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Isolation and Magnetic Properties of Heterocycle-Carrying *N*-Alkoxyarylaminyl Radicals[1]

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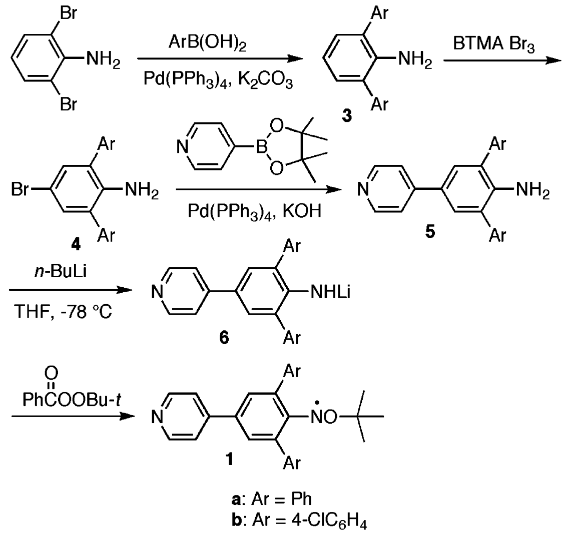
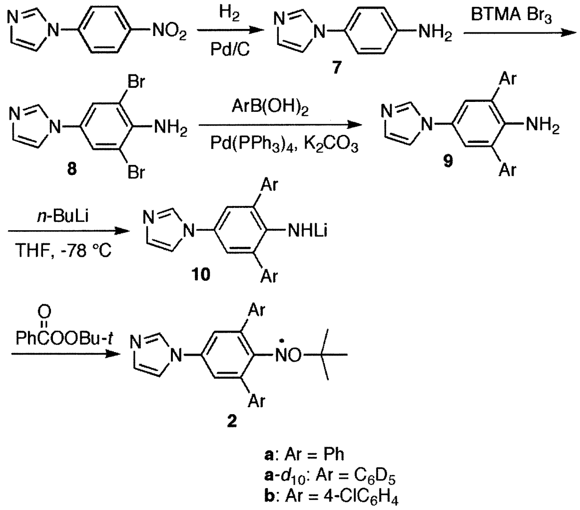
Abstract: Two *N-tert*-butoxy-2,6-diaryl-4-(4-pyridyl)phenylaminyls (**1**) and three *N-tert*-butoxy-2,6-diaryl-4-(1*H*-imidazol-1-yl)phenylaminyls (**2**) were prepared by the reaction of the lithium salts of the corresponding anilines with *tert*-butyl peroxybenzoate. Although **1** could not be isolated as radical crystals, **2** was successfully obtained as red crystals. The X-ray crystallographic analysis and magnetic susceptibility measurements were performed for one isolated radical.

Although a variety of thioaminyl radicals (R$\dot{\text{N}}$SR′) have been isolated as radical crystals,[2] *N*-alkoxyaminyls (R$\dot{\text{N}}$OR′), the isoelectronic radicals of thioaminyls, were unsuccessful in isolation for a long time despite a number of ESR studies on *N*-alkoxyaminyls.[3] However, quite recently, the first isolation of *N*-alkoxylaminyls was accomplished by our group. The isolated *N*-alkoxyaminyls are *N-tert*-butoxy-2,4,6-triaryl-, *N-tert*-butoxy-2-*tert*-butyl-4,6-diaryl-, and *N-tert*-butoxy-4-*tert*-butyl-2,6-diarylphenylaminyls[4] and *N-tert*-butoxy-2-*tert*-butyl- and *N-tert*-butoxy-2,6-di-*tert*-butyl-1-pyrenylaminyls, which are sterically protedted.[5] Interestingly, the isolated *N*-alkoxyaminyls were shown to be oxygen-insensitive, even in solution. Isolable and oxygen-insensitive free radicals have attracted increasing much attention as a spin source or building blocks of the magnetic materials.[6] In the present study, we prepared two kinds of heterocycle-carrying *N-tert*-butoxyarylaminyls, *N-tert*-butoxy-2,6-diaryl-4-(4-pyridyl)phenylaminyls (**1**) and *N-tert*-butoxy-2,6-diaryl-4-(1*H*-imidazol-1-yl)phenylaminyls (**2**). Although **1** could not be obtained as crystals, **2** was successfully isolated as red crystals. Herein, we report the isolation, the X-ray crystallographic analysis, and the magnetic measurements of **2**.

