Exceptionally persistent and oxygen-insensitive 2,7-di-*tert*-butylpyren-1-oxyl radical: synthesis, dimerization, EPR and ENDOR spectra

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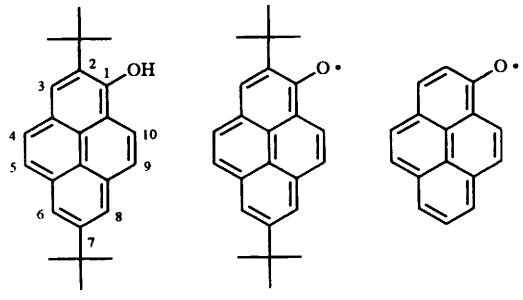
Oxidation of 2,7-di-*tert*-butyl-1-hydroxypyrene 1 yields the exceptionally persistent and oxygen-insensitive 2,7-di-*tert*-butylpyren-1-oxyl radical 2 whose EPR and ENDOR spectra give the following proton hyperfine coupling (hfc) constants: 0.526, 0.445, 0.426, 0.386, 0.157, 0.107, 0.088 and 0.0054 mT (g = 2.0037). The assignments of the protons are accomplished by measuring the EPR and ENDOR spectra of partly deuteriated 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyren-1-oxyl radical. Radical 2 is isolated as a dimer which is in equilibrium with 2 in solution, even at low temperatures. The thermodynamic parameters for the equilibrium are determined to be 7.2 ± 2.0 kJ mol^{-1} (ΔH) and −35 ± 15 J mol^{-1} K^{-1} (ΔS), respectively. The very low ΔH and negative ΔS values are briefly discussed.

Aroxyl radicals are a family of well known oxygen-centred free radicals which have been widely investigated using EPR spectroscopy for a long time.[1] Although non-protected aroxyls are short-lived, appropriate protection of the active sites against homolytic attack drastically changes them to quite persistent species. Examples are typically illustrated by stable aroxyl radicals such as 2,4,6-tri-*tert*-butylphenoxyl,[2] galvinoxyl[3] and their analogues.[4] Recent stable free radical chemistry has been strongly stimulated by the expectation that stable free radical crystals might be organic (molecule-based) ferromagnets since several nitroxides and nitronyl nitroxides, including 2-(*p*-nitrophenyl)nitronyl nitroxide, have been shown to be purely organic ferromagnets at cryogenic temperature.[5] As part of a programme directed towards purely organic magnetism,[6] we have searched for a new class of stable (isolable) free radicals and have found that 2,7-di-*tert*-butylpyren-1-oxyl **2**, one of the aroxyl radical family, is quite persistent, even in the presence of oxygen. As seen from the structure, the aroxyl is electronically stabilized by the large π-pyrene system. Unfortunately, this radical is not monomeric in the solid state, but the dimer isolated has been shown to have a quite low ΔH and negative ΔS values for the dimer ⇌ radical equilibrium. Herein we report the synthesis and EPR/ENDOR spectra of **2**, isolation of the dimer and the ΔH and ΔS values for the equilibrium.



1 **2** **3**

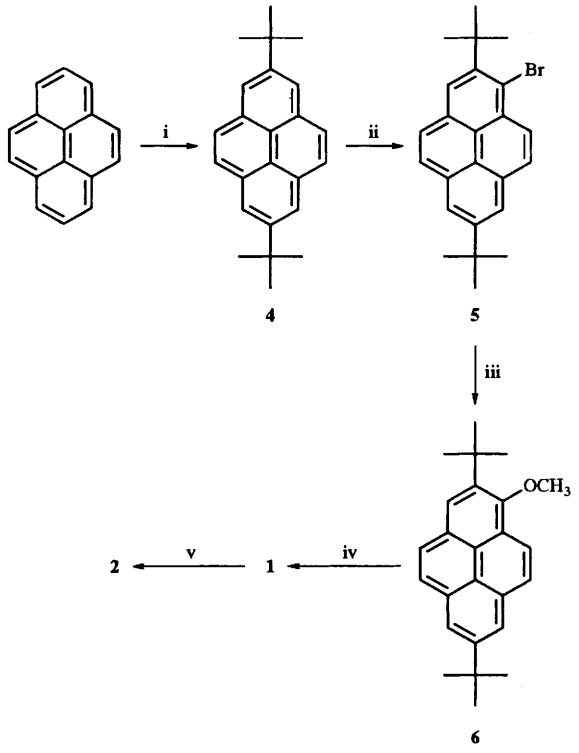
Results and discussion

Preparation of 2,7-di-*tert*-butyl-1-hydroxypyrene 1

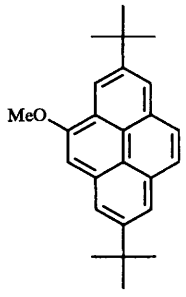
Compound **1** was prepared according to the route shown in Scheme 1. Treatment of 2,7-di-*tert*-butylpyrene with an equivalent amount of Br_2 gave a mixture of at least five products. Repeated chromatography of the mixture gave 2,7-di-*tert*-butyl-1-bromopyrene **5** in 64% yield. The structural determination of **5** was made by ^{1}H NMR spectroscopy. The peaks due to the two *tert*-butyl groups at C-2 and C-7 were observed at 1.57 and 1.79 ppm as a singlet. For the seven aromatic protons, one singlet, two doublets with J = 1.8 Hz and four doublets with J = 9.2 Hz were observed in the low field region. The singlet peak at 8.25 ppm was assigned to the proton at C-3. On the other hand, the four doublet peaks with J = 9.2 Hz at 7.96, 8.03, 8.10 and 8.68 ppm were assigned to the protons at C-4, C-5, C-9 and C-10 and the other two doublet peaks with J = 1.8 Hz were assigned to the protons at C-6 and C-8. On the basis of this unequivocal assignment we could confirm the structure of **5**.

