Molecular Electronics

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Intramolecular Spin Transfer in a Spiro-Fused Bis(triarylamine)**

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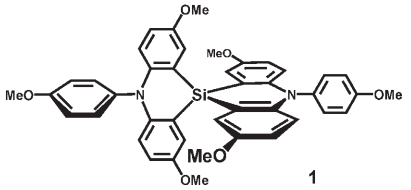
Organic intervalence systems are receiving increasing attention because they provide valuable insight into intramolecular charge-transfer (ICT) phenomena.[1] The intervalence systems are composed of redox-active units and bridging units. Upon partial oxidation (or reduction) of the redox-active units, various facets of ICT phenomena emerge depending on the strength of the electronic coupling between the redox-active units.[2,3] Owing to the accessibility of several oxidation states, oligo(aryl amine)s have attracted considerable interest. In particular, radical cations of *para*-phenylenediamine (PDA) derivatives, with two redox-active units, are considered the simplest organic intervalence systems.[1,4,5] The stability of the radical cations can be explained by the delocalization of the generated radical spin over the two redox-active units. In connection with the formidable challenges associated with the development of molecular-based electronic devices, many kinds of organic intervalence compounds, including PDA derivatives, are investigated for charge and/or spin transport in molecular wires.[4–18]



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Recently, we reported the synthesis of the spiro-fused bis(triarylamine) **1** and the magnetic properties of the dication $\mathbf{1}^{2+}$.[19] The spiro molecule **1** has a unique structure in which two redox-active triarylamine based π systems are linked perpendicularly to one another through a spiro Si atom. The orthogonality results in the interesting interaction observed between the two redox-active π systems. In fact, $\mathbf{1}^{2+}$ was found to be a stable diradical with a spin-triplet multiplicity due to the ferromagnetic interaction between the two radical spins generated.[19] The two triarylamine moieties and the spiro Si atom in **1** can be regarded as the redox-active units and the bridging unit in the intervalence system, respectively. We know from our previous electrochemical studies[19] that the difference between the first and second oxidation potentials of **1** is relatively large (160 mV). This result shows the existence of electronic coupling between the two triarylamine moieties in **1**. Furthermore, the spiro structural motif and its suitability for molecular electronics have already been discussed from both theoretical[20] and experimental[21] viewpoints. Therefore, we examined intramolecular spin transfer (IST) in $\mathbf{1}^{+}$.

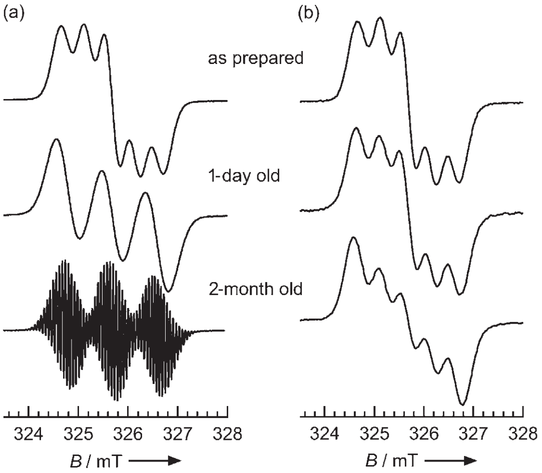

Figure 1. Temporal ESR spectral changes of $\mathbf{1}^{+}$ in a) CH_2Cl_2 (recorded at 295 K) and b) *n*-butyronitrile (recorded at 293 K).

The radical cation $\mathbf{1}^{+}$ was prepared by the chemical oxidation of **1** with tris(4-bromophenyl)aminium hexachloroantimonate at 195 K in dichloromethane or *n*-butyronitrile. As shown in Figure 1, the ESR spectrum of as-prepared $\mathbf{1}^{+}$ exhibited a five-line pattern in both solvents at room temperature. This spectrum can be explained mainly by the hyperfine coupling with the two equivalent nitrogen nuclei ($a_N \approx 0.84$ mT) in the two triarylamine moieties. Contrary to our expectation, however, the stability of $\mathbf{1}^{+}$ depends strongly on the solvent used. The originally light-blue-colored solution gradually turned turquoise, in spite of being kept under anaerobic conditions. In particular, when CH_2Cl_2 was used as the solvent, the signal intensities of the central three lines decreased rapidly, and the spectral shape changed to a three-line pattern within a day. Moreover, a well-resolved multiline pattern containing many hyperfine structures appeared within

