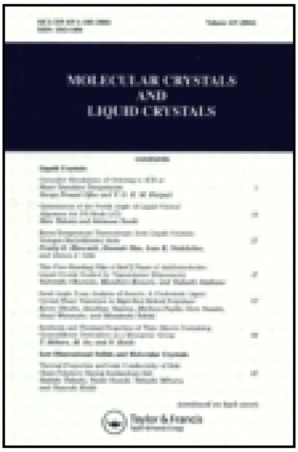

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Hydrogen-Bonded Open-Shell Molecules: Synthesis and Physical Properties of the Oxophenalenoxyl-Based Radical with Hydroxyl Group

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Hydrogen-Bonded Open-Shell Molecules: Synthesis and Physical Properties of the Oxophenalenoxyl-Based Radical with Hydroxyl Group

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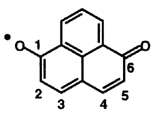
Abstract: As a new precursor for a hydrogen-bonded open-shell system, we have designed and synthesized 2,5,8-tri-*tert*-butyl-4,9-dihydroxyphenalenone **1** from commercially available 2,7-dimethoxynaphthalene in nine steps. The neutral radical generated from **1** with active PbO_2 exhibits higher stability compared with other 6-oxophenalenoxyl derivatives in the solid state. From the results of ESR and ENDOR/TRIPLE spectroscopies and MO calculations, the structure of the radical is identified to be monoradical **2** with a hydroxyl group.

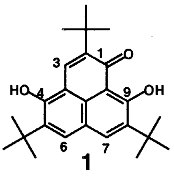
Keywords phenalenyl; 6-oxophenalenoxyl; hydroxyl group; ESR; ENDOR/TRIPLE; hydrogen-bonded monoradical

INTRODUCTION

An organic stable radical plays an important role in the recent development of molecule-based magnetism. Efforts to obtain molecular crystals and molecular assemblies possessing organic radical and/or paramagnetic metal ion as spin sources have made great strides in various strategies [1]. A number of organic crystalline ferromagnets have been reported so far [2]. Among them, a hydrogen-bonded ferromagnet [3] has drawn much attention, because a hydrogen-bonded interaction does not only contribute to controlling supramolecular crystal structures of organic radicals but also induce the intermolecular spin polarization. Aiming to develop building blocks for spin-mediated new molecular functionality, we have recently designed and synthesized 6-oxophenalenoxyl derivatives as a novel stable neutral radical based on phenalenyl skeleton, which possess similar electronic characteristics to those of galvinoxyl [4]. In such 6-oxophenalenoxyl chemistry, 2,5,8-tri-*t*-butyl-4,9-dihydroxyphenalenone **1** has been designed, enabling us to introduce hydrogen-bonded functionality to 6-oxophenalenoxyl systems. We report on the synthesis and characterization of the new stable radical **2** as studied by ESR, electron-nuclear multiple resonance (ENDOR/TRIPLE) experiments and theoretical MO calculations.



6-oxophenalenoxyl



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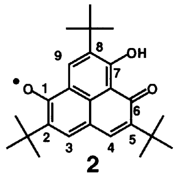
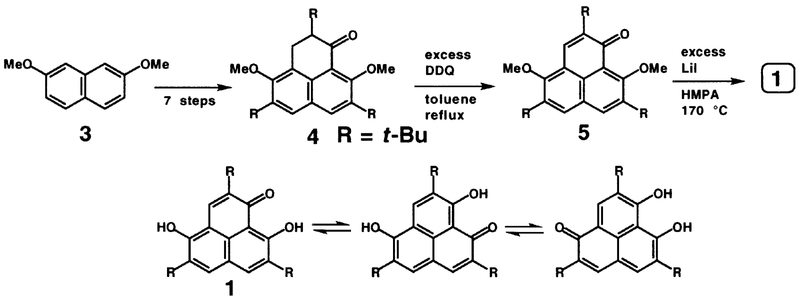


2

RESULTS AND DISCUSSION

The dihydroxyphenalenone derivative **1** as a radical precursor was quantitatively prepared from dimethoxyphenalanone **4** in two steps (see Scheme 1). The dimethoxyphenalanone **4** was prepared from commercially available 2,7-dimethoxynaphthalene (**3**) according to the reported method [4]. The obtained **1** shows strong intramolecular hydrogen bonding and intramolecular keto-enol tautomerization, which were observed by IR and ^{1}H NMR measurements (see Scheme 1).



SCHEME 1 Synthetic method and intramolecular keto-enol tautomerization for **1**

The radical **2** was obtained by the treatment of **1** with large excess amounts of active PbO_2 as black green-colored powder. The radical is stable in air at room temperature in the solid state for a month and is more stable under inert gas atmosphere.