The bromopyrene **5** was then allowed to react with a large excess of MeONa in the presence of CuI. After chromatography, 2,7-di-*tert*-butyl-1-methoxypyrene **6** was separated as a mixture from 2,7-di-*tert*-butyl-4-methoxypyrene **7**. The ^{1}H NMR measurement of the mixture revealed that the molar ratio of **6** to **7** was 92:8. Since the by-product **7** had a very similar polarity, the separation of **6** from the mixture by chromatography was very tedious. Repeated chromatography of the mixture gave pure **6** and **7** in 89 and 7.3% yields, respectively. Compound **7** is an isomer of **6** whose formation requires a cation migration from C-3 to C-4. Demethylation of **6** was performed by treating **6** with BBr_3 at room temperature to give **1** in 92% yield. The ^{1}H and ^{13}C NMR spectra of **1** showed quite broad signals, particularly for the peaks arising from the aromatic protons and carbons due to the presence of a small amount of a paramagnetic species **2**.

Since isolation of pure **5** and **6** from the corresponding reaction mixtures was very tedious owing to the formation of by-products having a very similar polarity, as mentioned above, their isolation procedures were simplified as follows: first, after bromination, the reaction mixture obtained was only chromatographed once and the resultant separated raw product of **5** (*ca.* 80% purity) was subjected to the next reaction, without further purification. However, **6** was separated as a mixture of **6**



Scheme 1 *Reagents and conditions:* i, Bu^{t}Cl, $AlCl_3$, CH_2Cl_2, room temp., 5 h; ii, Br_2, CH_2Cl_2, room temp., 3 h; iii, CH_3ONa, CuI, MeOH–DMF, 80 °C, 18 h; iv, BBr_3, CH_2Cl_2, room temp., 2 h; v, PbO_2, benzene



and **7** in a molar ratio of 92:8 by the first chromatograph. The molar ratio is similar to that obtained with the use of pure **5**. Second, the mixture of **6** and **7** was then subjected to the demethylation reaction, without further purification. However, pure **1** was quite easily separated by the first chromatograph. The total yield of **1** from 2,7-di-*tert*-butylpyrene was 49%, which was similar to that (52%) for the above procedure.

Generation and EPR and ENDOR spectra of 2

Oxidation of **1** was accomplished in benzene using PbO_2 as oxidant. When PbO_2 was added to a stirred light-yellow solution of **1**, the solution immediately turned dark yellowish-green and the resulting coloured solution gave an intense EPR signal due to **2**. The UV–VIS spectrum of **2** showed absorption peaks at 435, 412, 363 and 348 nm (in benzene). As shown in Fig. 1, the EPR spectrum of **2** was very complex owing to the presence of many inequivalent protons. We therefore analysed the EPR spectrum by computer simulation and the proton hyperfine coupling (hfc) constants 0.532, 0.449, 0.430, 0.389, 0.164, 0.110 and 0.095 mT (g = 2.0037) were obtained.

In order to ascertain the hfc constants determined by EPR spectroscopy, ENDOR measurements of **2** were carried out at −90 °C in toluene. As shown in Fig. 2, 200 accumulations with a low frequency modulation depth (50 kHz) gave an ENDOR spectrum with a relatively good signal-to-noise ratio. In the

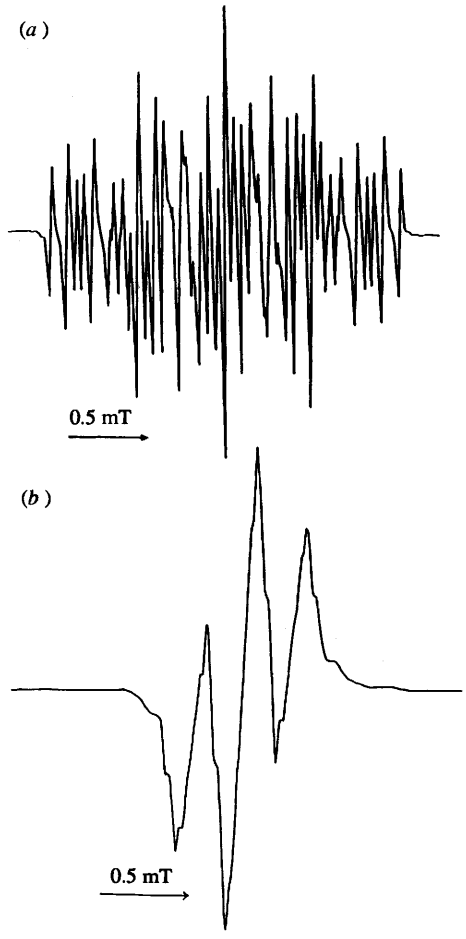


Fig. 1 (*a*) EPR spectrum of **2** in benzene at 20 °C; (*b*) EPR spectrum of **13** in benzene at 20 °C

