Design and synthesis of diphenyldiazomethanes possessing stable aminoxyl radicals: photolytic generation of quartet species and their reaction with C_{60}

Kenji Matsuda,† Gilles Ulrich and Hiizu Iwamura *,‡

Institute for Fundamental Research in Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Diphenyldiazomethanes possessing stable *tert*-butylaminoxyl and Ullman's 'nitronyl nitroxide' § radicals were prepared. The corresponding diphenylcarbenes substituted with the free radicals were generated by photolysis of the parent diazomethanes. From EPR fine structures and their temperature dependence, the carbene and the radical centers were shown to couple ferromagnetically in these molecules as expected from the topological symmetry of the π-framework. These diazo compounds were reacted with C_{60} to afford a fulleroid carrying one to four nitronylaminoxyl groups.

Introduction

Connection of carbene centers *via* *m*-phenylene and/or benzene-1,3,5-triyl groups has been successfully used to construct high-spin organic molecules and is considered to be one of the promising strategies for eventual construction of photogenerated organic ferromagnets.[1] Whereas the final target molecule in this strategy is a two dimensional network such as **1**, we started from the construction of pseudo-two dimensional polycarbenes such as the dendritic and cyclic ones which make up **1**. In these studies the importance of the topological symmetry was emphasized.[1e] However, there seemed to be a limitation of strategies in forming extended dendritic structures;[1f,g] highly branched dendritic polydiazo compounds gave photoproducts exhibiting spin multiplicities less than those expected for the corresponding polycarbenes. Intramolecular cross-linking between the carbene centers appeared to limit their extension to highly branched polycarbenes.

More recently another strategy of constructing extended systems of well-defined dimensionality by coordination of triplet diaminoxyl and quartet triaminoxyl radicals with magnetic metal ions proved to be useful in ordering the 2p spins of the former and the 3d spins of the latter in a ferrimagnetic fashion.[2] A 2:3 complex from a quartet triaminoxyl radical and bis(hexafluoroacetylacetonato)manganese(II) showing a magnetic transition temperature of 46 K forms a notable landmark of such studies.[2e]

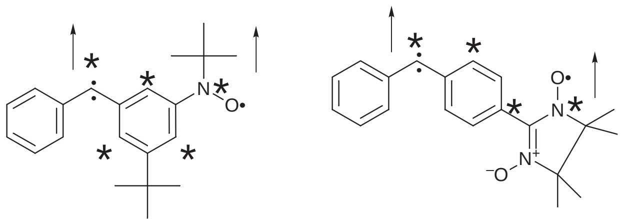
To construct advanced magnetic materials, it is necessary to understand the magnetic interaction in the heterospin species having two or more kinds of spin and reflect them in the new molecular design. We have already worked with a number of possible spin species: organic radicals, carbenes or nitrenes, cation or anion radicals and magnetic metal ions. Systems of heterospin species can exhibit more than one functionality due to differences in their stability, photoresponse, redox potential, Lewis acidity, *etc*. This paper will focus on such a system of heterospin species.

Buckminsterfullerene was also taken into account as a potential precursor for anion radicals.[3] Some C_{60} derivatives have interesting physical properties such as superconductivity[4] or ferromagnetism.[5] Wudl and co-workers reported that a charge transfer salt made of C_{60} and tetrakis(dimethylamino)ethylene had an unusually high ferromagnetic transition temperature (16.1 K) for a purely organic compound.[5a] However the saturation magnetization of this sample corresponds only to 4% of the stoichiometric amount of spins. The correlation of the structure and the mechanism of the development of ferromagnetism has been investigated by Tokumoto and co-workers[5b,c] who concluded that this magnetic material has spin-glass-like behavior.

Results and discussion

Molecular design and synthesis of the precursors

We wish to report the syntheses of the *tert*-butylaminoxyl substituted diphenylcarbene **2** and Ullman's 'nitronyl nitroxides' substituted diphenylcarbenes§ **3** and **4**. These compounds represent heterospin species in that they possess both a triplet carbene capable of being generated photochemically and a stable aminoxyl radical capable of forming complexes with Lewis-acidic magnetic metal ions. The regiochemistry is designed on the basis of topological symmetry that would allow the two kinds of spin to couple strongly in a ferromagnetic fashion within the molecules of **2**, **3** and **4**. As the photolysis of the diazo group is expected to generate the triplet carbene, the positions of the diazo groups and the aminoxyl radicals should be controlled by the topological symmetry of the π-conjugated systems. The radical moiety and the diazo group were thus connected through the *m*-phenylene group in the case of *tert*-butylaminoxylcarbene.[6a] The *p*-phenylene group was used in the case of nitronylaminoxylcarbene[6b] (Scheme 1). Another *tert*-butyl group was introduced into **2** in order to stabilize the *N*-*tert*-butylaminoxyl.



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Scheme 1 Schematic representation of spin polarization by topological symmetry

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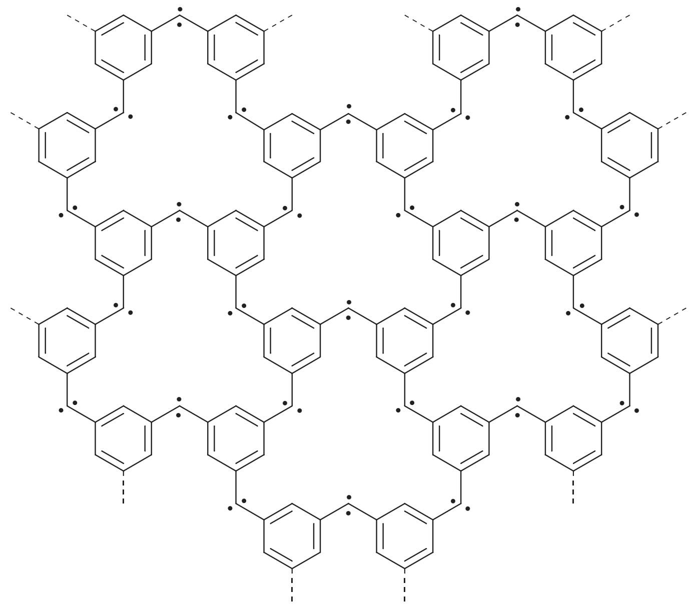
† Present address: Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

‡ Present address: National Institution for Academic Degrees, 4259 Nagatsuta, Midori-ku, Yokohama, 226 Japan.

§ The IUPAC name for nitroxide is aminoxyl.



