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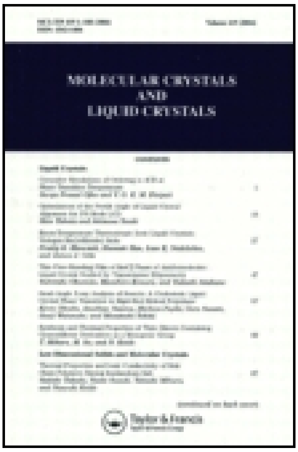

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New Stable Oxophenalenoxyl: Preparation and Characterization of a 4-Oxophenalenoxyl Derivative

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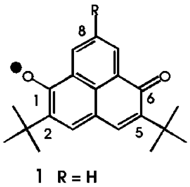
A 4-oxophenalenoxyl derivative, 2,5,8-tri-*tert*-butyl-4-oxophenalenoxyl, was prepared for the first time. This radical was successfully isolated in solid state. Its electronic spin structure was unequivocally characterized by means of liquid-phase ESR, ENDOR/TRIPLE measurements and DFT calculations.

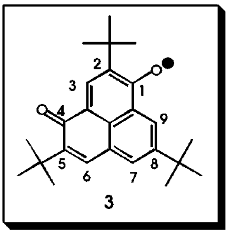
Keywords: 4-oxophenalenoxyl; 6-oxophenalenoxyl; stable neutral radical; ESR, ENDOR/TRIPLE spectra

INTRODUCTION

The preparation of new open-shell organic molecules and the elucidation of their electronic properties are important issues in the research field of molecule-based magnetic materials. Phenalenyl systems have drawn great attention as possible components for intriguing spin-mediated molecular functionalities[1,2]. We have recently achieved the synthesis and characterization of 2,5-di-*tert*-butyl-6-oxophenalenoxyl derivatives **1** and **2** as novel stable π-conjugated neutral radicals based on the phenalenyl skeleton[3]. These derivatives are stabilized by both the extended delocalization of the unpaired electron and the bulky *tert*-butyl groups on the appropriate positions. The extended delocalization is ascribable to the heteroatomic effects of the introduced oxygen atoms. Successful isolation of these derivatives demonstrated that oxophenalenoxyl is a promising system for the preparation of new stable neutral radicals, encouraging us to isolate other oxophenalenoxyl systems. In the present paper we report the synthesis, stability and electronic features of 2,5,8-tri-*tert*-butyl-4-oxophenalenoxyl (**3**).



1 R = H
2 R = *tert* -Bu



3

RESULTS AND DISCUSSION

The preparation of the radical precursor **6** was efficiently carried out by

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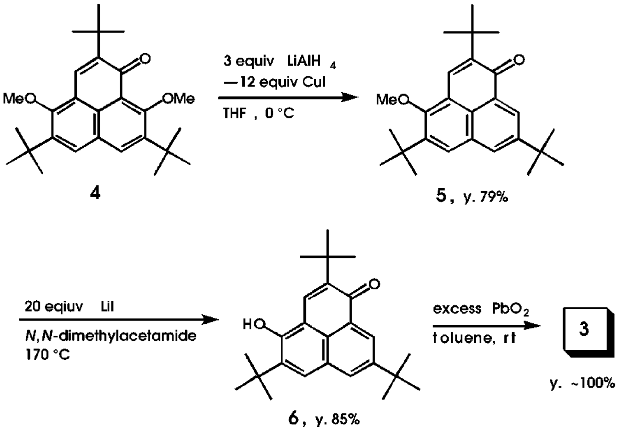
use of the following two-step reactions from 2,5,8-tri-*tert*-butyl-4,9-dimethoxyphenalenone (**4**) [4] as shown in Scheme 1: (i) regioselective reductive demethoxylation by the treatment of **4** with $LiAlH_4$–CuI reagent in THF[5] (ii) demethylation by an excess amount of LiI in *N*,*N*-dimethylacetamide. The structural determination of the mono-methoxyphenalenone derivative **5** was made by means of the NMR analysis based on the NOESY data, which gave reasonable assignments of all protons including *tert*-butyl groups. The treatment of **6** with an excess amount of active PbO_2 in toluene at room temperature gave the desired radical **3** as a green solid in quantitative yield. In the solid state, the radical **3** exhibits high stability in the absence of atmospheric oxygen, and most of radicals remains unchanged in air atmosphere for a few weeks at room temperature. In a degassed toluene, however, the radical **3** decomposed in a few days, while 6-oxophenalenoxyl derivatives **1** and **2** are stable for a long time under the same conditions.



