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Synthesis and magnetic behaviour of poly(1,3-phenylene)-based polyradical carrying *N*-*tert*-butylaminoxyl radicals

Hiroyuki Oka,[a] **Tomoki Tamura,**[a] **Yozo Miura***[a] **and Yoshio Teki**[b]

[a]*Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558–8585, Japan*
[b]*Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558–8585, Japan*

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The synthesis and magnetic behaviour of poly[6-(*N*-oxyl-*N*-*tert*-butylamino)biphenyl-3,3′-ylene] **2** are described. Polyradical **2** was prepared by the Pd-catalyzed polycondensation of *N*-*tert*-butyl-2,4-dibromoaniline and 1,3-phenylenebis(trimethylene boronate), followed by oxidation with 3-chloroperoxybenzoic acid. The degree of polymerisation determined by SEC (size exclusion chromatography) was ~18. Polyradical **2** was stable in both solution and the solid state. The spin concentrations of **2** determined by EPR and SQUID were 0.75 and 0.82 spin per repeating unit, respectively. Magnetic susceptibility (χ) measurements on **2** were carried out on a SQUID magnetometer and these showed that the magnetic interaction between the unpaired electron spins was antiferromagnetic ($\theta = -0.98$ K). The fact that no ferromagnetic interaction was observed was ascribed to a twisting of the nitroxide moieties from the π-conjugated main chain, and this was confirmed by X-ray crystallographic analysis of the corresponding model monoradical, *N*-*tert*-butyl-*N*-(2,4-diphenylphenyl)aminoxyl.

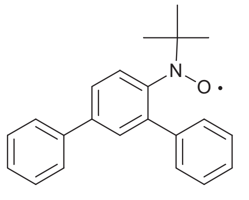
The potential of organic ferromagnetism has stimulated recent interest in polyradicals, and a wide variety of π-conjugated spin systems has been investigated.[1] Intramolecular ferromagnetic interaction through π-conjugation is considered crucial for ferromagnetism. Thus, a wide variety of theoretical and experimental studies has been done on π-conjugated systems,[2] and the 1,3-phenylene unit has been shown to be the best ferromagnetic coupler.[3] Many 1,3-phenylene connected polycarbenes[4] and 1,3-phenylene connected poly(triarylmethyl polyradical)s[5] have been synthesized by stepwise methods, and it has been shown that the polycarbenes and poly(triarylmethyl polyradical)s are in high-spin ground states. However, since their spin centers are in the main chains, failure in generation of the carbene or radical species, or their decomposition, leads to interruption of π-conjugation. Furthermore, carbene is unstable at room temperature, and triarylmethyl radicals are not stable in the presence of oxygen.

In the present study we report the first synthesis of a poly(1,3-phenylene)-based polynitroxide. We prepared **2** with a high spin concentration by the palladium-catalyzed polycondensation[6–8] of *N*-*tert*-butyl-2,4-dihaloaniline **3** with 1,3-phenylenebis(trimethylene boronate) **5**, followed by oxidation. Although a variety of polyradicals including poly(phenylacetylene)-,[9] poly(1,3-phenyleneethynylene)-,[10] and poly(phenylenevinylene)-based polyradicals[11] have been prepared, poly(1,3-phenylene)-based polyradicals have never been reported. Since polyradical **2** has its spin centers in the side chain, the absence of some spin centers does not result in interruption of π-conjugation.

Results and discussion

Design of polyradicals

Synthesis of high spin organic molecules is aimed at topological symmetry,[2] and, with this in mind, we can draw three structures for poly(1,3-phenylene)-based polyradicals (A, B and C, in Fig. 1). Since the radical groups are substituted at the 2- or 6-position to the 1,3-phenylene coupler, the polyradicals have a nondisjoint structure favourable to induction of a strong ferromagnetic interaction between the unpaired electron spins.[12] In the structure A, all radical groups are at the 2-position, and in the structure C, half of the radical groups are at the 2-positions. Since the 2-position is surrounded by the neighboring two 1,3-phenylene couplers, serious steric congestion is anticipated at this position. This steric congestion may lead to significant twisting of the radical group from the poly(1,3-phenylene) π-conjugated system if the radical groups are bulky like *N*-*tert*-butylaminoxyl. This may weaken the strong ferromagnetic interaction between the unpaired electrons through π-conjugation. We therefore decided to prepare a polyradical having structure B.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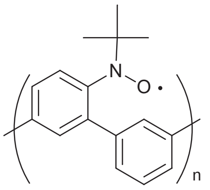

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Synthesis of monoradical 1

Monoradical **1** was synthesized according to Scheme 1. Treatment of *N*-*tert*-butylaniline[13] with two equiv. of benzyltrimethylammonium tribromide ($BTMABr_3$)[14] in CH_2Cl_2–MeOH gave **3a** in 93% yield as a colorless oil. The corresponding tribromo compound was not observed even with excess $BTMABr_3$ (3.3 equiv.). This is probably due to the presence of a bulky *N*-*tert*-butyl group. The Pd-catalyzed cross-coupling reaction of **3a** with phenylboronic acid in benzene–H_2O at reflux temperature for 24 h under nitrogen gave **4** in 85% yield. In the IR spectrum of **4** an absorption peak due to νNH was observed at 3415 cm^{-1}. Although the ^1H NMR spectrum was very complex, the ^{13}C NMR spectrum gave the expected 2 and 14 peaks in the aliphatic and aromatic regions, respectively. Elemental analysis also confirmed our expectations.

