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Magnetic Interaction between Two Triplet Nitrene Units through Diphenylsilane and 1,2-Diphenyldisilane Couplers

Takatsugu Doi, Andrew S. Ichimura, Noboru Koga, and Hiizu Iwamura*

Contribution from the Department of Chemistry, Faculty of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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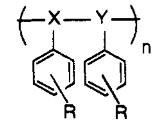
Abstract: *m,m*′-, *m,p*′-, and *p,p*′-Bis(azidophenyl)dimethylsilanes **1a** and 1,2-bis(azidophenyl)-1,1,2,2-tetramethyldisilanes **2a** were prepared, and the dipolar and exchange couplings in the corresponding dinitrenes **1n** and **2n** generated photochemically were investigated by means of EPR spectroscopy at cryogenic temperatures. The powder pattern fine structures due to the quintet states with $|D/hc| = 0.158$ and $0.172\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.014$ and $0.009\ \mathrm{cm}^{-1}$ were observed for *p,p*′-**2n** and *m,m*′-**2n**, respectively. Temperature dependences of the EPR signal intensities due to the high-spin states revealed that the two nitrene centers separated by the disilane linkage interact antiferromagnetically in *p,p*′-**2n** and *m,m*′-**2n** and ferromagnetically in *m,p*′-**2n**. The energy differences between the singlet and quintet states ($\Delta E_{S\text{-}Q}$) were estimated to be -300 and $0 > \Delta E_{S\text{-}Q} > -3.4$ cal/mol for *p,p*′-**2n** and *m,m*′-**2n**, respectively. Comparison with the monosilanes which have no interaction except for a weak dipolar coupling in *m,p*′-**1n** suggested that the σ–π conjugation in the PhSiSiPh moiety may play an important role in this through-bond interaction. The observed regioselectivity of the ground-state spin multiplicity and the necessity for σ–π overlap in providing through-bond exchange coupling were bolstered by semiempirical CI calculations.

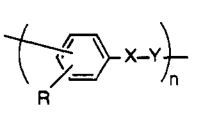
Introduction

One of the promising structures leading to organic molecules with high-spin ground states is a π-conjugated polymer having open shell centers as pendants in the side chains.[1] In order to foresee and predict the magnetic properties of such polymers, it is necessary to understand how two open-shell centers would couple through a magnetic coupler in a model diradical possessing a partial structure of the polymer chain.

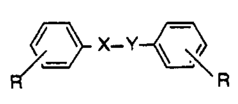
Dimer structures **D** would serve as prototypes for judging the sign and magnitude of the intramolecular coupling in polyradicals **P** and **P′**. Poly(phenylsilane)s have been taken into account in this study as versatile polymer main chains[2] for making potentially high-spin organic polymers. A nitrene has been chosen for a spin-carrying center, R, since the precursor azide is readily introduced and the interaction between two nitrene centers through a π-conjugated framework is known to be strong compared with that of persistent nitroxides.[3] We report here the regioselectivity in the exchange coupling between the two nitrene units in isomeric 1,2-bis(nitrenylphenyl)-1,1,2,2-tetramethyldisilanes **2n** as prototypes for such polymers **P** (XY = Si–Si). The results will be compared with those of the corresponding dinitrenes of monosilanes **1n** and the classically conjugated stilbenes **D**(XY = CH=CH)[4] and tolanes **D** (XY = C≡C)[5] reported previously.



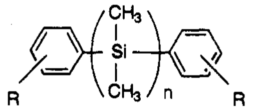
P



P′



D



n=1 n=2

R= N: **1n** **2n**

Results and Discussion

Diazidomonosilanes and Diazidodisilanes. The isomeric 1,2-bis(bromophenyl)disilanes (**2b**) and bis(bromophenyl)monosilanes (**1b**) were prepared by coupling[6] of the corresponding (bromophenyl)lithium with the chlorosilanes. Dibromides **1b** and **2b** were then dilithiated with *n*-butyllithium in diethyl ether at −78 °C and allowed to react with *p*-tosyl azide to give the isomeric diazidodisilanes (*p,p*′-**2a**, *m,m*′-**2a**, and *m,p*′-**2a**) and diazidomonosilanes (*p,p*′-**1a**, *m,m*′-**1a**, and *m,p*′-**1a**) as summarized in Scheme I. Analytically pure samples were obtained by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 as eluent. Diazide derivatives were used for EPR measurements immediately after the purification. The UV–visible absorption spectra of the azides *p,p*′-**2a** and *p,p*′-**1a** in *n*-hexane showed absorption maxima at 266 and 240 nm, respectively. The observed red shift of the former compared with that of the latter is ascribed to the σ–π conjugation of substituted phenyldisilane moieties,[7] suggesting possible magnetic interactions between the two nitrene centers in **2n** as there are in stilbenes and tolanes.

