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SPIN ALIGNMENT IN A MODEL COMPOUND OF ORGANIC FERRIMAGNETS

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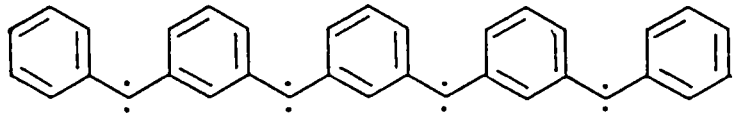
Abstract Exchange interaction via an ether bridge between magnetic moieties in organic high-spin molecules has been studied by single-crystal ESR. Whether it is ferromagnetic or antiferromagnetic depends on the substituted position of the bridge, showing the important role of topology in spin alignment. This behavior is satisfactorily interpreted as due to superexchange mechanism. Using the antiferromagnetic bridge, a model compound for a unit of organic ferrimagnets is designed and its spin structure is determined.

INTRODUCTION

We have been studying a series of high-spin hydrocarbons designed by exploiting topological symmetry of their pi electron network as well as localized spins at divalent carbon atoms in the network.[1] These high-spin molecules have been successfully detected and characterized up to a nonet hydrocarbon



by ESR spectroscopy.[1-5] Recently, these organic high-spin molecules have attracted increasing theoretical interest as models for organic ferromagnets.[6-16] Our strategy to organic ferromagnets may be termed as an intramolecular or through-bond approach in contrast to intermolecular or through-space approaches which utilizes the charge transfer stabilization between adjacent sites in a crystal.[17-19]

Most of the high-spin molecules investigated have quasi one-

dimensional spin structures. Since it is widely known that purely one-dimensional spin systems do not show spontaneous magnetization,[20] one has to extend these to higher dimensional spin structures in order to obtain organic ferro-, antiferro- and ferrimagnetism as bulk matter. There may be two approaches for realizing such higher-dimensional spin ordering. One is to extend a pi electron network to higher dimensions in such a way that its topological symmetry makes spins parallel according to the principle already established.[1,6,7] The other is to introduce weak magnetic interaction between the chains with quasi one-dimensional spin structures. This auxiliary interaction may be obtained by exploiting a functional group such as the ether or methylene bridge as shown in Figure 1, which gives a picture for spin alignment in a magnetic polymer where spins are interacting through chemical bonds. However, little has been known on the role of such bridges in the spin alignment of organic high-spin molecules.

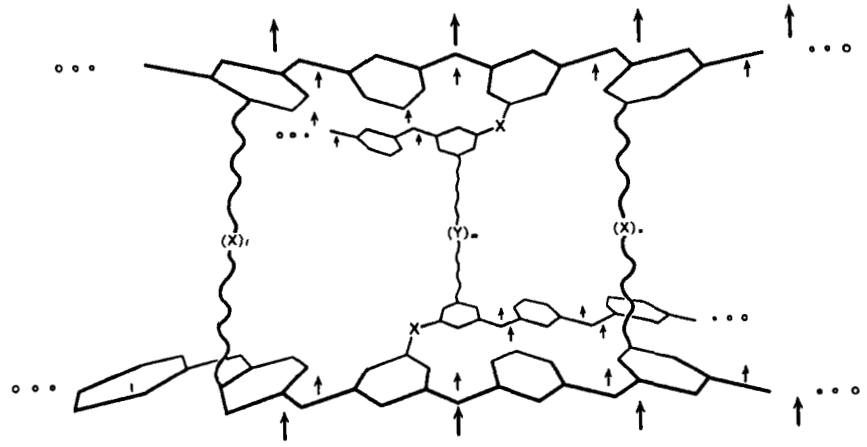


FIGURE 1. A model for a higher-dimensional spin structure.