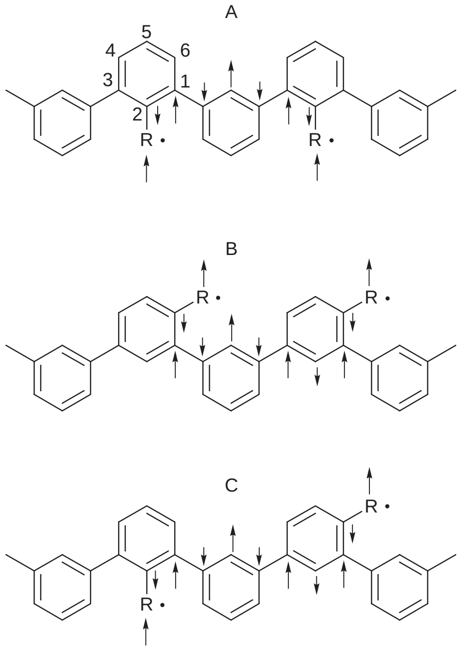
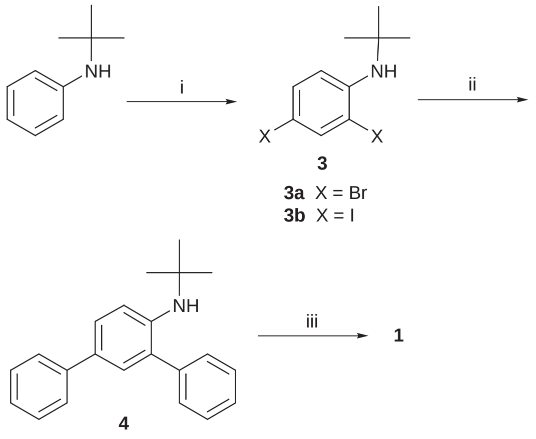


Fig. 1 Structures of poly(1,3-phenylene)-based polyradicals.

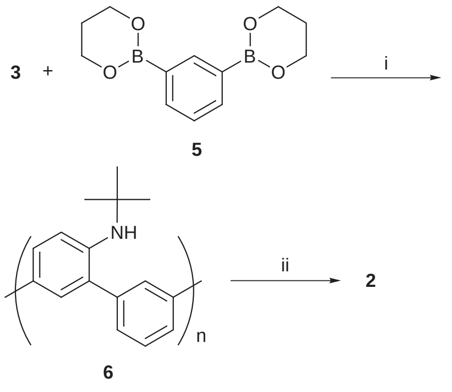
A solution of **4** and 3-chloroperoxybenzoic acid in CH_2Cl_2 was stirred for 30 min at room temperature and, after evaporation, the residue was chromatographed on silica gel with CH_2Cl_2–hexane (1:5) as the eluant to give **1** in 70% yield. Recrystallization from hexane gave deep red prisms with mp 94–96 °C. The IR spectrum showed the complete disappearance of an absorption peak due to νNH at 3415 cm^{-1}, and the elemental analysis was satisfactory. The purity of the radical determined by EPR was ~100%. Monoradical **1** was very stable in both solution and solid state over a long period.

Synthesis of polymer 6

Polymer **6** was prepared by the Pd-catalyzed polycondensation of **3** with 1,3-phenylenebis(trimethylene boronate) **5** (Scheme 2).[15] A mixture of **3**, **5**, $Pd(PPh_3)_4$, K_2CO_3 and Bu_4NCl was refluxed in benzene, toluene or DMF–H_2O at 80–110 °C under nitrogen. Bu_4NCl was added as a phase transfer catalyst.[16] After 3–7 days, the organic layer was separated, concentrated, and chromatographed on silica gel. Elution with benzene gave low molecular weight materials containing catalysts, and elution with ethyl acetate gave polymer **6**. The molecular weight (M_n) of **6** was determined by SEC with polystyrene standard in THF. Reprecipitation of the polymer from CH_2Cl_2–hexane gave a light yellow powder. The results of polycondensation are summarized in Table 1.



Scheme 1 *Reagents and conditions*: i, $BTMABr_3$ or $BTMAICl_2$, $CaCO_3$, CH_2Cl_2–MeOH, room temp; ii, $C_6H_5B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, benzene–H_2O, reflux; iii, $3\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, room temp.



Scheme 2 *Reagents and conditions*: i, $Pd(PPh_3)_4$, K_2CO_3, Bu_4NCl, benzene–H_2O, reflux; ii, $3\text{-}ClC_6H_4CO_3H$, CH_2Cl_2, room temp.

As shown in Table 1, the polycondensation of dibromo compound **3a** with **5** gave a higher molecular weight material than that from the diiodo compound **3b**. To examine solvent effects on the molecular weights of polymers obtained, the polycondensations were carried out in benzene–H_2O, toluene–H_2O and DMF–H_2O, and the highest molecular weight polymer was obtained in benzene–H_2O. Furthermore, the polycondensations were carried out in different ratios of **5**/**3** (0.77, 1.0 and 1.3) and, when the ratio was 1.3, the highest molecular weight polymer was obtained. Polymer **6** was soluble in benzene, $CHCl_3$, CH_2Cl_2 and THF, but insoluble in MeOH, hexane and acetone.

The IR spectrum of **6** showed an absorption peak due to νNH at 3417 cm^{-1}. In the ^1H NMR spectrum the aromatic region (7.0–7.8 ppm) was complex and assignment was difficult, but a singlet due to the *t*-Bu group and a broad singlet due to NH were observed at 1.30 and 4.08 ppm, respectively. Furthermore, no signals due to the trimethylene in the boronate were observed. The ^{13}C NMR spectrum was also complex in the aromatic region (115–145 ppm), possibly arising from head-to-tail, head-to-head and tail-to-tail connections between **3** and **5** (Fig. 2). However, the magnetic behavior of **2** should not be seriously affected because topological symmetry indicates that all these connections would give intramolecular ferromagnetic interactions although steric strain in the head-to-head connection may reduce the effective π-conjugation.

