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Synthesis and characterization of poly(1,3-phenylene)-based polyradicals carrying cyclic aminoxyls

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The synthesis and magnetic properties of poly(2,2,4,4-tetramethyl-*N*-yloxy-1,4-dihydro-2*H*-3,1-benzoxazine-6,8-diyl-1,3-phenylene) (**4**) are described. Polyradical **4** was prepared by the Pd-catalyzed cross-coupling reaction of 6,8-dibromo-2,2,4,4-tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazine and bis(trimethylene) 1,3-phenylenediboronate, followed by oxidation with *m*-chloroperoxybenzoic acid. The number average molecular weights of **4** determined by SEC (size exclusion chromatography) were ~4120 (15 repeating units), and the spin concentrations determined by EPR were up to 0.75 spin per repeating unit. The EPR spectrum of **4** in a toluene glass matrix showed the $\Delta M_S = 2$ forbidden transition at $g = 4.0$. A Curie plot of the $\Delta M_S = 2$ signal intensity *vs.* $1/T$ gave a straight line, suggesting that the polyradical is in a triplet ground state or a nearly degenerate singlet–triplet state.

Introduction

In the study of organic ferromagnetism, polymeric ferromagnets have attracted much attention in recent years because their Curie temperatures are expected to be much higher than those of organic radical crystals,[1,2] which makes them potentially very useful as magnetic materials. A wide variety of π-conjugated spin systems, including poly(phenylacetylene)-based,[3] poly(1,3-phenyleneethynylene)-based[4] and poly(phenylenevinylene)-based polyradicals[5] and poly(triarylmethyl) polyradicals,[6] have been designed on the basis of the π-topological symmetry rule[7] and synthesised. In a previous paper[8] we reported the first synthesis of a poly(1,3-phenylene)-based polyradical having the structure of **1**. The 1,3-phenylene unit has been shown to be one of the best ferromagnetic couplers by theoretical studies[9] and by magnetic studies on polycarbenes[10] and poly(triarylmethyl) polyradicals.[6] Although the spin concentration of **1** was very high (82%), no ferromagnetic interaction was observed. This was attributed to the interruption of π-conjugation due to a serious twisting between the N–O moieties and the poly(1,3-phenylene) backbone. This feature was confirmed by X-ray crystallographic analysis of the corresponding model radical **2**, which showed a dihedral angle of 68.5° between the N–O$^\bullet$ moiety and the benzene ring. To overcome this problem we decided to prepare polyradicals having a planar cyclic aminoxyl as the dangling aminoxyl,[11] and we focused on **3** and **4** as poly(1,3-phenylene)-based polyradicals (Chart 1).[12] We first investigated the stabilities of the corresponding model radicals **5** and **6**. Although **5** was not sufficiently stable to be isolated, **6** was very stable and could be isolated as radical crystals. On the basis of these results we prepared **4**. Herein we report the synthesis of **4** and its magnetic properties, along with the synthesis of **6** and its X-ray crystallographic study.

Results and discussion

Syntheses of radicals 5 and 6 and their stabilities

The preparation of **5** is shown in Scheme 1.[13] Compound **7** was prepared by the reported method.[14] Reduction of **7** with 5% Pd/C gave **8** in 97% yield, and treatment of **8** with benzyltri-

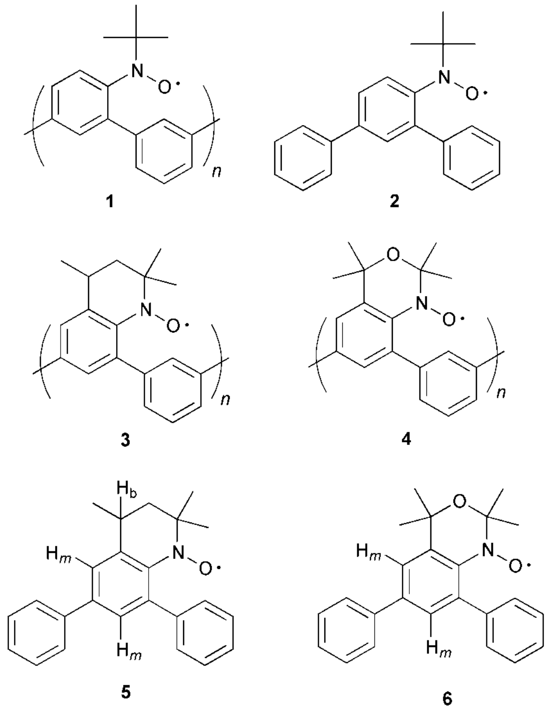
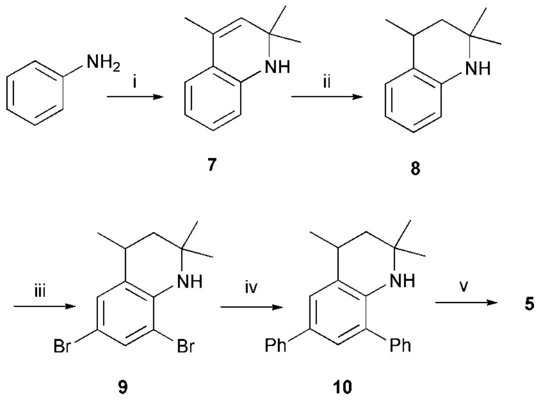


