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Synthesis of Phenylnitroxides Bridged by an sp^3-Linkage

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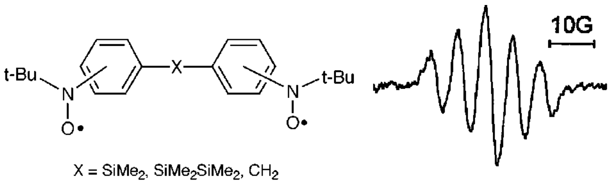
ABSTRACT



X = SiMe$_2$, SiMe$_2$SiMe$_2$, CH$_2$

Silicon- and carbon-bridged phenylnitroxides were synthesized. They exhibited similar ESR profiles independent of the nature of the sp^3 bridge and the substitution mode of the phenylene units. The spectra revealed a quintet signal at room temperature, which became a broad triplet by lowering the temperature. Accumulated ESR measurements at 77 K led to the successful observation of a signal at $\Delta m_s = 2$, indicating that the triplet state was involved in this system.

There has been an interest in the $\sigma-\pi$ conjugated organosilicon compounds, in which orbital interaction between the Si σ-orbital and carbon π-electron system takes place to provide the potential utilities of the compounds as novel functional materials.[1] For example, it has been demonstrated that polymers composed of a regularly alternating arrangement of organosilicon and π-conjugated carbon units can be used as organic electric semiconductors, photoconductors, and hole- and electron-transporting materials. An advantage of the use of $\sigma-\pi$ conjugated system, in particular for polymeric materials, is the high solubility of the materials in common organic solvents arising from the flexibility of the backbone, which is difficult to be gained by usual π-conjugated systems unless they have long flexible side chains.

On the other hand, several approaches have been examined to obtain high-spin organic molecules by using a variety of conjugated spin couplers in both experimental and theoretical aspects.[2] However, those reported so far have been rather restricted to π-conjugated systems, and only a little is known about the $\sigma-\pi$ systems as spin couplers. One example comprises phenylnitrenes bridged by a disilanylene unit, reported by Iwamura et al.[3] Of those, bridging the phenylnitrene units by meta and para substitution modes results in the high-spin coupling of the nitrenes.

In the course of studies to explore further the utilities of $\sigma-\pi$ system,[1] we prepared compounds having two phenylnitroxide units linked by a mono- or disilanylene bridge, in the hope of obtaining the information for the potential utilities

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(1) (a) Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379. (b) Ishikawa, M.; Ohshita, J. Silicon and Germanium Containing Conductive Polymers. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, Chapter 15. (c) *Inorganic and Organometallic Polymers*; ACS Symposium Series 368; Zeldin, M., Wynne, H. K. J., Allcock, R., Eds.; American Chemical Society: Washington, DC, 1988. (d) *Silicon-Based Polymer Science*; Advances in Chemistry Series 224; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990.

(2) For recent works, see: (a) Ducasse, L.; Fritsch, A. *Chem. Phys. Lett.* **1998**, *286*, 183. (b) Nishide, H.; Doi, R.; Oyaizu, K. Tsuchida, E. *J. Org. Chem.* **2001**, *66*, 1680. (c) Rajca, A.; Rajca, S.; Wougsriratanakul, J. *J. Am. Chem. Soc.* **1999**, *121*, 6308. (d) Miyasaka, M.; Yamazaki, T.; Tsuchida, E.; Nishide, H. *Macromolecules* **2000**, *33*, 8211. (e) Chapyshev, S. V.; Walton, R.; Sanborn, J. A.; Lahti, P. M. *J. Am. Chem. Soc.* **2000**, *122*, 1580. (f) Domingo, V. M.; Burdous, X.; Brillas, E.; Carilla, J.; Rius, J.; Terrelles, X.; Juliá, L. *J. Org. Chem.* **2000**, *65*, 6847. (g) Domingo, V. M.; Alemán, C.; Brillas, E.; Juliá, L. *J. Org. Chem.* **2001**, *66*, 4058. (h) Nishide, H.; Maeda, T.; Oyaizu, K.; Tsuchida, E. *J. Org. Chem.* **1999**, *64*, 7129. (i) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942. (j) Itoh, T.; Matsuda, K.; Iwamura, H.; Hori, K. *J. Am. Chem. Soc.* **2000**, *122*, 2567.

(3) Doi, T.; Ichimura, A.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 8928.

