

Control of the “Superexchange” Interaction through Diphenyl Sulfide 4,4'-Diyl Magnetic Coupler by Changing the Oxidation State and Conformation of the Sulfur Atom

Kenji Matsuda, Takehiro Yamagata, Tomoo Seta, Hiizu Iwamura,* and Kenzi Hori†

Contribution from the Institute for Fundamental Research in Organic Chemistry, Kyushu University, Fukuoka 812-81, Japan

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Abstract: The exchange interaction between two triplet carbene centers through diphenyl sulfide 4,4'-diyl, its sulfoxide and sulfone analogs, and thioxanthene 2,7-diyl coupling units was studied. These dicarbenes were generated by photolysis of the corresponding bisdiazio precursors in MTHF matrices at cryogenic temperatures. From the temperature dependence of the ESR signals it was found that the dicarbene jointed through the sulfide group has a quintet ground state; it serves as a ferromagnetic coupler. On the other hand, as the oxidation state or the geometry of the sulfur atom was changed to sulfoxide, sulfone, and thioxanthene groups, antiferromagnetic interaction was observed between the two diphenylcarbene units. The magnitude of the exchange interaction J/k was determined to be 11, -30 , -92 , and -21 K for diphenyl sulfide, sulfoxide, sulfone 4,4'-diyl, and thioxanthene 2,7-diyl couplers, respectively. In the ESR spectra of sterically unconstrained sulfide and its analogs the isolated triplet signals were rather strong. In the thioxanthene analog, however, this ratio of the isolated triplet signals to those of the other spin multiplicities was smaller. The isolated triplets were attributed to the conformation where the two phenyl rings were perpendicular to each other. It was demonstrated that the magnetic interaction could be tailored from ferro- to antiferromagnetic coupling by changing the oxidation state or geometry of the sulfur atom.

Introduction

The design and synthesis of polyradicals having high-spin ground states are subjects of great importance for deepening our understanding of chemical bonds and developing potential organic magnetic materials.^{1–4} In such systems, the control of topological symmetry in alternant hydrocarbon polyradicals, namely, connectivity of the radical centers through π -cross-conjugated chains and networks, is a guiding principle for aligning electron spins in parallel. Some of the highlights in these studies include poly(trityl radicals) ($S = 4$)^{3g} and polycarbenes ($S = 9$)^{2j,l} in which the open shell centers are joined

through *m*-phenylene and 1,3,5-benzenetriyl units. Since chains and networks consisting of carbon atoms only have a number of limitations from a preparative point of view, the introduction of heteroatoms such as nitrogen, oxygen, and sulfur is considered to be of help in expanding the scope of the structural variation. However, the role of heteroatoms in coupling the spins in polymer **1**, for example, is not as clearly understood as in hydrocarbons. The role of bridging heteroatom ligands in effecting the magnetic coupling in bi- and polynuclear magnetic metal complexes is interpreted in terms of “superexchange”.⁵ Our naive question was if we might be able to interpret the coupling in organic polyradicals containing heteroatoms in a similar fashion via the filled π orbital localized on the sulfur atom.

Diphenyl ether 4,4'-diyl unit in dicarbene **2** is reported by Itoh et al.⁶ to couple two carbene centers antiferromagnetically. This was explained in terms of the superexchange or hyper-

† Current address: Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755 Japan.

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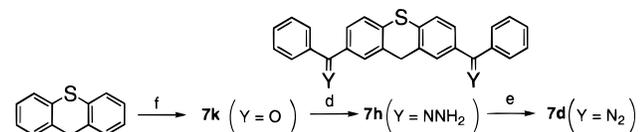
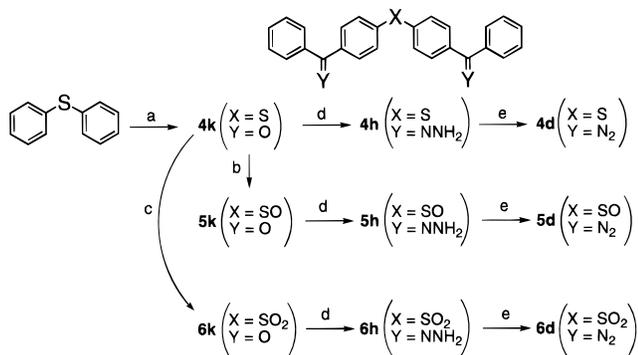
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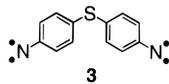
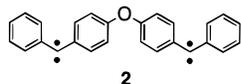
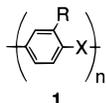
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Scheme 1^a



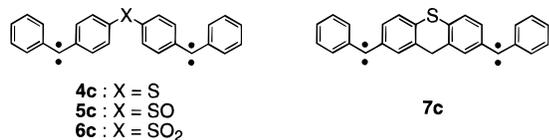
^a Reagents and conditions: (a) PhCOCl, CCl₄, 44%; (b) H₂O₂, acetone, 40%; (c) *t*-BuOCl, CH₂Cl₂, 46%; (d) N₂H₄, N₂H₄·HCl, DMSO; (e) BaMnO₄, CH₂Cl₂, or HgO, CH₂Cl₂, 29–58%, two steps; (f) PhCOCl, PhNO₂, 40%.

conjugation on the oxygen atom. On the other hand Kaise, Yabe et al.⁷ found that two triplet nitrene centers appeared to be coupled ferromagnetically in dinitrene **3**. Sulfur is on the third row of the periodic table and so is able to have high oxidation states. Effect of the oxidation state and/or geometry of the sulfur atom in diphenyl sulfide 4,4'-diyl coupler has now been studied.⁸



Results and Discussion

Synthesis of the Precursors. Diazo precursors **4d–7d** were synthesized according to Scheme 1. Diphenyl sulfide was treated with benzoyl chloride to give bis(*p*-benzoylphenyl) sulfide **4k**.⁹ Oxidation of sulfide **4k** with hydrogen peroxide or *tert*-butyl hypochlorite afforded bis(*p*-benzoylphenyl) sulfoxide **5k** or sulfone **6k**.¹⁰ The diketone of thioxanthone **7k** was synthesized from thioxanthone. Ketones **4k–7k** were converted to the corresponding hydrazones and then to the corresponding diazo compounds **4d–7d** (Scheme 1).



