

Magnetic Interactions in Insulating BEDT-TTF Salts

Takehiko Mori¹

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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Inter-dimer magnetic interactions J in BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) salts in the Mott insulator regime are estimated from the intermolecular overlap integrals. The estimated J values are compared with the experimental results, and the stable spin alignment and the dimensionality of the spin systems are discussed. © 2002 Elsevier Science (USA)

Key Words: charge transfer salts; π d-interaction; Mott insulator; molecule-based magnetism.

INTRODUCTION

Charge-transfer salts of BEDT-TTF and the derivatives are well known because of their superconducting properties (1–3). Recently, however, interest in the interplay between electrical conduction and magnetism in BEDT-TTF salts involving magnetic anions (4, 5) has been aroused. In particular, many intriguing phenomena, including coexistence of superconductivity and antiferromagnetism, as well as field-induced superconductivity, have been found in BETS (bis(ethylenedithio)tetraselenafulvalene) salts (6, 7). Magnetic interactions in these compounds are basically explained by the RKKY-type interaction mediated by the π d-coupling between the donor and the magnetic anion (8), though the direct magnetic interaction between the anions plays an important role in the antiferromagnetic states. To understand these phenomena, it is essential to examine magnetic properties of the π -system without magnetic anions; that is, what magnetic structure the π -system prefers, and how strong is the magnetic interaction. There are many BEDT-TTF compounds which do not include magnetic anion, but whose π -system is located in the Mott insulator regime (4, 9). From the high-temperature susceptibility values, these compounds are regarded as having entirely localized $S = \frac{1}{2}$ spins. Transfer integrals, energy band structures, and Fermi surface of BEDT-TTF salts are well investigated both from theoretical and experimental points of view (1–3, 10). Quantitative treatment of π -spin

system is, however, relatively difficult, because in the usual quarter-filled conductors, it is not the single donor but a dimer that holds a localized spin. Magnetic interactions J between the donors are easily estimated from the intermolecular transfer integrals, but magnetic interactions between the dimers are not straightforwardly obtained. This paper is an attempt to determine the stable magnetic structures of these π -systems, and to quantitatively estimate the magnitudes of the magnetic interactions.

ITINERANT π -SYSTEM

Magnetic properties of conduction electron are represented by response of conduction electrons to a magnetic impurity atom. When a magnetic moment S_d is placed at $r = 0$ in conduction electrons, spin of the surrounding conduction electron is polarized according to $m(r) = 2 \times (J_{\pi d}/g\mu_B)\chi(r)S_d$. This means that the conduction electron at $r = 0$ feels an internal field $2(J_{\pi d}/g\mu_B)S_d$, which is in turn transmitted in proportion to $\chi(r)$. The spin susceptibility $\chi(r)$ for isotropic free electrons with spherical Fermi surface is well known as the RKKY interaction (11). This has been extended to general Fermi surface (12),

$$\chi(r) = \Sigma A \cos(2k_F r)/(2k_F r)^3, \quad [1]$$

where A is a parameter depending on the direction of r , and is decided by the band structure. This equation represents that $\chi(r)$ has a negative (antiferromagnetic) peak at $2k_F r = \pi$ in each direction, and if a peak of up spin is located at $r = 0$, the adjacent peak of down spin appears at $r = \pi/2k_F$. As a simple example, in a $1/n$ -filled one-dimensional system ($k_F = \pi/an$), the down spin appears at $r = an/2$.² For a quarter-filled ($n = 4$) system, this gives $r = 2a$. Even if the magnitude of the spin polarization is not one complete spin ($S = \frac{1}{2}$), we may consider spin density

²For half-filling, $r = a$, each site has alternating spin. Aromatic hydrocarbons are regarded as the special case, where each carbon gives up one π -electron. In the π -band, the lower half of the bonding nature is occupied, whereas the antibonding half is empty. The resulting half-filled situation leads to the alternating alignment of up and down spins.