The elemental analysis of **6** showed the presence of bromine (3.24%). This indicates that the polycondensation is terminated by bromine. Accordingly, the observed values (C, 83.23; H, 7.36; N, 5.24; Br, 3.24%) were not in satisfactory agreement with the calculations [C, 86.06; H, 7.67; N, 6.27% for $(C_{16}H_{17}N)_n$]. However, taking the presence of bromine of 3.24% into account, the observed results give satisfactory agreement with the calculations. For example, polymer **7** gave C, 83.41; H, 7.48; N, 6.18; Br, 2.94%, and polymer **8** gave C, 83.31; H, 7.47; N, 6.07; Br, 3.15%. Polymer **8** may be formed by deboronation of **9**.

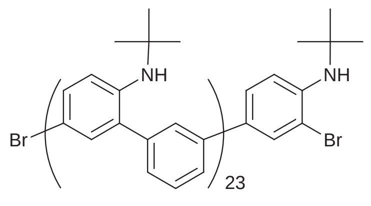
Oxidation of 6

Oxidation of **6** was carried out with 3-chloroperoxybenzoic acid in the same manner as for **1** (Scheme 2). A solution of **6** and 3-chloroperoxybenzoic acid in CH_2Cl_2 was stirred for 30 minutes at room temperature and the light red mixture was washed with an aqueous Na_2CO_3 (10%) solution and brine, and dried ($MgSO_4$). After concentration, the residue was reprecipitated from CH_2Cl_2–hexane to give **2** as a light red

Table 1 Results of the Pd-catalyzed polycondensation of **3** with **5**

Run	3	5/3	Solvent	T/°C	t/d	Yield (%)[a]	M_n[b]	M_w[b]	M_w/M_n[b]	DP
1[c]	**3a**	1.0	benzene	80	3	36	1320	2210	1.67	5.9
2[c]	**3b**	1.0	benzene	80	3	30	1050	1690	1.61	4.7
3[c]	**3a**	1.0	toluene	110	3	45	1030	1670	1.62	4.6
4[c]	**3a**	1.0	DMF	100	3	43	700	1020	1.46	3.1
5[d]	**3a**	0.77	benzene	80	3	29	1200	1750	1.46	5.4
6[e]	**3a**	1.3	benzene	80	3	31	2470	3760	1.52	11.1
7[e]	**3a**	1.3	benzene	80	7	18	4070	5960	1.46	18.2

[a] Yield after reprecipitation from CH_2Cl_2–hexane. [b] Determined by SEC. [c] **3**, 2.0 mmol; **5**, 2.0 mmol, $Pd(PPh_3)_4$, 0.12 mmol; K_2CO_3, 8.0 mmol; Bu_4NCl, 5.3 mmol; solvent, organic solvent (20 cm^3)–H_2O (4.0 cm^3). [d] **3**, 2.0 mmol; **5**, 1.5 mmol, $Pd(PPh_3)_4$, 0.12 mmol; K_2CO_3, 6.0 mmol; Bu_4NCl, 4.0 mmol; solvent, benzene (15 cm^3)–H_2O (3.0 cm^3). [e] **3**, 2.0 mmol; **5**, 2.6 mmol, $Pd(PPh_3)_4$, 0.12 mmol; K_2CO_3, 10.4 mmol; Bu_4NCl, 6.9 mmol; solvent, benzene (26 cm^3)–H_2O (5.2 cm^3).



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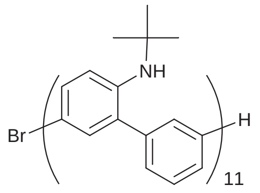

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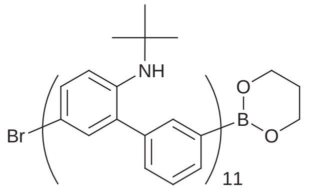

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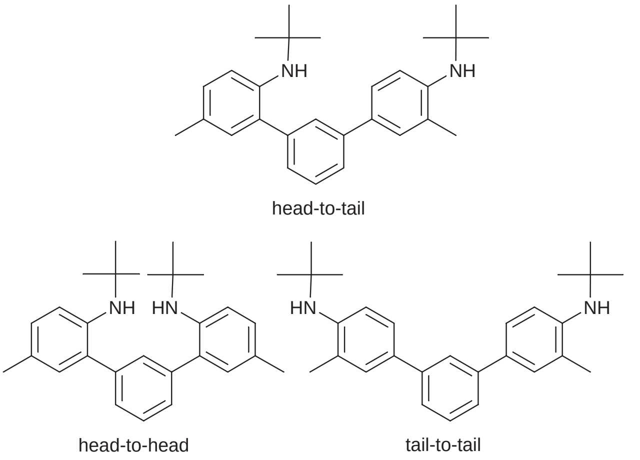

Fig. 2 Three kinds of connection between monomers in polymer **6**.

powder in 50% yield. Polyradical **2** was soluble in organic solvents such as benzene, CH_2Cl_2, $CHCl_3$ and THF. The IR spectrum of **2** indicated the complete disappearance of the absorption peak due to νNH at 3417 cm^{-1} observed for **6**.