Diazo compounds were characterized by NMR, IR, and UV–vis spectroscopy. ¹H and ¹³C NMR spectra were fully assigned. HH-COSY and relay shift correlation spectrum of **7k** clearly

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Figure 1. ESR spectra of the photoproducts of **4d** in 10 mM MTHF matrix (9.42 GHz) (a) at 9.7 K and (b) at 34.1 K. Signals denoted T_i, T_r, and Q are assigned to isolated triplet, thermally populated triplet, and quintet signals, respectively.

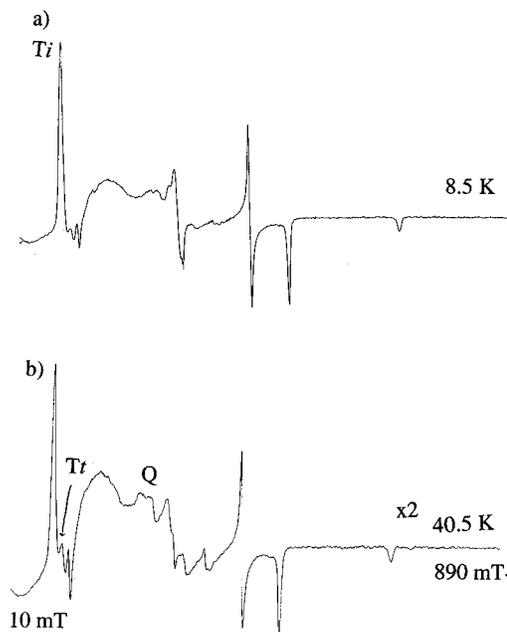


Figure 2. ESR spectra of the photoproducts of **5d** in 10 mM MTHF matrix (9.41 GHz) (a) at 9.7 K and (b) at 34.1 K. Signals denoted T_i, T_r, and Q are assigned to isolated triplet, thermally populated triplet, and quintet signals, respectively.

showed from the correlation signal between positions 1 and 9 that the benzoyl substituents were at the 2,7-positions (see Supporting Information). For diazo compounds **4d–7d** IR spectra showed absorptions at about 2040 cm⁻¹, confirming the presence of diazo groups. Moreover the sulfoxide group in **5d** and sulfone group in **6d** were confirmed by absorptions at 1050 cm⁻¹ and 1154, 1312 cm⁻¹, respectively. UV–vis spectra showed *n*- π^* absorption maxima at 502–524 nm and slightly blue-shifted as the oxidation state of the sulfur atom increased. Diazo compounds **4d–7d** were rather stable and could be kept in a refrigerator for weeks.

ESR Measurement of the Dicarbenes. Photolyses of diazo compounds **4d–7d** were carried out in 2-methyltetrahydrofuran (MTHF) solid solutions in an ESR cavity at 9 K by using light ($\lambda > 420$ nm) from a high-pressure mercury lamp for 60–150 min. ESR spectra of dicarbenes **4c–7c** are shown in Figures 1–4. The observed spectral patterns did not change from initial to later stages of the irradiation and were found to consist of three sets of signals due to an isolated triplet, a thermally populated triplet, and a quintet species. From the resonance field, the signal around 90 mT (marked T_i) was assigned to the $-z$ transition of an isolated triplet species. The signal around 280 mT (marked Q) was assigned to the quintet of the interacting dicarbene in reference to those of the corresponding biphenyl dicarbenes.¹¹ The additional signal (marked T_r) beside the

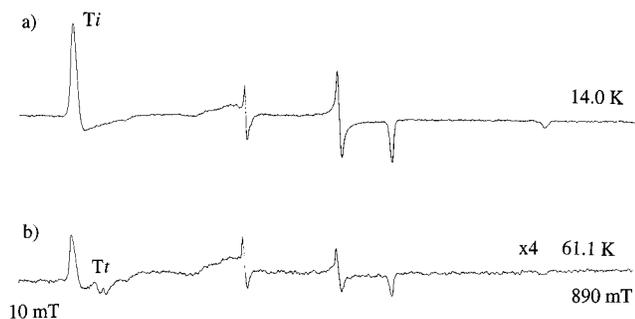


Figure 3. ESR spectra of the photoproducts of **6d** in 10 mM MTHF matrix (9.41 GHz) (a) at 9.7 K and (b) at 34.1 K. Signals denoted T_i and T_r are assigned to isolated triplet and thermally populated triplet, respectively.

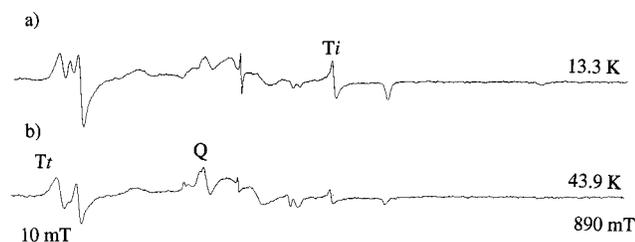


Figure 4. ESR spectra of the photoproducts of **7d** in 10 mM MTHF matrix (9.41 GHz) (a) at 13.3 K and (b) at 43.9 K. Signals denoted T_i , T_r , and Q are assigned to isolated triplet, thermally populated triplet, and quintet signals, respectively.

