ($2M^+$ + Na, 100%), 245 (M^+ + Na, 43%), 223 (M^+, 28%). Found: C, 54.0; H, 6.5; N, 25.1. $C_{10}H_{14}N_4O_2$ requires C, 54.05; H, 6.3; N, 25.2%.

6-(4-Diphenylaminophenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**10**): From 4-diphenylaminobenzaldehyde, pale yellow needles (0.40 g, 60%) from ethyl acetate/methanol, m.p. 157–158°C. IR: ν_{max}/cm^{-1} 3249 m, 3035w, 1627 m, 1602 s, 1493 s, 1279 s, 759 m, 701 m. NMR: δ_H (250 MHz; DMSO-d_6) 2.99 (6 H, s, 2 × CH_3), 7.40–7.60 (14H, m); δ_C (62.9 MHz; DMSO-d_6) 38.1, 69.2, 123.2, 124.9, 127.2, 129.3, 147.4, 154.6. MS: *m/z* (ESI +) 769 ($2M^+$ + Na, 100%), 396 (M^+ + Na, 91%), 374 (M^+ + 1, 70%). Found: C, 70.0; H, 6.0; N, 18.4. $C_{22}H_{23}N_5O$ requires C, 70.4; H, 6.2; N, 18.8%.

6-Ferrocenyl-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**11**): From ferrocenecarbaldehyde, dark prisms (3.05 g, 76%) (from ethyl acetate/methanol), m.p. 116–118°C. IR: ν_{max}/cm^{-1} 3210 m, 3087 m, 1636 s, 1994 m, 1428 m, 1391 m. NMR: δ_H (250 MHz; $CDCl_3$) 3.17 (6 H, s, 2 × CH_3), 4.21 (6 H, s), 4.28 (2 H, t, *J* = 1.5 Hz), 4.35 (2 H, d, *J* = 8.2 Hz, 2 × NH), 4.55 (1 H, t, *J* = 8.2 Hz, H-6); δ_C (62.9 MHz; $CDCl_3$) 38.2, 65.4, 66.3, 68.4, 68.5, 83.1, 155.3. MS: *m/z* (ESI +) 315 (M^+ + 1, 58%), 199 (24), 186 (23), 143 (38), 116 (40), 104 (100), 89 (73). Found: C, 53.85; H, 5.9; N, 17.6. $C_{14}H_{18}FeN_4O$ requires C, 53.5; H, 5.7; N, 17.8%.

Radicals **12–15** were generated and used immediately for ESR studies without further purification.

Typical procedure. 2,4-dimethyl-6-(2-pyridyl)-3-oxoverdazyl (**12**):[1] 2,4-Dimethyl-6-(2-pyridyl)-1,2,4,5-tetrazinan-3-one (**2**) (120 mg, 0.58 mmol) and $NaIO_4$ (142 mg, 0.67 mmol) were stirred in water (50 ml) for 2 h, then extracted with CH_2Cl_2 (3 × 30 ml). The combined extracts were dried with anhydrous Na_2SO_4, filtered, and concentrated to yield the title compound (0.11 g, 93%) as a yellow viscous oil. ESR: 11 line group.

2,4-Dimethyl-6-(6-methyl-2-pyridyl)-3-oxoverdazyl (**13**): 2,4-Dimethyl-6-(6-methyl-2-pyridyl)-1,2,4,5-tetrazinan-3-one (**3**) (0.25 g, 1.13 mmol) and $NaIO_4$ (0.36 g, 1.70 mmol) in water (60 ml) yielded

‡ Preferred (IUPAC) name: 3-(1,5-dimethyl-6-oxo-1,2,4,5-tetrazinan-3-yl)-4-hydroxybenzoic acid.

the title compound (71 mg, 29%) as a red viscous oil. ESR: 11 line group.

2,4-Dimethyl-6-(4-pyridyl)-3-oxoverdazyl (**14**): 6-(4-Pyridyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**4**) (90 mg, 0.43 mmol) and $NaIO_4$ (107 mg, 0.5 mmol) in water (25 ml) yielded the title compound (78 mg, 87%) as a red viscous oil. ESR: 11 line group.

6-(3,5-Di-t-butylphenyl)-2,4-dimethyl-3-oxoverdazyl (**15**): 6-(3,5-Di-*t*-Butylphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**5**) (100 mg, 0.32 mmol), $NaIO_4$ (77 mg, 0.36 mmol) and water (25 ml) formed the title compound (0.65 g, 66%) as an orange-red viscous oil. ESR: 11 line group.