Chart 1

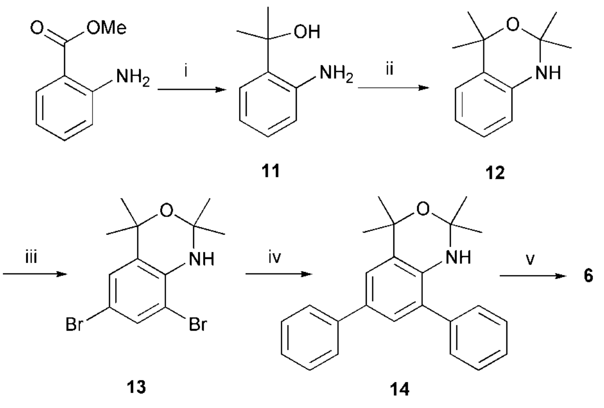


Scheme 1 *Reagents and conditions*: i, acetone, I_2, 170–175 °C; ii, H_2, 5% Pd/C; iii, $BTMABr_3$, $CaCO_3$, CH_2Cl_2–CH_3OH, room temp.; iv, $PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, benzene–EtOH–H_2O, reflux; v, MCPBA, CH_2Cl_2.

methylammonium tribromide ($BTMABr_3$)[15] gave **9** in 88% yield. The Pd-catalyzed cross-coupling reaction of **9** with two equivalents of phenylboronic acid in benzene–EtOH–H_2O gave **10** in 80% yield.[16,17] Oxidation of **10** was carried out by addition of *m*-chloroperoxybenzoic acid (MCPBA, 1.1 equiv.) to a solution of **10** in CH_2Cl_2, and the mixture was stirred for 30 min. After evaporation of CH_2Cl_2 under reduced pressure, the residue was chromatographed on alumina with CH_2Cl_2–hexane. Although flash column chromatography gave an almost pure radical solution (inspected by TLC), gradual decomposition of radical took place during concentration of the solution, and crystallization of the residue showed further decomposition. Such instability of **5** can be attributed to the presence of the benzylic hydrogen. On the basis of this result we abandoned the preparation of polyradical **3**.

In contrast, radical **6** was very stable and could be isolated as radical crystals. The preparation of **6** is shown in Scheme 2.[18] Methyl anthranilate was treated with an excess of methylmagnesium iodide to give **11** as a colorless oil in 77% yield. Amino alcohol **11** was treated with an excess of acetone at the reflux temperature in the presence of acetic acid to give **12** as colorless prisms in 86% yield. Treatment of **12** with $BTMABr_3$ gave **13** in 77% yield,[15] and Pd-catalyzed cross-coupling reaction of **13** with phenylboronic acid gave **14** in 76% yield.[16,17] Oxidation of **14** with MCPBA in CH_2Cl_2 gave **6** in 78% yield. Radical **6** was stable both in solution and in the solid, and the crystals could be stored without decomposition for a long period.

EPR spectra of **5** and **6** were measured at 20 °C using benzene as the solvent. As shown in Fig. 1(a), the spectrum of **5** is split into 1 : 2 : 1 triplets of 1 : 1 doublets of a 1 : 1 : 1 triplet. Computer simulation of this spectrum gave $a_N = 1.05$, $a_H = 0.26$ (1 H) and 0.11 mT (2 H) ($g = 2.0055$). The proton giving an a_H of 0.26 mT is assigned to the benzylic proton H_b (see Chart 1) and the two protons giving an a_H of 0.11 mT to the aromatic protons (H_m) *meta* to N–O$^\bullet$. The EPR spectrum of **6** is split into 1 : 2 : 1 triplets of a 1 : 1 : 1 triplet [Fig. 1(b)]. Computer simulation gave $a_N = 1.06$ and $a_H = 0.11$ mT (2 H) ($g = 2.0055$). The two protons giving an a_H of 0.11 mT were assigned to H_m (see Chart 1). Thus, it is obvious that the unpaired electron is considerably delocalized on the adjacent benzene ring in both radicals.



Scheme 2 *Reagents and conditions*: i, MeMgI, ether, 0 °C and then room temp.; ii, acetone AcOH, benzene, reflux; iii, $BTMABr_3$, $CaCO_3$, CH_2Cl_2–CH_3OH, room temp.; iv, $PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, EtOH–H_2O, reflux; v, MCPBA, CH_2Cl_2.

