

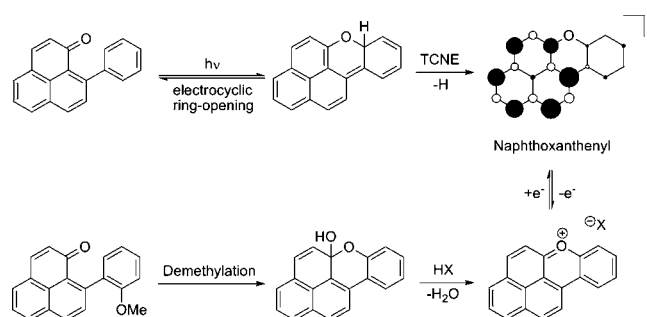
Naphthoxanthenyl, a New Stable Phenalenyl Type Radical Stabilized by Electronic Effects

Ommid Anamimoghadam,[†] Mark D. Symes,[†] Christoph Busche,[†] De-Liang Long,[†] Stuart T. Caldwell,[†] Cristina Flors,^{‡,§} Santi Nonell,[‡] Leroy Cronin,^{*,†} and Götz Bucher^{*,†}

WestCHEM, School of Chemistry, University of Glasgow, Joseph-Black-Building, University Avenue, Glasgow G12 8QQ, United Kingdom, and Grup d'Enginyeria Molecular, Institut Químic de Sarrià, Universitat Ramon Llull, E-08017 Barcelona, Spain
goebu@chem.gla.ac.uk

Received April 22, 2013

ABSTRACT



Naphthoxanthenyl **1** is a new stable phenalenyl-type radical. Electrochemical studies indicate that **1** has two reversible redox processes that occur on comparatively short time scales. Crystals containing **1** can be grown by electrocrystallization, suggesting that they are conductive.

Stable π -conjugated radicals constitute promising building blocks for spin carriers in next generation functional materials involving magnetic systems.^{1–3} Effective radical spin carriers must show high stability and persistence, but for applied aspects, communication between spins must also be possible.⁴ In this regard, delocalized radicals based on phenalenyl (PLY) hold a significant advantage over

both metal ions and nitroxyl radicals, which are currently the most widely used spin carriers.⁵ The ability of PLY to exhibit such metal-like behavior was first suggested by Haddon,⁶ who also pointed out PLY's potential for derivatization and its ability to form stable radicals, cations, and anions with invariant bond orders.

In order to design stable PLY-type radicals, it is necessary to prevent the formation of σ -dimers.⁷ PLY itself undergoes dimerization between the α -positions and subsequent oxidative cyclization to form dibenzoperylene in the solid state.⁸ PLY-type radicals substituted with sterically hindering groups as such as *tert*-butylated PLY form paramagnetic π -dimers that are predicted to show aromaticity between the π -planes.^{9,10} Alternatively, PLY radicals can be stabilized electronically via incorporating

[†] University of Glasgow.

[‡] Universitat Ramon Llull.

[§] Current address: IMDEA Nanociencia, C/Faraday 9, E-28049 Madrid, Spain.

(1) Müllegger, S.; Rashidi, M.; Fattinger, M.; Koch, R. *J. Phys. Chem. C* **2012**, *116*, 22587.

(2) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443.

(3) Kubo, T.; Katada, Y.; Shimizu, A.; Hirao, Y.; Sato, K.; Takui, T.; Uruichi, M.; Yakushi, K.; Haddon, R. C. *J. Am. Chem. Soc.* **2011**, *133*, 14240.

(4) Morita, Y.; Suzuki, S.; Sato, K.; Takui, T. *Nat. Chem.* **2011**, *3*, 197.

(5) Morita, Y.; Nishida, S. Phenalenyls, Cyclopentadienyls, and Other Carbon-Centered Radicals. In *Stable Radicals: Fundamental and Applied Aspects of Odd-Electron Compounds*; Hicks, R. G., Ed.; John Wiley & Sons: Chichester, 2010; p 81.

(6) Haddon, R. C. *Nature* **1975**, *256*, 394.

(7) Reid, D. *Q. Rev. Chem. Soc.* **1965**, *19*, 274.

(8) Small, D.; Rosokha, S. V.; Kochi, J. K.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 11261.

