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HIGHLY STABILIZED PHENOXYL RADICALS WITH HYDROGEN-BONDING CAPABILITY

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Abstract. The syntheses of 4-(1H-benzimidazol-2-yl)-2,6-di-*tert*-butyl-phenoxyl and 4-(1H-5,6-dimethyl-benzimidazol-2-yl)-2,6-di-*tert*-butyl-phenoxyl radicals (**1-2**) by oxidation of the corresponding phenols is described. The radicals are stable enough to retain color for weeks in the solid state in air under some conditions. Their hydrogen bonding functionality offers prospects for use in molecular magnetic materials.

One recent strategy to control intermolecular interactions in molecular magnetic materials has been to use stable radicals with attached hydrogen bonding moieties. Both Sugawara[1] and Cirujeda et al.[2] have shown that phenolic groups can be attached to nitronylnitroxides to induce more effective exchange coupling between organic radicals in the solid state. Yoshioka[3] has shown that a nitronylnitroxide radical functionalized with a benzimidazole group yields a solid state stable ferromagnetically exchange-coupled system. Given the possibilities for controlled crystal engineering of solids through the use of hydrogen bonding,[4] it is not surprising that this approach is being applied to the design of electronic and magnetic materials. Herein we report the synthesis of unusually stablized phenoxyl radicals that incorporate benzimidazole and 5,6-benzimidazole hydrogen-bonding groups. The final products **1** and **2** – are unusually persistent even in air, and so may have use as spin bearing units in molecular magnetic materials.

The generation of radicals **1-2** requires the syntheses of appropriate *tert*-butylated phenols **3-4** (Figure 1) by condensation-cyclization of the appropriate *ortho*-diamine with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.[5] The original report of **3** describes a 9% yield, which improved to 44% through a more prolonged reaction time with exposure to air. Synthesis of **4** is accomplished in the same fashion using commercially available 4,5-dimethyl-1,2-diaminobenzene (Aldrich). Multigram quantities of **3-4** are readily made by this method. All spectra and physical characteristics are in accord with the expected structures, and previously unreported **4** is analytically pure to within typical limits. Both are high melting solids, in accord with their expected hydrogen bonded natures.

Compounds **3** and **4** both show[6] the typical, sharp –OH stretch of sterically hindered phenols at about 3600 cm^{-1} in the FT-IR spectrum, as well as broader –NH stretching at 3300 cm^{-1}. Oxidation of the phenols can be carried out by stirring over lead dioxide in dimethylsulfoxide, ether, or benzene for 30-60 min.[6] The oxidations are slowest in benzene, apparently due to the low solubility of the precursors. The final solutions of radicals **1** and **2** are deeply colored, ranging from azure to indigo depending on concentration and choice of solvent. The solutions retain their

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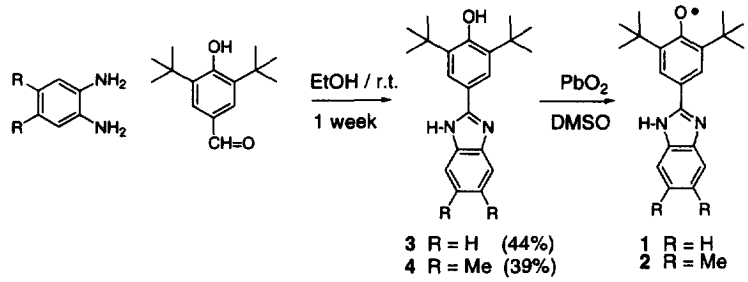


Figure 1. Synthesis of phenoxyl radicals **1-2**.

colors even in air for days, unlike the situation for the vast majority of phenoxyl radicals, which decompose upon exposure to air for a few hours at most.[7] Radical **1** can be recovered as a lavender powder after being generated in DMSO by precipitation with added water and careful vacuum drying. The color of **1** does not fade after weeks in air in the samples made with DMSO solvent. Radical **2** is a persistently azure-blue powder when generated in DMSO. FT-IR spectra of both systems shows a complete loss of the –OH stretching band, and retention of the N-H band, and production of a new band at about 1730 cm^{-1} associated with the C-O of the phenoxyl radicals, which has partial C=O character. HPLC of the radicals shows only one peak for each. The strength of the N-H and C-O bands in the radical samples varies somewhat as a function of the solvent used for oxidation (ether, benzene, DMSO). The most stable preparations of the radicals appear to incorporate solvent into the solid, judging by elemental analyses showing the presence of 5-15% DMSO by weight of sulfur despite days of vacuum drying, and the decomposition of samples that were crystallized multiple times in efforts to remove DMSO.

