New isoindoline aminoxyl based polyradicals for spin probes and molecular magnetic materials

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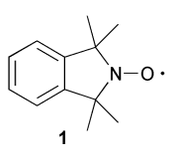
The synthesis of a range of aminoxyl polyradicals based on the isoindoline aminoxyl moiety is described. Friedel–Crafts alkylation reactions between 1,1,3,3-tetramethylisoindolin-2-yloxyl (**1**) and suitable haloalkanes were used to prepare three new biradicals and one new triradical. Standard methods[11] for the synthesis of nitronyl aminoxyls and iminyl aminoxyls were employed to prepare two novel tridentate biradical derivatives of **1**. Also a novel isoindoline-like fused biradical was prepared. The room temperature solution EPR spectra of all radicals are reported and reveal a wide range of exchange coupling constants. The crystal structure determinations of two of these compounds, 1,1-bis(1′,1′,3′,3′-tetramethylisoindolin-2′-yloxyl-5′-yl)ethane (**3**) and 1,2,3,5,6,7-hexahydro-1,1,3,3,5,5,7,7-octamethylbenzo[1,2-*c*:4,5-*c*′]dipyrrol-2,6-diyloxyl (**15**), are reported.

Introduction

1,1,3,3-Tetramethylisoindolin-2-yloxyl (**1**) aminoxyls exhibit superior EPR linewidths as well as excellent thermal and chemical stability compared to commercially available aminoxyls.[1] Their stability, relative ease of synthesis and functionalisation make them ideal candidates for use in many biological, chemical and materials science applications.



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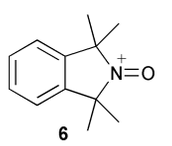
A broad range of aminoxyls has received attention in the field of molecular magnetism with encouraging results arising from many structural variations of the aminoxyl radical. Isoindoline aminoxyls have provided the basis for much research in the area of radical trapping[2–5] and spin probes,[6–8] however their application to the field of molecular magnetism has been largely overlooked. The use of aminoxyl polyradicals as coupling units for magnetic metal ions has received much attention and represents a promising approach for the preparation of functional molecular magnetic materials.[9]

We have successfully synthesised a range of isoindoline aminoxyl polyradicals which may find use in a range of fields applicable to aminoxyl radicals. Of primary interest is the field of molecular magnetism, although the polyradicals prepared may also prove to be useful as spin probes. Recent spin probe studies have mainly focused on monoradicals. However, the advantages of using biradicals as spin probes have previously been outlined.[10] Notably the presence of exchange interactions contributing to the EPR spectrum of biradicals may represent another method for obtaining environmental information from spin probes.

Results and discussion

Bis(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)methane (2)

The Friedel–Crafts alkylation reaction between **1** and dichloromethane gave biradical **2** as the sole isolated reaction product in 16% yield (45% based on consumed starting material, Scheme 1). This type of Friedel–Crafts alkylation is known, however yields are typically higher. In this case low yields can be attributed to acid mediated oxidation of the aminoxyl **1** to the corresponding oxoammonium ion **6**, evident by the deep red colouration of the reaction solution. The aromatic ring of **6** would be less reactive towards electrophilic substitution due to the influence of the cationic oxoammonium group.



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The solution EPR spectrum of **2** in toluene-*d8* (Fig. 1) exhibits five resolved resonances characteristic of an aminoxyl biradical system where $|J_0| \approx a_N$.[10] In systems where $|J_0| \approx a_N$, $|J_0|$ can be accurately determined by spectral simulation due to the sensitivity of the spectrum to changes in J_0. The ability to accurately determine J_0 presents possibilities for spin labelling applications where changes in J_0 may relate to variations in certain environmental conditions. An investigation of the variable temperature EPR behaviour of biradical **2** with analysis of J_0 values that support this will appear in a later publication.

1,1-Bis(1′,1′,3′,3′-tetramethylisoindolin-2′-yloxyl-5′-yl)ethane (3)

The Friedel–Crafts alkylation reaction between **1** and 1,2-dichloroethane affords the 1,1-substituted dimer in 15% yield (45% based on consumed starting material). The observed substitution is expected to arise from rapid rearrangement of the initial carbocation adduct to give the more stable benzylic carbocation.

Crystals suitable for X-ray crystallography were obtained by slow evaporation from a cyclohexane–dichloromethane (1 : 1) solution of **3**.

