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Electrochemical Studies of Verdazyl Radicals

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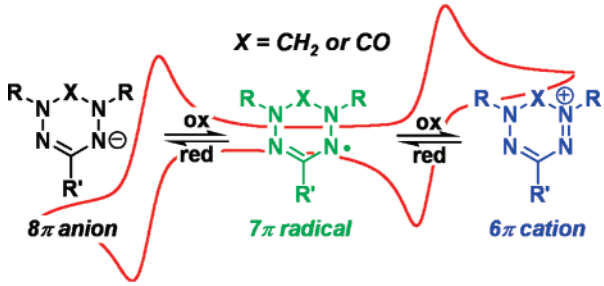
ABSTRACT



The redox properties of verdazyl radicals are presented using cyclic voltammetry techniques. These radicals can be reversibly reduced as well as oxidized. Electron-donating and -withdrawing substituents have significant effects on the oxidation and reduction potentials as well as the cell potential ($E_{cell} = |E_{ox}° - E_{red}°|$) for these radicals; a correlation between the electron spin distribution and redox properties is developed.

Stable radicals[1] have long been of fundamental interest and find a broad array of uses including as ligands for transition metals,[2] as spin labels,[3] as components of magnetic or conducting materials,[4] and as mediators of living radical polymerization processes[5] Much of the interest in, and utility of, stable radicals stems directly from the unpaired electron inherent to these species. However, stable radicals are also often redox-active, and electrochemical studies of many kinds of stable radicals have been reported.[6] The redox properties of stable radicals are central to, e.g., their intramolecular electron-transfer chemistry,[7] their efficacy as building blocks for single-component molecular conductors,[8] and their potential use as active components of organic-based batteries.[9]

Verdazyls (**1**, **2**) are the only family of neutral radicals whose stability rivals that of the well-known nitroxides (including nitronyl nitroxides); both verdazyls and nitroxides are sterically unprotected radicals, air- and water-stable, and resistant toward dimerization.[10] The main foci of research

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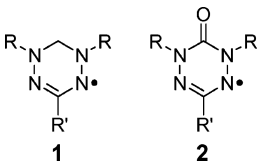
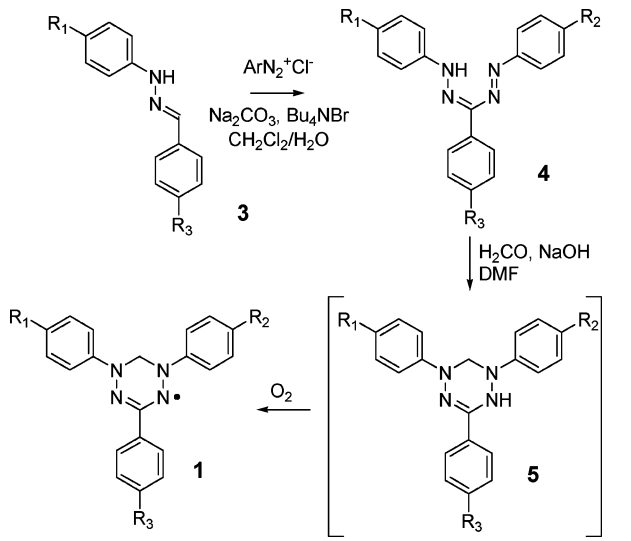
on verdazyls have been their magnetic properties[11] and coordination chemistry.[12] The redox properties of specific verdazyl derivatives have been reported,[13] but there have been no systematic studies. Herein we present electrochemical studies on a range of verdazyl radicals with a view to correlating redox properties with molecular structure.



1 **2**

Methylene-bridged triaryl verdazyls **1** were prepared using established procedures.[10a] Formazans **4** (prepared by reactions of hydrazones **3** with diazonium salts[14]) react with formaldehyde in the presence of base to produce tetrahydrotetrazines **5** which are oxidized in air to give the verdazyls **1** (Scheme 1). This is a broadly applicable procedure for

Scheme 1



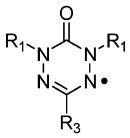
the synthesis of verdazyls, although with some limitations when strong electron-withdrawing groups are present. In one case ($R_1 = R_2 = NO_2$, $R_3 = Me$) the formazan **4n** could not be made, while other formazans with electron-withdrawing groups (**4f**, **j**, **k**, **l**, **m**) could be successfully prepared but could not be converted to the corresponding verdazyl radicals (Table 1).