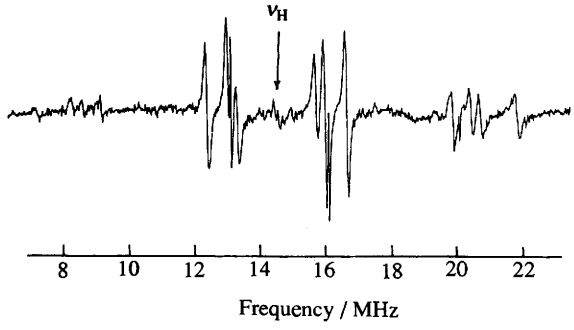


Fig. 2 ENDOR spectrum of **2** in toluene at −90 °C

figure, eight pairs of peaks were observed, which substantiated the hfc constants determined by EPR spectroscopy (see Table 1). The innermost pair of peaks (0.149 MHz, 0.0053 mT) was assigned to the protons of a *tert*-butyl group (probably at C-2).

Spin-density calculation

The spin-density distribution on pyren-1-oxyl radical **3** was calculated by the McLachlan–Hückel and INDO methods. For the McLachlan–Hückel method the following parameters were used: $\alpha_O = \alpha + 0.2\beta$ and $\beta_{C\text{-}1\text{-}O} = 0.9\beta$ (λ = 1.0). Although the INDO calculations gave considerable deviations from the experimental results, the McLachlan–Hückel method yielded a satisfactory agreement with the experiment. The results from the McLachlan–Hückel calculations are listed in Table 2.

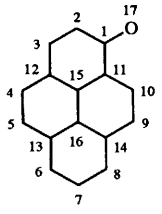
Among the hydrogen-bearing carbons in **2** (C-3–C-6 and C-8–C-10), the positions of high-spin density are C-5, C-6, C-8 and C-9, while the positions of low-spin density are C-3, C-4 and C-10. Accordingly, the protons with a large hfs constant

Table 1 EPR and ENDOR spectral data of 2,7-di-*tert*-butylpyren-1-oxyl **2** and 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyren-1-oxyl **13** radicals

Radical	Method[a]	$a_{3\text{-H}}$/mT	$a_{4\text{-H}}$, $a_{10\text{-H}}$/mT	$a_{5\text{-H}}$, $a_{9\text{-H}}$/mT	$a_{6\text{-H}}$, $a_{8\text{-H}}$/mT	a_H(Bu^t)/mT	g
2	EPR[b]	0.095	0.164, 0.110	0.532, 0.389	0.449, 0.430		2.0037
2	ENDOR[c]	0.088	0.157, 0.107	0.526, 0.386	0.445, 0.426	0.0054	
13	ENDOR[c]	0.088	—	—	0.444, 0.422	0.0053	

[a] The method for determination of the hfc constants. [b] In benzene at 20 °C. The hfc constants are determined by computer simulation. [c] In toluene at −90 °C.

Table 2 Spin density distribution in **3** calculated by the McLachlan–Hückel MO method



Position	Calculated spin density (calculated hfc constant)[a]	Observed hfc constant (a_H/mT)[b]
1	−0.057	—
2	0.169	—
3	−0.065 (0.177)	0.088
4	−0.052 (0.140)	0.157 or 0.107
5	0.159 (−0.430)	0.526 or 0.386
6	0.161 (−0.433)	0.445 or 0.426
7	−0.045 (0.120)	—
8	0.161 (−0.435)	0.445 or 0.426
9	0.161 (−0.434)	0.526 or 0.386
10	−0.044 (0.120)	0.157 or 0.107
11	0.152	—
12	−0.036	—
13	−0.033	—
14	0.159	—
15	−0.036	—
16	0.004	—
17(O)	0.243	

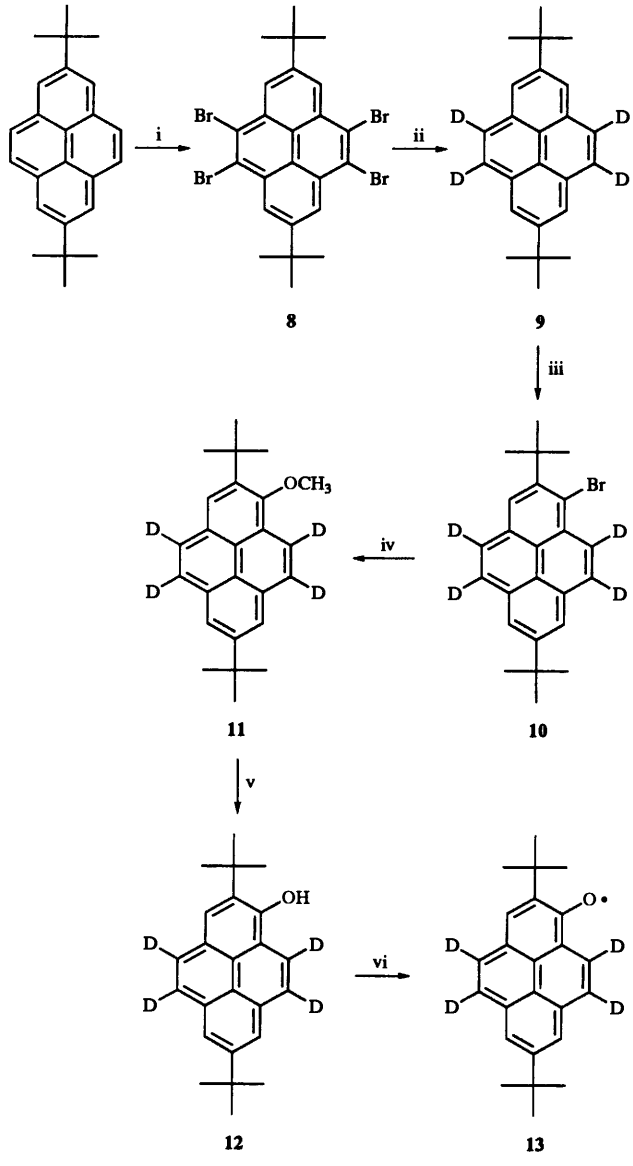
[a] The a_H values are derived using equation $a_H = -2.7\,\rho_c^{\pi}$. [b] The values for **2** determined by ENDOR spectroscopy.

