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Synthesis of An Azobenzene Derivative Bearing Two Stable Nitronyl Nitroxide Radicals as Substituents and Its Magnetic Properties

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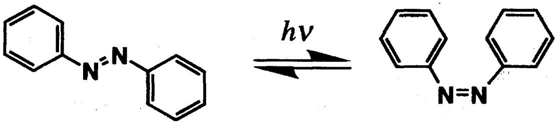
3,4′-Bis(4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1-oxyl-3-imidazolio-2-yl)azobenzene (**1**) was synthesized starting from 3,4′-dimethylazobenzene via the diformyl derivative. Biradical **1** crystallized as dark blue-green needles; its crystal structure was determined by the X-ray crystallography. X-band ESR spectra of biradical **1** in the degassed toluene solution were measured in the temperature range 10—300 K. At 300 K the ESR spectrum showed nine lines centered at $g = 2.006$ ($a_N = 3.7$ G). At 10 K the ESR spectrum showed a fine structure with zero-field splitting (zfs) parameters $|D/hc| = 0.0026$ cm^{-1} and $|E/hc| = 0.00014$ cm^{-1}. Magnetic susceptibility measurements revealed that the two radical centers coupled in a ferromagnetic way and the through-bond exchange interaction was determined to be $2J/k_B = 8.36 \pm 0.26$ K with a Weiss constant $\theta = -0.39 \pm 0.01$ K. Photochromic reaction was monitored by ESR and UV-vis spectroscopy.

Since molecule-based magnets were brought to realization in the late eighties-early nineties,[1] how to provide additional properties to them has been an interdisciplinary topic of great interest in chemical science.[2] By taking advantage of the versatility of organic molecules, efforts have been made to combine photochromism, thermochromism, conductivity, non-linear optical properties, etc. with the magnetic properties.

When two spins are placed in proper sites on an organic π-conjugated molecular framework, the spins can couple in ferro- or antiferromagnetic fashion according to the spin coupling unit.[3,4] Stilbene-3,4′-diyl and 3,3′-diyl[4] are typical ferro- and antiferromagnetic coupling units, respectively. The functionalization of such coupling units is the second step of this research.[5] Azobenzenes are known as photochromic compounds which undergo *cis–trans* structural isomerization by light; therefore many applications have been performed (Scheme 1).[6] We focused our attention on this point to control magnetic properties. Whereas the two forms have the same connectivity for the two attached radical centers, namely, azobenzene-3,4′-diyl should serve as a ferromagnetic coupling unit irrespective of the geometrical isomerism, the efficiency as a π-spin coupling unit should be very much reduced in the *cis* form due to the reduced conjugation from steric hindrance.[7]



Scheme 1. Photoisomerism of azobenzene.

In this paper we will discuss the design, synthesis, and magnetic properties of azobenzene bearing the Ullman's nitronyl nitroxide,[8] focusing on the photochromism of the azobenzene moiety.

Results and Discussion

Synthesis of the Biradical. Biradical **1** having the azobenzene skeleton was synthesized according to Scheme 2; the two methyl groups of 3,4′-dimethylazobenzene were transformed to the nitronyl nitroxide radicals. *p*-Toluenediazonium chloride–zinc chloride adduct (**2**) and *m*-tolylmagnesium bromide (**3**) gave 3,4′-dimethylazobenzene (**4**),[9] which was treated with *N*-bromosuccinimide (NBS) and *α,α′*-azobisisobutylonitrile (AIBN) to give 3,4′-bis(bromomethyl)azobenzene (**5**). The compound **5** was reacted with sodium acetate in *N,N*-dimethylformamide (DMF) to afford 3,4′-bis(hydroxymethyl)azobenzene (**6**). Swern oxidation of **6** gave 3,4′-diformylazobenzene (**7**).[10] A treatment of **7** with 2,3-dimethyl-2,3-bis(hydroxyamino)butane in methanol followed by oxidation with sodium periodate, gave biradical **1**. All compounds were obtained as stable solids and could be kept in a refrigerator for months. Compounds **1**—**7** were characterized by NMR (except for **1**), IR, HR-FAB Mass, and UV-vis spectroscopy. ^{1}H and ^{13}C NMR spectra were fully assigned. The FAB$^+$ mass spectra of **1** exhibited intense molecular ion peaks ($[M+H]^+$) plus characteristic major fragments which are due to the successive loss of four oxygen atoms.

