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Ferromagnetic Behavior of Formyl-Group-Carrying Stable Thioaminyl Radicals[1]

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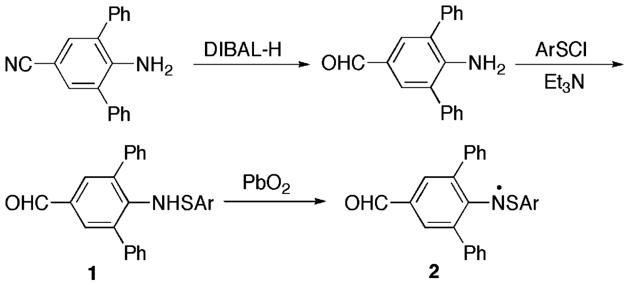
Abstract: Four formyl-group-carrying thioaminyl radicals were generated, and one radical could be isolated as radical crystals. Magnetic susceptibility measurements of the isolated radical showed a ferromagnetic regular linear-chain interaction of $2J/k_B = 3.2$ K, which was explained in terms of the X-ray crystallographic results.

Thioaminyl radicals have attracted much attention as a family of isolable and oxygen-inert radicals having a delocalized π-spin system.[2] Isolable and oxygen-inert radicals are important as a spin source or building blocks in the study of molecule-based magnetism.[3,4] Although much effort has been paid to finding new stable free radicals, isolable and oxygen-inert free radicals are still rare. In the present work we prepared formyl-group-carrying thioaminyl radicals because we planned to prepare thioaminyl-verdazyl or thioaminyl-nitronyl nitroxide diradicals. Among four kinds of formyl-substituted thioaminyls prepared, one radical could be isolated as radical crystals, and its X-ray crystallographic analysis was successfully performed. The magnetic susceptibility measurements with a superconducting quantum interference device (SQUID) magnetometer showed that the isolated radical was ferromagnetic, and the ferromagnetic behavior could be satisfactorily explained on the basis of the X-ray crystallographic results. Although we have so far found nine ferromagnetic thioaminyls,[1,5−9] their X-ray crystallographic analyses were unsuccessful for a long time because they did not give high-quality single crystals. Fortunately, however, we quite recently succeeded in the X-ray analysis for one ferromagnetic radical,[1] *N*-(2-pyridythio)-2,6-diphenyl-4-cyanophenylaminyl, and its magnetic behavior could be analyzed on the basis of the X-ray results. The present paper reports the second successful results.

SCHEME 1



a: Ar = 3-$NO_2C_6H_4$
b: Ar = 4-$NO_2C_6H_4$
c: Ar = 2,4-$Cl_2C_6H_3$
d: Ar = 3,5-$Cl_2C_6H_3$

N-(Arylthio)-2,6-diphenylanilines (**1**), the corresponding precursors of *N*-(arylthio)-2,6-diphenyl-4-formylphenylaminyls (**2**), were prepared according to Scheme 1. Treatment of 4-cyano-2,6-diphenylaniline with diisobutylaluminum hydride (DIBAL-H) in toluene gave 4-formyl-2,6-diphenylaniline in 86% yield. The precursors **1** were obtained in 22−31% yields by the reaction of 4-formyl-2,6-diphenylaniline with 3-nitro-, 4-nitro-, 2,4-dichloro-, and 3,5-dichlorobenzenesulfenyl chlorides in dry ether in the presence of Et_3N.

Oxidation of **1** was performed with PbO_2 using benzene as the solvent. When PbO_2 was added to the stirred colorless (**a**, **c**, **d**) or light yellow (**b**) mixtures of **1** and K_2CO_3, they immediately turned to dark green, and an intense ESR signal was observed from the resultant colored solutions. TLC analysis showed formation of the two new colored compounds, **2** (green) and **3** (orange). In the case of **1c**, both the compounds (**2c** and **3c**) could be isolated by chromatography. However, in the cases of **1a**, **1b**, and **1d**, pure radical crystals could not been obtained despite much effort. This is in part due to a partial decomposition of the radicals during chromatography.