The solution EPR spectrum of **3** in toluene-*d8* (Fig. 1) exhibits five resolved resonances, again characteristic of an aminoxyl biradical system where $|J_0| \approx a_N$.

The crystal structure analysis confirmed in the first instance the presence of the 1,1-aminoxyl disubstitution rather than the expected 1,2-disubstitution (Fig. 2). The presence of two molecules of the compound in the orthorhombic unit cell (space

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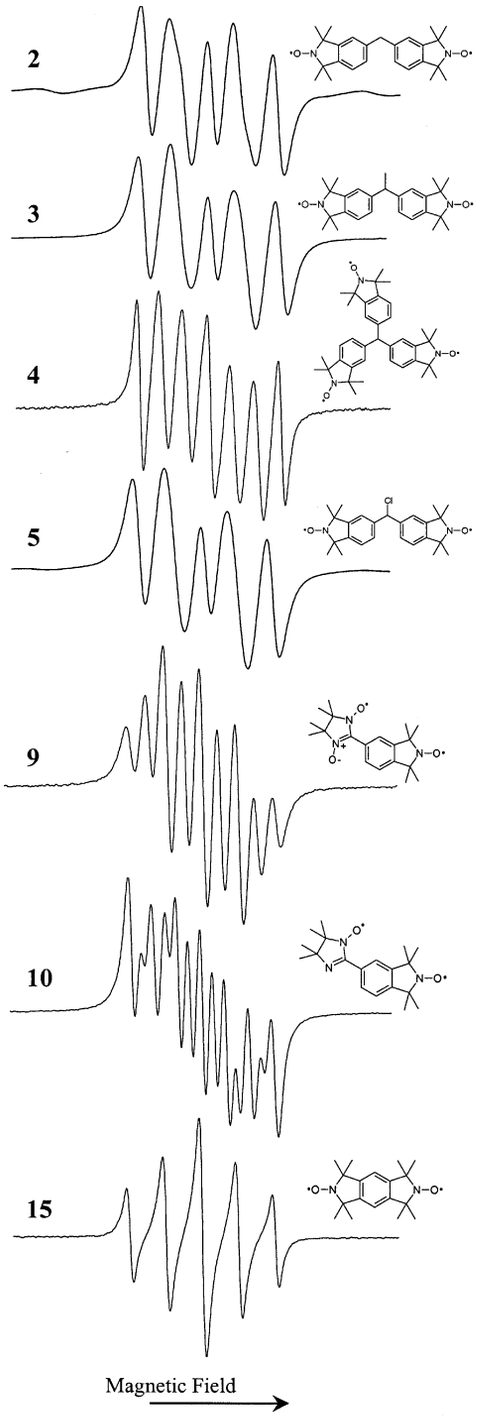


Fig. 1 X-Band EPR spectra of radicals **2**–**5**, **9**, **10** and **15** in toluene (298 K).

group *Pnn*2) means that the two aminoxyl substituents are related by 2-fold rotational symmetry, with the central linking carbon (C61) constrained to this axis. To achieve this, the second ethane carbon (C62) must be disordered over two sites (S.O.F. = 0.5) related by 2-fold symmetry. Fig. 2 shows only one of the disordered sites for this second carbon. Also as a consequence of this disorder, not all of the protons on the chain could be located by difference methods.

Tris(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)methane (4) and chlorobis(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)methane (5)

The preparation of the triradical **4**, using chloroform as the Friedel–Crafts haloalkane, was analogous to that for the biradicals **2** and **3**. The yield for the preparation was 26% despite the reaction being less selective. Biradical **5** was also isolated in 3.6% yield.

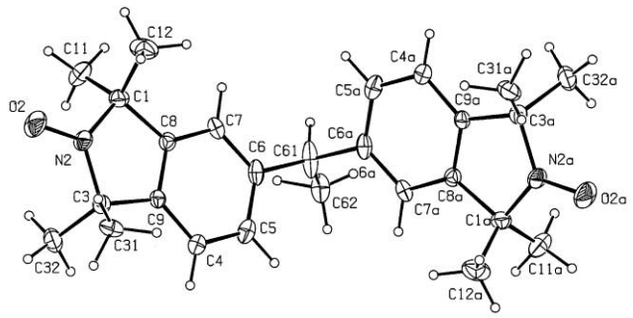
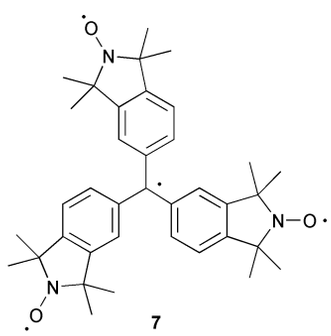


Fig. 2 Molecular configuration and atom numbering scheme for **3** viewed down the approximate 2-fold rotational axis. Only one site of the disordered atom (C62) is shown. Non-hydrogen atoms are shown as 30% probability ellipsoids.