The spin concentration of **2** was determined by EPR. When the mole ratio of the 3-chloroperoxybenzoic acid to **6** was 1.0–1.3, the spin concentration was 1.89×10^{21} spins g^{-1} (0.75 spin per repeating unit). On the other hand, when a greater or lesser amount of 3-chloroperoxybenzoic acid was used, the spin concentrations were lower. In the use of a lesser amount of 3-chloroperoxybenzoic acid a strong absorption peak due to νNH was observed in the IR spectrum of the polyradical obtained, and in the case of a greater amount of 3-chloroperoxybenzoic acid the colour of the polyradical obtained was not light red, but dark brown. This indicates that the aminoxyl moieties formed are in part decomposed by further oxidation with the excess 3-chloroperoxybenzoic acid. The SEC curve of **2** was almost identical with that of **6**, indicating that no polymer chains were cleaved or bridged during the oxidation.

EPR and UV–VIS spectra

EPR measurements of **1** and **2** were carried out at 20 °C using benzene as the solvent. The spectra are shown in Figs. 3a and 3b. Monoradical **1** showed a 1 : 1 : 1 triplet spectrum with a_N = 1.48 mT at g = 2.0061 (Fig. 3a). In the case of **2**, on the other hand, the 1 : 1 : 1 triplet was smeared out, and the spectrum was a single peak with a peak-to-peak width of 0.82 mT (g = 2.0061), as shown by Fig. 3b. This is due to the occurrence of exchange narrowing because the spin concentration of **2** is very high (1.89×10^{21} to 2.07×10^{21} spins g^{-1}).

The UV–VIS spectra of **1**, **2**, **4** and **6** were measured using CH_2Cl_2 as the solvent. The spectra are shown in Fig. 4. The extinction coefficients (ε) for **2** are corrected for the spin concentration determined by EPR measurement. The UV–VIS spectrum of **4** showed two λ_{max} at 231 (ε 21500 dm^3 mol^{-1} cm^{-1}) and 301 nm (21800), and that of **1** showed a λ_{max} at 246 nm (33000) and three shoulders at 301 (3340), 399 (120) and 483 nm (70) (Fig. 4a). These shoulders are due to the aminoxyl group (inset, Fig. 4a). On the other hand, two λ_{max} were observed at 234 (24200) and 306 nm (25600) for **6**,

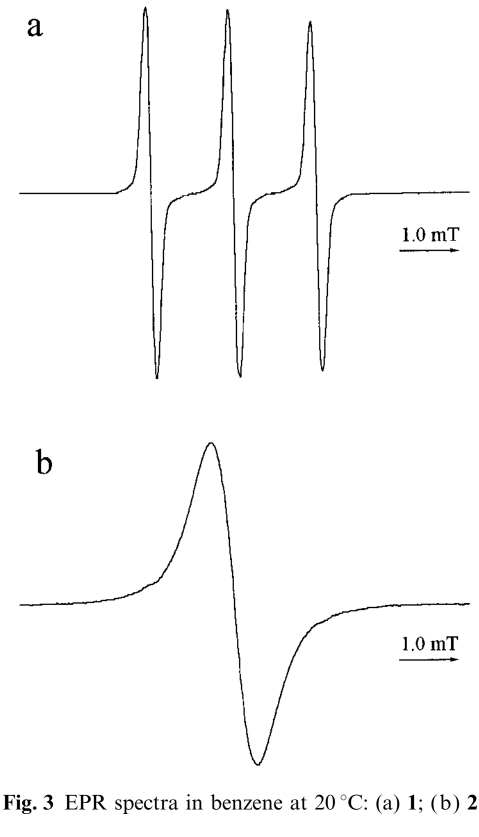

Fig. 3 EPR spectra in benzene at 20 °C: (a) **1**; (b) **2**.

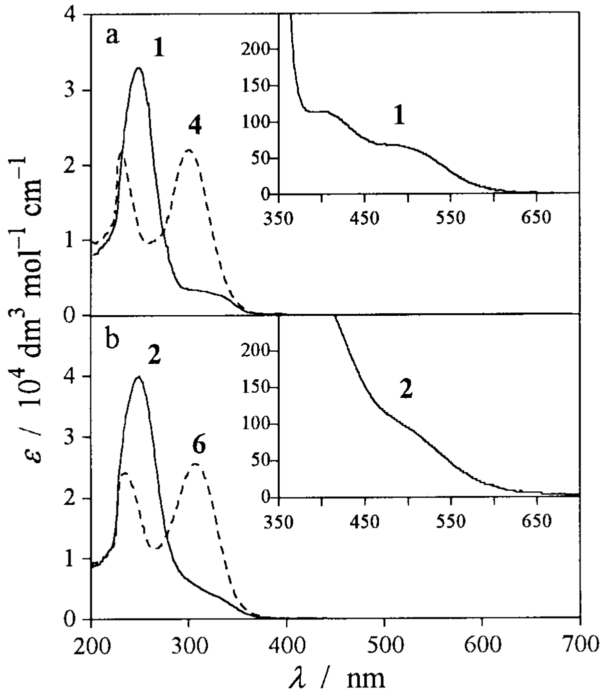

Fig. 4 UV–VIS spectra in CH_2Cl_2 at 20 °C: (a) **1** (solid line) and **4** (dotted line); (b) **2** (solid line) and **6** (dotted line). Extinction coefficient ε for **2** is corrected for the spin concentration determined by EPR spectroscopy.

and a peak was observed at 248 nm (40000) for **2**. However, the three shoulders in the spectrum of **2** were not clearly observed. The UV–VIS spectrum of **2** is almost identical with that of **1**, indicating that polyradical **2** has the expected structure. Since **2** has a cross-conjugated structure, no bathochromic shifts were observed.

Magnetic susceptibility measurements

Magnetic susceptibility measurements on **2** were carried out with a SQUID at 1.8–300 K. The diamagnetic contribution from the sample was estimated from Pascal's constants.