¹Fax: +81-3-5734-3657. E-mail: takehiko@o.cc.titech.ac.jp.

waves (SDW) with such periodicity that two molecules hold one spin unit. In quarter-filled salts with strong dimerization, we may consider that each dimer has one spin unit.

As another approach, once we know the band structure, we can calculate $\chi(\mathbf{q})$ as we have done in Ref. (8). The maximum of $\chi(\mathbf{q})$ affords the q -vector of the antiferromagnetic order. The results agree with the above simple consideration. The calculated $\chi(\mathbf{q})$, however, has a very broad peak, and this method is not practical to determine the stable magnetic structure of the π -system. Furthermore, the $\chi(\mathbf{q})$ value calculated from the band structure is a bare value without considering the effect of correlation, so that this method is inappropriate to the quantitative estimation of the magnetic instability.

From this perspective, we can unambiguously determine the periodicity of SDW from the band filling, whereas we cannot estimate the magnitude of magnetic interactions from the itinerant electron picture. Then next we assume entirely localized π -electrons.

INTER-DIMER MAGNETIC INTERACTIONS

When we consider each dimer as having one spin unit, as happens in a strongly dimerized quarter-filled system, we have to estimate inter-dimer J from the intermolecular transfer integrals t . If the dimerization is sufficiently strong, we can estimate inter-dimer J values from the intermolecular transfer integrals and the on-site Coulomb repulsion U on the basis of the Hubbard model for two couples of dimers (13). By applying the perturbation theory to a two-site two-electron system, M. Mori *et al.* have carried out such a calculation, and have obtained the representation of inter-dimer J (14). Actual systems are, however, not so strongly dimerized so that the inter-dimer transfer is comparable to the intra-dimer transfer. Such systems are more appropriately regarded as alternating chains with quarter filling. Nonetheless, the systems are in the insulating states, and the observed susceptibility has been analyzed on the basis of one- or two-dimensional Heisenberg model, as if each dimer had an entirely localized spin. Then the problem is how we can relate such effective J values to the intermolecular transfers or other quantities. Yoneyama *et al.* have measured magnetic susceptibility of many insulating BEDT-TTF compounds, and have semi-quantitatively compared the sum of absolute values of the transfer integrals $\Sigma|t|$ (9). Here we show a different approach.

The orbital of a dimer is generally represented as $\phi_A = (\chi_1 + e^{i\theta}\chi_2)/\sqrt{2}$ and $\phi_B = (\chi_3 + e^{i\theta}\chi_4)/\sqrt{2}$ (Fig. 1), where χ_1 - χ_4 are molecular orbitals (HOMO) of the molecules 1-4, and the phase factor $e^{i\theta}$ is ± 1 (or $\theta = 0$ and π) for bonding and antibonding combinations of these orbitals. We first consider Fig. 1(a), where two interactions p and q remain

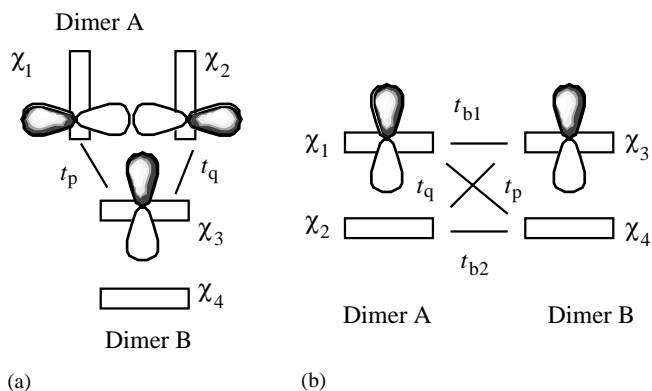


FIG. 1. Dimer model of π -system.

