Long-Range Magnetic Interactions in *trans*-1,4-Cyclohexylene- and 1,3-Adamantylene-bis(*p*-nitrenylbenzene) by π–σ–π Hyperconjugation
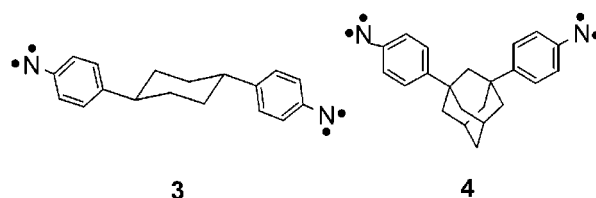
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ABSTRACT

Di(phenylnitrene)s linked with *trans*-1,4-cyclohexylene (3) and 1,3-adamantylene (4) units were generated photochemically at cryogenic temperatures. The EPR spectra are attributed to quintets. The temperature dependence of the signal intensities indicates that both quintets are thermally accessible states with energy gaps ΔE(S–Q) = 138 and 300 J mol^{-1}, respectively. DFT calculations showed that the magnetic interactions originated in the π–σ–π hyperconjugative through-bond interactions.

Considerable efforts to make molecule-based ferromagnetic substances during the past two decades have brought about a deep understanding of π-conjugative open-shell systems such as non-Kekulé molecules and homologous high-spin molecules.[1] Thus, the correlation between the topology of π-systems and their ground-state spin-multiplicity is now well understood and makes it possible to design spin alignment in π-systems bearing many radical sites.

In contrast to such spin communication through π-conjugative linkers, that through σ-bonds has received little attention as linkers for magnetic molecules.[2] This is understandable because biradicals separated with a long alkyl chain were known to have very small energy gaps between singlet and triplet states; e.g., the magnetic-field dependence of reaction products derived from such the biradicals is caused by S–T energy gaps as small as $g\beta H$ (< several J mol^{-1}).[2d,e] Even though the interaction between spin sites through σ-bonds is expected to be weak, we think that exploring spin alignment through σ-bonds is worthwhile in designing functional magnetic molecules[3] because of the diversity of conformational and electronic properties of the σ-bonds.

Here we describe spin communication through σ-bonds using dinitrenes incorporated into *trans*-1,4-cyclohexylene and 1,3-adamantylene skeletons, which have conformations appropriate for π–σ–π interactions.[4]
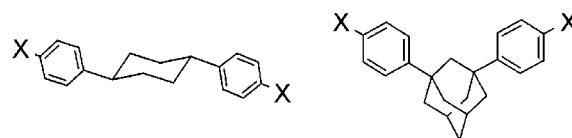
1:	X = N$_3$	2:	X = N$_3$
3:	X = Ṅ•	4:	X = Ṅ•
5:	X = ĊH$_2$	6:	X = ĊH$_2$

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The irradiation of *trans*-1,4-(*p*-azidophenyl)cyclohexane **1** in a 2-methyltetrahydrofuran (MTHF) glass at 15 K (310−350 nm of a 500 W Hg arc) produced an EPR spectrum (X-band) with a wide magnetic field (0−900 mT). The spectrum persisted at least 1 h at temperatures up to 70 K and was similar to those thus far assigned to quintet dinitrenes[5] (Figure 1a), resulting from interactions between
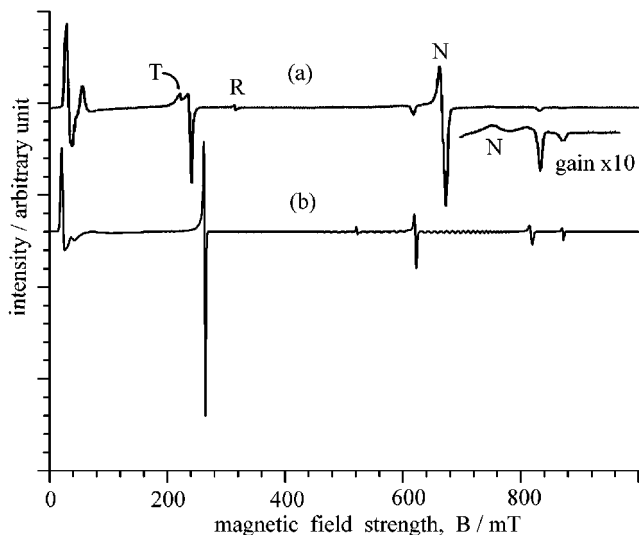