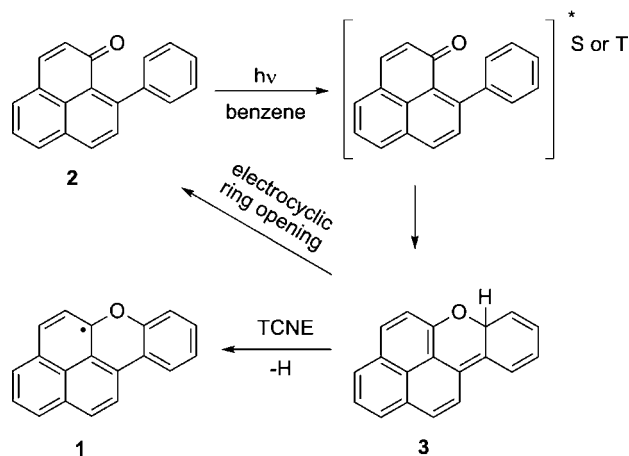
(9) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakushi, K.; Ouyang, J. *J. Am. Chem. Soc.* **1999**, *121*, 1619.

heteroatoms to decrease the spin densities at the α -positions. 1,9-Dithiophenalenyl as well as 1,6,7,9-tetrathio-phenalenyl represent the pioneering and only examples of stable PLY species stabilized solely through electronic effects.^{11,12}

We now wish to report on the synthesis and electrochemical studies of a new radical, naphthoxanthenyl (**1**), which incorporates a PLY core, and is further stabilized via a xanthene substructure. **1** is the first example of a PLY radical that is stabilized solely through the electronic effects of a single oxygen atom and a Clar sextet, and furthermore this stabilization is achieved without the use of any sterically hindering substituents. This makes **1** an excellent candidate for use as a spin carrier in molecular electronics, as it lacks bulky substituents which could inhibit interspin communication.¹³

Radical **1** was synthesized using two different routes. Photolysis of a solution of 9-phenylphenalenone (**2**)¹⁴ in benzene in the presence of tetracyanoethylene (TCNE) yielded **1** (Scheme 1), via transient 1*H*-2-oxa-benzpyrene (**3**)¹⁵ with a weak C(sp³)–H bond (UM05-2X/6-31G(d): BDE_{calcd} = 28.8 kcal mol^{−1}).^{16,17} This is distinctly lower than the C(sp³)–H bond dissociation enthalpy in phenalene (64 kcal mol^{−1}).¹⁸ The intramolecular addition of a triplet ketone to a β -phenyl ring is known as β -phenyl quenching (BPQ).^{19–22} In the absence of added quenchers, intermediate **3** rapidly decays by electrocyclic ring opening, yielding **2**. In the presence of TCNE, the labile C(sp³)-bound hydrogen atom of **3** is transferred to the TCNE molecule, yielding **1**.¹⁵ The formation of **1** was confirmed by ESR spectroscopy (*vide infra*).

Scheme 1. Photochemical Approach to **1** via β -Phenyl Quenching



(10) Suzuki, S.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *J. Am. Chem. Soc.* **2006**, *128*, 2530.

(11) Beer, L.; Mandal, S. K.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. *Cryst. Growth Des.* **2007**, *7*, 802.

(12) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

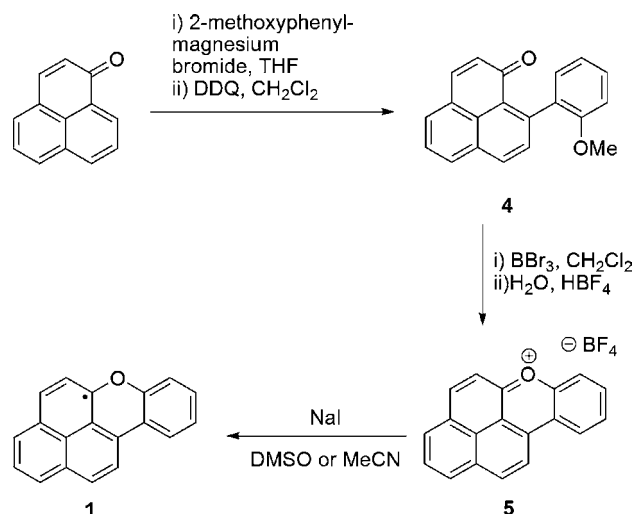
(13) Shun, Z.; Wu, J. *J. Mater. Chem.* **2012**, *22*, 4151.

(14) Quiñones, W.; Escobar, G.; Echeverri, F.; Torres, F.; Rosero, Y.; Arango, V.; Cardona, G.; Gallego, A. *Molecules* **2000**, *5*, 974.

