PERKIN 2 COMMUNICATION

Synthesis of two novel *para*-extended bisaroxyls and characterization of their triplet spin states

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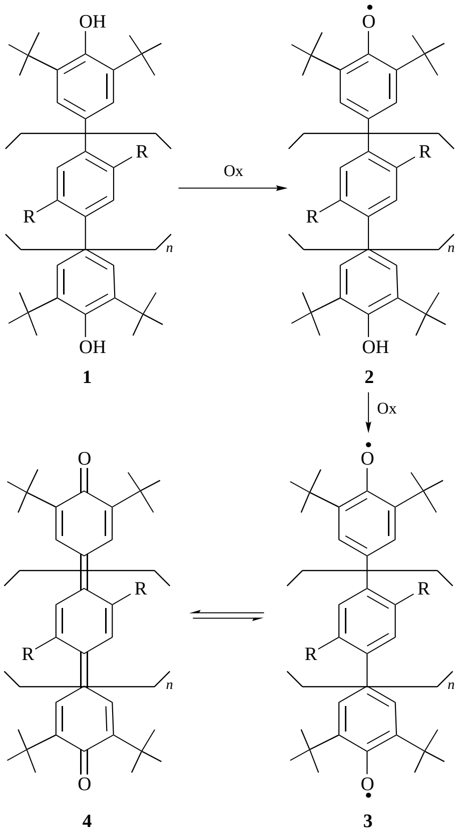
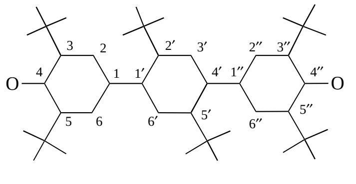
2′,3,3″,5,5′,5″-Hexa-*tert*-butyl-1,1′:4′,1″-terphenyl-4,4″-dioxyl 3c and 3,3′′′′,5,5′′′′-tetra-*tert*-butyl-1,1′:4′,1″:4″,1′′′:4′′′,1′′′′-quinquephenyl-4,4′′′′-dioxyl 3e, obtained by oxidation of the corresponding biphenols 1c and 1e, show thermally excited triplet spin states.

Radical centres, separated by suitable spacers, constitute one of the basic principles in the design of organic molecular ferromagnets.[1] Thus, 2,6-di-*tert*-butylphenoxyl radical systems,[2,3] connected by *m*-phenylene units in the 4 positions, have been largely used to synthesize oligo-radicals with triplet, quartet and quintet ground states.[4–7] We are currently investigating biradical systems **3**, in which two phenoxyl radicals are coupled by various *p*-arylene spacers, in order to clarify the prerequisites necessary for such spacers also to act as ferromagnetic couplers. Whereas the biphenyl and terphenyl species **3a** and **3b**, respectively, quantitatively exist as extended quinones **4a** and **4b** (EPR silent, aside from traces of mono-radical impurities in **4b**[8]), the *p*-quaterphenylene system **d** is able to exist in an equilibrium of biradical (**3d**) and quinone (**4d**) states.[9] In order to favour the biradical/triplet state **3** over the quinonoidal singlet state **4** further, an effective π-orbital overlapping must be prevented, *e.g.* by twisting or extending the linear aromatic spacer system. Therefore, we synthesized the compound series **c** and **e**† and characterized the radical species **2** and **3** by EPR–ENDOR and voltammetry.