between the dimers. Putting the above orbitals in the usual formulation of exchange interaction ($J = -2t^2/\Delta$) (15), in which the transfer integral t is given by $\int \phi_A \mathbf{H} \phi_B d\tau$, the inter-dimer interaction is

$$J_{AB} = -2 \left(\int \phi_A \mathbf{H} \phi_B d\tau \right)^2 / \Delta \\ = - (2/\Delta) \frac{1}{4} (t_p^2 + t_q^2 + 2t_p t_q \cos\theta). \quad [2]$$

Here Δ is twice that of the intra-dimer transfer in the limit of strong dimerization (16). When only one transfer t_p is significant between the dimers, this relation becomes simple

$$J_{AB} = -2t_p^2/4\Delta = J_p/4. \quad [3]$$

Then the inter-dimer J_{AB} is one quarter of the intermolecular J_p . This is because each molecule of the dimer holds 50% spin.

When the dimer has a bonding orbital, that is $\theta = 0$, Eq. [2] gives

$$J_{AB} = -2(t_p + t_q)^2/4\Delta, \quad [4]$$

whereas for the antibonding orbitals

$$J_{AB} = -2(t_p - t_q)^2/4\Delta. \quad [5]$$

When t_p and t_q have similar magnitudes, these two are much different. These results correspond to the large U limit of M. Mori's results obtained from the two-site two-electron Hubbard model (14). In the usual quarter-filled dimers, the hole resides on the antibonding combinations of HOMO, so that Eq. [5] holds. In practical calculations, however, we should carefully examine the phase factors because we usually take such HOMO phases as the intra-dimer overlap becomes positive (as shown in Fig. 1(a)). If two molecules forming the dimer are connected by an inversion center, as happens frequently, the phases of p orbitals are inverted like Fig. 1(a). In this case, the

antibonding combination formally corresponds to $(t_p + t_q)^2$ (Eq. [4]).

The case of Fig. 1(b) becomes,

$$J_{AB} = -(2/\Delta)\frac{1}{4}|t_{b1} + t_{b2} + t_p e^{i\theta} + t_q e^{-i\theta}|^2. \quad [6]$$

This gives equations similar to Eqs. [4] and [5].

If the dimer is placed in an infinite chain, θ of the Bloch function may change from zero to π . On account of this ambiguity, if we neglect the cross terms in Eq. [2] or [6], the inter-dimer interaction is

$$J_{AB} = -(2/\Delta)\frac{1}{4}\Sigma t_p^2 = (\frac{1}{4})\Sigma J_p. \quad [7]$$

This means that the dimer $S = \frac{1}{2}$ spin resides on each molecule in 50% probability irrespective of the phase of the electron. Fortunately, in practical cases, many inter-dimer interactions are mediated by a single transfer integral, and unambiguously obtained by Eq. [3]. For other cases, we shall compare values estimated from Eqs. [4], [5], and [7], with experiments.

In the following, HOMO of an isolated BEDT-TTF molecule is calculated by the extended Hückel method (1), from which the intermolecular overlap integrals S are obtained. The transfer integrals t are estimated from these overlap integrals by using $t = ES$ and $E = -10$ eV, Δ is assumed to be 1 eV similar to Ref. (8).

INDIVIDUAL EXAMPLES

β' -(BEDT-TTF)₂AuCl₂

β' -(BEDT-TTF)₂AuCl₂ is a strongly dimerized insulator (9, 17), and judging from the magnetic susceptibility (9.0×10^{-4} emu/mol) at room temperature, the magnetic moment on a dimer is more than 85% of the entirely localized $S = \frac{1}{2}$ spin. As shown in Table 1 and Fig. 2(a), the intra-dimer overlap $a1$ (27.4×10^{-3}) overwhelms the other interactions. The inter-dimer interactions are evaluated as in Table 1 and Fig. 2(b). J_a and J_q are unambiguously obtained from Eq. [3]. For J_c , we show three different estimations from Eqs. [4], [5], and [7]. Because the intra-