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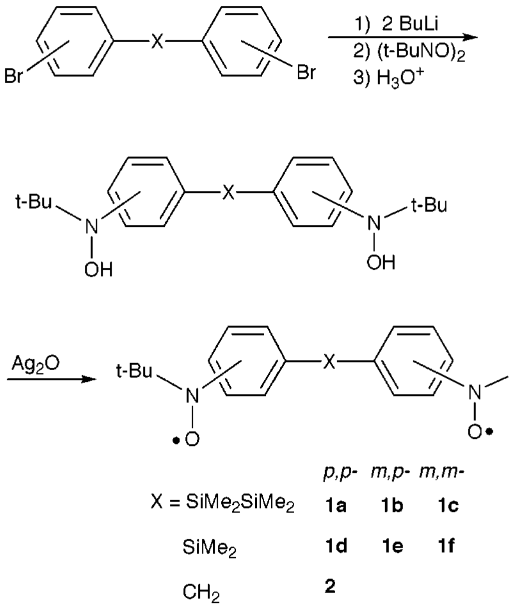
Scheme 1



of $\sigma-\pi$ conjugated systems as flexible high-spin couplers.[4] We also prepared methylene-bridged phenylnitroxides, for comparison.

Bridged phenylnitroxides **1a**−**f** were obtained, as shown in Scheme 1 and Table 1. Thus, di(lithiophenyl)di- and monosilanes were treated with *tert*-butylnitroso dimer to afford the corresponding hydroxylamines. The hydroxylamines were then treated with excess silver oxide until the O−H stretching absorptions in the IR spectra disappeared.[5] Compounds **1a**,**d** were obtained as orange to red solids by recrystallization in high yields. Compounds **1b**,**c**,**e**,**f** could be isolated by alumina column chromatography as viscous red oils, but they slowly decomposed by standing them in the condensed phase. Carbon-bridged phenylnitroxide **2** was even less stable and could not be isolated. Therefore, these compounds were subjected to the following ESR experiments after removal of inorganic salts by filtration without further purification, which also gave sufficient data without any signals due to the monoradicals (vide infra). The phenylnitroxides were characterized by IR spectrometry and elemental analysis, except for **2**.

Table 1. Preparation and ESR Data for Compounds **1**, **2**, and **3**

		ESR data		
compd	yield/%[a]	*g*	hfc/G[c]	distance/Å[d]
1a	68	2.0068	5.96	12.0
1b	26	2.0069	6.37	10.7
1c	21	2.0069	5.93	10.6
1d	73	2.0066	5.80	10.4
1e	85	2.0073	6.11	10.0
1f	95	2.0077	6.60	9.1
2	ni[b]	2.0071	6.17	10.5
3d	ni[b]	2.0073	12.22	

[a] Isolated yield. [b] ni = not isolated. [c] hfc at room temperature. [d] Intramolecular distance between radicals estimated by the ESR spectrum at 77 K.

The crystal structure of **1a** was determined by a single-crystal Xray diffraction study, and the ORTEP drawing is depicted in Figure 1.[6] As can be seen in Figure 1, the phenylnitroxide groups are located in a trans fashion with respect to the Si−Si bond which possesses a gauche configuration. The Si−Si bond is almost perpendicular to

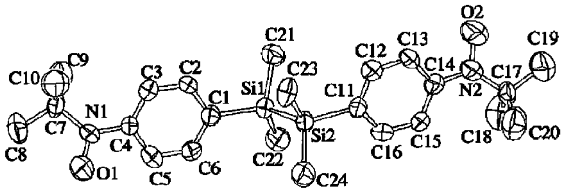


Figure 1. ORTEP drawing of compound **1a**. The thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−Si2 = 2.344(4), Si1−C1 = 1.887(9), Si1−C21 = 1.87(1), N1−O1 = 1.27(1), N1−C4 = 1.41(1), N1−C7 = 1.49(1), N2−O2 = 1.28(1), N2−C14 = 1.41(1), N2−C17 = 1.47(1), Si2−Si1−C1 = 108.4(3), Si1−Si2−C11 = 107.4(3), O1−N1−C4 = 116.1(8), O1−N1−C7 = 117.3(7), C4−N1−C7 = 126.6(8), O2−N2−C14 = 115.3(9), O2−N2−C17 = 116.5(8), C14−N2−C17 = 128.1(9).