Table 1. Resonance Magnetic Field for Dicarbenes **4c–7c**

compd	ESR resonance field (mT)		
	$T_i (-z)^a$	$T_r (-z)$	Q
4c	85	112	264
5c	94	114	284
6c	89	120	not obsd
7c	92	78	285

^a Signals denoted T_i , T_r , and Q are assigned to isolated triplet, thermally populated triplet, and quintet signals, respectively. For the assignment of the signals, see text.

isolated triplet signals was assigned to the thermally populated triplet signals due to the interacting dicarbene. These kinds of thermally populated triplet signals are reported in the interacting bis(trimethylenemethane)-type tetraradical.^{4d} While the intensity of the isolated triplet signals was strong in the ESR spectra of the dicarbenes **4c–6c**, that of dicarbene **7c** was very weak. The meaning of this observation will be discussed later. In the ESR spectra of the dicarbenes **5c–7c**, one more signal was observed around 100 mT. This signal was tentatively assigned to a forbidden band ($\Delta m_s = 2$) due to the thermally populated triplet species. The resonance fields of **4c–7c** are summarized in Table 1.

The plots of the ESR signal intensity vs reciprocal temperature are shown in Figures 5–8. The signals due to the isolated triplets obeyed Curie–Weiss laws in the temperature ranges 10–50 K for dicarbene **4c** and **6c** and 20–50 K for **5c** and **7c**, respectively. The quintet and thermally populated signals showed different behavior depending upon the dicarbene species. The quintet signal due to **4c** obeyed a Curie–Weiss law, but the thermally populated triplet signal grew in, reached a maximum intensity at ca. 45 K, and then decreased as the temperature was increased (Figure 5). For **5c**, the thermally populated triplet signal showed maximum intensities at ca. 50 K, whereas quintet signal grew up to 50 K (Figure 6). For **6c**,

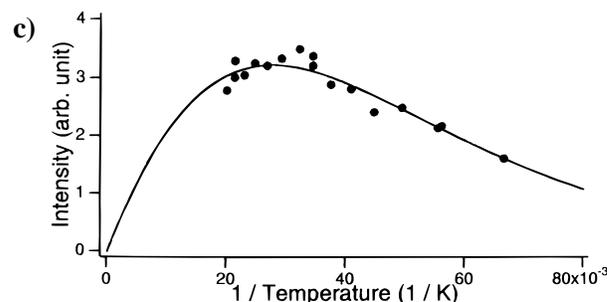
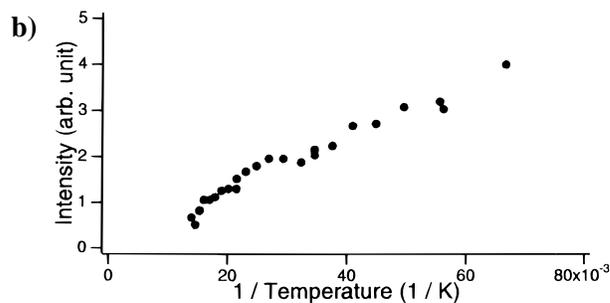
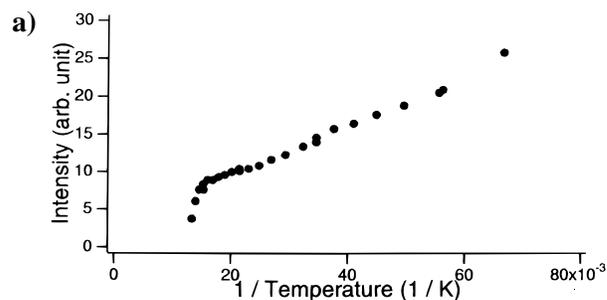


Figure 5. Plots of the intensities of the ESR signal at (a) 85 mT (T_i) due to the isolated triplet, (b) 264 mT (Q) due to the ground state quintet, and (c) 112 mT (T_r) due to the thermally populated triplet of **4c** vs reciprocal of temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie–Weiss law.

neither thermally populated triplet nor thermally populated quintet signals were observed up to 37 K. However, the thermally populated triplet signal appeared above 39 K and started to increase with increasing temperature (Figure 7). For **7c**, the isolated signal was very small compared to the other carbenes described above. Therefore the temperature dependence of the isolated triplet signal was measured on the y transition (469 mT). The position of the thermally populated triplet signal shifted to the lower field. The behavior of the temperature dependent signals was similar to the case of **5c**, the thermally populated triplet signal showed maximum intensities at ca. 30 K, and the quintet signal intensity increased to 50 K (Figure 8). From these observations, **4c** was concluded to have quintet ground states: ferromagnetic interaction between two carbenes, while **5c**, **6c**, and **7c** have singlet ground states: antiferromagnetic interaction between the two carbenes.