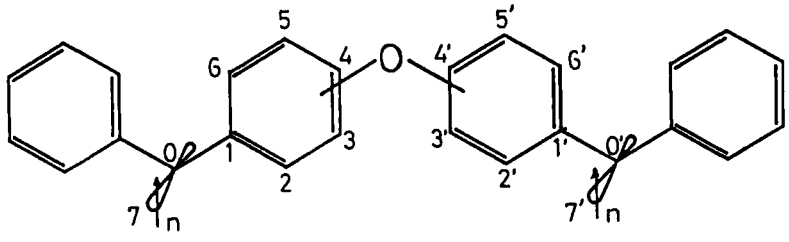
As part of a program examining the alignment of electron spins via such functional groups, we have synthesized a group of model compounds composed of two triplet moieties connected by the

ether bridge and studied their spin alignment by a single-crystal ESR technique. It is shown that the role of bridges making spins ferromagnetic or antiferromagnetic depends on the topology of the bridging position and that this role can be satisfactorily interpreted by a Heisenberg model Hamiltonian. On the basis of the role of bridges so studied, we have designed and synthesized a model compound for studying the fundamental magnetic interaction in organic ferrimagnets.

ROLE OF OXYGEN BRIDGE IN SPIN ALIGNMENT

Model Compounds

As a simplest model, we have chosen a,a'-bis(phenylmethylene)-diphenylether (a,a'-BPDE; a,a'=3,4)



in which spins in each of the two triplet diphenylmethylene moieties interact via an oxygen atom. The composite carbenes, a,a'-BPDE, were formed by the photolysis of the corresponding diazo precursors which were synthesized from a-hydroxybenzophenone and a'-bromobenzophenone (a,a'=3,4). The diazo precursors were oriented in single crystals of benzophenone ($P2_12_12_1$ space group), which were irradiated at 4.2 K with a 500 W high-pressure mercury lamp equipped with a Toshiba UV39 filter.

Magnetic Interactions as Determined by ESR

ESR measurements were made at a K-band frequency (24-25 GHz) on a JEOL-3BX spectrometer with a home made TE_{011} cavity. Figure 2 shows the temperature dependence of the ESR spectra from 4,4'-BPDE with the external magnetic field along the b axis of a benzophenone crystal.

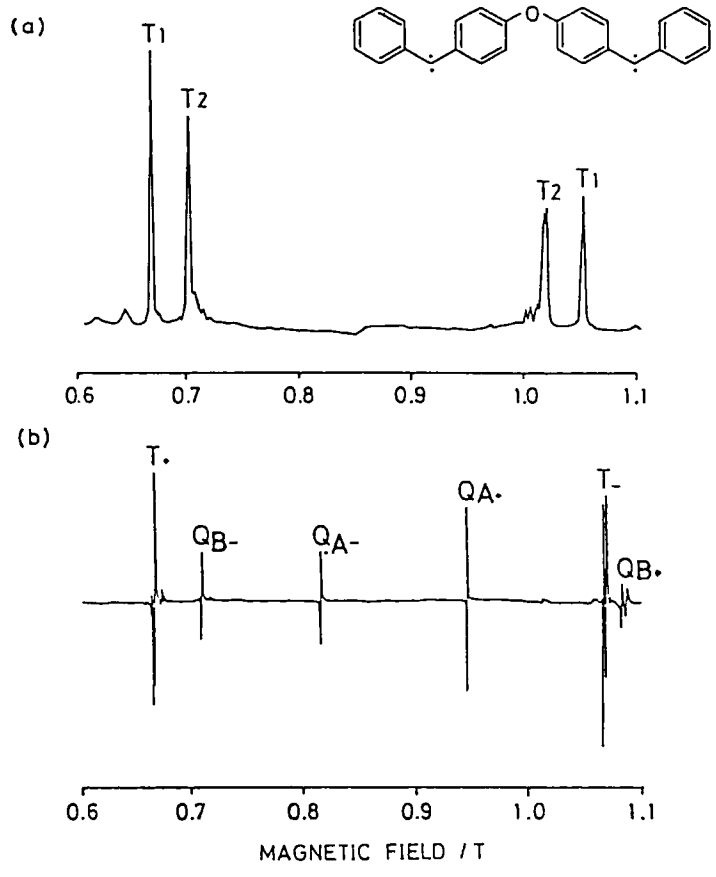


FIGURE 2. ESR spectra of 4,4'-BPDE. H//b axis.
(a) Observed at 4.2 K immediately after photolysis.
(b) Observed at 77 K.

