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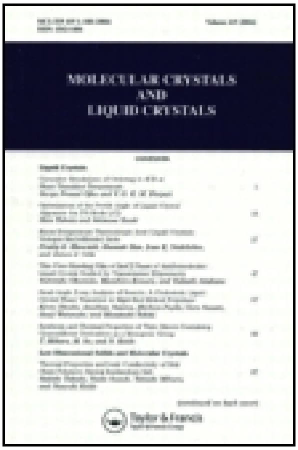

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Intra- and Inter-Molecular Exchange on Symmetrical Hydrazine Diradical Dications and Comparison of the Magnetic Exchange with ET Parameters Derived from their Optical Spectra

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Intra- and Inter-Molecular Exchange on Symmetrical Hydrazine Diradical Dications and Comparison of the Magnetic Exchange with ET Parameters Derived from their Optical Spectra

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The spin alignment in a charged molecular field is important research issue in the molecular magnetism. In order to clarify the interrelation between spin alignment and the charged molecular field, we have investigated intra- and inter-molecular exchanges on some Hydrazine diradical dictations **1** - **3** shown in Scheme 1 (see texts) by ESR and magnetic susceptibility measurement. The magnetic behavior of the dication salt **1** has been well analyzed using the alternating linear chain models with $J_{intra}/k_B = -106$ K, $J_{inter}/k_B = -49$ K and an alternating parameter $\alpha=0.46$. The magnetic property of **3** has been also fitted to the alternating chain model with $J/k_B = -106$ K $J_{inter}/k_B = -42$ K ($\alpha=0.40$). On the other hand, **2** gives a robust triplet ground state with larger energy separation from other spin states. The energy separation has been estimated to be larger than 300 cm^{-1} ($J_{intra}/k_B > +190$ K) from the temperature dependence of the ESR signal intensity. These findings indicate that the sign of the intramolecular exchange depends on the linking position (*m*- or *p*-) of the hydrazine cation group, i.e. the topology of the π orbital network even in the cationic molecular field. The magneto-optical correlation is also discussed based on the intramolecular electron transfer (ET) parameters.

Keywords: Stable Dication Diradical; Intramolecular Exchange; Electron Transfer; Spin Alignment

INTRODUCTION

Stable cation and dication radical salts are interesting materials and contribute to the understanding of the intra- and intermolecular spin alignment in the charged molecular field. They provide, therefore, an important research field on organic magnetism. The hydrazine diradical dications shown in Scheme 1 are

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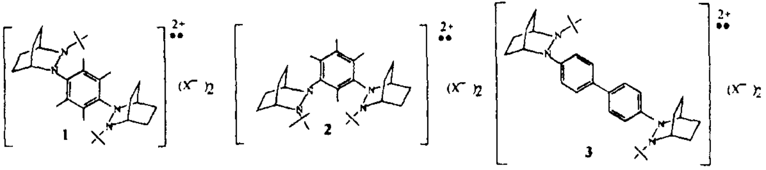
exceptionally persistent and can be isolated as pure cation radical salts [1]. In addition, intramolecular charge transfer bands have been observed in their uv-vis. optical spectra. Therefore, these dication salts are interesting materials for the study of the relationship between the intramolecuar charge- transfer (CT)/electron-transfer (ET) and the intramolecular magnetic exchanges. In this paper, we report the magnetic behavior and the electronic structures of the hydrazine dication salts.

Scheme 1 Stable Dication Radicals Studied in This Work



EXPERIMENTAL

The synthetic procedures of the Hydrazine diradical dications were published in our previous paper [1]. The rigid-glass and powder ESR and the magnetic susceptibility measurement were carried out in order to determine the intra- and inter-molecular magnetic exchange interactions. The temperature dependence of the magnetic susceptibility was measured from 1.8 K to 300 K using powder samples with a Quantum-Design MPMS SQUID magnetometer (MPMS2/MPMS XL5/MPMS7). All ESR experiments were carried out with a Bruker ESP300 spectrometer equipped with an Oxford variable temperature controller ESR 910. For the rigid-glass solvent, we chose acetnitrile, butylnitrile, methylene chloride (1: 1: 1) mixed solvent.

RESULTS AND DISCUSSION

Results of ESR and Magnetic Susceptibility Measurements

Temperature dependence of $\chi_{mol}T$ of dication salt **1** is shown in Figure 1.

Magnetic behavior has been well analyzed using one-dimensional antiferromagnetic behavior which have described in terms of alternating linear chain models with J_1/k_B = -106 K, J_2/k_B = -49 K and an alternating parameter α=0.46. A preliminary analysis to estimate the intramolecular exchange using the dimer model has given J_{intra}/k_B = -103 K [2].