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(4) Iwamura et al. mentioned that they have synthesized compound **1a** and determined the crystal structure by an Xray diffraction study (ref 3). However, no detailed description has been given so far.

(5) An illustrative procedure for the preparation of **1** is as follows. To a solution of 1.0 g (2.33 mmol) of 1,2-bis(4-bromophenyl)-1,1,2,2-tetramethyldisilane in 8 mL of ether was added 3.0 mL (4.80 mmol) of an *n*-butyllithium/hexane solution (1.6 M) at −78 °C, and the mixture was gradually warmed to room temperature over a period of 1 h. To this was added a solution of 0.52 g (3.04 mmol) of 2-methyl-2-nitrosopropane dimer in 8 mL of THF at −78 °C, and the mixture was stirred at room temperature for 1 h. The mixture was hydrolyzed with aqueous ammonium chloride and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was recrystallized from acetone to give 0.75 g (73 % yield) of 1,2-bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]-1,1,2,2-tetramethyldisilane as a pale yellow solid: mp 208−209 °C; MS *m*/*z* 444 (M$^+$); ^{1}H NMR (δ in THF-d_8) 0.31 (s, 12H), 1.13 (s, 18H), 7.19 (d, 4H, J = 8.09 Hz), 7.25 (d, 4H, J = 8.09 Hz), 7.35 (s, 2H, OH); ^{13}C MNR (δ in THF-d_8) −3.54, 26.56, 60.50, 124.69, 133.69, 134.44, 152.47; ^{29}Si NMR (δ in THF-d_8) −22.65; IR 3228 cm^{-1} (O−H); UV (in THF) λ_{max} 265 nm. Anal. Calcd for $C_{24}H_{40}N_2O_2Si_2$: C, 64.81; H, 9.07; N, 6.30. Found: C, 65.11; H, 9.06; N, 6.25. To a solution of 50 mg (0.11 mmol) of 1,2-bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]-1,1,2,2-tetramethyldisilane in 5 mL of ether was added a large excess amount (100 mg, 0.78 mmol) of Ag_2O, and the mixture was stirred for 30 min at room temperature. The mixture was filtered and the solvent was evaporated; then the residue was recrystallized from hexane to give 34 mg (68 % yield) of **1a** as a red needle crystal: mp 129−133 °C; MS *m*/*z* 442 (M$^+$); λ_{max} (in cyclohexane) 311.2 nm. Anal. Calcd for $C_{24}H_{38}N_2O_2Si_2$: C, 65.10; H, 8.65; N, 6.33. Found: C, 65.12; H, 8.68; N, 6.26. IR spectrum of **1a** reveled no absorptions in the region of O−H stretching.

(6) Crystal data for **1a**: $C_{24}H_{38}O_2N_2Si_2$, M_W = 442.75, space group $P2_1/c$ with a = 7.459(2) Å, b = 17.920(2) Å, c = 20.139(1) Å, β = 93.22(1)°, V = 2687.5(6) Å^3, Z = 4, density (calcd) = 1.094 g/cm^3, $F(000)$ = 960.00, μ(Mo Kα) = 1.52 mm^{-1}. A total of 6633 intensity data were collected on a Rigaku AFC7R diffractometer using a 0.8 × 0.1 × 0.1 mm^3 sized crystal; 1884 unique reflections with $I > 1\sigma(I)$ (reflns/para = 7.0) were used in refinement; R = 7.9, R_w = 8.3%.

