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Redox-based spin diversity: a reversible topological spin switching in oxophenalenoxyl systems

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Abstract

A 6-oxophenalenoxyl system is found to be the first example of the molecular system with redox-based spin diversity nature. To generalize this nature, we focus on the 3-oxophenalenoxyl system as a topological isomer of 6-oxophenalenoxyl system. The radical dianion derivative **3** which is the redox state in the 3-oxophenalenoxyl system was successfully generated by the reduction of the corresponding hydroxyphenalenone **5** with potassium mirror. Our ESR/ENDOR/TRIPLE measurements and DFT calculation of **3** demonstrated that the 3-oxophenalenoxyl system has also redox-based spin diversity nature. In addition, for the elucidation of the interplay between spin and charge fluctuation in **3**, we discuss a VB approach derived from MO calculations.

Keywords: Oxophenalenoxyl; Radical dianion; Redox-based spin diversity; Spin structure; Charge fluctuation; Density functional calculation

1. Introduction

Exotic molecular systems with dynamic magnetic properties controlled by external stimuli are current issues in the progress in molecule-based magnetic materials [1,2]. We have designed and synthesized some neutral stable radicals as the spin sources [3]. A 6-oxophenalenoxyl derivative **1** has been prepared as a stable neutral radical [4], and recently we have demonstrated that the 6-oxophenalenoxyl system is the first example which shows the reversible topological switching of the spin density distribution in the spin-delocalized molecular system by controlling redox processes [5]. We have termed this spin switching nature as redox-based spin diversity [5]. To generalize this nature, we focus on a 3-oxophenalenoxyl system as a topological isomer of 6-oxophenalenoxyl. We have already reported the generation of 3-oxophenalenoxyl derivative **2** [6]. In the present paper, we report the generation and the characterization of the radical dianion **3** as a redox species derived from the 3-oxophenalenoxyl system by ESR measurements and DFT calculation. Furthermore, the interplay between the spin and charge in the radical dianion **3** and **4** plays an important role in their electronic structures [7]. Thus, a result obtained by the VB method for **3** in terms of MO calculations is also discussed.

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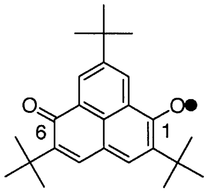

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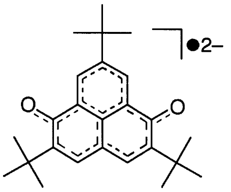

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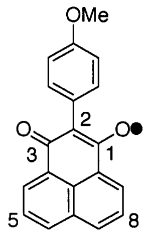

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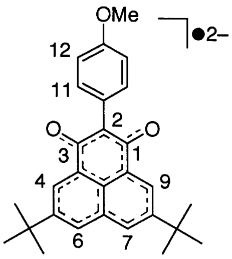

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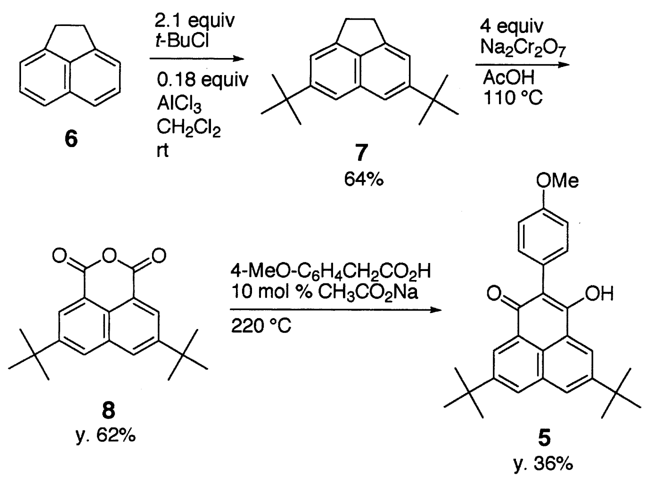
2. Results and discussion

