Pergamon

Tetrahedron Letters 42 (2001) 7991–7995

TETRAHEDRON LETTERS

6-Oxophenalenoxyl derivatives covalently linked to TTF moieties: synthesis, ESR/ENDOR measurements, and DFT calculations†

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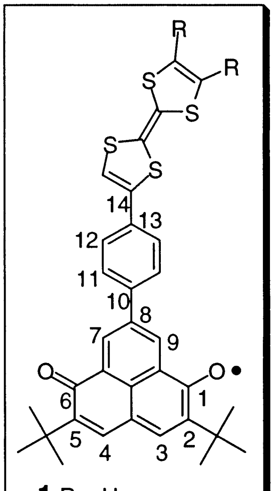
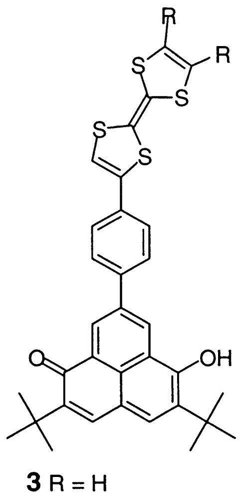
Received 25 June 2001; revised 17 August 2001; accepted 21 August 2001

Abstract—The efficient synthesis, characterization, and electronic properties of new 6-oxophenalenoxyls covalently linked to TTF moieties are described in terms of Stille-coupling reactions, ESR/^{1}H-ENDOR techniques, and DFT calculations. © 2001 Elsevier Science Ltd. All rights reserved.

The importance of organic neutral radicals, such as a triarylmethyl, nitroxide, phenoxyl, and conjugated multi-heteroatom radicals, has been growing in the field of organic-based magnetic materials as spin sources.[1,2] Recently, introduction of an electron-donor site (e.g. TTF) or an electron-withdrawing site (e.g. benzoquinone) into organic radicals has opened new possibilities for the realization of ferromagnetic-conducting organic materials by the use of charge-transfer interactions combined with effective spin alignment.[3] For the past decade, our theoretical examinations by ab initio molecular orbital calculations have suggested the importance of intramolecular magnetic interactions within component radical ions as well as intermolecular and interchain magnetic interactions.[4] Our recent efforts to acquire new stable neutral radicals based on an oxophenalenoxyl system[5] have enabled us to design and synthesize new derivatives with an electron-donor site, i.e. 6-oxophenalenoxyls having a tetrathiafulvalene (TTF) or an ethylenedithio–TTF (EDT–TTF) moiety, **1** and **2**. This paper deals with the synthesis and characterization of their spin structure.



1 R = H
2 R—R = S(CH$_2$)$_2$S



3 R = H
4 R—R = S(CH$_2$)$_2$S

The radical precursors, **3** and **4**, were prepared from the dimethoxyformylnaphthalene derivative **5**[5c] in seven steps or from the 8-(iodophenyl)-6-hydroxyphenalenone derivative **13** in a more convergent fashion (Scheme 1). The aldol reaction of the aldehyde **5** with zinc enolates generated from iodophenyl-substituted ethyl acetate with lithium diisopropylamide (LDA) followed by the addition of zinc chloride proceeded quantitatively. The

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Keywords: neutral radicals; organic-based magnetic materials; 6-oxophenalenoxyl; ^{1}H-ENDOR/TRIPLE spectroscopies; DFT calculations.

