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Generation and ESR Spectrum of a Persistent and Oxygen-Insensitive Free Radical. 2,7-Di-*t*-butyl-1-pyrenoxy

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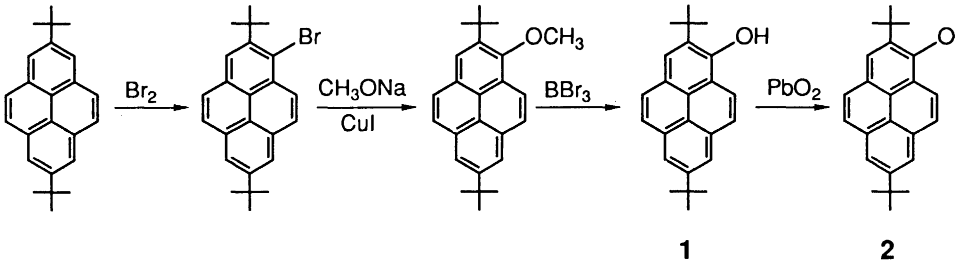
Oxidation of 2,7-di-*t*-butyl-1-hydroxypyrene yields persistent and oxygen-insensitive 2,7-di-*t*-butyl-1-pyrenoxy radical (**2**) with the following ESR parameters: (a_H) 0.532, 0.449, 0.430, 0.389, 0.164, 0.110, and 0.095 mT (a_H), and 2.0037 (g). Radical **2** is isolated as a diamagnetic dimer which, upon dissolution, dissociates into **2** at room temperature. The ΔH and ΔS values for the dimer $\rightleftarrows$ 2 radical equilibrium are determined to be 7.2 ± 2.0 kJ mol^{-1} and -35 ± 15 J mol^{-1} K^{-1}, respectively. The negative ΔS value is briefly discussed.

Radical persistence is a function of electronic stabilization and steric protection. Thus, pertinent combinations of the two factors have sometime produced exceptionally persistent free radicals. Typical examples are 2,2-diphenyl-1-picrylhydrazyl, nitroxides, 2,4,6-tri-*t*-butylphenoxy, and 1,3,5-triarylverdazyls.1) The recent chemistry of stable free radicals is largely stimulated by the suggestion that free radical materials including radical crystals and polymeric polyradicals might be possible ferromagnets.2) However, the development in the organic ferromagnetic chemistry has been seriously limited by the unavailability of stable free radicals having suitable structures and sufficient stabilities for construction of ferromagnetic materials.3) As part of the program directed toward the syntheses of ferromagnetic materials, we have searched for stable free radicals and have found some novel isolable radicals.4) Herein we report the generation and characterization of 2,7-di-*t*-butyl-1-pyrenoxy (**2**), a novel persistent and oxygen-insensitive free radical.

2,7-Di-*t*-butyl-1-hydroxypyrene (**1**) was obtained according to the route shown in Scheme 1. Thus, treatment of 2,7-di-*t*-butylpyrene with a slightly excess of bromine gave 2,7-di-*t*-butyl-1-bromopyrene in 64% yield after column chromatographic separation. The bromopyrene was allowed to react with a large excess of sodium methoxide in the presence of CuI, yielding 2,7-di-*t*-butyl-1-methoxypyrene in 56% yield. Demethylation of 2,7-di-*t*-butyl-1-methoxypyrene using BBr_3 gave **1** in 92% yield.5)

Oxidation of **1** was performed in benzene with PbO_2. When PbO_2 was added to a stirred solution of **1**, the light yellow solution immediately turned dark greenish yellow and gave an intense ESR signal due to **2**. As found in Fig. 1, the ESR spectrum is very complex due to the presence of many unequivalent pyrene ring protons. We therefore analyzed the ESR spectrum with the aids of computer simulation and the following hyperfine splitting (hfs) constants were obtained: a_H (1H) = 0.532, 0.449, 0.430, 0.389, 0.164, 0.110, and 0.095 mT (g = 2.0037).

The UV-visible spectrum of **2** in benzene is illustrated in Fig.2. The spin concentration of this solution was determined to be 1.85 x 10^{-5} mol dm^{-3} by ESR.[6] As found in Fig. 2, radical **2** gives absorption peaks at 412 and 435 nm in the visible region, which correspond to the yellow color of **2** in solution.



1 **2**

Scheme 1.