The ESR spectrum observed immediately after photolysis at 4.2 K is shown in Figure 2(a); this consists of two kinds of ground-state triplet signals denoted by T_1 and T_2. They were ascribed to para-substituted diphenylmethylene formed as byproducts which was generated by the thermal decomposition of one diazo group during the preparation of mixed crystals. With increasing the crystal temperature from 4.2 K, a new pair of lines marked with $T_{\pm}$ first appeared at 20 K and then those labeled by $A_{\pm}$ and $B_{\pm}$ at 31 K. While these lines increased their intensities on heating, the first triplet signals T_1 and T_2 markedly diminished. The spectrum observed at 77 K is shown in

Figure 2(b). The above temperature dependence was completely reversible in the range of 4.2 K and 77 K. From the analysis of the angular dependence of the spectra described below, the $T_{\pm}$ pair and the four lines $A_{\pm}$ and $B_{\pm}$ were attributed to a triplet state and a quintet state of 4,4'-BPDE, respectively, the quintet state being higher in energy.

The observed ESR spectra and their angular dependence were described well by the effective spin Hamiltonian

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

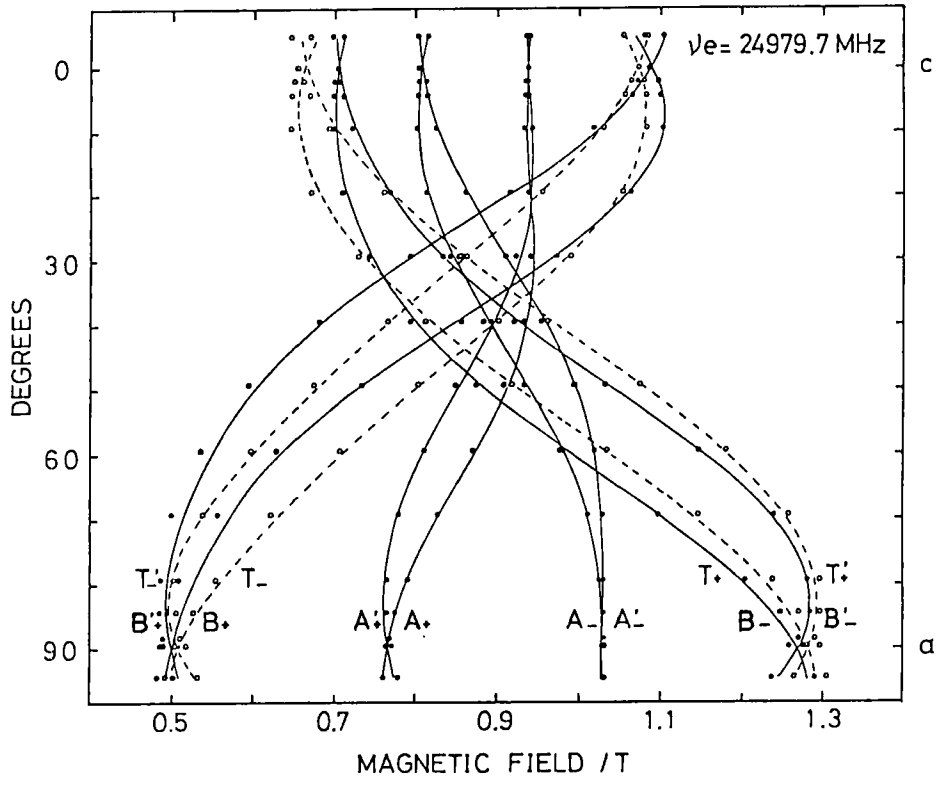


FIGURE 3. Angular dependence of the resonance field in the ca-plane at 77 K. The solid and open circles are the observed values and the solid and broken lines are the calculated values for the quintet and triplet states, respectively.

