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Synthesis and properties of 1,3-diphenyl-5-(benzothiazol-2-yl)-6-R-verdazyls

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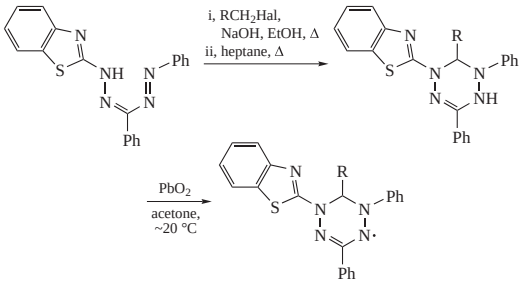
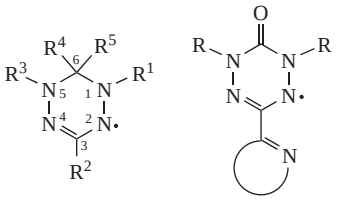
Novel 1,3-diphenyl-5-(benzothiazol-2-yl)-6-R-verdazyls, stable free radicals, were synthesized from the corresponding formazans by alkylation followed by cyclization and oxidation of the intermediate leucoverdazyls (yields 78–93%). The radicals were characterized by ESR, electronic and IR spectroscopy, mass spectrometry, X-ray diffraction (for one of them) and cyclic voltammetry. The resulting verdazyls are stable under ordinary conditions and are reduced more readily but more difficult to oxidize than the triphenylverdazyl analogue.



Verdazyl free radicals attract attention due to high chemical stability, magnetic properties, synthetic potential and ability to form metal complexes with strong magnetic exchange.[1–6] They are used as stabilizers, spin markers and building blocks for the creation of molecular magnets and switches in various fields of chemistry, physics and biology. Verdazyls with a saturated carbon atom at 6-position (Kuhn verdazyls) **1** and 6-oxoverdazyls **2** are most popular. Verdazyls are characterized as relatively weakly-basic ligands. Incorporation of chelating substituents into their structure resulted in active development of the coordination chemistry of these compounds.[1,3,7,8] For example, complexes of various metals with 1,5-dialkyl-6-oxoverdazyls **2** containing N-heterocyclic moiety (pyridin-2-yl, pyrimidin-2-yl, imidazol-2-yl) at 3-position were reported.[1,3] A first complex of 1,5-diphenyl-3-(pyridin-2-yl)verdazyl (**1**, $R^1 = R^3 = Ph$, $R^2 = Py$, $R^4 = R^5 = H$) with $PdCl_2$ was described recently.[9]



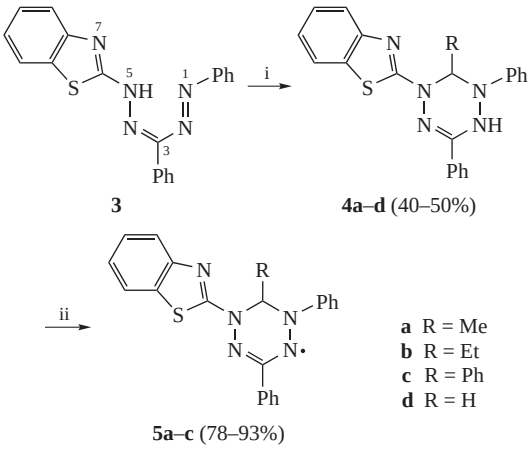
1 **2**

Verdazyls with an N-heterocyclic moiety at 1(5)-position can also be of interest as ligands for metal complexes. Only one example of such compounds, a tetrazolyl-containing verdazyl, was reported, but its complexing properties were not studied.[10]

Previously, we synthesized 1,3-diaryl-5-(benzothiazol-2-yl)-formazans and showed that the metal complexes of these compounds were formed with participation of the benzothiazole nitrogen atom.[11,12] The coordination capability of this heterocycle, along with that of 1,3-thiazole, was noted.[13] It was reasonable to assume that incorporation of a benzothiazole substituent at the tetrazine ring of verdazyls would allow one to use them for synthesizing metal complexes. Furthermore, it has been shown for a series of Kuhn verdazyls that their properties are strongly affected by the substituent at C^6: even its insignificant modification may change the crystal packing and magnetic properties.[14,15] The purpose of this communication is to describe the synthesis, structure and properties of novel 1,3-diphenyl-5-(benzothiazol-2-yl)-6-R-verdazyls with various substituents at 6-position (Scheme 1).

The starting formazan **3** synthesized by a reported technique[16] was alkylated by various alkylating agents under conditions reported elsewhere[17] while tuning the optimum reaction time (Scheme 1).

Subsequent cyclization of *N*-alkylformazans in heptane and purification by column chromatography gave leucoverdazyls **4a–d** that were characterized by elemental analysis, IR, electronic and NMR spectroscopy and by mass spectrometry. The structure



3 **4a–d** (40–50%)

5a–c (78–93%)

Scheme 1 *Reagents and conditions:* i, RCH_2Hal, NaOH, EtOH, Δ, then heptane, Δ; ii, PbO_2, acetone, ~20 °C.