SCHEME 1



SCHEME 2



Radicals **1** and **2** were prepared by the reaction of the lithium salts (**6** and **10**) of 2,6-diaryl-4-(4-pyridyl)phenylanilines (**5**) or 2,6-diaryl-4-(1*H*-imidazol-1-yl)phenylanilines (**9**) with *tert*-butyl peroxybenzoate in THF at −78 °C.[4,5,7] The preparation of **5** and **9** is shown in Schemes 1 and 2. When a THF solution of *tert*-butyl peroxybenzoate was added to a solution of **6** or **10** in THF, the resultant mixtures immediately showed a characteristic red color. The appearance of the red color clearly indicates the generation of *N*-alkoxyarylaminyls, and the radicals were separated by column chromatography. Although the pyridine ring-carrying *N-tert*-butoxyaryl-

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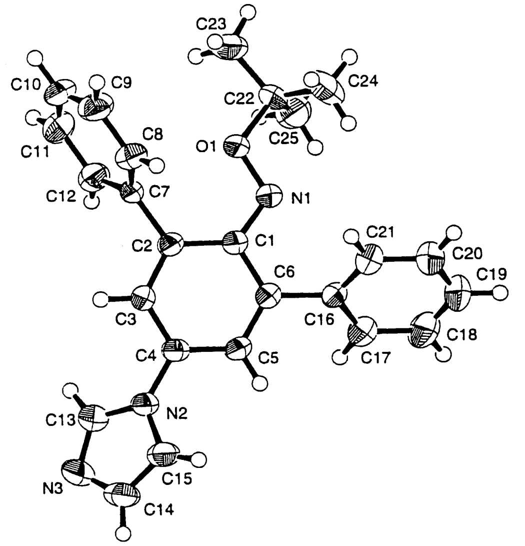


FIGURE 1. ORTEP drawing of **2a** at 50% probability.

aminyls could not be obtained as crystals despite much effort, the imidazole ring-carrying *N-tert*-butoxyarylaminyls **2** were successfully isolated as red needles (**2a**) or red microcrystals (**2b**) in 13−14% yield. In the case of **1**, the radicals were obtained as a viscous red oil, which never solidified. HPLC analysis of the red oil indicated that it contained considerable amounts of impurities which could not be removed by column chromatography.

Since recrystallization of **2a** from hexane gave good single crystals suitable for the X-ray crystallographic analysis, the X-ray crystallographic analysis could be successfully carried out. The ORTEP drawing is depicted in Figure 1. The small torsion angle of 3.7° for C2−C1−N1−O1 indicates that N1 and O1 are planar to ring A defined by C1−C6. On the other hand, the dihedral angle between ring A and the imidazole ring is 37°, exhibiting that the unpaired electron spin can be delocalized to the imidazole ring to some extent. In contrast, the large dihedral angles between ring A and ring B defined by C7−C12 (50°) and between ring A and ring C defined by C16−C21 (71°) strongly suggest that the delocalization of the unpaired electron spin onto rings B and C are very small or negligibly small.

The ESR spectra of **1** showed a broad 1:1:1 triplet, and no hyperfine splittings due to aromatic protons were observed. On the other hand, the ESR spectra of **2** were split by the interaction with some aromatic protons although the splittings were quite poor. A typical ESR spectrum of **2a** is illustrated in Figure 2, and the hfc constants and *g* values for **1** and **2** are summarized in Table 1.

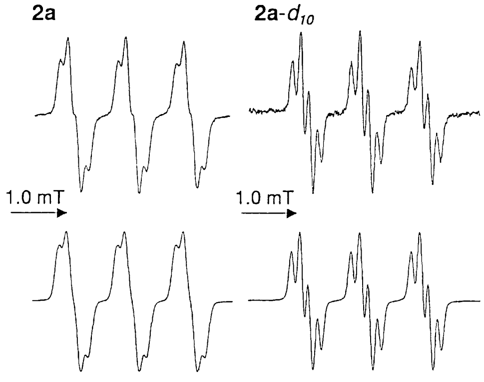


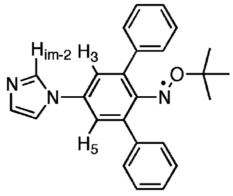
FIGURE 2. ESR spectra of **2a** and **2a**-d_{10} in benzene: (a) an observed spectrum of **2a** (upper) and computer simulation (bottom); (b) an observed spectrum of **2a**-d_{10} (upper) and computer simulation (bottom).

