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FERROMAGNETIC INTERMOLECULAR INTERACTION IN ORGANIC CRYSTALS

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Abstract The galvinoxyl radical is shown to have ferromagnetic intermolecular interaction in the solid state. The interaction extends one-dimensionally with the exchange energy of $2\mathcal{J}_F \simeq 1.5$ meV between the neighboring radicals. The ferromagnetic interaction is interpreted by a combined effect of intramolecular spin polarization and intermolecular charge-transfer interaction.

INTRODUCTION

There has been a growing interest in organic ferromagnetism. As the ferromagnetism is a property of bulk materials, it is of great importance to study the conditions under which the ferromagnetic (FM) intermolecular interaction is realized in a solid state. The aim of the present study is to learn or extract the conditions from detailed study on organic radicals which are known, albeit very rare, to exhibit FM intermolecular interaction. We have chosen the galvinoxyl radical as a typical example, because it is stable and has somewhat large FM interaction, though a crystal is known to show a phase transition at 85 K.

Galvinoxyl (4-[[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)phenoxy, see Figure 1) exhibits distinguished magnetic behavior. The temperature dependence of the magnetic susceptibility follows the Curie-Weiss law above 85 K with a positive Weiss constant (19 K).[1-3] The crystal of this radical undergoes a first-order phase transition at 85 K[4,5] and most of the paramagnetism disappears below 85 K.

In this communication, we summarize our experimental results for the FM intermolecular interaction of galvinoxyl. A simple interpretation of the interaction is given on the basis of INDO MO calculations

and intermolecular overlap integrals. The conditions for the FM coupling in galvinoxyl are discussed.

RESULTS AND DISCUSSION

We have initiated the study by examining the effect of an impurity on the phase transition. The closed-shell compound, hydrogalvinoxyl (see Figure 1), was chosen as an impurity. Hydrogalvinoxyl has the molecular and crystal structures similar to those of galvinoxyl and its crystal is known not to exhibit a phase transition.

Magnetic susceptibility[2,3]

The temperature dependence of paramagnetic susceptibilities χ_p of the 4:1, 6:1, 9:1 and 19:1 mixed crystals was examined from 2 to 300 K. The result for the 6:1 mixed crystal is shown in Figure 1, where the susceptibility of the neat galvinoxyl crystal is also given in the inset as the reference. In the 6:1 and 4:1 mixed crystals, the phase transition due to galvinoxyl is no more present and the susceptibilities follow the Curie-Weiss law over the whole temperature range. The Weiss constants are obtained to be about 7 and 5 K for the 6:1 and 4:1 mixed crystals, respectively. In contrast, the 9:1 and 19:1 mixed crystals undergo the phase transition when the samples are well annealed, but it is found that the transition is easily quenched by rapid cooling. The quenched state is a supercooled state and stable below 55 K.[5] The Weiss constants are obtained to be about 7 and 6 K for the supercooled states of the 9:1 and 19:1 mixed crystals, respectively.

We have thus learned from these that the phase transition can be suppressed by making a mixed crystal of galvinoxyl with a small amount of hydrogalvinoxyl and the FM interaction can be kept working to a sufficiently low temperature for studying the interaction in detail.

Magnetization[2,3]

The field strength dependence of the magnetizations M of the 4:1, 6:1 and supercooled 9:1 mixed crystals were measured at about 2 and 5 K. The results at 2 K are shown in Figure 2, where the magnetization is normalized by the saturation value M_s in each case. The magnetization curves at 5 K are essentially in agreement with those at 2 K. The magnetization saturates rather fast and does not show hysteresis.