X-Ray Crystal Structure of Biradical 1. The structure of **1** has been determined by X-ray analysis at −145 °C. Single crystals of **1** were dark blue-green needles, orthorhombic

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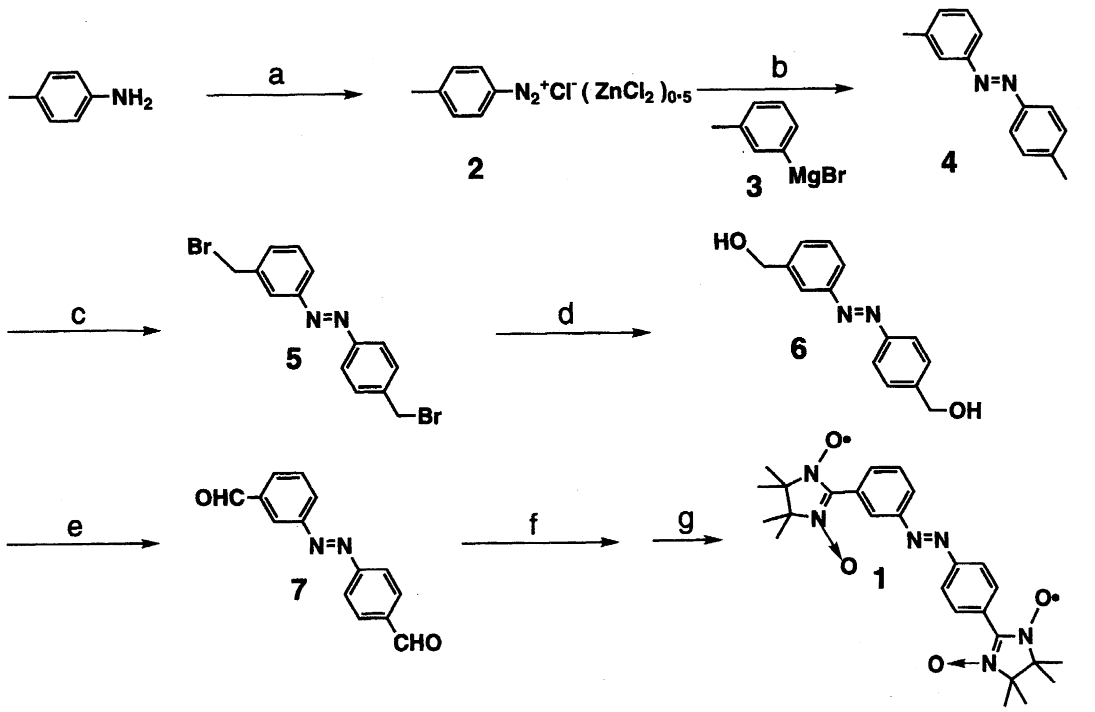

Scheme 2. Synthesis of biradical **1**. Reagents and conditions: (a) HCl, $NaNO_2$, H_2O, $ZnCl_2$, 94%; (b) *m*-tolylmagnesium bromide **3**, THF, HCl, 94%; (c) NBS, AIBN, CCl_4, reflux, 80%; (d) CH_3COONa, DMF, 100 °C, 92%; (e) Swern oxidation, oxalyl chloride, CH_2Cl_2, DMSO, TEA, 66%; (f) 2,3-bis(hydroxyamino)-2,3-dimethylbutane, MeOH, 50 °C; (g) $NaIO_4$, CH_2Cl_2, H_2O, 21%; NBS = *N*-bromosuccinimide, AIBN = azobisisobutyronitrile, DMF = dimethylformamide.

space group *Pbca* (#61), with a = 23.613(3), b = 17.257(4), c = 12.598(2) Å, V = 5133(1) Å^3, Z = 8. Crystallographic details and selected bond distances and angles are listed in Tables 1, 2, and 3, respectively.

Table 1. Crystallographic Details

Empirical formula	$C_{26}H_{32}N_6O_4$
Formula weight	492.58
Indexing images	3 oscillations @ 4.0 min
Data images	18 exposures @ 30.0 min
T/°C	−145
Radiation	Mo $K\alpha$
Space group	*Pbca* (#61)
a/Å	23.613(3)
b/Å	17.257(4)
c/Å	12.598(2)
V/Å^3	5133(1)
Z	8
D_c/g cm^{-3}	1.275
μ/mm^{-1}	0.88
F(000)	2096.00
No. observations ($I > 3.00\sigma(I)$)	4398
No. of params	454
Goodness of Fit Indicator	1.96
R[a)]	0.044
R_w[b)]	0.062

a) $R = \sum||F_o|-|F_c||/\sum|F_o| = 0.044$.
b) $R_w = \sqrt{\sum w(|F_o|-|F_c|)^2/\sum wF_o^2} = 0.062$.

Table 2. Selected Bond Lengths (Å) of Biradical **1**

Atom	Atom	Distance
O(1)	N(3)	1.282(2)
O(2)	N(4)	1.286(2)
O(3)	N(5)	1.288(2)
O(4)	N(6)	1.283(2)
C(13)	N(3)	1.352(2)
C(13)	N(4)	1.355(2)
C(20)	N(5)	1.348(2)
C(20)	N(6)	1.357(2)
N(3)	C(14)	1.509(2)
N(4)	C(15)	1.505(2)
N(5)	C(21)	1.502(2)
N(6)	C(22)	1.509(2)
C(4)	C(13)	1.463(2)
C(9)	C(20)	1.464(2)
N(1)	C(1)	1.431(2)
N(2)	C(7)	1.443(2)
N(1)	N(2)	1.253(2)

The crystal structure is reproduced in Fig. 1. The azobenzene moiety has a thermodynamically more stable *trans* configuration. The dihedral angle between the two phenyl rings was 5.4°. The angles between the plane of the phenyl groups and the plane through the –N=N– unit were 4.48 and 9.19°. The dihedral angles between the nitronyl nitroxide and the phenyl rings were 32.6° and 33.5°. The modest dihedral angles suggest that the *trans*-azobenzene-3,4′-diyl unit should serve as a ferromagnetic coupling unit.