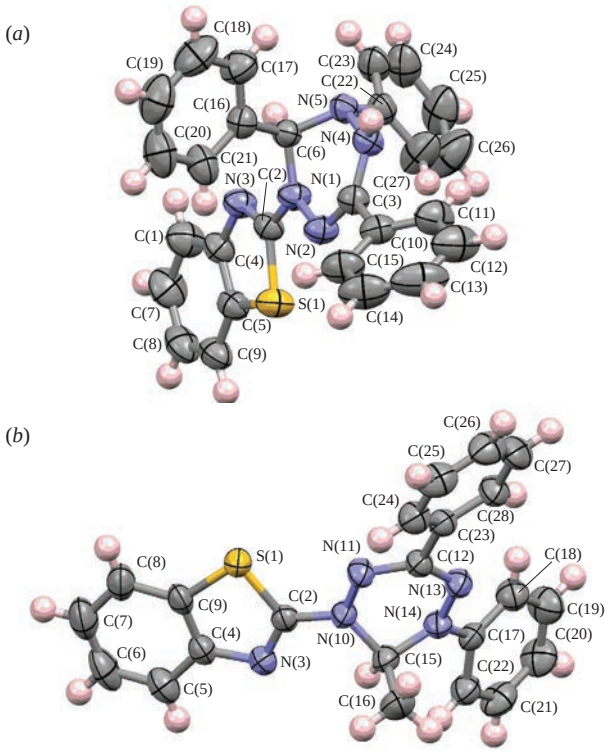


Figure 1 Molecular structures of (*a*) leucoverdazyl **4c** and (*b*) verdazyl **5a**.

of leucoverdazyl **4c** was confirmed by single crystal X-ray diffraction [Figure 1(*a*)].†

Leucoverdazyls **4a**–**d** are more stable in air at room temperature than their aryl analogues.[18] For their oxidation, K_3FeCN_6, PbO_2 and benzoquinone were tested. The best results were achieved with excess PbO_2 (for the syntheses, see Online Supplementary Materials).

The ability of leucoverdazyls to undergo oxidation and the stability of verdazyls depend on the substituents at 6-position. For R = Alk or Ph, verdazyl formation was observed even during formazan alkylation. In fact, verdazyl **5c** (R = Ph) was isolated from the reaction mixture in 15% yield, along with leucoverdazyl.

† *Crystal data.* XRD analysis of **4c** and **5a** was accomplished on an Xcalibur 3 automated four-circle diffractometer with a CCD-detector by a standard procedure [295(2) K, MoKα irradiation, graphite monochromator, ω-scans with 1° steps]. The structure was solved and refined with the SHELXTL program package.[23] All non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms at C–H bonds were calculated in the riding model, in isotropic approximation with the C_{sp^2}–H distance of 0.93 Å.

The crystal of **4c** ($C_{27}H_{21}N_5S$) is triclinic, space group $P\bar{1}$, a = 9.628(6), b = 20.276(7) and c = 20.609(10) Å, α = 113.87(4)°, β = 100.70(5)°, γ = = 101.12(4)°, V = 3451(3) Å^3, Z = 6. An empirical absorption correction was applied (μ = 1.439 mm^{-1}). At the angles 4.23° < θ < 66.60°, 72549 reflections were measured, 12057 unique reflections (R_{int} = 0.0507) among them, 8050 reflections with $I > 2\sigma(I)$. Completeness to θ = 66.60° is 98.7%. GOOF = 1.008 at F^2; final R values [$I > 2\sigma(I)$]: R_1 = 0.0458, wR_2 = 0.1149; R value (all reflections): R_1 = 0.0612, wR_2 = 0.1185, largest diff. peak/hole 0.394/–0.198 eÅ^{-3}.

The crystal of **5a** ($C_{22}H_{18}N_5S$) is monoclinic, space group $P2_1/c$, a = 12.822(5), b = 15.861(10) and c = 12.021(3) Å, β = 114.92(3)°, V = = 2216.9(18) Å^3, Z = 4. An empirical absorption correction was applied (μ = 1.412 mm^{-1}). At the angles 4.72° < θ < 66.19°, 19378 reflections measured, 3836 unique (R_{int} = 0.0722), 2140 reflections with $I > 2\sigma(I)$. Completeness to θ = 66.19° is 98.8%. GOF = 1.002 at F^2; final R values [$I > 2\sigma(I)$]: R_1 = 0.0464, wR_2 = 0.1013; R value (all reflections): R_1 = = 0.0688, wR_2 = 0.1046, largest diff. peak/hole 0.22/–0.23 eÅ^{-3}.