The structure of **2c** was confirmed by the IR spectrum showing no NH absorption peak and by satisfactory elemental analyses. Later, the radical structure was unequivocally determined by X-ray crystallography, as described below.

The structure of **3c** was determined by its ^1H NMR (400 MHz) and mass spectra, elemental analysis, and later by X-ray crystallography, indicating that the 4-formylanilino group is converted into the *p*-benzoquinone monoimine structure, with a loss of the formyl group. To clarify whether **3c** is formed via **2c** or not, **2c** was treated with PbO_2 in benzene under atmospheric conditions, and chromatography of the resultant mixture gave **3c** in 58% yields. This reaction was also carried out under a

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(1) ESR Studies of Nitrogen-Centered Free Radicals. 57. Part 56. Miura, Y.; Oyama, Y.; Teki, Y. *J. Org. Chem*., **2003**, *68*, 1225.

(2) Miura, Y. *Trends Org. Chem*. **1997**, *6*, 197. Miura, Y. *Recent Res. Dev. Org. Chem*. **1998**, *2*, 251.

(3) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, Basel, 1999.

(4) Proceedings of the 7th International Conference on Molecule-Based Magnets; *Polyhedron* **2001**, *20*, 1115−1784.

(5) Teki, Y.; Itoh, K.; Okada, A.; Yamakage, H.; Kobayashi, T.; Amaya, K.; Kurokawa, S.; Ueno, S.; Miura, Y. *Chem. Phys. Lett*. **1997**, *270*, 573.

(6) Miura, Y.; Momoki, M.; Nakatsuji, M.; Teki, Y. *J. Org. Chem*. **1998**, *63*, 1555.

(7) Miura, Y.; Kurokawa, S.; Nakatsuji, M.; Ando, K.; Teki, Y. *J. Org. Chem*. **1998**, *63*, 8295.

(8) Miura, Y.; Tomimura, T.; Teki, Y. *J. Org. Chem*. **2000**, *65*, 7889.

(9) Nakatsuji, M.; Miura, Y.; Teki, Y. *J. Chem. Soc., Perkin Trans. 2* **2001**, 738.

10.1021/jo0300789 CCC: $25.00

SCHEME 2

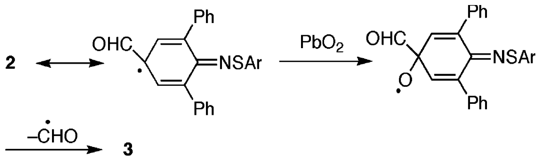


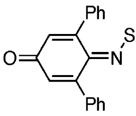
TABLE 1. ESR Parameter for 2 in Benzene Measured at 20 °C[a,b]

radical	a_N	a_H[c]	g
2a[d]	0.864		2.0061
2b[d]	0.861		2.0058
2c[e]	0.850	0.130 (2H),[f] 0.090 (1H)[g]	2.0059
2d[e]	0.860	0.130 (2H),[f] 0.095 (3H)[h]	2.0059

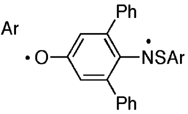
[a] The hfc constants are given in mT. [b] The g values were determined by comparison with Fremy's salt (g = 2.0057) in an aqueous dilute K_2CO_3 solution. [c] The numbers in parentheses refer to the number of equivalent protons. [d] The hyperfine splittings due to aromatic protons were not observed. [e] The proton hfc constants are determined by computer simulation. [f] Due to the anilino meta protons. [g] Due to the phenylthiyl ortho proton. [h] Due to the phenylthiyl ortho and para protons.

nitrogen atmosphere, and the same compound was obtained in a similar yield. On the basis of the above results we conclude that **3** is formed via **2** and the *p*-benzoquinone monoimine oxygen comes from the PbO$_2$ used as the oxidant. Although we cannot provide a clear mechanism for formation of **3** at the present time, a plausible mechanism is drawn in Scheme 2.

