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Detection of New Neutral Radicals: 2-Phenyl- and 2-*p*-Methoxyphenyl-3-oxophenalenoxyl Radicals

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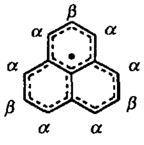
Abstract: New neutral radicals, 2-phenyl and 2-*p*-methoxyphenyl derivatives of 3-oxophenalenoxyl radical, were detected by ESR measurement. The radicals were generated by thermal decomposition of the dimers of the corresponding radicals and by oxidation of 2-phenyl-3-hydroxyphenalenone.

We have designed 3-oxophenalenoxyl radical **2** as a new neutral radical based on the phenalenyl skeleton.[1] The spin density of phenalenyl radical **1** is mainly localized on the six α-carbon atoms. Such a characteristic spin distribution has been well recognized in conjugated electronic systems containing the phenalenyl skeleton.[2] In sharp contrast, the important localized structures **2a** and **2b** suggest that the spin density of **2** is localized on a β-carbon atom at C-2, but not on the α-carbon atoms. In this context, an appropriate substituent on 2-position is necessary to reduce kinetic instability for the study of the basic chemical and physical properties of **2**. We now report on the first detection of 2-phenyl and 2-*p*-methoxyphenyl derivatives of 3-oxophenalenoxyl radical, **3a** and **3b**, by ESR spectroscopy from the corresponding dimers **5a** and **5b** and the hydroxyphenalenone **4a**.



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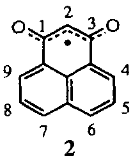

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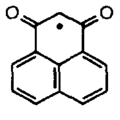
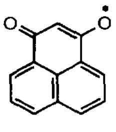
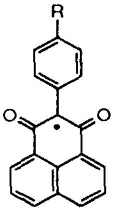


2a

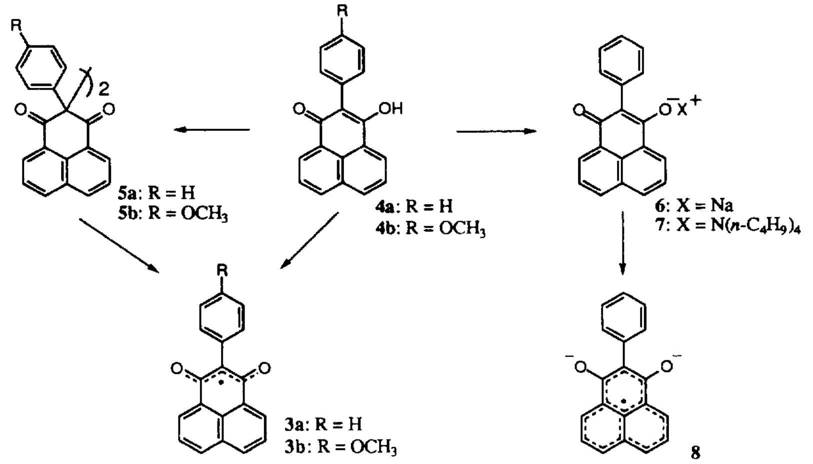


2b



3a: R = H
3b: R = OCH_3

2-Phenyl-3-hydroxyphenalenone derivatives **4a** and **4b** were prepared by the same procedure described in the literature.[3] The dimers **5a**[4] and **5b** were obtained by treatment of **4a** and **4b**, respectively, with a large excess amount of oxidants under argon atmosphere using the three different procedures: a) PbO_2, benzene, room temperature, 12 h; b) Ag_2CO_3, benzene, reflux, 3 h; c) $K_3[Fe(CN)_6]$, aqueous KOH solution and benzene, room temperature, 12 h. The products were purified by silica gel column chromatography with $CHCl_3$ as eluent (yield 53–67%). The structures of **5a** and **5b** were determined primarily by ^1H and ^{13}C NMR, IR, FD-mass spectra, and elemental analyses.[5] The hydroxyphenalenone **4a** was also converted to the sodium salt **6**[6] by treatment with NaOMe in MeOH at room temperature under argon atmosphere (quantitative yield), which was subsequently converted to the ammonium salt 7[6] by treatment with (n-C_4H_9)$_4$NCl in CH_3CN at room temperature under argon atmosphere (quantitative yield).