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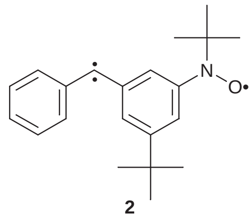

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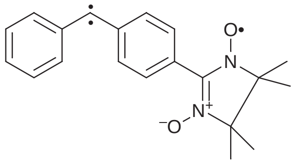

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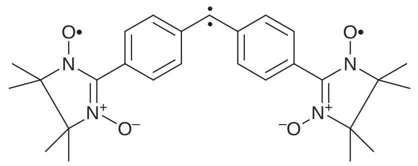

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The synthetic route to the diazo compound **2d** is described in Scheme 2. 3,5-Dibromo-*tert*-butylbenzene was first synthesized from *tert*-butylbenzene and converted to *N*-(3-bromo-5-*tert*-butylphenyl)-*N*-(*tert*-butyldimethylsiloxy)-*tert*-butylamine **5**.[7] The monobromo compound **5** was lithiated and reacted with benzaldehyde to give alcohol **6** which was then oxidized with pyridinium dichromate to give ketone **7**. Treatment of **7** with hydrazine monohydrate gave hydrazone **8** which was deprotected by the reaction with tetra-*n*-butylammonium fluoride and then oxidized by yellow mercury oxide to give [3-(*N*-ylooxy-*tert*-butylamino)-5-*tert*-butylphenyl]phenyldiazomethane **2d**. In the last oxidation step, both the hydrazone and the hydroxyamine groups were oxidized simultaneously to the diazo and aminoxyl groups, respectively. The diazo compound **2d** was obtained as a red oil showing an IR absorption at 2039 cm^{-1} and a UV–VIS absorption at 520 (sh) nm. An EPR spectrum of **2d** consisted of three sets of quartet lines at 178.3 K (Fig. 1a). The hyperfine couplings with one nitrogen ($\alpha_N = 12.3$ G) and two *ortho* and one *para* hydrogens ($\alpha_{ortho\text{-}H} = \alpha_{para\text{-}H} = 2.0$ G) were determined by simulation. An EPR spectrum with a hyperfine structure of nitrogen having a random orientation in solid solution was obtained at 8.3 K.

Synthesis of the diazo compounds **3d** and **4d** was performed according to Scheme 3. A simultaneous oxidation was also performed to obtain the nitronylaminoxyl and the diazo moieties. The diazo compound **3d** was confirmed by IR, UV, HRMS and EPR spectra. The IR absorption of the diazo group was observed at 2039 cm^{-1}. UV–VIS absorptions were observed at 550 (sh), 607 (800), 645 (840) and 720 (sh) nm. An EPR spectrum of **3d** measured at 174 K consisted of five lines having hyperfine coupling with two equivalent nitrogens ($\alpha_N = 7.4$ G) as shown in Fig. 1b. An EPR spectrum of **4d** measured at room temperature showed nine lines with hyperfine coupling with four equivalent nitrogens ($\alpha_N = 3.7$ G).

Photolysis and EPR spectra

Photolysis of **2d** in 2-methyltetrahydrofuran (MTHF) solid solution was performed at 8.1 K in an EPR cavity. Light from a high pressure mercury lamp attached with a sharp cut filter ($\lambda > 480$ nm) was irradiated. An EPR spectrum after photolysis is shown in Fig. 2a. The spectrum resembled closely that of the monoanion of *m*-phenylenebis(phenylmethylene) **22**, reported to have a quartet ground state.[8] Three *x*, *y* and *z* lines, an extra line and a set of forbidden bands were assigned, suggesting the photolysate has a quartet state. The appearance of the off-axis extra line indicates that the observed fine structure pattern arises from a species with the half-integral spin of 3/2.[8] Temperature dependence of the signal intensity due to the xy_1 transition obeyed a Curie law up to 50 K demonstrating that the quartet state was a ground state.

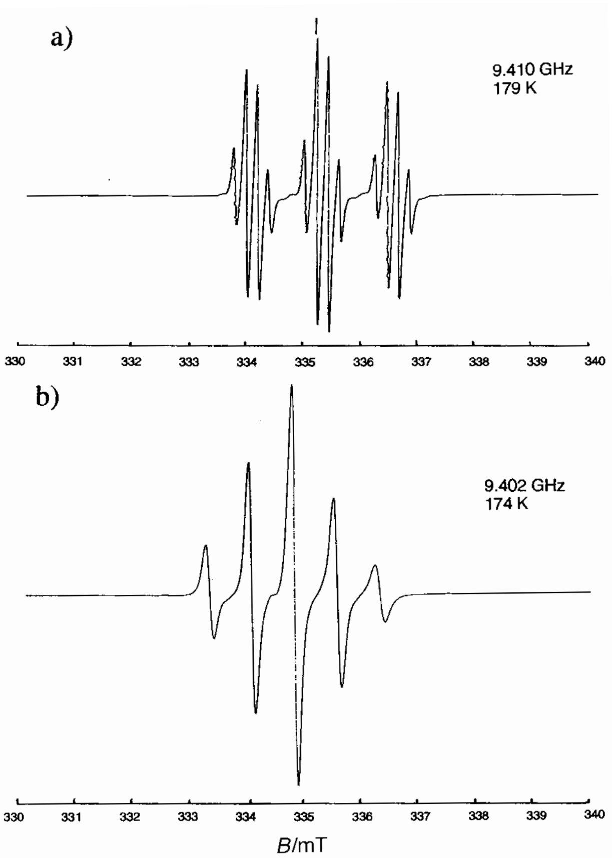
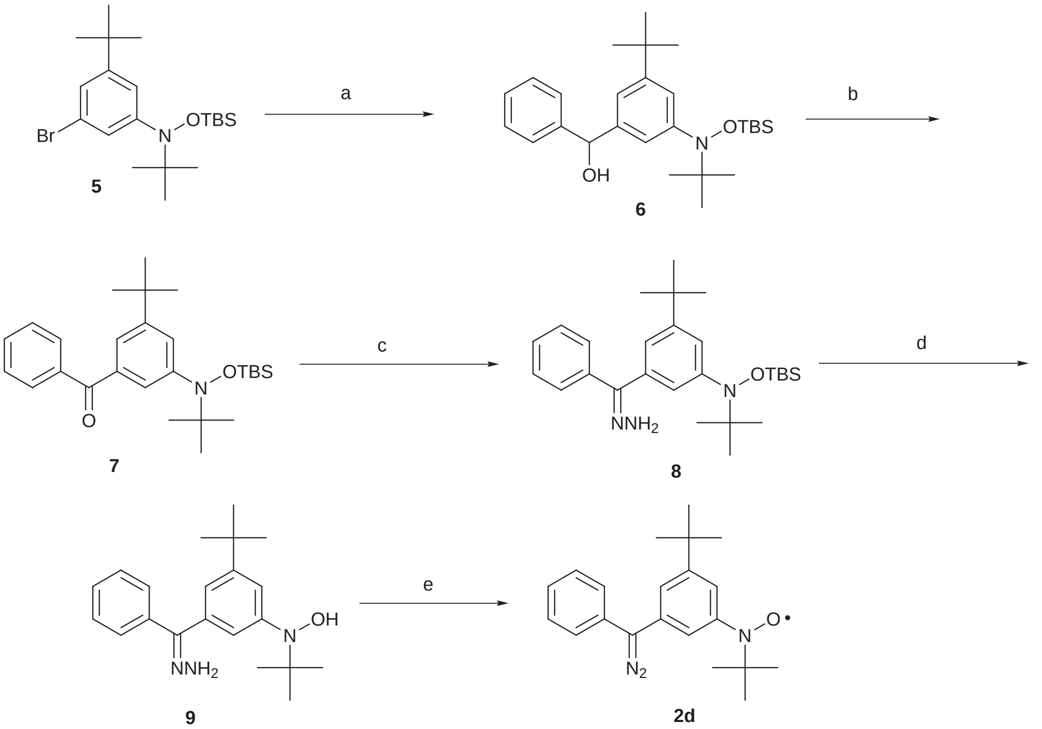
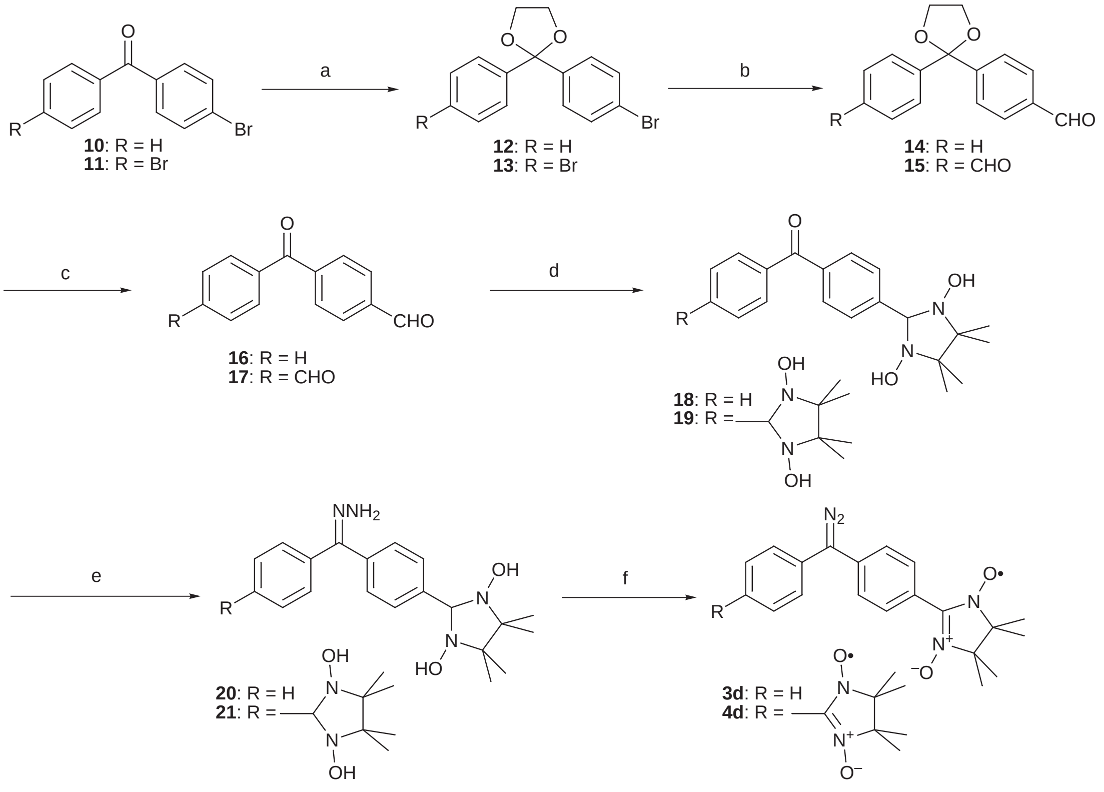