2.1. Synthesis of 3-hydroxyphenalenone derivative 5

A 5,8-*tert*-butylated 3-hydroxyphenalenone derivative **5** has been designed as a precursor of **3** in view of the improvement of the solubility and stability of the corresponding radical dianion by the introduction of *tert*-butyl groups. The reaction of acenaphthene (**6**) with *tert*-butyl chloride in the presence of aluminium chloride gave the di-*tert*-butylated product **7**, which was oxidized to 3,6-di-*tert*-butyl-1,8-naphthalic anhydride (**8**) with sodium dichromate in acetic acid at 110 °C [8]. The synthesis of **5** was accomplished by condensation of **8** with 4-methoxyphenylacetic acid in the presence of a catalytic amount of sodium acetate at 220 °C [9] (Scheme 1).



Scheme 1.

2.2. Generation and measurements of the ESR/ENDOR/TRIPLE spectra of the radical dianion 3

The radical dianion **3** was generated by the treatment of **5** with potassium mirror in a degassed diglyme solution (1×10^{-3} M) in a sealed tube at room temperature. Fig. 1 shows the ESR spectrum (a) observed for the radical dianion **3**, and the simulated one (d). The spectral simulation was made on the basis of two sets of isotropic hyperfine coupling constants (hfccs) due to the four protons on the phenalenyl skeleton and a set of hfcc due to two protons on the phenylene moiety obtained by ^{1}H ENDOR/TRIPLE spectroscopy (Fig. 1 b and c). The relative signs of the hfccs for **3** were determined by invoking ^{1}H TRIPLE resonance measurements. Interestingly, these ESR measurements demonstrate that an unpaired electron of **3** does not couple with the nuclear spin of the potassium cation, while that of the radical dianion **4** does in the 6-oxophenalenoxyl system [5]. This difference is attributable to the difference of the electronic structure of the ion pair(s), which are governed by negative charge distribution depending on the positions of two oxygen atoms [10]. The decrease in the signal intensities of **3** was not observed for a few months at room temperature in sealed tube, being indicative of the high stability in degassed solution.

To assign the hfccs used for the spectral simulation, the π-spin density of the radical dianion **3** was calculated by using Gaussian 98 with the UBLYP/6-31G**//UBLYP/6-31G** methods (Fig. 2), in which two *tert*-butyl groups of **3** were replaced with hydrogen atoms. On the basis of these calculations, the assignment of the hfccs was made, and the result was summarized in Table 1. Agreement between the experimental and theoretical values is satisfactory. These results indicate that the reduction of 3-hydroxyphenalenone derivatives **5** by potassium mirror gives the corresponding radical dianion **3** as a single paramagnetic species, while the structure and equilibration nature of the ion pair(s) are uncertain. Our ESR/ENDOR/TRIPLE measurements and calculations confirmed that the topological symmetry of the π-electron network in the radical dianion system is in contrast with that of the neutral radical system [11]. This result demonstrates that the 3-oxophenalenoxyl system has the redox-based spin diversity nature similar to the 6-oxophenalenoxyl system.

2.3. Valence bond approach in terms of the MO calculation

To understand electronic structure of the ion pair(s) and π-electronic network of these radical dianion **3**, the clarification of the interplay between the highly delocalized nature of the unpaired electron and charge fluctuation is an essential issue. However, it seems to