It was also possible to prepare **1** in a four-step synthesis (Scheme 2), starting from phenalene. The well-established Michael-type Grignard addition²³ of 2-methoxyphenylmagnesium bromide to the 9-C position of phenalene, followed by oxidation with DDQ, gave 9-(2-methoxyphenyl)-phenalene (**4**) (X-ray data included in the Supporting Information (SI)). Demethylation of **4** using BBr₃ in dichloromethane resulted in cyclization to naphthoxanthenium bromide. Naphthoxanthenium bromide is very soluble in water and can be isolated through extraction and subsequent precipitation by means of counterion exchange with HBF₄ to yield naphthoxanthenium tetrafluoroborate (**5**) as orange crystals. The yield over four steps was 36%, and the neutral radical could be generated by one-electron reduction of **5**, e.g. using sodium iodide in acetonitrile or DMSO.

Single crystals of **5** were obtained by recrystallization from acetone (see SI). The X-ray analysis indicates interplanar distances between 3.294 and 3.372 Å, indicating a π -stacked structure with considerable interaction between the π -planes (see SI).

Scheme 2. Synthesis of **5** and Reduction to **1**



Solutions of **5** in acetone or acetonitrile are easily reduced by adding NaI, yielding brown-greenish solutions

(15) The transient species derived from the photolysis of **2** has been previously ascribed to an intramolecular charge transfer intermediate (Flors, C.; Ogilby, P. R.; Luis, J. G.; Grillo, T. A.; Izquierdo, L. R.; Gentili, P. L.; Bussotti, L.; Nonell, S. *Photochem. Photobiol.* **2006**, *82*, 95). Our results now suggest that this species in fact is the oxabenzpyrene **3**.

(16) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(18) Bausch, M. J.; Gostowski, R.; Jirka, G.; Selmarten, D.; Winter, G. *J. Org. Chem.* **1990**, *55*, 5805.

(19) Wismontski-Knittel, T.; Kilp, T. *J. Phys. Chem.* **1984**, *88*, 110.

(20) Samanta, S.; Mishra, B. K.; Pace, T. C. S.; Sathyamurthy, N.; Bohne, C.; Moorthy, J. N. *J. Org. Chem.* **2006**, *71*, 4453.

(21) Bucher, G. *J. Phys. Chem. A* **2008**, *112*, 5411.

(22) Smith, M. J.; Bucher, G. *J. Phys. Chem. A* **2010**, *114*, 10712.

(23) Koelsch, C. F.; Anthes, J. A. *J. Org. Chem.* **1941**, *6*, 558.

containing radical **1**. Upon evaporation of the solvent, a black solid with a bronze luster is obtained. Both the solution and the solid are paramagnetic and ESR active. Figure 1 shows a highly resolved ESR spectrum obtained using DMSO as solvent which shows hyperfine couplings. The signal has a g -value of 2.0027 and a total width of 32 G. The complexity is due to hyperfine coupling with the 11 nonequivalent protons of the NX molecule. However, solutions of **1**, generated either photochemically from **2** or by reduction of **5** with NaI in DMSO, are brown, not green.²⁴ The UV/vis spectrum of a sample of **1** generated by NaI reduction of **5** in DMSO is shown in Figure 2. Cation **5** has a sharp λ_{max} at 457 nm, which is no longer visible in the reduced sample. Instead, λ_{max} values at 372, 395, and 412 nm were detected. Also, moderate absorption is shown between 440 and 520 nm, and low absorption, up to 700 nm.²⁵ Given the absence of bands due to cation **5**, the synthesis of **1** from **5** using NaI appears essentially quantitative.

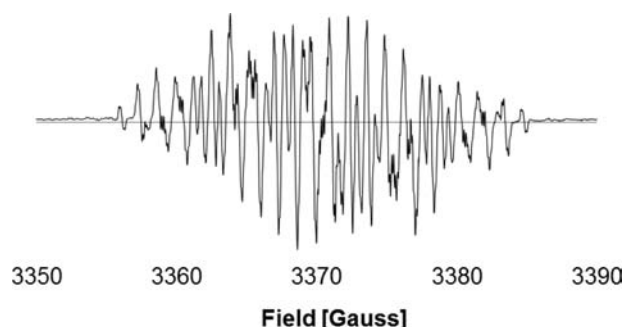


Figure 1. ESR spectrum of **1** in degassed DMSO solution, ambient temperature.

