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Intramolecular π-Dimerization in a 1,1′-Bis(verdazyl)ferrocene Diradical

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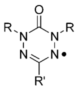
Most radicals dimerize to form a two-center, two-electron bond. However, many delocalized radicals associate to form cofacially aligned "π-dimers" or π-stacks in condensed phases. The principal driving force for π-dimerization arises from orbital overlap of SOMOs with π-symmetry which are delocalized over several atoms, and the strength of π-dimerization tends to be low (often reversible in solution) compared to σ-bond formation.[1] The unconventional bonding in π-dimers has attracted considerable interest,[2] and radical (ion) π-dimers or π-stacks are of central importance to a range of solid-state charge transport[3] and magnetic[4] phenomena. A variety of features can suppress dimerization, such as the presence of charge on the radical (i.e., radical ions[5]), steric protection,[6] resonance delocalization,[7] or spiroconjugation.[8] Verdazyls **1** are unusual in that they show no tendency to π-dimerize (or associate in any other way) despite lacking any of the factors listed above. Herein we report the characterization of 1,1′-bis(verdazyl)ferrocene **2**, a diradical containing two verdazyl centers that form *intramolecularly associated* π-dimers in the solid state, the first such association of verdazyl radicals. Ferrocene-based *mono*verdazyl **3** is also presented as a model system for diradical **2**.



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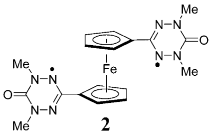

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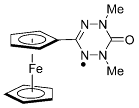

3

Diradical **2** and monoradical **3** were synthesized using standard protocols for the synthesis of 3-substituted-1,5-dimethyl-6-oxo-verdazyls,[9] starting from 1,1′-ferrocenedicarboxaldehyde and ferrocenedicarboxaldehyde, respectively. Compounds **2** and **3** were isolated as air-stable maroon and green crystals, respectively. The X-ray crystal structure of **2** (Figure 1) reveals that in the solid state the two verdazyl rings are nearly perfectly eclipsed over one another (i.e., an intramolecular π-dimer is formed). The torsion angles between each verdazyl ring and the cyclopentadienide (Cp) ring to which they are attached are very close to zero. The two verdazyls appear to be drawn in toward one another: The interannular N−N distances average 3.15 Å, smaller than the standard interplanar Cp−Cp separation (∼3.3 Å) in ferrocenes. The internal structural parameters of the verdazyls are within the normal range for verdazyls,[10] but the methyl and carbonyl groups are noticeably bent out of the verdazyl plane; for example, the carbonyl oxygen atoms are 3.645 Å apart, or ∼0.4 Å further apart than pairs of nitrogen atoms. This effect probably arises from a combination of steric and rehybridization[5] effects.

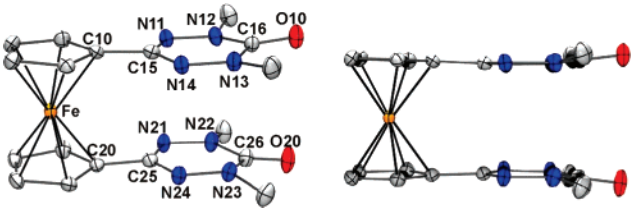

Figure 1. ORTEP drawing (50% probability ellipsoids) of **2**. Left: Partial labeling scheme. Right: Side view. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) O10−C16 1.220(3), O20−C26 1.210(3), N11−N12 1.367(3), N11−C15 1.331(3), N13−N14 1.375(3), N14−C15 1.335(3), N21−N22 1.369(3), N21−C25 1.329(3), N23−N24 1.375(3), N24−C25 1.328(3), C10−C15 1.470(3), C20−C25 1.474(3). Interannular distances (Å) C10−C20 3.249, C15−C25 3.144, N11−N21 3.119, N14−N24 3.149, N12−N22 3.136, N13−N23 3.196, C16−C26 3.365, O10−O20 3.645

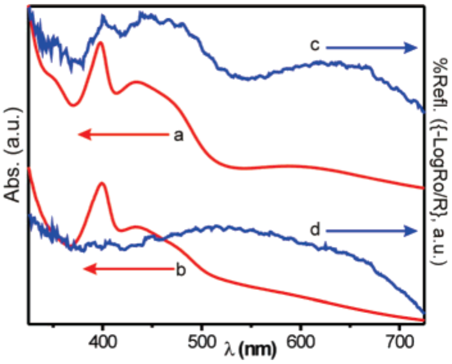

Figure 2. Solution absorption spectra of **3** (a) and **2** (b) and corresponding solid state diffuse reflectance spectra: (c) = **3**; (d) = **2**.