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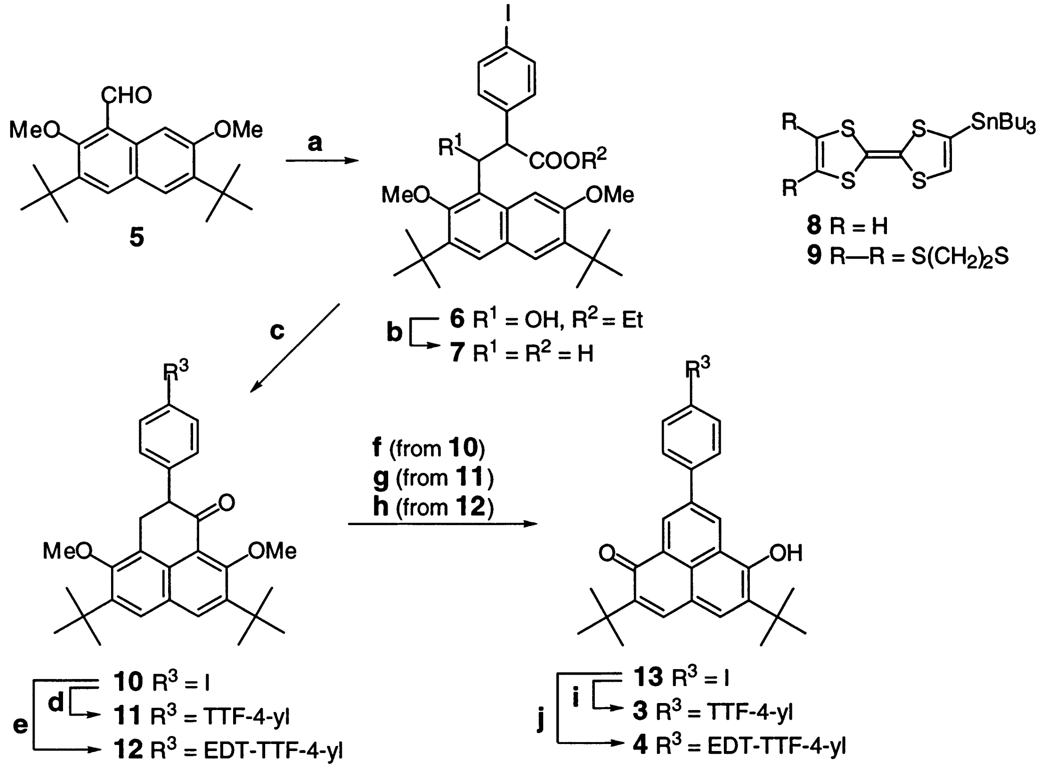
† This paper is dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

PII: S0040-4039(01)01564-7



Scheme 1. *Reagents and conditions*: (a) 2.0 equiv. LDA–$ZnCl_2$–4-I-$C_6H_4CH_2COOEt$, THF, −78°C, 96%; (b) (i) 1.5 equiv. Et_3SiH, 4.5 equiv. CF_3COOH, CH_2Cl_2, rt; (ii) 9.3 equiv. KOH, EtOH–H_2O, 100°C, 76%; (c) (i) excess $(COCl)_2$, 65°C; (ii) 3.5 equiv. $AlCl_3$, CH_2Cl_2, −78°C, 77%; (d) 12 mol% $Pd(PPh_3)_4$, **8**, toluene, 120°C, 63%; (e) 12 mol% $Pd(PPh_3)_4$, **9**, toluene, 120°C, 36%; (f) (i) 20 equiv. $NaBH_4$, EtOH, rt; (ii) 40 equiv. LiI, *N*,*N*-dimethylacetamide, 170°C; (iii) 5% aq. $NaHSO_3$, rt, 85%; (g) (i) 5.7 equiv. $LiAlH_4$, THF, rt; (ii) 20 equiv. LiI, HMPA, 170°C; (iii) pH 7.0 phosphate buffer solution, rt, 53%; (h) (i) 73 equiv. $NaBH_4$, EtOH, rt; (ii) 50 equiv. LiI, *N*,*N*-dimethylacetamide, 170°C, (iii) pH 7.0 phosphate buffer solution, rt, 76%; (i) (i) NaOMe, THF, rt; (ii) concentration in vacuo at rt; (iii) 2 mol% $Pd(PPh_3)_4$, 10 mol% CuI, **8**, THF, 80°C, 90%; (j) (i) NaOMe, THF, rt; (ii) concentration in vacuo at rt; (iii) 10 mol% $Pd(PPh_3)_4$, 49 mol% CuI, **9**, THF, 80°C, 33%.

aldol product **6** was converted to the phenalanone derivative **10** by reductive removal of the hydroxyl group, de-esterification, and cyclization by Friedel–Crafts reaction. TTF or EDT–TTF was introduced into **10** by the Stille reaction using tributyltin derivatives **8** or **9** in the presence of $Pd(PPh_3)_4$. Reduction and demethylation of the coupling products **11** and **12** afforded the desired 6-hydroxyphenalenone derivatives **3** and **4** as reddish–orange powders.[6] Alternatively, in order to open up a more convergent way to the radical precursors **3** and **4**, we designed a direct coupling reaction between iodophenyl-substituted 6-hydroxyphenalenone derivative **13** and **8** (or **9**). Under the above-mentioned coupling conditions, the reaction of **13** with **8** gave **3** in less than 10% yield. After extensive efforts we found the key element for the coupling reaction lay in the conversion of the hydroxyl group into the corresponding anion and addition of a copper salt; thus, the reaction of the sodium salt of **13** and **8** (or **9**) in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI in THF gave the desired coupling product **3** (or **4**) effectively. The electronic spectrum of **3** (or **4**) measured as a CH_2Cl_2 solution gave a superposition of spectra from 8-phenyl-6-hydroxyphenalenone[7] and TTF (or EDT–TTF), indicating weak intramolecular interaction between 6-hydroxyphenalenone and the TTF moieties.