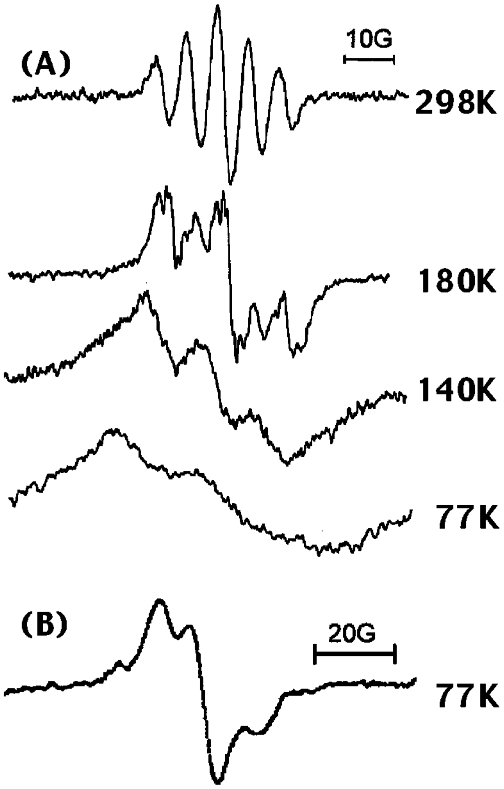

Figure 2. ESR spectra of compound **1a**. (A) $\Delta m_s = 1$ transition in benzene and (B) $\Delta m_s = 2$ transition in 2-methyltetrahydrofuran at 77 K.

the attached phenylene rings, with angles of 91.17° and 86.82° between the Si−Si−C(ipso) planes and mean planes of the phenyl rings, to permit the maximum overlap of the Si−Si σ-orbital and the π-orbital. The nitroxide units in **1a** are planar as indicated by the sum of the angles around the nirtogen atoms of 360.0° for N1 and 359.9° for N2, and the nitroxide planes are a little twisted with respect to the phenylene rings. The angles of the mean planes of nitroxides and the adjacent phenylene planes are 31.80° for nitroxide of N1 and 23.18° for that of N2, presumably due to the steric repulsion between the *tert*-butyl group and phenylene ortho-protons.

Compounds **1a**−**f** and **2** exhibited essentially the same ESR profiles, independent of nature of the sp^3-linkage (X) and the substitution modes of the phenylene units. The spectra showed an intense quintet signal with hfc of ~6 G in the $\Delta m_s = 1$ region ($g \approx 2.0$) at room temperature (Table 1). Since the ESR spectrum of monoradical t-Bu(HO)N-*p*-C_6H_4-$SiMe_2$-*p*-$C_6H_4N(O^•)$t-Bu (**3d**), prepared by the reaction of Ag_2O with a large excess of the precursor, bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]dimethylsilane, revealed a triplet signal with the hfc of approximately twice as large as that of **1d**, the hfc of **1a**−**f** and **2** is most likely to be due to the coupling with two magnetically equivalent nitrogens. This clearly indicates that the intramolecular spin exchange integral (J) is sufficiently large when compared with the nitrogen coupling constant (a), i.e., $a/J \approx 0$.[7] The absence of evident influence of the structure of the bridged nitroxides **1a**−**f** and **2** on the ESR profiles would indicate that the $\sigma-\pi$ conjugation does not play an important role in the spin exchange, although the crystal structure of **1a** geometrically permits the $\sigma-\pi$ conjugation, as mentioned above.

Interestingly, the ESR signals of bridged nitroxides **1a**−**f** and **2** were broadened and became a triplet on cooling, as illustrated in Figure 2A for **1a**. The broadening of the lines is presumably attributable to the anisotropic interactions owing to immobilizing the molecules by lowering the temperature. On the other hand, the changes of the ESR signals from quintet to triplet may be best explained by taking account of the conformational flexibility of these compounds which may exert influence on the degree of the spin localization. Thus, at room temperature free rotation around the nitroxide−phenylene bonds would allow the nitroxide spins to delocalize over the phenylene rings to some extent, giving rise to the possible through-space interaction between the spins. However, at low temperature, the rotation would be frozen with twisting between the nitroxide planes and the adjacent phenylene rings, respectively, due to the steric repulsion, as observed for the crystal structure of **1a**. As the result, the spins are more localized on the nitroxide units and hence rather isolated from each other, relative to those at higher temperature. Figure 3 shows the changes of heats of formation for a model compound with the function of nitroxide−phenylene twisting angles, derived from MO calculations. As can be seen in Figure 3, the energy minimum was obtained with a twisting angle of 34°.

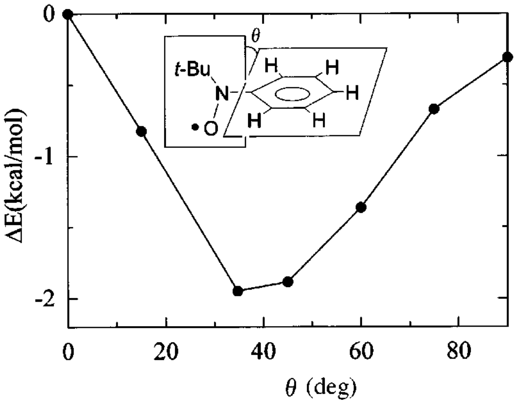

Figure 3. Plots of dihedral angles of C(*β*)−C(α)−N−O vs relative heats of formation for the model compound presented, derived from MO calculations at level of B3LYP/6-31G using the Gaussian 98 software. For the calculations, the dihedral angle was rotated from 0° to 90° and bond lengths, angles, and the other dihedral angles were optimized at this level.