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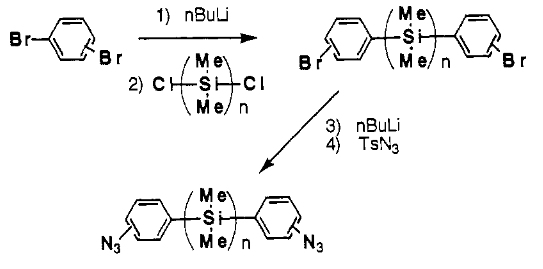
Scheme I



n = 1 **1a**
n = 2 **2a**

EPR Measurements. Dinitrenes (**2n** and **1n**) were produced by irradiation of solid solutions of the corresponding diazides in 2-methyltetrahydrofuran (MTHF) or ethanol-d_6 (ca. 6 mmol/L) with a Pyrex-filtered high-pressure mercury lamp with or without additional filters in an EPR cavity at cryogenic temperatures.

When a solid solution of *p,p′*-**2n** in ethanol-d_6 was photolyzed, several signals appeared in addition to the X (= Y) transitions due to an isolated triplet nitrene at 679 mT (Figure 1a). Similar spectra were also obtained in MTHF matrices and were independent of the irradiation wavelength. The additional signals were found to be classified into two groups by the temperature dependence of their spectral intensities in the range 10–93 K. The signal intensity at 243 mT and those at 16.4, 283, 636, and 842 mT increased reversibly with increasing temperatures (Figure 1a′) and reached maxima at 30 and 86 K, respectively (Figure 2), suggesting that the signals are due to thermally populated species. The latter signals are characteristic of quintet dinitrenes,[4,5,8] and zero-field splitting values (zfs) were determined to be $|D/hc| = 0.158$ cm^{-1} and $|E/hc| = 0.014$ cm^{-1} by applying a third-order perturbational method to the highest-field Z transition ($m_S = -2 \rightarrow -1$) and next highest-field Y transition ($m_S = 1 \rightarrow 2$).[5,9] Interaction between two triplet centers gives rise to six nonionic electronic states in which two are singlet, three are triplet, and one is quintet. As far as a weak interaction between two triplet centers each of which has strong one-center coupling is concerned, as in these dinitrenes, these six states are reduced to one each of singlet, triplet, and quintet states. The energy differences of the quintet $\Delta E_{\mathrm{S-Q}}$ ($-6J$) and triplet $\Delta E_{\mathrm{S-T}}$ ($-2J$) states from a ground singlet state were estimated on the basis of a weakly interacting two-triplet model as described by eq 1,

$$I = \frac{5C\exp(-6J/RT)}{T[5\exp(-6J/RT) + 3\exp(-2J/RT) + 1]} \qquad (1)$$

where I and C are an EPR signal intensity due to the quintet state and a proportionality constant, respectively. By assuming that the signal at 243 mT was due to the thermally populated triplet, we calculated the $\Delta E_{\mathrm{S-T}}$ and, consequently, $\Delta E_{\mathrm{S-Q}}$ values to be approximately −100 and −300 cal/mol, respectively. The $\Delta E_{\mathrm{S-Q}}$ value of −290 cal/mol was determined independently from the temperature dependence of the other signals due to the quintet state and is in good agreement with that derived from the excited triplet. Therefore, the assignment of the two sets of the signals to the thermally populated triplet and quintet states of *p,p′*-**2n** is justified.