Fig. 1 (a) EPR spectrum of the diazo compound **2d** at 179 K (9.410 GHz); (b) EPR spectrum of the diazo compound **3d** at 174 K (9.402 GHz)



Scheme 2 *Reagents and conditions*: (a) Bu^{n}Li, THF and then PhCHO, 83%; (b) PDC, CH_2Cl_2, 53%; (c) $H_2NNH_2{\cdot}H_2O$, EtOH, 81%; (d) TBAF (5 equivs.), THF; (e) HgO, CH_2Cl_2, 27%, two steps



Scheme 3 *Reagents and conditions*: (a) ethylene glycol, TsOH, benzene, 70–72%; (b) Bu^{n}Li, DMF, 80–100%; (c) $HClO_4$, CH_2Cl_2, 77–88%; (d) 2, 3-bis(hydroxyamino)-2,3-dimethylbutyl sulfate, MeOH, 55–67%; (e) $H_2NNH_2{\cdot}H_2O$, EtOH, 31–46%; (f) HgO, CH_2Cl_2, 63–80%

A pair of signals were observed for each transition for **2**, indicating that there were two or more conformers of the quartet species present. From the signal spacing of the highest-field z_3 resonances at 619 and 634 mT and lowest-field z_1 signal at 113 mT, the *D* values were obtained as 0.118 and 0.125 cm^{-1} for the two species. Approximate *E* values of 0.0035 and 0.0060 cm^{-1}, respectively, were obtained by simulation on the basis of a perturbation treatment by using a program written by Itoh and co-workers.[9] These *D* values are close to that of **22**, *i.e.* 0.120 cm^{-1}.[8] While the conformation of *m*-phenylenebis(phenylmethylene) **23** is reported to be asymmetric,[10] **22** is said to have a symmetric conformation.[8] Two conformers with high and low axial symmetry may be involved in **2**.

The EPR spectrum of the photoproduct of **3d** shown in Fig. 2b also has a fine structure characteristic of a quartet state and was assigned to the carbene **3**. In the case of the carbene **3**,

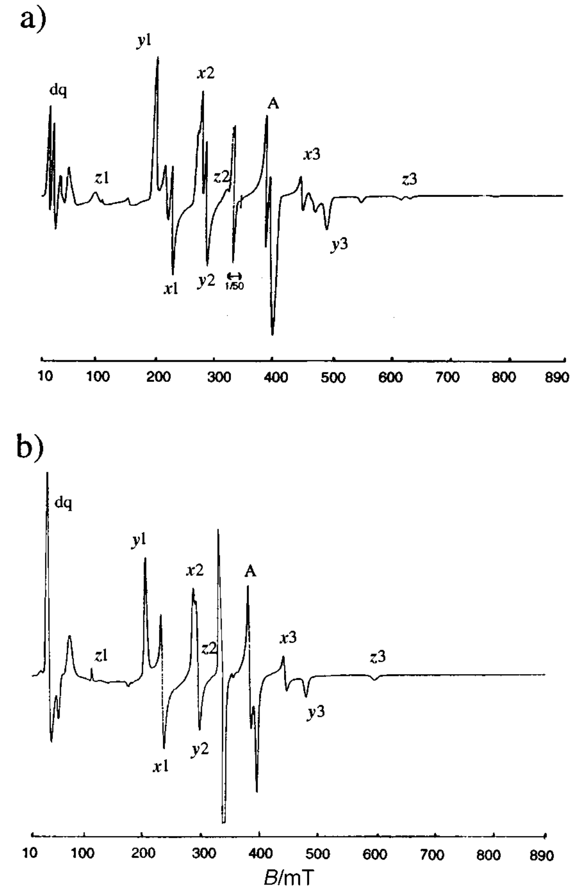
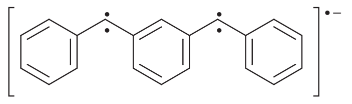


Fig. 2 (a) EPR spectrum of the carbene **2** at 8.1 K (9.412 GHz). dq and A denote a forbidden band and an extra line, respectively. The appearance of the off-axis extra lines assures that the observed fine structure pattern arises from the species with the half-integral spin of 3/2; (b) EPR spectrum of the carbene **3** at 6.3 K (9.406 GHz). dq and A denote a forbidden band and an extra line, respectively.