can be assigned to those attached to C-5, C-6, C-7 and C-8, while the protons with a small hfs constant can be assigned to those attached to C-3, C-4 and C-9. Further strict assignments are impossible unless the pyrene ring is partly deuteriated.

Generation of the 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyren-1-oxyl radical 13 and its EPR and ENDOR spectra

We therefore decided to prepare the 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyren-1-oxyl radical **13** as a partly deuteriated 2,7-di-*tert*-butylpyren-1-oxyls, starting from 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyrene **9**[7] (Scheme 2). The synthesis of 2,7-di-*tert*-butyl-1-hydroxy(4,5,9,10-$^2H_4$)pyrene **12** was accomplished by following the procedure for the corresponding non-labelled compounds, except for the demethylation step. When demethylation of **11** was carried out using BBr_3 in the same manner as for **6**, a significant decrease in the isotope purity (68%) of the product was observed. This decrease was ascribable to the acidic conditions in the demethylation reaction. Accordingly, the demethylation was carried out in basic conditions using EtSNa as a demethylation agent,[8] and **12** at 84% isotope purity was obtained in 90% yield. Since this isotope purity is very similar to that (87%) of the starting compound **9**, this result indicates that no significant decrease in the isotope purity takes place in the demethylation step.

The EPR and ENDOR spectra of **13** were recorded using the same experimental conditions as for **2**. The EPR spectrum is shown in Fig. 1 and the ENDOR spectrum in Fig 3. As shown in Fig. 3, the ENDOR spectrum gave four pairs of peaks with hfc constants 0.444, 0.422, 0.088 and 0.0053 mT for the 3-H,



Scheme 2 *Reagents and conditions:* i, Br_2, $FeCl_3$, CCl_4, room temp., 4 h; ii, 4.2% Na/Hg, CH_3OD–benzene, reflux, 4 h; iii, Br_2, CH_2Cl_2, 0 °C, 0.5 h and room temp., 3 h; iv, CH_3ONa, CuI, MeOH–DMF, 80 °C, 18 h; v, EtSNa, DMF, reflux, 3 h; vi, PbO_2, benzene

6-H, 8-H and *tert*-butyl protons, respectively. By using the hfc constants due to the three aromatic protons (0.444, 0.422 and 0.088 mT) and those due to 5-D and 9-D [0.081 (= 0.154 × 0.526 mT) and 0.059 mT (= 0.154 × 0.386 mT)], the experimental EPR spectrum was satisfactorily reconstructed. The small deviations in the wings from the observed spectrum were ascribed to the incomplete deuteriation at the 4, 5, 9 and 10 positions.

Comparison of hfc constants between **2** and **13** allowed assignments of the protons to be made. The MO calculations (Table 2) predict that among C-3–C-6 and C-8–C-10, the four positions of the higher spin densities are C-5, C-6, C-8 and C-9, while the three positions of the low spin densities are C-3, C-9

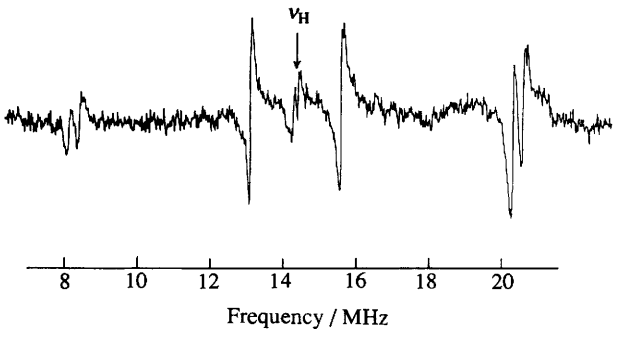


Fig. 3 ENDOR spectrum of **13** in toluene at −90 °C

and C-10. Therefore, we can unequivocally confirm that the hfc constants of 0.532 and 0.389 mT are assigned to 5-H and 9-H, and those of 0.449 and 0.430 mT to 6-H and 8-H. On the other hand, the hfc constant of 0.095 mT can be assigned to 3-H, and those of 0.164 and 0.110 mT to 4-H and 10-H. The results are summarized in Table 1.