In the ^1H NMR spectrum of **3c** (see Supporting Information), the singlet due to the meta protons (2H) of the benzoquinone monoimine at 6.63 ppm and the multiplets due to the 2- and 6-phenyl protons (10H) at 7.43−7.53 ppm were significantly broadened. We previously observed a similar phenomenon for **4**.[10] A plausible explanation for the broadened ^1H NMR spectrum may be formation of diradical **3c′**, though the diradical was not detected by ESR, probably due to the very low concentration.

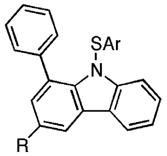


3



3'

(**c**: Ar = 2,4-Cl$_2$C$_6$H$_3$)



4 (R = *t*-Bu, Ph)

The ESR spectra of **2** were measured at room temperature using benzene as the solvent. The ESR parameters are summarized in Table 1. Although the ESR spectra of **2a** and **2b** were a broad 1:1:1 triplet, the other two radicals, **2c** and **2d**, showed additional hyperfine splittings due to aromatic protons. A typical ESR spectrum of **2c** is shown in Figure 1. The spectrum is split into a 1:1:1 triplet, and each component of the 1:1:1 triplet is further split into a broad 1:3:3:1 quartet. Computer simulation of the spectrum gave a_N = 0.850, a_H (2H) = 0.130, and a_H (1H) = 0.090 mT (g = 2.0059).

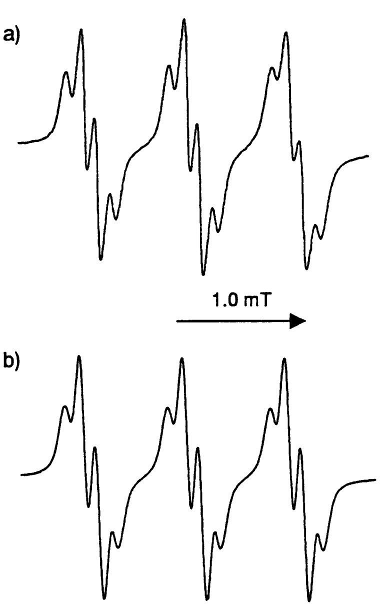


FIGURE 1. ESR spectrum of **2c** in benzene at 20 °C: (a) observed spectrum; (b) computer simulation.

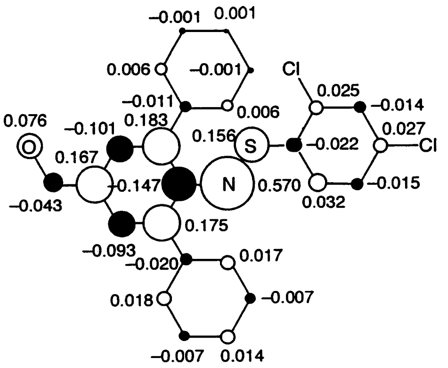


FIGURE 2. The total atomic spin densities in **2c**. The spin density calculations based on the density functional theory were performed by the UBecke 3LYP hybrid method using the 6-31G basis set.

The spin density distribution for **2c** was calculated by the DFT UBecke 3LYP hybrid method using the 6-31G basis set. The X-ray crystallographic structure was used without further optimization of structure. All the MO calculations were carried out on Gaussian 98.[11] The total atomic spin densities are depicted in Figure 2, and the calculated hyperfine coupling (hfc) constants are compared with the observed values in Table 2. As found in Table 2, the calculated hfc constants are in satisfactory

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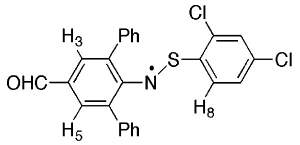
(10) Miura, Y.; Momoki, M. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1185.

(11) All calculations were carried out on *Gaussian 98*, Version A.9; Frisch, M, J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1998.