Figure 1. (a) X-band EPR spectrum of **3** obtained after UV irradiation (310−350 nm) of **1** in a 2-methyltetrahydrofuran matrix for 50 min at 15 K (recorded at 15 K, $\nu = 9.0051$ GHz, power = 0.1 mW, modulation = 1 mT). R, N, and T denote doublet and mononitrene impurities, and a triplet of **3**, respectively. Simulation[6] was performed with ZFS parameters of $|D/hc| = 0.320$ and $|E/hc| = 0.0003$ cm^{-1} (b).

two open shell units. This was confirmed by a simulated spectrum[6] ($|D/hc| = 0.320$, $|E/hc| = 0.0003$ cm^{-1}, Figure 1b) for randomly oriented quintet molecules using the Hamiltonian of the following equation:

$$H = D\{S_z^2 - S(S+1)/3\} + E(S_x^2 - S_y^2) + g\beta BS \quad (1)$$

The D value obtained is consistent with that estimated from the sum of D tensors of component triplet mononitrenes ($D^t = 0.9708$ cm^{-1}) by the Itoh model:[7] $D^q = (D^t_a + D^t_b)/6 = 0.32$ cm^{-1} (sum of tensors, rotational angle = 180°).

The temperature dependence of signal intensity (I_Q) for the quintet fitted an equation for a thermally accessible

quintet state with an energy separation between the singlet and quintet $\Delta E_{(S-Q)} = 6J = -138$ J mol^{-1}: $I_Q = $ constant/$T\{\exp(-3x) + 3\exp(-2x) + 5\}$, where $x = -2J/RT$.

According to density functional calculations[8] (open-shell singlet and triplet states at the U-B3LYP/6-31G* level) for a model diradical **5**, in which nitrenic atoms in **3** are replaced by methylene in order to eliminate complexity arising from localized spins on nitrogen atoms, **5** has a bisected conformation about the C1(and C4)-phenyl bond and is suitable to hyperconjugative coupling with π-NBMOs. The bisected conformation is the same as that of 1,4-diphenyl-cyclohexane obtained by X-ray crystallography (Supporting Information) Thus, both the HOMO(α) and HOMO-1(α) orbitals of the triplet **5** are coextensive and are constructed with an antibonding connection between the π-NBMOs and hyper-conjugative σ-bonds (Figure 3a,b). In contrast, those of the
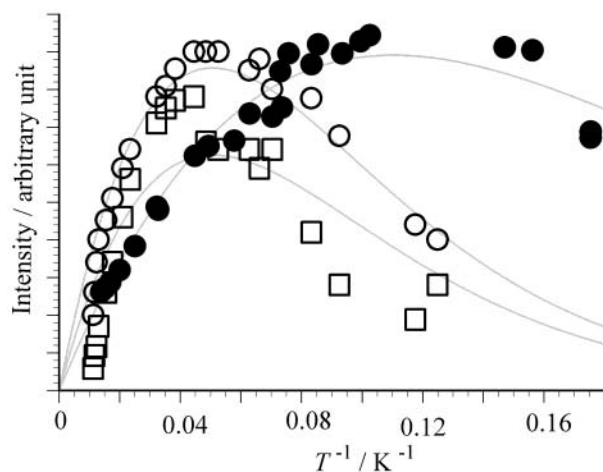

Figure 2. Curie plots for the EPR signals of **3** and **4**. For **3**, signals at 247.7 mT (solid circles) are shown with a fitting curve (eq 2 in text) with $J = -23$ J mol^{-1}. For **4**, signals at 295.8 and 233.2 mT (quintet, open circles and squares, respectively) are plotted with a fitting curve ($J = -50$ J mol^{-1}).