In the crystal packing as shown in Fig. 2, two NO terminals in a given nitronyl nitroxide unit had an intermolecular contact to make a head-to-tail zigzag one-dimensional chain.

Table 3. Selected Angles (deg) of Biradical **1**

Atom	Atom	Atom	Angle
N(6)	C(20)	N(5)	108.9(1)
C(20)	N(6)	O(4)	125.9(1)
C(20)	N(5)	O(3)	126.6(1)
C(20)	N(6)	C(22)	122.4(1)
C(20)	N(5)	C(21)	112.2(1)
N(3)	C(13)	N(4)	108.7(1)
C(13)	N(3)	O(1)	126.8(1)
C(13)	N(4)	O(2)	126.8(1)
C(13)	N(4)	O(15)	111.3(1)
C(13)	N(3)	C(14)	111.0(1)
C(1)	N(1)	N(2)	113.1(1)
C(7)	N(2)	N(1)	113.8(1)

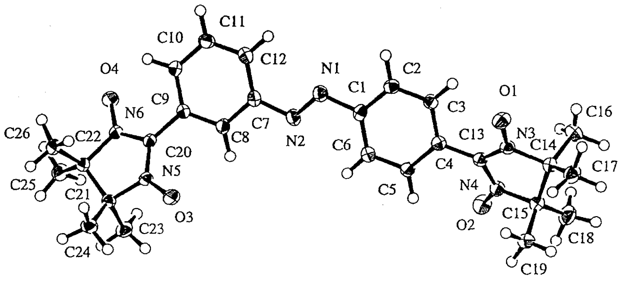

Fig. 1. ORTEP diagram illustrating the molecular structure of **1** from the X-ray single crystal analysis.

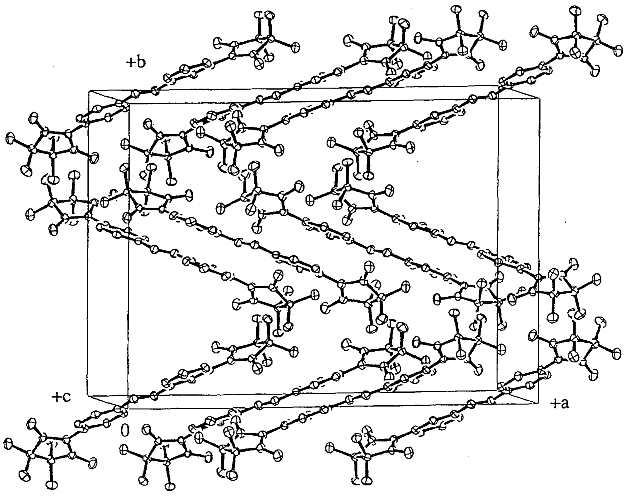

Fig. 2. Molecular stacking of **1** in crystal.

The molecules of biradical **1** were arranged centrosymmetrically in the unit cell. There is no short contact less than 3.2 Å.

ESR Measurement of 1. X-band ESR spectra of biradical **1** in the degassed toluene solution were measured in the temperature range 10—300 K. At 300 K, the ESR spectrum centered at $g = 2.006$ consisted of a nine-line signal in a ratio of $1:4:10:16:19:16:10:4:1$ ($|a_N| = 3.7$ G) due to the hyperfine coupling with four equivalent nitrogen nuclei (Fig. 3a). The a_N value and the splitting into nine lines suggested that the exchange interaction is larger than the hyperfine interaction ($|J| \gg |a_N|$). At 10 K, ESR spectra of **1** in toluene solid solution showed fine structures due to dipolar coupling of the unpaired electrons at $g = 2$ and $\Delta m_S = 2$ transitions at about 165 mT (Fig. 3b). This signal was assigned to a forbidden band due to the triplet species. The zero-field splitting (zfs) parameter $|D/hc|$ was determined to be 0.0026 cm^{-1} from the separation of the highest-field (H_Z) and lowest field (H_{-Z}) resonances. The $|E/hc|$ parameter was also obtained from the signals due to the x and y transitions in the $\Delta m_S = 1$ region to be 0.00014 cm^{-1}. Application of a point-dipole approximation to the above D value suggests that the distance between the spin centers is 9.98 Å.