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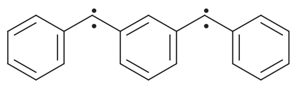


23

one conformer was observed: $D = 0.113\ \mathrm{cm}^{-1}$, $E = 0.006\ \mathrm{cm}^{-1}$. Because the nitronylaminoxyl is symmetric with respect to rotation around the symmetric axis of the five-membered ring, there is only one possible conformation.

C_{60} carrying nitronylaminoxyl

C_{60} species carrying one to four nitronylaminoxyl radicals were synthesized by the reaction between C_{60} and diphenyldiazomethane carrying nitronylaminoxyl radical and were characterized by spectroscopic, electrochemical and magnetic methods.

In order to functionalize C_{60} from a magnetic point of view, we started to attach stable free radicals to C_{60}.[11] The diphenyldiazomethane derivatives are suitable precursors to derivatize C_{60}.[12] Diphenyldiazomethanes **3d** and **4d** should afford C_{60} derivatives substituted with free radicals. **3d** and C_{60} were mixed in toluene at room temperature. Purification of the reaction products by column chromatography (silica, toluene : CH_2Cl_2 = 1 : 1) gave monoadduct **24** and bisadducts **25**. Reaction of bis(nitronylaminoxyl) **4d** and C_{60} also gave monoadduct **26** and bisadducts **27** (Scheme 4). Bisadducts **25** and **27** are mixtures of stereoisomers. FAB mass spectroscopy showed satisfactory peaks for all the compounds. The UV–VIS spectrum of **24** and C_{60} was very similar in the short-wavelength region to other C_{60}–diazo adducts, suggesting that the C_{60} moiety in **24** has a [5,6] open structure[12] and that basic electronic structure was retained.

EPR spectra of **24**, **25** and **26** were measured at room temperature in degassed toluene (Fig. 3). While the spectrum of **24** consisted of five lines ($\alpha_N = 7.4$ G), **26** consisted of nine lines ($\alpha_N = 3.4$ G), suggesting the exchange interaction in **26** through the spiro carbon was larger than the hyperfine coupling ($|J| > |\alpha_N|$). The EPR spectrum of **25** consisted of nine distorted lines. The distortion of the signals may be attributed to the presence of isomers for bisadduct **25** which have different exchange interactions. For most of the isomers of **25**, the exchange interaction between spins through the C_{60} skeleton was found to be rather small ($J \approx |\alpha_N|$).

Molar magnetic susceptibility χ_M of **24** was measured by a SQUID susceptometer at the field strength of 5000 G. The $\chi_M T$ value at 200 K was 0.371 emu K mol^{-1} in good agreement with a theoretical value of 0.375 emu K mol^{-1} for isolated monoradicals. Judging from the almost horizontal $\chi_M T$ *vs.* T plot, any intermolecular interaction between free radical molecules was very small in this system.

Cyclic voltammetry of **24** and **26** has been performed in *o*-dichlorobenzene with 0.1 M $Bu^n{}_4NClO_4$ as a supporting electrolyte (Fig. 4). The first reduction potentials of **24** and **26** were observed at −0.90 V *vs.* Ag/Ag$^+$, which is rather close to that of C_{60} (−0.89 V *vs.* Ag/Ag$^+$). Since the interaction between C_{60} and the free radical part would shift the reduction potential of C_{60} to a more negative value,[13] the donor–acceptor interaction between C_{60} and the nitronylaminoxyl unit is estimated to be small. The reduction wave for the nitronylaminoxyl was observed between the first and second reduction potential of C_{60} as a shoulder. Reduction at a potential in between those of C_{60} and nitronylaminoxyl would produce a diradical. A study of the charge-transfer salt thus obtained is in progress.

Conclusions

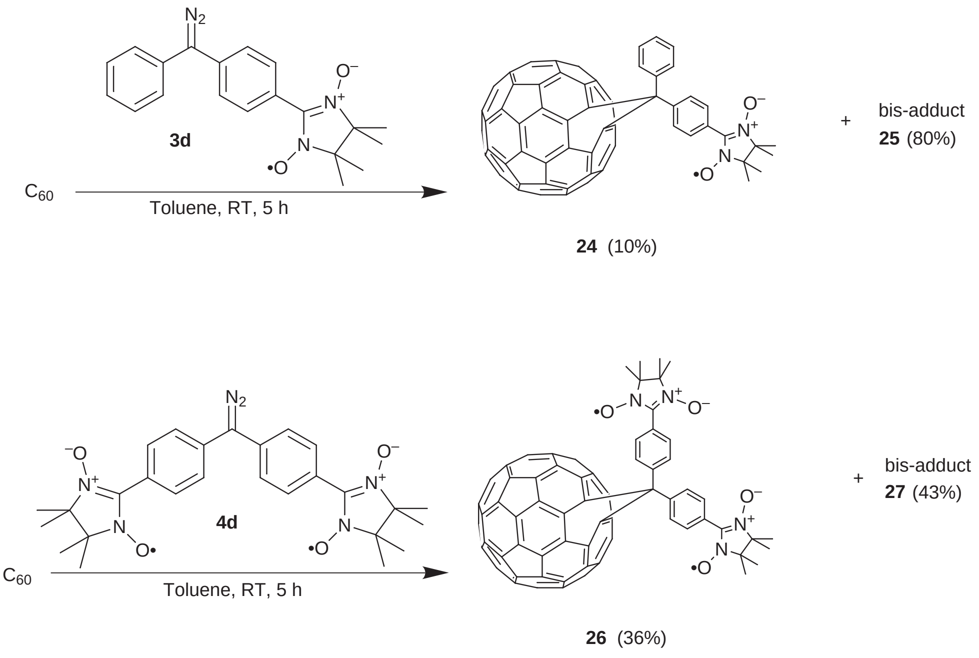
We have designed and synthesized diphenyldiazomethanes substituted with aminoxyl radicals. EPR spectra of the photoproducts of these compounds showed intramolecular ferromagnetic interaction between the carbene and organic radical centers according to the spin-polarization of the π-electrons. These systems are hybrid between stable and Lewis-basic aminoxyl radicals and photo-generated carbene centers. Such hybrid systems will be useful in constructing multifunctionalized magnetic materials. These diazo compounds reacted with C_{60} to afford C_{60}-substituted stable radicals.