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two months (Figure 1 a). The well-resolved ESR spectrum of the 2-month-old sample in CH_2Cl_2 was found to be identical to that of the tri-*p*-anisylamine radical cation ($a_N = 0.902$ mT, $a_{H(ortho)} = 0.185$ mT, $a_{H(meta)} = 0.059$ mT, $a_{H(methoxy)} = 0.059$ mT; Figure 2). This temporal spectral change in CH_2Cl_2 is closely related to the decomposition process of $\mathbf{1}^+$ to the tri-*p*-anisylamine radical cation. Thus, we could follow the Si–C bond-cleavage process in detail through the change in the ESR spectrum. On the other hand, it was found that the spectral change is much slower for the sample in *n*-butyronitrile than for the sample in CH_2Cl_2: The spectrum of the sample in *n*-butyronitrile retains the five-line pattern even after 2 months (Figure 1 b).

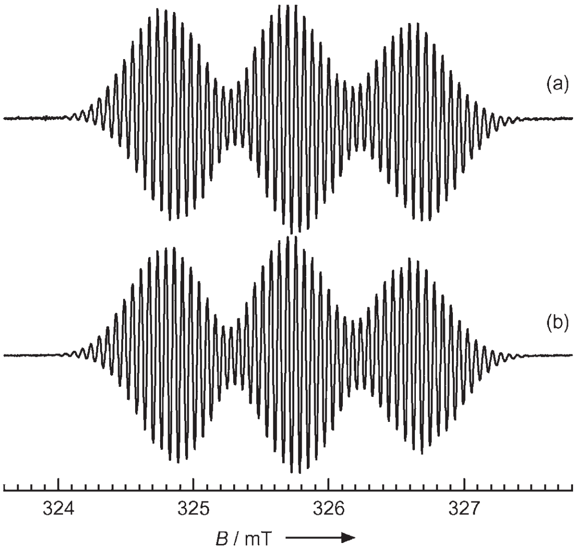


Figure 2. Comparison of the ESR spectra of a) 2-month-old $\mathbf{1}^+$ and b) the tri-*p*-anisylamine radical cation in CH_2Cl_2 at 295 K.

The IST process in $\mathbf{1}^+$ was studied by variable-temperature ESR spectroscopy. As described in the preceding section, as-prepared $\mathbf{1}^+$ was found to be considerably stable in *n*-butyronitrile. Hence, the thermal ESR spectral change of $\mathbf{1}^+$ was monitored in the temperature range from 324 to 203 K in *n*-butyronitrile. We checked that the line shape observed at 293 K remained unchanged throughout a series of measurements. The signal intensities of the central three lines decreased gradually with decreasing temperature (Figure 3). Such a temperature-dependent (or thermal) spectral change indicates clearly that the five-line pattern at room temperature is induced by thermally activated IST between the two redox-active units. Closer inspection revealed a difference in the temporal and thermal spectral changes: In the case of the thermal spectral change, the signal intensity of the third line decreases before a significant change is observed in the second and fourth lines, whereas the second and fourth lines decrease most rapidly in intensity in the case of the temporal spectral change. The coagulation of *n*-butyronitrile prevented us from observing the ESR spectrum below 200 K, at which temperature the unpaired electron in $\mathbf{1}^+$ is fully localized on one triarylamine moiety on the ESR timescale.

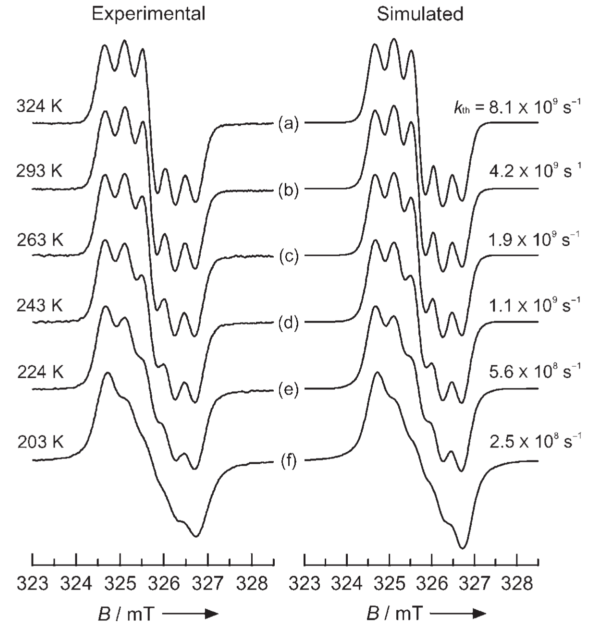
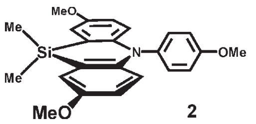


Figure 3. Temperature-dependent change in the ESR spectrum of $\mathbf{1}^+$ in *n*-butyronitrile (left), and simulated spectra (right); k_{th} values [s^{-1}], line widths [mT]: a) 8.1×10^9, 0.083 at 324 K; b) 4.2×10^9, 0.087 at 293 K; c) 1.9×10^9, 0.093 at 263 K; d) 1.1×10^9, 0.105 at 243 K; e) 5.6×10^8, 0.122 at 224 K; f) 2.5×10^8, 0.170 at 203 K.