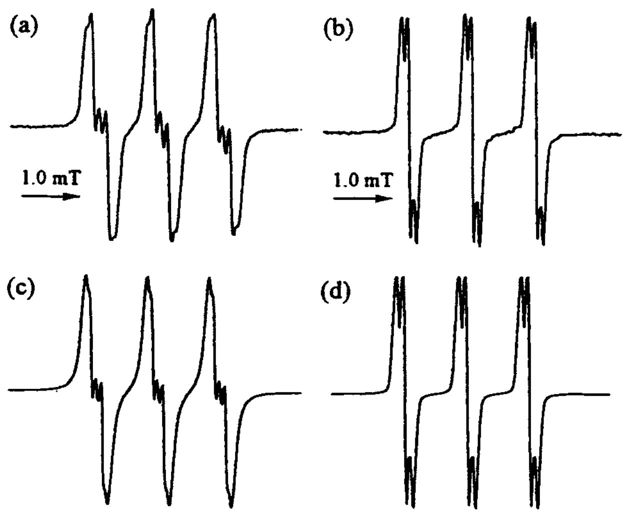


Fig. 1 EPR spectra of **5** and **6** in benzene at 20 °C. (a) Observed spectrum of **5**; (b) observed spectrum of **6**; (c) computer-simulated spectrum for **5**; (d) computer-simulated spectrum for **6**.

X-Ray crystallographic analysis of 6

Upon recrystallization from MeOH, **6** gave red prisms suitable for single crystal X-ray crystallographic analysis. The corresponding ORTEP drawing is shown in Fig. 2. The dihedral angle between the plane consisting of C1–N1–O1 and ring A (C1–C6) is 26.8°, which is much smaller than that of **2** (68.5°). On the other hand, the dihedral angles in **6** between the A and B (C7–C12) benzene rings and between the A and C (C13–C18) benzene rings are 42.4° and 53.7°, respectively, which are 14.2° and 7.8° larger than those of **2**. The latter large dihedral angle can be explained by the steric repulsions between ring C and

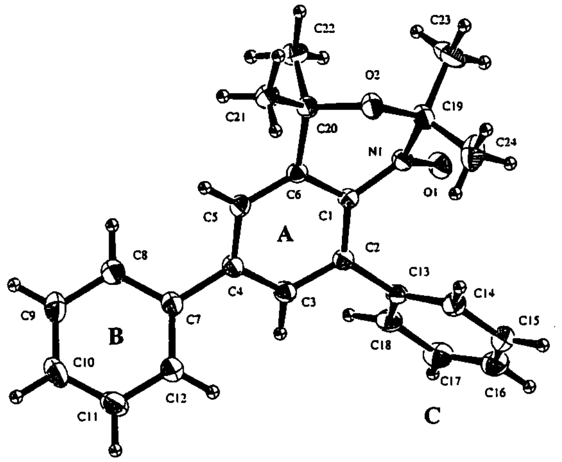


Fig. 2 ORTEP drawing of **6**. Planes A, B and C are the benzene rings comprised of C1–C6, C7–C12 and C13–C18, respectively. Selected bond lengths, bond angles and torsion angles are as follows: N1–O1 1.276(2), C1–N1 1.406(2), C19–N1 1.489(2) Å; C1–N1–O1 121.2(2), C19–N1–O1 117.0(2)°; O1–N1–C1–C2 25.1(3), O1–N1–C1–C6 −152.2(2), O1–N1–C19–O2 168.0(2)°.

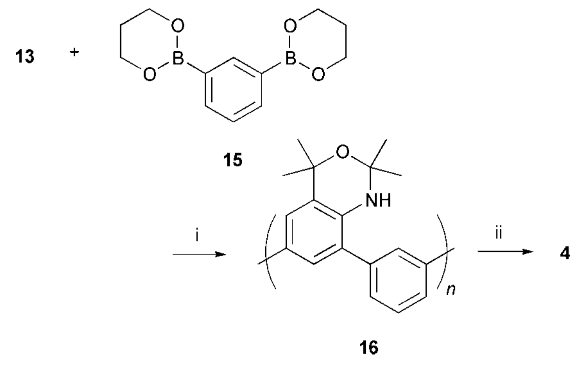
one of the two methyl groups at C19. However, the former large dihedral angle cannot be unequivocally explained. On the basis of the above X-ray crystallographic results, it is concluded that although rings B and C are considerably twisted away from ring A, the aminoxyl moiety is approximately planar with respect to ring A. Consequently, magnetic interactions between the unpaired electron spins through π-conjugation can be expected for **4**.

Synthesis and characterization of polymer 4

The synthesis of **4** is shown in Scheme 3. Precursor polymer **16** was prepared by the Pd-catalyzed cross-coupling reaction of **13** with bis(trimethylene) 1,3-phenylenediboronate (**15**).[19] A mixture of **13** (1.0 equiv.), **15** (1.3 equiv.), Bu_4NCl (5.2 equiv.), $Pd(PPh_3)_4$ (0.060 equiv.) and K_2CO_3 in H_2O–THF was refluxed with stirring for 3 days under N_2. Bu_4NCl was added as a phase-transfer catalyst. The organic layer was extracted with benzene, and the benzene extract was washed with aqueous 5 wt% NaCN to remove the catalyst. Precipitation from THF–MeOH and then THF–hexane gave **16** as a colorless powder in 60% yield. Polymer **16** was soluble in benzene, ethyl acetate, $CHCl_3$, CH_2Cl_2, and THF, but insoluble in hexane and MeOH. The number average molecular weight (M_n) of **16** determined by size exclusion chromatography (SEC) using polystyrene standards was 4000, which corresponds to 15.1 repeating units.