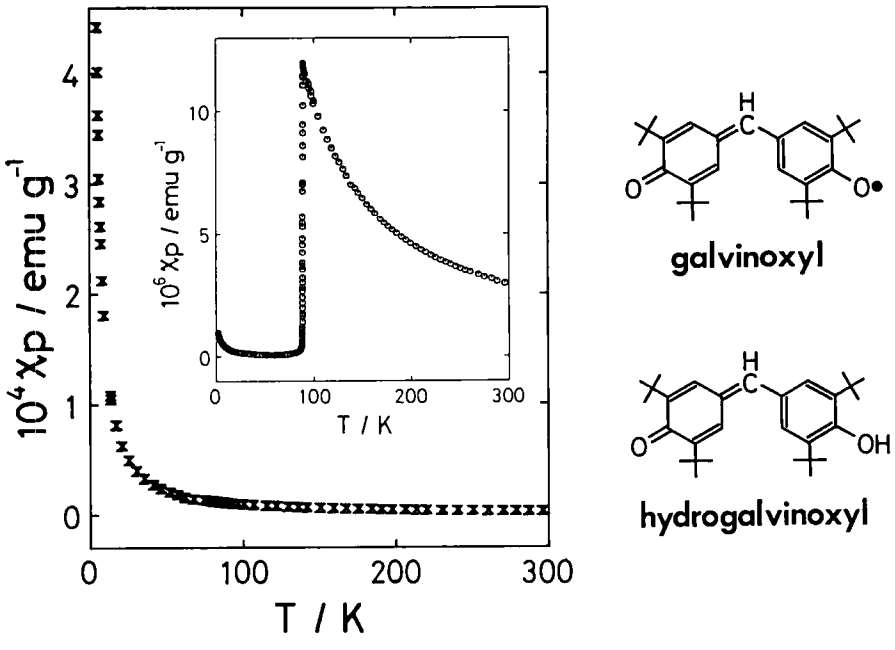

FIGURE 1. Temperature dependence of paramagnetic susceptibility of the 6:1 mixed crystal. The inset shows that of neat galvinoxyl.

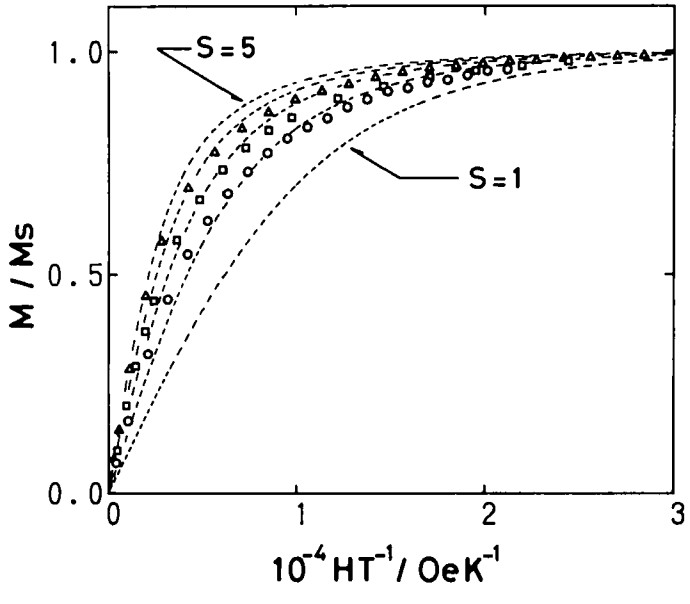

FIGURE 2. Field dependence of the magnetizations of 4:1 (○), 6:1 (□) and supercooled 9:1 (△) mixed crystals at about 2 K. The dashed lines represent the theoretical curves (see text).

Therefore, the spin system in these mixed crystals is regarded as being in a paramagnetic state with high-spin multiplicity. The high-spin multiplet state must be formed by the FM intermolecular interaction which is larger than the thermal energy corresponding to 2 and 5 K. The magnetization measurements have thus given a firmed evidence for the FM interaction between the galvinoxyl radicals.

Analysis of the magnetization curves would provide further insight into the nature of the interaction. The magnetization of paramagnetic species may be given by

$$M = M_s B_J(x) \qquad \text{with} \qquad x = Jg\mu_B H/kT, \tag{1}$$

where J is the quantum number of the total angular momentum and $B_J(x)$ is the Brillouin function for J. The broken curves in Figure 2 are the theoretical ones for $J = S = 1$, 2, 3, 4 and 5 (with $L = 0$). The observed magnetization curves of the 4:1, 6:1 and 9:1 mixed crystals are corresponding to the theoretical curves for $S = 2$, 3 and 4, respectively. This suggests that the mixed crystal of n:1 mixing ratio results in the multiplet state of $S = n/2$. The FM interaction extends over about n radicals in the n:1 mixed crystal. This linear relationship corresponds to the statistics for a one-dimensional system.