The synthesis of triradical **4** was of particular interest since it represents a potential precursor for a triphenylmethyl type carbon centred radical. Our attempts at preparing tetraradical **7** have so far proven unsuccessful.



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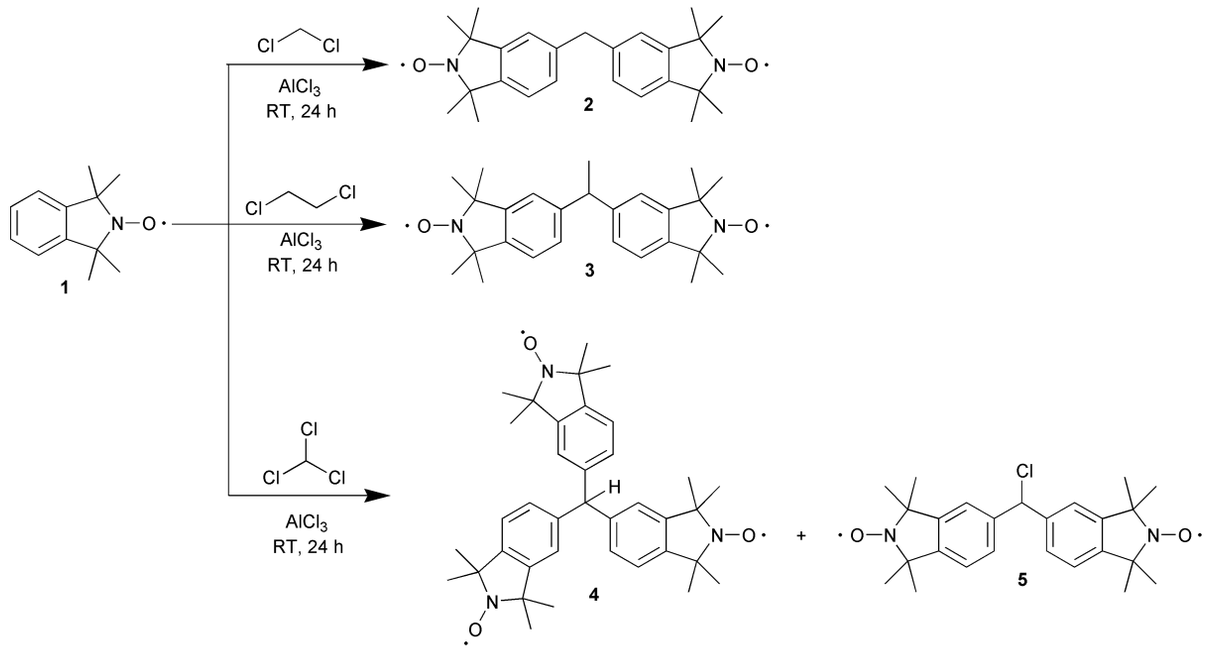
The solution EPR spectrum of **4** in toluene-*d8* (Fig. 1) exhibits seven resolved resonances as expected for an aminoxyl triradical where $|J_0| \approx a_N$.

The solution EPR spectrum of **5** in toluene-*d8* (Fig. 1) exhibits five resolved resonances characteristic of an aminoxyl biradical system where $|J_0| \approx a_N$.