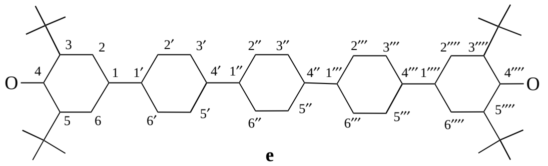
The EPR spectra of **3c**,**e** in toluene exhibited broad absorption signals ($\Delta H = 5$ G) at 293 K, resulting from dipole broadening in the biradicals. These signals were superimposed by hyperfine structure signals of the mono-radicals **2c**,**e** with the same *g*-factors ($g_{\mathbf{2c}} = 2.00448$, $g_{\mathbf{2e}} = 2.00422$) as the biradicals. They presumably originated from a partial oxidation of the corresponding bisphenols **1c**,**e**. ENDOR-spectra in toluene at 233 K gave the following coupling constants (in G, 1 G = 9.3408×10^{-5} cm^{-1}): for **2c** $a_{\mathbf{H2,6}} = 1.69$, $a_{\mathbf{H6'}} = 0.50$, $a_{\mathbf{H3'}} = 0.21$ and $a_{\mathbf{H\text{-}Bu}^t} = 0.09$, and for **2e** $a_{\mathbf{H2,6}} = 1.83$, $a_{\mathbf{H2',6'}} = 1.60$, $a_{\mathbf{H3',5'}} = 0.71$, $a_{\mathbf{H2'',6''}} = 0.32$, $a_{\mathbf{H3'',5''}} = 0.13$ and $a_{\mathbf{H\text{-}Bu}^t} < 0.10$.

Toluene solutions of **3c** or **3e** were frozen in the EPR cavity at 77 K. The resulting matrices revealed characteristic $\Delta m_s = 1$ transitions (zero field splitting, zfs) centred at 3310 G along with forbidden, but strong $\Delta m_s = 2$ transitions (half-field reson-





c



e

a $n = 0$
b $n = 1$, R = H
c $n = 1$, R = Bu^t
d $n = 2$, R = H
e $n = 3$, R = H

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† 3,5-Di-*tert*-butyl-4-(trimethylsilyloxy)phenylboronic acid and 1,4-dibromo-2,5-di-*tert*-butylbenzene or 4,4″-dibromoterphenyl reacted *via* Pd-catalyzed cross coupling (Suzuki reaction) in toluene to yield 67% of bis($OSiMe_3$) protected **1c** (mp 262 °C) or 53% of bis($OSiMe_3$) protected **1e** (mp 280 °C), respectively. Cleavage of the $SiMe_3$ groups with excess diluted aqueous HCl in boiling THF gave 80% of **1c** (mp 355 °C, from toluene) or 98% of **1e** (mp 320 °C, from ethyl acetate). The biphenols **1c** and **1e** show the expected ^1H and ^{13}C NMR spectra and elemental analyses. The biradicals **3c** and **3e** were prepared by oxidation of toluene solutions of **1c** and **1e** with PbO_2 or aqueous KOH–$K_3Fe(CN)_6$ in an EPR tube under argon *via* the intermediary mono-radicals **2c** and **2e**. For the preparation of the powder samples of **3c**,**e**, 6.0 g of $K_3Fe(CN)_6$ and 5.0 g of KOH in 40 ml of water were added to a solution of 0.1 g (0.167 mmol) of **1c** in 100 ml toluene, or 0.5 g (0.783 mmol) of **1e** in 100 ml toluene, each under argon. After shaking well for 5 min, the organic phase was separated under argon and again oxidized with fresh $K_3Fe(CN)_6$ and KOH–H_2O. Then, the organic phase was separated, dried over $CaCl_2$ and the toluene removed *in vacuo*, yielding **3c** (83 mg, 83%) or **3e** (460 mg, 92%).

