Intramolecular Spin Interactions through Cumulative Double Bonds

Takehiro Yamagata, Hideyuki Tukada,[†] and Keiji Kobayashi*
Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
[†]*Graduate School of Integrated Sciences, Yokohama City University, Kanazawa-ku, Yokohama 236*

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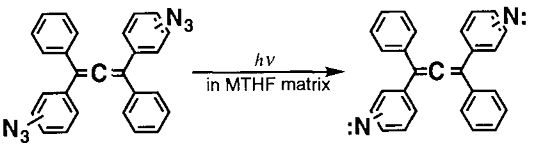
Cumulative double bonds were proved to act as a ferromagnetic spin coupler between both sides of π-conjugated spins, as investigated by temperature dependence of quintet ESR signals of three isomeric dinitrene species in which two spin centers are incorporated in a tetraphenylallene framework.

In the past decade significant progress in the spin interactions has been made toward exploring high-spin molecular materials and organic ferromagnets. A variety of π–conjugated systems have been investigated as spin coupling paths, particularly, in view of their topological property. For these conjugated hydrocarbons a spin polarization mechanism fundamentally accounts for intramolecular spin interactions on arrays of adjacent carbon atoms in planar π–conjugated systems.[1] The effects of torsion in π–conjugation have recently been discussed.[2] On the other hand, there has been no investigation on spin coupling through an orthogonally fixed π–system that is also an important constituent unit of π–systems as cumulative double bonds. In this paper we wish to report the first experimental results for the spin coupling via a cumulene-type conjugation by the use of three isomeric dinitrene species **1a**, **1b**, and **1c**, in which spin centers are incorporated in a tetraphenylallene framework.



2a : *p, p'*-
2b : *m, m'*-
2c : *m, p'*-

1a : *p, p'*-
1b : *m, m'*-
1c : *m, p'*-

Dinitrenes **1a**, **1b**, and **1c** were generated by photolysis of diazides[3] **2a**, **2b**, and **2c**, respectively, in 2-methyltetrahydrofuran (MTHF) matrices at cryogenic temperature: the dilute frozen solution (ca 2~10 × 10^{-3} M) of the diazide in a quartz cell was irradiated in an ESR cavity with a high pressure mercury lamp.

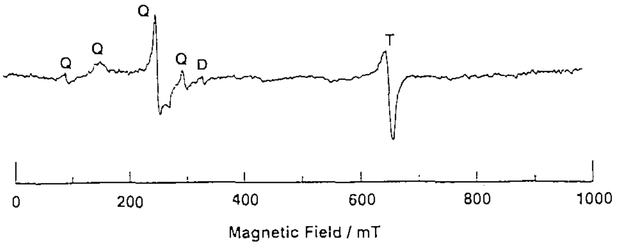


Figure 1. ESR spectrum obtained after irradiation of diazides **2a** in MTHF glass at about 10 K along with the signal assignment. D = doublet, T = triplet, Q = quintet.

The ESR spectrum from the photolysis of *p,p'*- isomer **2a** at about 8 K for 70 min is shown in Figure. 1. The resonance signal at 648.5 mT is assigned to transitions of triplet mononitrene and the peak at 323.8 mT is to a doublet radical. Other observed resonances, i.e. the intense signal at 241.4 mT and some of the weak signals at 288.2, 144.6 and 84.9 mT, are characteristic signals of the quintet dinitrene species;[4] various types of dinitrenes have been characterized so far by the X-band spectrometer.[5]

In order to determine whether the observed quintet state is a ground state or a thermally excited one, the temperature dependence of the signal intensities was investigated by monitoring the signal at 241.4 mT. The signal intensity decreased reversibly with increasing temperatures in the range 7.8-54.7 K. The plot of quintet signal intensity vs the reciprocal of temperature showed a linear relation in accordance with a Curie's law, as shown in Figure 2 (a), and no thermally populated signals were detected. Above 65 K, their signals disappear irreversibly from the ESR spectrum. From these results we concluded that the quintet state of *p,p'*-isomer **1a** is the ground state, although an exact degeneracy with the corresponding singlet state cannot be excluded.[6] The signal at 648 mT ascribed to triplet impurity shows also linear decrease with the reciprocal of temperature,