When the magnetic interactions among the unpaired electron spins are smaller than the energy of the thermal fluctuation kT, and the orbital angular momentum is neglected, the magnetic susceptibility χ is expressed by eqn. (1),

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

$$\frac{1}{\chi} = \frac{T-\theta}{C} \tag{2}$$

where N is Avogadro's number, μ_B is the Bohr magneton, g is the Landé factor and θ is the Weiss temperature; $N\mu_B{}^2 g^2 S(S+1)/3k$ is called the Curie constant, C.

The χ–T and χT–T plots for a polyradical with a spin concentration of 0.75 spin per repeating unit ($M_n = 4070$) are shown in Fig. 5. The χT–T plot of **2** (inset, Fig. 5) shows a downward turn in the temperature region below 30 K, indicating an antiferromagnetic interaction between the unpaired electron spins. The χ–T plot was analyzed according to the Curie–Weiss law [eqn. (2)], and the Curie and Weiss constants were determined to be $C = (1.29 \pm 0.01) \times 10^{-3}$ emu g^{-1} K and $\theta = -0.98 \pm 0.01$ K, respectively. From the Curie constant the spin concentration of **2** was estimated to be 0.82 spin per repeating unit, which was somewhat higher than that determined by EPR (0.75 spin per repeating unit). A similar magnetic behaviour (antiferromagnetic) was also observed for a polyradical with a lower M_n of 2470.

In spite of the high spin concentration, polyradical **2** was antiferromagnetic. We ascribed this to twisting of the aminoxyl moieties from the poly(1,3-phenylene) π-conjugated system. The ferromagnetic interaction between the unpaired electron spins through π-conjugation may be weaker than, and masked by, antiferromagnetic through-space interactions. Any significant twisting of the aminoxyl groups from the π-conjugated system would reduce the ferromagnetic interaction between the unpaired electron spins. This twisting of the aminoxyl moieties is suggested by the large a_N value (1.48 mT) of **1** since the magnitude of 1.48 mT is larger than those for planar *N*-alkyl-*N*-phenylaminoxyl (1.18–1.20 mT).[17] To confirm this twisting, we performed X-ray crystallographic analysis on **1**.

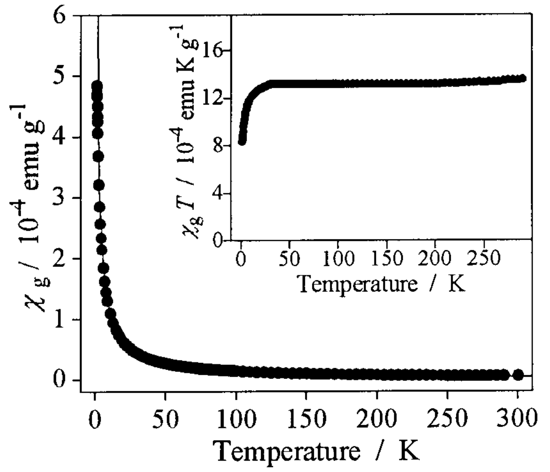

Fig. 5 χ–T and χT–T plots of **2**. The solid line in the χ–T plot is calculated from the Curie–Weiss law.

X-Ray crystallographic analysis

Recrystallization of **1** from hexane gave deep red prisms suitable for X-ray crystallographic analysis. The ORTEP drawing is shown in Fig. 6. Since the *tert*-butyl group was disordered over the three sites with occupancies of 0.70, 0.13 and 0.17, only the *tert*-butyl group with an occupancy of 0.70 is drawn for clarity. The dihedral angle between planes A (C1–C6) and B (C7–C12) is 45.9°, and that between planes A and C (C13–C18) is 28.2°. On the other hand, the dihedral angle

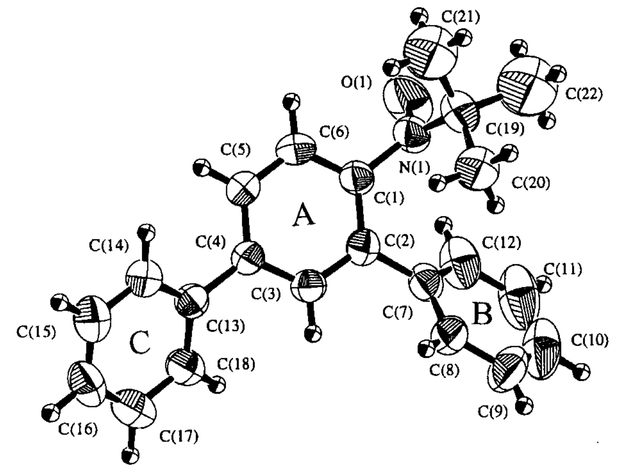

Fig. 6 ORTEP drawing of **1**. Only the *tert*-butyl group with an occupancy of 0.7 is drawn for clarity. Planes A, B and C are the benzene rings comprised of C1–C6, C7–C12 and C13–C18, respectively. Plane D is comprised of C1–N1–O1. The dihedral angles between planes A and B, planes A and C and planes A and D are 45.8, 28.2 and 68.5°, respectively. Selected bond lengths, bond angles and torsion angles are as follows: N1–O1 1.277(5), C1–N1 1.438(5) and C19–N1 1.494(3) Å; C1–N1–O1 116.7(1) and C19–N1–O1 118.6(5)°; C2–C1–N1–O1 111.5(2) and C6–C1–N1–O1 −68.5(2)°.

between planes A and D (C1–N1–O1) is 68.5°. Therefore, the extent of the delocalization of the unpaired electron from the N–O moiety to the benzene ring A is reduced to 13.4% (by a factor of $\cos^2 68.5°$) of the planar structure. This reduces the ferromagnetic interaction between the unpaired electron spins through the conjugated π-system. Consequently, the absence of the intramolecular ferromagnetic interaction can be ascribed to the unexpectedly large twisting of the N–O moieties from the poly(1,3-phenylene) π-conjugated system.