The crystal structure is known at room temperature[6] and at 210 K[7] as the monoclinic C2/c system. The radicals stack one-dimensionally along the c axis. For the n:1 mixed crystal, it is quite natural to assume that a stacking chain of galvinoxyl is partitioned into segments consisting of n radicals on the average. The fact that the n:1 mixed crystal is characterized approximately by the multiplicily of $2S + 1 = n + 1$ implies that all the radicals in a segment are coupled ferromagnetically and the segments are magnetically isolated from each other. Therefore, it is concluded that the FM interaction observed in the present temperature region works essentially in one-dimension, most probably along the c axis.

Electron Paramagnetic Resonance (EPR)[8]

Galvinoxyl is known to exhibit an EPR absorption characteristic of triplet species when it is diluted in hydrogalvinoxyl.[9] Figure 3(a) shows the X-band EPR absorption spectrum of the 4% mixed crystals (powder) of galvinoxyl at 13 K. The fine structure typical of triplet species in a powder sample is clearly observed at the wings of the

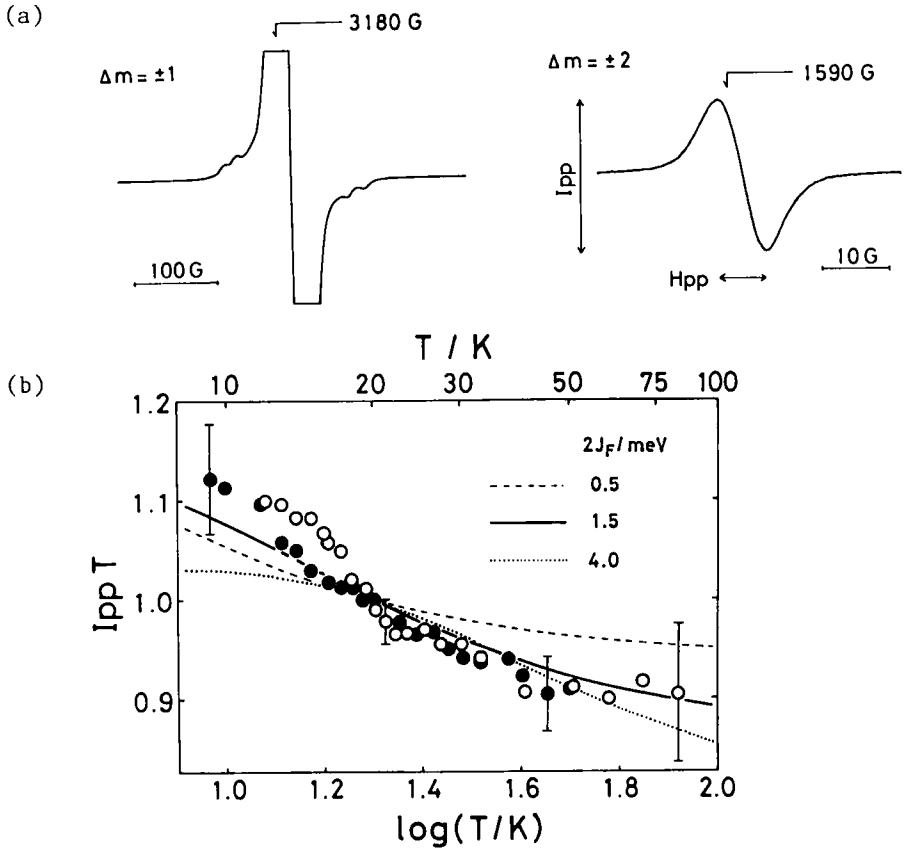

FIGURE 3. EPR spectrum at 13 K (a) and $I_{pp}T$ vs. log$T$ plots (b) of the powder sample of 4% galvinoxyl diluted in hydrogalvinoxyl. The open and closed circles represent different runs for the same specimen. The calculated curves using Eq. (2) with $2J_F$ = 0.5, 1.5 and 4.0 meV are shown.

strong central signal due to the radicals isolated in the matrix. The $\Delta m = \pm 2$ transitions are also observed at the half field. These signals are characteristic of triplet species and are due to the radical pairs statistically present in the dilute mixed crystal.