The ESR spectra of $\mathbf{1}^+$ in *n*-butyronitrile at various temperatures were simulated successfully by the use of the ESR-EXN program.[22] This program gives the ESR line shape when an intramolecular dynamic spin exchange exists between the multiple redox-active sites. The first-order rate constants (k_{th}) for the thermally activated IST process between the two triarylamine moieties were determined by comparison of the experimental and simulated ESR spectra (Figure 3). For example, the IST rate constant (k_{th}) of $\mathbf{1}^+$ in *n*-butyronitrile was estimated to be $4.2 \times 10^9\ s^{-1}$ at 293 K. The simulations were conducted by using the hyperfine coupling constants in Table 1. The hyperfine constants for N and H_a were determined uniquely from the experimental spectra. However, the other hyperfine constants could not be estimated owing to the broad line widths of the spectra. Hence, they were estimated from the density functional calculation for the radical cation of the segmental model compound **2**.[23]



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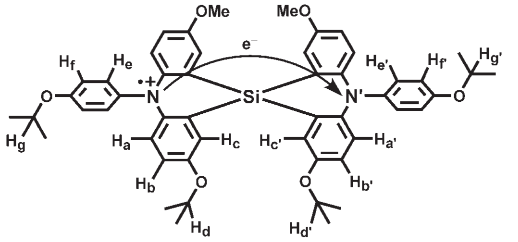
In this way, reasonable values were obtained for H_b, H_d, and H_f from the calculated data, whereas those for H_c, H_e, and H_g were found to be negligible. Therefore, the contributions from the latter hydrogen nuclei were incorporated in the line width of the spectral simulation. The Eyring plot gave a clear linear relationship between $\ln(k_{th}/T)$ and $1/T$ (Figure 4).[20] From this relationship, the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) for the barrier to thermally activated IST were

Table 1: Hyperfine coupling constants for 1^+ in *n*-butyronitrile used for the ESR simulations.



Nucleus	Position	Number of equivalent nuclei	Coupling constant [mT]
N	–	2	0.844
H	a, a′	4	0.290
H	b, b′	4	0.060
H	d, d′	12	0.085
H	f, f′	4	0.051
H	c, e, g, c′, e′, g′	–	ca. 0

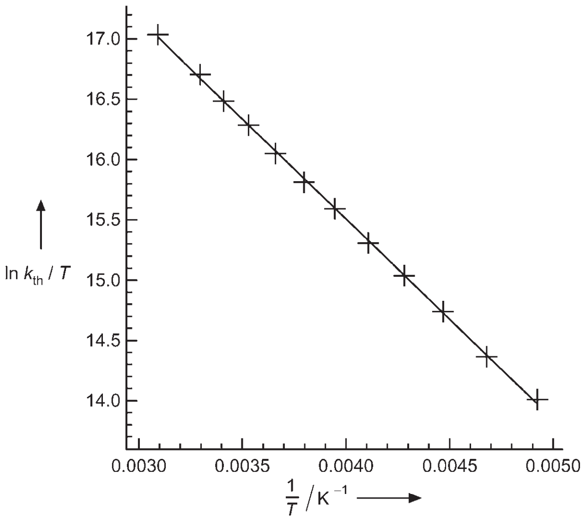


Figure 4. Eyring plot of the IST rate constant (k_{th}) for 1^+ obtained from simulations of the ESR spectrum.