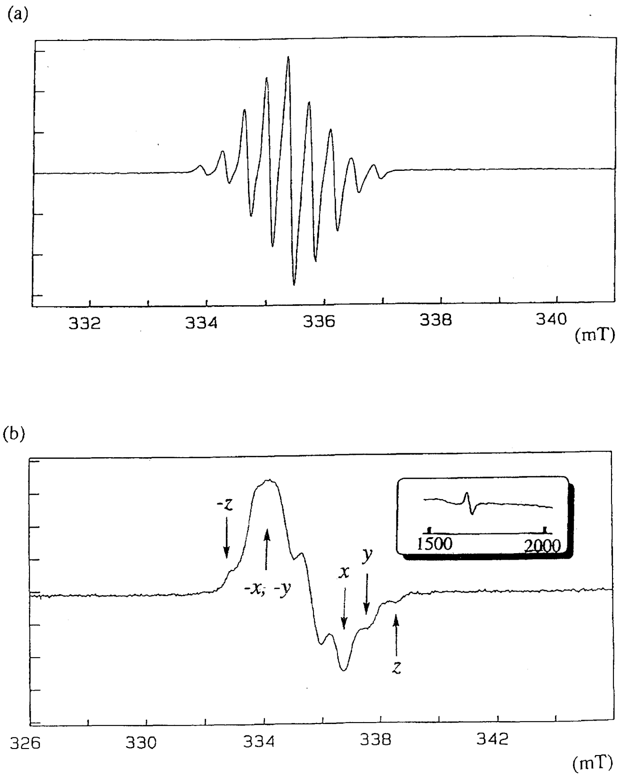

Fig. 3. ESR spectra of **1** in 10 mmol dm^{-3} toluene matrix. a) at 300 K (9.437 GHz) and b) at 10 K (9.442 GHz). Signal assignment was indicated as x, y, and z. The signal in the center originated from impurity. The inset shows the $\Delta m_S = 2$ region.

The plot of the ESR signal intensity due to the triplet species vs the reciprocal of temperature is shown in Fig. 4. The temperature dependence of the spectrum obeyed a Curie law in the temperature range 40—100 K. The plot is linear, suggesting that the triplet state is a ground state or that singlet and triplet states are almost degenerate.

Magnetic Susceptibilities of Biradical 1. The magnetic interaction in the nitroxide biradical **1** was studied by temperature dependence of its magnetic susceptibility χ_{mol} in the temperature range 2—300 K at a constant magnetic field of 5000 Oe on a Quantum Design MPMS-5S SQUID magnetometer/susceptometer. A microcrystalline sample was employed for the measurement. The temperature dependence of the molar magnetic susceptibility (χ_{mol}) of **1** is shown in the form of $\chi_{\text{mol}}T$ vs. T plot in Fig. 5. The $\chi_{\text{mol}}T$ values

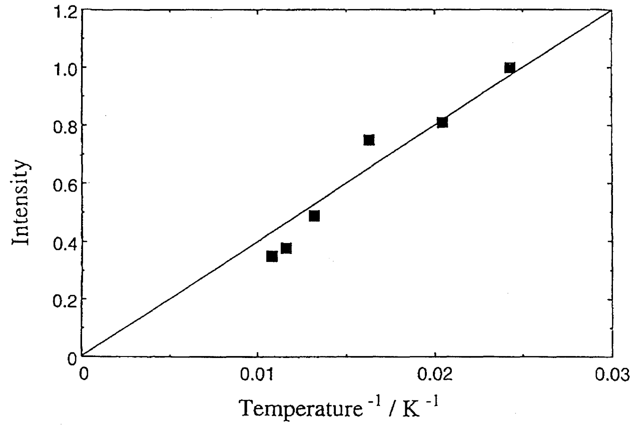

Fig. 4. Plots of the intensity of the g = 2 region in the ESR signal of **1** vs. reciprocal of temperature in 12—100 K in toluene glass.

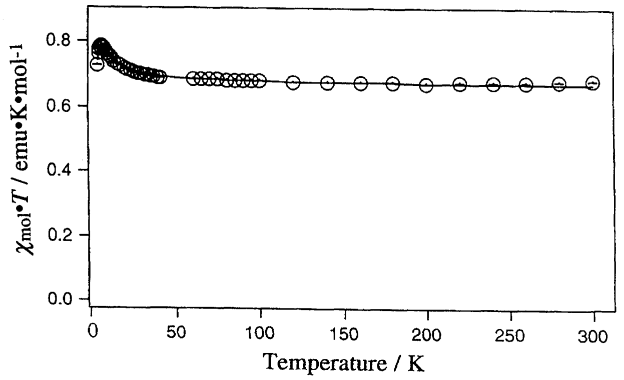

Fig. 5. Temperature dependence of $\chi_{\text{mol}}T$ of dinitroxide **1** at the field of 5000 Oe. The solid curve is theoretical one as described in the text.

remained almost constant in the temperature range 50—300 K. The observed $\chi_{\text{mol}}T$ value of 0.75 emu K mol^{-1} showed a good fit to the theoretical value for a biradical with uncoupled two spins. As the temperature was decreased below 50 K, the $\chi_{\text{mol}}T$ values increased continuously to a maximum of 0.787 emu K mol^{-1} at 4.5 K and then started to decrease. Operations of intramolecular ferromagnetic coupling and intermolecular antiferromagnetic coupling were suggested.