Figure 3(b) shows the temperature dependence of the peak-to-peak intensity I_{pp} of the $\Delta m = \pm 2$ transitions in the low temperature region, where the linewidth is independent of temperature. The quantity $I_{pp}T$ is proportional to the population in the triplet state. The fact that $I_{pp}T$ increases with decreasing temperature indicates that the ground state is the triplet state, which should be associated with the thermally accessible excited singlet state.

When the spin system is in thermal equilibrium between the ground triplet and the excited singlet states, the EPR absorption intensity may be given by

$$I \propto [7\{3 + \exp(-2\mathcal{J}_F/k7)\}]^{-1}, \quad (2)$$

where $\mathcal{J}_F$ (>0) is the FM coupling constant. $2\mathcal{J}_F$ is estimated to be 1.5 ± 0.7 meV from the fitting of the data in Figure 3(b) with Eq. (2).

FM Intermolecular Interaction of Galvinoxyl[10]

The molecular orbital energies of galvinoxyl have been calculated by using INDO method. The calculation is based on the molecualr structure of galvinoxyl in the high-temperature phase. Figure 4(a) shows the energies of topmost occupied and low-lying unoccupied orbitals of π-character, where the orbitals for one of the spin directions are combined by the broken lines with those for the opposite spin direction of similar orbital shape.

It is noticed that the orbital energies of SOMO-α and NLUMO-α are closely correspond to those of NHOMO-β and SOMO-β, respectively. This

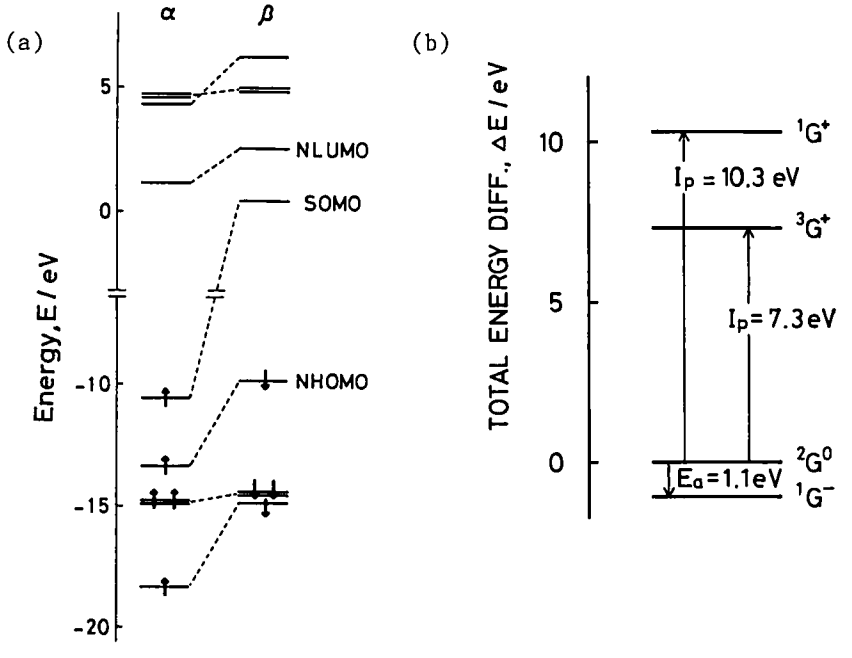

FIGURE 4. (a) Orbital energies and electronic configuration of galvinoxyl in the $^2G^0$ ground state. (b) Total energy differences of galvinoxyl in various states.

should be related to the molecular structure of galvinoxyl. Galvinoxyl has an extended π-conjugation system, which should decrease the energy separation between the frontier orbitals. Further, galvinoxyl contains two carbonyl groups having n-electrons and the spin polarization (intramolecular exchange interaction) should be enhanced through the n-π interaction.