Isolation of dimer

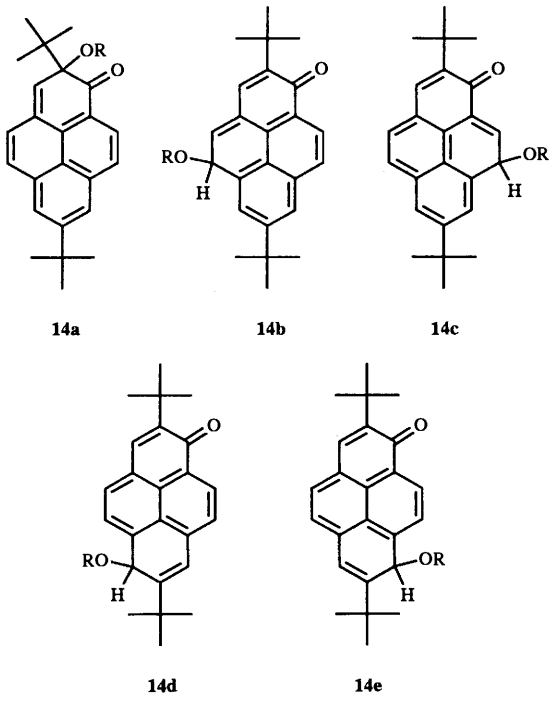
Pyrenoxyl radical **2** is quite persistent, even in the presence of oxygen. This was shown by a simple kinetic experiment. The concentration of the radical in benzene was followed by EPR spectroscopy as a function of time at 20 °C under atmospheric conditions. Although the EPR measurements were continued for 5 h, no reduction in the EPR signal intensity was observed. Furthermore, it was shown that radical **2** was stable, even upon heating at 80 °C for 5 h in benzene under atmospheric conditions.

For comparison, sterically unprotected pyren-1-oxyl radical **3** was generated by PbO_2 oxidation of 1-hydroxypyrene in benzene. In contrast to **2**, this radical was quite unstable and gave a very weak EPR spectrum showing the presence of impurities. Hence, the determination of the hfc constants for **3** was abandoned.

The exceptionally persistent property of **2** prompted us to isolate it. A solution of **1** was treated with PbO_2 in benzene in the presence of K_2CO_3 and the benzene was removed by freeze-drying. The resulting green crystalline powder was crystallized from hexane to give greenish-black fine needles in 58% yield. In the IR spectrum of the isolated compound the peak due to the stretching vibration of O–H completely disappeared (in the IR spectrum of **1** it appeared strongly at 3550 cm^{-1}) and two new strong peaks appeared at 1640 and 1630 cm^{-1}. The new two peaks are typical of those due to dienone (or polyenone). Also, the elemental analysis of the isolated compound gave satisfactory agreements with the values calculated as dimer or radical.

To determine whether the material isolated is monomeric radical or dimer, the spin concentrations were measured for the solid and solution samples. The magnetic susceptibility measurements showed that the spin concentration of the solid sample corresponded to 4% of the value calculated by assuming that the crystals consist of the radical alone. On the other hand, the EPR measurements showed that the spin concentration of the solution sample corresponded to *ca.* 58% of the theoretical value. On the basis of this result we determined that the compound isolated was a dimer containing a small amount (*ca.* 4%) of radical. In the same manner, dimer **15** comprising of **13**, was also prepared by PbO_2 oxidation of **12** in benzene.

As plausible structures for the dimers, **14a–e** are proposed for the dimer from **2** on the basis of the IR results and elemental analyses. The absorption peaks at 1640 and 1630 cm^{-1} in the IR spectrum indicate the presence of dienone (or polyenone). For phenoxyl radicals, the X-ray crystallographic analyses of their corresponding dimers have shown that dimerization takes place at the position *para* or *ortho* to the oxygen.[1,9] This is also taken



14a **14b** **14c** **14d** **14e**

R: 2,7-di-*tert*-butylpyren-1-yl

into account in the drawing of the possible dimer structures. Among the possible five structures **14d** and **14e** may be excluded since there are serious steric repulsions between the RO and neighbouring *tert*-butyl groups. For further reliable structural assignments of the dimer, ^{13}C CP/MAS NMR spectra of **14** were recorded at room temperature. Although the spectra were obtained by 9040 accumulations with a pulse-interval of 4 s, they were quite broad; the peaks at 32.2 and 35.3 ppm could be assigned to the primary and quarternary carbons of the *tert*-butyl groups by comparison with the ^{13}C solution NMR spectrum of **6** and the peak at 182.8 ppm could be assigned to the carbonyl carbon, but the absorptions due to aromatic carbons gave only three broad peaks in the region 121–144 ppm. Therefore, we could confirm the presence of a carbonyl group, but the structure of **14** could not be determined by the ^{13}C CP/MAS NMR spectra. Although effort has been paid to obtain a sufficiently large single crystal suitable for the X-ray crystallographic analysis, all attempts were unsuccessful.

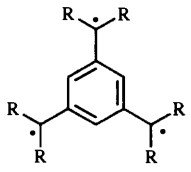
Measurements of equilibrium constants

The equilibrium constants (K) for the dimer $\rightleftharpoons$ 2 radical equilibrium were measured in the temperature range 193–293 K, using toluene as solvent, by the EPR method, and ln K was plotted against $1/T$ (γ = 0.998). From the slope and intercept of the plot the enthalpy of dissociation (ΔH) and the entropy of dissociation (ΔS) were determined from eqn. (2) to be 7.2 ± 2.0 kJ mol^{-1} and −35 ± 15 J K^{-1} mol^{-1}, respectively, where R is the gas constant and T is the absolute temperature.