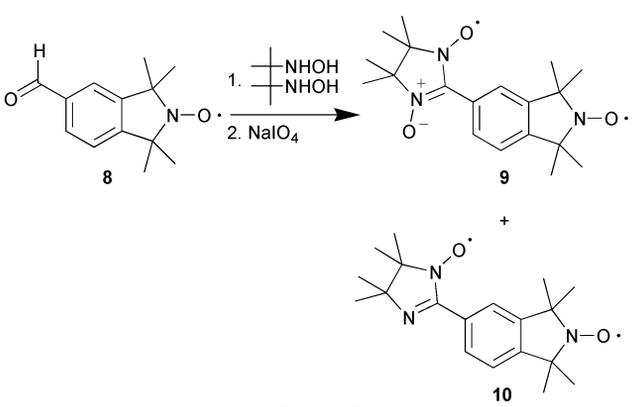
5-(4′,4′,5′,5′-Tetramethyl-1′-oxido-3′-oxylimidazolin-2′-yl)-1,1,3,3-tetramethylisoindolin-2-yloxyl (9) and 5-(4′,4′,5′,5′-tetramethyl-1′-oxylimidazolin-2′-yl)-1,1,3,3-tetramethylisoindolin-2-yloxyl (10)

The nitronyl aminoxyl (**9**) and iminyl aminoxyl (**10**) derivatives of **1** were prepared by an Ullmann nitronyl aminoxyl synthesis.[11] The aldehyde precursor **8** was prepared according to our previously reported method.[12] The oxidation reaction yields both **9** and **10** (Scheme 2), the relative proportions of which are dependent on reaction temperature. The observed yields are typical for nitronyl aminoxyl syntheses.[11]

The solution EPR spectrum of nitronyl aminoxyl **9** in toluene-*d8* (Fig. 1) exhibits nine resonances indicative of a system containing three nitrogen nuclei with two different a_N values, where $a_{N(1)} \approx 2 \times a_{N(2)}$, and $|J_0| \gg a_N$. One a_N value arises from the nitronyl aminoxyl group (a_N = 7.2 G) and the other from the isoindoline aminoxyl group (a_N = 14.4 G). The solution EPR spectrum of iminyl aminoxyl **10** in toluene-*d8* (Fig. 1) exhibits 13 resonances which arise from three different a_N values, where $a_{N(1)} \approx 2 \times a_{N(2)} \approx 3 \times a_{N(3)}$, and $|J_0| \gg a_N$. Two of the a_N values (9.4 and 4.7 G) are associated with the iminyl aminoxyl while the third (14.1 G) is associated with the isoindoline aminoxyl. It is difficult to obtain values for J_0 from the EPR spectrum when $|J_0| \gg a_N$ since the spectra in this regime are relatively insensitive to changes in J_0.



Scheme 1



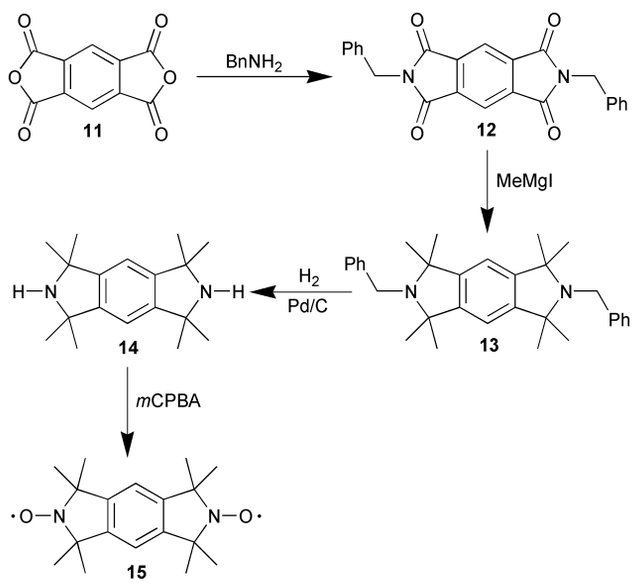
Scheme 2

1,2,3,5,6,7-Hexahydro-1,1,3,3,5,5,7,7-octamethylbenzo-[1,2-*c*:4,5-*c*′]dipyrrole-2,6-diyloxyl (15)

The novel fused biradical was prepared using methods similar to those used for the preparation of the related monoradical TMIO (**1**).[13] Benzylation of pyromellitic dianhydride (**11**) was achieved by treatment with benzylamine in glacial AcOH to give **12** in 90% yield (Scheme 3). The octamethyl species **13** was prepared by the exhaustive methylation of **12** with MeMgI in boiling toluene and was isolated and purified in 4.6% yield. The low yield for **13** reflects both the difficult nature of this type of methylation procedure and the limited solubility of the products. The analogous step involving the addition of four methyl groups in the synthesis of TMIO (**1**) affords yields of <40%.[13]

Hydrogenation of **13** at 50 psig over 5% Pd/C in glacial AcOH afforded diamine **14** in 90% yield. The material was used as is without further purification for the next step. Oxidation of diamine **14** with *m*CPBA in THF afforded biradical **15** in 63% yield. Biradical **15** has only limited solubility in most common organic solvents. Recrystallisation could be achieved from several solvents including MeCN, toluene and DMF. However to obtain crystals suitable for X-ray crystallography a solution of **15** in boiling DMF was cooled extremely slowly (>16 h) in an oil bath, yielding small yellow needles.

