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# Dimer Formation and Detection of Neutral Radical: 2,5-Dimethyl-6-oxophenalenoxyl Radical

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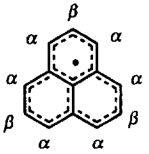
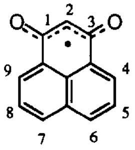
***Abstract:*** New neutral radical, 2,5-dimethyl-6-oxophenalenoxyl radical was generated by oxidation of 2,5-dimethyl-6-hydroxyphenalenone. The ESR data and MO calculations show the direct evidence for spin distribution on the *β*-positions of the phenalenyl moiety.

In a previous paper,[1] we reported on the design and detection of new neutral radicals, 2-phenyl and 2-*p*-methoxyphenyl derivatives of 3-oxophenalenoxyl, **3a** and **3b**. The ESR spectral data showed that the spin density was delocalized mostly on the substituent phenyl group, which indicates the exclusive spin delocalization on a *β*-position, C-2 of the phenalenyl moiety. This is in sharp contrast with the spin distribution of the parent phenalenyl radical **1**, which shows larger distribution on the *α*-carbon atoms. In order to further explore such examples of the spin distribution on the *β*-positions, we have designed an additional new neutral radical, 6-oxophenalenoxyl radical **4**. The important localized structures **4a–c** suggest larger spin density on the *β*-positions, C-2, 5 and quaternary C-3a. We now report on the dimer formation and detection of a new neutral radical, 2,5-dimethyl-6-oxophenalenoxyl radical **5**.



**1**



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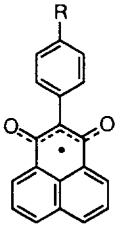
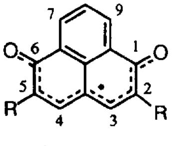
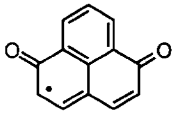


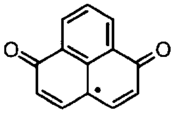
**3a**: R = H
**3b**: R = OCH$_3$



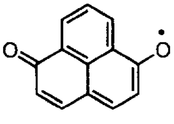
**4**: R = H
**5**: R = CH$_3$



**4a**

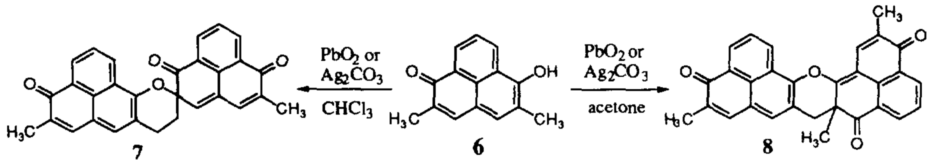


**4b**

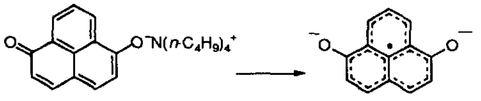


**4c**

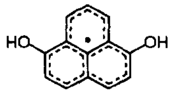
2,5-Dimethyl-6-hydroxyphenalenone **6**[2] was prepared from 3,6-dimethyl-2,7-naphthalenediol[3] and 1,3,3-trimethoxypropene[4] using a similar procedure reported in the literature for the synthesis of the parent 6-hydroxyphenalenone.[5] In the case of the oxidation of the 3-hydroxyphenalenone derivatives, we obtained the dimeric compound formed by the C–C coupling at C-2 because of the large spin population on C-2 of the 3-oxophenalenoxyl radical.[1] In order to understand the chemical reactivity of the 6-oxophenalenoxyl radical derivatives, the oxidation reactions of **6** were carried out with a large excess amount of oxidants under argon atmosphere using two different procedures: i) $PbO_2$, $CHCl_3$ or acetone, room temperature, 12 h; ii) $Ag_2CO_3$, $CHCl_3$, reflux, 12 h. The spiro type dimeric compound **7** was obtained as a yellow solid by the reactions in $CHCl_3$ ($PbO_2$, yield 75%; $Ag_2CO_3$, yield 76%),[6] and the condensed type dimeric compound **8** was obtained as an orange solid by the reaction in acetone (yield 56%).[7] The structures of the dimeric compounds were characterized by $^1H$ and $^{13}C$ NMR, IR, and FAB-mass spectra.[8]