The solution UV−visible spectrum of monoradical **3** (Figure 2a) has absorption maxima at 396 and 470 nm, which can be assigned to verdazyl-based electronic transitions, and a typical ferrocene-based absorption 450 nm. The peak at 590 nm is not native to either ferrocene or verdazyl chromophores and appears to be a charge-transfer band; λ max for this peak is solvent-dependent. The solution spectrum of diradical **2** (Figure 2b) shows qualitatively similar features, although the CT band is much broader and less well-defined. However, the solid state electronic spectra are markedly different. The reflectance spectrum of monoradical **3** (Figure 2c) closely resembles the corresponding solution spectrum. In contrast, the two verdazyl-based peaks in the solution spectrum of **2** are absent in the reflectance spectrum (Figure 2d) and are replaced by a broad maximum at ∼520 nm. We assign this new peak as a HOMO → LUMO of the *π-dimer*, where the two frontier orbitals

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are linear combinations of the verdazyl π-SOMO. From this we can also infer that that **2** does *not* exist as a π-dimer in solution.

EPR spectroscopic studies qualitatively support the supposition that the two verdazyls are uncoupled in solution. The solution EPR spectrum (see Supporting Information) consists of a broad (~300 G wide) featureless signal upon which is superimposed a complex multiplet that contributes <1% of the total signal intensity. Inspection of the latter component reveals that it is nearly identical in pattern to verdazyl monoradicals.[9] This signal can therefore be attributed to a small amount of doublet ($S = {}^{1}/_{2}$) verdazyl-based impurity. The broad signal is consistent with a randomly oriented triplet species with a spin−spin dipolar interaction that is not averaged out by the molecular tumbling.[11] The lack of spectral features precludes determination of zero field splitting parameters, and variable temperature studies were thwarted by the rapid crystallization of **2** upon cooling. The EPR spectrum of **2** immobilized in a polystyrene matrix was similarly lacking in fine structure, suggesting that a distributiaon of conformations (facilitated by rotational motion about the verdazyl−Cp bonds and about the iron−Cp axis) persists here too.

Solid state magnetic susceptibility data for **2** indicate that the material is diamagnetic from 300 K down to cryogenic temperatures, indicative of strong antiferromagnetic exchange ($J \geq -2000$ cm^{-1}) between radical centers. The small paramagnetic component seen at cryogenic temperatures is ascribed to a small fraction of $S = {}^{1}/_{2}$ impurities, consistent with the solution EPR spectrum. Through-bond contributions to the magnetic coupling should be small, based on the weak ($|J| < 10$ cm^{-1}) intramolecular magnetic interactions in (non-π-dimerized) ferrocene-bridged nitronyl nitroxide-[11] or triarylmethyl-[12] based diradicals. Thus, the diamagnetism can be ascribed to strong antiferromagnetic exchange resulting from the π-dimer structure.[13]

The solution magnetic properties of **3** and **2** were studied using Evans' method. Monoradical **3** has a μ_{eff} value of 2.39 BM, significantly higher than the expected spin-only value of 1.73. This is attributed to spin−orbit coupling arising from nonzero spin density on the iron nucleus (Evans method produces a μ_{eff} of 3.63 BM for Fc^+PF_6^-). The solution moment of diradical **2** is 3.17 BM, higher than the spin-only values for either noninteracting radicals ($\mu_{\text{eff}} = 2.45$) *or* a ground state triplet diradical ($\mu_{\text{eff}} = 2.83$). The spin−orbit contributions to the magnetic moment do not permit quantitative analysis of the spin energetics, but the very weak through-bond interactions in other ferrocene diradicals (see above) suggest that the verdazyl moieties in **2** are probably very weakly coupled to one another. In any event, the solution magnetic properties of **2** are clearly distinct from the diamagnetic solid-state behavior and lend support to the notion that the π-dimer structure of **3** is not maintained in solution.

Pyridinyl diradicals[14] and oligothiophene diradical dications[15] tethered to flexible polymethylene [$(\text{CH}_2)_n$] chains undergo intramolecular π-dimerization, whereas verdazyl diradicals linked by flexible chains do not.[16] In the former systems, there is an intrinsic driving force for association; intermolecular π-dimers of these native (nontethered) radicals are well-known. In contrast, there are no documented examples of verdazyl-based dimers. The structure of **2** must arise from a combination of solid-state packing effects and the *relatively* conformationally restricted nature of the ferrocene spacer. The eclipsed structure permits a more compact packing mode, and the face-to-face distance between Cp rings is near ideal to permit orbital overlap between verdazyl π-SOMOs. This contrasts the structures of 1,1′-disubstituted ferrocenes with planar π-conjugated groups: Stacking of the two π-substituents is rare, and in these cases the aromatic units typically have significant torsion angles (<15°) with the Cp to which they are attached, leading to "slipped" stacks of the two substituents.[17]

In summary, we present the first π-dimer of a verdazyl radical, an achievement facilitated in the solid state through intramolecular association of two verdazyls connected to a ferrocene moiety. Future efforts will be aimed at elucidating other aspects of the ferrocene−verdazyl interaction in ferrocene-based diradicals and monoradicals.

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Supporting Information Available: Synthetic and characterization details for **2** and **3** and CIF file for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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