The solution EPR spectrum of **15** in toluene-*d8* (Fig. 1) exhibits five resonances (1 : 2 : 3 : 2 : 1) characteristic of an aminoxyl biradical system where $|J_0| \gg a_N$. Systems such as these are of interest in the field of molecular magnetism where high exchange interactions are desired.



Scheme 3

The crystal structure of **15** shows the biradical aminoxyl which is centrosymmetric and planar and lies on a crystallographic inversion centre (Fig. 3). The poor refinement residual is

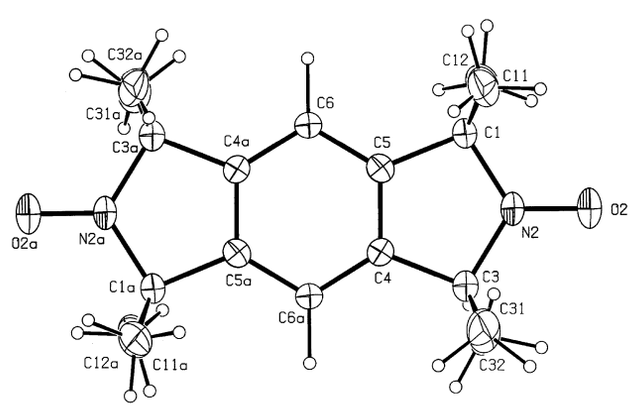


Fig. 3 Molecular configuration and atom numbering scheme for **15** (30% probability ellipsoids).

due to a combination of poor crystal quality and considerable thermal motion, particularly in the methyl substituents.

Experimental

NMR Spectra were recorded on a Varian Unity 300 spectrometer. EPR spectra were recorded on a Brüker ESP 300E EPR spectrometer (X-band, ~9.2 GHz) using an EIP 548B microwave frequency counter and a Brüker O35M gaussmeter for microfrequency calibration.

Bis(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)methane (2)

To a solution of **1** (1.00 g, 5.26 mmol, 1 equiv.) in CH_2Cl_2 (10 cm^3) was added $AlCl_3$ (2.80 g, 21.0 mmol, 4 equiv.). The mixture was stirred at room temperature under an atmosphere of argon for 24 h. The dark red mixture was poured slowly onto ice with stirring. The layers were separated and the aqueous portion was extracted with $CHCl_3$ (3 × 5 cm^3). The combined organics were washed with sat. NaCl (10 cm^3), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Chromatography (SiO_2; 40 : 60 : 0.5 EtOAc–*n*-hexane–MeOH) gave starting material **1** (662 mg, 3.48 mmol) followed by biradical **2**, which was recrystallised as fine yellow crystals from hexane (163 mg, 0.416 mmol, 16%), mp 156 °C (decomp.) (Found: C, 76.3; H, 8.5; N, 6.4. $C_{25}H_{32}N_2O_2$ requires C, 76.5; H, 8.2; N, 7.1%); *m*/*z* 392 (100%), 377 (75%), 362 (40%), 347 (71%), 332 (34%), 317 (12%) (fused ring N-containing compounds frequently give poor combustion analysis and so high resolution EI MS was also run); EI MS found M^+ 392.245929 (1.1 ppm from calc. mass for $C_{25}H_{32}N_2O_2$); g = 2.00580, a_N = 14.0 G (toluene-*d8*, 293 K).