Effect of Oxidation State on Sulfur Atom in Superexchange Interaction. According to the theory of two weakly interacting robust triplets,^{6,12} for which spin Hamiltonian is given by eq 1, antiferromagnetic interaction ($J < 0$) leads to a ground singlet state with excited triplet and quintet states that are higher in energy by $-2J$ and $-6J$, respectively, from the ground state, where J is the exchange integral of two electrons, one on each

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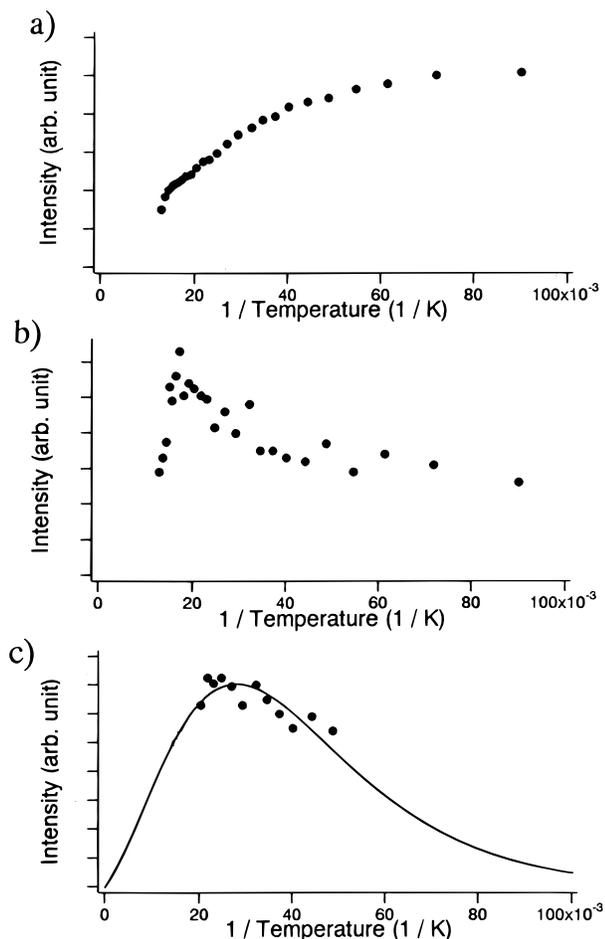


Figure 6. Plots of the intensities of the ESR signal at (a) 94 mT (T_i) due to the isolated triplet, (b) 284 mT (Q) due to the thermally populated quintet, and (c) 111 mT (T_i) due to the thermally populated triplet of **5c** vs reciprocal temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie–Weiss law.

of the carbene centers. When a ferromagnetic interaction ($J > 0$) is operative, a quintet ground state with excited triplet and singlet states higher in energy by $4J$ and $6J$, respectively, is observed. The observed data were analyzed in terms of the Bleaney–Bowers-type thermal distribution among the three states:¹³ for **4c**,

$$\mathbf{H} = -2JS_1 \cdot S_2 \quad (1)$$

$$I(T_i) = \frac{C}{T} \frac{3 \exp(-4J/kT)}{5 + 3 \exp(-4J/kT) + \exp(-6J/kT)} \quad (2)$$

and for **5c**, **6c**, and **7c**,

$$I(T_i) = \frac{C}{T} \frac{3 \exp(2J/kT)}{1 + 3 \exp(2J/kT) + 5 \exp(6J/kT)} \quad (3)$$

Fitting of the observed intensity data for thermally populated triplets to these equations in the temperature ranges where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie–Weiss laws gave exchange integral J/k values of 11, -30 , -92 , and -21 K for **4c–7c**, respectively (Figures 5–8). The fitting of the thermally populated quintet signal for **5c** and **7c** could not be accurately performed because of the decomposition of the carbenes.

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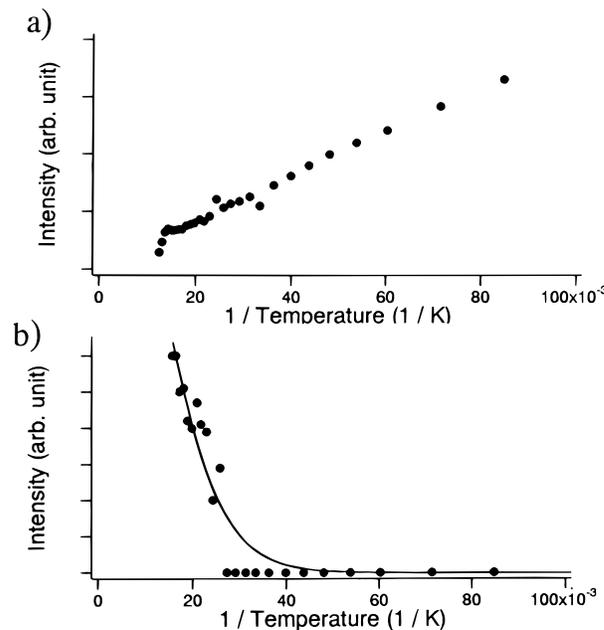


Figure 7. Plots of the intensities of the ESR signal at (a) 89 mT (T_i) due to the isolated triplet and (b) 120 mT (T_i) due to the thermally populated triplet of **6c** vs reciprocal of temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie–Weiss law.

Correlation between the Ground States and Their Geometry.

In order to understand the relationship between the ground states of the carbenes and the geometry around the bridging fragment, the geometries of **4d**, **5d**, and **7d** which are parent molecules of the observed carbenes, were optimized by using *ab initio* molecular orbital (MO) calculations on the GAUSSIAN94 program.¹⁵ The 3-21G* basis sets were used to optimize geometries since higher basis sets handle such big molecules containing four phenyl rings with some difficulty.¹⁶ We chose the parent diazo compounds to estimate the conformations of the carbenes, because the carbenes were safely assumed to take the conformers very similar to those of the parent diazo compounds in the temperature range where photolyses of the diazo compounds were carried out and the carbenes were studied; in this temperature region no effect of the annealing on the resonance fields was observed, and the temperature dependence on the signal intensities was reversible.