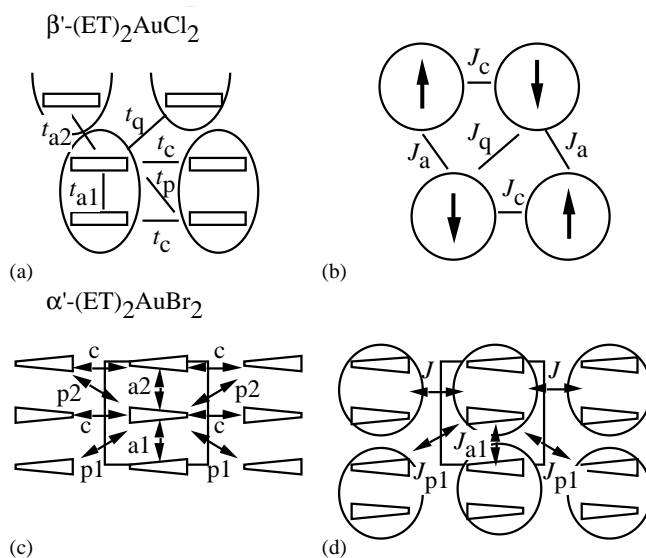


FIG. 2. (a) Donor arrangement of β' -(BEDT-TTF)₂AuCl₂, and (b) the dimer model. (c) Donor arrangement of α' -(BEDT-TTF)₂AuBr₂, and (d) the dimer model.

dimer overlap $a1$ is taken positive, the value from Eq. [4] (71 K) corresponds to the antibonding orbitals. If we take this estimation, the transverse interaction J_c (71 K) becomes even larger than J_a (58 K). This does not seem quite reasonable, so that it may be better to use the value of Eq. [7] (31 K).

Since J_q (9 K) is much smaller than J_a (58 K) and J_c (31 K), the system may be approximated as a two-dimensional square lattice formed by the network of J_a and J_c . A stable spin structure is depicted in Fig. 2(b). Here, the small J_q is frustrated.

The magnetic susceptibility makes a broad maximum around 110 K. Since an ideal two-dimensional square-lattice Heisenberg system shows a susceptibility maximum at $T_{\max} = -1.8975 J/k_B$ (18), the observed maximum gives $J/k_B = -58$ K. This is in good agreement with the calculated J_a and J_c . This compound shows considerable low-dimensional character in the magnetic susceptibility, and a three-dimensional antiferromagnetic transition takes place at 28 K. This temperature is related to the inter-sheet J , which we cannot estimate in the present calculation. We may have to take into account transport through the nonmagnetic anions to estimate the inter-sheet J .

α' -(BEDT-TTF)₂AuBr₂

Another example α' -(BEDT-TTF)₂AuBr₂ is shown in Table 2 and Fig. 2(c) (3). If we take the $a2$ interaction as dimer, the inter-dimer interactions make a chain with J along the c -axis (Fig. 2(d)). This J is 216 K from Eq. [4], or 92 K from Eq. [7]. If we adopt the former estimation, the combined overlap integral $2S_c + S_{p2} = 19.3 \times 10^{-3}$ is even

TABLE 1
Overlap Integrals S and Inter-Dimer Magnetic Interactions
in β' -(BEDT-TTF)₂AuCl₂ (Figs. 2(a) and 2(b))

Interaction	$S(\times 10^{-3})$	Inter-dimer J	$-J/k_B$ (K)	Eq.
$a1$	27.4	J_a	$2t_{a2}^2/4\Delta$	58 [3]
$a2$	10.0	J_c	$2(2t_c + t_p)^2/4\Delta$	71 [4]
c	2.3		$2(2t_c - t_p)^2/4\Delta$	2 [5]
p	6.5		$2(2t_c^2 + t_p^2)/4\Delta$	31 [7]
q	-2.0	J_q	$2t_q^2/4\Delta$	9 [3]

Note. The transfer integrals t are estimated from the overlap integrals S by using $t = ES$ and $E = -10$ eV.