We attempted generation of **3a** and **3b** using three methods and their detection by ESR measurement. Firstly, we performed thermal decomposition of the corresponding dimers **5a** and **5b** in 1-methylnaphthalene (or in diphenyl ether) in a cell under argon atmosphere. The ESR signals appeared above 120 °C (or 90 °C) and disappeared after about 3 h probably due to consecutive reactions. The ESR data obtained are listed in Table 1. Figure 1 shows the ESR spectrum obtained by thermal decomposition of **5a** and the simulated spectrum calculated by using the values given in Table 1. The data strongly suggest the formation of our desired neutral radicals **3a** and **3b** (see below). Secondly, we performed oxidation of **4a** with PbO_2 in 1-methylnaphthalene (or in diphenyl ether) in a cell. The ESR signals appeared above 110 °C and the spectrum observed at 150 °C was similar to that of **3a** obtained by thermal decomposition of **5a**. Finally, we attempted to generate the radical **3a** through the electrochemical reaction of the anion **6** and **7**. The redox potentials of **7** measured by cyclic voltammetry were:[7] $E_1^{\mathrm{ox}} = +0.28$ (irreversible), $E_1^{\mathrm{red}} = -2.21$, $E_2^{\mathrm{red}} = -2.78$ (irreversible) V. The irreversible nature of the half-wave potential curve in the oxidation region indicates that the neutral radical **3a** seems to be unstable in this condition. The ESR signals detected can be assigned to a dianion radical species **8**, but not to the neutral radical (Table 1).[8] Such behavior is consistent with the results of cyclic voltammetry.

Table 1. ESR data for the 3-oxophenalenoxyl radicals **3a** and **3b** generated by thermal decomposition of dimers **5a** and **5b**, and the dianion radical **8**

	A_H /mT[a]							g	T/K[b]
Radical	o	m	p	4,9	5,8	6,7	OCH_3		
3a	0.300	0.138	0.363					2.0046	433
	(+0.299)	(−0.106)	(+0.365)	(+0.016)	(−0.016)	(+0.021)			
3b	0.300	0.075					0.075	2.0038	403
	(+0.300)	(−0.100)		(+0.017)	(−0.016)	(+0.022)			
8				0.475	0.063	0.550		2.0044	243
	(−0.017)	(+0.000)	(−0.014)	(+0.475)	(−0.130)	(+0.550)			

[a] Values in parentheses are calculated by a simple HMO-McLachlan method for **3a** with Q_{CH} = 2.46 mT, **3b** with Q_{CH} = 2.50 mT, and **8** with Q_{CH} = 2.33 mT. [b] Temperature giving sufficiently clear spectra to be analyzed.

The coupling constants of **3a** and **3b** calculated by a simple HMO-McLachlan method[9] were in agreement with the measured values as shown in Table 1. Figure 2 shows SOMOs of the neutral radicals **1**, **2**, **3a**, and LUMOs of **2** and **3a**. In contrast to the parent phenalenyl **1** which possesses the coefficients only on the six α-carbon atoms, the SOMO of 3-oxophenalenoxyl radical **2** possesses the largest coefficient on a β-carbon atom at C-2, the small coefficients on the two α-carbon atoms at C-1 and C-3, and negligibly small coefficients on the other α-carbon atoms. As is consistent with the large coefficient of C-2, the 2-phenyl-substituted radicals **3** showed relatively large coupling constants of the protons on *o*- and *p*-positions of the substituent phenyl ring, while the coupling constants of six protons of the naphthalene moiety were not observed because of a very small spin density (Table 1).[10] Such a contrastive spin distribution of **3** to **1** indicates an important contribution of a localized structure **2a**. The spin delocalization into a phenyl ring like the benzyl radical contributes to stabilize radical **3**. The results of the ESR measurement and the spin density calculation by a simple HMO-McLachlan method show the high spin polarized nature of the radicals **3** which is important for obtaining magnetically interesting materials in the future.[11] In sharp contrast, the dianion radical **8** generated by electrochemical reaction possesses relatively large coupling constants of the protons at α-carbon atoms of the phenalenyl moiety. Such a spin distribution is consistent with the feature of SOMO of **8** which corresponds to LUMO of **3a**, and can be predicted from an important localized structure **8** in which two anions are localized in oxygen atoms and a radical is distributed on the α-carbon atoms of the phenalenyl moiety.