SCHEME 1 Synthetic method of radical **3**

A hyperfine ESR spectrum of **3** observed from a degassed toluene solution of the isolated radical (5 x 10^{-5} M) at 243 K was shown in Figure 1A. In order to determine the magnitudes and relative signs of hfcc's, the liquid-phase ^{1}H-ENDOR/TRIPLE spectra were measured (Figure 1C, D). The ^{1}H-ENDOR spectrum showed four pairs of sharp lines and a pair of broad lines attributed to the four protons on the phenalenyl skeleton and *tert*-butyl protons, respectively. Furthermore, the ^{1}H-TRIPLE spectrum confirmed the relative signs of hfcc's of all the protons to be the same. The observed ESR spectrum was successfully simulated by use of the hfcc's obtained from the

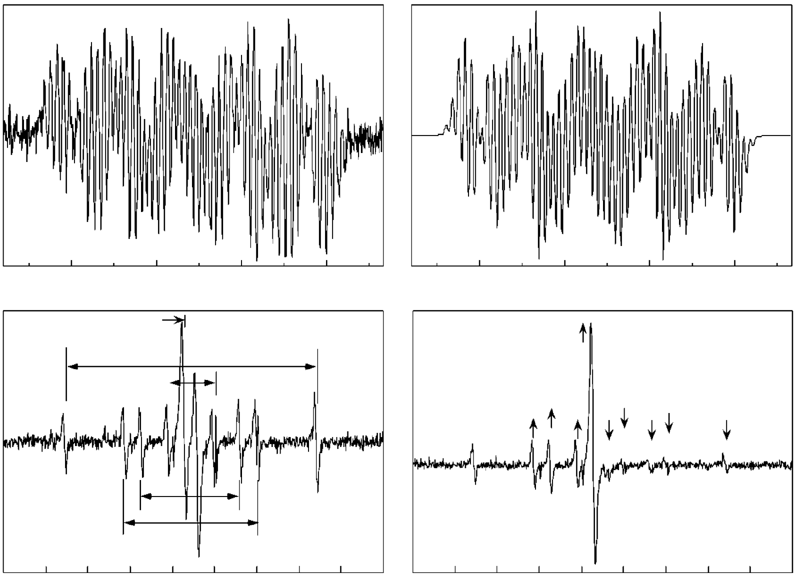


FIGURE 1 Observed hyperfine ESR (**A**), ^{1}H-ENDOR (**C**) and ^{1}H-TRIPLE (**D**) spectra in toluene (5 x 10^{-5} M) at 243 K, and simulated ESR spectrum (**B**); The microwave frequency used for the ESR measurement was 9.490406 GHz. The observed *g*-value is 2.0052.

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^{1}H-ENDOR spectrum (Figure 1B). The assignment of hfcc's was made with the help of the spin density distribution calculated in terms of a local spin density functional theory by using *Gaussian* 94 with the SVWN/6-31G**//SVWN/6-31G** method (Figure 2). The experimental and calculated values of hfcc's were summerized in Table 1. Agreements between the experimental and theoretical values are satisfactory. Although the 4-oxophenalenoxyl system has π-delocalized nature, the degree of its π-spin delocarization over the whole phenalenyl skeleton is smaller than that of 6-oxophenalenoxyl as shown in Figure 2.

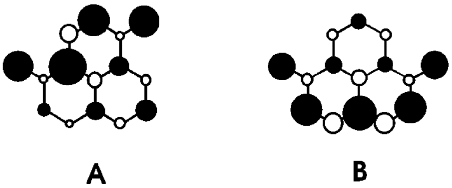

FIGURE 2 The spin density distribution of 4-oxophenalenoxyl (**A**) and 6-oxophenalenoxyl (**B**) calculated by a local spin density functional theory by using *Gaussian* 94 with the SVWN/6-31G**//SVWN/6-31G**. Vacant and filled circles denote negative and positive π-spin density, respectively.

TABLE 1 Observed and calculated proton hfcc's for **3**

	A_{H}/mT						
	3	6	7	9	2-*t*-Bu	5-*t*-Bu	8-*t*-Bu
observed[a]	+0.214	+0.039	+0.112	+0.084	+0.011	–[c]	–[c]
calculated[b]	+0.221	+0.039	+0.098	+0.073	–	–	–

[a]The observed hfcc's were determined by ^{1}H-ENDOR/TRIPLE and simulated ESR spectra. [b]The calculated hfcc's were obtained by the DFT method and McConnell equation, $A_{\alpha\text{-H}} = \rho Q$ ($Q = -3.5$ mT). [c]The magnitude and sign were experimentally unknown.

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In summary, we have succeeded in the preparation, isolation and characterization of a 4-oxophenalenoxyl derivative **3**. In spite of the comparable stability to a 6-oxophenalenoxyl derivative **2** in the solid state, **3** shows notably lower stability in the solution state. Such unstability is likely to be caused by the difference of the extended nature of the π-spin delocalization. Further progress toward the crystal structural analysis and magnetic properties of the radical **3** will be reported in due course.

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