singlet state are spatially separated into individual π-radical sites, with no interaction between radical sites. The energy gap between the singlet and triplet states in **5** is estimated

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(6) Computer simulations were performed with an EPR simulation program suite, XSophe-Sophe-XeprView (v.1.0.1) developed by Prof. G. R. Hanson (University of Brisbane, Australia) and Bruker Analytik GmbH, using a full-matrix diagonalization method for $S = 2$. Wang, D.; Hanson, G. R. *J. Magn. Reson., Ser. A* **1995**, *117*, 1.

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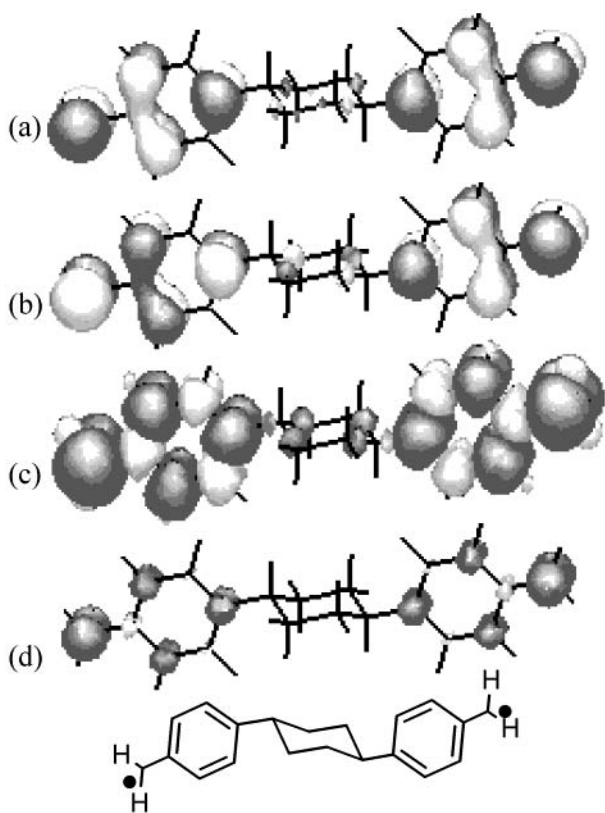
Figure 3. DFT calculations at U-B3LYP/6-31G* level of theory for triplet **5**. HOMO(α) (No. 72, -4.6925 eV) (a) and HOMO-1(α) (No. 71, -4.7631 eV) (b) are depicted with isodensity surfaces at 0.03 electrons/au^3. Isosurface of spin density at 0.001 and 0.01 electrons/au^3 are shown in (c) and (d), respectively. Black and white surfaces indicate α and β spins, respectively. Calculations were performed with Gaussian98W,[8] and the results were visualized with WinMOPAC (v.3, Fujitsu Ltd.).

Figure 4. (a) X-band EPR spectrum of **4** obtained after UV irradiation (310$-$350 nm) of diazide **2** in a 2-methyltetrahydrofuran matrix for 60 min at 15 K (recorded at 15 K, $\nu = 9.0040$ GHz, power $= 0.2$ mW, modulation $= 1$ mT). R and N denote doublet and mononitrene impurities, respectively. Simulated spectrum[6] was obtained by use of the Hammiltonian shown in text and ZFS parameters of $|D/hc| = 0.220$ and $|E/hc| = 0.013$ cm^{-1} (b), and $|D/hc| = 0.325$ and $|E/hc| = 0.0003$ cm^{-1} (c), respectively.

to be 80 J mol^{-1} ($J = -40$ J mol^{-1}) at the U-B3LYP/6-31G* level and is comparable to the experimentally obtained $\Delta E_{(S-Q)}$ for the dinitrene **3**.

