Effect of the Oxidation State of the Sulfur Atom on the Exchange Interaction between Two Triplet Carbene Units through Diphenyl Sulfide *p,p'*-Diyl Couplers

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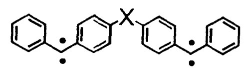
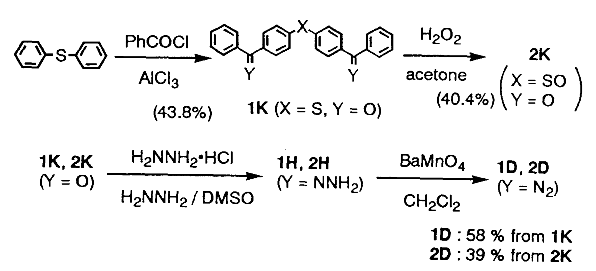
The exchange interaction between two triplet carbene centers through diphenyl sulfide *p,p'*-diyl and the corresponding sulfoxide coupling units was studied. While the former was found to be a ferromagnetic coupler, the latter was found to be an antiferromagnetic coupler.

While a diphenyl ether *p,p'*-diyl unit is reported to couple two carbene centers antiferromagnetically,[1] the corresponding sulfur analog appears to connect two triplet nitrene centers ferromagnetically.[2] In order to find the generality and scope of the latter trend, the effect of the oxidation state of the sulfur atom in diphenyl sulfide *p,p'*-diyl coupler has been studied.

Diazo precursors **1 D** and **2 D** were synthesized according to Scheme 1. Diphenyl sulfide was treated with benzoyl chloride to give 4,4'-dibenzoyldiphenyl sulfide **1 K**.[3,4] Oxidation of 4,4'-dibenzoyldiphenyl sulfide **1 K** with hydrogen peroxide afforded 4,4'-dibenzoyldiphenyl sulfoxide **2 K**.[5] Both **1 K** and **2 K** were converted to the corresponding hydrazones and then to the corresponding diazo compounds **1 D** and **2 D**[6,7] (Scheme 1).



1C : X=S
2C : X=SO



Scheme 1.

Photolyses of diazo compounds **1 D** and **2 D** were carried out in 2-methyltetrahydrofuran (MTHF) solid solutions in an ESR cavity at 9 K by using light (λ > 480 nm) from a high-pressure mercury lamp for 90 and 150 min, respectively, to give ESR spectra as shown in Figure 1. The observed spectral patterns did not change from the initial to later stages of the irradiation and were found to consist of three sets of signals assigned in reference to those of the corresponding ether dicarbenes.[1] In **1 C**, the signal at 85 mT (marked T_i) obeyed Curie-Weiss law and was assigned to the isolated triplet, originating from the conformers in which the intramolecular interaction was very small. As the temperature was raised, the signal at 112 mT (marked T_t) appeared, increased, reached a maximum and then decreased, suggesting the thermally populated triplet. The signal at 264 mT (marked Q) obeyed Curie-Weiss law, which was assigned to the ground state quintet of the interacting dicarbene. For **2 C**, the signals at 94 mT and 111 mT (marked T_i and T_t, respectively) showed the same behavior as the signal at 85 mT and 112 mT of **1 C**. Thus they were assigned to isolated triplet and thermally populated triplet, respectively. But the signal at 284 mT (marked Q) appeared, increased, reached a maximum and then decreased as the temperature was raised. This signal was assigned to the thermally populated quintet.

