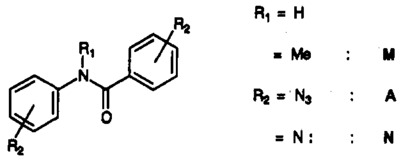
Isomeric *N*-(Nitrenophenyl)nitrenobenzamides. Comparison of the Energy Differences between Their Singlet and Quintet States Obtained Computationally and Experimentally

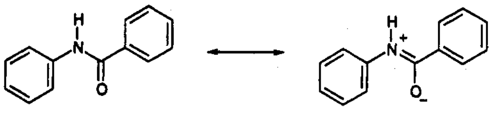
Andrew S. Ichimura, Kazunori Ochiai, Noboru Koga, and Hiizu Iwamura*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113 Tokyo, Japan

Received November 18, 1993 (Revised Manuscript Received February 28, 1994●)

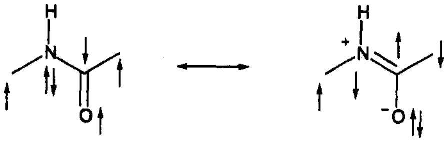
Summary: The sign and magnitude of the intramolecular magnetic coupling between the two triplet nitrene units through the benzanilide chromophore have been studied by temperature dependence of their EPR fine structures. The results that the interactions are ferromagnetic in the *m,p′* and *m′,p* isomers and antiferromagnetic in the *p,p′* and *m,m′* isomers were corroborated by semiempirical CI calculations.





X

Y



For the construction of high-spin organic molecules[1] with a long-range goal of constructing organic ferromagnets,[2] various magnetic couplers[3] that connect radical centers ferromagnetically have been proposed and their sign and magnitude of the coupling have been investigated. The amide bond is a synthetically attractive magnetic coupler which has the potential of forming polyamide bonds as well as hydrogen bonds, thus enabling the spin alignment along the chain as well as between the neighboring chains. As a first step, the effectiveness of the amide bond as an exchange coupler has to be evaluated. For this purpose, we selected isomeric benzanilides N having a nitrene unit on each benzene ring and studied their EPR fine structures. We wish to report here the sign and magnitude of their spin exchange interaction predicted by semiempirical CI calculations and obtained by EPR experiments.

The amide bond is expressed by two resonance structures, X and Y. In principle, the extent of π-conjugation through the C–N bond should determine the strength of the exchange interaction between two triplet nitrenes. The π-conjugation in resonance structure Y has an obvious similarity to stilbene. For dinitrene derivatives of stilbene, a simple parity-based model[4] for predicting the ground-state spin quantum number is easily applied to the different isomers. Starting from one of the nitrene centers, the different atoms are alternantly starred and unstarred such that no starred or unstarred atoms are adjacent. Then the spin quantum number S is given simply by $S = (n^* - n^\circ)/2$, and for stilbene dinitrenes[5], $S_{p,m'} = 2$ and $S_{m,m'} = 0$ as was observed experimentally.[3d] By direct analogy, the ground-state regioselectivity of the fully π-conjugated structure Y is expected to be identical to the stilbene derivatives. At the other extreme, resonance structure X might be thought of as a three-π-electron coupler where the lone pair of nitrogen would act a two-electron superexchange center. Applying the formula outlined above to the hypothetical situation of localized structure X, the *p,p′* and *m,m′* isomers are predicted to be high spin while the *p,m′* and *m,p′* isomers would be low spin, the exact opposite of the fully π-conjugated case.

Since the amide bond exists somewhere between the extremes of X and Y, the effectiveness of the amide bond as an exchange coupler was first tested by means of PM3/CI calculations,[6] and the results are listed in Table 1. Qualitatively, the *p,m′* and *m,p′* isomers are predicted to be high spin, the *p,p′* isomer is a ground-state singlet, and the *m,m′* isomer has nearly degenerate quintet, triplet, and singlet states or may be low spin. On the basis of these results, we expected the amide bond to behave like the C═C double bond in stilbene in coupling two phenylnitrene units.