1,1-Bis(1′,1′,3′,3′-tetramethylisoindolin-2′-yloxyl-5′-yl)ethane (3)

To a solution of **1** (1.00 g, 5.26 mmol, 1 equiv.) in 1,2-dichloroethane (10 cm^3) was added $AlCl_3$ (2.80 g, 21.0 mmol, 4 equiv.). The mixture was stirred at room temperature under an atmosphere of argon for 24 h. The dark red mixture was poured slowly onto ice with stirring. The layers were separated and the aqueous portion was extracted with $CHCl_3$ (3 × 5 cm^3). The combined organics were washed with sat. NaCl (10 cm^3), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Chromatography (SiO_2; 40 : 60 : 0.5 EtOAc–hexane–MeOH) gave starting material **1** (550 mg, 2.89 mmol) followed by the biradical **3**, which was recrystallised as yellow hexagonal prisms by slow evaporation from a cyclohexane–dichloromethane (1 : 1) solution (155 mg, 0.382 mmol, 15%), mp 218 °C (dec.); EI MS M^+ 406.262124 (−0.2 ppm from calc. mass for $C_{26}H_{34}N_2O_2$); g = 2.00582, a_N = 14.0 G (toluene-*d8*, 293 K).

Tris(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)methane (4) and chlorobis(1′,1′,3′,3′-tetramethylisoindolin-2′-yloxyl-5′-yl)-methane (5)

To a solution of **1** (2.00 g, 10.5 mmol, 1 equiv.) in $CHCl_3$ (20 cm^3) was added $AlCl_3$ (4.63 g, 34.7 mmol, 3.3 equiv.). The mixture was stirred at room temperature under an atmosphere of argon for 24 h. The dark green mixture was poured slowly onto ice with stirring. The layers were separated and the aqueous portion was extracted with $CHCl_3$ (3 × 20 cm^3). The combined organics were washed with sat. NaCl (50 cm^3), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Chromatography (SiO_2; 20 : 20 : 60 : 0.5 DCM–EtOAc–*n*-hexane–MeOH) gave starting material **1** (444 mg, 2.34 mmol) followed by biradical **5** (82 mg, 0.190 mmol, 3.6%) then triradical **4** (533 mg, 0.918 mmol, 26%).

Biradical **5**: Recrystallisation from *n*-hexane gave yellow needles, mp 180–182 °C; EI MS M^+ 426.20835 (2.22 ppm from mass calc. for $C_{25}H_{31}N_2O_2Cl$); g = 2.00582, a_N = 13.9 G (toluene-*d8*, 293 K).

Triradical **4**: Slow evaporation from a 1 : 1 DCM–*n*-hexane mixture gave yellow prisms, mp >180 °C (slow decomp.); EI MS M^+ 580.35497 (1.82 ppm from mass calc. for $C_{37}H_{46}N_3O_3$); g = 2.00582, a_N = 14.1 G (toluene-*d8*, 293 K).

5-(4′,4′,5′,5′-Tetramethyl-1′-oxido-3′-oxylimidazolin-2′-yl)-1,1,3,3-tetramethylisoindolin-2-yloxyl (9) and 5-(4′,4′,5′,5′-tetramethyl-1′-oxylimidazolin-2′-yl)-1,1,3,3-tetramethylisoindolin-2-yloxyl (10)

To a solution of 5-formyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (**8**, 90 mg, 412 μmol, 1 equiv.) in MeOH (2 cm^3) was added 2,3-bis(hydroxyamino)-2,3-dimethylbutane (85 mg, 574 μmol, 1.4 equiv.). The mixture was stirred at room temperature for 22 h whereupon the solvent was removed under vacuum. The residue was taken up in $CHCl_3$ (3 cm^3), cooled to 0 °C then $NaIO_4$ (180 mg, 842 μmol) in H_2O (2 cm^3) was added with stirring over 5 min. The solution was stirred at 0 °C for a further 15 min. The mixture was diluted with H_2O (3 cm^3) and extracted with $CHCl_3$ (3 × 10 cm^3). The combined organic extracts were washed with sat. NaCl (2 × 15 cm^3), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Chromatography (SiO_2; 40 : 60 : 0.2 EtOAc–*n*-hexane–MeOH) gave iminyl aminoxyl **10** (32 mg, 97 μmol, 24%) followed by nitronyl aminoxyl **9** (18 mg, 52 μmol, 13%).

Nitronyl aminoxyl **9**: Slow evaporation from a 1 : 1 DCM–*n*-hexane mixture gave dark blue prisms, mp 209 °C (decomp.); EI MS M^+ 345.205330 (−0.3 ppm from calc. for $C_{19}H_{27}N_3O_3$); g = 2.00677, $a_{N(1)}$ = 14.4 G, $a_{N(2)}$ = 7.2 G, $a_{N(3)}$ = 7.2 G (toluene-*d8*, 293 K).