Table 1. List of Substituents for Verdazyls **1** and Precursors **3**−**5**

derivative	R_1	R_2	R_3	derivative	R_1	R_2	R_3
a	H	H	H	**h**	Me	Me	H
b	OMe	OMe	Me	**i**	Me	Me	Cl
c	Me	Me	Me	**j**[a]	Me	Me	CN
d	H	H	Me	**k**[a]	Me	Me	NO_2
e	Cl	Cl	Me	**l**[a]	Me	Me	CF_3
f[a]	CN	CN	Me	**m**[a]	CF_3	CF_3	Me
g	Me	Me	OMe	**n**[b]	NO_2	NO_2	Me

[a] Formazan **4** prepared, but verdazyl **1** synthesis was unsuccessful. [b] Formazan synthesis unsuccessful.

A smaller series of 6-oxoverdazyls **2** was also prepared. 1,3,5-Triphenyl-6-oxoverdazyl **2a** was prepared according to Milcent's procedure[15] with some modifications (see Supporting Information). 1,5-Dimethyl-3-phenyl-6-oxoverdazyl **2b** was the lone *N*,*N*′-dimethylverdazyl employed in this study; the stability of *N*-*N*-dimethyl-substituted verdazyls varies widely depending on R_3 in unpredictable ways. The remaining oxoverdazyls **2c**−**2f** have isopropyl groups on the nitrogens, which are much more robust.[16] Derivatives **2c**,[17] **2d**, and **2e**[16] were prepared as reported, while **2f** is a new verdazyl radical derivative.



2a $R_1 = R_3 = Ph$,
2b $R_1 = Me$, $R_3 = Ph$
2c $R_1 = {}^iPr$, $R_3 = Ph$
2d $R_1 = {}^iPr$, $R_3 = 2$-pyridyl
2e $R_1 = {}^iPr$, $R_3 = 2$-imidazolyl
2f $R_1 = {}^iPr$, $R_3 = N$-methyl-2-imidazolyl

The electrochemical properties of radicals **1a**−**e**, **g**−**i**, and **2a**−**2f** were studied using cyclic voltammetry; data are summarized in Table 2. With few exceptions, verdazyls display fully reversible oxidation and reduction processes. Reversibility of the redox processes were confirmed as

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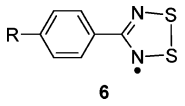
Table 2. Electrochemical Parameters[a] for Verdazyl Radicals

cmpd	$E_{ox}°$	$E_{red}°$	E_{cell}	cmpd	$E_{ox}°$	$E_{red}°$	E_{cell}
1a	−0.22	−1.23	1.01	**1i**	−0.26	−1.26	1.00
1b	−0.39	−1.33	0.94	**2a**	+0.44	−0.94	1.38
1c	−0.31	−1.29	0.99	**2b**	+0.27	−1.28	1.55
1d	−0.24	−1.26	1.02	**2c**	+0.18	−1.38	1.56
1e	−0.15	−1.14	0.98	**2d**	+0.20	−1.36	1.55
1g	−0.30	−1.26[b]	n.a.	**2e**	+0.24	−1.25[b]	n.a.
1h	−0.29	−1.27	0.98	**2f**	+0.23	−1.31	1.54

[a] Potentials are reported in V vs Fc/Fc^+. CVs were performed in MeCN solution with 0.1 M Bu_4NBF_4 as electrolyte and at a scan rate of 100 mV/s. [b] Irreversible process, cathodic peak potential only given.

follows: (1) the ratio of anodic:cathodic peak currents was approximately 1; (2) peak potentials were independent of scan rate; and (3) the peak-to-peak separations were comparable to that of the ferrocene/ferrocenium redox couple run under the same conditions.