Figure 9 displays the optimized structures. It is quite interesting that the Ph–C(N₂)–Ph fragments of the parent molecules exhibit almost the same geometry since there are no differences in bond lengths and angles except for the Ph–S–Ph moiety. The change in the Ph–S–Ph angles causes a distinct difference between **4d** and **5d**, i.e., the geometrical relationship of the phenyl group bridged by the S atom. In order to clarify

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(16) We also optimized H(N₂)C–C₆H₅–X–C₆H₅–C(N₂)H (X = S, SO) at the 6-31G* level of theory and obtained similar results. The dihedral angles for X = S and SO were calculated to be 88.3° and 105.0°, respectively.

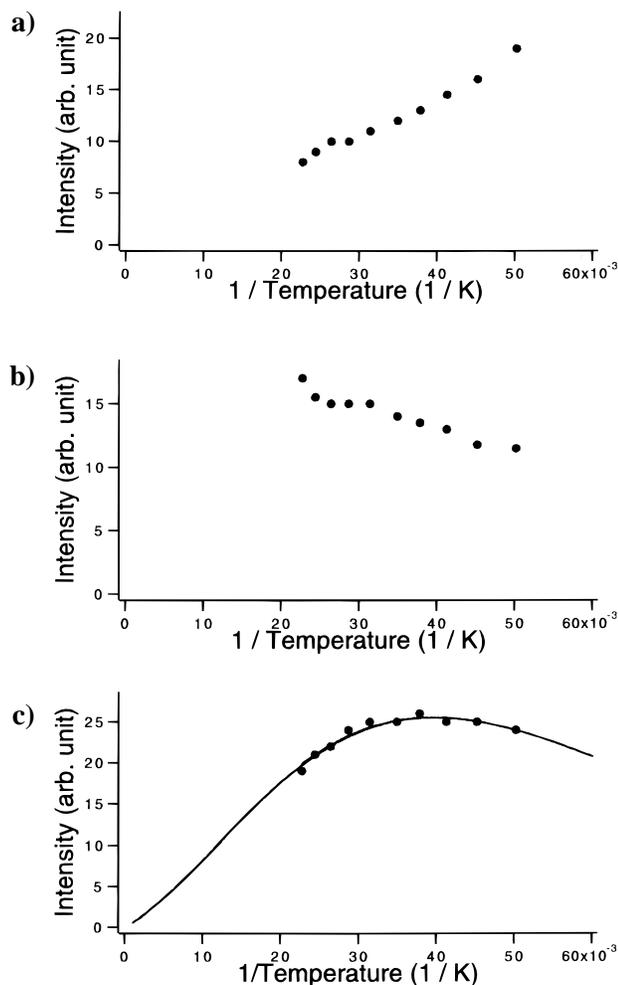


Figure 8. Plots of the intensities of the ESR signal at (a) 469 mT (T_i) due to the isolated triplet, (b) 285 mT (Q) due to the thermally populated quintet, and (c) 78 mT (T_1) due to the thermally populated triplet of **7c** vs reciprocal of temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie–Weiss law.

these differences, we used the dihedral angle and torsion angle (Table 2). Torsion angle is defined as the angle between the phenyl ring and the CSC plane. Plus and minus signs correspond to con- and disrotations, respectively. The two phenyl rings in **4c** are in conrotation and takes an almost perpendicular geometry; the torsion angle is calculated to be +61.3°. This geometry is considered to be related to the exchange interaction.

The two phenyl rings are disrotated in the optimized geometry of **5d** and **7d**; torsion angles were calculated to be -99.8° and -39.0° for **5d** and **7d**, respectively. We can consider a kind of the conjugative interaction as shown schematically in Scheme 2. This kind of resonance structure stabilizes the singlet ground state. The semiempirical PM3-CI calculation of the dinitrene **3** showed⁷ that the energy gaps between singlet and quintet states are dependent on the torsion angle of two phenyl rings. Fang et al. have described the correlation between torsion angle and the magnetic interaction.¹⁷

The magnitude of this singlet ground state stabilization should not be very large because the rings do not take the coplanar geometry shown in Figure 9. However, this is large enough to reverse the ordering of the small singlet–quintet energy gap.

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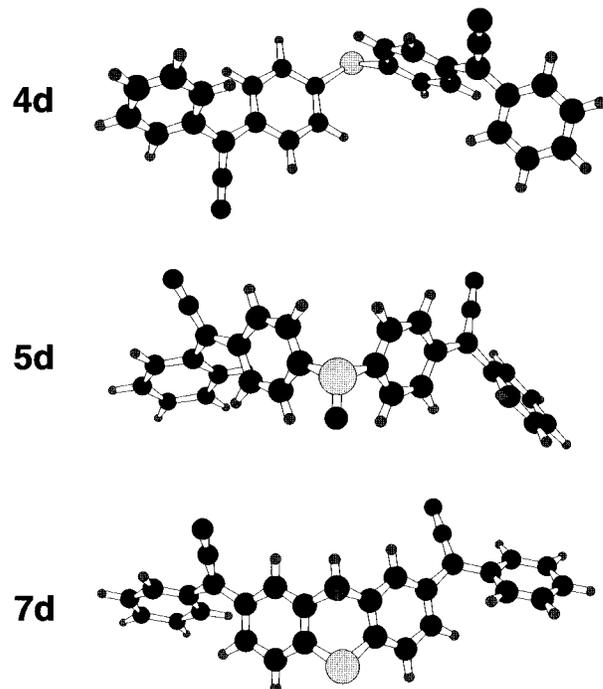


Figure 9. Optimized structure of **4d**, **5d**, and **7d**. The 3-21G* basis sets were served to optimize geometries.