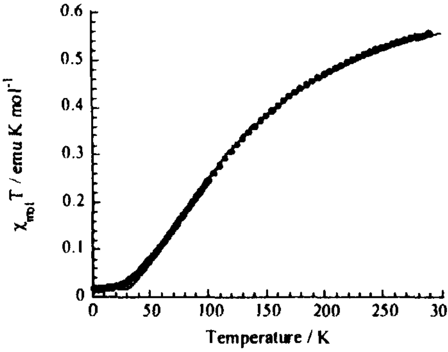


FIGURE 1 $\chi_{mol}T$ vs. T Plot for Polycrystalline $1^{2+}(Ph_4B^-)$

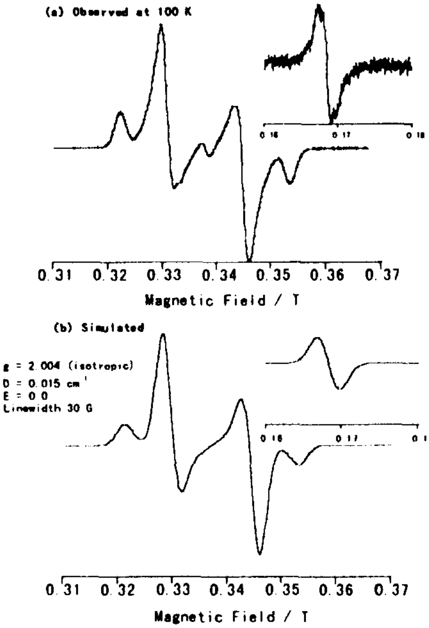


FIGURE 2 Typical ESR spectrum of 1^{2+} in a 1:1:1 acetonitrile, butylnitrile, methylene chloride rigid glass matrix

After the preliminary report [2], we obtained out more accurate data given in this work using higher-field SQUID magnetometer (MPMS7). The two exchange interactions of J_1 and J_2 are assigned to be intra- and inter-molecular exchanges, respectively, with the help of the following ESR data. In order to extract the intramolecular exchanges between two Hydrazine cations, we carefully measured the temperature dependence of the

ESR signal intensity in the diluted rigid glass sample in which the influence of the inter-molecular exchange is negligible. The typical ESR spectra of **1** observed at ca. 100 K in a 1:1:1 acetonitrile, butylnitrile, methylene chloride rigid-glass is shown in Figure 2. The accurate determination of the g-value and fine-structure parameters was carried out by a ESR simulation using the effective spin Hamiltonian,

$$H = \beta \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2). \qquad (1)$$

The g, D and E values are determined to be g = 2.004 (isotropic), D= 0.015 cm^{-1}, E= 0.0 cm^{-1}, respectively. The temperature dependence of the signal intensity is shown in Figure 3 as well as the fitting using a singlet-triplet model, which gives the intra-molecular exchange of -89.3 K. This value is close to that of J_1 in magnitude as well as its sign (antiferro-magnetic) obtained from the magnetic susceptibility data of the powder sample of **1**. Therefore, we can safely assign J_1 to be intra-molecular exchanges (J_{intra}) and the remain J_2 to be intermolecular one (J_{inter}).

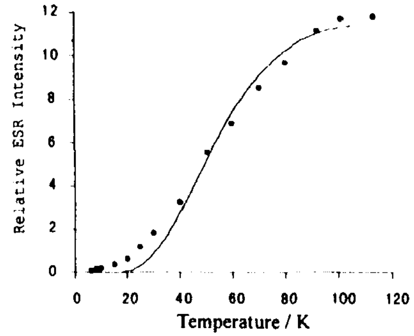


FIGURE 3 Temperature dependence of ESR signal intensity

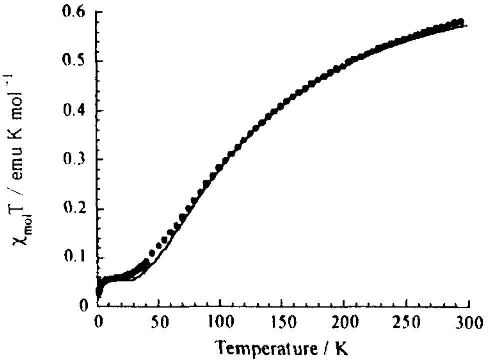
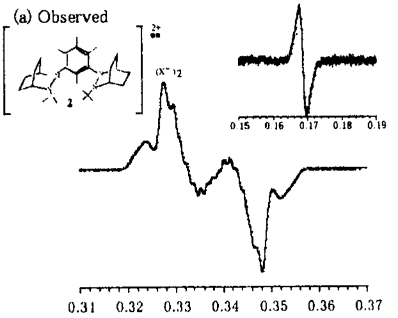