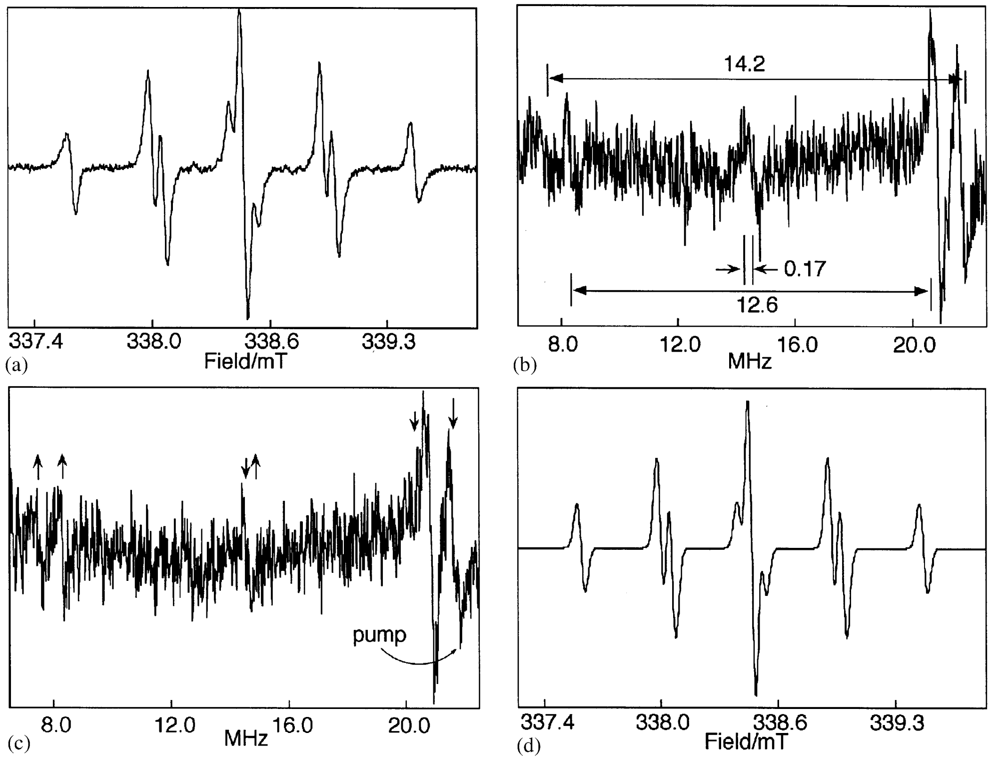


Fig. 1. Hyperfine ESR spectrum (a), ^{1}H ENDOR (b), and ^{1}H TRIPLE spectra (c; pump frequency, 21.6 MHz) observed for **3** in diglyme (1×10^{-3} M) at 295 K; microwave frequency used was 9.5156215 GHz, and a simulated ESR spectrum (d).

be difficult to evaluate them experimentally and theoretically in terms of MO calculations alone. Thus, we have calculated contributing weights of any possible resonance structures based on the VB method in terms of Hückel-MO calculations, utilizing classical canonical resonance structures in a more quantitative fashion [12]. We have already shown the spin delocalization nature in 6-oxophenalenoxyl neutral radical system by this method [4b]. The resonance structures of the radical dianion in 3-oxophenalenoxyl system with the contributing weights calculated by the same method are shown in Fig. 3. The resonance structures α–δ which keep the naphthalene moiety in the phenalenyl skeletons show the important contributions, whereas ε and ζ show relatively small contributions due to the breaking of the naphthalene rings [13]. It is intriguing that the structure with one negative charge on an oxygen atom and the other on a carbon atom in the phenalenyl skeleton shows the most important contribution. The charge fluctuation of the radical dianion in this system has been calculated in terms of DFT by UBLYP/6-31G**//UBLYP/6-31G** method. Fig. 4 shows that the negative charges lie dominantly on the oxygen atoms, but appreciable amounts of the negative charge are found on the phenalenyl skeletons in the 3-oxophenalenoxyl system. This result is harmony with the result of the VB calculation, indicating that the negative charges are delocalized on the phenalenyl skeleton as well as oxygen atoms similar to the spin density.

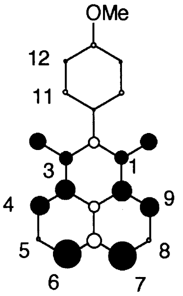


Fig. 2. π-spin density distribution of **3** (unsubstituted at 5- and 8-positions) calculated by UBLYP/6-31G**//UBLYP/6-31G**. Vacant and filled circles denote negative and positive π-spin density.