TABLE 1. ESR Parameters of 1 and 2 in Benzene at Room Temperature

radical	a_N[a,b]	a_H[a]	g
1a	0.992		2.0042
1b	0.992		2.0042
2a	1.016		2.0042
2a-d_{10}[c]	1.016	0.160 (2H),[d] 0.100 (1H)[e]	2.0042
2b	1.020		2.0042

[a] Hyperfine coupling constants are given in mT. [b] Due to the NO nitrogen. [c] The hyperfine coupling constants are determined by computer simulation. [d] Due to the anilino meta protons. [e] Due to the proton attached to the imidazole 2-position.

TABLE 2. Comparison of the Observed and Calculated Hfc Constants for 2a



position	calcd hfc const[a,b]	obsd hfc const[b,c]
N[d]	1.364	1.016
H_3	0.240	0.160[e]
H_5	0.238	0.160[e]
H_{im-2}	−0.042	0.100[e]

[a] The MO calculations were performed with the DFT UBecke 3LYP hybrid method using the 6-31G basis set. [b] Given in mT. [c] The hfc constants are given in the absolute value. [d] The value for the NO nitrogen. [e] The values for **2a**-d_{10} are shown.

No or poor splittings due to the aromatic protons observed for **1** and **2** can be in part ascribed to the presence of many protons with unresolved small hyperfine splittings. To improve the broad spectrum to a sharper one, the 2- and 6-phenyl groups were deuterated. The ESR spectrum of the 2- and-6-phenyl-deuterated radical, **2a**-d_{10}, is shown in Figure 2. Computer simulation of the ESR spectrum of **2a**-d_{10} gave $a_N = 1.020$, a_H (2H) = 0.160, a_H (1H) = 0.100 mT. The protons with a hfc constant of 0.160 mT are assigned to the anilino meta protons, H_3 and H_5, and the proton with a hfc constant of 0.100 mT is assigned to H_{im-2} attached to C2 of the imidazole ring (see Table 2).[8] The assignment of H_{im-2} is based on the MO calculations by the DFT UBecke 3LYP method using the 6-31G basis set.[9] The highest spin-density position in the imidazole ring predicted by the MO calculations is the 2-position. The calculated spin density distribution for **2a** is depicted in Figure 3, and comparison of the observed hfc constants with the calculated ones is made in Table 2. As found in Table 2, the calculated hfc constants are in satisfactory agreement with the observed values, suggesting that the present DFT calculations are reliable.

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(8) The numberings, H2 and C2, do not coincide with the numberings in the ORTEP drawing shown in Figure 1.

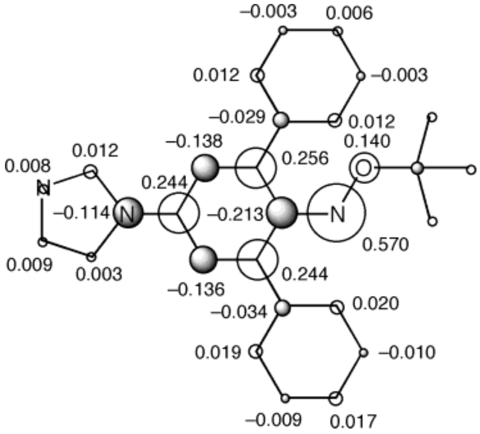

FIGURE 3. Spin density distribution of **2a** calculated by the DFT UBecke 3LYP hybrid method using the 6-31G basis set.

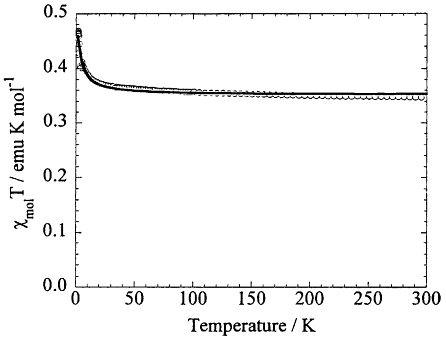

FIGURE 4. $\chi_{mol}T$ vs T plot for **2a**. The theoretical line is calculated by the dimer model with $2J/k_B = 3.4$ K.