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

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

Note that ΔH is unusually low and ΔS is negative. The very low ΔH value can be explained as the result of the great electronic stabilization of **2** by the pyrene ring. On the other hand, the negative ΔS is quite strange because the ΔS values for dimer $\rightleftharpoons$ radical equilibria are positive with few exceptions[10,11] because the dissociation is the process yielding two radical molecules from one molecule of dimer. It is obvious that the



16

R: 4-biphenyl

C–O bond in dimer **14** is very weak and much longer than the usual C–O bond on the basis of the very low ΔH value. If considerable solvation of the radical molecules relative to the dimer molecules takes place, the ΔS value will be reduced. However, the negative ΔS value cannot be sufficiently explained only by solvation. We wish to explain the negative ΔS value as follows: because the C–O bond in **14** is loose, **14** can adopt many conformers and this leads to an increase in entropy of **14**. If the increase in entropy is sufficiently large, the ΔS value for the equilibrium will become a negative value. Kothe *et al.* reported a very low ΔH (*ca.* 0 kJ mol^{-1}) value and negative ΔS value (-74 J K^{-1} mol^{-1}) for the equilibrium of 1,3,5-benzenetriyltris[di(*p*-diphenyl)methyl] radical **16**.[10] They termed this kind of bonding 'entropy bonding' on the basis of the nearly zero ΔH and negative ΔS values.

Experimental

All mps were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were run for samples as KBr pellets on a JASCO A-202 spectrophotometer. UV–VIS spectra were measured with a Shimadzu UV-2200 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL α-400 spectrometer (400 MHz) with $SiMe_4$ as internal reference; *J* values are given in Hz. ^{13}C CP/MAS NMR spectra were obtained on a Bruker DSX300 spectrometer with hexamethylbenzene as external reference. Mass spectra were measured with a JEOL JMS-01 SA-2 spectrometer at 75 eV using a direct inlet system. EPR spectra were recorded on a JEOL JES-ME-3X or Bruker ESP 300 spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. Hyperfine splitting constants and *g* values were determined by the simultaneous measurements with Fremy's salt (a_N = 1.309 mT; g = 2.0055) in K_2CO_3 aqueous solution as reference. ^{1}H ENDOR spectra were recorded at -90 °C on a Bruker 300/350 ENDOR spectrometer equipped with a TM_{011} mode microwave cavity operating at X-band.

2,7-Di-*tert*-butylpyrene was obtained by the reported method. 2,7-Di-*tert*-butyl(4,5,9,10-$^2H_4$)pyrene **9** (isotope purity 87%) was prepared by treating 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene with CH_3OD in the presence of 4.2 wt% Na–Hg, according to our previous method.[7] Dry *N*,*N*-dimethylformamide (DMF) was obtained by distillation from CaH_2. Anhydrous MeOH was obtained by distillation from $Mg(OMe)_2$. Column chromatography was performed on silica gel (Waco gel C-200).

Preparation of 2,7-di-*tert*-butyl-1-bromopyrene 5

To a stirred solution of **4** (10.0 g, 31.8 mmol) in CH_2Cl_2 (300 cm^3) was added dropwise at 0 °C over 30 min a solution of bromine (5.1 g, 32 mmol) in CH_2Cl_2 (50 cm^3). After the mixture was stirred for 3 h at room temperature, it was poured into a large amount of 1 mol dm^{-3} NaOH ice–water. The CH_2Cl_2 layer was separated, washed with brine (2 × 100 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the solid residue (13.4 g) was refluxed in hexane (150 cm^3) for 5 min and cooled to room temperature. After the undissolved products were filtered off, the filtrate was evaporated and the residue was repeatedly chromatographed on silica gel with hexane. Recrystallization from EtOH gave pure **5** (8.04 g, 64%) as colourless prisms, mp 162–164 °C; δ_H($CDCl_3$) 1.57 (9 H, s, Bu^t), 1.79 (9 H, s, Bu^t), 7.96 (1 H, d, *J* 9.2, ArH), 8.03 (1 H, d, *J* 9.2, ArH), 8.10 (1 H, d, *J* 9.2, ArH), 8.20 (1 H, d, *J* 1.8, ArH), 8.21 (1 H, d, *J* 1.8, ArH), 8.25 (1 H, s, ArH) and 8.68 (1 H, d, *J* 9.2, ArH) [Found: C, 73.7; H, 6.75 (M$^+$, 392). $C_{24}H_{25}Br$ requires C, 73.28; H, 6.41%].