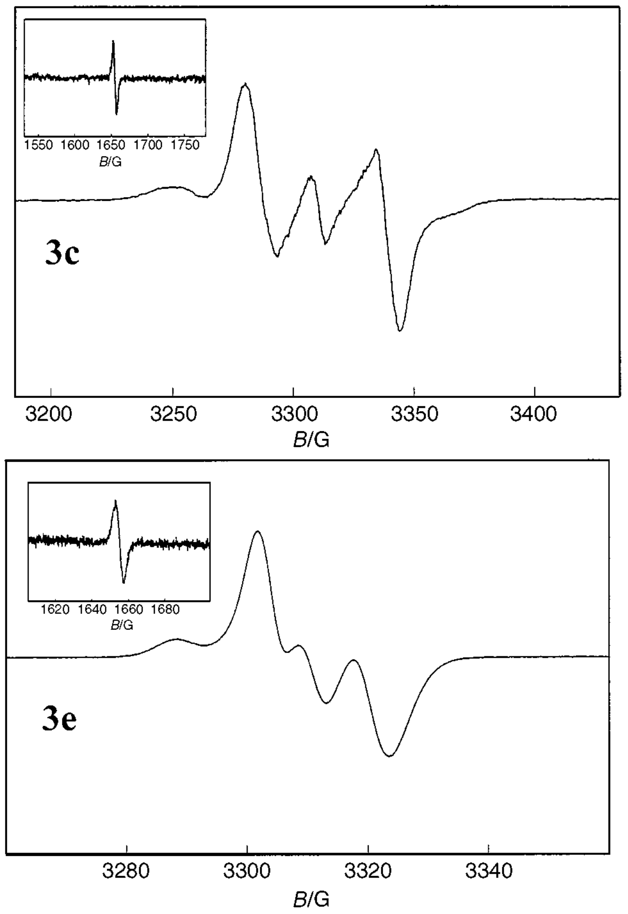

Fig. 1 Matrix EPR spectrum of **3c** and **3e** (zfs) with half-field resonance (hfr) (see insets)

ance, hfr) at 1655 G (see insets in Fig. 1). The typical zfs pairs of lines corresponding to the orientations of the triplet species (g-factor anisotropy) are described by zfs parameters ***D*** and ***E*** (**3c**: $|D/hc| = 0.0053$ cm^{-1}, $|E/hc| = 0$ cm^{-1}; for **3e**: $|D/hc| = 0.0018$ cm^{-1}, $|E/hc| = 0$ cm^{-1}). The two signals in the centres of each spectrum of Fig. 1 may again be attributed to the mono-radicals **2c**,**e**. The unsymmetrical nature of the matrix spectrum of **3e** may be attributed to a g-factor anisotropy. In sealed samples at 25 °C, these central signals increase with time, even under an inert atmosphere and in the dark, with a simultaneous decrease of the zfs signals. Also the total signal intensity decreases, therefore, reversible association of the biradicals by partial spin coupling to double- and oligo-radicals may take place within several days. This would explain the absence of any zfs and hfr in EPR spectra of powders of **3c**,**e** and the rather low susceptibility of those powders as measured by a SQUID magnetometer: for **3c**, $\chi_{\mathrm{mol}} = 1.54 \times 10^{-2}$ emu mol^{-1} at 5 K; for **3e**, $\chi_{\mathrm{mol}} = 6.68 \times 10^{-3}$ emu mol^{-1} at 5 K. After redissolution of the powders in toluene, we can again find zfs and hfr of **3c**,**e** in the matrix formed at 77 K.

By comparing the radical intensity of **3c**,**e** with that of a 1,3,5-triphenylverdazyl solution by double integration of the zfs we estimate a biradical concentration of 94% of **3c** and 96% of **3e** at room temperature. Furthermore, we detect a low concentration of the mono-radical (<5% of the total EPR signal) and do not find any indication of a quinonoid structure **4** by IR spectrometry. If the observed D value is explained in terms of a point-dipole approximation[10] [D (G) = 27 810/r^3], the distance r between the two radical centres can be estimated for **3c** as 7.9 Å and for **3e** as 11.4 Å. From X-ray analysis of single crystals of **1e** and the bis dimethyl ether of **1c** we measured the O···O distance 14.16 Å for **1c**(Me$_2$) and 22.64 Å for **1e**. This shows again that the point dipole model is not stringent in the case of biradicals with delocalized spins.[11] The value of E = 0 cm^{-1} for both compounds indicates axial symmetry of the biradicals in the matrix.[12] The ground state multiplicity and the singlet–triplet gap $\Delta E_{\mathrm{T-S}} = 2J$ was determined from the temperature *vs.* intensity plots (Fig. 2).[13] The non-linearity of the curves in the range of 93–293 K clearly indicates singlet ground states for **3c** and **3e** which are in thermal equilibrium with their triplet states. For this case, the intensity I of the triplet EPR-signal is given by eqn. (1)[14] where J is the exchange coupling between the