In the EPR spectrum of *m,m′*-**2n**, signals due to a quintet state were also observed but the spectral shape in the field range 100–320 mT was sample-dependent. A sample in MTHF showed an EPR spectrum corresponding to $|D/hc| = 0.172$ cm^{-1} and $|E/hc| = 0.009$ cm^{-1} as shown in Figure 1b. After annealing at 64 K, the quintet signals changed to a reproducible broad signal at 206 mT. The sample dependence of the quintet signals right after the photolysis of the *m,m′*-isomer is considered to be caused by its conformation in frozen solvents. Similar behavior was also observed in the *m,m′*-isomers of stilbene[4] and tolane[5] systems. Both the signal intensities before and after annealing decreased in accordance with Curie's law in the range 10–64 K, suggesting either that the two nitrene centers interact in a ferromagnetic fashion or that the spin states are nearly degenerate with $0 > \Delta E_{\mathrm{S-Q}} > -3.4$ cal/mol. The latter is more likely the case, although the dipolar coupling is similar in magnitude to the *p,p′*-isomer.

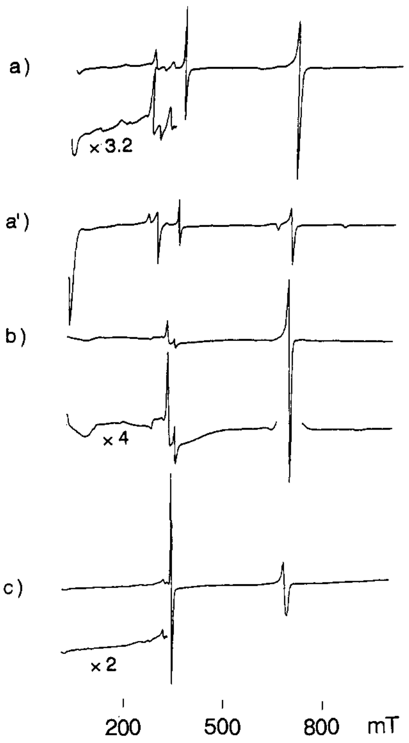


Figure 1. X-band (9.4249 GHz) EPR spectra of *p,p′*-**2n** in frozen C_2H_5OH-d_6 (a) at 28 K and (a′) at 78 K. Spectra at 10 K due to *m,m′*- and *m,p′*-isomers are given in (b) and (c), respectively.

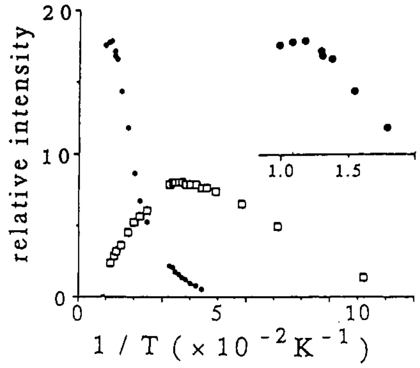


Figure 2. Plots of the signal intensities at 243 mT (□) and 284 mT (●) due to *p,p′*-**2n** vs the inverse of temperature.

When *m,p′*-**2a** was irradiated under similar conditions, a weak signal at 313 mT and a strong sharp one at 338 mT appeared together with an isolated triplet signal at 682 mT with $|D/hc| = 0.968$ cm^{-1} and $|E/hc| = 0.00$ cm^{-1} (Figure 1c). In the temperature range 10–90 K, no new signals appeared and the observed signal intensities decreased in accordance with Curie's law. Although a signal due to a fortuitously formed photobyproduct in a doublet state often appears at these field positions in the photolysis of phenyl azides under similar conditions, there is circumstantial evidence which permits the assignment of the observed signals at 313 and 338 mT to a quintet species. Firstly, the spectral shape consisting of a set of a sharp signal and a weak one is very

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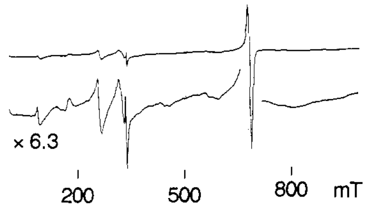

Figure 3. X-band (9.4820 GHz) EPR spectrum of *m,p′*-**1n** in frozen MTHF at 10 K.

similar to those of the *m,p′*-isomers of the stilbene and tolane systems,[4,5] in which the sharp signal appeared at 308 mT. Secondly, this set of signals appeared by longer wavelength irradiation ($\lambda > 400$ nm), while the signal at $g = 2$ was not observed in *p,p′*- and *m,m′*-isomers under similar irradiation conditions. The ratio of the sharp (338 mT) to weak (313 mT) signal intensities was not wavelength-dependent ($\lambda > 360$ nm). Lastly, although these quintet signals are somewhat different from those of the *p,p′*- and *m,m′*-isomers, the temperature dependence of the EPR signals for the *p,p′*- and *m,m′*-isomers demonstrated that exchange coupling through the disilane bond does in fact take place, so that there is every reason to expect an interaction between the nitrenes of the *m,p′*-isomer.