Four isomeric diazides of benzanilides A as precursors of dinitrenes N were prepared by treating the corresponding diaminobenzanilides[7] with sodium nitrite and sodium azide according to the method reported previously.[3a] Azides

---

● Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Super-high-spin molecules ($S \geq 7/2$): Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1990**, *112*, 4074. Sasaki, S.; Iwamura, H. *Chemistry Lett.* **1992**, 1759. Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484. Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *114*, 1884. Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872. Dougherty, D. A.; Jacobs, S. J.; Silverman, S. K.; Murray, M. M.; Shultz, D. A.; West, A. P., Jr.; Clites, J. A. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 289. Rajca, A.; Utamapanya, S. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 305.

(2) Real ferromagnets due to monoradicals at subliquid He temperature: (a) Turek, P.; Nozawa, K.; Shiomi, K.; Awaga, K.; Inabe, T.; Maruyama, Y.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *180*, 327. Tamaru, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *86*, 401. (b) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczwe, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301. (c) Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147. (d) Nogami, T.; Tomioka, K.; Ishida, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Chem. Lett.* **1994**, 29.

(3) (a) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33. (b) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547. (c) Doi, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993** *115*, 8928. (d) Ling, C.; Minato, M.; Lahti, P. M.; Willigen, H. V. *J. Am. Chem. Soc.* **1992**, *114*, 9959. (e) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744. (f) Doi, T.; Inoue, K.; Koga, N.; Iwamura, H. Unpulished results.

(4) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(5) A nitrene center contributes a total spin of $S = 1$ so that the result of $S = (n^* - n^\circ)/2$ should be multiplied by a factor of 2 for dinitrenes.

(6) Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Phys. Org. Chem.*, in press.

(7) Dezern, J. F. *J. Poly. Sci., Part A, Poly. Sci.* **1988**, *26*, 2157.

0022-3263/94/1959-1970$04.50/0

Table 1. Signs and Energy Differences, ΔE_{SQ} (cal/mol), between the Singlet and Quintet States of Isomeric Dinitrenes

	Computed		Experimental	
	sign	ΔE_{SQ}	sign	ΔE_{SQ}
p,p'-**N**	−	170	−	>180
p,m'-**N**	+	160	+	>238[a]
m,p'-**N**	+	70	+	>238[a]
m,m'-**N**	degenerate	3	−	39

[a] This value was estimated from the highest temperature, 80 K, at which the quintet state was observed before decomposition and at which no signal due to a thermally excited triplet state could be detected.

A were purified by column chromatography on aluminum oxide and used for EPR measurements immediately after the purification.[8]

Irradiation (λ > 380 nm) of **A** in 2-methyltetrahydrofuran (MTHF) matrices at 10 K in an EPR cavity produced the corresponding dinitrenes **N**. The EPR spectra from *p,p'*-**A** revealed two signals at 667.3 and 681.1 mT due to the *X* (= *Y*) transitions of triplet mononitrenes. In comparison with the mononitrene signals observed in the other isomers, those at lower and higher fields are assigned to the mononitrenes at the *p*- (aniline side) and *p'*-positions (benzoyl side), respectively. It was only after raising the temperature to about 75 K in the dark that additional weaker signals grew in at 15.0, 272.3, and 653.3 (very weak) mT. They (Figure 1a) were reproducible after two annealing/cooling cycles and are interpreted to be from a thermally populated quintet state of dinitrene *p,p'*-**N**,[3] since the intensity of these signals increased reversibly in the temperature region 75–85 K. The signal intensities started to decrease irreversibly at above 90 K because of chemical decomposition of the nitrene centers. Thus, it was not possible to determine the temperature at which the intensity of the quintet signals reached a maximum, but its lower limit was estimated to be 90 K. These EPR results[9] suggest that the two nitrene centers in *p,p'*-**N** couple in an antiferromagnetic fashion to produce a ground-state singlet with the quintet state lying above the singlet state by >180 cal/mol.