The ^1H and ^{13}C NMR spectra of **16** were measured using $CDCl_3$ as the solvent. In the aliphatic region of the ^1H NMR spectrum, two singlet peaks with equal intensity were observed at 1.40 and 1.62 ppm, which were assigned to two kinds of methyl protons. On the other hand, the aromatic region was very complex and assignment of the peaks was impossible. This is due to the presence of three possible kinds of connection between the repeating **16** units (head-to-tail, head-to-head, and tail-to-tail).[8] However, the 1 : 2 ratio of the integrated peak intensity of the aromatic to aliphatic protons was in agreement with the calculations (6 H : 12 H). The ^{13}C NMR spectrum showed four peaks in the range of 29–82 ppm and they were assigned to the methyl carbons. In contrast, the aromatic region was complex, as in the ^1H NMR spectrum, and no aromatic carbon could be assigned. In the head-to-head connection the magnetic interaction may be considerably weakened due to twisting from steric congestion.

Elemental analysis of **16** gave C, 81.16; H, 7.09; N, 5.15; Br, 1.34%, showing the presence of a small amount of Br. Thus, it is suggested that the polycondensation is in part terminated by the unit of **13**. Since the values calculated by taking into account the presence of Br at 1.34% are 80.38 (C), 7.12 (H) and 5.21% (N), the observed C percentage deviates by 0.78% from calculation. We assume that this is due to the influence of the polymer end structure.



Scheme 3 *Reagents and conditions*: i, $Pd(PPh_3)_4$, K_2CO_3, Bu_4NCl, THF–H_2O, reflux; ii, MCPBA, CH_2Cl_2.

Oxidation of polymer 16

Oxidation of **16** was carried out with MCPBA in CH_2Cl_2. 1.1 Equivalents of MCPBA (per mol of **16**) were added to a colorless CH_2Cl_2 solution of **16** and the mixture was stirred at room temperature for 30 minutes under N_2. After the resulting red solution had been washed with aqueous Na_2CO_3 and brine, the mixture was poured into a large excess of hexane to give **4** as a light red powder in 37% yield. The polyradical was soluble in benzene, CH_2Cl_2, $CHCl_3$, and THF, but insoluble in hexane and MeOH.

The IR spectrum of **4** showed complete disappearance of the peak due to NH observed for **16**. The M_n determined by SEC was 4120, which agreed with that of **16** (4000), indicating that no cleavage or bridging of the polymer chain had occurred during oxidation with MCPBA.

The spin concentrations of **4** were determined by EPR using 1,3,5-triphenylverdazyl as the reference and using the same solvent, EPR tube and EPR settings. The spin concentrations depended on the amounts of MCPBA added. When the molar amount of MCPBA was 1.1 equiv., the spin concentrations were in the range 1.40×10^{21} (0.65 spin per repeating unit) to 1.61×10^{21} spin g^{-1} (0.75). However, a large amount of MCPBA or a small amount of MCPBA decreased the spin concentration of the resulting polyradicals. The appropriate amount of MCPBA was *ca.* 1.1 equiv. per repeating unit of **16**.

EPR and UV–VIS spectra of 4

The EPR spectrum of **4** in benzene gave a simple singlet peak with with a peak-to-peak line width of 0.64 mT ($g = 2.0056$), and the hyperfine couplings due to nitrogen and protons were completely smeared out. Such a phenomenon is often observed for polyradicals with a high spin concentration and can be explained in terms of the occurrence of exchange narrowing.

UV–VIS spectra of polyradical **4**, model monoradical **6** and precursor polymer **16** were measured using CH_2Cl_2 as the solvent (Fig. 3). Precursor polymer **16** showed absorption peaks at 231 (ε 20300 mol^{-1} dm^3 cm^{-1}) and 296 nm (17200). On the other hand, polyradical **4** showed absorption peaks at 234 (ε 20000 mol^{-1} dm^3 cm^{-1}), 337 (10900), and 498 nm (310), which are very similar to those of **6** [236 (ε 18800 mol^{-1} dm^3 cm^{-1}), 335 (20700), 495 nm (435)]. The absorptions with a low absorption coefficient at 498 (**4**) and 495 nm (**6**) are characteristic of aminoxyl radicals, and are not observed in the UV–VIS spectrum of **16**.

Glass matrix EPR measurements of polyradical

Glass matrix EPR measurements were carried out for the polyradical **4** using toluene as the matrix at 5–70 K. Under these conditions intermolecular through-space (usually antiferromagnetic) interactions are negligible. As shown in the inset

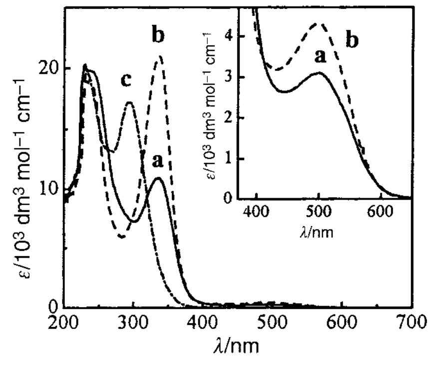


Fig. 3 UV–VIS spectra of (a) **4**, (b) **6** and (c) **16** in CH_2Cl_2. The absorption coefficient ε for **4** has been corrected for the spin concentration determined by EPR spectroscopy. The inset shows an expansion of the visible region.