The data were analyzed in terms of a modified singlet–triplet two-spin model (the Bleaney–Bowers-type) in which spins S_1 and S_2 coupled ferromagnetically within a biradical molecule by exchange interaction J (Eq. 1).

$$\chi_{\text{mol}}T = f\frac{2N_g^2\mu_B{}^2T}{k(T-\theta)}\cdot\frac{1}{3+\exp(-2J/k_BT)}. \qquad (1)$$

Here θ indicates a Weiss constant employed to describe the additional intermolecular antiferromagnetic interaction by a mean field theory. A purity factor f was introduced for more realistic fitting. The best fit parameters obtained by means of a least-squares method were $2J/k_B = 8.36\pm0.26$ K, $\theta = -0.39\pm0.01$ K, and $f = 0.89\pm0.002$. The ground state of the biradical is a triplet, as predicted by the topology rule. When compared with the strong ferromagnetic couplings in stilbene-2,3′-bis(*N*-*t*-butylaminoxyl) and -3,4′-bis(phenylcarbene),[4] the observed ferromagnetic coupling in **1** is rather weak. Since the dihedral angle between the two phenyl rings and those between the nitronyl nitroxide and the phenyl rings are not large, it is not very likely that the *trans*-azobenzene-3,4′-diyl unit itself is responsible for the attenuated interaction. A plausible reason why the interaction is weak is the fact that the carbon atoms of the nitronyl nitroxide radical units that are attached to the azobenzene-3,4′-diyl coupler have a negative spin density. If radical centers or atoms having a reasonable fraction of positive spin density were attached directly to the azobenzene coupler, the magnitude of the ferromagnetic coupling should have been greater.

***Cis–Trans* Photoisomerization of Biradical 1.** *Cis–*

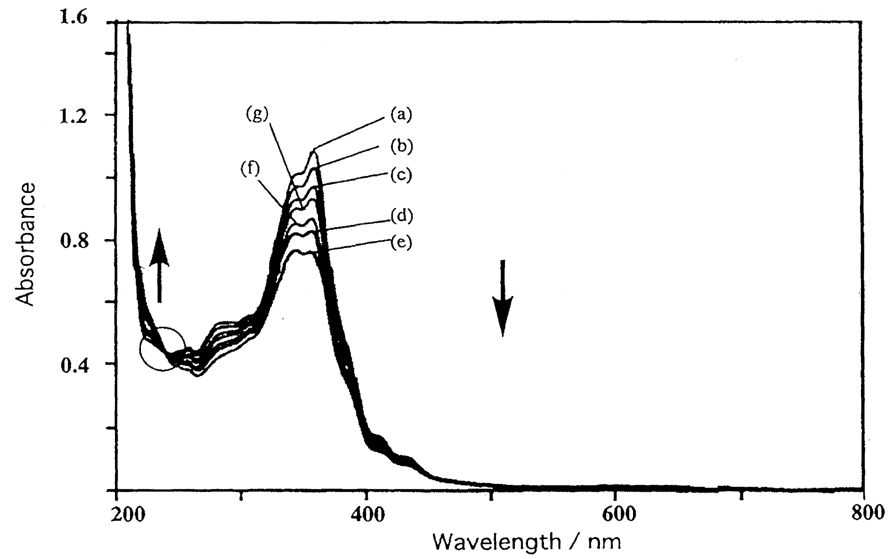

Fig. 6. UV-vis spectrum of biradical **1** in cyclohexane (0.03 mmol dm^{-3}) at room temperature. The arrows show the spectral change due to the irradiation at 365 nm: a) before irradiation, b) after irradiation for 10 min, c) 20 min, d) 1 h, e) 2 h, f) after stopping the irradiation and left for 1 d, g) 2 d.

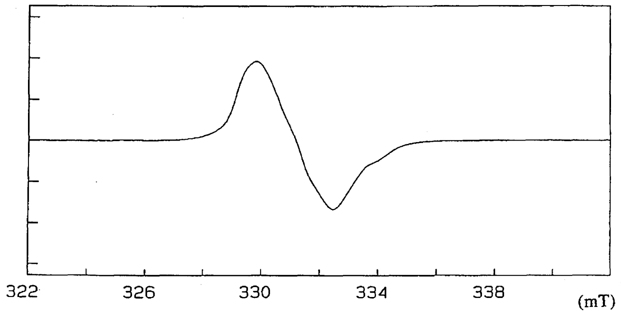

Fig. 7. ESR spectrum of **1** in toluene after irradiation at room temperature and then frozen at 10 K (9.324 GHz).