In the solid state, radical **1**, generated by reduction of **5**, is remarkably stable, and the black material can be heated under air to $T = 495$ K (melting point: $T = 422$ K) with an increase of the ESR intensity.²⁶ ESR spectra of solid samples containing **1**, thus generated, do not show hyperfine coupling. The ESR spectrum of **1** obtained by reduction of **5** (shown in Figure 1) and a spectrum obtained by photolysis of **2** in benzene in the presence of TCNE are identical. The ESR spectrum can be approximately simulated using four different hyperfine coupling constants of 5.9 (4H), 2.3 (2H), 1.9 (1H), and 1.5 G (2H), which agree well with predictions from B3LYP/eprII calculations (see SI).^{27,28}

(24) The green color of samples obtained in acetone or acetonitrile is likely due to CT complexes between cation **5** and radical **1**.

(25) We note that no σ -dimer formed from **1** would be expected to absorb at $\lambda = 700$ nm.

(26) This might indicate some formation of dimers in the crystal (π or less likely σ), which for entropic reasons is broken up at high T .

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(28) Barone, V. Structure, Magnetic Properties and Reactivities of Open-Shell Species from Density Functional and Self-Consistent Hybrid Methods. In *Recent Advances in Density Functional Methods: Part I*; Chong, D. P., Ed.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 1996; Vol. 1, p 287.

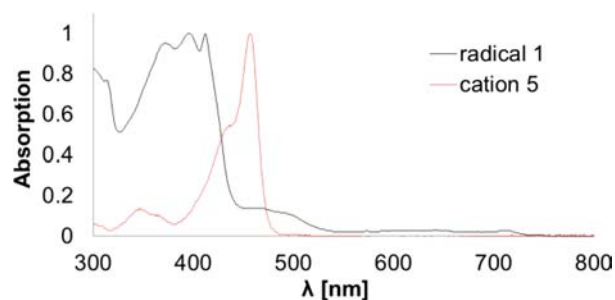


Figure 2. UV/vis spectrum of **1** in DMSO at room temperature showing a complete depletion of **5** after reduction using NaI at 40 °C after 3 h.

Investigation of **5** with cyclic voltammetry (CV) under Ar revealed two reversible reduction/oxidation steps (Figure 3). The potential for the reduction of the cation resulting in the radical was $E_{1/2}(\text{1}) = -0.52$ V, and for the formation of the anion resulting from the reduction of the radical it was $E_{1/2}(\text{2}) = -1.66$ V (all potentials vs the ferrocene/ferrocenium couple, Fc/Fc⁺). For open-shell polyaromatic species, the difference in redox potentials between the cation/radical couple and the radical/anion couple can be taken as a measure of the pairing energy required to place a second electron in the SOMO of the radical. In our case, we find that this value equates to 1.14 V, which is in a range typical for phenalenyl-type radicals.²⁹ Moreover, this magnitude represents an approximation for the on-site Coulombic repulsion energy U , a parameter which is important for molecular conductors in the solid state.³⁰

In contrast to the situation under Ar, when the CV was recorded under an atmosphere of air, the redox wave centered around -0.52 V remained unchanged and fully reversible, but the second reduction at -1.66 V became irreversible and multiple new peaks appeared below -1 V vs ferrocene/ferrocenium. This suggests that (at least on the time scale of the CV) radical **1** is stable under ambient conditions, whereas the corresponding anion is prone to rapid aerial degradation.

The kinetics of the redox processes shown in Figure 3 were probed by examining the scan-rate dependence of CVs of **5** at a Pt microelectrode under an atmosphere of Ar. As the scan rate was increased, the splitting of the anodic and cathodic peak potentials increased only marginally for both reduction processes (cation + electron \rightarrow neutral compound and then neutral compound + electron \rightarrow anion), even at scan rates as high as 2000 V s^{-1} . The resulting “trumpet plots” for these reduction processes (see SI)^{31,32} allowed an electrochemical rate constant, k , to be obtained for both reduction events of **5** by fitting the

(29) Nakasuji, K.; Kubo, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1791.

(30) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12* (3), 79.

(31) Laviron, E. *J. Electroanal. Chem.* **1979**, *101*, 19.

(32) Costentin, C.; Robert, M.; Savéant, J.-M.; Teillout, A.-L. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 11829.