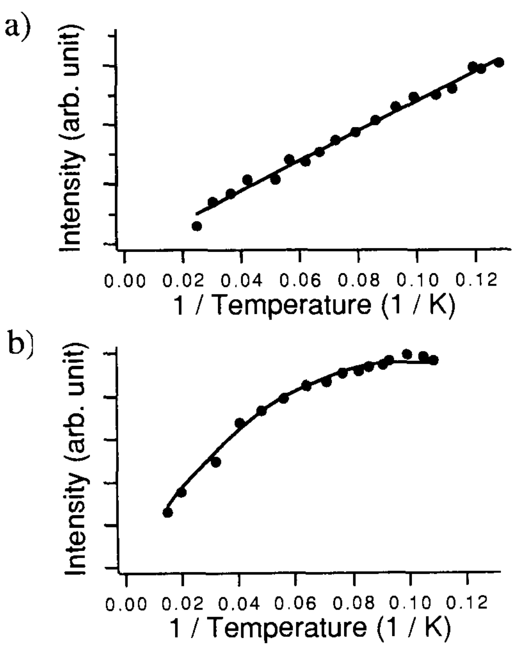


Figure 2. Plots of the signal intensities due to quintet signal vs the inverse of temperature for **1a** (a) and **1c** (b).

while its behavior is independent of quintet signals, indicating that the observed triplet is not a thermally excited triplet of the dinitrene but a triplet of the mononitrene. No sign of stepwise generation of the dinitrene from the mononitrene was detected.

The variable-temperature experiments of UV-irradiated **2b** demonstrated likewise that the quintet state of *m,m'*-isomer **1b** is a ground state or the spin states are nearly degenerate.

When **2c** was irradiated under similar conditions (at 9.2 K, for 210 min), the ESR signals assigned to the quintet state of *m,p'*- dinitrene **1c** were observed besides the signals due to a doublet and to two triplets, which are assigned to each of *p*- and *m*-substituted mononitrenes, respectively. In contrast to dinitrenes **1a** and **1b**, the observed signal intensities of quintet **1c** at 292.4 mT increase and reach a maximum at about 10 K and then decrease as the temperature is raised. In this measurement we applied an appropriate low microwave power to avoid saturation of the signal intensities. In Figure 2 (b) the results are depicted in an intensity vs reciprocal temperature plots form. After annealing the solid solutions, reproducible signal intensities were recorded in the temperature range 9.2-70.7 K. Thus it is evident that quintet state of dinitrene is populated thermally. The curve fitting of the observed data was undertaken to a Bleaney-Bowers type equation,[7] describing the temperature dependence of the signal intensity I due to the excited quintet state. The fitting curve is also indicated in Figure 2 (b). Thus $J/k_B = -2.8$ K was estimated for the energy gap $E = 6J$.

The present experimental results of **1a**, **1b**, and **1c** are consistently rationalized in terms of spin polarization, as schematically illustrated in Figure 3 for **1a**. Along planar π–conjugated hydrocarbon the triplet nitrene unit would propagate spin polarization toward the central sp carbon atom of the cumulative π–bonds, which depends on the topological pattern of the nitrene substitution. For unpaired electrons in orthogonal orbitals on the same site high-spin state is stabilized by exchange interaction; triplet carbene $:CH_2$ is a relevant example. A similar situation could reasonably be assumed at the sp carbon atom in **1a**, **b** and **c** acting as a ferromagnetic spin coupler, since its π orbitals are restricted to being orthogonal.

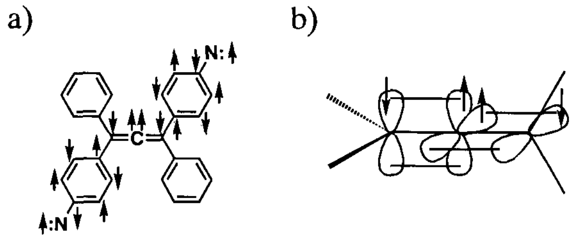


Figure 3. (a) Schematic representation of intramolecular spin allignment for **1a**. (b) Ferromagnetic spin coupling via the sp carbon atom of cumulative double bonds.

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References and Notes

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3 The precursors of dinitrenes, diazides **2a**, **2b**, and **2c**, were prepared by dilithiation of the corresponding dibromide, followed by the reaction with *p*-tosyl azide in the presence of $Na_4P_2O_7$. The diazides exhibited characteristic IR absorptions at 2120-2160 cm^{-1} ascribed to azide functionality and also ^{13}C NMR signals at about 210 ppm due to the central sp carbon atom.

4 The highest-field Z transition and the next highest-field Y transition were not observed in the spectra of the three dinitrene species except for **1b**, wherein the peak ascribed to the next higest-field transition could be observed at around 650 mT.

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6 The energy gap between the singlet and quintet states of **1a** and **1c** was calculated by the use of the RHF PM3 (open 4,4) method in the MOPAC 93 program package. For **1a** quintet state is slightly stable ($\Delta E_{Q\text{-}S}$ = 0.4 kcal/mol), while for **1b** there is no energy gap ($\Delta E_{Q\text{-}S}$ = 0.0 kcal/mol).

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This paper is dedicated to Professor Michinori Ōki on the occasion of his 70th birthday.