Summary

A poly(1,3-phenylene)-based aminoxyl polyradical with a high spin concentration was prepared by the Pd-catalyzed polycondensation of *N-tert*-butyl-2,4-dibromoaniline and 1,3-phenylenebis(trimethylene boronate), followed by oxidation with 3-chloroperoxybenzoic acid. The SQUID measurements of the polyradical showed a weak antiferromagnetic interaction between the unpaired electron spins. The lack of ferromagnetic interaction was explained in terms of twisting of the aminoxyl moieties from the poly(1,3-phenylene) π-conjugated system. This twisting of the aminoxyl moiety was confirmed by X-ray crystallographic analysis of the corresponding model monoradical. We are now synthesizing planar aminoxyl radicals having cyclic structures, to maximize the likelihood of a ferromagnetic interaction.

Experimental

Melting points were measured on a Yanaco micro-melting point apparatus and are uncorrected. FT-IR and UV–VIS spectra were run on a JASCO FT/IR-230 and a Shimadzu UV-2200 spectrophotometer, respectively. ^{1}H 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. Size exclusion chromatography (SEC) was run on a TOSOH 8020 series instrument equipped with TSKgelG5000HHR, GMultiporeHXL-M and TSKgelGMHHR-L columns calibrated with polystyrene standards, eluting with THF. Detection was made with a Tosoh refractive-index detector RI 8020. EPR spectra were recorded on Bruker ESP 300 spectrometer operated at the X band. The spin concentrations of the polyradicals were determined by the double integrated EPR spectra of the sample using benzene as the solvent. The calibration curve was drawn with 1,3,5-triphenylverdazyl solutions using the same EPR cell and solvent and the same instrument setting as for the sample measurements. The 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 samples was estimated from Pascal's diamagnetic constants.

Materials

N-tert-Butylaniline,[13] benzyltrimethylammonium tribromide ($BTMABr_3$),[14] benzyltrimethylammonium dichloroiodate ($BTMAICl_2$),[18] phenylboronic acid,[19] 1,3-phenylenebis(trimethylene boronate)[8] and $Pd(PPh_3)_4$[20] were prepared according to reported methods. Bu_4NCl and 3-chloroperoxybenzoic acid (purity ~70%) were commercial grade. Column chromatography was carried out on Fuji Silysia BW-127ZH silica gel (Fuji-Davison Chem. Co., Ltd). Ether refers to diethyl ether.

N-tert-Butyl-2,4-dibromoaniline 3a

To a stirred solution of *N-tert*-butylaniline (3.84 g, 25.7 mmol) in CH_2Cl_2 (250 cm^3)–MeOH (100 cm^3) were added $BTMABr_3$ (22.0 g, 56.5 mmol) and $CaCO_3$ powder (6.22 g, 62.2 mmol) at room temperature. After the mixture was stirred for 30 min, the $CaCO_3$ powder was filtered off, and the filtrate was evaporated. An aqueous $NaHSO_3$ solution (10%, 170 cm^3) was then added, and the mixture was extracted with ether. The ether layer was washed with brine, dried ($MgSO_4$) and evaporated, and the residue was chromatographed on silica gel with CH_2Cl_2–hexane (1:6) as the eluant to give **3a** in 92.6% yield (7.30 g, 23.8 mmol) as a colorless oil. ν_{max} (KBr)/cm^{-1} 3406 (NH); δ_H ($CDCl_3$) 1.38 (9H, s, *t*-Bu), 4.3 (1 H, br s, NH), 6.82 (1H, d, *J*.8.8, ArH), 7.22 (1H, dd, *J* 2.4 and 8.8, ArH) and 7.54 (1H, d, *J* 2.4, ArH).

N-tert-Butyl-2,4-diiodoaniline 3b

To a stirred solution of *N-tert*-butylaniline (4.0 g, 26.8 mmol) in CH_2Cl_2 (500 cm^3)–MeOH (300 cm^3) were added $BTMAICl_2$ (28.0 g, 80.4 mmol) and $CaCO_3$ powder (10.5g, 105 mmol) at room temperature. After the mixture was stirred for 24 h, the $CaCO_3$ powder was filtered off, and the filtrate evaporated. An aqueous $NaHSO_3$ solution (10%; 180 cm^3) was then added, and the mixture was extracted with ether. The ether layer was washed with brine, dried ($MgSO_4$), evaporated and chromatographed on silica gel with benzene–hexane (1:1) to give **3b** in 51.3% yield (5.52 g, 13.8 mmol) as a light yellow oil. ν_{max} (KBr)/cm^{-1} 3390 (NH); δ_H ($CDCl_3$) 1.39 (9H, s, *t*-Bu), 4.20 (1 H, br s, NH), 6.65 (1H, d, *J* 8.5, ArH), 7.39 (1H, dd, *J* 8.5 and 2.4, ArH) and 7.91 (1H, d, *J* 2.4, ArH).