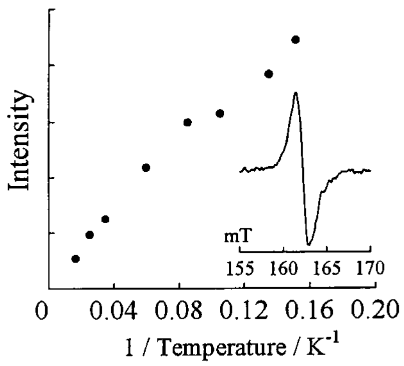


Fig. 4 Plots of intensity of absorption due to the $\Delta M_s = 2$ forbidden transition against T^{-1}. The inset shows the EPR spectrum of **4** at 163 mT in a toluene glass matrix at 5.5 K.

of Fig. 4, a clear absorption peak due to the $\Delta M_s = 2$ forbidden transition was observed at the $g = 4$ region. The $\Delta M_s = 2$ forbidden signal was measured in the temperature range 5 to 70 K, and a Curie plot of the signal intensity *versus* $1/T$ was drawn. As shown in Fig. 4, a linear relationship was observed, suggesting that **4** is in a triplet ground state or a nearly degenerate singlet–triplet state.

SQUID measurements of polyradical

Magnetic susceptibility measurements on **4** were carried out with a SQUID at 1.8–300 K. The diamagnetic contribution from the sample was estimated from Pascal's constants.

The χT *versus* T plots for **4** with a spin concentration of 0.75 per repeating unit ($M_n = 4120$) are shown in Fig. 5. In the high temperature region the χT value is constant, giving 0.27 emu K mol^{-1} as the Curie constant [eqn. (1)].

$$C = N\mu_B^2 g^2 S(S+1)/3k \qquad (1)$$

From this value the spin concentration of **4** [eqn. (2)] was estimated to be 0.72 spin per repeating unit, in agreement with that (0.75 spin per repeating unit) determined by EPR.

$$\chi = \frac{N\mu_B^2 g^2 S(S+1)}{3k}\frac{1}{T-\theta} \qquad (2)$$

$$\frac{1}{\chi} = \frac{T-\theta}{C} \qquad (3)$$

The χT value was constant in the temperature range 300–20 K and decreased with decreasing temperature below 20 K, indicating that the magnetic interactions are antiferromagnetic. To estimate the magnitude of the antiferromagnetic interaction, the χ^{-1} values were plotted against T [eqn. (3)], and the Weiss temperature (θ) was determined to be -1.1 K (Fig. 5). Since in the glass matrix EPR measurements the sample is diluted with toluene, intermolecular through-space (usually) antiferromagnetic interaction is removed. On the other hand, in the SQUID measurements the intermolecular antiferromagnetic through-space interaction appears because bulk samples are used. If the through-bond interactions are weak, this will be masked by the intermolecular through-space antiferromagnetic interaction. Such a situation represents the present case. It is therefore strongly suggested that, even if **4** is in a triplet or higher spin ground state, the ferromagnetic interactions through π-conjugation are weak or very weak.

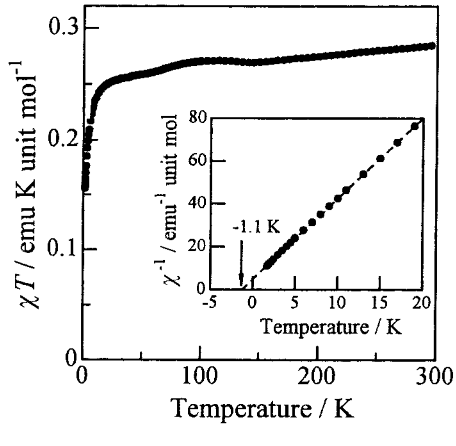


Fig. 5 χT *vs.* T plot for **4** in bulk. The inset shows plots of χ^{-1} *vs.* T.

Conclusion

A poly(1,3-phenylene)-based polyradical carrying cyclic aminoxyls with a spin concentration of up to 75% per repeating unit was prepared by Pd-catalyzed cross-coupling of **13** and **15**, followed by oxidation with MCPBA. In toluene glass matrix EPR measurements the polyradical showed an absorption peak due to the $\Delta M_s = 2$ forbidden transition in the $g = 4$ region. The Curie plots of the signal intensity *versus* $1/T$ suggested that **4** is in a triplet ground state or a nearly degenerate singlet–triplet state.

Experimental

Materials

1,2-Dihydro-2,2,4-trimethylquinoline (**7**),[14] benzyltrimethylammonium tribromide ($BTMABr_3$),[15] bis(trimethylene) 1,3-phenylenediboronate (**15**),[19] phenylboronic acid[20] and $Pd(PPh_3)_4$[21] were prepared according to the reported methods. Methyl anthranilate, *m*-chloroperoxybenzoic acid (MCPBA, purity ~ 70 wt%), CH_3I, and Bu_4NCl were commercial grade. 2,2,4,4-Tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazine **12** was prepared by reaction of methyl anthranilate with MeMgI, and subsequent treatment with acetone based on the procedures reported by Rassat *et al.*.[18] Silica gel and alumina column chromatography was carried out on Fiji Silysia BH-127ZH silica gel and Merck aluminium oxide 90.