Experimental

Materials

^{1}H and ^{13}C NMR spectra were recorded on JEOL GX-270 and EX-270 instruments. *J* values are given in Hz. IR spectra were obtained on a Hitachi I-5040 spectrometer. UV–VIS spectra were recorded on a Hitachi U-3300 Spectrophotometer. Mass spectra were obtained using JEOL JMS-SX102L, JEOL JMS-SX/SX102A and JEOL HX-110 instruments. Melting points are not corrected.

Diethyl ether and tetrahydrofuran (THF) used in the reactions were distilled, under a dry nitrogen atmosphere, from lithium aluminum hydride just before use. 2-Methyltetrahydrofuran (MTHF) used in the magnetic measurements was purified by successive distillation from lithium aluminum hydride under a nitrogen atmosphere and from sodium–benzophenone ketyl under a dry nitrogen atmosphere. *N*,*N*-



Scheme 4 Reactions of **3d** and **4d** with C_{60}

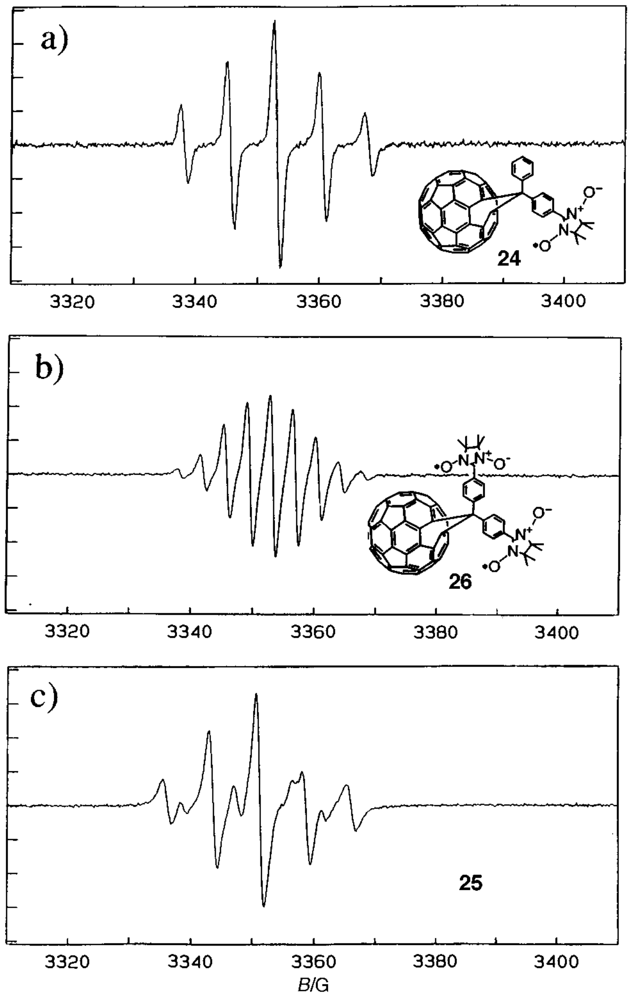


Fig. 3 EPR spectra of nitronylaminoxyl radicals **24** (9.43 GHz), **25** (9.44 GHz), and **26** (9.43 GHz), measured at room temperature in toluene

Dimethylformamide (DMF) was distilled under reduced pressure from calcium hydride. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified. Anhydrous magnesium sulfate was used as the drying agent.

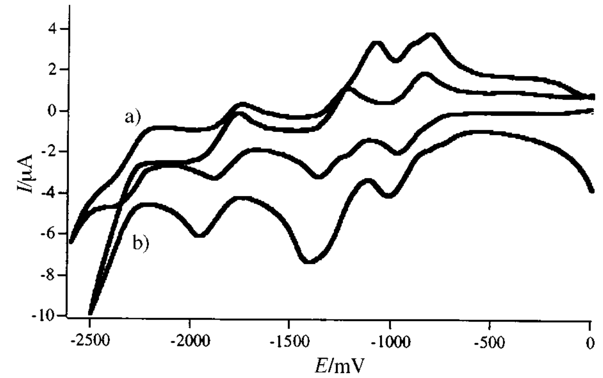


Fig. 4 Cyclic voltammograms of **24** (a) and **26** (b) in *o*-dichlorobenzene with 0.1 M $Bu^n_4NClO_4$ as a supporting electrolyte at Pt working and counter electrodes. Potentials were measured *vs.* Ag/Ag^+ reference electrode. Scan rate was 100 mV s^{-1}.

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) using UV light as a detector. Column chromatography was performed on silica gel (E. Merck, 70–230 mesh) or neutral alumina (ICN, activity grade IV).

3-(*N-tert*-Butyldimethylsiloxy-*N-tert*-butylamino)-5-*tert*-butylbenzophenone 7. A solution of bromo compound **5**[7] (1.00 g, 2.41 mmol) in dry THF (20 ml) at −78 °C was treated with *n*-butyllithium (1.58 ml, 1.6 M in hexane, 2.53 mmol) and stirred at −78 °C for 45 min. Benzaldehyde (0.24 ml, 2.41 mmol) was added at −78 °C, and the resulting mixture was allowed to warm to 25 °C. The reaction mixture was poured into aqueous ammonium chloride, extracted with diethyl ether, washed with brine and water, dried and concentrated. Purification by column chromatography (silica, hexane : CH_2Cl_2 = 1 : 1) gave alcohol **6** (780 mg, 83%) as a pale yellow oil. A solution of alcohol **6** (780 mg, 2.41 mmol) in dichloromethane (10 ml) was treated with pyridinium dichromate (1.0 g, 2.65 mmol) and stirred for 3 h. After filtration the resulting solution was diluted with water, extracted with diethyl ether, washed with water, dried and concentrated. Purification by column chromatography (silica, hexane : dichloromethane = 2 : 1) gave ketone **7** (410 mg, 53%) as a pale yellow oil. ν(NaCl)/cm^{-1} 2959, 2930, 2905, 2857, 1663; δ_H(270 MHz, $CDCl_3$) −0.11 (br s, 6 H, Si-Me), 0.89 (s, 9 H, Si-Bu^t), 1.09 (s, 9 H, N-Bu^t), 1.34 (s 9 H, Bu^t), 7.36 (br s, 1 H, Ar), 7.46 (t, *J* 7.3, 2 H, Ar), 7.55–7.63 (m, 3 H, Ar), 7.79 (d, *J* 7.7, 2 H, Ar); *m*/*z* (FAB HRMS) (M^+) 439.2894, calc. for $C_{27}H_{41}NO_2Si$ 439.2906.