Next we examined spin alignment through a 1,3-adamanthylene linker, which has a rigid W-letter skeleton connecting the open shell units. The photolysis of 1,3-di(*p*-azidophenyl)adamantane **2** gave a quintet dinitrene **4** at 15 K in MTHF (Figure 1a). The EPR spectrum fitted to two sets of quintet ZFS parameters, $|D/hc| = 0.325$, $|E/hc| = 0.0003$ cm^{-1}, and $|D/hc| = 0.220$, $|E/hc| = 0.013$ cm^{-1} (Figure 4b,c). Both have an identical energy gap of $\Delta E_{(S-Q)}$

$= 300$ J mol^{-1}, as determined from an analysis of the Curie plots (Figure 2).

The two quintet species can be attributed to rotamers around C$-$Ph bonds. X-ray crystallographic analysis for 1,3-diphenyladamantane (see Supporting Information) gave a single rotamer around C$-$Ph bonds, in which two phenyl rings are eclipse to the C1$-$C2$-$C3 plane and other C$-$C bond, respectively. Molecular mechanics calculations (MM2) for 1,3-diphenyladamantan showed that four stable rotamers around the Ph$-$C bond having the eclipsed conformations lay within 0.6 kJ mol^{-1} of steric energies. Applying the Itoh model to the four possible rotamers of the dinitrene **4**, D^q can be estimated to be $0.25-0.20$ cm^{-1} from the D^t tensor ($D^t = 0.9828$ cm^{-1}). These D^q values are not far from those observed in **4**, and thus further structural identification about conformation of **4** is difficult.

DFT calculations (U-B3LYP/6-31G*) for model diradical **6** were carried out for one of the eclipsed conformers (Figure 5). The HOMO(α) is constructed with two NBMOs and a pseudo p-orbital at the C2 atom (Figure 5b). The energy gap $\Delta E_{(S-T)}$ for this conformer of **6** was 120 Jmol^{-1} ($J = -60$ Jmol^{-1})

The energy gaps in **3** and **4** are appreciably smaller than those in conjugated diradicals such as *m*-quinodimethane ($\Delta E_{(S-T)} = 40$ kJ mol^{-1});[9] however, they are comparable to those of some perturbed π-diradicals such as *m*-bis(phenothiazino)benzene diradical dication ($\Delta E_{(S-T)} = 118$ J mol^{-1})[10]

(8) The DFT calculation at the B3LYP/6-31G* level of theory were carried out by a Gaussian 98W program package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
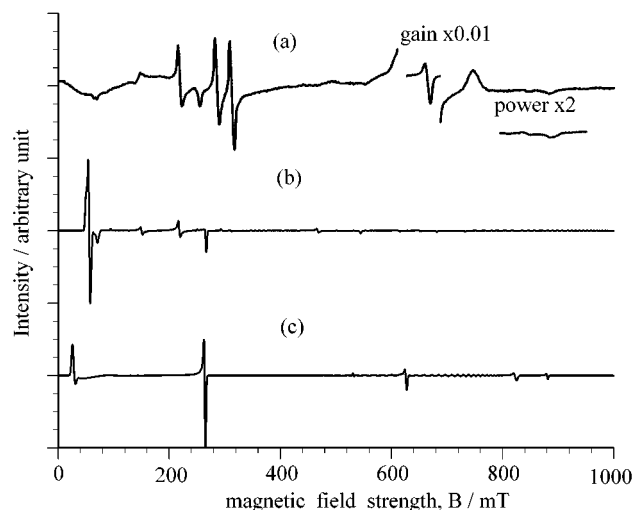
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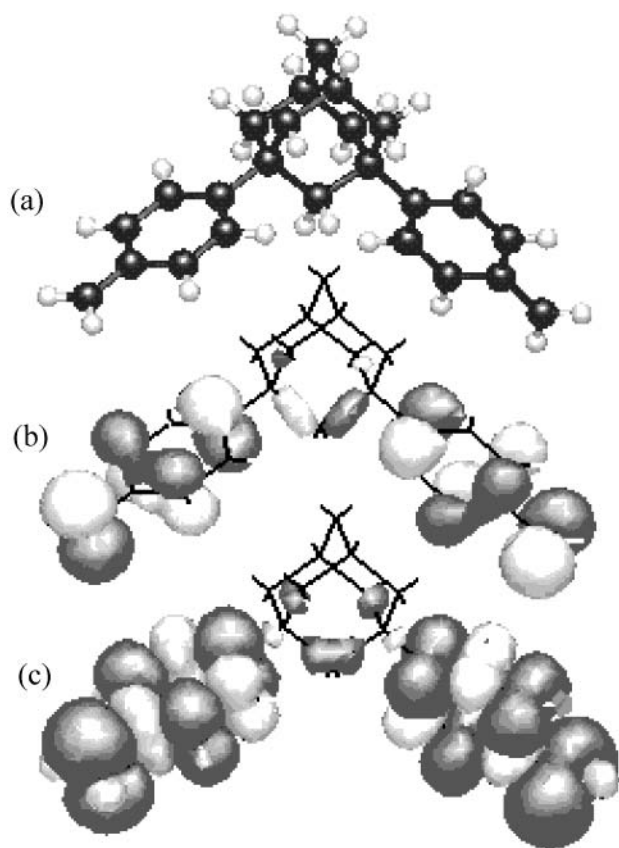
Figure 5. DFT calculations at U-B3LYP/6-31G* level of theory[8] for triplet **6**. The most stable conformer is shown in this figure. HOMO(α) (b) and spin population (c) are shown with electron density of 0.03 electrons/au^3 and 0.001 electrons/au^3, respectively. Black and white surfaces in (c) indicate α and β spins, respectively.