The magnetic susceptibility measurements were carried out for **2a** with a superconducting quantum interference device (SQUID) in the temperature range 1.8−300 K. The diamagnetic components were estimated by the Pascal sum rule. In Figure 4, the $\chi_{mol}T$ vs T plot is depicted (χ_{mol}: the molar magnetic susceptibility). The radical purity estimated from the $\chi_{mol}T$ value (0.350 emu K mol^{-1}) in the high-temperature region was 93% (the Curie constant for the paramagnetic 1/2 spin system is 0.376 emu K mol^{-1}). Figure 4 shows that the $\chi_{mol}T$ value is constant in the temperature range 30−300 K and increases slightly below 30 K. Since the X-ray crystal structure of **2a** shows the formation of dimer, the observed magnetic behavior was analyzed using the dimer model, and a good agreement of the experimental data with the theoretical curve was obtained when $2J/k_B$ was 4.6 K (38 J mol^{-1}). As described in Figure 5, the two radical molecules contact between N2- - -C14′ and C14- - -N2′ with a distance of 3.47 Å to form a dimer, which is stacked along the *c*-axis. The nearest distance between the dimers is 5.99 Å, which is too long to interact. The calculated spin densities at N2 and C14 are −0.114 and +0.009. According to the McConnell rule,[10] the interaction within the dimer is ferromagnetic, in agreement with the observation. However, since the spin density on C14 is very low, the observed weak interaction can be explained by the very low spin density on C14.

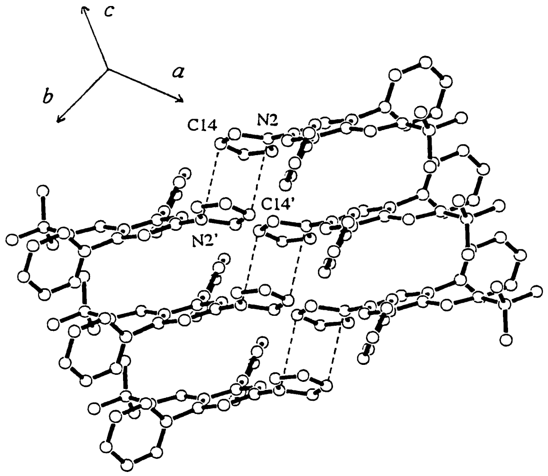

FIGURE 5. Dimer structure determined by the X-ray crystallography and the packing mode of the dimers. The distances between N2- - -C14′ and C14- - -N2′ are both 3.47 Å.

In conclusion, two pyridine ring-carrying *N*-alkoxyarylaminyls **1** and three imidazole ring-carrying *N*-alkoxyarylaminyls **2** were prepared by the reaction of the lithium salts of the corresponding anilines with *tert*-butyl peroxybenzoate, and the imidazole ring-carrying *N-tert*-butoxyarylaminyls could be isolated as radical crystals. The magnetic susceptibility measurements showed that **2a** interacts ferromagnetically. Analysis of the $\chi_{mol}T$ vs T plots using the dimer model gave $2J/k_B = 3.4$ K as the ferromagnetic interaction within the dimers.

Experimental Section

General Methods. 4-(1*H*-Imidazol-1-yl)aniline (**7**) was obtained by reduction of 4-(1*H*-imidazol-1-yl)-1-nitrobenzene[11] with Pd/C in THF (yield 99%).[12]

2,6-Dibromo-4-(1*H*-imidazol-1-yl)aniline (8). A mixture of 4.73 g (30 mmol) of **7**, 26.6 g (67 mmol) of BTMA Br_3, and 7.60 g of $CaCO_3$ in 150 mL of CH_2Cl_2 and 60 mL of MeOH was stirred at room temperature for 2 h. After filtration, the filtrate was washed with 10% $NaHSO_3$ and extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were then washed with brine, dried ($MgSO_4$), evaporated, and chromatographed on silica gel with ethyl acetate. Crystallization from hexane−ethyl acetate gave **8** as colorless prisms in 52% yield: mp 172−173 °C; ^1H NMR ($CDCl_3$) δ 4.69 (s, 2H), 7.14 (s, 1H), 7.17 (s, 1H), 7.45 (s, 2H), 7.70 (s, 1H). Anal. Calcd for $C_9H_7Br_2N_3$: C, 34.10; H, 2.23; N, 13.26. Found: C, 34.22; H, 2.35; N, 13.47.