The first term represents the electronic Zeeman energy and the others the fine-structure energy. Figure 3 shows the angular dependence of the resonance fields of the $\Delta M_S = \pm 1$ allowed transitions for the rotation of the magnetic field in the ca plane. A third-order perturbation calculation with S = 1 for $T_{\pm}$ and S = 2 for $A_{\pm}$ and $B_{\pm}$ reproduced well the observed values as shown in this figure. The spin Hamiltonian parameters determined are: g = 2.003, D = $\mp$0.38821 cm^{-1}, and E = $\pm$0.01437 cm^{-1} for S = 1, and g = 2.003, D = $\pm$0.1288 cm^{-1}, and E = $\mp$0.00085 cm^{-1} for S = 2. In addition, the principal axes of the fine structure tensor D_T for S = 1 agree with those of the tensor D_Q for S = 2, indicating that both the triplet and quintet states arise from the same molecule.

Weakly Interacting Model

The fine structure tensors determined above show that $\mathbf{D}_T$ and $\mathbf{D}_Q$ are coaxial and $\mathbf{D}_T = -3\,\mathbf{D}_Q$. This particular relationship between the triplet and quintet states can be understood by a weakly interacting model between the high-spin systems.[1] The analysis based on this model clearly interprets not only the above properties of the fine structure tensors but also the nature of the magnetic interaction via the oxygen bridge.

The spins in BPDE may be regarded as composed of two groups of spins within each of which the spins strongly couple to form a triplet state; on the other hand, these groups couple weakly with each other via the oxygen bridge. The spin Hamiltonian for this system may be written as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{int} \tag{2}$$

where

$$\mathcal{H}_i = g_i\beta\mathbf{H}.\mathbf{S}_i + \mathbf{S}_i.\mathbf{D}_i.\mathbf{S}_i, \qquad i = 1, 2 \tag{3}$$

$$\mathcal{H}_{int} = -2J^{eff}\,\mathbf{S}_1.\mathbf{S}_2. \tag{4}$$

$\mathcal{H}_i$ stands for the spin Hamiltonian of the triplet groups, and $\mathcal{H}_{int}$ for that of interaction between these groups. Since we assume weak interaction, only a scalar exchange interaction is

taken into account. For the present model $S_1 = S_2 = 1$, and $g_1 = g_2 = g = 2.003$. Using the transformation properties of angular momentum and tensor operators, the Hamiltonian can be rewritten with the total spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ as

$$\mathcal{H} = -J^{eff}\,[S(S+1) - 4] + g\,\beta\mathbf{H}.\mathbf{S} + \mathbf{S}.\mathbf{D}_S.\mathbf{S}, \qquad (5)$$

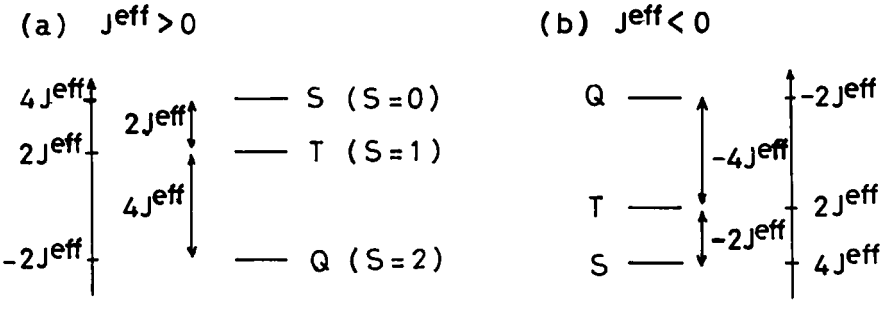
where $\mathbf{D}_S$ for S = 1 and 2 are respectively given by

$$\mathbf{D}_T = (1/6)(\mathbf{D}_1 + \mathbf{D}_2), \qquad (6)$$

$$\mathbf{D}_Q = (-1/2)(\mathbf{D}_1 + \mathbf{D}_2). \qquad (7)$$

From Eqs. (6) and (7) we obtain the observed relationship $\mathbf{D}_T = -3\,\mathbf{D}_Q$. It should be noted that such a relationship between the fine structure tensors is characteristic of the spin sublevels arising from the weakly interacting triplet pairs.