trans photoisomerization of the azobenzene biradical **1** was monitored by using ESR and UV spectroscopy. The irradiation using 360—400 nm light generated from a Xe lamp combined with Kenko U-360 filter was carried out for the cyclohexane solution of **1** (0.03 mmol dm^{-3}) in a quartz cell at room temperature for 2 h. UV-vis spectra before and after irradiation are shown in Fig. 6. During the irradiation, the absorption at 343 nm decreased and the absorption (shoulder) at ca. 230 nm increased with an isosbestic point at ca. 240 nm, suggesting the transformation of the skeleton from *trans* to *cis* form. After we halted the irradiation, the absorptivity at 343 nm recovered 50% of the decreased value in 48 h. The irradiation using monochromatic light at 345 nm and 415 nm from a Hitachi F-3010 spectrofluorimeter was also carried out and gave a similar behavior, as shown in Fig. 6. The conversion was effected more by 345 nm light than 415 nm light. The absorptivity at 343 nm recovered 75% (in the case of excitation with 345 nm) and 50% (in the case of excitation with 415 nm) of the decreased value in 48 h at room temperature, respectively. These transformations could be repeated at least five times without decomposition.

The effect of irradiation upon a solution of **1** in toluene has been studied by ESR spectroscopy under various conditions. No noticeable change was detected in a nine-line ESR spectrum after irradiation at 360—400 nm for 2 h at room temperature, presumably because the exchange interactions for both isomers should be much larger than the hyperfine coupling. Irradiation at 10 K in an ESR cavity also did not change the spectrum of **1**, probably because the reorganization of the molecular structure due to the *cis–trans* isomerization was frozen out under these conditions.

When a solution of **1** (0.04 mmol dm^{-3}) was irradiated in the same condition of UV-vis measurement for 19 h at room temperature in toluene and then frozen at 10 K, we measured the EPR spectrum again. The fine structure which was observed in the pure *trans* form was replaced by a broad single line (Fig. 7). Since the distance between the two unpaired electrons should be different in the two geometric isomers, the fine structure should be different. Since the conversion is not complete, the spectrum must have become unresolved.

Conclusion

A new biradical **1** with a photochromic spin coupler, 3,4′-bis(4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1-oxyl-3-imidazolio-2-yl)azobenzene, was synthesized and its molecular structure and magnetic properties were studied. The radical centers were found to couple ferromagnetically in the *trans*-isomer. The *trans* to *cis* forward and backward geometrical isomerizations were observed by UV-irradiation and thermal reactions, respectively. EPR spectra at cryogenic temperature differed between before and after irradiation. This is attributed to the difference of the distance between the two unpaired electrons before and after irradiation. Since the conversion is not complete, the spectrum must have become unresolved. In order to make use of this property, it is required that the photoisomerization should proceed at low temperature efficiently.

Experimental

A. Materials. ^{1}H NMR spectra were recorded on a JEOL EX-270 NMR spectrometer and ^{13}C NMR were recorded on a Brucker DRX 600 spectrometer. 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.

Tetrahydrofuran (THF) and 2-Methyltetrahydrofuran (MTHF) were distilled from sodium diphenylketyl under a dry nitrogen atmosphere. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure from calcium hydride. 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 (E. Merck, 70—230 mesh) or neutral alumina (ICN, activity grade IV).

3,4′-Dimethylazobenzene 4. To a stirred solution of *p*-toluidine (5 g, 46.6 mmol) in 20 mL of water was added 37% hydrochloric acid (7.7 mL, 93.0 mmol) and this mixture was stirred at room temperature in the open air. When all the solid had dissolved the solution was cooled to 0 °C. Sodium nitrite (3.09 g, 46.0 mmol) in 10 mL of water was added to the reaction mixture slowly. This required about thirty to forty minutes. The temperature during the reaction was kept below 5 °C. A cooled saturated solution of zinc(II) chloride in 10 mL of water was poured into the solution of diazonium salt until the white precipitate was formed. After two hours, the precipitate was filtrated and washed with cold ethanol and ether to give *p*-toluenediazonium chloride zinc chloride adduct **2** (9.7 g, 94%) as a white powder.[12)]

m-Tolylmagnesium bromide (**3**) was prepared from magnesium turnings (0.88 g, 36 mmol) and *m*-bromotoluene (6.21 g, 36 mmol) in 30 mL of THF. The Grignard reagent **3** was added to the solution of **2** in 300 mL of THF through the Teflon® tube under nitrogen atmosphere. This process required about twenty minutes. The color changed from white to red. After the mixture was stirred overnight, 100 mL of THF and 5 mL of 37% of hydrochloric acid was added. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with water, dried, concentrated and applied to column chromatography (silica, hexane : dichloromethane = 5 : 1). Evaporation of the solvent gave 3,4′-dimethylazobenzene (**4**) (7.1 g, 94%) as an orange powder;[13,14)] mp 53.4—55.1 °C; IR (KBr) ν 3020, 2920, 821 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 2.42$ (s, 3 H), 2.44 (s, 3 H), 7.24—7.32 (m, 3 H), 7.37 (t, $J = 8.2$ Hz, 1 H), 7.69 (d, 2 H), 7.82 (d, $J = 8.57$ Hz, 2 H); ^{13}C NMR (150.9

MHz, $CDCl_3$) $\delta = 21.4$, 21.5, 120.4, 122.7, 122.8, 128.9, 129.7, 131.5, 138.9, 141.4, 150.8, 152.8. FAB HRMS $(m+1)/z$ Calcd for $C_{14}H_{15}N_2$: M, 211.1235. Found: m/z 211.1242.