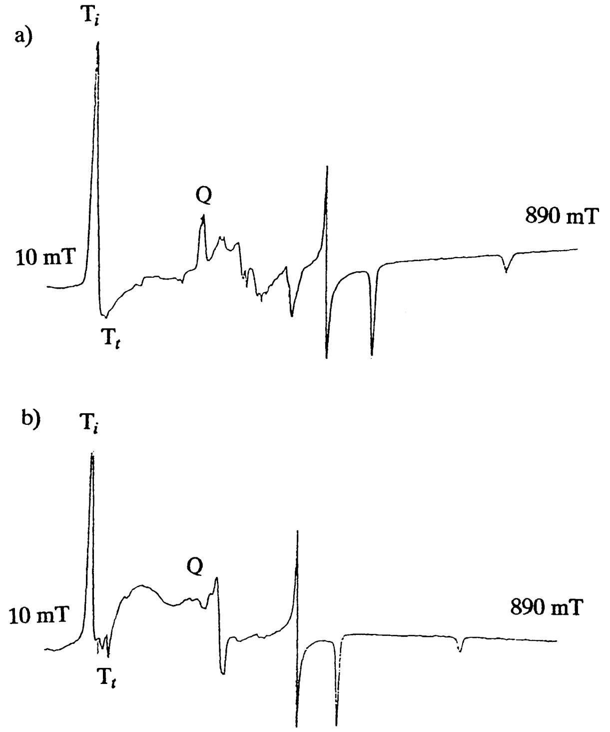


Figure 1. ESR spectra of the photoproducts of a) **1 D** in 10 mM MTHF matrix at 9.5 K, 9.42 GHz, and b) **2 D** in 10 mM MTHF matrix at 8.5 K, 9.41 GHz. Signals denoted T_i, T_t, and Q are assigned to isolated triplet, thermally populated triplet, and quintet signals, respectively.

The plots of the ESR signal intensity vs the reciprocal of temperature are shown in Figures 2 and 3. The signals due to the isolated triplets obeyed Curie-Weiss laws in the temperature ranges 10-50 and 20-50 K for **1 C** and **2 C**, respectively. The quintet signal due to **1 C** obeyed a Curie-Weiss law, but thermally populated triplet signal grew in, reached a maximum intensity at ca. 45 K, and decreased as the temperature was increased. For **2 C**, the thermally populated triplet and quintet signals showed maximum intensities at ca. 50 and 60 K, respectively. From these observations, **1 C** and **2 C** were concluded to have quintet and singlet ground states, respectively.

According to a theory of two weakly interacting triplets,[8] antiferromagnetic interaction (J < 0) leads to a ground singlet state with excited triplet and quintet states higher in energy by $-2J$

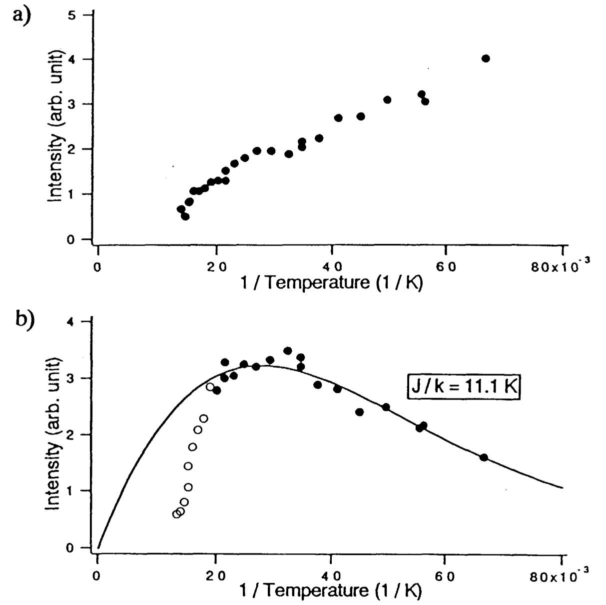


Figure 2. Plots of the intensities of the ESR signal at a) 264 mT (Q) due to the ground state quintet and b) 112 mT (T_t) due to the thermally populated triplet of **1 C** vs reciprocal of temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range (shown by closed circle) where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie-Weiss laws.

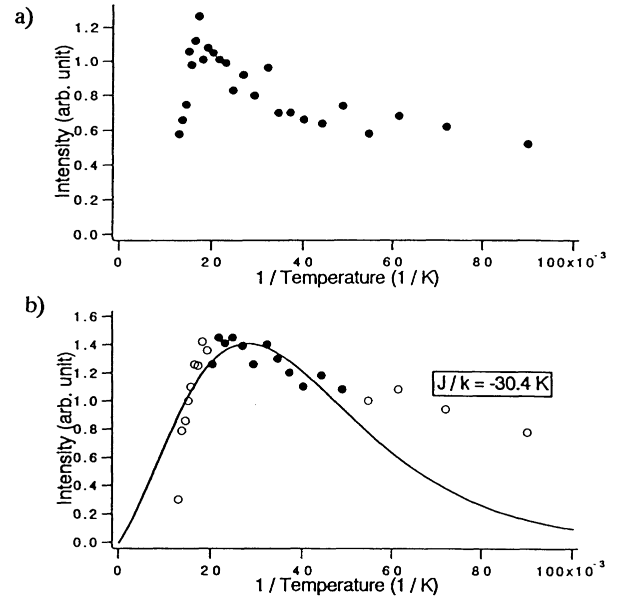


Figure 3. Plots of the intensities of the ESR signal at a) 284 mT (Q) due to the thermally populated quintet and b) 111 mT (T_t) due to the thermally populated triplet of **2 C** vs reciprocal of temperature. The fitting of a theoretical curve for thermally populated triplet signals was performed in the temperature range (shown by closed circle) where the dicarbene was chemically intact and the isolated triplet signals obeyed Curie-Weiss laws.