Preparation of 2,7-di-*tert*-butyl-1-methoxypyrene 6

To a MeONa solution, prepared from absolute MeOH (171 cm^3) and Na (4.3 g), were added dry DMF (171 cm^3), **5** (6.90 g, 17.5 mmol) and CuI (4.0 g, 21.0 mmol). After the resulting mixture was heated at 80 °C for 18 h under nitrogen, it was cooled and poured into a large amount of ice–water to give a powder. The powder collected was dissolved in CH_2Cl_2 (250 cm^3) and the organic layer separated was washed with 1 mol dm^{-3} HCl (150 cm^3) and brine (150 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the solid residue was repeatedly chromatographed on silica gel with 1:3 benzene–hexane to give **6** (5.39 g, 89%) and **7** (0.44 g, 7.3%). Recrystallization from hexane afforded **6** as colourless fine prisms, mp 145–147 °C; δ_H($CDCl_3$) 1.55 (9 H, s, Bu^t), 1.62 (9 H, s, Bu^t), 4.09 (3 H, s, OMe), 7.91 (1 H, d, *J* 9.2, ArH), 7.94 (1 H, d, *J* 9.2, ArH), 8.01 (1 H, d, *J* 9.2, ArH), 8.11 (1 H, s, ArH), 8.13 (1 H, d, *J* 1.8, ArH), 8.14 (1 H, d, *J* 1.8, ArH) and 8.22 (1 H, d, *J* 9.2, ArH); δ_C($CDCl_3$) 31.3, 31.9, 35.2, 35.6, 63.6, 121.7, 121.9, 123.0, 123.7, 124.1, 124.9, 126.2, 127.0, 127.1, 127.3, 130.5, 130.9, 140.2, 148.9 and 154.4 [Found: C, 87.0; H, 8.25 (M$^+$, 344). $C_{25}H_{28}O$ requires C, 87.16; H, 8.19%].

2,7-Di-*tert*-butyl-4-methoxypyrene 7

Recrystallization from hexane–benzene gave colourless prisms, mp 214–216 °C; δ_H($CDCl_3$) 1.56 (9 H, s, Bu^t), 1.58 (9 H, s, Bu^t), 4.20 (3 H, s, OMe), 7.28 (1 H, s, ArH), 7.98 (2 H, s, ArH), 8.03 (1 H, d, *J* 1.8, ArH), 8.09 (1 H, d, *J* 1.8, ArH), 8.19 (1 H, d, *J* 1.8, ArH) and 8.59 (1 H, d, *J* 1.8, ArH) [Found: C, 87.0; H, 8.3 (M$^+$, 344). $C_{25}H_{28}O$ requires C, 87.16; H, 8.19%].

Preparation of 2,7-di-*tert*-butyl-1-hydroxypyrene 1

To a stirred solution of **6** (0.52 g, 1.51 mmol) in CH_2Cl_2 (40 cm^3) was added dropwise, at 0 °C, a solution of BBr_3 (3.8 g, 15 mmol) in CH_2Cl_2 (10 cm^3). After the mixture was stirred at room temperature for 2 h, it was poured into a large amount of ice–water. The organic layer was extracted with CH_2Cl_2 (2 × 50 cm^3) and the combined extract was washed with brine (100 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the solid residue was chromatographed on silica gel with 1:1 benzene–hexane to give **1** (0.46 g, 92%). Recrystallization from hexane afforded **1** as light yellow prisms, mp 231–233 °C; ν_{max}/cm^{-1} 3550 (OH), 2950 (Bu^t); δ_H($CDCl_3$) 1.57 (9 H, s, Bu^t), 1.67 (9 H, s, Bu^t), 5.82 (1 H, br s, OH) and 7.7–8.3 (7 H, br, ArH) [Found: C, 87.3; H, 8.1 (M$^+$, 330). $C_{24}H_{26}O$ requires C, 87.23; H, 7.93%].

A convenient procedure for preparation of 1

To a stirred solution of **4** (10.0 g, 31.8 mmol) in CH_2Cl_2 (300 cm^3) was added dropwise at 0 °C over 30 min a solution of Br_2 (5.1 g, 32 mmol) in CH_2Cl_2 (50 cm^3). After the mixture was stirred for 3 h at room temperature, it was poured into a large amount of 1 mol dm^{-3} NaOH ice–water solution. The CH_2Cl_2 layer was separated, washed with brine (2 × 100 cm) and dried ($MgSO_4$). After filtration and evaporation, the solid residue (13.4 g) was refluxed in hexane (150 cm^3) for 5 min and cooled to room temperature. After the undissolved products were filtered off, the filtrate was evaporated and the residue was chromatographed on silica gel with hexane to give a raw product of **5** (10.1 g).

To a MeONa solution, prepared from absolute MeOH (250 cm^3) and Na (6.2 g), were added dry DMF (250 cm^3), **5** (10.1 g) and CuI (5.86 g, 30.7 mmol). After the resulting mixture was heated at 80 °C for 18 h under nitrogen, it was cooled and poured into a large amount of ice–water to give a powder. The powder collected was dissolved in CH_2Cl_2 (300 cm^3) and the

separated organic layer was washed with 1 mol dm^{-3} HCl (200 cm^3) and brine (200 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the solid residue was chromatographed on silica gel with 1:3 benzene–hexane to give a mixture (6.56 g) of **6** and **7**. The ^1H NMR measurement of the mixture showed the ratio of **6** to **7** was 92:8.

To a stirred solution of the mixture of **6** and **7** (6.56 g) in CH_2Cl_2 (440 cm^3) was added dropwise, at 0 °C, a solution of BBr_3 (44 g, 15 mmol) in CH_2Cl_2 (70 cm^3). After the mixture was stirred at room temperature for 3 h, it was poured into a large amount of ice–water. The organic layer was extracted with CH_2Cl_2 (2 × 100 cm^3) and the combined extract was washed with brine (100 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the solid residue was chromatographed on silica gel with 1:1 benzene–hexane to give **1** (5.15 g, 15.6 mmol). The total yield of 2,7-di-*tert*-butylpyrene was 49%.