Table 2. Total Energies and Geometrical Parameters^a in the Optimized Geometries of **4d**, **5d**, and **7d**

	4d	5d	7d
total energy	-1601.59057	-1675.98846	-1639.25940
S–C	1.781	1.778	1.775
C–N	1.286	1.287	1.286
\angle CSC	101.8	98.8	98.6
dihedral angle 1 ^b	93.3	104.1	132.2
torsion angle ^c	+61.3	-99.8	-39.0
dihedral angle 2 ^d	59.3	59.7	59.1

^a Energies in Hartree unit, lengths and angles in Å and deg units.

^b Dihedral angles of the two phenyl planes connected with the S atom.

^c The angles between two phenyl rings and CSC plane. Plus and minus signs correspond to con- and disrotations, respectively. ^d The average dihedral angles of the two phenyl planes in the Ph-C(N₂)-Ph fragments.

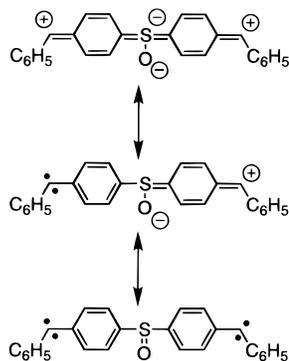
The adjacent phenyl rings may also help to stabilize the singlet states of **5c** and **7c**. Considering this effect, it is highly likely that the opposite magnetic interaction was observed between two carbenes in **4c** and **5c**.

Observed Strong Isolated Triplet Signals. For dicarbene **4c–6c** strong signals assigned to isolated triplet species were observed. Such signals are also observed for oxygen-linked dicarbene **2**. Itoh et al. explained this phenomenon in terms of a monocarbene due to incomplete photolysis.⁶ We measured the ESR spectra of the carbenes under different conditions of photolysis for various specimens and on different concentration of the sample. However, there was no evidence for a transformation from monocarbene to dicarbene even under prolonged irradiation. Therefore the signals are assigned to the dicarbene.

The calculated structure of **4c** and **5c** showed that the two phenyl rings were perpendicular to each other; the dihedral angle was nearly 90° (Table 2). It is suggested that the isolated triplet signals should be attributed to the conformers where the two phenyl rings were perpendicular to each other. When the two diphenylcarbene units are connected by the vinylene double bond,¹⁸ isolated triplet signals are in fact very small when

(18) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 1266.

Scheme 2



compared to analogs having a sulfide coupler. The two phenyl rings of thioxanthene **7c** are fixed to an envelope form as the thioxanthene ring should shallow boat form; a dihedral angle was 132.2°. In the ESR spectrum of **7c**, isolated triplet signal was weaker compared to those of **4c–6c**. This observation supports the interpretation about the origin of the isolated triplet signal.

Conclusions

Four dicarbenes possessing diphenyl sulfide, sulfoxide, and sulfone 4,4'-diyl and thioxanthene 2,7-diyl coupling units were photochemically generated. From the temperature dependence of the ESR signal intensity the exchange coupling constants J/k were determined: 11 K in diphenyl sulfide 4,4'-diyl: -30 K sulfoxide: -92 K sulfone: -21 K thioxanthene 2,7-diyl. Thioxanthene derivative **7c** has an additional methylene bridge *meta* to the carbene centers. However the superexchange interaction through this *meta*-methylene moiety is estimated to be very small and therefore we may neglect the effect of the methylene group.¹⁴ It was demonstrated that the superexchange interaction could be controlled by changing the oxidation state or either geometry of the sulfur atom. Unlike alternant hydrocarbon systems, the spin systems which include heteroatom cannot be predicted by the topological symmetry alone. In the case of the interaction through sulfur atom, the geometry played an important role in determining the value of the exchange interaction.

Experimental Section

A. Materials. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-270 and JEOL EX-270 instruments. IR spectra were obtained on a Hitachi I-5040 spectrometer. UV-vis spectra were recorded on a Hitachi U-3300 spectrophotometer. Melting points are not corrected.

Benzoyl chloride and dimethyl sulfoxide (DMSO) were distilled under reduced pressure from calcium hydride. 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. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified. Anhydrous magnesium sulfate was used as the drying agent.

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 (Wakogel C-200, 200 mesh) or neutral alumina (ICN, activity grade IV).

Bis(*p*-benzoylphenyl) Sulfide (4k).⁹ To a stirred slurry of aluminum trichloride (8.6 g, 64.5 mmol) in 35 mL of carbon tetrachloride was added benzoyl chloride (7.2 mL, 62 mmol) at 5 °C. Diphenyl sulfide (4.7 mL, 28 mmol) was added to the mixture at 5 °C dropwise for 2 h. After the mixture was stirred for 24 h at 20 °C, the reaction mixture was poured into aqueous hydrochloric acid. The mixture was extracted

with dichloromethane, washed with aqueous hydrochloric acid, aqueous sodium carbonate, and water, dried, and concentrated. Column chromatography (silica, hexane:dichloromethane = 7:3) gave sulfide **4k** (4.87 g, 44%) as a white solid: mp 169.0–169.9 °C; IR (KBr) ν 3050, 1650, 1590 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.45–7.53 (m, 8H, Ar-H), 7.61 (t, J = 7.3 Hz, 2 H, Ar-H), 7.76–7.82 (m, 8 H, Ar-H); ¹³C NMR (67.8 MHz, CDCl₃) δ 128.3, 129.9, 130.3, 130.9, 132.5, 136.3, 137.2, 140.3, 195.6. Anal. Calcd for C₂₆H₁₈O₂S: C, 79.16; H, 4.60; S, 8.13. Found: C, 79.40; H, 4.82; S, 8.25.