The radicals **1** and **2** were obtained as dark-green solids by treatment of the corresponding hydroxyl compounds **3** and **4** with a large excess of active PbO_2[8] in benzene at room temperature in quantitative yields.[9] The two radicals are stable in the crystal form in the absence of atmospheric oxygen. Under an air atmosphere, these radicals decompose slowly in the solid state, but most of the radical remains unchanged for a few days. Both radicals are stable for a long period of time in degassed toluene, but decompose under an air atmosphere.[10] Fig. 1 shows well-resolved hyperfine ESR spectra (**a**) observed for **1** and **2** in degassed toluene, and the simulated ones (**d**). The spectral simulations were made based on a set of isotropic hyperfine coupling constants (hfcc's) obtained by ^{1}H-ENDOR/TRIPLE spectroscopies (Figs. 1**b** and **c**). The relative signs of the hfcc's were determined by invoking ^{1}H-TRIPLE resonance measurements. The spin Hamiltonian parameters and proton assignments for **1** and **2** are summarized in Table 1. Theoretically calculated values for the hfcc's in Table 1 were made in terms of the McLachlan method.[11] Agreement between the experimental and theoretical values is satisfactory. These results show that the unpaired electron is mainly delocalized on the 6-oxophenalenoxyl skeleton, but significant delocalization into the phenylene moiety was also demonstrated.

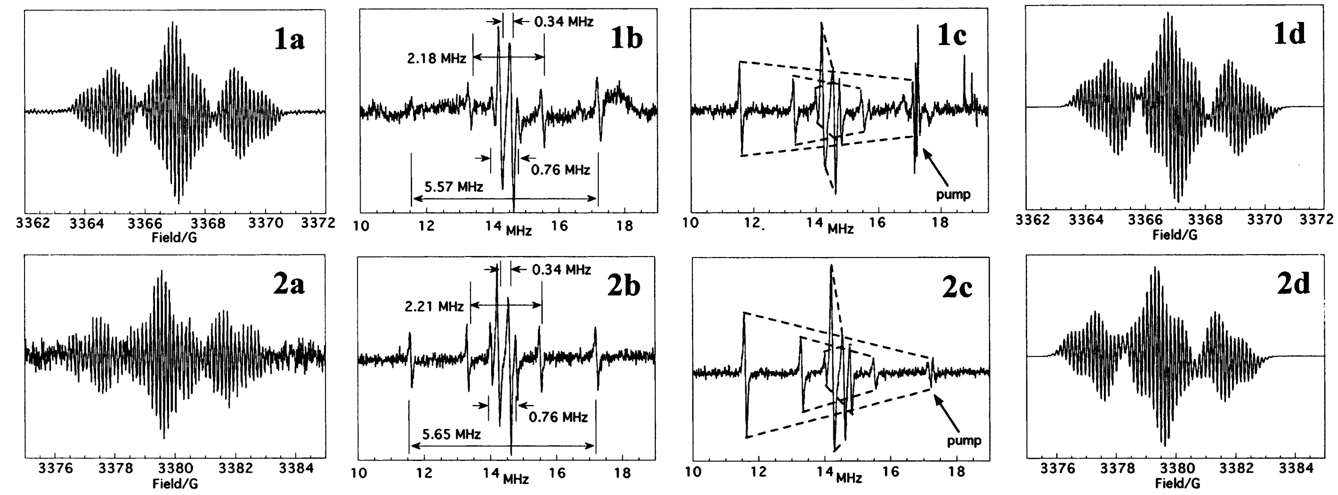


Figure 1. Hyperfine ESR (**1a**, 290 K; **2a**, 288 K), ENDOR (**1b** and **2b**, 260 K), and ^{1}H-TRIPLE spectra (**1c** and **2c**, 260 K) observed for **1** in toluene (3.6×10^{-5} M) and **2** in toluene (3.0×10^{-4} M) at the indicated temperatures; microwave frequency used was 9.448005 GHz (for **1**) and 9.483965 GHz (for **2**), and simulated ESR spectrum (**1d** and **2d**). In spectra **1c** and **2c**, the arrows designate the pump frequencies (17.22 MHz for **1**; 17.23 MHz for **2**) and the dashed lines represent the TRIPLE effects appearing in the pairs of ENDOR signals.