**7** **6** **8**



**9** **10**



**11**

The formation of the dimeric compounds strongly suggests the existence of the radical species **5** as an intermediate. Therefore, we tried to detect the radical **5** by ESR spectroscopy by heating a suspended solution of **6** and $PbO_2$ in 1-methylnaphthalene or diphenyl ether in a cell under argon atmosphere. The ESR data are listed in Table 1. Figure 1 shows the ESR spectrum of **5** obtained at 100 °C in 1-methylnaphthalene and a simulated spectrum calculated by using the values given in Table 1. The coupling constants of **5** calculated by a simple HMO-McLachlan method are in good agreement with the experimental values. No signals were detected by the oxidation reactions of the parent 6-hydroxyphenalenone with $PbO_2$ or $NiO_2$ under similar conditions. We also tried to generate the neutral radical **4** from the tetra-*n*-butylammonium salt of 6-oxyphenalenone anion **9** by an electrochemical reaction. Though the signals assignable to **4** were not detected, a dianion radical **10** was observed. A simple HMO-McLachlan calculation supported the observed coupling constants (Table 1).

Figure 2 shows SOMOs of the neutral radicals **1**, **2**, **4**, and LUMO of **4**. The largest coefficients in SOMO of **4** are on the $\beta$-carbon atoms of C-2, 5, and on quaternary C-3a, and the small coefficients on the $\alpha$-carbon atoms C-3, 4, 7, and 9. Thus, in addition to 3-oxophenalenoxyl radical **2**, 6-oxophenalenoxyl radical **4** is also expected to possess an opposite spin distribution to that of the parent phenalenyl **1**. Such an opposite spin distribution can be predicted from the important localized structures **4a–c**. The experimental results for **5** showed that this is the case. The more extended nature of the $\pi$-conjugated system of 6-oxophenalenoxyl compared with that of 3-oxophenalenoxyl might enhance the stability of the radical **5**. In fact, we could observe ESR signals at a lower temperature (100 °C) for **5** than that for **3a** (160 °C). The radical **5** as well as **3** shows the high spin polarized nature which is important for obtaining magnetically interesting materials in the future.[10] The spin density of the dianion **10** is localized on the α-carbon atoms of the phenalenyl moiety similar to that of the parent phenalenyl radical **1** and to that of 1,6-dihydroxyphenalenyl radical **11**.[11] Such a spin distribution of **10** is consistent with the feature of LUMO of **4** which corresponds to SOMO of **10**.

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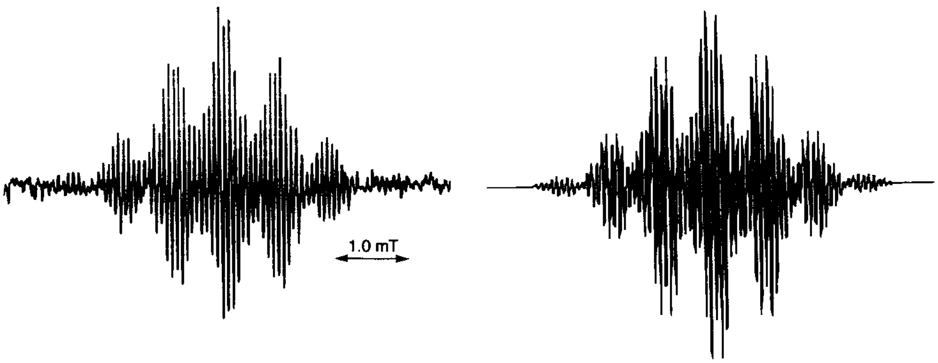
**Table 1.** ESR data for the 6-oxophenalenoxyl radical **5** and the dianion radical **10**.

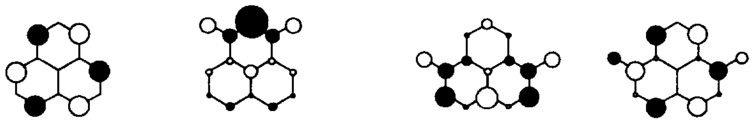
| | $A_H$ /mT[a] | | | | | $g$ | $T$/K |
|---|---|---|---|---|---|---|---|
| Radical | 2,5 | 3,4 | 7,9 | 8 | 2,5–$CH_3$ | | |
| **5** | | 0.225<br>(–0.256) | 0.075<br>(–0.074) | 0.150<br>(+0.123) | 0.738 | 2.0061 | 373 |
| **10** | 0.113<br>(–0.122) | 0.463<br>(+0.512) | 0.563<br>(+0.513) | 0.150<br>(–0.153) | | 2.0056 | 243 |

[a] Values in parentheses are calculated by a simple HMO-McLachlan method for **5** with $Q_{CH}$ = 3.99 mT and for **10** with $Q_{CH}$ = 2.42 mT.



(a) (b)

Figure 1. (a) ESR spectrum and (b) simulated spectrum of **5**.