Instruments

FT-IR spectra were run on a JASCO FT/IR-230 spectrometer. UV–VIS spectra were obtained with a Shimadzu UV-2200 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a JEOL α-400 spectrometer (400 MHz) with Me_4Si as the internal reference; *J* values are given in Hz. EPR spectra were measured with a Bruker ESP 300 spectrometer operated at the X band. The spin concentrations were determined by the double integrated EPR spectra of the sample in benzene. The calibration curve was drawn with 1,3,5-triphenylverdazyl solutions using the same EPR cell, solvent and instrument settings as for the sample measurements. SEC was recorded with a Tosoh 8020 series instrument using TSK-gel G5000HHR, GMutiporeHXL-M, and GMHHR-L columns calibrated with polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020. Magnetic susceptibility measurements were carried out on a Quantum Design SQUID MPMS2 system in the temperature range 1.8–300 K. The diamagnetic contribution of the sample was estimated from Pascal's diamagnetic constants.

1,2,3,4-Tetrahydro-2,2,4-trimethylquinoline 8

H_2 was bubbled into a stirred mixture of **7** (8.66 g, 50 mmol) and Pd/C(5 wt%, 2.13 g) in EtOH (100 cm^3) at room temperature until the complete disappearance of **7** (*ca.* 5 h). Filtration and evaporation of the reaction mixture gave **8** as a light yellow oil in 97% yield.

6,8-Dibromo-1,2,3,4-tetrahydro-2,2,4-trimethylquinoline 9

To a solution of 1,2,3,4-tetrahydro-2,2,4-trimethylquinoline (5.26 g, 30.0 mmol) in CH_2Cl_2 (150 cm^3)–MeOH (60 cm^3) were added BTMABr$_3$ (25.74 g, 66.0 mmol) and $CaCO_3$ powder (6.60 g, 66.0 mmol) at room temperature. After the mixture was stirred for 30 min, the $CaCO_3$ powder and solvent were removed, and an aqueous 10% $NaHSO_3$ solution (100 cm^3) was added. The aqueous solution was extracted with ether, and the ether layer was washed with water and dried ($MgSO_4$). After evaporation under reduced pressure, the residue was recrystallized from EtOH to give **9** in 88% yield (8.79 g, 26.4 mmol) as colorless prisms with mp 71–72 °C. ν_{max}(KBr)/cm^{-1} 3400 (NH); δ_H ($CDCl_3$) 1.18 (3 H, s, CH_3), 1.31 (3 H, s, CH_3), 1.33 (3 H, d, *J* 6.3, CH_3), 1.41 (1 H, dd, both *J* 12.7, C**H**H), 1.74 (1 H, ddd, *J* 12.9, 5.3 and 2.0, CH**H**), 2.92 (1 H, dqd, *J* 12.9, 6.3 and 5.3, CH), 4.26 (1 H, s, NH), 7.20 (1 H, s, ArH), 7.37 (1 H, d, *J* 2.0, ArH) (Found: C, 43.41; H, 4.54; N, 4.23. $C_{12}H_{15}Br_2N$ requires C, 43.27; H, 4.54; N, 4.21%).

6,8-Diphenyl-1,2,3,4-tetrahydro-2,2,4-trimethylquinoline 10

To a solution of **9** (1.00 g, 3.00 mmol) in benzene (45 cm^3) were added a solution of phenylboronic acid (1.10 g, 9.00 mmol) in EtOH (4.5 cm^3), an aqueous 2 M K_2CO_3 solution (9 cm^3), and $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol). After the resulting heterogeneous mixture had been purged with nitrogen, it was gently refluxed for 24 h with stirring under N_2. After cooling, the organic layer was separated, and the aqueous solution was extracted with benzene. The combined benzene solutions were dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed on silica gel with CH_2Cl_2–hexane (1 : 3) as the eluant to give **10** in 80% yield (0.790 g, 2.41 mmol). Mp 96–97 °C; ν_{max}(KBr)/cm^{-1} 3400 (NH); UV–VIS (CH_2Cl_2) λ_{max} 231 (ε 26000 mol^{-1} dm^3 cm^{-1}) and 304 nm (21200); δ_H ($CDCl_3$) 1.17 (6 H, s, CH_3), 1.45 (3 H, d, *J* 6.3, CH_3), 1.51 (1 H, dd, both *J* 12.7, C**H**H), 1.78 (1 H, dd, *J* 13.2 and 5.4, CH**H**), 3.04 (1 H, dqd, *J* 12.7, 6.3 and 5.4, CH), 4.00 (s, NH, 1H), 7.21 (1 H, d, *J* 2.0, ArH), 7.24 (1 H, d, *J* 2.0, ArH), 7.37 (3 H, t, *J* 7.8, ArH), 7.43–7.47 (5 H, m, ArH), 7.56 (2 H, d, *J* 7.8, ArH); δ_H ($CDCl_3$) 20.50, 28.07, 28.21, 31.44, 44.24, 49.37, 124.87, 125.72, 125.85, 126.31, 126.58, 126.97, 127.09, 128.55, 128.85, 128.90, 129.39, 139.74, 140.20, 141.62 (Found: C, 87.94; H, 7.72; N, 4.25. $C_{24}H_{25}N$ requires C, 88.03; H, 7.70; N, 4.28%).