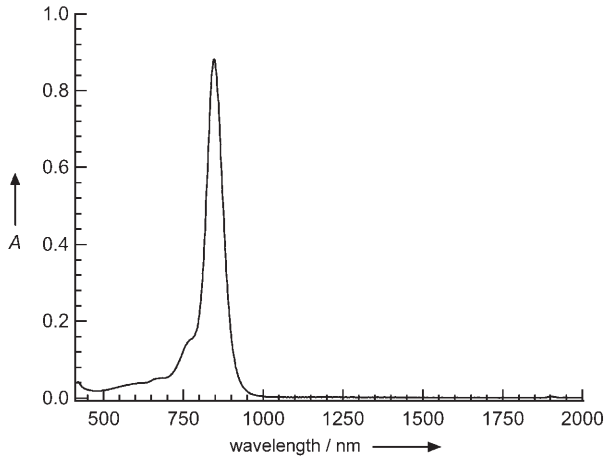


Figure 5. Vis/NIR spectrum of as-prepared 1^+ in *n*-butyronitrile at room temperature. NIR = near infrared.

estimated to be 3.3 kcal mol^{-1} and −3.2 cal K^{-1} mol^{-1}, respectively.

Finally, the optical-absorption spectrum of the chemically oxidized sample of **1** used for the ESR measurements was recorded in the Vis/NIR region (Figure 5). An intense absorption band characteristic for radical cations of triarylamines was observed at 847 nm.[24] However, the intervalence-charge-transfer (IVCT) band associated with the IST process was not detectable in the NIR region (ca. 2000 nm). We also measured the absorption spectrum of a sample of **1** that had been oxidized electrochemically by the use of an optically transparent thin-layer electrochemical (OTTLE) cell. Again, no IVCT band was detected. The same sample was checked immediately by ESR spectroscopy, and the observed ESR spectrum was the same as that of the as-prepared sample in Figure 1. In the classical Marcus–Hush two-state theory,[2] the optical-transition energy at the IVCT band maximum is equal to the Marcus reorganization energy λ. Triarylamines have a relatively low internal reorganization energy λ_v,[25] and the spiro compounds have rigid structures. Hence, it is expected that the small geometrical change between the neutral and cationic states of **1** is associated with a very low value of λ.[26] Therefore, the IVCT band in $\mathbf{1}^+$ could be shifted to the normal IR region instead of the near IR region. With the aim of determining precisely the electronic-coupling parameter in $\mathbf{1}^+$, a search for the IVCT band on the basis of IR spectroscopy is in progress.

This radical cation $\mathbf{1}^+$ of a spiro-fused bis(triarylamine) provides an example of intramolecular spin transfer (IST) in an organic intervalence system connected through an orthogonal structure. The expected IVCT band in the NIR region was not observed in the absorption spectrum of $\mathbf{1}^+$. However, variable-temperature ESR spectroscopy revealed the thermally activated IST process in the as-prepared radical cation $\mathbf{1}^+$. Hence, $\mathbf{1}^+$ can be regarded as an intriguing IVCT system.

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[23] The geometrical optimization of **1** was carried out at the hybrid HF/DF (B3LYP)/6-31G* level of theory by using the Gaussian 98 program package: Gaussian 98 (Revision A.07), M. J. Frisch et al..

[24] Owing to the instability of $\mathbf{1}^+$, the absorption spectrum with an intense band due to $\mathbf{1}^+$ changed gradually with an isosbestic point at 794 nm. The concomitant appearance of a band at 745 nm corresponds to the formation of the tri-*p*-anisylamine radical cation. This observation is consistent with the decomposition of $\mathbf{1}^+$ into the tri-*p*-anisylamine radical cation. The decomposition process was also observed in the ESR spectrum (see Figure 1).

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[26] The enthalpy contribution to λ'_v, the internal reorganization energy λ_v for $\mathbf{1}^{0/+}$, can be estimated theoretically by using the Nelsen method. Moreover, the remaining external solvent reorganization energy is estimated to be approximately 8 kcal mol^{-1} in MeCN: S. F. Nelsen, M. N. Weaver, Y. Luo, J. R. Pladziewicz, L. K. Ausman, T. L. Jentzsch, J. J. O'Konek, *J. Phys. Chem. A* **2006**, *110*, 11665 – 11676, and references therein. The DFT calculations for the segmental model compound **2** at the (U)B3LYP/6-31G* level gave a small λ'_v value of 2200 cm^{-1} (6.3 kcal mol^{-1}), which corresponds to the IR region. From the nonadiabatic rate equation (N. Sutin, *Prog. Inorg. Chem.* **1983**, *30*, 441 – 498), the electronic coupling for $\mathbf{1}^+$ is estimated to be 0.03–0.22 kcal mol^{-1} (11–78 cm^{-1}), which is small enough for the IST of $\mathbf{1}^+$ to be treated nonadiabatically. Hence, the ε_{max} for the IVCT band is predicted to range from 2 to 79 $\text{M}^{-1}\,\text{cm}^{-1}$. The molar absorptivity might be so small that it is impossible to detect such a weak IVCT band.