1-(SOMO) 2-(SOMO) 4-(SOMO) 4-(LUMO)

Figure 2. SOMOs and/or LUMO of the phenalenyl radicals, **1**, **2**, and **4**.

## REFERENCES AND NOTES

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2 **6**: $^1$H NMR (acetone-$d_6$, 30 °C) $\delta$ 2.06 (3H, s), 2.43 (3H, s), 7.59 (2H, s), 7.75 (1H, t, $J$ = 7.3 Hz), 8.48 (1H, d, $J$ = 7.3 Hz), 8.62 (1H, d, $J$ = 7.3 Hz); IR (KBr) 1633, 3195 cm$^{-1}$; MS (FAB) *m/z* 225 (M$^+$ + H).

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8 **7**: $^1$H NMR (CDCl$_3$, rt) $\delta$ 8.64 (1H, dd, $J$ = 7.2, 1.0 Hz), 8.55 (1H, dd, $J$ = 7.2, 1.0 Hz), 8.53 (1H, dd, $J$ = 7.9, 1.5 Hz), 8.29 (1H, dd, $J$ = 7.6, 1.5 Hz), 7.73 (1H, t, $J$ = 7.2 Hz), 7.70 (1H, dd, $J$ = 7.9, 7.6 Hz), 7.50 (1H, d, $J$ = 1.0 Hz), 7.39 (1H, s), 7.28 (1H, d, $J$ = 1.0 Hz), 6.85 (1H, s), 2.98 (2H, t, $J$ = 6.8 Hz), 2.33 (2H, t, $J$ = 6.8 Hz), 2.21 (3H, d, $J$ = 1.0 Hz), 2.21 (3H, d, $J$ = 1.0 Hz); $^{13}$C NMR (CDCl$_3$, rt) $\delta$ 195.38 (C), 185.71 (C), 183.70 (C), 151.79 (C), 138.96 (CH), 138.26 (CH), 137.72 (C), 136.62 (CH), 134.47 (C), 133.73 (C), 132.96 (CH), 132.26 (CH), 131.50 (CH), 130.31 (CH), 129.63 (CH), 129.49 (C), 129.06 (C), 128.34 (CH), 128.12 (C), 127.51 (C), 127.15 (C), 126.49 (CH), 124.15 (C), 121.46 (C), 114.97 (C), 80.65 (C), 29.60 (CH$_2$), 21.06 (CH$_2$) 16.57 (CH$_3$), 16.50 (CH$_3$); IR (KBr) 1575, 1634, 1699 cm$^{-1}$; MS (FAB) *m/z* : Found: 445.14432 (M$^+$ + H). Calcd for C$_{30}$H$_{21}$O$_4$ (M$^+$ + H): 445.14398. **8**: $^1$H NMR (CDCl$_3$, rt) $\delta$ 8.71 (1H, dd, $J$ = 6.9, <1.0 Hz), 8.69 (1H, dd, $J$ = 7.2, <1.0 Hz), 8.61 (1H, dd, $J$ = 7.9, 1.5 Hz), 8.28 (1H, dd, $J$ = 7.5, 1.5 Hz), 8.15 (1H, d, $J$ = 1.2Hz), 7.93 (1H, t, $J$ = 7.2, 6.9 Hz), 7.63 (1H, dd, $J$ = 7.9, 7.5 Hz), 7.55 (1H, d, $J$ = 1.2 Hz), 7.50 (1H, s), 3.47 (1H, d, $J$ = 6.8 Hz), 3.22 (1H, d, $J$ = 6.8 Hz), 2.33 (3H, d $J$ = 1.2 Hz), 2.24 (3H, d, $J$ = 1.2 Hz), 1.54 (3H, s); $^{13}$C NMR (CDCl$_3$, rt) $\delta$ 197.32 (C), 185.44 (C), 183.83 (C), 159.19 (C), 147.42 (C), 137.68 (CH), 136.08 (C), 135.89 (C), 135.13 (C), 133.71 (CH), 131.39 (CH), 131.39 (CH), 130.87 (CH), 129.85 (C), 129.56 (CH), 129.24 (C), 127.62 (CH), 127.46 (CH), 127.24 (CH), 125.82 (C), 124.55 (C), 122.68 (C), 115.08 (C), 106.70 (C), 45.25 (C), 31.07 (CH$_2$), 24.21 (CH$_3$), 17.06 (CH$_3$), 16.53 (CH$_3$); IR (KBr) 1576, 1623, 1689 cm$^{-1}$; MS (FAB) *m/z* : Found: 445.14301 (M$^+$ + H). Calcd for C$_{30}$H$_{21}$O$_4$ (M$^+$ + H): 445.14398.

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