Bis(*p*-benzoylphenyl) Sulfoxide (5k). To a stirred solution of sulfide **4k** (197 mg, 0.50 mmol) in 2 mL of acetone and 5 mL of dichloromethane was added 0.1 mL of 30% solution of hydrogen peroxide in water and stirred at room temperature for 2 weeks. The reaction mixture was poured into aqueous sodium sulfate and extracted with dichloromethane, washed with water, dried, and concentrated. Column chromatography (silica, hexane:dichloromethane = 7:3) gave sulfoxide **5k** (82.9 mg, 40%) as a white solid: mp 162.3–162.9 °C; IR (KBr) ν 3050, 1650, 1590, 1060 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.49 (t, J = 7.5 Hz, 4 H, Ar-H), 7.62(t, J = 6.6 Hz, 2 H, Ar-H), 7.76–7.83 (m, 8H, Ar-H), 7.90 (d, J = 8.4 Hz, 4 H, Ar-H); ¹³C NMR (67.8 MHz, CDCl₃) δ 124.4, 128.4, 130.0, 130.8, 133.0, 136.6, 140.2, 149.1, 195.3. Anal. Calcd for C₂₆H₁₈O₃S: C, 76.08; H, 4.42; S, 7.81. Found: C, 75.88; H, 4.45; S, 8.00.

Bis(*p*-benzoylphenyl) Sulfone (6k). To a stirred solution of sulfide **4k** (2.5 g, 6.33 mmol) in 30 mL of dichloromethane was added *tert*-butylhypochlorite (13.7 g, 126 mmol) and stirred for 2 weeks. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (silica, dichloromethane) to give sulfone **6k** (1.24 g, 46%) as a white powder: mp 200.2–201.0 °C; IR (KBr) ν 3090, 3060, 1670, 1319, 1170 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.50 (t, J = 7.3 Hz, 4 H, Ar-H), 7.64 (t, J = 7.6 Hz, 2 H, Ar-H), 7.78 (d, J = 6.9 Hz, 4 H, Ar-H), 7.91 (d, J = 8.3 Hz, 2 H, Ar-H), 8.10 (d, J = 8.3 Hz, 4 H, Ar-H); ¹³C NMR (67.8 MHz, CDCl₃) δ 127.9, 128.6, 130.1, 130.6, 133.4, 136.2, 142.1, 143.9, 207.0. Anal. Calcd for C₂₆H₁₈O₄S: C, 73.22; H, 4.25. Found: C, 73.26; H, 4.23.

Bis[*p*-(α -hydrazinobenzyl)phenyl] Sulfide (4h). To a solution of sulfide **4k** (103 mg, 0.26 mmol) in 1.5 mL of anhydrous hydrazine and 6.0 mL of dry DMSO was added hydrazine monohydrochloride (140 mg, 2.0 mmol). After stirring at 90 °C under argon atmosphere for 0.5 h, the reaction mixture was poured into water. The mixture was extracted with ether, washed with water, dried, and concentrated to give bishydrazone **4h** (111 mg) as a colorless oil: IR (KBr) ν 3400, 3060, 1590, 1570 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 5.38–5.52 (m, 4 H, NH₂), 7.13–7.57 (m, 18 H, Ar).

Bis[*p*-(α -hydrazinobenzyl)phenyl] Sulfoxide (5h). To a solution of sulfoxide **5k** (101 mg, 0.25 mmol) in 1.5 mL of anhydrous hydrazine and 6.0 mL of dry DMSO was added hydrazine monohydrochloride (150 mg, 2.2 mmol). After stirring at 90 °C under argon atmosphere for 18 h, the reaction mixture was poured into water. The mixture was extracted with ether, washed with water, dried, and concentrated to give bishydrazone **5h** (112 mg) as a white oil: IR (KBr) ν 3380, 3050, 1570, 1550, 1040 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 5.30–5.59 (m, 4 H, NH₂), 7.13–7.91 (m, 18 H, Ar).

Bis[*p*-(α -hydrazinobenzyl)phenyl] Sulfone (6h). To a solution of sulfone **6k** (2.0 g, 4.7 mmol) in 30 mL of anhydrous hydrazine and 100 mL of dry DMSO was added hydrazine monohydrochloride (5.0 g, 73 mmol). After stirring at 110 °C under argon atmosphere for 24 h, the reaction mixture was poured into water. The mixture was extracted with ether, washed with water, dried, concentrated, and column chromatography (silica, dichloromethane:diethyl ether = 7: 3) to give bishydrazone **6h** (1.16 g) as a white solid: IR (KBr) ν 3413, 1318, 1152 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 5.30–5.70 (m, 4 H, NH₂), 7.20–8.23 (m, 18 H, Ar).

Bis[*p*-(α -diazobenzyl)phenyl] Sulfide (4d). To a solution of bishydrazone **4h** (43 mg, 0.10 mmol) in 6 mL of dichloromethane was added barium manganate (90 mg) in the dark and stirred 3 h at room temperature with monitoring the reaction by the thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography (alumina act. IV, hexane:dichloromethane = 2:1) gave bisdiazobenzyl compound **4d** (24 mg, 58%, 2 steps) as a deep red viscous oil: IR (KBr) ν 2920, 2040, 1590 cm⁻¹; UV-vis (CH₂Cl₂) $\lambda_{max}(\epsilon)$ 292

(29700), 523 (244) nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.20–7.25 (m, 6 H), 7.27–7.32 (m, 4 H), 7.35–7.43 (m, 8 H).