Iminyl aminoxyl **10**: Recrystallisation from *n*-hexane gave orange–red clusters, mp 199–201 °C (Found: C, 69.1; H, 8.4; N, 12.8. $C_{19}H_{27}N_3O_2$ requires C, 69.3; H, 8.3; N, 12.8%); g = 2.00516, $a_{N(1)}$ = 14.1 G, $a_{N(2)}$ = 9.4 G, $a_{N(3)}$ = 4.7 G (toluene-*d8*, 293 K).

N,*N*′-Dibenzylpyromellitimide (12)

To a stirred solution of pyromellitic dianhydride (**11**, 9.6 g, 0.044 mol, 1 equiv.) in glacial AcOH (50 mL) was added dropwise benzylamine (14.6 mL, 0.134 mol, 1.5 equiv.). A white precipitate rapidly formed and the mixture was stirred for a further 30 min at room temperature. The white precipitate was collected by vacuum filtration to yield *N*,*N*′-dibenzylpyromellitimide (**12**, 15.7 g, 0.0396 mol, 90%). Recrystallisation from toluene gave colourless needles, mp 301–302 °C (Found: C, 72.6; H, 4.1; N, 7.1. $C_{24}H_{16}N_2O_4$ requires C, 72.7; H, 4.1; N, 7.1%); ^{1}H NMR ($CDCl_3$) δ 4.85 (s, 4H, CH_2), 7.32–7.43 (m, 10H, ArH), 8.25 (s, 2H, ArH).

2,6-Dibenzyl-1,2,3,5,6,7-hexahydro-1,1,3,3,5,5,7,7-octamethylbenzo[1,2-*c*:4,5-*c*′]dipyrrole (13)

Magnesium turnings (19.6 g, 0.81 mol, 16 equiv.) and a few crystals of iodine were placed in a flame dried Grignard apparatus under a positive pressure of Ar. Anhydrous Et_2O (~300 mL) and a few drops of iodomethane were added to initiate the reaction. The remaining iodomethane (51.0 mL, 0.81 mol, 16 equiv. total) and anhydrous Et_2O (1.5 L total) were added to maintain a constant rate of reaction. When addition of the reagents was complete the mixture was stirred until all activity subsided. Ether was removed by distillation until the temperature of the mixture reached 80 °C. A solution of *N*,*N*′-dibenzylpyromellitimide (**12**, 20.0 g, 0.050 mmol, 1 equiv.) in anhydrous toluene (1 L) was added to the methyl Grignard solution (~60 °C) at a rate which maintained a constant temperature. When addition was complete, solvent was distilled until the temperature of the reaction mixture reached 110 °C. The reaction mixture was refluxed for two hours, then concentrated by distillation. After cooling, the reaction was diluted with hexane fraction (1.5 L) and mixed thoroughly. The resultant purple slurry was vacuum filtered through Celite and the

residue was washed with hexane fraction (~500 mL). Residues were deactivated with *i*-PrOH and air was bubbled through the filtrate overnight. The filtrate was passed through a column of basic alumina and solvent was removed under vacuum to yield crude **13**. Recrystallisation from MeCN gave **13** (1.06 g, 2.34 mmol, 4.6%) as colourless prisms, mp 213–215 °C (Found: C, 76.3; H, 8.5; N, 6.4. $C_{25}H_{32}N_2O_2$ requires C, 76.5; H, 8.2; N, 6.1%); ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 24H, CH_3), 4.00 (s, 4H, CH_2), 6.8 (s, 2H, ArH), 7.3–7.50 (m, 10H, ArH) ppm; ^{13}C NMR ($CDCl_3$) δ 28.5 (CH_3), 46.0 (CH_2), 65.2 (quat. C), 126–129 (ArC), 143–148 (ArC) ppm.