Oxidation of 10

MCPBA (0.52 g) was added to a solution of **10** (0.33 g, 1.00 mmol) in CH_2Cl_2 (30 cm^3), and the mixture was stirred for 30 min under N_2. After evaporation under reduced pressure, the residue was quickly chromatographed on alumina gel with CH_2Cl_2–hexane (1 : 1). During concentration of the eluate with an evaporator under reduced pressure, **5** was partially decomposed. Crystallization of the residue resulted in further decomposition.

2-(2-Hydroxypropan-2-yl)aniline 11

A solution of 17.5 g (120 mmol) of methyl anthranilate in 100 cm^3 dry ether was added dropwise at 0 °C to a solution of MeMgI in 300 cm^3 of dry ether (prepared from 12.6 g of Mg and 480 mmol of CH_3I) and the mixture was stirred for 1 h at room temperature. The usual work-up and chromatography on silica gel with 3 : 1–benzene–ethyl acetate gave **11** in 77% yield (13.9 g, 91.9 mmol) as a colorless oil. δ_H ($CDCl_3$) 1.63 (6 H, s, CH_3), 2.24 (1 H, br s, OH), 4.62 (2 H, br s, NH_2), 6.61 (1 H, d, *J* 7.8, ArH), 6.67 (1 H, t, *J* 7.8, ArH), 7.05 (1 H, t, *J* 7.8, ArH), 7.10 (1 H, d, *J* 7.8, ArH).

2,2,4,4-Tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazine 12

To a solution of 17.6 g (116 mmol) of **11** in 260 cm^3 benzene were added 17.3 cm^3 (229 mmol) acetone and 10.2 cm^3 (176 mmol) of CH_3COOH at room temperature. The mixture was then refluxed for 5.5 h using Dean–Stark apparatus and cooled. After 5% $NaHCO_3$ (180 cm^3) had been added, the mixture was washed with brine, dried, and evaporated, and the residue was chromatographed on silica gel with 3 : 1 benzene–ethyl acetate to give **12** in 86% yield (9.49 g, 99 mmol) as colorless prisms with mp 67–68 °C. δ_H ($CDCl_3$) 1.45 (6 H, s, CH_3), 1.54 (6 H, s, CH_3), 3.84 (1 H, br s, NH), 6.62 (1 H, d, *J* 7.8, ArH), 6.82 (1 H, t, *J* 7.8, ArH), 7.06 (1 H, t, *J* 7.8, ArH), 7.07 (1 H, d, *J* 7.8, ArH).

6,8-Dibromo-2,2,4,4-tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazine 13

To a solution of 5.00 g (26.0 mmol) of **12** in CH_2Cl_2 (150 cm^3)–MeOH (60 cm^3) were added 22.2 g (58.0 mmol) of BTMABr$_3$ and 7.0 g (70 mmol) of $CaCO_3$ powder at room temperature. After the mixture had been stirred for 1.5 h, $CaCO_3$ powder was removed by filtration and the filtrate was evaporated under reduced pressure. Aqueous 10% $NaHSO_3$ (120 cm^3) was added and the mixture was extracted with CH_2Cl_2 and dried ($MgSO_4$). After filtration and evaporation, the residue was chromatographed on silica gel with benzene to give **13** in 77% yield (7.00 g, 20.1 mmol) as colorless prisms with mp 55–57 °C. ν_{max}(KBr)/cm^{-1} 3380 (NH); δ_H ($CDCl_3$) 1.45 (6 H, s, CH_3), 1.52 (6 H, s, CH_3), 4.48 (1 H, s, NH), 7.12 (1 H, d, *J* 2.0, ArH), 7.44 (1 H, d, *J* 2.0, ArH) (Found: C, 41.23; H, 4.17; N, 3.95. $C_{12}H_{15}Br_2NO$ requires C, 41.29; H, 4.33; N, 4.01%).