Table 1
Observed and calculated hfccs of proton and potassium cation for **3**

A (mT)			*T* (K)	*g*-Value
H(4, 9)	H(6, 7)	H(11)		
−0.505[a]	−0.450[a]	+0.006[a]	295	2.0034
−0.505[b]	−0.255[b]	+0.011[b]		

[a] The hfccs were determined by ^{1}H ENDOR spectra in a diglyme solution at 295 K. The relative signs of hfccs were determined in terms of ^{1}H TRIPLE spectroscopy.

[b] These hfccs were calculated for **3** by using Gaussian 98 with UBLYP/6-31G**//UBLYP/6-31G** method with help of McConnell's equation ($Q = -2.35$ mT).

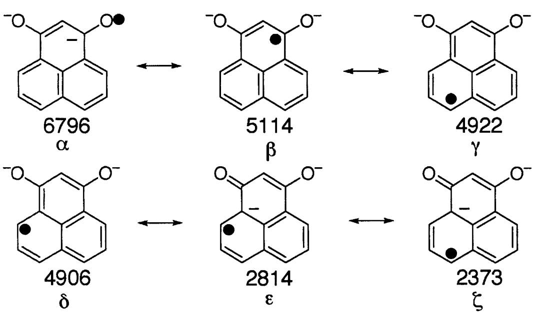


Fig. 3. Resonance structures and their relative contributing weights of the radical dianions in the 3-oxophenalenoxyl system calculated by the VB method in terms of Hückel-MO calculations ($\alpha_{C-O} = 1.5\ \beta$, $\alpha_O = \alpha + 1.0\ \beta$, $\alpha_{C(C-O)} = \alpha + 0.2\ \beta$).

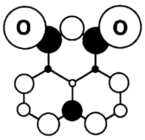


Fig. 4. Charge fluctuation of the radical dianion in 3-oxophenalenoxyl system calculated by UBLYP/6-31G**//UBLYP/6-31G**. Vacant and filled circles denote negative and positive charge.

3. Conclusion

Our ESR/ENDOR/TRIPLE measurements and DFT calculation have demonstrated that the π-spin structure of the radical dianion **3** are in remarkable contrast with that of the corresponding neutral radical system [11], indicating that the 3-oxophenalenoxyl system is another example of the redox-based spin diversity systems similar to the 6-oxophenalenoxyl one [5]. In addition, the relationship between spin and charge was evaluated by both the VB method in terms of the MO calculations and the DFT calculation, demonstrating that the negative charges are delocalized on the phenalenyl skeleton similar to the spin density.

This study serves for the realization of new magnetic materials with interesting functionalities such as the molecular magnets controlled by externally injected electrons and the organic molecular battery by excess electrons.

4. Experimental

DFT calculations were made using Gaussian 98 [14]. 3,6-Di-*tert*-butyl-1,8-naphthalic anhydride (**8**) was synthesized from acenaphthene (**6**) according to the literature procedures [8]. ^{1}H NMR spectra were recorded at 270 MHz with $CDCl_3$ as solvent and Me_4Si or residual solvent as an internal standard. Infrared spectra were recorded using KBr plates. EI-MS spectra were recorded at 70 eV. Melting points were measured with a hot-stage apparatus and are uncorrected. Elemental analyses were performed at the Analytical center of Graduate School of Science, Osaka University. The liquid-phase ESR, ENDOR, and ^{1}H TRIPLE spectra were recorded on Bruker ESR/ENDOR spectrometers ESP 300/350. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots became clearly visible. Silica gel 60 (100–200 mesh) was used for column chromatography. Deactivated silica gel was prepared by mixing with 6% water. Diglyme was distilled over lithium aluminum hydride followed by distilling over Na–K alloy. The cell **A** and the tube **B** were used for the generation of radical dianion (Fig. 5).