Despite our convictions that the *m,p′*-isomer is ferromagnetically coupled and the *m,m′*-isomer exhibits a nearly degenerate or weak antiferromagnetic interaction, our results do not unambiguously prove that this is the case. The signal intensities of both isomers displayed Curie law behavior, which can be interpreted as nearly degenerate electronic states.[10] Unfortunately, a thermally populated triplet was not observed in either one of these isomers.

Isomeric monosilanes **1n** were also irradiated under similar conditions and their reactions followed by EPR measurements. Both *p,p′*- and *m,m′*-**1n** produced similar EPR spectra after photolysis which consisted solely of an isolated triplet nitrene with $|D/hc| = 0.977$ cm^{-1}and $|E/hc| = 0$ cm^{-1} and $|D/hc| = 0.997$ cm^{-1}and $|E/hc| = 0$ cm^{-1} for *p,p′*- and *m,m′*-**1n**, respectively. As shown in Figure 3, the *m,p′*-isomer of **1n** did have a very weak quintet signal in the field range 90–320 mT together with the much stronger isolated triplet nitrene. The lack of EPR signals due to a quintet state of *p,p′*- and *m,m′*-**1n** and the very weak quintet signal of *m,p′*-**1n**, strongly suggest that a possible superexchange interaction through one Si atom is almost nonexistent, effectively isolating the two nitrenes.

Semiempirical MO Study. Semiempirical CI calculations were carried out with MOPAC[11] to predict which conformation would most likely reproduce the observations from EPR experiments. The quintet geometry of each isomer (*m,m′*, etc.) was optimized at the three fixed conformations shown in Figure 4, and the energy differences between the singlet and quintet states of the dinitrenes are reported in Table I.

It was expected that the isomers of **2x** would have the largest through-bond interaction and energy differences because the σ–π overlap for this conformer is maximal. The semiempirical predictions for conformer **2x** compare favorably with the experimental results for each isomer. A singlet ground state was predicted for *p,p′*-**2x** at –320 cal/mol, in close agreement with the experimentally determined value. The *m,m′*- isomer was predicted to have degenerate electronic states, while *m,p′*-**2x** was found to favor a ground-state quintet but by a small energetic margin. The latter value is consistent with one possible interpretation of the experimental data in which the nitrenes are weakly ferromagnetically coupled in the *m,p′*-isomer. The predicted ground-state multiplicity for each isomer parallels the computed values for stilbene and tolane dinitrenes, except that in the latter series of molecules, the *m,p′*-isomers are predicted to favor the quintet state by a much larger amount.[4,5,12] This level of theory cannot be considered definitive but is suggestive of a smaller interaction in the *m,p′*-isomer relative to in the *p,p′*-isomer.

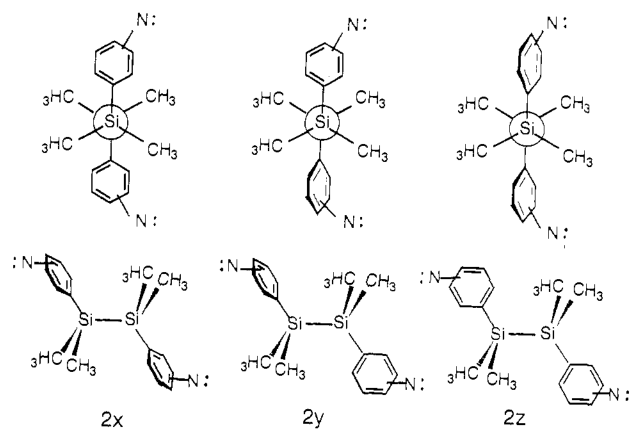
2x 2y 2z

Figure 4. Three fixed conformations of **2n** used for calculating the ground-state multiplicity.

Table I. Energy Differences $\Delta E_{S\text{–}Q}$ (cal/mol) between the Singlet and Quintet States of **2n** and **1n** Computed at Various Conformations

	p,p′	*p,m′*	*m,m′*
2n[a]	–290	>0	$0 < \Delta E < -3.4$
2x	–320	68	<1
2y	<1	0	0
2z	<1	15	0
1x	27	14	4
1y	139	3	8
1z	262	5	16

[a] Experimental data.