N-tert-Butyl-2,4-diphenylaniline 4

To a solution of **3a** (0.92 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 K_2CO_3 solution (2 mol dm^{-3}; 9 cm^3) and $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol). The resulting heterogeneous mixture was purged with nitrogen, and then gently refluxed for 24 h with stirring under nitrogen. 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 (2:1) to give **4** in 85.0% yield (0.77 g, 2.55 mmol). Recrystallization from hexane gave colorless prisms. Mp 107–109 °C; ν_{max} (KBr)/cm^{-1} 3415 (NH); λ_{max} (CH_2Cl_2)/nm 231 (ε/dm^3 mol^{-1} cm^{-1} 21500) and 301 (21800); δ_H ($CDCl_3$) 1.32 (9H, s, *t*-Bu), 7.06 (1H, d, *J* 8.3, ArH), 7.23 (1H, t, *J* 7.8, ArH), 7.34–7.47 (9H, m, ArH) and 7.06 (2H, d, *J* 7.3, ArH); δ_C ($CDCl_3$) 30.04, 51.28, 114.58, 126.03, 126.23, 126.59, 127.27, 128.58, 128.88, 129.09, 129.49, 129.67, 129.97, 139.86, 140.99 and 143.49 (Found: C, 87.51; H, 7.28; N, 4.59. $C_{22}H_{23}N$ requires C, 87.66; H, 7.69; N, 4.65%).

N-tert-Butyl(2,4-diphenyl)phenylaminoxyl 1

3-Chloroperoxybenzoic acid (~70%) (0.52 g, ~2.1 mmol) was added to a solution of **4** (0.30 g, 1.00 mmol) in CH_2Cl_2 (25 cm^3) and stirred for 30 min, all at room temperature. After evaporation, the residue was chromatographed on silica gel with CH_2Cl_2–hexane (6:1) to give **1** in 70.0% yield (0.22 g, 0.70 mmol). Recrystallization from hexane gave deep red prisms. Mp 94–96 °C; a_N (benzene)/mT 1.48 (g 2.0061); λ_{max} (CH_2Cl_2)/nm 246 (ε/dm^3 mol^{-1} cm^{-1} 33000), 301 (3340), 399 (120) and 483 (70) (Found: C, 83.36; H, 6.71; N, 4.38. $C_{22}H_{22}NO$ requires C, 83.51; H, 7.01; N, 4.43%).

Polycondensation of 3 and 5. A typical procedure

To a solution of **3a** (0.61 g, 2.0 mmol) in benzene (26 cm^3) were added 1,3-phenylenebis(trimethylene boronate) (0.64 g, 2.6 mmol), an aqueous K_2CO_3 solution (2 mol dm^{-3}; 5.2 cm^3), Bu_4NCl (1.93 g, 6.9 mmol) and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for a week with stirring under nitrogen. After cooling, the mixture was extracted with benzene, and the benzene layer was washed with brine and dried ($MgSO_4$). After filtration, the benzene was evaporated and the residue chromatographed on silica gel with ethyl acetate. The material separated was refluxed in MeOH for 10 min to give a light yellow powder. It was then dissolved in CH_2Cl_2 (4 cm^3) and the solution was poured into hexane (20 cm^3) to give a light yellow powder, which was collected by filtration and dried *in vacuo*. Yield 17.9% (0.080 g, 0.36 mmol); ν_{max} (KBr)/cm^{-1} 3417 (NH); λ_{max} (CH_2Cl_2)/nm 234 (ε/dm^3 mol^{-1} cm^{-1} 24200) and 306 (25600); δ_H ($CDCl_3$) 1.30 (9H, s, *t*-Bu), 4.08 (1H, s, NH), 7.05 (1H, d, *J* 7.8, ArH) and 7.25–7.74 (6H, m, ArH); δ_C ($CDCl_3$) 29.63, 115.45, 119.88, 123.09, 124.60, 125.47, 126.66, 126.77, 126.97, 127.19, 128.22, 128.53, 128.81, 129.26, 129.37, 130.31, 130.61, 131.53, 131.99, 132.09, 132.53, 139.54, 140.41, 141.12 and 141.57 (Found: C, 83.23; H, 7.36; N, 5.24; Br, 3.24. $(C_{16}H_{17}N)_n$ requires C, 86.06; H, 7.67; N, 6.27%). $M_n = 4070$ ($n = 18.2$), $M_w = 5960$ and $M_w/M_n = 1.46$.

Oxidation of 6

3-Chloroperoxybenzoic acid (~70%) (0.12 g, ~0.49 mmol) was added to a solution of **6** (0.10 g, 0.42 unit mmol) in CH_2Cl_2 (20 cm^3), and the resulting mixture was stirred for 30 min, all at room temperature. The mixture was then washed with an aqueous Na_2CO_3 solution (10%; 10 cm^3 × 2) and brine, and dried ($MgSO_4$). After filtration, the filtrate was evaporated under reduced pressure and the residue dissolved in CH_2Cl_2 (5 cm^3). The solution was poured into hexane (50 cm^3) to give **2** as a light red powder, which was collected by filtration and dried *in vacuo*. Yield 50.0% (0.050 g, 0.21 mmol); λ_{max} (CH_2Cl_2)/nm 248 (ε/dm^3 mol^{-1} cm^{-1} 40000) (Found: C, 75.50; H, 6.36; N, 4.97; Br, 5.07. $(C_{16}H_{16}NO)_n$ requires C, 80.64; H, 6.77; N, 5.88%). The spin concentrations determined by EPR and SQUID were 1.89×10^{21} and 2.07×10^{21} spins g^{-1}, respectively.

Crystal structure determination of 1†

Crystal data: $C_{22}H_{22}NO$, $M = 316.4$, monoclinic, $a = 11.282(1)$, $b = 7.602(2)$, $c = 21.513(1)$ Å, $\beta = 95.38(1)°$, $V = 1836.8(4)$ $Å^3$, space group $P2_1/n$, $Z = 4$, $D_c = 1.14$ g cm^{-3}, $F(000) = 676$ and μ(Cu-Kα) = 5.38 cm^{-1}.