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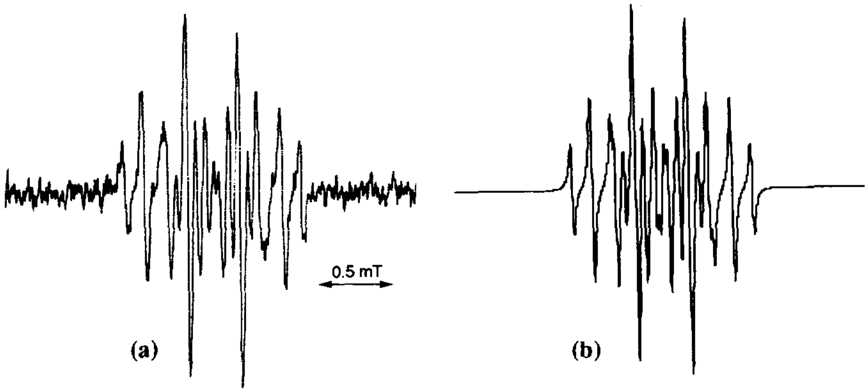
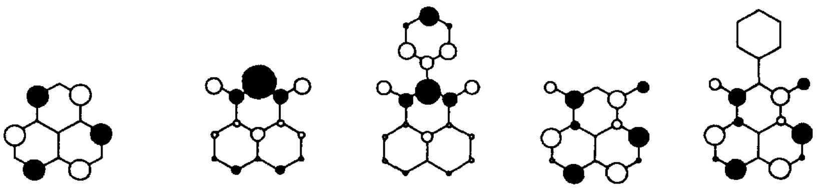


Figure 1. (a) ESR spectrum and (b) simulated spectrum of **3a**.



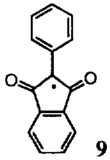
1-(SOMO) **2-(SOMO)** **3a-(SOMO)** **2-(LUMO)** **3a-(LUMO)**

Figure 2. SOMOs and/or LUMOs of the phenalenyl radicals **1**, **2**, and **3a**.