In particular, the spin polarization effect in galvinoxyl appears notably in the relation between SOMO and NHOMO. The orbital energy of SOMO-α is even lower than that of NHOMO-β; this implies that the ionizaton of galvinoxyl would occur from NHOMO-β, leaving the triplet state cation behind. Figure 4(b) shows the differences of the total energies calculated by INDO method among neutral galvinoxyl ($^2G^0$), closed-shell anion ($^1G^-$), closed-shell cation ($^1G^+$) and open-shell cation ($^3G^+$) of galvinoxyl. The prominent feature of this figure is that the energy of the closed-shell cation is higher than that of open-shell cation. This happens partly by overestimation of the spin polarization effect in UHF calculation, but suggests considerably large contribution from the intramolecular exchange effect. From these characteristics of the electronic structure of galvinoxyl, it is expected that NHOMO-β and NLUMO-α contribute to the intermolecular interaction as well as the up- and down-spin levels of SOMO.

The charge-transfer (CT) interaction, which is common to organic solids, is observed even in crystals of free radicals. Figure 5 shows schematically the electronic configurations of the ground and low-lying excited states in a radical pair.[11] They are drawn in a spin-unrestricted picture. Configurations NT and NS are the no-bond structures. NT is the triplet while NS is the singlet state, and they are nearly degenerate. S_0 is a singlet CT structure ($^1G^+ \cdot {}^1G^-$) where CT occurs from SOMO-α to SOMO-β in the different radicals in pair. The configuration interaction between S_0 and NS results in the stabilization of NS. Namely, the overlap between SOMOs always makes the intermolecular magnetic coupling antiferromagnetic (AFM).

The other configurations presented in Figure 5 also show the CT structures, although their contribution is usually ignored. However, in the case of galvinoxyl, the triplet CT configurations, T_1 ($^3G^+ \cdot {}^1G^-$) and T_2, are expected to be well stabilized as discussed above and

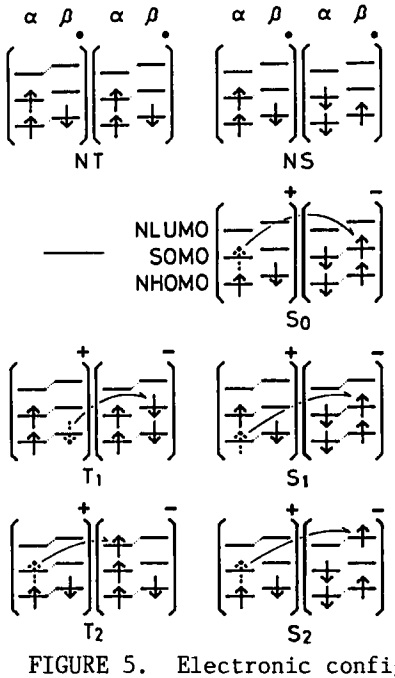

FIGURE 5. Electronic configurations in a radical pair coupled by the CT interaction.

TABLE 1 Overlap integrals for various CT configurations.

Config.	Integral type	Overlap
S_0	<SOMO-α |SOMO-β >	0.72×10^{-3}
T_1	<NHOMO-β|SOMO-β >	1.60×10^{-3}
S_1	<NHOMO-α|SOMO-β >	0.87×10^{-3}
T_2	<SOMO-α |NLUMO-α>	2.73×10^{-3}
S_2	<SOMO-α |NLUMO-β>	1.33×10^{-3}

become energetically as favorable as S_0 for configuration interaction with the no-bond structures. T_1 and T_2 thus stabilize NT and bring about the FM intermolecular interaction.