TABLE 2. Calculated hfc Constants for 2c and Comparison with Observed Values



position	calcd hfc constant[a,b]	obsd hfc constant[a,c]
N1	0.7708	0.850
S1	0.2547	
H_3	0.2334	0.130
H_5	0.1977	0.130
H_8	−0.0733	0.082

[a] The hfc constants are given in mT. [b] The hfc constants are calculated by the UBecke 3LYP hybrid method using the STO 6-31G basis set. [c] The hfc constants are shown in absolute values.

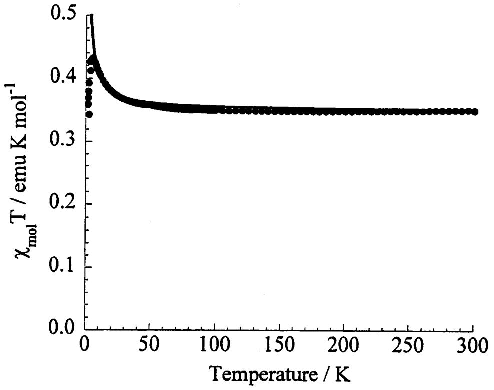


FIGURE 3. $\chi_{mol}T$ vs T plots of **2c**. The solid curve is the theoretical values calculated using eq 1.

agreement with the observed ones, strongly suggesting that the spin density distribution shown in Figure 2 is reliable.

Magnetic susceptibility (χ) measurements for **2c** were carried out using polycrystalline samples with SQUID. The diamagnetic components were estimated by the usual Pascal sum rule. Figure 3 shows $\chi_{mol}T$ vs T plots. The $\chi_{mol}T$ value at the high-temperature region (~300 K) is 0.350 emu K mol^{-1}, which corresponds to 93% of the Curie constant (0.376 emu K mol^{-1} for the $S = 1/2$ spin system), indicating the purity of the radical is 93%.

The $\chi_{mol}T$ is constant in the temperature range from 300 to 50 K and below 50 K $\chi_{mol}T$ increases with decreasing temperature and gives a maximum in $\chi_{mol}T$ at 10 K. Below 10 K, the $\chi_{mol}T$ decreases with decreasing temperature. This magnetic behavior suggests that the intrachain interaction is ferromagnetic and the interchain interaction is antiferromagnetic. As found in Figure 4, the radical molecules are stacked along the *a* axis in a zigzag fashion. Taking this X-ray result into account we analyzed the ferromagnetic behavior with the regular Heisenberg model[12] (eq 1), and the best-fit value of the regular linear-chain interaction, $2J_1/k_B$, was determined to be +3.2 K (27 cal mol^{-1}).

$$\boldsymbol{H} = -2J_1\Sigma\boldsymbol{S}_i\cdot\boldsymbol{S}_j \qquad (1)$$

The nearest distances between the neighboring radical molecules are found for S1··· C5′ (3.76 Å), S1··· C4′ (4.06 Å), N1··· C5′ (4.26 Å), S1··· C19′ (4.29 Å), and S1··· C6′ (4.34 Å). The spin densities on those atoms predicted by the above MO calculations are 0.156 (S1), 0.570 (N1), 0.167 (C4), −0.093 (C5), and 0.175 (C6), respectively. According to the McConnell rule,[13] the contacts through S1··· C5′, S1··· C19′, and N1··· C5′ are ferromagnetic, and the contracts through S1··· C4′ and S1··· C6′ are antiferromagnetic. Since the above analysis shows that the intrachain interaction is ferromagnetic, the contacts through S1··· C5′, S1··· C19′, and N1··· C5′are dominant.