A spin polarization mechanism accounts for the observed ground-state multiplicities of many π-conjugated radicals including stilbenes and tolanes.[13] The total spin populations of the silicon atoms were obtained from PM3 unrestricted Hartree–Fock (UHF) calculations on the conformers **2x** and were much smaller in magnitude than those of the neighboring phenyl carbon atoms. The spin populations of the Si atoms were of the same sign for the *p,p′*- and *m,m′*-isomers, while the Si spin populations of the *m,p′*-isomer were opposite in sign, suggesting that a parity-based exchange coupling mechanism may be operative in **2n**.

For there to be any through-bond interaction between the nitrene centers of **2z** requires superexchange through two sets of Si–methyl p-orbitals which have the proper symmetry to overlap with the phenyl π-system. However, such interactions were found to be very weak computationally, as indicated by the prediction of essentially zero energy differences between the electronic states. The orthogonal orientation of the atomic orbitals on silicon and of the phenyl groups of **2y** most likely prevents favorable σ–π overlap, and hence, nearly degenerate states are predicted regardless of the isomer considered. These computations suggest that the most likely carriers of the EPR signals are the **2x** isomers and that conformation is extremely important for magnetic interactions to occur. Stabilization of radical centers by the σ-π captodative effect has been proposed by Sakurai et al.[14] Our X-ray crystallographic structure of 1,2-bis[*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl]-1,1,2,2-tetramethyldisilane revealed that the

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[10] For a discussion of the complications involved in using EPR spectral data for determining the ground state, see: (a) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley and Sons: NewYork, 1988; Vol. 2, pp 462–469. (b) Iwamura, H.; Koga, N. *Acc. Chem. Res.*, **1993**, *26*, 346.

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Table II. ΔE_{S-Q} (cal/mol) Values for *m,m'*-Isomers of Various Magnetic Couplers XY

XY				
Si	Si—Si	C≡C—C≡C	C≡C	C=C (*trans*)
0	$0 > \Delta E > -3.4$	−90	−180	−240[a]

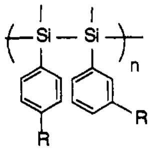
[a] Unpublished results. EPR spectra of *m,m'*-dinitrenostilbene under similar conditions showed two sets of signals due to the quintet species at least. Data obtained from the quintet having a slightly stronger antiferromagnetic interaction are listed.

molecule did indeed assume this conformation (**2x**) in the crystalline state,[15] although the exchange interaction was smaller than that in *p,p'*-**2n** by an order of magnitude.[15]

Three conformations of the monosilane dinitrenes were also optimized. The phenyl rings and the silicon atom were initially constrained to be coplanar (**1x** in Table I) followed by rotation of one phenyl ring by 90° (**1y**) and then rotation of both groups to 90° (**1z**) relative to those in **1x**. The computed ΔE_{S-Q}s for the monosilane-coupled dinitrenes **1n** were all found to favor a ground-state quintet, by a small amount, for each isomer of the three individually optimized conformations.[16] However, the size of the ΔE_{S-Q}s for the *m,p'*- and *m,m'*-isomers did not change with conformation, while two of the *p,p'*-**1n** conformers had larger computed energy gaps. At the semiempirical computational level, it is usually the case that the ΔE_{S-Q} of each isomer is affected by rotation about certain bonds, provided that the exchange interaction is significant enough to allow distinction between the various isomers.[12b] Hence, it is not clear that the efficiency of exchange coupling is modified by conformation for the monosilanes since the ΔE_{S-Q} shifted for only one isomer. The lack of any quintet EPR signal for the *p,p'*-isomer further implies that the consistent favoring of the quintet state may be a spurious computational result. The generally small values of the ΔE_{S-Q}s and the apparent insensitivity to conformation suggest that the electronic states may be considered to be nearly degenerate in energy for each monosilane isomer.

Conclusion

It is concluded that the two nitrene centers in **2n** interact with each other through the conjugation of the Si–Si σ bond with the π-orbitals of the phenyl rings. The structure of high-spin poly(phenylsilane)s should have an alternating structure, **P''**, where



P''

R is the radical center. As summaried in Table II, the efficiency of the disilane unit as a magnetic coupler is concluded to be 1–2 orders of magnitude smaller.