In order to compare the magnitudes of the transfer integrals for the CT configurations in Figure 5, the intermolecular overlap integrals between the interacting orbitals were calculated by using the MOs obtained by INDO method. The results are listed in Table 1. The overlap integrals for T_1 and T_2 are larger than those for the singlet configurations. Taking account of the stabilization of T_1 and T_2, it is concluded that the AFM coupling derived from the resonance of S_0 with NS is surpassed by the FM coupling derived from the resonance of T_1 and T_2 with NT, resulting in the net FM exchange.

From these considerations, we can summarize that the FM intermolecular interaction of galvinoxyl should originate in the resonance with the triplet CT excited states stabilized by the intramolecular exchange interaction. The FM interaction is regarded as a combined effect of the intramolecular spin polarization and the intermolecular CT interaction.

Conditions for FM Intermolecular Interaction

The molecular structure desirable for the FM intermolecular exchange coupling is discussed by reffering to the case of galvinoxyl. Firstly, a planer π-radical is favorable for a large intermolecular interaction. Secondly, a large spin polarization and closely spaced energy levels of frontier orbitals are indispensable for stabilization of the triplet CT states. The spin polarization could be enhanced by introducing substituent groups having n-electrons such as nitro, nitroso and carbonyl groups. Developed π-conjugation should decrease the energy separation between the frontier orbitals.

In regard to small energy separation, it is to be noted that the use of a radical having unpaired electrons in the degenerate orbitals is not always promissing for FM coupling. The degeneracy is the extreme limit of small energy separation of the frontier orbitals, but does not always guarantee large intramolecular exchange interaction. For FM coupling, the exchange interaction should overcome the energy level splitting due to the Jahn-Teller effect; this holds in the case of the complex of decamethylferrocene-TCNE,[12] because the exchange interaction is mainly between the d-orbitals on the one-center Fe atom.

From these, we propose the odd-alternant system having developed π-conjugation and the substituents with n-electrons as a good candidate for the FM radical. In the odd-alternant system, there is an additional advantage for intermolecular overlap as follows. The large electron densities in SOMO appear alternately along the bonded atoms; on the other hand, NHOMO and NLUMO provide large densities on the atoms where the electron densities are small in SOMO. Therefore, the appearance of large intermolecular overlap between SOMO and NHOMO and/or NLUMO should inevitably result in small overlap between SOMOs of interacting radicals, making the CT contribution from S_0 small.

Other Radicals with FM Coupling

Keeping the conditions described above in mind, Dr. Awaga has recently examined the magnetic properties of nitronyl nitroxide (2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide, see Figure 6(a)) and found the FM intermolecular interaction of $2\mathcal{J}_F/k \simeq 1$ K.[13]

French group[14] has studied the magnetic properties of TANOL

(a) (b)

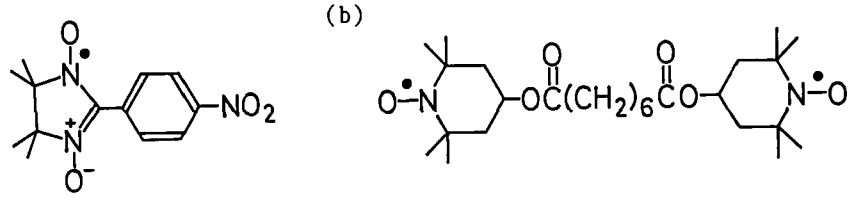

FIGURE 6. Molecular structures of nitronyl nitroxide (a) and TANOL suberate (b).

suberate (bis(2,2,6,6-tetramethylpiperidin-4-yl-1-oxyl) suberate, see Figure 6(b)) in detail and shown that it is an organic metamagnet below 0.39 K. The TANOL radicals on the crystallographic ac plane are ferromagntically coupled while AFM interaction operates along the b axis. The FM interaction in this radical would be interpreted just by the potential exchange, because the distances between the N-O groups of neighboring radicals on the ac plane are so large that the overlaps of MOs on the neighboring radicals are quite small ($\sim 10^{-4}$) and the CT contribution should be negligibly small.

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