*4.1. Synthesis of 2,5-di-tert-butyl-3-hydroxy-2-(4′-methoxyphenyl)phenalenone (**5**)*

A naphthalic anhydride **8** (1.0 g, 3.2 mmol), 4-methoxyphenylacetic acid (536 mg, 3.2 mmol) and anhydrous sodium acetate (26 mg, 0.32 mmol) were placed in a 50-ml Schlenk tube and stirred at 220 °C for 6 h. This reaction mixture was cooled to room temperature and directly subjected to silica gel column chromatography with a 10:1–5:1 mixture of hexane and ethyl acetate as eluent, to give 3-hydroxyphenalenone derivative **5** (480 mg, 36%) as a orange powder: m.p.: 120–124 °C; $R_f = 0.38$ (hexane:ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$) δ 8.67 (d, $J = 2.0$ Hz, 1), 8.35 (d, $J = 1.8$ Hz, 1), 8.10 (d, $J = 2.0$ Hz, 1), 8.01 (d, $J = 1.8$ Hz, 1), 7.37 (dd,

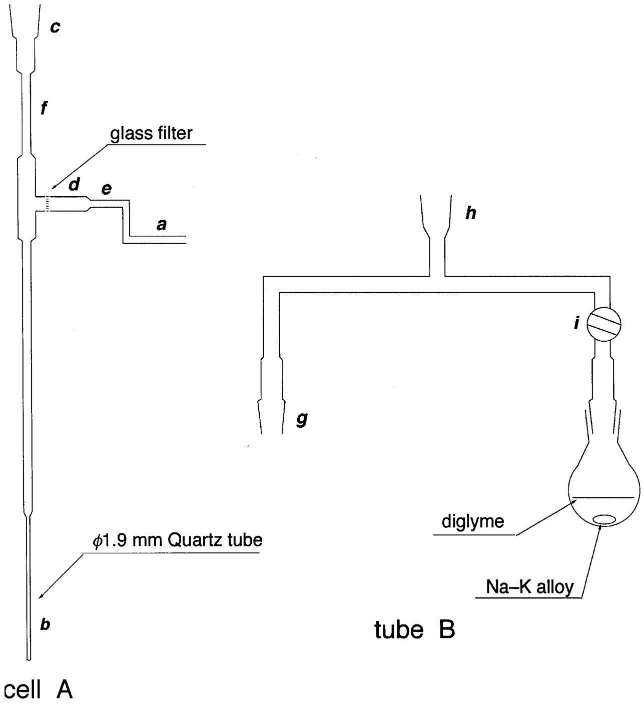


Fig. 5. The apparatus for the generation of the radical dianion.

$J = 13.4$, 2.1 Hz, 2), 7.08 (dd, $J = 13.4$, 2.1 Hz, 2), 6.14 (s, 1), 3.88 (s, 3), 1.49 (s, 9), 1.47 (s, 9); EI-MS *m/z* 414 (M^+, 100%), 399 (M^+—CH_3); IR (KBr) 2965, 1579 cm^{-1}; *Anal.* Calc. for $C_{28}H_{30}0_3$: C, 81.13; H, 7.30; N, 0.00. Found; C, 80.49; H, 7.15; N, 0.00.

*4.2. Generation of dipotassium 5,8-di-tert-butyl-2-(4′-methoxyphenyl)phenalenyl-1,3-bis(olate) (**3**)*

A piece of sodium was settled into the side arm ***e*** and sealed at ***a***. 3-Hydroxyphenalenone derivative **6** (0.2 mg, 5.0×10^{-4} mmol) was introduced into the cell ***b***. The cell **A** was connected at ***c*** with ***g*** of the tube **B** which was connected to a vacuum line at ***h***. Diglyme (0.5 ml) was introduced into the cell **A** by vacuum distillation. The solvent was degassed by a repeated freeze-pump-thaw method (3 times). The side arm was heated with a luminous flame to distill the potassium as a mirror onto the walls at ***d***. This side arm was removed by sealing at ***e***. Finally, the cell **A** was sealed at ***f***. The contact of the solution with a potassium mirror at ***d*** at room temperature for 3 min gave the radical dianion **3**.

5. Supplementary material

The material is available from the authors on request.

Acknowledgements

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