EPR spectra of *p,m'*-**N** and *m,p'*-**N** (Figure 1b and c) under similar conditions showed signals at 55.6, 122.0, 220.6, 308.0, 629.6, and 858.5 mT for *p,m'*-**N** and 54.2, 175.0, 222.5, 272.8, 609.0, and 858.8 mT for *m,p'*-**N** together with the signals due to isolated mononitrenes at 681.6 and 689.8 mT for *p,m'*-**N** and 667.3 and 695.3 mT for *m,p'*-**N**. The observed signals were characteristic of quintet dinitrenes,[3] and their zero field splitting parameters were determined to be $|D/hc|$ = 0.164 and 0.164 cm^{-1} and $|E/hc|$ = 0.0115 and 0.0117 cm^{-1} for *p,m'*-**N** and *m,p'*-**N**, respectively, by applying a third-order perturbational method to the highest-field *Z* transition ($m_S = -2 \rightarrow -1$) and next highest-field *Y* transition ($m_S = 1 \rightarrow 2$). These quintet signals decreased their intensities in the temperature range 10–90 K in accordance with the Curie law, suggesting either that the two nitrene centers interact in a ferromagnetic manner or that the states are nearly degenerate with the singlet states with 0 > ΔE_{SQ} > −20 cal/mol. In addition, no other signal which might be assigned to a thermally populated triplet dinitrene could be observed below 80 K. The linearity of the Curie plot and the absence of an excited triplet state strongly suggest that the amide bond permits a ferromagnetic interaction in phenylnitrenes *p,m'*-**N** and *m,p'*-**N**, producing a fairly robust quintet state. The ΔE_{SQ} value was estimated to be greater than 238 cal/mol on the basis of the thermal behavior of the quintet signals.

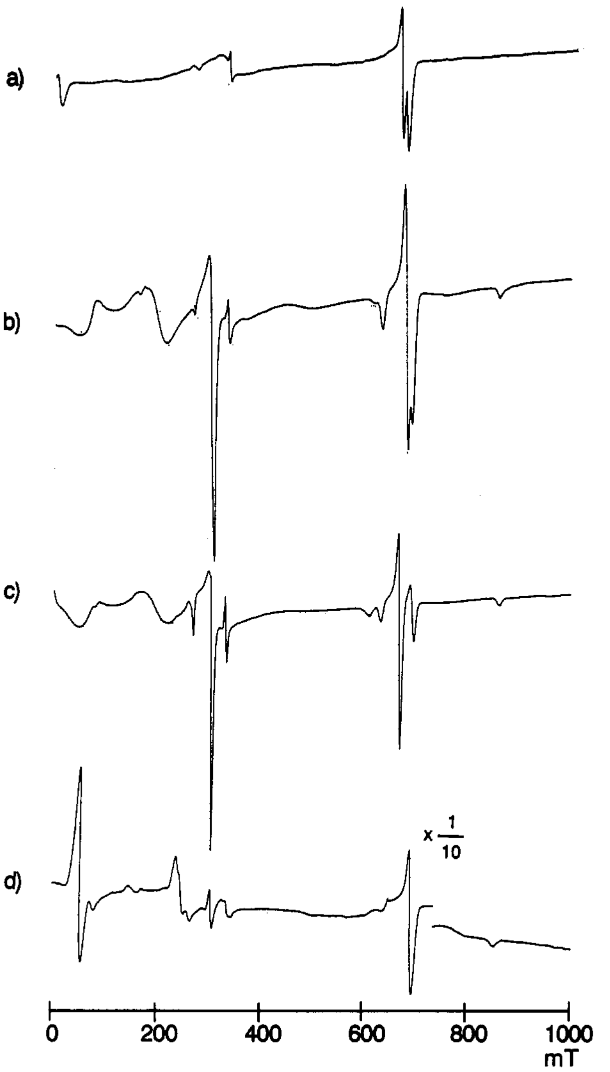


Figure 1. EPR spectra (ν = 9.42 GHz) obtained by photolyses of isomeric diazides **A**s at 10 K in MTHF matrices: (a) *p,p'*-**A** at 85 K, (b) *m,p'*-**A** at 10 K, (c) *p,m'*-**A** at 10 K, and (d) *m,m'*-**A** at 10 K.