and *p*-phenylene-2,2′-bis(1,1:3,3-di-2,2′-biphenylenepropenyl) ($\Delta E_{(S-T)}$ = 250 J mol^{-1}).[11]

Because both **3** and **4** have singlet ground states, an odd/even alternation rule on the ground-state spin-multiplicity vs the number of π-units is not invoked in systems constructed with σ-bonds, such as **3** and **4**. It is in contrast to the spin alignment in π-conjugative diradicals (i.e., $CH_2(C{=}CH_2)_nCH_2$).[1] It also opposes alternative spin polarization along σ-bonds from the radical center, which is widely recognized in monoradicals, as is proofed by the sign of hyperfine splitting constants.

In general, through bond (TB) and through space (TS) interactions[4] between radical sites stabilize a singlet state of biradicals tied with σ-bonds. The TB interaction destabilizes (at least) one NBMO by antibonding interactions with σ-bonds, which destabilizes a triplet state. The TS interaction stabilizes a singlet state through a direct antiparallel spin alignment between radical centers. As the TS interaction is expected to be small due to the spatial separation in **3** and **4**, and the HOMOs(α) clearly shows hyperconjugations, the lack of alternative spin multiplicities in **3** and **4** comes from the TB interactions. Thus, the antiferromagnetic interactions in the diradicals separated with σ-bonds will be common.

The importance of σ-bonds for spin alignment for sterically distorted conjugated biradicals linked with *m*-phenylene has recently been reported.[12] In this case, an inversion from ferro- to antiferr-magnetic interaction occurs along with the conformational change of open-shell π-systems. The conformational change is indicative of a change in mechanisms for spin alignment from π-conjugation to through-σ-bond interaction. In a similar way to the distorted π-systems, a diradical molecule separated with σ-bonds is potentially a molecular device that can tune the magnetic properties of the molecules in response to environmental changes of circumstances. The reason for this is that if the molecule has two conformers, one with an appropriate conformation for TB interaction and one without, then the magnetic properties will depend on the equilibrium between the conformers affected by the environment. Our results guarantee that appropriate σ-systems provide sufficient magnetic interactions and are the first step to realize the above devices.

Supporting Information Available: X-ray structural details (CIF format) for mother hydrocarbons, experimental procedures of the EPR measurement, and selected data of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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