3-(*N*-*tert*-Butyldimethylsiloxy-*N*-*tert*-butylamino)-5-*tert*-butylbenzophenone hydrazone 8. A solution of ketone **7** (480 mg, 1.09 mmol) and hydrazine monohydrate (12 ml) in ethanol (60 ml) was refluxed for 20 h. The reaction mixture was poured into water, extracted with dichloromethane, washed with water, dried and concentrated. No further purification was needed to give a pure mixture of two *syn*- and *anti*-isomers of hydrazone **8** (400 mg, 81%) as a pale yellow oil. ν(NaCl)/cm^{-1} 3401, 2959, 2928, 2857, 1586; δ_H(270 MHz, $CDCl_3$) −0.19 (br s, 6 H, Si-Me), −0.10 (br s, 6 H, Si-Me), 0.80 (s, 9 H, Si-Bu^t), 0.88 (s, 9 H, Si-Bu^t), 1.00 (s, 9 H, N-Bu^t), 1.10 (s, 9 H, N-Bu^t), 1.29 (s, 9 H, Bu^t), 1.31 (s, 9 H, Bu^t), 5.37 (s, 2 H, NNH_2), 5.40 (s, 2 H, NNH_2), 6.81–7.72 (m, 16 H, Ar); *m*/*z* (FAB HRMS) (MH^+) 454.3233, calc. for $C_{27}H_{44}N_3OSi$ 454.3253.

[3-(*N*-Ylooxy-*tert*-butylamino)-5-*tert*-butylphenyl]phenyldiazomethane 2d. A solution of hydrazone **8** (50 mg, 0.11 mmol) and tetrabutylammonium fluoride trihydrate (173 mg, 0.55 mmol) in dry THF (2 ml) was stirred for 5 h. The reaction mixture was poured into aqueous sodium carbonate, extracted with Et_2O, washed with water, dried and concentrated. Purification by column chromatography (alumina, CH_2Cl_2) gave hydroxylamine **9** which colorized spontaneously on standing. A solution of **9** and ethanolic potassium hydroxide (20 drops) in dichloromethane (8 ml) and diethyl ether (2 ml) was treated with yellow mercury(II) oxide in the dark. The reaction mixture was stirred for 24 h in the dark and filtered. After concentration, purification by column chromatography (alumina act. IV, hexane : CH_2Cl_2 = 1 : 1) gave diazo compound **2d** (22 mg, 31%) as a red oil. ν(NaCl)/cm^{-1} 2965, 2870, 2039, 1661; λ_{max}(CH_2Cl_2)/nm 520 (sh); EPR (benzene) 1 : 3 : 3 : 1 : 1 : 3 : 3 : 1 : 1 : 3 : 3 : 1, 12 lines, $g = 2.006$, $a_N = 12.3$ G, $a_H = 2.0$ G.

2-Phenyl-2-(4-bromophenyl)-1,3-dioxolane 12. A solution of 4-bromobenzophenone **10** (13.00 g, 50 mmol, purchased from Wako Chemical), ethylene glycol (3.0 ml, 55 mmol), and toluene-*p*-sulfonic acid monohydrate (100 mg, 0.53 mmol) in benzene (20 ml) was refluxed for 48 h with a Dean–Stark condenser. The reaction mixture was poured into aqueous sodium bicarbonate, extracted with diethyl ether, washed with aqueous sodium bicarbonate and water, dried and concentrated. Purification by column chromatography (silica, hexane : CH_2Cl_2 = 3 : 1) gave dioxolane **12** (10.70 g, 70%) as a white powder: mp 55.0–55.7 °C; ν(KBr)/cm^{-1} 2996, 2892, 1590; δ_H($CDCl_3$) 3.99 (s, 4 H, CH_2-CH_2), 7.24–7.49 (m, 9 H, Ar); *m*/*z* (HRMS) 304.0099, calc. for $C_{15}H_{13}O_2Br$ 304.0099.

2-Phenyl-2-(4-formylphenyl)-1,3-dioxolane 14. A solution of bromo compound **12** (10.00 g, 32.8 mmol) in dry THF (100 ml) at −78 °C was treated with *n*-butyllithium (22.0 ml, 1.6 M in hexane, 35.2 mmol) and stirred at −78 °C for 30 min. The solution turned deep blue and DMF (2.7 ml, 35.2 mmol) was added at −78 °C, and the resulting mixture was allowed to warm to 25 °C. The reaction mixture was poured into aqueous ammonium chloride, extracted with diethyl ether, washed with brine and water, dried and concentrated. No further purification was needed to give pure aldehyde **14** (8.31 g, 100%) as a white powder: mp 61.7–63.4 °C; ν(KBr)/cm^{-1} 2950, 2897, 2834, 1698; δ_H($CDCl_3$) 4.08 (s, 4 H, CH_2-CH_2), 7.27–7.87 (m, 9 H, Ar), 10.00 (s, 1 H, CHO); *m*/*z* (FAB HRMS) (MH^+) 255.1015, calc. for $C_{16}H_{15}O_3$ 255.1021.

4-Formylbenzophenone 16. A solution of dioxolane **14** (17.00 g, 67 mmol), in dichloromethane (500 ml) was treated with conc. $HClO_4$ (70%) (45 ml) for 1 h in an ice bath, and then 2 h at room temperature. The reaction mixture was poured into aqueous sodium bicarbonate, extracted with dichloromethane, washed with aqueous sodium bicarbonate and water, dried and concentrated. No further purification was necessary to give ketone **16** (11 g, 77%) as a white crystal: mp 66.5–67.0 °C; ν(KBr)/cm^{-1} 3059, 2811, 2724, 1709, 1651; δ_H($CDCl_3$) 7.51 (t, *J* 7.9, 2 H, Ar), 7.64 (t, *J* 7.3, 1 H, Ar), 7.82 (d, *J* 6.9, 2 H, Ar), 7.93 (d, *J* 8.3, 2 H, Ar), 8.01 (d, *J* 8.3, 2 H, Ar), 10.14 (s, 1 H, CHO); *m*/*z* (HRMS) 210.0680, calc. for $C_{14}H_{10}O_2$ 210.0681.

4-(4,4,5,5-Tetramethyl-1,3-dihydroxyimidazolidin-2-yl)benzophenone 18. A solution of aldehyde **16** (380 mg, 1.8 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane dihydrogen sulfate[14] (900 mg, 3.6 mmol), and potassium carbonate (540 mg, 3.6 mmol) in methanol (45 ml) was refluxed for 24 h. The reaction mixture was poured into water, extracted with dichloromethane, washed with water, dried and concentrated. Purification by column chromatography (silica, CH_2Cl_2 : Et_2O = 4 : 1) gave bishydroxylamine **18** (340 mg, 55%) as a white powder: mp 136.5 °C (decomp.); ν(KBr)/cm^{-1} 3424, 2980, 2918, 1645; δ_H([$^2H_6$]DMSO) 1.06 (s, 6 H, CH_3), 1.10 (s, 6 H, CH_3), 4.61 (s, 1 H, CH), 7.58–7.74 (m, 9 H, Ar), 7.89 (s, 2 H, N-OH); *m*/*z* (FAB HRMS) (MH^+) 341.1865, calc. for $C_{20}H_{25}O_3N_2$ 341.1861.