TABLE 2
Overlap Integrals S and Inter-Dimer Magnetic Interactions
in α' -(BEDT-TTF) $_2$ AuBr $_2$ (Figs. 2(c) and 2(d))

Interaction	$S(\times 10^{-3})$	Inter-dimer J	$-J/k_B$ (K)	Eq.
$a1$	5.4	J	$2(2t_c + t_{p2})^2/4\Delta$	216 [4]
$a2$	11.9		$2(2t_c - t_{p2})^2/4\Delta$	139 [5]
c	8.7		$2(2t_c^2 + t_{p2}^2)/4\Delta$	92 [7]
$p1$	1.9	J_{a1}	$2t_{a1}^2/4\Delta$	17 [3]
$p2$	1.9	J_{p1}	$2t_{p1}^2/4\Delta$	2 [3]

Note. The transfer integrals t are estimated from the overlap integrals S by using $t = ES$ and $E = -10$ eV.

larger than the intra-dimer overlap $S_{a2} = 11.9 \times 10^{-3}$, contradicting with the dimer model. Then it may be safe to adopt the simple sum of J (Eq. [7]). The other interactions, J_{a1} (17 K) and J_{p1} (2 K), are regarded as interchain interactions. Since an one-dimensional Heisenberg chain makes a susceptibility maximum at $T_{\max} = -1.282 J/k_B$ (19), the observed susceptibility maximum at 80 K affords $J/k_B = -62$ K. This value is smaller than the calculation, probably because the intra-dimer interaction $a2$ is not sufficiently larger than the inter-dimer interactions.

We can similarly analyze many other examples presented in Ref. (9). If the dimerization is insufficient, the J values calculated under the above dimer approximation are larger than the experimentally determined J values. If we take account of this possible overestimation coming from the insufficient dimerization, the above calculation gives a good rough estimation of the observed magnetic interactions. Furthermore, this semi-quantitative estimation is sufficient to determine the stable spin alignment, and affords a satisfactory insight into the dimensionality of the magnetic systems.

κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]X [$X = Cl$ and Br]

These are famous superconductors, but are located on the border to the Mott insulator regime (16). Based on the overlap integrals in Ref. [2], the inter-dimer interactions are estimated as shown in Table 3. Since the intra-dimer

TABLE 3
Inter-Dimer Magnetic Interactions in
 κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]X [$X = Cl$ and Br] (Fig. 3)

Interaction	$S(\times 10^{-3})$		Inter-dimer J	$-J/k_B$ (K)		Eq.	
	$X = Cl$	Br		$X = Cl$	Br		
$a1$	27.3	26.5	J_p	$2(t_p + t_q)^2/4\Delta$	25	29	[4]
$a2$	10.4	9.8		$2(t_p - t_q)^2/4\Delta$	120	125	[5]
p	10.5	10.9		$2(t_p^2 + t_q^2)/4\Delta$	73	78	[7]
q	-3.9	-3.8	J_C	$2t_{b1}^2/4\Delta$	63	56	[3]

interaction is large, the dimer model is a good approximation. Inter-dimer interactions are very simple (Fig. 3); there are only two interactions: the oblique one (P) and the horizontal one (C). Because the intra-dimer overlap is taken positive, $(t_p + t_q)^2$ (Eq. [4]) corresponds to the antibonding combination, but t_p and t_q have different signs, then $(t_p + t_q)^2$ is smaller than $(t_p - t_q)^2$. If we take $(t_p + t_q)^2$ as J_p , this is even smaller than J_C . This result seems, however, unreasonable because even the single p interaction is larger than $b1$. Then we shall use the simple sum of J (Eq. [7]).