Solution phase electron spin resonance (ESR) spectroscopy was carried out on degassed benzene solutions of **1-2** at room temperature at about 9.8 GHz (Figure 2). Both spectra show spin delocalization from the phenoxyl unit onto the benzimidazole ring. Hyperfine coupling constants (hfc's) were obtained using lineshape fitting programs by Duling[8] and Kirste,[9] and are displayed in Figure 2. Spin counting experiments versus TEMPO standard solutions in benzene at room temperature showed essentially quantitative spin production under these conditions. The same ESR spectra are obtained by redissolving aged solid samples of **1**, even after two months of standing in air.

The ESR spectrum of **1** is relatively complex by comparison to that of **2**. We interpret this to support the presence of hydrogen atom hfc at the 5,6-positions positions in **1**, with unresolvably small methyl group hfc in **2**. The major hfc in **1** are assigned to the *meta*-hydrogens of the phenoxyl ring (due to typical negative spin density production by spin polarization at these sites), the nitrogen atoms in the imidazole ring, and the 4,7-hydrogens on the benzimidazole unit. The small but resolvable hfc at the 5,6-hydrogens of the benzimidazole unit complete the hfc which lead to the spectrum of **1**. Elimination of the latter hfc in the spectrum of **2** simplifies that spectrum to seven resolved lines. The hfc analysis of the two spectra are supported by the similarity of corresponding hfc's: $a_{meta\text{-}H}(\mathbf{1})$ = 1.87 G (2H) vs. $a_{meta}(\mathbf{2})$ = 2.17 G (2H) , $a_N(\mathbf{1})$ = 1.26 G vs. $a_N(\mathbf{2})$ = 1.53 G, $a_{N[\text{-}H]}(\mathbf{1})$ = 0.5-0.7 G vs. $a_{N[\text{-}H]}(\mathbf{2})$ = 0.89 G, $a_{4,7\text{-}H}(\mathbf{1})$ = 1.2-1.3 G vs. $a_{4,7\text{-}H}(\mathbf{2})$ = 1.26 G. In both spectra, the correlation coefficient of the fit was >0.98.

The observed hfc's are interpretable in terms of typical spin density arguments, with some perturbation by the imidazole unit of the benzimidazole moiety. EPR-II/B3LYP density functional computations for **1** using an AM1-

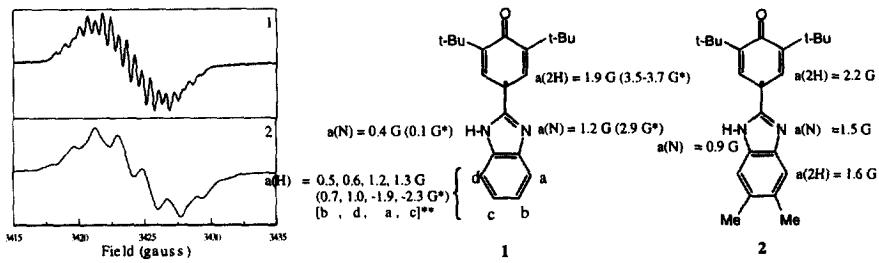
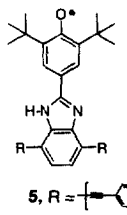
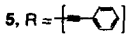


Figure 2. Experimental ESR spectra for **1-2** and hfc assignments from lineshape fitting (simulation methodology of ref 9 for **1**, ref 8 for **2**). *Density functional predicted hfc using EPR-II/B3LYP method of Gaussian 98.[10] **Computed hfc assignments for a(H) on the benzimidazole ring.

UHF optimized geometry were carried out using Gaussian 98.[10] The computations were in reasonable accord with the experimental results, showing delocalization of spin density onto the benzimidazole ring in a manner consistent with the observed hyperfine splitting. The results augment typical observations that the phenoxyl radical can be substantially delocalized,[7] placing appreciable spin density beyond the phenoxyl ring itself.