FIGURE 4 $\chi_{mol}T$ vs. T plot for polycrystalline **3**[2]

The magnetic property of **3** has been also fitted to the alternating chain model with $J_{intra}/k_B = -106$ K $J_{inter}/k_B = -42$ K (α=0.40) as shown in Figure 4. On the other hand, **2** gives a robust triplet ground state with larger energy separation from other spin states. Figure 5 shows a typical ESR spectrum of **2** and a plot of the ESR signal intensity vs. the reciprocal of temperature. The energy separation has been estimated to be larger than 260 cm^{-1} ($J_{intra}/k_B > +190$ K) from the temperature dependence of the ESR signal intensity. The ESR and magnetic exchange data obtained are summarized in Table 1. In conclusion, the *m*-linking hydrazine dication diradical has a high-spin triplet ground state and *p*-phenylene or *p*-biphenyl linking compounds have low-spin singlet ground states with low-lying triplet excited state. This finding indicates that the sign of the intramolecular exchange depends on the linking position (*m*- or *p*-) of the hydrazine cation group, i.e. the topology of the π orbital network even in the cationic molecular field. This situation is similar to the case of high-spin dicarbenes and their topological isomers, i.e., *m*-phenylenbis(phenylmethylene), *p*-phenylenbis(phenylmethylene) [4-7]. Similarity to the phenylene/biphenyl


(a) Observed

(b) ESR Signal Intensity

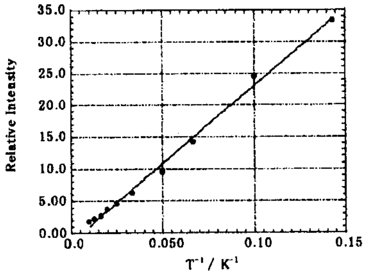


FIGURE 5 Typical ESR spectrum of 2^{2+} in the rigid glass and temperature dependence of ESR intensity

linked dicarbenes, the spin polarization mechanism is predominant over the spin delocalization mechanism even in the ionized molecular field. This conclusion is the same with that of our previous work of the organic ions with quartet high-spin states [8]. However, the charge-transfer band was observed in the hydrazine dication diradical cases in their optical spectra. This indicates that the charge-transfer (CT)/electron transfer (ET) mechanism gives an important contribution to the intramolecular spin alignment and the magnetic exchanges.

Table 1 Summary of the Magnetic Properties and ESR Data of the Dication Biradicals

	Charge	Magnetic Behavior		D, E and J_{intra}	$<\bar{r}>$
1	dication	Alternating Chain Ground State : S =0	$J_{intra}/k_B = -106.2$ K $J_{inter}/k_B = -48.9$ K $\alpha = 0.46$	$D = 0.0150$ cm^{-1} $E = 0.0$ cm^{-1} $J_{intra}/k_B = -89.3$ K	5.63 Å
2	dication	Curie-Weiss Ground State : S = 1	$\theta = -0.3$ K	$D = 0.0129$ cm^{-1} $E = 0.0011$ cm^{-1} $J_{intra}/k_B > 300$ K	5.92 Å
3	dication	Alternating Chain	$J_{intra}/k_B = -106.0$ K $J_{inter}/k_B = -42.4$ K $\alpha = 0.40$	$D = 0.0051$ cm^{-1} $E = 0$ cm^{-1} $D = 0.0062$ cm^{-1} $E = 0$ cm^{-1} $J_{intra}/k_B = -104.6$ K	8.07 Å 7.55 Å

ET Mechanism and Topological Nature of the Intramolecular Spin Alignment

The consistency between the ET mechanism and the topological nature of the intra-molecular magnetic exchange can be understood as follows. The sign of the intramolecular exchange is consistent with the exchange derived from ET mechanism by taking the superexchange mechanism through phenyl and biphenyl groups into account as shown in Figure 6. Thus, the unpaired electron can transfer to the linking pπ orbital through *p*-phenylene and *p,p'*-biphenylene groups and vice versa. Figure 6 is the case of *m*-phenylene linked Hydrazine dication diradical. In this case, we consider the electron transfer from Hydrazine site to the phenylene coupler and vice versa. In case of both hydrazine sites having the parallel spin configuration (triplet spin configuration), both unpaired electron can transfer simultaneously to phenylene coupler and interact each other, leading to the superexchange through the phenylene coupler and resulting the stabilization of the parallel spin configuration. On the other hand, in case of antiparallel spin configuration, only the unpaired spin in one side of hydrazine radicals can move to the phenylene coupler and that in another side can not transfer simultaneously. In such a case, the superexchange mechanism can not work well and the stabilization energy is about one half of that of the triplet spin configuration.