Table 1. Proton hfcc's and *g*-values for **1** and **2**

Compound	A_H/mT[a]				*g*-Value
	3, 4	7, 9	2, 5-*t*-Bu	11	
1	+0.201	+0.078	+0.013	−0.026	2.0043
	(+0.210)	(+0.076)			
2	+0.201	+0.079	+0.012	−0.026	2.0045
	(+0.210)	(+0.076)			

[a] Hfcc's were determined by ^{1}H-ENDOR spectra in toluene at 260 K and simulation successfully reproducing the ESR hyperfine spectra. The relative signs of the hfcc's were determined in terms of ^{1}H-TRIPLE spectroscopy. Values in parenthesis were calculated by the HMO–McLachlan method[11] using the following parameters: $\lambda=1.2$, $Q=-2.6$ mT.

If one oxidation state from the TTF donor group with suitable counter ions is realized, relatively strong intramolecular spin interactions between the neutral radical and the donor radical cation due to a spin polarization effect through the π-electron network can be expected. We carried out the theoretical studies based on ab initio molecular orbital and density functional theories to evaluate the magnetic interaction. We at first assumed the structure to be planar for molecule **1**. The evaluated effective exchange integrals between the two radical sites were found to be −153.75 and −64.50 cm^{-1} by using UHF (ab initio MO) and UB3LYP/6-31G (DFT) methods, respectively. Both calculated results imply that antiferromagnetic interaction is feasible. Next, the conformational effect around the single bond between the phenylene and TTF groups (C13–C14), caused by different dihedral angles, was investigated. The magnetic interactions evaluated by the UB3LYP/6-31G method were −44.21, −12.16 and 2.22 cm^{-1} for 30, 60 and 90°, respectively. Interestingly, for the perpendicular structure a small ferromagnetic interaction was induced. It is important for the evaluation of the magnetic interaction to take SOMO–SOMO interactions into account.[3d,3f,4c] We emphasize also the considerations in terms of the spin density distributions. Fig. 2 shows the spin densities of the diradical cation evaluated by UB3LYP/6-31G for singlet and triplet states corresponding to the planar (**A**) and perpendicular structures (**B**), respectively. It is noteworthy that the feasible local ferromagnetic coupling on C13 and C14 carbon atoms due to the same sign of spin densities on two carbon atoms in Fig. 2**B** contributes greatly to the whole ferromagnetic interaction of the two radical sites, while the whole antiferromagnetic interaction seen in Fig. 2**A** is found to arise from the different sign of the π-spin densities on C13 and C14. It is demonstrated that the induced spin densities around the rotation axis is essential for intramolecular magnetic interactions.[12]

The oxidation potentials measured by cyclic voltammetry (CV) on the anion salts, $\mathbf{3}^{-}\cdot(\mathrm{Et_4N^+})$[13] and $\mathbf{4}^{-}\cdot(\mathrm{Et_4N^+})$,[13] were found to be −0.23, −0.04, +0.19 V and −0.24, +0.06, +0.24 V, respectively.[14] These three reversible cyclic voltammograms are attributable to the one-electron oxidation from the anions of 6-hydroxyphenalenone moieties, the first and second oxidations of TTF and EDT–TTF moieties, respectively.[15] These observations suggest sufficient donor ability of **1** and **2** to form CT complexes with appropriate acceptors. Actually, some CT complexes were obtained both from