The room-temperature ESR spectrum in toluene exhibited broad 6-lines with satellite 8-lines (see Figure 1). A frozen matrix spectrum at 140 K gave only a broad single line in the g = 2 region with no indication for high-spin electronic states. The spectral simulation was performed based on a set of isotropic hyperfine coupling constants (hfcc) obtained by ^{1}H ENDOR/TRIPLE spectroscopies (see Figure 2). The origin of the satellite 8-lines is reasonably assigned to the ^{13}C nuclei with natural isotopic abundance from the spectral simulation.

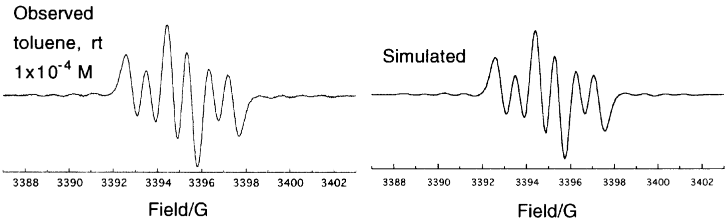


FIGURE 1 ESR spectrum observed for **1** in toluene at room temperature (left) and simulated one (right); The microwave frequency used was 9.523596 GHz. Satellite lines were attributed to ^{13}C hyperfine interactions.

The ENDOR/TRIPLE spectra of **2** measured in toluene at 200 K are shown in Figure 2. The spectrum (left) shows three pairs of intense sharp ENDOR signals and a weak pair in the middle. The intense signals are due to the phenalenyl ring protons, the weak signals are attributable to the two *tert*-butyl groups in the 2 and 5 positions on the phenalenyl skeleton and OH proton. The relative signs of the proton hfcc were unambiguously determined by general TRIPLE experiments in toluene at 200 K; the spin densities of three protons on the phenalenyl skeleton have the equal sign. The hfcc and g-value are summarized in Table 1.

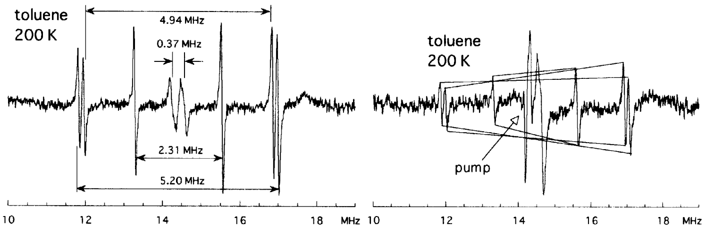


FIGURE 2 ^{1}H ENDOR (left) and TRIPLE (right) spectra observed for **2** in toluene at 200 K.

TABLE 1 Proton hfcc and *g*-value for **2**

A_H/mT					
3,4	9	2,5-*t*-Bu	8-*t*-Bu	OH	*g*-value
+0.185, +0.176	+0.082	-0.013	[a]	[a]	2.0042

[a] The values of hfcc were not determined.

As shown in Figure 3, the π-spin density distribution of **2** calculated by an HMO-McLachlan method using the standard parameters (λ = 1.2) is depicted. For the reason of the existence of three tautomers for dihydroxyphenalenone **1**, three possible structures of the monoradical species generated from **1** might be expected. The HMO-McLachlan calculation for the spin densities of monoradical species which fully agrees with the ENDOR/TRIPLE experimental results gave the structure of **2**. The π-spin density predicted by a DFT method also supported this result. Thus, we concluded the structure of the stable radical to be **2**, which has a similar π-spin distribution to that of 6-oxophenalenoxyl derivatives [4].

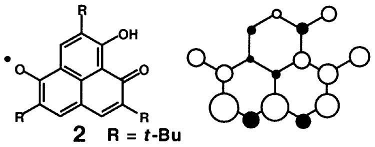


FIGURE 3 The π-spin density distribution for **2**.

In summary, we have synthesized a stable neutral radical, 2,5,8-tri-*tert*-butyl-7-hydroxy-6-oxophenalenoxyl **2** and characterized the electronic spin structure by ESR, ENDOR/TRIPLE and HMO-McLachlan calculation. The electronic structure of the radical **2** is similar to that of other 6-oxophenalenoxyl systems, which possess electronic characteristics of galvinoxyl. The radical **2** is the first 6-oxophenalenoxyl system with a hydrogen-bonded site. For further study of the solid state properties of **2**, the measurements of magnetic susceptibility and X-ray crystal structure analysis for **2** are in progress.

Acknowledgments

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