A deep red prismatic crystal with dimensions of 0.20 × 0.40 × 0.60 mm was selected. The reflection data were collected on a Rigaku AFC7R diffractometer (50 kV, 200 mA) with graphite monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å) at 23 ± 1 °C. The ω–2θ scan mode was used with the scan speed of 14° min^{-1} and the scan width of $(1.73 + 0.3 \tan\theta)°$. Of 2836 reflections measured up to $2\theta = 113.2°$ 2677 were unique ($R_{int} = 0.008$), 1894 of which were considered as observed ($I > 3\sigma(I)$). An empirical absorption correction based on the Ψ scan was applied. The maximum and minimum transmission factors are 0.93 and 1.00.

The structure was solved by the direct method [SHELXS86] and refined on *F* by the least-squares [TEXSAN] using anisotropic thermal parameters for non-hydrogen atoms.[21] The *tert*-butyl group is disordered over the three sites with occupancies of 0.70, 0.13 and 0.17. Their C atoms were placed at an idealized position and in the final cycles of the refinement their parameters were fixed. The hydrogen atoms were placed at a calculated position (C–H = 0.96 Å) with $B_{iso}(H) = 1.2$ B_{iso}(C) and their parameters were not refined. The hydrogen atoms bound to C(23–28) with an occupancy of 0.13 or 0.17 were excluded from the refinement. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $\omega = 1$ was used. The final agreement indices based on 1894 reflections for 210 parameters were 0.086 and 0.080 with GOF 5.64. The maximum and minimum residual electron densities were 0.39 and -0.26 e $Å^{-3}$. Several high peaks were still found near the *tert*-butyl group. The maximum shift of the parameters in the final refinement was less than their errors ($\Delta/\sigma = 0.30$).

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References

1. J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201; H. Iwamura and N. Koga, *Acc. Chem. Res.*, 1993, **26**, 346; J. A. Crayston, A. Iraqi and J. C. Walton, *Chem. Soc. Rev.*, 1994, 147; P. M. Lahti, *Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, New York and London, 1996, vol. 2, pp. 1484–1494; Y. Miura, *ibid.*, vol. 9, pp. 6686–6695; *Proceedings of the Symposium of the 5th International Conference on Molecule-based Magnets, Mol. Cryst. Liq. Cryst.*, 1997, **305**, 1; **306**, 1.
2. N. Mataga, *Theor. Chim. Acta*, 1968, **10**, 372; A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297.
3. S. Kato, K. Morokuma, D. Feller, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1983, **105**, 1791; P. M. Lahti and A. S. Ichimura, *J. Org. Chem.*, 1991, **56**, 3030; R. C. Fort, Jr., S. J. Getty, D. A. Hrovat, P. M. Lahti and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 7549.
4. P. S. Zuev and R. S. Sheridan, *Tetrahedron*, 1995, **51**, 11337; Y. Teki, I. Fujita, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 11499 and references cited therein.
5. A. Rajca, *Chem. Rev.*, 1994, **94**, 871.
6. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
7. Y. Miura, H. Oka and M. Momoki, *Synthesis*, 1995, 1419.
8. Y. Miura, H. Oka and M. Morita, *Macromolecules*, 1998, **31**, 2041.
9. A. Fujii, T. Ishida, N. Koga and H. Iwamura, *Macromolecules*, 1991, **24**, 1077; Y. Miura, M. Matsumoto and Y. Ushitani, *Macromolecules*, 1993, **26**, 2628; Y. Miura, M. Matsumoto, Y. Ushitani, Y. Teki, T. Takui and K. Itoh, *Macromolecules*, 1993, **26**, 6673; H. Nishide, T. Kaneko, M. Igarashi, E. Tsuchida, N. Yoshioka and P. M. Lahti, *Macromolecules*, 1994, **27**, 3082, and references cited therein.
10. Y. Miura, Y. Ushitani, K. Inui, Y. Teki, T. Takui and K. Itoh, *Macromolecules*, 1993, **26**, 3698; Y. Miura and Y. Ushitani, *Macromolecules*, 1993, **26**, 7079; Y. Miura, T. Issiki, Y. Ushitani, Y. Teki and K. Itoh, *J. Mater. Chem.*, 1996, **6**, 1745, and references cited therein.
11. H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida and P. M. Lahti, *J. Am. Chem. Soc.*, 1996, **118**, 9695, and references cited therein.
12. W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1977, **99**, 4587.
13. E. R. Biehl, R. Patrizi and P. C. Reeves, *J. Org. Chem.*, 1971, **36**, 3252.
14. S. Kajigaeshi, T. Kakinami, H. Tokikawa, T. Hirakawa and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2667; S. Kajigaeshi, T. Kakinami, K. Inoue, M. Kondo, H. Nakamura, M. Fujikawa and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 597.
15. M. Remmers, M. Shultze and G. Wegner, *Macromol. Rapid. Commun.*, 1996, **17**, 239; F. E. Goodson, T. I. Wallow and B. M. Novak, *Macromolecules*, 1998, **31**, 2047.
16. A. B. Charette and A. Giroux, *J. Org. Chem.*, 1996, **61**, 8718.
17. A. R. Forrester, J. M. Hay and R. H. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press, London and New York, 1968, pp. 202–203.
18. S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 600.
19. R. M. Washburn, E. Levens, C. F. Albright and F. A. Billig, *Org. Synth.*, 1963, **Coll. Vol. IV**, 68.
20. D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
21. All calculations were performed using the Molecular Structure Corporation's TEXSAN crystallographic software package.

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