REFERENCES AND NOTES

1. Reid, D. H. *Quart. Rev.* **1965**, *19*, 274.
2. Gerson, F.; Knobel, J.; Metzger, A.; Murata, I.; Nakasuji, K. *Helv. Chim. Acta* **1984**, *67*, 934. Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1982**, *104*, 1432. Nakasuji, K.; Yoshida, K.; Murata, I. *Chem. Lett.* **1982**, 969. Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136.
3. Ayyangar, N. R.; Joshi, S. V.; Lugade, A. G. *Indian J. Chem., Sect. B* **1981**, *20B*, 1043. Awad, W. I.; Aly, O. M. *J. Org. Chem.* **1960**, *25*, 1872.
4. Meirovics, I.; Vanags, G. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1965**, 579. In this report the structure of **5a** was characterized by IR spectrum and elemental analysis.
5. **5a**: ^{1}H NMR ($CDCl_3$, –50 °C) δ 6.84 (2H, m), 7.14 (2H, m), 7.28 (4H, m), 7.43 (2H, m), 7.66 (2H, dd, *J* = 8.3, 7.3 Hz), 7.72 (2H, dd, *J* = 8.3, 7.3 Hz), 8.12 (2H, dd, *J* = 8.3, 1.1 Hz), 8.18 (2H, dd, *J* = 8.3, 1.1 Hz), 8.41 (2H, dd, *J* = 7.3 1.1 Hz), 8.43 (2H, dd, *J* = 7.3, 1.1 Hz); ^{13}C NMR (CD_2Cl_2, rt) δ 199.31 (C) , 191.70 (C), 134.01 (CH), 134.59 (CH), 132.88 (C), 132.45 (C), 130.17 (CH), 129.63 (C), 129.41 (C), 129.27 (CH), 128.66 (CH), 128.30 (C), 128.23 (CH), 127.37 (CH), 127.10 (CH), 126.99 (CH), 76.84 (C); IR (KBr) 1695, 1668, 1622, 1579, 1493 cm^{-1}; MS (FD) *m/z* 543 (M^+ + H, 100%); Anal. Calcd for $C_{38}H_{22}O_4{\bullet}2C_6H_6$: C, 85.94; H, 4.90. Found: C, 85.84; H, 5.06. **5b**: ^{1}H NMR ($CDCl_3$, -50 °C) δ 3.74 (6H, s), 6.62 (2H, dd, *J* = 9.0, 2.9 Hz), 6.74 (2H, dd, *J* = 9.0, 2.6 Hz), 6.81 (2H, dd, *J* = 8.8, 2.9 Hz), 7.33 (2H, dd, *J* = 8.8, 2.6 Hz), 7.68 (2H, dd, *J* = 8.2, 7.2 Hz), 7.72 (2H, dd, *J* = 8.2, 7.2 Hz), 8.14 (2H, dd, *J* = 8.2, 1.1 Hz), 8.19 (2H, dd, *J* = 8.2, 1.1 Hz), 8.39 (2H, dd, *J* = 7.2, 1.1 Hz), 8.46 (2H, dd, *J* = 7.2, 1.1 Hz); ^{13}C NMR ($CDCl_3$, 30 °C) δ 199.26 (C), 191.62 (C), 159.24 (C), 133.98 (CH), 133.40 (CH), 133.15 (CH), 132.52 (C), 130.05 (CH), 129.47 (C), 129.24 (C), 128.76 (CH), 128.16 (C), 126.70 (CH), 126.43 (CH), 123.49 (C), 112.60 (CH), 75.61 (C), 54.98 (CH_3); IR (KBr) 1697, 1667 cm^{-1}; MS (FD) *m/z* 603 (M^+ + H, 100%); Anal. Calcd for $C_{38}H_{22}O_4{\bullet}2C_6H_6$: C, 82.30; H, 5.05. Found: C, 82.14; H, 5.23.

   At room temperature ^{1}H NMR spectra of **5a** and **5b** showed broad signals. Therefore, we measured at –50 °C to obtain sharp signals. The X-ray crystal structure analysis for **5b** showed the dimeric structure unambiguously.
6. The salts **6** and **7** were identified by ^{1}H, ^{13}C NMR and IR spectra.
7. Conditions: Bu_4NClO_4 (0.1 mol dm^{-3}), THF, –30 °C, GC working electrode and Pt counter electrode. Potentials were measured against a Ag/Ag^+ electrode and converted to the values vs. SCE (Fc/Fc^+ = 0.31 V).
8. Conditions: Bu_4NClO_4 (0.1 mol dm^{-3}), **7** (1–10 mmol dm^{-3}), THF or CH_2Cl_2, –30 °C, Au working and counter electrodes.
9. McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.
10. Harnack, C.; Krull, W.; Lehnig, M.; Neumann, W. P.; Zarkadis, A. K. *J. Chem Soc. Perkin Trans. 2* **1994**, 1247. The coupling constants reported for 2-phenyl-1,3-indanedionyl radical **9** are similar to those of **3a**.
11. Yamaguchi, K.; Fueno, T.; Nakasuji, K.; Murata, I. *Chem. Lett.* **1986**, 629. Awaga, K.; Sugano, T.; Kinoshita, M. *Chem. Phys. Lett.* **1987**, *141*, 540.



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