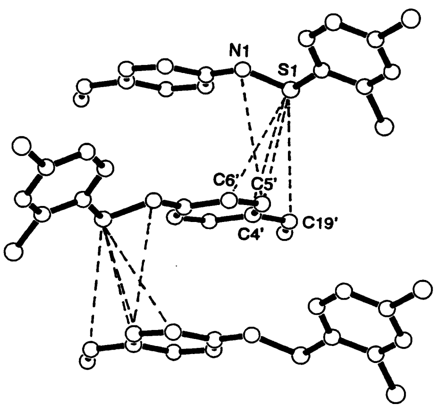


FIGURE 4. Stacking mode of **2c** along the *a* axis. The contacts between S1··· C5′ (3.76 Å), N1··· C5′ (4.26 Å), and S1··· C19′ (4.29 Å) are shown to be ferromagnetic, whereas the contacts between S1··· C4′ (4.06 Å) and S1··· C6′ (4.34 Å) are shown to be antiferromagnetic (see text).

In conclusion, we have successfully isolated a formyl-group-carrying thioaminyl radical, and the regular linear-chain ferromagnetic interaction could be satisfactorily explained by the X-ray crystal structure. This is the second ferromagnetic thioaminyl whose magnetic behavior could be explained by the X-ray crystallographic results. The magnetic data analyzed on the basis of the X-ray crystallographic structures are particularly important for robust developments of the magnetic study.

Experimental Section

General Procedure for Preparation of *N*-(Arylthio)-4-formyl-2,6-diphenylanilines (1). A solution of arenesulfenyl chloride (10 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of 4-formyl-2,6-diphenylaniline (2.00 g, 7.3 mmol) and Et_3N (4.0 mL) in dry ether (300 mL) at 0 °C. After being stirred for 2 h at the same temperature, the mixture was filtered and evaporated. The residue was then chromatographed on alumina with 4:5 (**1a**), 3:1 (**1b**), 1:3 (**1c**), or 1:1 CH_2Cl_2/hexane (**1d**) at room temperature (**1a** and **1b**) or 0 °C (**1c** and **1d**). Compounds **1a** and **1b** were further purified with a recycle preparative HPLC instrument.

Isolation of *N*-[(2,4-Dichlorophenyl)thio]-4-formyl-2,6-diphenylphenylaminyl (2c). A mixture of **1** (100 mg) and K_2CO_3 (300 mg) in benzene (10 mL) was vigorously stirred. After PbO_2 (2.5 g) was added during 0.5 min in some portions, the mixture was further stirred for 1 min and filtered. After the benzene was removed by freeze-drying, the residue was subjected to chromatography on alumina. Elution of the green zone with benzene gave **1c** in 56% yield, and subsequent elution of the orange zone with ethyl acetate gave **3c** in 18% yield. Data for **2c**: dark green needles (from hexane/ethyl acetate); mp

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(12) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *A135*, 640.
(13) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

128−130 °C; IR (KBr) 1680 cm^{-1} (CHO); UV−vis (benzene) 394 (15200), 445 (12800), 572 (2980, s), 656 nm (5590 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{25}H_{16}Cl_2NOS$: C, 66.82; H, 3.59; N, 3.12. Found: C, 66.64; H, 3.70; N, 3.06.

***N*-[(2,4-Dichlorophenyl)thio]-2,6-diphenyl-*p*-benzoquinone Monoimine (3c):** orange prisms (from hexane/ethyl acetate); mp 185−186 °C; IR (KBr) 1625 cm^{-1} (C=O); FABMS *m*/*z* 436 (M$^+$ + 1, 26); ^{1}H NMR ($CDCl_3$) δ 6.63 (br s, 2H), 6.70 (d, $J = 8.8$ Hz, 1H), 6.85 (dd, $J = 8.8$ and 2.0 Hz, 1H), 7.16 (d, $J = 2.0$, 1H), 7.43−7.53 (br m, 10H). Anal. Calcd for $C_{24}H_{15}Cl_2NOS$: C, 66.06; H, 3.46: N, 3.21. Found: C, 65.87; H, 3.68; N, 3.21.

Supporting Information Available: Preparation of 4-formyl-2,6-diphenylaniline and **1a**−**d**, ^{1}H NMR spectrum of **3c**, and X-ray crystallographic data of **2c** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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