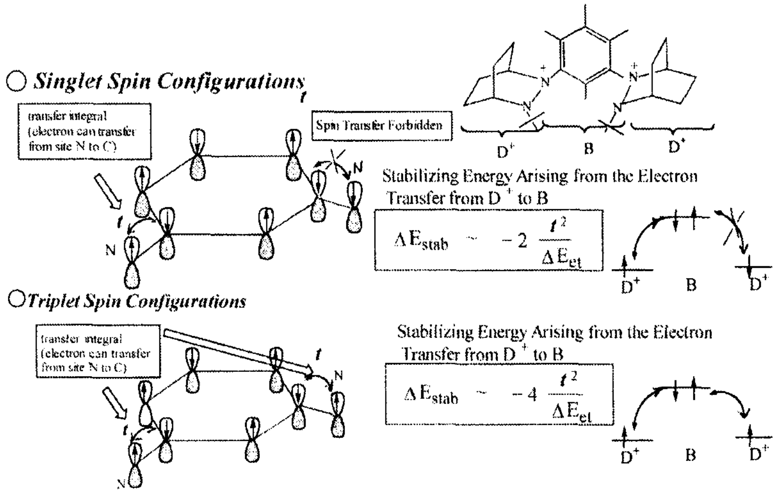


FIGURE 6 Magnetic exchange arising from a ET mechanism

Therefore, in *m*-phenylene case, the ET mechanism followed by the superexchange stabilize the triplet spin configuration, which is the same effect as that of the spin polarization mechanism. According to the similar considerations, we can show that in cases of the *p*-phenylene and *p*-biphenyl coupler, the singlet spin configuration is stabilized by both ET mechanism and spin poralization effect. Although we have treated only the dominant Valence Bond (VB) structures [9] and their spin correlation [9,10] in this explanation, the salient nature of the ET and superexchange mechanism and the resulting spin alignment may be described well in this picture.

Comparison of the Magnetic Exchange with ET Parameters

Considering antiferromagnetic exchange interactions in *p*-stacked crystals, Soos pointed out an approximate relationship using the transition energy of charge transfer (CT) band ($h\nu_{CT}$): $J \sim V^2/h\nu_{CT}$ [11]. For an intramolecular ET system, the stabilization of the adiabatic minima relative to parabolic diabatic (V=0) is given by $-V^2/(\lambda + \Delta G^0)$, where λ is the vertical recognization energy and ΔG^0 is the free energy change for the reaction and $h\nu_{CT} = \lambda + \Delta G^0$. Okamura and co-workers [12] gave eq. (2) which describes the stabilization of a diradical pair where the singlet state is stabilized by ET and the triplet state is not.

$$|E(\text{singlet}) - E(\text{triplet})| = V^2/(\lambda + \Delta G^0) \qquad (2)$$

Since our case is three state system (one is a molecular orbital of the phenylene or biphenyl spin coupler and other two are localized singly occupied molecular orbital on each hydrazine cations), the stabilization energy is slightly different with Okamura's case which is a two-state system. Making the same assumption as Okamura and extending the formula toward three state system, the following eq. (3) is obtained:

$$2J \sim |E(\text{singlet}) - E(\text{triplet})| = 2V(1^{2+})^2/(\lambda + \Delta G^0)\,. \qquad (3)$$

V and $\lambda + \Delta G^0$ is estimated from a CT band of $\mathbf{1}^{2+}$ with λ_{max} = 446 nm ($h\nu_{CT}$ =22400 cm^{-1}), bandwidth at half-height of 5500 cm^{-1} ($2\Delta\nu_{1/2}$) and ε_{max} of 2100 $M^{-1}cm^{-1}$. V was estimated to be 1330 cm^{-1} by using the following Hush's formula [13].

$$V \sim 0.0206(h\nu_{CT}\,\Delta\nu_{1/2}\,\varepsilon_{max})^{1/2}/d \qquad (4)$$

Because the concept of an average ET distance (*d*) appears close to the concept of an average distance between the electrons in a triplet diradical, we have used the triplet form of $\mathbf{1}^{2+}$ as a model to estimate the *d* value. The average distance was estimated to be 5.62 Å from the D value determined by ESR fine structure [1]. These formulas give an estimate of the exchange J derived from CT mechanism to be $|J_{CT}| \sim 80$ cm^{-1} (115 K) which is the same order in magnitude of the observed intramolecular exchange (89.3 K) of **1**. This finding indicates that the ET mechanism plays an important role in the intramolecular spin alignment of hydrazine dication diradicals.

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