General Procedure for Preparation of 9. A mixture of 1.00 g (3.2 mmol) of **8**, 8.2 mmol of arylboronic acid, 3.5 g of K_2CO_3 in 40 mL of benzene, 20 mL of water, and 5 mL of EtOH was stirred for 30 min, and 0.29 g (0.25 mmol) of $Pd(PPh_3)_4$ was

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added. The resultant mixture was then purged with N_2 and refluxed for 24 h with stirring. The mixture was washed with brine, dried ($MgSO_4$), evaporated, and chromatographed on alumina with CH_2Cl_2. Crystallization from hexanes−ethyl acetate gave **9** as colorless needles.

2,6-Diphenyl-4-(1*H*-imidazol-1-yl)aniline (9a): yield 70%; mp 159−160 °C; ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 2H), 7.15 (s, 2H), 7.16 (t, $J = 1.2$ Hz, 1H), 7.23 (t, $J = 1.2$ Hz, 1H), 7.39−7.54 (m, 10H), 7.78 (t, $J = 1.2$ Hz, 1H). Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.49. Found: C, 81.21; H, 5.74; N, 13.43.

2,6-Di(phenyl-*d*$_5$)-4-(1*H*-imidazol-1-yl)aniline (9a-*d*$_{10}$): yield 94%; mp 161−162 °C; ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 2H), 7.15 (s, 2H), 7.17 (t, $J = 1.2$ Hz, 1H), 7.23 (t, $J = 1.2$ Hz, 1H), 7.79 (t, $J = 1.2$ Hz, 1H). Anal. Calcd for $C_{21}H_7D_{10}N_3$: C, 78.47; H, 5.33; N, 13.07. Found: C, 78.55; H, 5.64; N, 12.99.

2,6-Bis(4-chlorophenyl)-4-(1*H*-imidazol-1-yl)aniline (9b): yield 88%; mp 197−199 °C; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 2H), 7.12 (s, 2H), 7.17 (s, 1H), 7.21 (s, 1H), 7.45 and 7.48 (each d, $J = 8.8$ Hz, 8H), 7.77 (s, 1H). Anal. Calcd for $C_{21}H_{15}Cl_2N_3$: C, 66.33; H, 3.98; N, 11.05. Found: C, 66.41; H, 4.21; N, 10.97.

General Procedure for Isolation of 2. A solution of 300 mg of **9** in 40 mL of anhyd THF was cooled to 78 °C under N_2, and 0.78 mL of a hexane solution of butyllithium (1.56 M) was added. After the solution was stirred for 15 min at the same temperature, a solution of 0.36 g (1.92 mmol) of *tert*-butyl peroxybenzoate in 5 mL of dry THF was added dropwise, and the resultant mixture was stirred for 1 h at the same temperature. The mixture was then gradually warmed to room temperature, washed with 10% $Na_2S_2O_3$, extracted with benzene, and dried ($MgSO_4$). After evaporation, the residue was chromatographed on silica gel cooled to 0 °C with 2:3 hexanes−ethyl acetate and crystallized from hexane.

***N*-*tert*-Butoxy-4-(1*H*-imidazol-1-yl)-2,6-diphenylphenylaminyl (2a):** red needles; yield 14%; mp 118−119 °C; UV−vis (benzene) λ_{max} 322 (ϵ/L cm^{-1} mol^{-1} 17100), 371 (7080), 514 nm (1410). Anal. Calcd for $C_{25}H_{24}N_3O$: C, 78.51; H, 6.32; N, 10.99. Found: C, 78.50; H, 6.46; N, 10.81.

***N*-*tert*-Butoxy-4-(1*H*-imidazol-1-yl)-2,6-bis(4-chlorophenyl)phenylaminyl (2b):** red microcrystals; yield 13%; mp 151−152 °C; UV−vis (benzene) λ_{max} 316 (ϵ/L cm^{-1} mol^{-1} 15 900), 375 (7390), 512 nm (1430). Anal. Calcd for $C_{25}H_{22}Cl_2N_3O$: C, 66.52; H, 4.91; N, 9.31. Found: C, 66.77; H, 5.07; N, 9.06.

Supporting Information Available: Preparation of **4** and **5** and X-ray crystallographic data of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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