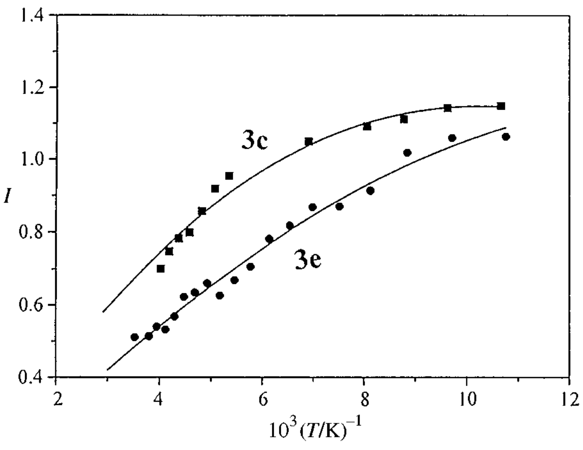

Fig. 2 Curie law plots of EPR intensity (I) *vs.* $1/T$ for biradicals **3c**,**e**

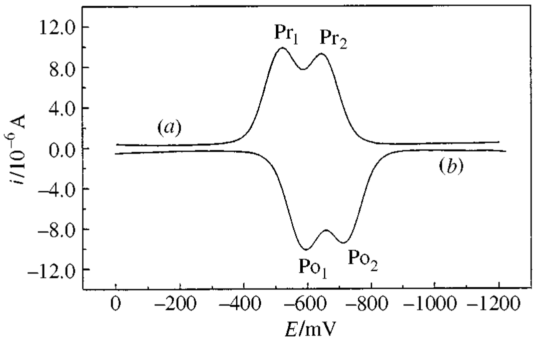

Fig. 3 DPV of 0.5 mM **3c** at a Pt electrode in pyridine solution containing 0.1 M NBu$_4$PF$_6$; reference electrode Ag/Ag$^+$ (0.01 M AgClO$_4$, in MeCN with 0.1 M NBu$_4$PF$_6$), pulse amplitude 50 mV, pulse width 200 ms, scan rate 20 mV s^{-1}, potential sweep (*a*) 0 to −1.2 V, (*b*) −1.2 to 0 V

$$IT = C[3\exp(-2J/RT)]/[1 + 3\exp(-2J/RT)] \qquad (1)$$

unpaired electrons T, the absolute temperature and $R = 1.987$ cal mol^{-1} K^{-1}. Non-linear least-squares curve fitting of the data in Fig. 2 to eqn. (1) yields $J = -156 \pm 4$ cal mol^{-1} (-55 cm^{-1}) for **3c** and $J = -103 \pm 2$ cal mol^{-1} (36 cm^{-1}) for **3e**.

The cyclic (CV) and differential-pulse (DPV) voltammetry of **3c** (Fig. 3) in pyridine solution show two peak couples ($E^{\circ 1} = -0.56$ V; $E^{\circ 2} = -0.68$ V *vs.* Ag$^+$/Ag). In contrast to **3c** and other extended quinones,[8,9] **3e** exhibits only one reduction and re-oxidation peak ($E^\circ = -0.55$ V). With increasing scan rate, the reduction and re-oxidation peaks of **3c**,**3e** are shifted towards more negative and more positive potentials, respectively. Controlled-potential electrolysis (CPE) at −1.0 V proves a one-electron transfer for each peak couple of **3c** and a formal two-electron transfer for the peak couple of **3e**. Apparently, the first and second reduction steps of **3e** occur at potentials very close together. This is a consequence of the lower interaction of the electrons in **3e** (low D and J values) according to which both radical centres are reduced independently.

From the structure of **1c** and **1e** and the experimental results of CV, DPV and CPE measurements, the electrochemical reduction in both cases can be denoted as a quasi-reversible electron transfer (EE) process.

In summary, our results reveal that p-arylene units, although producing an antiferromagnetic ground state, may cause effective ferromagnetic coupling since the triplet state is strongly populated at temperature >200 K if the arylene spacer is twisted (**3c**) or extended by two or three benzene rings (**3d** and **3e**).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/95. Supplementary data are also available (suppl. no. 57269, 4 pp.) from the British Library. For details of the Supplementary Publications scheme see ‘Instructions for Authors’ as above.

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