From Eq. (5) we have the following scheme depending upon whether the sign of J^{eff} is positive (ferromagnetic) or negative (antiferromagnetic). Hence, if J^{eff} assumes a negative value, the

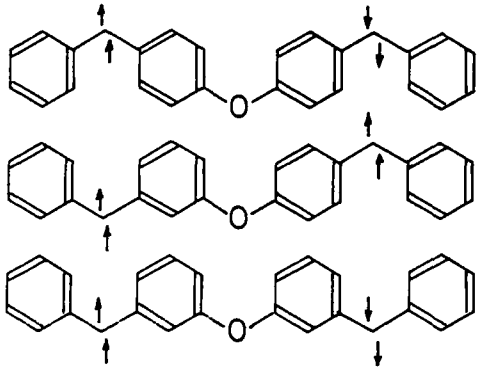


energy levels of the spin system are located as shown in Scheme (b). The observed temperature dependence clearly shows that the spin alignment in 4,4'-BPDE corresponds to this case, i.e., antiferromagnetic. The $2J^{eff}$ value was estimated to be -15 cm^{-1} from the temperature dependence of the triplet and quintet signal intensities.

On the other hand, similar ESR experiments on 3,4'-BPDE showed that this molecule is ground state-quintet and that its spin alignment corresponds to Scheme (a), i.e., ferromagnetic,

the $2J^{eff}$ value being 7 cm^{-1}. In the case of 3,3'-BPDE, ESR measurements indicated scheme (b). However, the triplet and quintet energy levels observed are so close with each other that the determination of J^{eff} was difficult from intensity measurements down to 2 K.

The above experimental results are summarized below:



4,4'-BPDE: antiferromagnetic

3,4'-BPDE: ferromagnetic

3,3'-BPDE: (antiferromagnetic)

This clearly shows that the role of the oxygen bridge on spin alignment is dependent on the position of the bridge, indicating the importance of topology similarly to the case of spin alignment in pi electron networks. The mechanism of spin exchange via the oxygen bridge is discussed below.

SUPEREXCHANGE MECHANISM

Heisenberg Model

In a previous paper,[16] we have shown that a method for obtaining exact numerical solution of the Heisenberg Hamiltonian is useful for the prediction of energy levels of organic high-spin molecules, and that it elucidates both the ground and low-lying excited spin states of pi electron networks with non-bonding orbitals (n orbitals) in a molecular plane. Calculation of the spin states of a,a'-BPDE has revealed that this method also serves to deal with the weak interaction via the oxygen bridge.

As described in the previous paper,[16] the spin coupling in a molecule is characterized, in valence bond theory, by the Heisenberg Hamiltonian

$$\mathcal{H} = -2 \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \qquad (8)$$

where $\mathbf{S}_i$ ($\mathbf{S}_j$) is the spin operator associated with the carbon site i (j) in the molecule. Magnetically, we may regard a,a'-BPDE as composed of two high-spin moieties A and B which interact weakly via the oxygen bridge. Then this Hamiltonian may be divided into three parts;

$$\mathcal{H} = -2 \sum_{i,j\subset A} J_{ij}^{A} \mathbf{S}_i \cdot \mathbf{S}_j - 2 \sum_{i,j\subset B} J_{ij}^{B} \mathbf{S}_i \cdot \mathbf{S}_j - 2J_{kl}^{AB} \mathbf{S}_k \cdot \mathbf{S}_l \quad (9)$$

where the first and second terms correspond to the spin coupling within units A and B, respectively, and the third term to their weak magnetic interaction; k and l refer to the positions of A and B connected by the bridge. It is to be noted that in the present calculation only the one-center and nearest-neighbor interactions are taken into account.

For conjugated alternant hydrocarbons, the sign of J_{ij}^{A} and J_{ij}^{B} is negative for the pi-pi interaction ($J_{\pi\pi} = -J$, $J > 0$), whereas positive for the one-center n-pi interaction ($J_{n\pi} = J' > 0$) at divalent carbon atoms.[16] We introduce here the third parameter $J'' = J_{kl}^{AB}$ to describe the weak magnetic interaction between units A and B; the magnitude of J" is estimated below. Using the Lanczos method, we can exactly solve the Heisenberg Hamiltonian (9) for the ground and several low-lying excited states by numerical diagonalization of the matrix derived from the full basis set of the spin system $|S_{1z}, S_{2z}, \ldots, S_{Nz}\rangle$ ($S_{iz} = \pm 1/2$).[16]