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi I-5040 FT-IR spectrometer. ^{1}H NMR spectra were measured on a JEOL 280 Fourier transform spectrometer using either $CDCl_3$ or benzene-d_6 as solvent and referenced to TMS. Electronic spectra were measured on a JASCO UVDEC-610C spectrometer. EPR spectra were obtained on a Bruker ESP 300 X band spectrometer equipped with an Air Products LTD-3-110 liquid helium transfer system. Melting points were recorded on a MEL-TEMP. Mass spectra (MS) were obtained on a JEOL DATUM JMS-SX120; percent relative intensity is given in parentheses. Elemental analyses were performed in the analytical center of this department.

Materials. Unless otherwise stated, the preparative reactions were carried out under a dry, high-purity nitrogen atmosphere. Diethyl ether, benzene, toluene, tetrahydrofuran, and MTHF were distilled from sodium benzophenone ketyl. Reaction mixture was worked up by diluting with diethyl ether, if necessary, washing the organic layer with aqueous ammonium chloride, drying over magnesium sulfate, and evaporation of the solvent under reduced pressure using a rotary evaporator.

Bis(*p*-bromophenyl)dimethylsilane (*p,p'*-1b). A solution of 2.36 g (10.0 mmol) of *p*-dibromobenzene in 40 mL of diethyl ether was mixed with 6.4 mL (10.2 mmol) of *n*-butyllithium in hexane (1.6 M) at −78 °C. After the solution was stirred for 1 h, 0.71 g (5.5 mmol) of dichlorodimethylsilane in 10 mL of diethyl ether was added. The whole mixture was stirred for 10 h at room temperature. Recrystallization of the residue by usual workup from *n*-pentane gave 1.80 g (48.6%) of *p,p'*-**1b** as colorless crystals: mp 74.5–75.9 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.52 (s, 6H), 7.34 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H).

Bis(*m*-bromophenyl)dimethylsilane (*m,m'*-1b) was prepared in a manner similar to the *p,p'*-isomer. Purification was made by chromatography on silica gel with *n*-hexane elution to give colorless crystals (91.0% yield) of *m,m'*-**1b**: mp 47–51 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.55 (s, 6H), 7.23 (t, J = 8.5 Hz, 2H), 7.39 (s, 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz), 7.59 (s, 2H). Anal. Calcd for $C_{14}H_{14}Br_2Si$: C, 45.43;H, 3.81; Br, 43.17. Found: C, 45.36; H, 3.86; Br, 43.37.

(*m*-Bromophenyl)(*p*-bromophenyl)dimethylsilane (*m,p'*-1b). A solution of 0.71 g (3.01 mmol) of *m*-dibromobenzene in 20 mL of diethyl ether was mixed with 1.9 mL (3.0 mmol) of *n*-butyllithium in hexane (1.6 M) at −78 °C. After the solution was stirred for 30 min, 0.42 g (3.3 mmol) of dichlorodimethylsilane in 10 mL of diethyl ether was added. To the mixture was added a solution of (*p*-bromophenyl)lithium prepared from 0.71 g (3.0 mmol) of *p*-dibromobenzene. After the mixture was stirred for 1 h at room temperature, usual workup gave an oil which was purified by chromatography on silica gel with *n*-hexane elution. *m,p'*-**1b** was obtained in 66.4% yield: colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.54 (s, 6H), 7.20–7.59 (m, 8H).

Bis(*p*-azidophenyl)dimethylsilane (*p,p'*-1a). To a solution of 0.37 g (1.0 mmol) of *p,p'*-**1b** in 10 mL of THF was added 1.3 mL (2.1 mmol) of *n*-butyllithium in hexane (1.6 M) at −78 °C. After the solution was stirred for 1 h, a solution of 0.45 g (2.3 mmol) of *p*-tolylsulfonyl azide in 3 mL of THF was added at the same temperature. After being stirred for another 1.5 h, the mixture was allowed to warm to room temperature. Usual workup gave an oil which was purified by chromatography on silica gel with n-hexane elution; 70 mg (23.7%) of *p,p'*-**1a** was obtained as a pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.53 (s, 6H), 7.02 (d, J = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H). UV–visible (*n*-hexane) 240 nm ($\epsilon = 3.50 \times 10^4$); IR (neat) 2959, 2127, 2091 ($-N_3$), 1589, 1561, 1497, 1396, 1292, 1258, 1188, 1138, 829, 802, 775, 698 cm^{-1}; MS *m/z* calcd for $C_{14}H_{14}N_6Si$ 294.1049, found: 249.1095 (60).