6,8-Diphenyl-2,2,4,4-tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazine 14

To a solution 1.75 g (5.00 mmol) of **13** in 75 cm^3 benzene were added a solution of 1.85 g (15.0 mmol) of phenylboronic acid in 7.5 cm^3 of EtOH, 15 cm^3 of aqueous 2 M K_2CO_3, and 0.35 g (0.30 mmol) of $Pd(PPh_3)_4$. After the resulting heterogeneous mixture had been purged with N_2, it was gently refluxed for 24 h with stirring under N_2. After cooling, the organic layer was separated, and the aqueous layer was extracted with benzene. After the combined benzene layers had been dried ($MgSO_4$) and evaporated under reduced pressure, the residue was chromatographed on silica gel with benzene to give **14** in 76% yield (1.30 g, 3.79 mmol) as colorless needles with mp 150–151 °C. ν_{max}(KBr)/cm^{-1} 3370 (NH); δ_H ($CDCl_3$) 1.41 (6 H, s, CH_3), 1.65 (6 H, s, CH_3), 4.23 (1 H, s, NH), 7.25–7.32 (3 H, m, ArH), 7.41 (3 H, t, *J* 7.8, ArH), 7.47–7.48 (4 H, m, ArH), 7.58 (2 H, d, *J* 8.3, ArH); δ_C ($CDCl_3$) 29.25, 31.93, 74.14, 82.00, 123.04, 126.40, 126.51, 127.00, 127.42, 128.57, 128.68, 128.98, 129.23, 130.51, 131.23, 137.17, 138.69, 141.19 (Found: C, 84.10; H, 7.32; N, 4.02. $C_{24}H_{25}NO$ requires C, 83.93; H, 7.34; N, 4.08%).

6,8-Diphenyl-2,2,4,4-tetramethyl-1,4-dihydro-2*H*-3,1-benzoxazin-1-yloxyl 6

To a solution of 0.17 g (0.50 mmol) of **14** in 20 cm^3 of CH_2Cl_2 was added 0.13 g of MCPBA and the mixture was stirred for 30 min under N_2. After evaporation under reduced pressure, the residue was chromatographed on alumina gel with benzene–ethyl acetate (5 : 1), giving pure **6** in 78% yield (0.14 g, 0.39 mmol). Recrystallization from MeOH gave **4** as red prisms with mp 151–153 °C (Found: C, 80.20; H, 6.71; N, 3.85. $C_{24}H_{24}NO_2$ requires C, 80.42; H, 6.75; N, 3.91%).

Pd-Catalyzed polycondensation of 13 with 15

To a solution of 2.09 g (6.00 mmol) of **13** in 62.4 cm^3 of THF were added 1.92 g (7.80 mmol) of **15**, 62 cm^3 of aqueous 1 M

K_2CO_3, 8.67 g (31.2 mmol) of Bu_4NCl, and 0.42 g (0.36 mmol) of $Pd(PPh_3)_4$. After the resulting heterogeneous mixture had been purged with N_2, it was gently refluxed for three days, with stirring, under N_2. After cooling, the organic layer was extracted with benzene, and the benzene extract was washed with aqueous 5 wt% NaCN and brine, and dried ($MgSO_4$). After evaporation under reduced pressure, the residue was reprecipitated from THF (30 cm^3)–MeOH (300 cm^3) and THF (30 cm^3)–hexane (300 cm^3) to give **16** in 60% yield (0.95 g) as a colorless powder. ν_{max}(KBr)/cm^{-1} 3380 (NH); δ_H ($CDCl_3$) 1.40 (6 H, s, CH_3), 1.62 (6 H, s, CH_3), 4.29 (1 H, br s, NH), 7.34–7.69 (6 H, m, ArH); δ_C ($CDCl_3$) 29.28, 31.97, 74.14, 82.00, 123.29, 125.01, 125.56, 126.49, 127.14, 128.19, 128.44, 128.68, 129.00, 129.98, 130.20, 130.58, 130.79, 131.46, 131.69, 137.19, 139.59, 141.85; SEC (THF) $M_n = 4000$ ($n = 15.1$), $M_w/M_n = 1.35$ (Found: C, 81.16; H, 7.09; N, 5.15; Br, 1.34. $(C_{18}H_{19}NO)_n$ requires C, 81.47; H, 7.22; N, 5.28%).

Oxidation of 16

To a solution of 0.10 g of **16** in 30 cm^3 of CH_2Cl_2 was added 0.10 g of MCPBA and the mixture was stirred for 30 min under N_2. After the resulting solution had been washed with aqueous 10 wt% Na_2CO_3 and brine, it was dried over $MgSO_4$. After filtration, the filtrate was poured into a large excess of hexane, and the light red powder deposited was collected by filtration and dried *in vacuo* to give **4** in 37% yield (0.040 g) as a light red powder.

Crystallographic determination of 6

Crystal data: $C_{24}H_{24}NO_2$, $M = 358.46$, monoclinic, $a = 18.724(4)$, $b = 12.034(4)$, $c = 17.318(5)$ Å, $\beta = 96.80$ (2)°, $V = 3874$ (1) $Å^3$, $T = 23 \pm 1$ °C, space group $C2/c$, $Z = 4$, $\rho_c = 0.614$ g cm^{-3}, $F(000) = 764$ and $\mu(M_o\text{-}K_\alpha) = 0.39$ cm^{-1}. Of the 4608 reflections measured, 4459 were unique ($R_{int} = 0.009$), 2721 of which were considered as observed ($I > 3\sigma(I)$).

The structure was solved by direct methods[22] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at calculated positions and not refined. The final cycle of full-matrix least-squares refinement was based on 2721 reflections and 245 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.041$ and $R_w = 0.037$. GOF = 1.64.CCDC reference number 1145/277. See http://www.rsc.org/suppdata/jm/b1/b100060h/ for crystallographic files in .cif format.

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