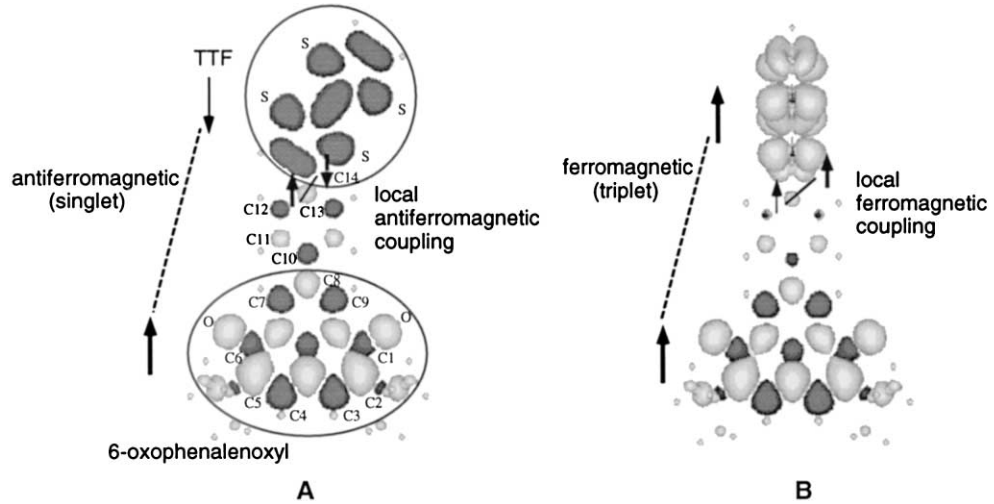


Figure 2. Spin densities of the diradical cation generated by one-electron oxidation from **1** evaluated by the UB3LYP/6-31G method for singlet and triplet states for the planar (**A**) and perpendicular (**B**) structures. White and black regions denote α and β spin densities, respectively, with a cut-off of 0.001.

3 and **4** with DDQ and F_4-TCNQ. Physical properties of these CT complexes will be reported in due course.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research on Priority Area 'Delocalized π-Electronic Systems' (No. 297) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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6. Selected physical and spectral data. Compound **3**: reddish–orange powder; mp 175°C; TLC $R_f=0.34$ (5:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.53 (s, 18), 6.35 (s, 2), 6.55 (s, 1), 7.39 (d, 2, $J=8.4$ Hz), 7.62 (d, 2, $J=8.4$ Hz), 7.63 (s, 2), 8.67 (s, 2); IR (KBr): 3600–3100, 2953, 1560 cm^{-1}; IR (CCl_2CCl_2): 3630, 2958, 1744 cm^{-1}; EI-MS, *m/z* 586 (M^+, 100%); FAB-MS, *m/z* 586 (M^+). Anal. calcd for $C_{33}H_{30}O_2S_4(H_2O)_{0.4}$: C, 66.72; H, 5.23; N, 0.00. Found: C, 66.99; H, 5.65; N, 0.00%. Compound **4**: orange powder; mp 143–144°C; TLC $R_f=0.54$ (CH_2Cl_2); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.56 (brs, 18), 3.32 (s, 4), 6.1–6.5 (br, 1), 7.3–7.4 (m, 2), 7.4–7.6 (m, 2), 7.6–7.8 (m, 2), 8.5–9.0 (br, 2); IR (KBr): 3600–3100, 2957, 1569 cm^{-1}; IR (CCl_2CCl_2): 3626, 2958, 1645 cm^{-1}; FAB-MS, *m/z* 676 (M^+). Anal. calcd for $C_{35}H_{32}O_2S_6(H_2O)_{0.5}$: C, 61.28; H, 4.85; N, 0.00. Found: C, 61.21; H, 4.77; N, 0.00%.
7. The preparation of 8-phenyl-6-hydroxyphenalenone will be reported elsewhere.
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9. Selected physical and spectral data. Compound **1**: dark-green solid; mp 76–78°C; TLC (alumina) $R_f = 0.62$ (3:1 hexane/ethyl acetate); IR (KBr): 2963, 1570 cm^{-1}. Anal. calcd for $C_{33}H_{29}O_2S_4(H_2O)_{0.3}$: C, 67.04; H, 5.05; N, 0.00. Found: C, 66.94; H, 4.88; N, 0.00%. Compound **2**: dark-green solid; mp 215–216°C; TLC (alumina) $R_f = 0.37$ (1:3 hexane/CH_2Cl_2); IR (KBr): 2962, 1592 cm^{-1}. Anal. calcd for $C_{35}H_{31}O_2S_6(H_2O)_{0.6}$: C, 61.21; H, 4.73; N, 0.00. Found: C, 61.25; H, 4.93; N, 0.00%.
10. The radical purity can be estimated by TLC analysis.
11. McLachlan, A. D. *Mol. Phys*. **1960**, *3*, 233–252.
12. Similar remarkable variations in intramolecular magnetic interaction for the rotation angle are also discussed in the case of the TTF–(α-nitronyl nitroxide) model molecule. See Ref. 4c.
13. These anion salts were prepared from **3** and **4** by the treatment of NaOMe and Et_4NCl in THF–MeOH.
14. CV was carried out by the following conditions: 3 mM in DMF with 0.1 M Et_4NClO_4 as supporting electrolyte at room temperature against Fc/Fc^+; Au working electrode and Pt counter electrode; 0.05 V/s.
15. The oxidation potentials of TTF and EDT–TTF under the same conditions were as follows: −0.09, +0.15 V; +0.02, +0.20 V.