3,4′-Bis(bromomethyl)azobenzene (5). A mixture of *N*-Bromosuccinimide (NBS) (0.93 g, 5.2 mmol) and α,α'-azobisisobutylonitrile (AIBN) (0.039 g, 2.62 mmol) were added to a solution of 0.5 g (2.38 mmol) of 3,4′-dimethylazobenzene **4** in 50 mL of CCl_4. The mixture was refluxed and irradiated (Xenon lamp, Pyrex filter) for 7 h with stirring under nitrogen atmosphere. After the reaction was complete the color changed from orange to deep red. The reaction mixture was filtrated, concentrated and purified by column chromatography (silica, hexane : dichloromethane = 5 : 1) to give 3,4′-bis(bromomethyl)azobenzene (**5**) (0.8 g, 92%) as a red powder; mp 85.3—85.5 °C; IR (KBr) ν 2930, 850 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 4.55$ (s, 2 H), 4.57 (s, 2 H), 7.49—7.55 (m, 4 H), 7.88—7.94 (m, 4 H); ^{13}C NMR (150.9 MHz, $CDCl_3$) $\delta = 32.6$, 32.7, 122.9, 123.3, 123.4, 129.6, 129.9, 131.6, 138.9, 140.8, 152.1, 152.7. FAB HRMS $(m+1)/z$ Calcd for $C_{14}H_{13}N_2Br_2$: M, 366.9446. Found: m/z 366.9431.

3,4′-Bis(hydroxymethyl)azobenzene (6). To a stirred solution of 3,4′-bis(bromomethyl)azobenzene (**5**) (1 g, 2.71 mmol) in 30 mL of DMF was added sodium acetate (1.84 g, 13.5 mmol) under nitrogen atmosphere. The mixture was stirred for three hours and the temperature during the reaction was kept at 100 °C. After the reaction mixture was concentrated, 10% of KOH in methanol was added and the solution was stirred for two hours in the open air. The reaction mixture was poured into aqueous sodium sulfate and extracted with ether and ethyl acetate, washed with water, dried and concentrated. Evaporation of the solvent gave 3,4′-bis(hydroxymethyl)azobenzene (**6**) (0.53 g, 80%) as a red powder. It contained a small amount of 3,4′-diformylazobenzene (**7**)·(**6**); mp 117.0—118.9 °C; IR (KBr) ν 3290, 2926, 2866, 1035 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.78$ (s, 2 H), 4.81 (s, 4 H), 7.53 (d, $J = 7.9$ Hz, 4 H), 7.87—7.94 (m, 3 H), 8.04 (s, 1 H); ^1H NMR (270 MHz, CD_3OD) $\delta = 4.69$ (s, 1 H), 4.70 (s, 1 H), 4.84 (s, 4 H), 7.49—7.54 (m, 4 H), 7.79—7.90 (m, 4 H); ^{13}C NMR (69.7 MHz, CD_3OD) $\delta = 65.5$, 65.6, 122.6, 123.7, 124.7, 129.3, 131.0, 131.3, 145.1, 147.2, 154.0, 155.0. FAB HRMS $(m+1)/z$ Calcd for $C_{14}H_{15}N_2O_2$: M, 243.1133. Found: m/z 243.1125.