4-(4,4,5,5-Tetramethyl-1,3-dihydroxyimidazolidin-2-yl)benzophenone hydrazone 20. A solution of ketone **18** (340 mg, 1.0 mmol) and hydrazine monohydrate (10 ml) in ethanol (50 ml) was refluxed for 24 h. The reaction mixture was poured into water, extracted with dichloromethane, washed with water, dried and concentrated. Purification by column chromatography (silica, CH_2Cl_2 : Et_2O = 3 : 2) gave a pure mixture of *syn*- and *anti*-isomers of hydrazone **20** (110 mg, 31%) as a white powder: mp 142.6 °C (decomp.); ν(KBr)/cm^{-1} 3364, 3266, 1578; δ_H([$^2H_6$]DMSO) 1.02–1.10 (m, 12 H, CH_3), 4.46 and 4.57 (s × 2, 1 H, CH), 6.19 (br s, 2 H, NNH_2), 7.17–7.69 (m, 9 H), 7.73 and 7.85 (s × 2, 2 H, N-OH); *m*/*z* (FAB HRMS) (MH^+) 355.2134, calc. for $C_{20}H_{27}O_2N_4$ 355.2109.

[4-(4,4,5,5-Tetramethyl-1-yloxy-3-oxidoimidazolin-2-yl)-phenyl]phenyldiazomethane 3d. A solution of hydrazone **20** (30 mg, 0.08 mmol) and ethanolic potassium hydroxide (5 drops) in dichloromethane (10 ml) and diethyl ether (2 ml) was treated with yellow mercury(II) oxide (100 mg) in the dark. The reaction mixture was stirred for 24 h in the dark and filtered. After concentration purification by column chromatography (alumina act. IV, hexane : CH_2Cl_2 = 1 : 1) gave nitronylaminoxyl radical **3d** (19 mg, 63%) as a green solid: mp 92.1 °C (decomp.); ν(NaCl)/cm^{-1} 2990, 2934, 2039, 1595, 1364; λ_{max}(CH_2Cl_2)/nm (ε/cm^3 mol^{-1} cm^{-1}) 282 (38 000), 353 (47 000), 550 (sh), 607 (800), 645 (840), 720 (sh); EPR (benzene) 1 : 2 : 3 : 2 : 1, five lines, $g = 2.006$, $\alpha_N = 7.4$ G. *m*/*z* (FAB HRMS) (MH^+) 350.1718, calc. for $C_{20}H_{22}O_2N_4$ 350.1742.

[4-(4,4,5,5-Tetramethyl-1-yloxy-3-oxidoimidazolin-2-yl)-phenyl]phenylfulleroid 24. A solution of diazo compound **3d** (100 mg, 0.29 mmol) and C_{60} (100 mg, 0.14 mmol) in toluene (50 ml) was stirred for 5 h. After concentration purification by column chromatography (silica, toluene : CH_2Cl_2 = 1 : 1) gave nitronylaminoxyl radical fulleroid **24** (40 mg, 10% based on C_{60}. See ref. 12 for the definition of fulleroid) and a stereoisomeric mixture of bisadduct **25** (150 mg, 80% based on C_{60}) as a brown–green powder. **24**: ν(KBr)/cm^{-1} 2922, 1362; λ_{max}-(cyclohexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 210 (141 000), 261 (116 000), 329 (38 700), 350 (sh), 371 (23 900), 429 (2240); EPR (toluene) 1 : 2 : 3 : 2 : 1, five lines, $g = 2.010$, $\alpha_N = 7.5$ G; *m*/*z* (FAB MS, *m*-NBA) $[M + H]^+$ 1042.9, calc. for $C_{80}H_{22}N_2O_2$ 1042.1. **25**: *m*/*z* (FAB MS, *m*-NBA) $[M + 3H]^+$ 1365.3, calc. for $C_{100}H_{45}N_4O_4$ 1365.4.

2,2′-Bis(4-bromophenyl)-1,3-dioxolane 13. A solution of 4,4′-dibromobenzophenone **11**¶,[15] (4.96 g, 15.7 mmol), ethylene glycol (2.6 ml, 47 mmol), and toluene-*p*-sulfonic acid monohydrate (100 mg, 0.53 mmol) in toluene (20 ml) was refluxed for 48 h with a Dean–Stark condenser. The reaction mixture was poured into aqueous sodium bicarbonate, extracted with diethyl ether, washed with aqueous sodium bicarbonate and water, dried and concentrated. Purification by column chrom-

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¶ Synthesized starting from *p*-dibromobenzene (Wako) *via* bis(4-bromophenyl)methanol. Benzophenone **11** is reported in reference 15.

atography (alumina, hexane:$CH_2Cl_2 = 3:1$) gave 2,2′-bis(4-bromophenyl)-1,3-dioxolane **13** (4.4 g, 72%) as a white powder: mp 94.6–96.3 °C; ν(KBr)/cm^{-1} 2903, 1583, 1475; δ_H($CDCl_3$) 4.04 (s, 4 H, $\mathrm{C}H_2$-$\mathrm{C}H_2$), 7.40 (AB quartet, $\Delta_{AB} = 27.1$ Hz, J_{AB} 7.7, 8 H, Ar); δ_C($CDCl_3$) 65.0, 118.6, 122.5, 127.8, 131.4, 140.8; *m*/*z* (FAB HRMS) (MH^+) 382.9257, calc. for $C_{15}H_{13}O_2Br_2$ 382.9283.

2,2′-Bis(4-formylphenyl)-1,3-dioxolane 15. A solution of dibromo compound **13** (4.00 g, 10.28 mmol) in dry THF (100 ml) at −78 °C was treated with *n*-butyllithium (14.15 ml, 1.6 M in hexane, 22.6 mmol) and stirred at −78 °C for 30 min. The temperature was then allowed to rise to −30 °C, and then cooled down again to −78 °C. DMF (1.7 ml, 22.6 mmol) was added at −78 °C, and the resulting mixture was allowed to warm slowly to 25 °C. The reaction mixture was poured into aqueous ammonium chloride, extracted with diethyl ether, washed with brine and water, dried and concentrated. A short chromatography (silica, pure dichloromethane) afforded pure 2,2′-bis(4-formylphenyl)-1,3-dioxolane **15** (2.37 g, 80%) as a white powder: mp 95.0–96.0 °C; ν(KBr)/cm^{-1} 2901, 1700, 1603; δ_H($CDCl_3$) 4.07 (s, 4 H, $\mathrm{C}H_2$-$\mathrm{C}H_2$), 7.75 (AB quartet, $\Delta_{AB} = 41.6$ Hz, J_{AB} 2.3, 8 H, Ar), 9.96 (s, 2 H, $\mathrm{C}H\mathrm{O}$); δ_C($CDCl_3$) 65.1, 126.0, 126.5, 129.7, 136.1, 147.7, 191.6; *m*/*z* (FAB HRMS) (MH^+) 283.0000, calc. for $C_{17}H_{15}O_4$ 283.0970.