Bis(*m*-azidophenyl)dimethylsilane (*m,m'*-1a) was prepared similarly to the corresponding *p,p'*-isomer by using *m,m'*-**1b** in place of *p,p'*-**1b**. After purification with column chromatography on silica gel, *m,m'*-**1a** was obtained as a pale yellow oil in 32.4% yield: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.55 (s, 6H), 7.04–7.58 (m, 8H); IR (neat) 2125, 2096 cm^{-1}; UV–visible (*n*-hexane) 252.4 nm; MS *m/z* calcd for $C_{14}H_{14}N_6Si$ 294.1049, found: 294.1030 (100).

(*m*-Azidophenyl)(*p*-azidophenyl)dimethylsilane (*m,p'*-1a) was prepared similarly to the corresponding *p,p'*-isomer by using *m,p'*-**1b** in place of *p,p'*-**1b**. After purification with column chromatography on silica gel, *m,p'*-**1a** was obtained as a pale yellow oil in 37.2% yield: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.54 (s, 6H), 7.00–7.49 (m, 8H); IR (neat) 2152, 2096 cm^{-1}; UV–visible (*n*-hexane) 255.6 nm; MS *m/z* calcd for $C_{14}H_{14}N_6Si$ 294.1049, found 294.1073 (100).

1,2-Bis(*p*-bromophenyl)-1,1,2,2-tetramethyldisilane (*p,p'*-2b). To a solution of 23.6 g (100 mmol) of *p*-dibromobenzene in 150 mL of diethyl ether was added 65 mL (104 mmol) of *n*-butyllithium in hexane (1.6 M) at −78 °C. After the solution was stirred for 1 h, 9.5 g (5.07 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane[17] in 100 mL of diethyl ether was added. The whole mixture was stirred for 1 h, during which time the temperature was allowed to rise to room temperature. Usual workup gave a colorless solid which was recrystallized from *n*-hexane to give 14

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[15] Doi, T.; Inoue, K.; Koga, N.; Iwamura, H. Unpublished results.

[16] As discussed in ref 12, a very small favoring of the quintet state at the semiempirical level sometimes occurs for difficult cases, which by comparison to other isomers is usually interpreted to imply the existence of nearly degenerate states.

[17] Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493. Sakurai, H.; Watanabe, T.; Kumada, M. *J. Organomet. Chem.* **1967**, *7*, 15.

g (64.0%) of *p,p'*-**2b** as colorless crystals: mp 78.9–79.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.30 (s, 12H), 7.19 (d, *J* = 8 Hz, 4H), 7.44 (d, *J* = 8 Hz, 4H). Anal. Calcd for $C_{16}H_{20}Si_2Br_2$: C, 44.87; H, 4.71; Br, 37.31. Found: C, 44.89; H, 4.63; Br, 38.39.

1,2-Bis(*m*-bromophenyl)-1,1,2,2-tetramethyldisilane (*m,m'*-2b) was prepared by using *m*-dibromobenzene in place of the *para* derivative in a method similar to that described above. *m,m'*-**2b** was obtained as colorless crystals: mp 65–69 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.32 (s, 12H), 7.17 (t, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.41 (s, 2H), 7.45 (t, *J* = 8.1 Hz, 2H); MS *m/z* calcd for $C_{16}H_{20}{}^{79}Br^{81}BrSi_2$ 427.9449, found 427.9415 (100). Anal. Calcd for $C_{16}H_{20}Br_2Si_2$: C, 44.87; H, 4.71; Br, 37.31. Found: C, 44.99; H, 4.70; Br, 37.61.