The superexchange interaction through the filled pi orbital localized on the oxygen atom is expected to play an important role in the spin coupling between the two diphenylmethylene moieties. From Anderson's formula,[22] this superexchange interaction can be expressed by[23]

$$J_{kl}^{AB} = J'' = -|b_{kl}|^2/U \quad (10)$$

where U is the repulsion of two electrons on the same site and b_{kl} the transfer integral for the electron that transfers, with preserving its spin, from the carbon site k to l connected with each other by the oxygen bridge. The magnitude of b_{ij} is proportional to the overlap integral between the p orbital on the

oxygen atom and that on the adjacent carbon atom, and it can be estimated to be 0.70 eV.[23] On the other hand, the electron repulsion U is approximately given by U = I - A = 10.84 eV, where I and A are the valence state ionization potential and the electron affinity of the carbon atom, respectively.[21] From these approximations we obtain -365 cm^{-1} or 0.045 eV for J_{kl} in Eq. (10).

In the previous paper[16] J was estimated to be 1.5 eV and J'/J to be 0.2, since these values gave the best fit to the energy and spin alignment of the pi network of high-spin molecules. It is known that the superexchange interaction is normally smaller than 2000 cm^{-1} and that its sign is negative or antiferromagnetic for the 180° superexchange.[24] Therefore, we have varied the J"/J ratio from 0 to -0.2 (J" < 0, and J > 0). Actually, we have calculated these quantities for a,a'-bis(methylene)diphenylether (a,a'-BMDE), in which each of the two end phenyl rings of a,a'-BPDE is replaced by a proton to reduce the dimensionality of the Hamiltonian matrix. This is because the dimensionality is given by 2^N, N being the number of of the sites, which is for a,a'-BPDE beyond the limit (N = 21) of our computer (HITAC S810/10).

It is reasonably expected that the electronic structure and spin distribution of a,a'-BMDE does not differ much from those of a,a'-BPDE through this replacement: we have confirmed such similarities using a UHF generalized Hubbard Hamiltonian approach[4] where the dimensionality expands much less rapidly with the increasing number of carbon sites.

Figure 4 depicts the energy level diagram for a,a'-BMDE as a function of J"/J. The solid curves represent the energy of the spin states near the ground state; these were calculated from the exact numerical solution of the Heisenberg Hamiltonian. The salient features of this diagram are consistent with our experimental results, i.e., the exchange via bridge is ferromagnetic for 3,4'-BPDE and antiferromagnetic for 4,4'- and probably also for 3,3'-BPDE. The arrow in Figure 4 indicates the position for J"/J = -0.030 which corresponds to J" = -365 cm^{-1} estimated above.

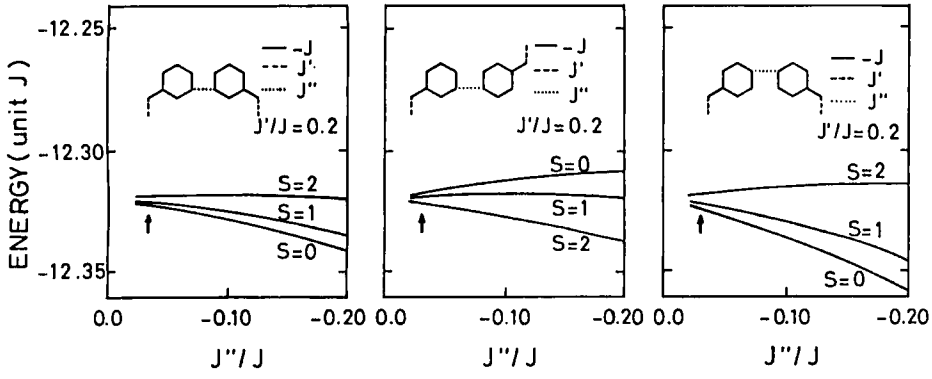


FIGURE 4. Energy level diagram for the ground and low-lying excited states as a function of J"/J. (a) 3,3'-BMDE, (b) 3,4'-BMDE, and (c) 4,4'-BMDE.