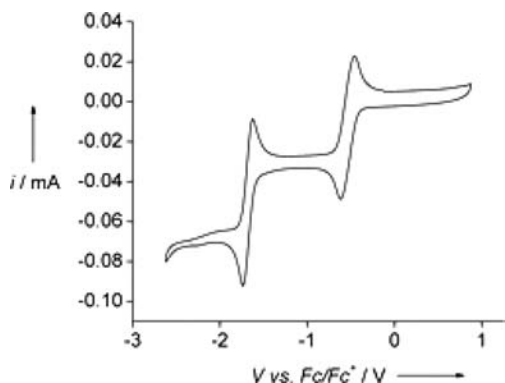


Figure 3. Cyclic voltammogram of **5** at room temperature obtained at a scan rate of 20 mV s^{-1} on a glassy carbon working electrode of area 0.071 cm^2 . Peaks are referenced to the Fc/Fc^+ couple (wave not shown).

experimental values to simulated CVs. Using the experimentally determined diffusion coefficient for **5** ($D_o = (3.7 \pm 0.6) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the radical cation and $D_o = (1.1 \pm 0.1) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the neutral compound, see SI), and assuming a transfer coefficient of $\alpha = 0.5$, values of k were obtained by simulating CVs to produce the curves shown in the SI, which best fit the experimental data points.³³ This analysis yielded a lower limit value of $k \approx 0.3 \text{ cm s}^{-1}$ for the first redox event (at $-0.52 \text{ V vs. Fc}/\text{Fc}^+$) and $k \approx 1 \text{ cm s}^{-1}$ for the second reduction process. The actual rates may in fact be faster than these lower bounds; however, we were unable to scan at faster sweep rates due to uncompensated resistance in the electrochemical cell, which acts to produce an artificial apparent slowing of k .³⁴ These data suggest that electron transfer between both **5** and **1** on the one hand and the electrode on the other is comparatively fast for an organic molecule, at least in part due to extensive charge delocalization which acts to minimize solvent reorganization factors during electron transfer.³⁵ This in turn suggests that, in solution at least, the conversion between **5** and **1** at a Pt electrode is both reversible and rapid.

(33) Symes, M. D.; Surendranath, Y.; Lutterman, D. A.; Nocera, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 5174.

(34) Roullier, L.; Laviron, E. *J. Electroanal. Chem.* **1983**, *157*, 193.

(35) Savéant, J.-M.; Tessier, D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 57.

(36) Batail, P.; Boubekeur, K.; Fourmigué, M.; Gabriel, J.-C. P. *Chem. Mater.* **1998**, *10*, 3005.

Electrocrystallization has proved to be a valuable technique for studying so-called organic metals,³⁶ such as PLY. During the process of electrocrystallization, ordered molecular assemblies are typically formed from mixed valence salts, giving extended crystalline structures that continue to grow on the electrode. Such materials are naturally conductive and could even possess superconductive properties.³⁷ When **5** was taken in an acetonitrile solution of $(\text{NBu}_4)\text{BF}_4$ and subjected to galvanostatic electrolysis, greenish-brown thread-like microcrystalline material was observed growing on the Pt cathode, reminiscent of samples of **1** obtained by chemical reduction of **5** (see SI). The similarity in appearance to **1** and deposition of the material on the cathode suggest that reduction of **5** to a species containing radical **1** is a key step in the formation of these conductive crystals. Hence, although we were unable to obtain crystals of sufficient quality to conduct an X-ray structure analysis, the very fact that compound **5** is amenable to reductive electrocrystallization indicates that conductive assemblies containing **1** can be readily obtained. This bodes well for potential applications for compound **1** and its derivatives in molecular electronics.

In summary, naphthoxanthenyl (**1**) represents the first example of a new class of stable oxygen-functionalized phenalenyl-type free radicals. The synthetic approach detailed herein provides great potential to prepare a plethora of promising analogs or functionalized derivatives of **1** for a variety of potential applications.

Acknowledgment. Part of this research was conducted within the Glasgow Centre for Physical Organic Chemistry in WestCHEM, as funded by EPSRC. Funding by the Spanish Ministerio de Economía y Competitividad (RYC-2011-07637) is acknowledged. We wish to express our gratitude to Micha Kunze and Dr. Chris Kay (University College, London), for pointing out DMSO as solvent for recording the ESR spectrum of **1**. We thank Dr. Dirk Grote (Ruhr-Universität Bochum) for the simulation of the ESR spectrum of **1**.

Supporting Information Available. Available detailed synthetic protocols for the syntheses of **4**, **5**, and **1**; spectroscopic data and crystallographic data for **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(37) Coronado, E.; Day, P. *Chem. Rev.* **2004**, *104*, 5419.

The authors declare no competing financial interest.