The oxidation potentials of the methylene-bridged verdazyls **1** occur between −0.39 to −0.15 V vs Fc/Fc^+, rendering them good electron donors (a few verdazyls have in fact been used as electron donors in charge-transfer salts[13c]). The reductions of these radicals occur at rather negative potentials (−1.14 to −1.33 V). Substituent effects are qualitatively predictable. For example, the series **1b**−**1c**−**1d**−**1e** consists of verdazyls with the same R_3 group (Me) and progressively more electron-withdrawing R_2 and R_2 substituents (OMe−Me−H−Cl). The oxidation potentials in this foursome rise from −0.39 V for **1b** to −0.15 V for **1e**, a range of nearly 250 mV. In comparison, electrochemical studies on 4-(*p*-phenyl substituted)-1,2,3,5-dithiadiazolyl radicals **6** showed a range of under 100 mV for a wider range of donating/withdrawing substituents, although in these compounds the substituents are attenuated because the point of attachment to the radical ring lies on a nodal plane (see below).[8a,18]



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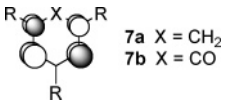
The reduction potentials also follow the expected trend and are affected qualitatively by the same magnitude, spanning from a low of −1.33 V for **1b** to a high of −1.14 V for **1e**. Substituent effects arising from changes in R_3 are qualitatively smaller than the effects of R_1 and R_2: The series **1g**−**1c**−**1h**−**1i** now have R_1 and R_2 fixed (Me) with R_3 following the same substituent progression (OMe−Me−H−Cl) and a smaller range of oxidation potentials (−0.30 for **1g** to −0.26 for **1i**). The irreversible nature of the reduction of **1g** precludes its inclusion in R_3 substituent effects, but the trend in reduction potentials for the remaining members **1c** (−1.29V)−**1h** (−1.27V)−**1i** (−1.26V) is similar to that discussed above for R_1/R_2 but smaller in magnitude. To some extent this may reflect the fact that the effects of R_1 and R_2 are being considered *collectively* (i.e., there are two substituents which can influence the redox properties). This can be deduced from the data for the series of verdazyls **1a**−**1d**−**1h**−**1c**, for which each member has one more *p*-methyl group than the one before it. Inspection of the oxidation and reduction potentials for these compounds suggests that each *p*-Me group lowers the oxidation potentials by ∼0.02 V (although the difference between **1d** and **1h** is larger at 0.05 V) and lowers reduction potentials by ∼0.02 V as well.

Overall the substituent effects appear to be mainly inductive in nature. This can be gleaned by inspection of the verdazyl singly occupied molecular orbital (SOMO)—the orbital involved for *both* oxidation and reduction processes—which is known to be a π^* orbital spanning the four nitrogen atoms (**7**). There are two nodal planes, one of which passes through the bond connecting the R_3 phenyl group to the verdazyl ring itself. This nodal plane should therefore preclude direct conjugative effects from this substituent. Para substituents R_1 and R_2 can, in principle, also affect the SOMO directly because the phenyl groups connect these substituents to the verdazyl at ring positions containing substantial contributions to the SOMO. This is borne out by comparison; for example, **1c** has *p*-OMe substituents which are inductively withdrawing but donating by resonance; the lower oxidation potential of **1c** compared to **1b** suggests that resonance effects are also important here.



7a X = CH_2
7b X = CO

The redox properties of the 6-oxoverdazyls **2** differ from those of the methylene-bridged verdazyls **1**. For comparative purposes the CVs of **1a**, **2a**, and **2b** are depicted in Figure

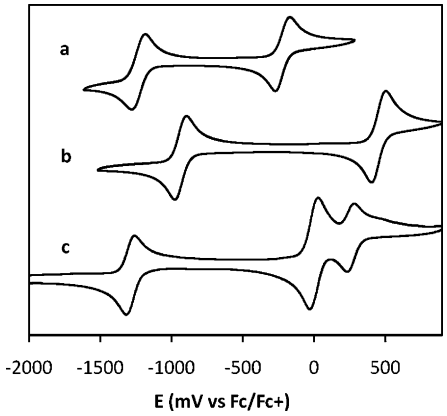


Figure 1. Cyclic voltammograms of (a) **1a**, (b) **2a**, and (c) **2b**. The redox event centered at 0 mV in (c) corresponds to the ferrocene/ferrocenium redox couple (ferrocene added as an internal reference). All CVs performed in MeCN solution at scan rates of 100 mV/s with 0.1 M Bu_4NBF_4 electrolyte.