The McLachlan-Hückel molecular orbital calculations for 1-pyrenoxy radical (**3**) performed using the following parameters: $\alpha_O = \alpha + 0.1\beta$, $\beta_{C1\text{-}O} = 0.9\beta$, and $\lambda = 1.0$ predict that, among the hydrogen - bearing carbons, the positions of high spin densities are C2, C5, C6, C8, and C9, while the positions of low spin densities are C3, C4, C7, and C10. Accordingly, the protons giving large hfs constants (0.532, 0.449, 0.430, and 0.389 mT) are assigned to one of those attached to C5, C6, C8, and C9, respectively, and the protons giving small hfs constants (0.164, 0.110, and 0.095 mT) are assigned to one of those attached to C3, C4, and C10, respectively. Further strict assignments are, however, impossible unless the pyrene ring is partially deuterated.

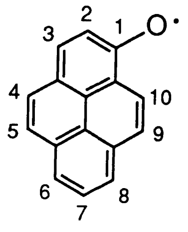
Interestingly, pyrenoxy radical **2** is quite persistent, even in the presence of oxygen. This is shown by a brief kinetic ESR measurement; a solution of **2** (3.20 x 10^{-4} mol dm^{-3}) in benzene was placed in an ESR cell and the intensity of the ESR signal was followed at 20 °C for 5 h, but no reduction in the ESR signal intensity was observed. Furthermore, it was found that the radical showed no decomposition, even after 5 h in refluxing benzene. On the basis of these results it is concluded that the radical is oxygen - insensitive and thermally very stable.

For comparison, a sterically unprotected pyrenoxy radical, **3**, was generated from 1-hydroxypyrene in an analogous manner to that for **2**. In contrast to **2**, the ESR signal due to **3** rapidly decayed during the ESR measurements and the spectrum was not clean owing to the presence of an impurity radical(s).

The noteworthy properties of **2** prompted us to isolate it. A solution of **1** in benzene was treated with PbO_2 in the presence of K_2CO_3. After filtration of the resulting dark green reaction mixture, the benzene was removed by the freeze - drying method and the resulting dark green crystalline powder was crystallized from hexane to give greenish black fine needles with mp 228 - 231 °C in 43% yield. In the IR spectrum no absorption due to the stretching vibration of OH at 3550 cm^{-1} was found. Also, the elemental analysis was in satisfactory agreement with the values calculated as the dimer or radical structure.[7]

Are the crystals isolated composed of radical or dimer ? To ascertain this point, the spin concentrations of the crystals in solid and in solution were determined by the magnetic susceptibility and ESR measurements. The magnetic susceptibility measurements of the solid sample were carried out in the temperature range 77 - 292 K using a magnetic torsion balance and gave the spin concentration of ~4 wt%. On the other hand, the spin concentration of the solution sample was measured by ESR and determined to be 59% of the value estimated by assuming that the crystals consist of radical alone.[8] From the results the crystals isolated were determined to be diamagnetic dimer crystals containing ~4 wt% of radical.

There are many possibilities for the dimer structure. The IR and elemental analyses are, however, helpless for the determination of the dimer structure. Although we have attempted the X-ray crystallographic analysis of the dimer crystal, it is still unsuccessful owing to no availability of sufficiently big crystals suitable for the X-ray crystallographic analysis.



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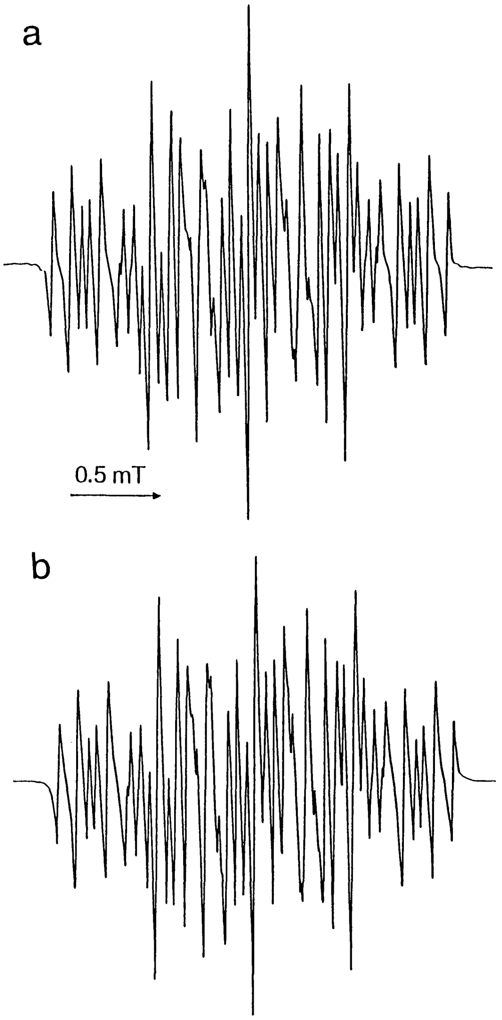

Fig. 1. ESR spectrum of **2** in benzene at 20 °C. (a) Experimental spectrum; (b) computer-simulated spectrum reconstructed using the parameters shown in the text.