5, R = 

A polymeric polyradical based upon radical **1** was recently reported[11] to have low (1 part in 60) spin count yields. In that report, the ESR spectrum of model compound **5** was given, and interpreted in terms of extensive spin delocalization from the phenoxyl unit onto the benzimidazole and attached polymer backbone. Our present study supports the previous assertion of spin delocalization onto the benzimidazole unit. The similarity of the ESR spectrum reported for **5** to that of **1** is notable, considering the different substitution patterns. The comparison of the spectra for monomeric **1** and **2** makes assignment of hfc less problematic than is the case for the more complex **5**, clarifying the nature of the spin delocalization. The high spin counts and long lifetimes of **1-2** encourage the use of these and related radicals for the construction of molecular magnetic materials. Future work will undertake study of the bulk magnetic properties of solid **1-2**, and efforts to obtain single crystals for analysis of their solid state packing motifs, especially the possible role of solvent incorporation as a stabilizing factor.

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6. **Experimental**. **4-(1H-benzimidazol-2-yl)-2,6-di-*tert*-butyl-phenol (3)**. 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde hemihydrate (486 mg, 2.0 mmol) was added portionwise to 1,2-phenylenediamine (216 mg, 2.0 mmol) dissolved in 2.5 mL of ethanol over 30 min. The reaction was stirred at room temperature for 7 days and filtered. The solid was recrystallized from DMF to give 141 mg (44%) of **3** as white needles (mp 350 °C(d), lit mp 347 °C[5b]). FTIR (KBr, cm^{-1}): 3630 (sh, O-H str), 3446 (br, s, N-H str), 2961 (s, C-H str). ^1H NMR(200 MHz, DMSO-d_6): δ 1.46 (s, 18 H), 7.10-7.20 (m, 2 H), 7.40-7.70 (m, 3 H), 7.95 (s, 2 H), 12.70 (s, 1H).

4-(1H-benzimidazol-2-yl)-2,6-di-*tert*-butyl-phenoxyl (1). Compound **3** (30 mg, 0.09 mmol) was dissolved in 4 mL of DMSO under argon and stirred with lead dioxide (87 mg, 0.37 mmol). The resultant deep blue solution was stirred at room temperature for 4 h, until IR spectroscopy showed disappearance of the sharp OH peak at 3630 cm^{-1}. The reaction was filtered, and 8 mL of distilled water was added to give an indigo precipitate. The solid was filtered and dried under vacuum to give **1** as a purple powder (27 mg, 90%, mp 310-312 °C). FTIR (KBr, cm^{-1}): 3399 (br, s, N-H str), 3026 (m, sp^2 C-H str), 2921 (s, sp^3 C-H str), 1731 (m, C-O str). UV-vis (λ_{max}, DMSO, nm): 269, 390, 428, 638 (w, br). MS(positive ion electrospray): expected for $C_{21}H_{25}N_2O$ m/z=323, found m/z=325 (parent+2H).

4-(1H-5,6-dimethylbenzimidazol-2-yl)-2,6-di-*tert*-butyl-phenol (4). 4,5-Dimethyl-1,2-phenylenediamine (272 mg, 2.0 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde hemihydrate (486 mg, 2.0 mmol) were dissolved in 50 mL of ethanol and stirred at room temperature under air for 7 days. The resultant precipitate was filtered washed with chloroform, and recrystallized from DMF-water to give 270 mg (39%) of **4** as a white, cottony solid (mp 342-344 °C(d)). FTIR (KBr, cm^{-1}): 3630 (sh, O-H str), 3400 (br, s, N-H str), 2921 (s, sp^3 C-H str). ^1H NMR(200 MHz, acetone-d_6): δ 1.50 (s, 18 H), 2.33 (s, 6 H), 6.45 (s, 1H), 7.21 (s, 1 H), 7.41 (s, 1 H), 8.04 (s, 2 H), 11.65 (s, 1H). Analysis calcd for $C_{23}H_{30}N_2O$, C 78.82, H 8.63, N 7.99; found C 78.58, H 8.65, N 7.97.

4-(1H-5,6-dimethylbenzimidazol-2-yl)-2,6-di-*tert*-butyl-phenoxyl (2). The same procedure used for radical **1** was carried out using phenol **4**, to yield **2** as a blue-green powder that decomposes on heating. FTIR (KBr, cm^{-1}): 3432 (br, s, N-H str), 2922 (s, sp^3 C-H str), 1731 (m, C-O str). UV-vis (λ_{max}, DMF, nm): 317, 331, 399, 665 (w, br). MS(positive ion electrospray): expected for $C_{23}H_{29}N_2O$ m/z=349, found m/z=351 (parent plus 2H).

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