In the EPR spectrum obtained after photolysis of *m,m'*-**A** under similar conditions (Figure 1d), two kinds of signals were observed together with a mononitrene signal at 686.6 mT. A set of the main signals at 46.7, 157, 234, 302, and 849 mT deviated from the Curie law and showed maximum intensities at about 13 K, while the intensities of the other signals at 70.9, 170, and 245 mT decreased linearly as the temperature was increased. The temperature dependence can be explained by assigning the former signals to a thermally populated quintet dinitrene with $|D/hc|$ = 0.161 and $|E/hc|$ = 0.012 cm^{-1}. The latter signals may be due to a thermally excited triplet state[9] or a quintet with smaller $|J|$ value than the former and nearly degenerate with a singlet. If the latter is the case, the two kinds of excited quintets might be due to different conformers of *m,m'*-**N** in frozen MTHF. Since the

---

[8] All the diazides gave satisfactory high-resolution MS and ^{1}H NMR data.

[9] In the EPR spectrum of *p,p'*-**N**, no signals due to a thermal triplet state which should lie by 4*J* below the quintet state could be detected. The lack of such signals suggested that they were either weak or broad and might be buried under the other signals. In ref 3b,c, weak signals at 237 and 243 mT, respectively, are suggested to be *X* transitions of the excited triplet dinitrenes.

temperature dependence of any signal intensity due to a quintet state that is formed by a weak interaction between two triplets and in equilibrium with the resulting singlet and triplet states is expressed by eq 1,[3] ΔE_{SQ} (=6J) for the main dinitrene was estimated to be 39 cal/mol by fitting eq 1 to the observed data

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

where I and C are the EPR signal intensity and a proportionality constant, respectively, and other symbols have their usual meanings.

The N-methyl derivative, *m,m'*-**MA**, of *m,m'*-**A** was also studied to rule out a possible photoenolization of the amide bond to form structure –N=C(OH)– which might have served as more efficient exchange coupler than the original –NHC(=O)–.[10] When photolyzed, *m,m'*-**MA** showed an EPR spectrum similar to that of *m,m'*-**A** and contained signals due to a quintet with $|D/\mathrm{hc}| = 0.168$ and $|E/\mathrm{hc}| = 0.016$ cm^{-1}. No maximum of the signal intensity was observed above 10 K indicating that the value of ΔE_{SQ} should be $0 > \Delta E_{SQ} \geq -20$ cal/mol. The magnitude of the coupling was somewhat reduced[11] but should be interpreted not to be fundamentally different from *m,m'*-**N**.

The sign of the exchange parameter J and the energy difference between the singlet and quintet states obtained experimentally are also summarized in Table 1. The experimental results support the qualitative predictions made by the semiempirical CI algorithm. On the basis of the above data, resonance structure Y contributes significantly in providing an coupling pathway. By comparison with the analogous *m,m'*-dinitrenes of stilbene[3f] or tolane[3a,b] where $\Delta E_{SQ} = -240$ and -200 cal/mol, respectively, the amide bond ($\Delta E_{SQ} = -39$ cal/mol) is concluded to be a weaker exchange coupler.[12]

We conclude that the amide bond is effective as an exchange coupler and warrants further investigation as a building block toward the design of molecular magnetic materials.

Acknowledgment. This work was supported by the Grant-in-Aid for Specially Promoted Research (No. 03102003) from the Ministry of Education, Science and Culture. Support is also acknowledged from the Japan Society for the Promotion of Science for a postdoctoral fellowship to A.S.I.

Supplementary Material Available: Intensity versus 1/T plots for the quintet signals and the EPR spectrum obtained by photolysis of *m,m'*-**MA** in MTHF matrix (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(10) This possibility was raised by a reviewer. A preliminary study of the photolysates of *m,m'*-**A** and **MA** in MTHF at 77 K revealed very similar weak absorptions at 400 nm but no strong and broad ones at 310 nm expected for the enolized products on the analogy of stilbenes and N-benzylideneanilines.

(11) For the decreased bond energy by N-methylation of the amides, see: Dorofeeva, I. B.; Kosobutskii, V. A.; Tarakanov, O. G. *Zh. Strukt. Khim.* **1982**, *23*, 56.

(12) Reduction to ca. 20% in the ΔE_{SQ} value does not deviate much from the degree of π-bonding in amides. See: Wiberg, K.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831.