and $-6J$, respectively, from the ground state, where J is the exchange integral of two electrons, one on each carbene centers. When ferromagnetic interaction ($J > 0$) was operative, quintet ground state with excited triplet and singlet state higher in energy by $4J$ and $6J$, respectively. The observed data were analyzed in terms of the Bleaney-Bowers-type thermal distribution among the three states:[9] for **1 C**,

$$I = \frac{C}{T}\frac{3\exp(-4J/kT)}{5 + 3\exp(-4J/kT) + \exp(-6J/kT)} \qquad (1)$$

and for **2 C**,

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

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 the exchange integral J/k values of 11.1 and -30.4 K for **1 C** and **2 C**, respectively (Figures 2b and 3b). The fitting of the thermally populated quintet signal for **2 C** could not be accurately performed because of the decomposition of the carbenes.

The contrasting ferro- and antiferromagnetic exchange interactions between the two 2p spins on the aromatic rings through the sulfide and sulfoxide groups may be attributed to the balance between the superexchange through the 3s and 3p electrons. While the 3s orbital is orthogonal to the 2p orbitals and contributes to the ferromagnetic coupling, the antiferromagnetic overlap of the 3p orbitals with the latter depends on the oxidation state and conformation of the sulfur compounds. The isolated triplet signals were rather intense in both cases; the amount of the conformers in which the interaction is minimal might be rather significant.

References and Notes

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3 W. Dilthey, L. Neuhaus, E. Reis, and W. Schommer, *J. Prakt. Chem.*, **124**, 114 (1930).
4 **1 K**: white solid; mp 169.0-169.9 °C; IR (KBr) ν 3050 (C-H), 1650 (C=O); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45-7.53 (m, 8 H, Ar), 7.61 (t, J = 7.3 Hz, 2 H, Ar), 7.76-7.82 (m, 8 H, Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 128.3, 129.9, 130.3, 130.9, 132.5, 136.3, 137.2, 140.3, 195.6; Anal. Found: C, 79.40; H, 4.82; S, 8.25%. Calcd for $C_{26}H_{18}O_2S$: C, 79.16; H, 4.60; S, 8.13%.
5 **2 K**: white solid; mp 162.3-162.9 °C; IR (KBr) ν 3050 (C-H), 1650 (C=O), 1060 (S=O); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.49 (t, J = 7.5 Hz, 4 H, Ar), 7.62 (t, J = 6.6 Hz, 2 H, Ar), 7.76-7.83 (m, 8H, Ar), 7.90 (d, J = 8.4 Hz, 4 H, Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 124.4, 128.4, 130.0, 130.8, 133.0, 136.6, 140.2, 149.1, 195.3; Anal. Found: C, 75.88; H, 4.45; S, 8.00%. Calcd for $C_{26}H_{18}O_2S$: C, 76.08; H, 4.42; S, 7.81%.
6 **1 D**: red oil; IR (KBr) ν 2920 (C-H), 2040 (N=N); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20-7.25 (m, 6 H, Ar), 7.30 (t, J = 6.2 Hz, 4 H, Ar), 7.35-7.43 (m, 8 H, Ar); UV-vis (CH_2Cl_2, λmax (ε)) 292 (29700), 523 (244).
7 **2 D**: red oil; IR (KBr) ν 3060 (C-H), 2040 (N=N), 1050 (S=O); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.22-7.34 (m, 10 H, Ar), 7.42 (t, J = 7.5 Hz, 4 H, Ar), 7.61 (t, J = 8.8 Hz, 4 H, Ar); UV-vis (CH_2Cl_2, λmax (ε)) 295 (56900), 333 (64600), 509 (174).
8 K. Itoh, *Pure Appl. Chem.*, **50**, 1251 (1978).
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