3,4′-Diformylazobenzene (7). A solution of oxalyl chloride (0.2 mL, 2.07 mmol) and CH_2Cl_2 (5 mL) was placed in a 30 mL three-neck round bottom flask equipped with an overhead mechanical stirrer, a thermometer and dropping funnels. Two funnels were prepared; one contained DMSO (0.17 mL, 2.2 mmol) dissolved in 0.5 mL of CH_2Cl_2 and the other contained 3,4′-bis(hydroxymethyl)azobenzene (**6**) (0.1 g, 0.5 mmol) dissolved in 1 mL of CH_2Cl_2. DMSO was added to the stirred oxalyl chloride solution at −50 to −60 °C under nitrogen atmosphere. The reaction mixture was stirred for 5 min and then alcohol was added within 5 min; then stirring was continued for additional 15 min. Triethylamine (5.0 mL, 50 mmol) was added and the reaction mixture was stirred for 5 min and then allowed to warm to room temperature. Water (5 mL) was then added and the aqueous layer was reextracted with additional CH_2Cl_2 (5 mL). The organic layers were combined, washed with saturated NaCl solution (10 mL), and dried. The concentrated solution was subjected to column chromatography (silica, hexane : dichloromethane = 1 : 1). Evaporation of the solvent gave 3,4′-diformylazobenzene (**7**) (0.08 g, 66%, two steps) as a red powder; mp 155.1—157.5 °C; IR (KBr) ν 2845, 2745, 1697 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.74$ (t, 1 H), 8.08 (m, 4 H), 8.22 (d, 1 H), 8.25 (d, 1 H), 8.45 (s, 1 H), 10.13 (s, 1 H), 10.16 (s, 1 H); ^{13}C NMR (150.9 MHz, $CDCl_3$) $\delta = 123.6$, 124.0, 129.1, 130.1, 130.8, 132.1, 137.4, 137.9, 152.8, 155.5, 191.5, 192.6. FAB HRMS $(m+1)/z$ Calcd for $C_{14}H_{11}N_2O_2$: M, 239.0820. Found: m/z 239.0816.

3,4′-Bis(4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1-oxyl-3-imidazolio-2-yl)azobenzene (1). To a stirred solution of 3,4′-diformylazobenzene (**7**) (0.42 g, 3.57 mmol) in 10 mL of methanol was added 2,3-dihydroxy-amino-2,3-dimethylbutane (0.63 g, 4.25 mmol). This mixture was stirred at 50 °C under nitrogen atmosphere. After being stirred overnight, it was then allowed to warm to room temperature. A white yellow precipitate was formed. The precipitate was collected by filtration and washed with hexane. To a solution of the precipitate in 100 mL of dichloromethane and 100 mL of water, $NaIO_4$ (1.7 g) was added. This mixture was stirred for 30 min at room temperature under nitrogen atmosphere. The reaction mixture was poured into water, extracted with CH_2Cl_2. The organic layer was washed with water, dried, concentrated, and applied to column chromatography (silica, hexane : dichloromethane = 1 : 1). After the resulting material was purified by GPC, evaporation of the solvent gave 3,4′-bis(4,5′-dihydro-4,4,5,5-tetramethyl-3-oxido-1-oxyl-3-imidazolio-2-yl)azobenzene **1** (0.36 g, 21%, two steps) as a dark green powder; mp 220.3—220.5 °C; IR (KBr) ν 3092, 2991, 1392, 1361 cm^{-1}. FAB HRMS $(m+1)/z$ Calcd for $C_{26}H_{33}N_6O_4$: M, 493.2563. Found: m/z 493.2579.

B. ESR Spectroscopy and Magnetic Measurements. Photolysis of azo compound **1** was carried out in MTHF matrices at 10 K in an ESR cavity. The light was obtained from a high-pressure mercury lamp with combination of a Kenko L-42 sharp cut filter and an quartz water filter. A Bruker ESP 300E spectrometer was used to obtain X-band ESR Spectra. Temperatures were controlled by an Oxford ESR-900 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 10—70 K were measured at appropriate power attenuation calibrated to exclude saturation effect. The temperatures were stepped up from 10 to 70 K with intervals of ca. 2 K. Since the temperature control was difficult and the reproducibility of the signal intensities was low, the Curie–Weiss law was tested for the triplet signals in the range 40—100 K.

Magnetic susceptibility data for microcrystalline samples of **1** was obtained on a Quantum Design MPMS-5S SQUID susceptometer at the field strength of 5000 Oe in the temperature range 5—300 K.

C. Crystallographic Structure Determinations. Crystallographic data are given in the Supporting Information. Crystals of **1** were grown from a concentrated hexane and dichloromethane solution at room temperature. A dark blue-green plate crystal of $C_{26}H_{32}N_6O_4$ having approximate dimensions of $0.3\times0.3\times0.1$ mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging-plate area detector with graphite monochromated Mo $K\alpha$ radiation. Indexing was performed from 3 oscillations which were exposed for 4.0 min. The crystal-to-detector distance was 110.0 mm with the detector at the zero swing position. Readout was performed in the 0.100 mm pixel mode. The data were collected at a temperature of −145 °C to a maximum 2θ value of 55.1°. A total of 185.00°-oscillation images were collected, each being exposed for 30.0 min. A total of 5551 reflections was collected. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $2.75150\times10^{-0.7}$). The structure was solved by direct methods[11] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 4398 observed reflections ($I > 3.00\sigma(I)$) and 454 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.28 to −0.16 e^{-} Å^{-3} respectively. All calculations were performed using the TEXAN Ver. 1.8 crystallographic software package of Molecular Structure Corporation. The complete $F_o - F_c$ data are deposited as Document No. 71068 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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12) This white powder may cause unexpected explosion.

13) The production of biaryl was suppressed by adding 25% excess of *p*-toluenediazonium chloride-zinc chloride adduct **2**.

14) Under more concentrated conditions, polymers were produced.