At 77 K, a signal ascribed to the $\Delta m_s = 2$ transition was also observed by accumulated measurements for all of the present bridged nitroxides **1a**−**f** and **2**, indicating that the

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(7) (a) Glarum, S. H.; Marshall, J. H. *J. Chem. Phys.* **1967**, *47*, 1374. (b) Luckhurst, G. R.; Pedulli, G. F. *J. Am. Chem. Soc.* **1970**, *92*, 4738.

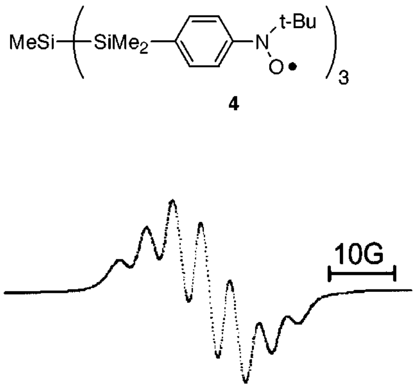

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Figure 4. Structure and ESR spectrum of compound **4** recorded at 298 K.

triplet spin states were involved in these systems (Figure 2B). Interspin distances were estimated from the intensity ratios of the $\Delta m_s = 2$ and $\Delta m_s = 4$ transition peaks in the ESR spectra as listed in Table 1,[8] which are a little shorter than the distances between the nitroxide units, derived from molecular modeling.[9] Similarly, the interunit distance observed in the crystal structure of **1a** (O1−O2 = 14.1 Å, N1−N2 = 13.0 Å) is slightly longer than the interspin distance based on its ESR spectrum (Table 1). This may be due to the delocarization of the spin density to the phenylene ring, although the contribution seems to be small.

It is also noteworthy that the spin distance for methylene-bridged compound **2** is calculated to be a little longer than that of the silylene analogue (**1d**), despite the shorter C−C bond length than that of Si−C. Although the origin of this disagreement is still unclear, there may be some electronic effects of the silylene bridge on the spin interaction. Enhancement of through-space $\pi-\pi$ interaction by a silylene bridge has been reported, previously.[10]

We also prepared compound **4**, having three phenyl nitroxide units linked by an organosilicon core. As expected, the ESR spectrum of **4** at 298 K revealed a septet signal at $g = 2.0071$ with an hfc of 4.40 G, which is approximately one-third of the hfc of mononitroxide **3d** (Figure 4). At 77 K, a signal due to the $\Delta m_s = 2$ transition was observed, similar to that for **1a**−**f** and **2**, although no signals in the region of $\Delta m_s = 3$ could be detected, probably due to the low intensity.

In conclusion, we have synthesized a series of sp^3-linkage-bridged phenylnitroxides and found that they exhibit temperature-dependent ESR profiles. It was also demonstrated that they involve triplet spin states. Detailed studies on the spin states of these systems are in progress and will be reported elsewhere.

Acknowledgment. We thank Sankyo Kasei Co. Ltd. and Sumitomo Electric Industry for financial support.

Supporting Information Available: Experimental procedures and spectral and analytical data for compounds **1a**−**f**, **2**, and **4**. Tables of crystal data, experimental conditions, and summary of structural refinement, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

[9] MOPAC/AM1 calculations on model compounds, (HO)HN-C_6H_4-X-C_6H_4NH(OH), where C_6H_4 = *m*- or *p*-phenylene, X = $(SiH_2)_{1,2}$ and CH_2, predicted the intramolecular distances of O−O = 13.0−14.6 Å for **1a**−**c**, 10.8−12.1 Å for **1d**−**e**, and 11.1 Å for **2** and N−N = 11.4−13.1 Å for **1a**−**c**, 10.2 Å for **1d**−**e**, and 9.8 Å for **2**, respectively.

[10] (a) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T. Y. *J. Am. Chem. Soc.* **1997**, *119*, 11321. (b) van Walree, C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.