1-(*m*-Bromophenyl)-2-(*p*-bromophenyl)-1,1,2,2-tetramethyldisilane (*m,p'*-2b). A solution of 0.49 g (2.08 mmol) of *m*-dibromobenzene in 20 mL of diethyl ether was mixed with 1.4 mL (2.24 mmol) of *n*-butyllithium in hexane (1.6 M) at −78 °C. The mixture was stirred for another hour. In a second flask, a solution of (*m*-bromophenyl)lithium prepared from 0.50 g (2.1 mmol) of *m*-dibromobenzene, as in *m,p'*-**1b**,was added to an ether solution of 0.39 g (2.1 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane. The mixture was stirred for 1 h at room temperature and then added to the mixture in the first flask. After the mixture was stirred for 1 h at room temperature, usual workup gave an oil which was purified by chromatography on silica gel with *n*-hexane elution. *m,p'*-**2b** was obtained in 68.3% yield: colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.308 (s, 6H), 0.313 (s, 6H), 7.15–7.45 (m, 8H); MS *m/z* calcd for $C_{16}H_{20}{}^{81}Br_2Si_2$ 429.9429, found 429.9474 (76.0).

1,2-Bis(*p*-azidophenyl)-1,1,2,2-tetramethyldisilane (*p,p'*-2a). Dibromide *p,p'*-**2b** (0.43 g, 0.1 mmol) was dissolved in 10 mL of dry THF and cooled at −78 °C in a dry ice/acetone bath. To this solution was added 1.3 mL of an *n*-hexane solution (1.6 M) of *n*-butyllithium dropwise, and the solution was stirred for 30 min; then, 5 mL of a THF solution of tosyl azide (0.41 g, 2.01 mmol) was added. After the solution was stirred for 1 h at −78 °C, a dry ice/acetone bath was removed and the reaction mixture was allowed to rise gradually to room temperature. A yellow solid was purified by silica gel column chromatography (eluent, *n*-hexane: CH_2Cl_2 = 1:1) to give a pale yellow solid of diazide *p,p'*-**2a** (0.055 g) in 16% yield: ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 12 H), 6.97 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 4H); IR (KBr) 2124, 2088 cm^{-1}; UV–visible (*n*-hexane) 264.4 nm (ϵ = 5.0 × 10^4); MS *m/z* calcd for $C_{16}H_{20}N_6Si_2$ 352.1288, found 352.1238 (23.3). Anal. Calcd for $C_{16}H_{20}N_6Si_2$: C, 54.51; H, 5.72; N, 23.84. Found: C, 54.22; H, 5.67; N, 24.08.

1,2-Bis(*m*-azidophenyl)-1,1,2,2-tetramethyldisilane (*m,m'*-2a). The corresponding dibromide *m,m'*-**2b** was used in place of *p,p'*-**2b**. After purification with silica gel column chromatography, *m,m'*-**2a** was obtained as a yellow oil in 30.5% yield: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 12H), 6.94 (s, 2H), 6.99 (d, *J* = 7.7 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H); IR (neat) 2165, 2106 cm^{-1}; UV–visible (*n*-hexane) 244.4 nm (ϵ = 6.4 ×10^4); MS *m/z* calcd for $C_{16}H_{20}N_6Si_2$ 352.1288, found 352.1299 (44.0).

1-(*m*-Azidophenyl)-2-(*p*-azidophenyl)-1,1,2,2-tetramethyldisilane (*m,p'*-2a). The corresponding dibromide *m,p'*-**2b** was used in place of *p,p'*-**2b**. After purification with silica gel column chromatography, *m,p'*-**2a** was obtained as a pale yellow oil in 64.4% yield: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.335 (s, 6H), 0.337 (s, 6H), 6.94–7.94 (m, 8H); IR (neat) 2098 cm^{-1}; UV–visible (*n*-hexane) 255.6 nm (ϵ = 4.87 × 10^4); MS *m/z* calcd for $C_{16}H_{20}N_6Si_2$ 352.1288, found 352.1308 (50.8).

Semiempirical CI Calculations. All semiempirical calculations were performed with MOPAC version 6.0[11] on the University of Tokyo's Hitachi M880 computer. The geometry of the quintet state of each species was optimized using a restricted open-shell SCF wave function employing the PM3 Hamiltonian. For the mono- and disilanes, the methyl groups were optimized once for each conformer without the presence of nitrene substituents and then the methyl C–H bonding parameters were held constant during subsequent optimization of all the other parameters. At each of the nine geometries so obtained, CI calculations were carried out to compute the energy differences between the quintet, triplet, and singlet states. Each state was assumed to be open-shell, that is, the OPEN(4,4) statement was used in conjunction with a five-orbital and six-electron active space. This procedure has been shown to yield qualitatively correct results in a number of cases where experimental data are known.[12b]

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