Preparation of 2,7-di-*tert*-butyl-1-hydroxy(4,5,9,10-$^2H_4$)pyrene 12

This partly deuteriated 2,7-di-*tert*-butyl-1-hydroxypyrene was prepared from 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyrene **9** by following the procedure for the corresponding non-deuteriated **1**, with some modifications. Thus, 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyrene (3.06 g, 9.61 mmol) was treated with Br_2 (1.6 g) in CH_2Cl_2 (110 cm^3) and the resulting raw 2,7-di-*tert*-butyl-1-bromo(4,5,9,10-$^2H_4$)pyrene **10** (3.10 g) was allowed to react with MeONa in the presence of CuI to give a mixture (1.85 g) of 2,7-di-*tert*-butyl-1-methoxy(4,5,9,10-$^2H_4$)pyrene **11** and 2,7-di-*tert*-butyl-4-methoxy(5,9,10-$^2H_3$)pyrene.

The mixture (1.85 g) of methoxypyrenes was dissolved in dry DMF (10 cm^3). This solution was then added to a suspension of EtSNa, prepared from ethanethiol (0.93 g) and 50 wt% NaH (0.8 g) in dry DMF (22 cm^3). The resulting mixture was then gently refluxed for 3 h and poured into 10% HCl ice–water solution (150 cm^3). The organic products were extracted with benzene (2 × 30 cm^3) and the combined benzene extract was washed with brine (100 cm^3) and dried ($MgSO_4$). After filtration and evaporation, the residue was chromatographed on silica gel with 1:1 benzene–hexane to give **8** (1.52 g, 4.90 mmol). The total yield of 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyrene was 51%. Recrystallization from hexane afforded light yellow prisms, mp 232–234 °C; ν_{max}/cm^{-1} 3550 (OH), 2950 (Bu^t) and 2250 (C–D); $\delta_H(CDCl_3)$ 1.57 (9 H, s, Bu^t), 1.67 (9 H, s, Bu^t), 5.81 (1 H, s, OH) and 8.10 (3 H, br s, ArH); *m/z* 336 (M^+ + 2, 7.1%), 335 (M^+ + 1, 36), 334 (M^+, 100), 333 (M^+ − 1, 54), 332 (M^+ − 2, 22) and 331 (M^+ − 3, 6.8) (Found: C, 86.3; H, 7.8. $C_{24}H_{22}D_4O$ requires C, 86.18; H, 7.84%).

Isolation of the 2,7-di-*tert*-butylpyren-1-oxyl radical dimer 14

Precursor **1** (100 mg, 0.30 mmol) was dissolved in benzene (10 cm^3) with stirring. After K_2CO_3 (1.0 g) and PbO_2 (0.8 g) were added, the resultant dark-green mixture was stirred for 2–2.5 min and filtered. The solvent was removed by freeze-drying and the resulting dark-green crystalline powder was crystallized from hexane to give **9** (0.058 g, 58%) as greenish-black fine needles, mp 228–231 °C; ν_{max}/cm^{-1} 2950, 1640, 1630, 1575, 1550, 1475, 1460, 1380, 1360, 1260, 1240, 1220, 1180, 1130, 910, 870, 770, 765, 735 and 685 (Found: C, 87.2; H, 7.7. $C_{48}H_{50}O_2$ requires C, 87.49; H, 7.65%).

Isolation of the 2,7-di-*tert*-butyl(4,5,9,10-$^2H_4$)pyren-1-oxyl radical dimer 15

Following the same procedure as for the preparation of **14**, dimer **15** was prepared. Thus, precursor **12** (0.100 g, 0.30 mmol) was treated with PbO_2 (0.8 g) for 2–2.5 min in benzene (10 cm^3) in the presence of K_2CO_3 (1.0 g). After filtration, the solvent was removed by freeze-drying and the resulting dark-green crystalline powder was crystallized from hexane to give **15** (0.054 g, 54%) as greenish-black fine needles, mp 224–227 °C; ν_{max}/cm^{-1} 2950, 2250, 1640, 1630, 1570, 1545, 1480, 1460, 1360, 1260, 1170, 1050, 870 and 650 (Found: C, 86.6; H, 7.5. $C_{48}H_{42}D_8O_2$ requires C, 86.44; H, 7.56%).

Magnetic susceptibility measurements

The magnetic susceptibility measurements of **9** were carried out on a Shimadzu MB2 magnetic torsion balance in the range 80–290 K. The diamagnetic contribution was estimated by measuring the diamagnetic susceptibility of **1** under the same measurement conditions.

Measurements of equilibrium constants

0.80 cm^3 of a toluene solution of **14** was placed in an EPR cell. After the sample solution was degassed and sealed, it was placed in the cavity of the EPR spectrometer and double integrated EPR spectra were recorded at six different temperatures between 20 and −70 °C. The calibration curve was drawn with 1,3,5-triphenylverdazyl[12] toluene solutions using the same EPR cell and solvent and the same instrument settings. This experiment was repeated for two different samples.

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