Sign of the Exchange Integral as Determined by Topology

Since J^{AB} represents the weak magnetic interaction via the bridge, it is evident that J^{AB} is much smaller than $J_{\pi\pi}$ and $J_{n\pi}$. Hence, the third term in the Heisenberg Hamiltonian in Eq. (9) may be regarded as a small perturbation. From this perturbation approach we can derive the equation[23]

$$J^{eff} = J_{kl}{}^{AB} \rho_k{}^{A} \rho_l{}^{B} / 4S_A S_B \qquad (11)$$

which relates the exchange integral J^{eff} in Eq. (5) to the product of the spin densities at the bridge positions k and l in units A and B, respectively. Figure 5 depicts the spin density distribution in the phenylmethylene moiety which was calculated from the exact numerical solution of the Heisenberg Hamiltonian. Since the spin densities at the 3- and 4-positions have the opposite sign to each other, $\rho_3{}^{A}\rho_4{}^{B}$ is negative, while both $\rho_3{}^{A}\rho_3{}^{B}$ and $\rho_4{}^{A}\rho_4{}^{B}$ are positive. From Eq. (10) $J_{kl}{}^{AB} < 0$ for the super-exchange mechanism, thus we have the conclusion that J^{eff} is ferromagnetic in 3,4'-BMDE while antiferromagnetic in 3,3'- and 4,4'-BMDE.

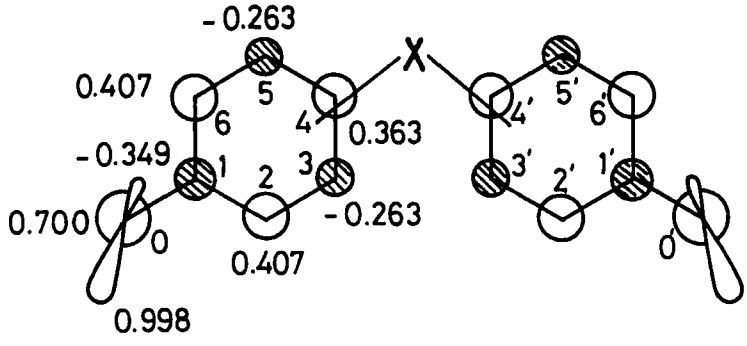


FIGURE 5. Spin density distribution in the phenylmethylene moiety.

From Eq. (12) we can evaluate J for a,a'-BMDE using J_{kl}^{AB} = = J" = -365 cm^{-1} and the spin density distribution shown in Figure 5. The calculated values are listed in Table I. Since the spin distribution of a,a'-BPDE is expected to be not much different from that of a,a'-BMDE as mentioned in the preceding section, we can compare these calculated exchange integrals with the values observed from a,a'-BPDE. It can be seen that agreement between theory and experiment is reasonably good considering the approximation introduced here.

TABLE I Calculated and observed exchange integrals ($2J^{eff}$) in cm^{-1} The calculated values are for BMDE and the observed values are for BPDE.

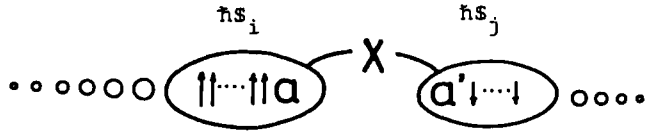
(a,a')	Calculated	Observed
3,3'	- 13	(- 3)
3,4'	+ 17	+ 7
4,4'	- 24	- 15

A MODEL COMPOUND OF ORGANIC FERRIMAGNETS

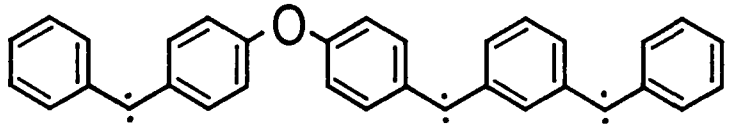
Organic ferrimagnetism appears to be also a target in the research field of organic magnetism. Buchachenko has proposed

ferrimagnetic mixed crystals composed of doublet radicals and triplet biradicals or polyradicals, anticipating the intermolecular exchange interaction in the crystal to be antiferromagnetic.[25] This idea may be classified as a through-space approach utilizing intermolecular exchange. We propose here, as a through-bond approach, ferrimagnetic macromolecules composed of different species of high-spin molecules by exploiting the intramolecular antiferromagnetic exchange interaction investigated above.[26]