Compounds **16**–**21** *Typical procedure. 6-(5-Carboxy-2-hydroxyphenyl)-2,4-dimethyl-3-oxoverdazyl* (**16**): To a stirred solution of 6-(5-carboxy-2-hydroxyphenyl)-2,4-dimethyl-1,2,4,5-tetrazinan-3-one (**6**) (80 mg, 0.30 mmol) in water (4 ml) and MeOH (2 ml) was added $NaIO_4$ (77 mg, 0.36 mmol) in water (2 ml). The reaction mixture was stirred at room temperature for 5 h and water (20 ml) was then added. The solution was extracted with Et_2O (3 × 25 ml) and the combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with Et_2O, to give the title compound (53 mg, 67%) as a red solid. IR: ν_{max}/cm^{-1} 3467 s, 2800–3600br, 1686 s. UV: λ_{max} (dioxan)/nm 553 (log ε 2.31), 516 (2.45), 493 sh (2.36), 417 (2.86), 310 sh (3.61), 295 (3.66). MS: *m/z* (ESI +) 263 (M^+, 100%), 248 (3), 218 (2). ESR: 11 line group.

6-(2-Hydroxyphenyl)-2,4-dimethyl-3-oxoverdazyl (**17**): Compound **7** (88 mg, 0.40 mmol) and $NaIO_4$ (101 mg, 0.47 mmol) gave the title compound (11 mg, 13%). IR: ν_{max}/cm^{-1} 3421 m, 1693 s. UV: λ_{max} (dioxan)/nm 525 (log ε 2.64), 419 (3.05), 393 sh (2.79), 299 (3.77), 288 sh (3.71), 258 sh (4.18), 250 (4.28). MS: *m/z* (ESI +) 220 ($M^+ + 1$, 100%). ESR: 11 line group.

6-(3-Hydroxyphenyl)-2,4-dimethyl-3-oxoverdazyl (**18**): Compound **8** (98 mg, 0.44 mmol) and $NaIO_4$ (113 mg, 0.53 mmol) gave the title compound (47 mg, 49%). IR: ν_{max}/cm^{-1} 3375 m, 1666 s. UV: λ_{max} (dioxan)/nm 524 sh (log ε 2.43), 494 (2.58), 414 (3.07), 402 (2.96), 394 (2.89), 288 (3.58). MS: *m/z* (ESI +) 219 (M^+, 100%). ESR: 11 line group.

6-(4-Hydroxyphenyl)-2,4-dimethyl-3-oxoverdazyl (**19**): Compound **9** (50 mg, 0.225 mmol) and $NaIO_4$ (58 mg, 0.269 mmol) gave the title compound (25 mg, 45%). IR: ν_{max}/cm^{-1} 3407 m, 1674 s, 1656 s. UV: λ_{max} (dioxan)/nm 519 (log ε 2.66), 418 (2.99), 394 sh (2.80), 261 (4.41). MS: *m/z* (ESI +) 219 (M^+, 100%), 163 (85), 91 (32). ESR: 11 line group.

6-(4-Diphenylaminophenyl)-2,4-dimethyl-3-oxoverdazyl (**20**): Compound **10** (55 mg, 0.15 mmol) and $NaIO_4$ (38 mg, 0.18 mmol) gave the title compound (11 mg, 20%). IR: ν_{max}/cm^{-1} 3055w, 1690 s. UV: λ_{max} (dioxan)/nm 517 (log ε 2.27), 320 (4.28), 295 sh (4.17), 280 sh (4.13), 226 (4.18). MS: *m/z* (ESI +) 370 (M^+, 100%). ESR: 11 line group.

3-Ferrocenyl-2,4-dimethyl-3-oxoverdazyl (**21**): Compound **11** (0.44 g, 1.41 mmol) and $NaIO_4$ (0.36 g, 1.69 mmol) gave the title compound (0.21 g, 48%). IR: ν_{max}/cm^{-1} 3106w, 1679 s. UV: λ_{max} (dioxan)/nm 396 (log ε 2.98), 271 (3.95), 242 (4.05). MS *m/z* (ESI +) 312 ($M^+ + 1$, 100%), 212 (43). ESR: 11 line group.

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