Spin alignment of the κ -phase is decided depending on whether J_C is larger or smaller than J_p (19). When J_C is

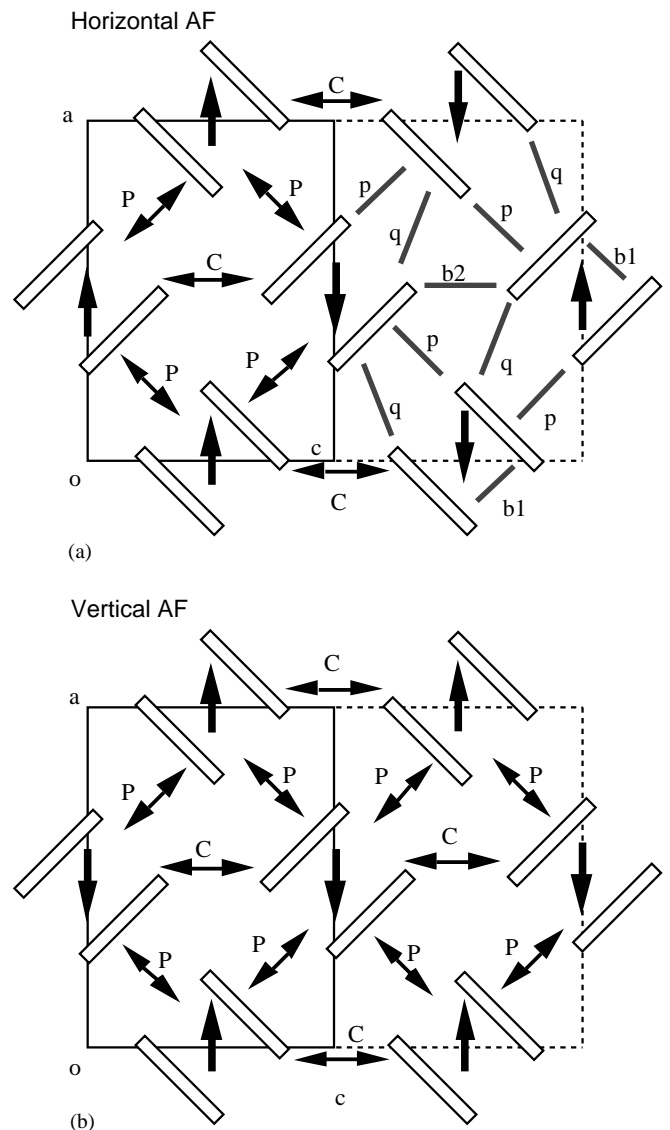


FIG. 3. Intermolecular interactions, $b1$, $b2$, p , and q (shaded in (a)), inter-dimer magnetic interactions P and C , and (a) horizontal and (b) vertical spin alignments in the κ -phase.

larger than J_P , alternating spin alignment along the c -axis is most important as shown in Fig. 3(a) (horizontal), and half of P interactions are frustrated. If J_C becomes smaller than J_P , however, all diagonal P interactions have antiferromagnetically coupled spins at the cost of the C interactions (Fig. 3(b) vertical). The present BEDT-TTF salts are expected to prefer the latter vertical spin structure, because J_C is smaller than J_P . By contrast, κ -type BETS salts prefer the former horizontal spin structure, because t_{b2} is larger than t_p and t_q (8).

CONCLUSIONS

In the present paper, we have examined a method to connect intermolecular transfers to inter-dimer magnetic interactions in quarter-filled π -systems. It seems practical to estimate the inter-dimer J from the simple sum of intermolecular J by using Eq. [7]. This seems to suggest that we have to make each electron localized on each *molecule*, removing the phase coherence, before taking account of dimerization and quarter filling. In the terminology of the Hubbard model, inclusion of off-site Coulomb repulsion V is probably essential, because these are quarter-filled systems. The present estimation has another merit, that is we do not need to pay attention to signs of the overlap integrals. This affords a good quantitative estimation of J if the dimerization is strong enough, but still tends to overestimate J when the dimerization is insufficient. In spite of the semi-quantitative nature, the stable spin alignment is easily predicted from this estimation. This kind of analysis is important to examine more complicated π d-systems (8).

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