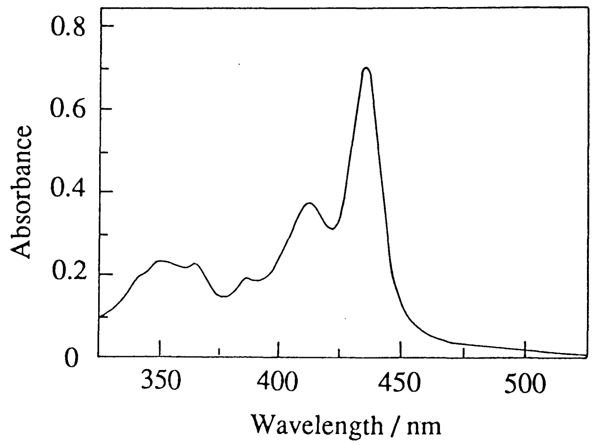

Fig. 2. UV-visible spectrum of **2** in benzene at 23 °C. This solution contains 1.85×10^{-5} mol dm^{-3} of **2** and 0.325×10^{-5} mol dm^{-3} of the dimer.

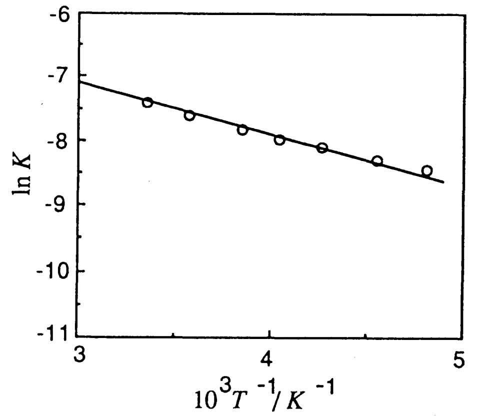

Fig. 3. Plots of ln$K$ vs T^{-1}.

The equilibrium constants (K) for the dimer $\rightleftarrows$ 2 radicals equilibrium were measured in the temperature range 298 - 208 K, using toluene as a solvent. The radical concentrations were determined by ESR. The ln$K$ vs $1/T$ plots are shown in Fig. 3. From the figure, the enthalpy of dissociation (ΔH) and the entropy of dissociation (ΔS) are determined to be 7.2 ± 2.0 kJ mol^{-1} and -35 ± 15 J mol^{-1} K^{-1}, respectively, using Eq. 2, where R is the gas constant and T is the absolute temperature.

$$K = \frac{[\text{radical}]^2}{[\text{dimer}]} \qquad (1)$$

$$\ln K = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \qquad (2)$$

This equilibrium is worth noting because ΔH is very low and ΔS is negative. Similar very low ΔH (~0 kJ mol^{-1}) and negative ΔS values (-74 J mol^{-1} K^{-1}) were found for 1,3,5-benzenetriyltris[di(p-diphenyl)methyl] radical by Kothe *et al.*[9] They termed this kind of bonding "entropy bonding" on the basis of the nearly zero ΔH and negative ΔS values. We assume that the negative entropy value is attributable to greater solvation of the radical molecules as compared with the dimer molecules. Further detailed studies are currently in progress.

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5) Light yellow prisms (from hexane); mp 233 - 235 °C; IR (KBr) 3550 cm^{-1} (OH); ^{1}H NMR (CDCl$_3$) δ 1.40 (s, *t*-Bu, 9H), 1.56 (s, *t*-Bu, 9H), 5.79 (br. s, OH, 1H), 7.7 - 8.3 (br, aromatic, 7H). Found: C, 87.34; H, 8.16%. Calcd for $C_{24}H_{26}O$: C, 87.23; H, 7.93%.

6) This radical solution was obtained by dissolving 0.0229 mmol of the dimer in 104.2 cm^3 (in total volume) of benzene.

7) Found: C, 87.16; H, 7.71%. Calcd for $(C_{24}H_{25}O)_{1\text{ and }2}$: C, 87.49; H, 7.65%.

8) When 15.1 mg of the crystals was dissolved in 104.2 cm^3 (in total volume) of benzene, the resulting solution gave a radical concentration of 2.60 x 10^{-4} mol dm^{-3} at 23 °C.

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