CCDC 1576715 and 1576716 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

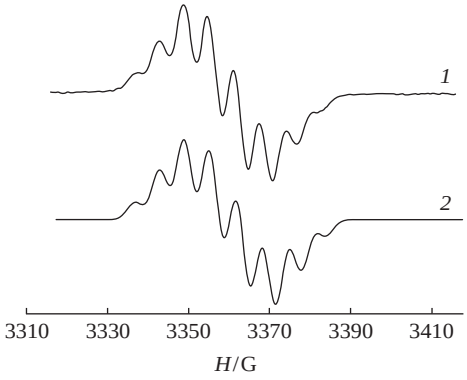


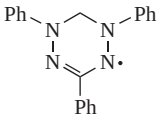
Figure 2 ESR spectrum of compound **5c**: (*1*) experimental in benzene at 15 °C and (*2*) simulated.

Table 1 Physicochemical properties of verdazyls **5a**–**c** and **6**.

Compound	ESR parameters					Electrochemical parameters		
	a_N/G	a_N/G	a_N/G	a_N/G	g	E_{ox}/V	E_{red}/V	E_{cell}/V
5a	6.61	6.07	5.97	4.10	2.00431	+0.05	–0.93	0.98
5b	6.48	6.02	5.93	3.80	2.00456	+0.04	–0.93	0.97
5c	6.25	6.03	5.84	3.67	2.00462	+0.10	–0.88	0.98
6[15]	6.0	6.0	5.8	5.8	2.0033	–0.22	–1.23	1.01

Note that verdazyl with R = H was prone to acid-induced disproportionation, similarly to Kuhn 1,5-diarylverdazyls.[2,18] At the same time, verdazyls **5a**–**c** are stable both in solid state for one month, in air at room temperature, and in solution (according to ESR data). Compounds **5** are dark green in crystals and green in organic solvents.

The structures of new radicals were studied by ESR, IR, electron absorption spectroscopy, mass spectrometry and single crystal X-ray diffraction (for **5a**) [(Figure 1(*b*)].† The ESR spectra of verdazyls **5**, like that of triphenylverdazyl **6**, consist of nine broad bands that result from coupling of the unpaired electron with four nitrogen atoms of the tetrazine ring.[9,18–20] The ESR spectrum and simulation for **5c** are shown in Figure 2. The spectral parameters of verdazyls **5a**–**c** are given in Table 1, along with those of radical **6**[15] provided for comparison.



6

However, replacement of the phenyl at N^5 by a benzothiazole moiety (verdazyls **5a**–**c**) led to a considerable a_N change in comparison with **6** (see Table 1). A similar effect was observed in 1,3-diphenyl-5-[2(1)-methyltetrazol-5-yl)]verdazyls. It is believed to be due to the electron-withdrawing properties of the heterocyclic substituent.[21]

The electronic spectra of compounds **5a**–**c** in acetone contain absorption bands in the 728–746 and 394–401 nm regions.

The electrochemical properties of radicals **5a**–**c** were studied using cyclic voltammetry and compared to those of **6**[22] (see Table 1, Figure 3). Verdazyls **5a**–**c** demonstrate fully reversible oxidation and reduction processes, similarly to radical **6**. The redox properties of **5a**–**c** are very similar. However, each redox process for these verdazyls is shifted to a more positive potential in comparison with the corresponding process of compound **6**.

The data obtained allow us to conclude that verdazyls **5a**–**c** are reduced more readily but more difficult to oxidize than **6** due

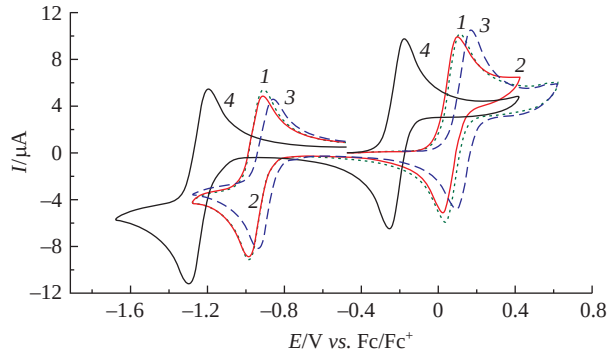


Figure 3 Cyclic voltammograms of (*1*) **5a**, (*2*) **5b** (*3*) **5c** and (*4*) **6**.

to the electron-withdrawing properties of the benzothiazole substituent. A similar effect was observed for 6-oxoverdazyls in comparison with Kuhn verdazyls,[22] as well as for the complex of a Kuhn verdazyl with Pd^{II}.[9] Note that the cell potentials ($E_{cell} = E_{ox} - E_{red}$) for compounds **5a**–**c** and **6** are similar (see Table 1).

In conclusion, novel verdazyls containing a benzothiazole moiety at a nitrogen atom of the tetrazine ring have been synthesized and characterized. These radicals are stable and the incorporation of a benzothiazole substituent resulted in considerable positive shifts of oxidation and reduction potentials in comparison with the triphenylverdazyl analogue.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.05.023.

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