Bis[*p*-(α -diazobenzyl)phenyl] Sulfoxide (5d). To a solution of bishydrazone **5h** (43 mg, 0.10 mmol) in 6 mL of dichloromethane was added barium manganate (90 mg) in the dark and stirred 3 h at room temperature with monitoring the reaction by the thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography (alumina act. IV, hexane:dichloromethane = 7:3) gave bisdiazio compound **5d** (24 mg, 39%, two steps) as a deep red viscous oil: IR (KBr) ν 3060, 2040, 1590, 1050 cm^{-1} ; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\epsilon)$ 295 (56900), 333 (64600), 509 (174) nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.22–7.34 (m, 10 H), 7.42 (t, $J = 7.5$ Hz, 4 H), 7.61 (t, $J = 8.8$ Hz, 4 H).

Bis[*p*-(α -diazobenzyl)phenyl] Sulfone (6d). To a solution of bishydrazone **6h** (300 mg, 0.66 mmol) in 50 mL of dichloromethane, 50 mL of benzene, and 50 mL of hexane was added barium manganate (2 g) in the dark, and the solution was stirred 18 h at room temperature with monitoring the reaction by the thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography (alumina act. IV, hexane:dichloromethane = 9:1) gave bisdiazio compound **6d** (170 mg, 29%, two steps) as a red powder: IR (KBr) ν 2043, 1586, 1154, 1312 cm^{-1} ; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\epsilon)$ 232 (27 000), 286 (23 000), 356 (36 000), 502 (310) nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.23–7.36 (m, 10 H), 7.45 (t, $J = 7.4$ Hz, 4 H), 7.87 (d, $J = 8.6$ Hz, 4 H); $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3) δ 63.4, 123.5, 126.5, 127.0, 127.4, 128.2, 129.3, 136.4, 137.2.

2,7-Dibenzoylthioxanthene (7k). To a stirred slurry of aluminum trichloride (2.0 g, 15 mmol) in 5 mL of nitrobenzene was added benzoyl chloride (1.8 mL, 15 mmol) at 5 °C. Thioxanthene (1.0 g, 5.0 mmol) was added to the mixture at 5 °C dropwise. After the solution was stirred for 24 h at 20 °C, the reaction mixture was poured into aqueous hydrochloric acid. The mixture was extracted with dichloromethane, washed with aqueous hydrochloric acid, aqueous sodium carbonate and water, dried, and concentrated. Column chromatography (silica, dichloromethane) gave sulfide **7k** (0.82 g, 40%) as a white solid: mp 175.5–176.5 °C; IR (KBr) ν 3058, 1647, 1593 cm^{-1} ; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 3.98 (s, 2 H, *CH*2), 7.45–8.96 (m, 16H, Ar-H); $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3) δ 38.6, 126.4, 128.3, 128.6, 129.5, 129.8, 132.4, 135.0, 136.2, 137.4, 138.3, 195.7. Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_2\text{S}$: C, 79.78; H, 4.46. Found: C, 79.73; H, 4.51.

2,7-Dibenzoylthioxanthene Dihydrazone (7h). To a solution of thioxanthene **7k** (200 mg, 0.49 mmol) in 3 mL of anhydrous hydrazine and 12 mL of dry DMSO was added hydrazine monohydrochloride (260 mg, 3.8 mmol). After stirring at 90 °C under argon atmosphere for 2 h, the reaction mixture was poured into water. The mixture was

extracted with ether, washed with water, dried, and concentrated. Column chromatography (silica, dichloromethane: $\text{Et}_2\text{O} = 3:1$) gave bishydrazone **7h** (180 mg, 84%) as a white powder: IR (KBr) ν 3391, 3281, 1580 cm^{-1} ; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 3.76–3.98 (m, 2 H, *CH*2), 5.42 (bs, 4 H, *NH*2), 7.10–7.65 (m, 16 H, Ar).

2,7-Bis(α -diazobenzyl)thioxanthene (7d). To a solution of bishydrazone **7h** (30 mg, 0.07 mmol) in 10 mL of dichloromethane was added yellow mercury oxide (200 mg) in the dark and the solution was stirred for 16 h at room temperature with monitoring of the reaction by thin layer chromatography (alumina). Filtration, concentration, and purification by chromatography (alumina act. IV, pentane) gave bisdiazio compound **7d** (10 mg, 34%) as a deep red solid: IR (NaCl) ν 3058, 3027, 2926, 2031, 1593 cm^{-1} ; UV-vis (CH_2Cl_2) $\lambda_{\text{max}}(\epsilon)$ 297 (32 000), 335 (sh), 524 (230) nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 3.83 (s, 2 H), 7.11–7.46 (m, 16 H); $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3) δ 37.8, 60.6, 121.8, 122.9, 123.6, 124.1, 125.9, 126.5, 127.5, 127.7, 129.3, 135.3.

B. ESR Measurement. Photolyses of diazo compounds **4d–7d** were carried out in MTHF matrices at 9 K in an ESR cavity. The light was obtained from a High-Pressure Mercury lamp by combination of a Kenko L-42 sharp cut filter and a quartz water filter. A Bruker ESP 300 spectrometer was used to obtain X-band ESR 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 ESR intensities for I - $1/T$ 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. 2 K. For the analysis of the intensity, the temperature region where the isolated triplet signal obeyed Curie–Weiss law was used.

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Supporting Information Available: 2D-HHCOSY and relay shift correlation NMR spectrum of NMR spectra of the ketone **6k** (2 pages). See any current masthead page for ordering and Internet access instructions.

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