1,2,3,5,6,7-Hexahydro-1,1,3,3,5,5,7,7-octamethylbenzo-[1,2-*c*:4,5-*c*′]dipyrrole (14)

A solution of diamine **13** (0.530 g, 1.17 mmol) in glac. AcOH was hydrogenated (50 psig) over a 5% Pd/C catalyst for 6 h. The solution was evaporated to dryness then taken up in 1 M HCl. The solution was filtered to remove residual catalyst then was made basic (pH 14) with 5 M NaOH. The solution was extracted with $CHCl_3$ (4 × 25 mL), evaporation of which gave **14** (0.287 g, 1.05 mmol, 90%) as a white solid. Recrystallisation from MeCN gave **14** as fine white crystals which sublimed at 200 °C. ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 24H, CH_3), 1.8 (s, 2H, NH), 6.8 (s, 2H, ArH) ppm; ^{13}C NMR ($CDCl_3$) δ 27.0 (CH_3), 65.0 (quat. C), 126.0 (ArC), 128–129 (ArC), 143–149 (ArC) ppm.

1,2,3,5,6,7-Hexahydro-1,1,3,3,5,5,7,7-octamethylbenzo-[1,2-*c*:4,5-*c*′]dipyrrole-2,6-diyloxyl (15)

3-Chloroperoxybenzoic acid (2.01 g, 11.6 mmol, 6 equiv.) was slowly added to a solution of diamine **14** (0.530 g, 1.95 mmol, 1 equiv.) in THF (100 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h then was allowed to warm to room temperature. The mixture was stirred at room temperature for a further 24 h. H_2O (50 mL) was added to the solution which was then acidified with 1 M HCl and extracted with $CHCl_3$ (4 × 20 mL). The combined organic extracts were washed with 2 M NaOH (3 × 20 mL). The organic extracts were evaporated to dryness to yield biradical **15** (0.370 g, 1.22 mol, 63%) as a yellow crystalline material. Recrystallisation from DMF gave **15** as small yellow needles, mp 230 °C (dec.); g = 2.006076, a_N = 14.0 G (toluene).

Crystallography †

Crystal data for (3). $C_{26}H_{34}N_2O_2$, M = 406.55, orthorhombic, space group *Pnn2*, (No. 34), a = 12.611(2), b = 16.164(2), c = 5.895(2) Å, V = 1201.7(3) Å^3, F(000) = 440, Z = 2, D_c = 1.124 g cm^{-3}, μ(Mo Kα) = 0.71 cm^{-1}, temperature 293(2) K; 1174 unique reflections measured [$2\theta_{max}$ 50°: h, 0 to 14; k, 0 to 19; l, 0 to 7]. Final $R1$ ‡ 0.057 (F); $wR2$ ‡ 0.172 (F^2) [899 observed with $I > 2.0\ \sigma(I)$; 142 refined parameters]; S = 1.42. Crystal size 0.50 by 0.25 by 0.15 mm.

Crystal data for (15). $C_{18}H_{26}N_2O_2$, M = 302.41, monoclinic, space group $P2_1/n$, (No. 14), a = 6.332(2), b = 13.403(2), c = 11.209(2) Å, β = 92.01(2)°, V = 950.7(4) Å^3, F(000) = 328, Z = 2, D_c 1.063 g cm^{-3}, μ(Mo Kα) = 0.69 cm^{-1}, temperature 293(2) K; 1833 reflections measured, 1676 unique (R_{int} = 0.035) [$2\theta_{max}$ 50°: h, 0 to 7; k, 0 to 15; l, −13 to 13]. Final $R1$* 0.073 (F); $wR2$* 0.202 (F^2) [509 observed with $I > 2.0\ \sigma(I)$]; S = 1.17. Crystal size 0.30 by 0.20 by 0.10 mm.

Data collection, structure solution and refinement

X-ray diffraction data for both compounds were measured on a Rigaku AFC7R diffractometer by using crystal monochromatized Mo Kα X-radiation (λ = 0.71073 Å) from a 12 kW rotating anode source. Negligible change in the intensities of three standards monitored throughout the data collection periods for both compounds (1.5% for **3** and 0.1% for **15**) indicated no significant crystal decomposition. Data were corrected for Lorentz and polarization effects and extinction but not for absorption The structures were solved by direct methods and refined by full-matrix least-squares (on F^2) using SHELXL-97[14] within TeXsan.[15] Figures were drawn using PLATON for Windows.[16] Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions in the refinements as riding models.

Full crystallographic details, excluding structure factor tables, 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*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference numbers 176995 and 176996.

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‡ $R1 = (\Sigma\ F_o - F_c)/(\Sigma\ F_o)$; $wR2 = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$.