4,4′-Diformylbenzophenone 17. A solution of dioxolane **15** (2.3 g, 8.15 mmol), in dichloromethane (100 ml) was treated with conc. $HClO_4$ (70%) (10 ml), cooled in an ice-bath for 1 h, then 2 h at room temperature. The reaction mixture was then poured into aqueous sodium bicarbonate, extracted with dichloromethane, washed with aqueous sodium bicarbonate and water, dried and concentrated. No further purification was necessary to obtain pure 4,4′-diformylbenzophenone **17** (1.720 g, 88%) as a white crystal: mp 160.3–162.4 °C; ν(KBr)/cm^{-1} 1697 (s), 1653 (s); δ_H($CDCl_3$) 7.99 (AB quartet, $\Delta_{AB} = 22.7$ Hz, J_{AB} 8.4, 8 H, Ar), 10.15 (s, 2 H, $\mathrm{C}H\mathrm{O}$); δ_C($CDCl_3$) 129.6, 130.4, 138.9, 141.4, 191.4, 194.9; *m*/*z* (FAB HRMS) (MH^+) 239.0709, calc. for $C_{15}H_{11}O_3$ 239.0708.

4,4′-Bis(4,4,5,5-tetramethyl-1,3-dihydroxyimidazolidin-2-yl)-benzophenone 19. A solution of dialdehyde **17** (1.5 g, 6.3 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane dihydrogen sulfate[14] (2.05 g, 13.8 mmol), in methanol (45 ml) was stirred for 48 h. Filtration of the white precipitate gave pure benzophenone **19** (2.1 g, 67%): mp 180.0 °C (decomp.); ν(KBr)/cm^{-1} 3437, 2978, 1651, 1375; δ_H([$^2H_6$]DMSO) 1.06 (s, 12 H, $\mathrm{C}H_3$), 1.10 (s, 12 H, $\mathrm{C}H_3$), 4.61 (s, 2 H, $\mathrm{C}H$), 7.70 (AB quartet, $\Delta_{AB} = 8.0$ Hz, J_{AB} 8.2, 8 H, Ar), 7.87 (s, 4 H, N-OH); δ_C([$^2H_6$]DMSO) 17.2, 24.3, 66.4, 89.9, 128.5, 129.2, 136.4, 146.9, 207.0; *m*/*z* (FAB HRMS) (MH^+) 499.2913, calc. for $C_{27}H_{39}O_5N_4$ 499.2921.

4,4′-Bis(4,4,5,5-tetramethyl-1,3-dihydroxyimidazolidin-2-yl)-benzophenone hydrazone 21. A solution of ketone **19** (1 g, 2.0 mmol) and hydrazine monohydrate (14 ml) in ethanol (40 ml) was refluxed for 24 h. The reaction mixture was poured into water. Filtration of the precipitate gave a pure mixture of *syn*- and *anti*-isomers of hydrazone **21** (470 mg, 46%) as a white powder: mp 203.2 °C (decomp.); ν(KBr)/cm^{-1} 3362, 3263, 1581; δ_H([$^2H_6$]DMSO) 1.02–1.10 (four-line multiplet, 24 H, $\mathrm{C}H_3$), 4.44 and 4.56 (s × 2, 2 H, $\mathrm{C}H$), 6.09–6.18 (three broad lines, 4 H, $\mathrm{NN}H_2$), 7.10–7.66 (m, 8 H), 7.69 and 7.83 (s × 2, 4 H, N-OH); *m*/*z* (FAB HRMS) (MH^+) 513.3165, calc. for $C_{27}H_{41}O_4N_6$ 513.3180.

4,4′-Bis(4,4,5,5-tetramethyl-1-yloxy-3-oxidoimidazolin-2-yl)-phenyldiazomethane 4d. A solution of hydrazone **21** (470 mg, 0.92 mmol) and ethanolic potassium hydroxide (20 drops) in dichloromethane (100 ml) and diethyl ether (20 ml) was treated with yellow mercury(II) oxide (1.2 g) in the dark. The reaction mixture was stirred for 24 h in the dark and filtered. After concentration purification by column chromatography (alumina act. IV, hexane:$CH_2Cl_2 = 1:1$) gave nitronylaminoxyl radical **4d** (370 mg, 80%) as a green solid: mp 182.0 °C (decomp.); EPR (toluene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.006$, $\alpha_N = 3.7$ G; *m*/*z* (FAB HRMS) (MH^+) 505.2574, calc. for $C_{27}H_{33}O_4N_6$ 505.2564.

4,4′-Bis(4,4,5,5-tetramethyl-1-yloxy-3-oxidoimidazolin-2-yl)-phenylfulleroid 26. A solution of diazo compound **4d** (84 mg, 0.16 mmol) and C_{60} (100 mg, 0.14 mmol) in toluene (50 ml) was stirred for 24 h. After concentration purification by column chromatography (silica, CH_2Cl_2) gave monoadduct fulleroid **26** (60 mg, 36% based on C_{60}) and a stereoisomeric mixture of bisadduct **27** (100 mg, 43% based on C_{60}) as a brown–green powder. **26**: EPR (toluene) 1:4:10:16:19:16:10:4:1, nine lines, $g = 2.006$, $\alpha_N = 3.4$ G; *m*/*z* (FAB MS, *m*-NBA) $[M + H]^+$ 1198.0, calc. for $C_{87}H_{33}N_4O_4$ 1197.3. **27**: *m*/*z* (FAB MS, *m*-NBA) $[M + 2H]^+$ 1675.2, calc. for $C_{114}H_{65}N_8O_8$ 1675.5.

EPR Spectra

Photolyses of diazo compounds were carried out in MTHF matrices at 9 K in an EPR cavity. The light (480 nm < λ) was obtained from a Super High Pressure mercury lamp with a Kenko Y-48 sharp-cut filter. A Bruker EPP 300 spectrometer was used to obtain X-band EPR spectra. Temperatures were controlled by an Air Products LTD-3-110 cryogenic temperature controller. The cryostat was maintained at high vacuum by a diffusion/rotary pump set.

The EPR intensities for Curie plots in the temperature range 9–70 K were measured at appropriate power attenuation calibrated to exclude saturation effects. The temperatures were stepped up from 9 to 70 K with intervals of *ca.* 5 K.

Cyclic voltammetry

Cyclic voltammetry was performed using the BAS CV-50W system with a three-electrode cell. The working electrode was a Pt wire with a diameter of 1.6 mm. Before each experiment, the electrode was polished sequentially with a 1 μ diamond slurry. The scan rate was 100 mV s^{-1} on saturated solutions of **1** with 0.1 M tetra-*n*-butylammonium perchlorate in acetonitrile. Potentials were scanned from 0.0 to 1.2 V with respect to the quasi-reference electrode in a single compartment cell fitted with platinum electrodes. The counter electrode was a platinum tab.

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