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1 as representative triarylverdazyl, triaryl-6-oxoverdazyl, and *N,N′*-dialkyl-3-aryl-6-oxoverdazyl radicals respectively. In general the oxoverdazyl radicals are considerably more difficult to oxidize; for example, the oxidation potential of **2a** is 660 mV more positive than that of **1a**. This is most likely due to the inductive electron-withdrawing effect of the carbonyl group in derivatives of **2**. Within the limited series of derivatives of **2a**, the effects of the C3 group on the redox properties are similar to those previously described for derivatives of **1**, i.e. electron-withdrawing groups (e.g., **2d**−**f**) are slightly more easily reduced and slightly more difficult to oxidize.

Table 2 also presents the cell potentials, E_{cell} for verdazyl radicals (where $E_{cell} = |E_{ox}^{\circ} - E_{red}^{\circ}|$). This parameter is believed to correlate with gas-phase IP-EA and/or disproportionation energies (the energy associated with the process $2R\bullet \rightarrow R^+ + R^-$) and is an important consideration in the design of neutral radical- based conductors.[8] The E_{cell} values for verdazyls **1** are all very close to 1.0 V and do not appear to be affected significantly—or systematically—by any of the para substituents. *N,N*-Dialkyl-6-oxoverdazyls have even larger E_{cell} values of ∼1.5 V, while the lone triaryl-6-oxoverdazyl **2a** has a cell potential of 1.38 V, intermediate between the other two classes of verdazyl.

Kaszynski has noted that "larger" (more delocalized) radicals tend to have lower disproportionation energies and smaller cell potentials.[19] In this respect, it is not surprising that the *N,N*-dialkyl-6-oxoverdazyls have larger cell potentials compared to those of verdazyls **1** or **2a**; triarylverdazyls have *N*-aryl groups onto which spin can delocalize. The cell potentials of 1,3,5-triphenyloxoverdazyl **2a** and its methylene-bridged counterpart **1a (**and by extension, other derivatives of triarylverdazyls **1)** bears some scrutiny. The cell potential of **2a** is much larger than that of **1a** despite the fact that the two radicals have essentially the same skeleton. The carbonyl group present in **2a** does not contribute to the radical SOMO and so should not add to the conjugation/delocalization in this radical.

The spin distributions in verdazyls **1** and **2** differ from one another: EPR hyperfine coupling constants (a_N) to the two different kinds of nitrogens are nearly the same in derivatives of **1**,[10a] whereas for the oxoverdazyls **2** the a_N values for the substituent-bearing nitrogen atoms are substantially smaller than the a_N's for the two-coordinate nitrogens.[10b] Thus, the amide-like nitrogens have comparatively more spin density in verdazyls of type **1** compared to that for **2a**. One consequence of this is that spin delocalization onto the *N*-aryl groups is greater for derivatives of **1**. This is indeed the case. A variety of EPR, ENDOR, and NMR studies confirm that the magnitude of hyperfine coupling constants to phenyl protons on N-aromatic groups is significantly larger (up to a factor of 2) for methylene-bridged vedazyls **1** compared to that for **2a**.[20] This suggests that there is a correlation between the spin distribution within the verdazyl heterocycle and the redox properties (in particular cell potential): methylene-bridged verdazyls **1** have a somewhat larger spin density on the amide-like nitrogens, facilitating more effective spin delocalization onto the *N*-aryl groups and leading to smaller cell potentials compared to that for **2a**.

In conclusion, we have described the first systematic study of the redox properties of verdazyls. Several features are worthy of comment here. (1) These radicals can be reversibly oxidized and reduced, and ring substituent effects as well as spin distribution contribute to the overall redox and cell potentials. (2) The methylene-bridged radicals **1** are oxidized at quite low potentials, highlighting their potential use as electron donors[13c] or as alternatives to nitroxide radicals as oxidation catalysts.[21] (3) The cell potentials for all verdazyls are rather larger than those found for other kinds of neutral radicals such as polycyclic thiazyl radicals or spirocyclic phenalenyls,[8] two classes of radicals which have been targeted as building blocks for conducting materials specifically because of their small cell potentials.

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Supporting Information Available: Experimental procedures, spectroscopic and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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