This concept is shown in the following diagram:



This is the minimum unit of such a organic ferrimagnet in which two non-identical high-spin moieties with spin multiplicities S_i and S_j are coupled by an antiferromagnetic bridge to yield the residual spin $|S_i - S_j|$. As a model compound we have synthesized a molecule shown below utilizing the oxygen bridge connecting



ground-state triplet diphenylmethylene and ground-state quintet m-phenylenebis(phenylmethylene) at the 4- and 4'-positions, respectively, and we designate it as 4T4'Q-ether for brevity.

The trisdiazo precursor was prepared from the corresponding 4-hydroxybenzophenone and 4-bromodiketone via the following sequence of reactions: Ullmann, condensation with hydrazine, and oxidation with activated MnO_2. Benzophenone was chosen as a host molecule for mixed single crystals. Experimental procedure is the same as that for a,a'-BPDE.

Figure 2 (a) shows a typical ESR spectrum observed at 4.2 K after photolysis with the external magnetic field applied parallel to the a axis of the host crystal. The spectrum

consists of the strong lines labeled by $T_{\pm}$ and the weak unlabeled lines. The latter were ascribed to byproducts identified as belonging to ground-state triplet and quintet carbenes whose diazo precursors were formed during preparation of mixed crystals.

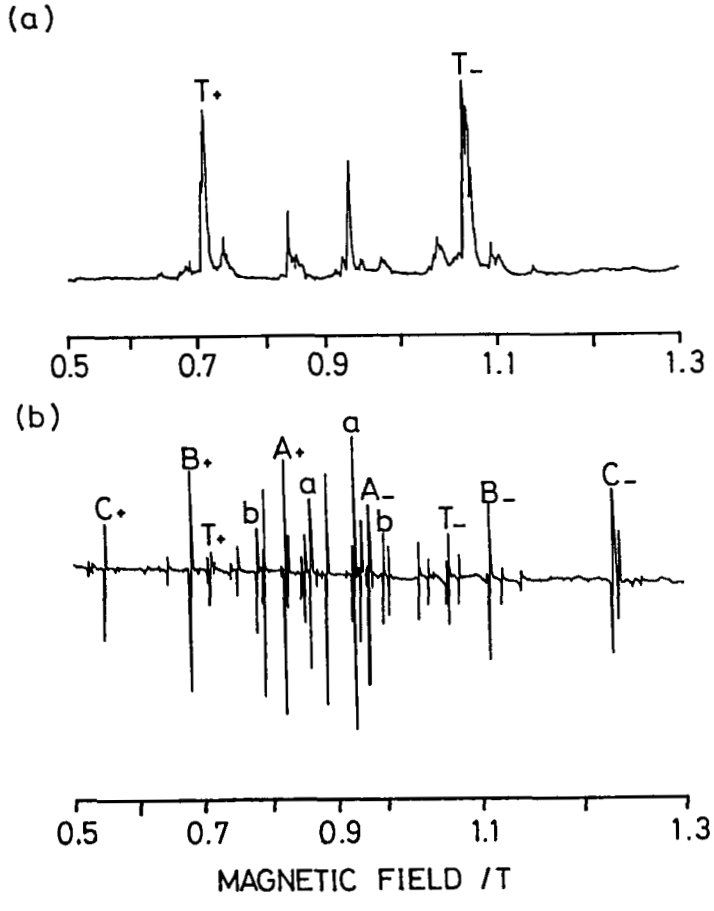


FIGURE 6. Temperature dependence of the ESR spectrum of 4T4'Q-ether. H//a. Observed at (a) 4.2 K immediately after photolysis and (b) 77 K.

The doublet signals $T_{\pm}$ was concluded as due to a triplet state, since the angular dependence of their resonance fields are well described by the spin Hamiltonian (1) with S = 1, g = 2.003, D_T = +0.24465 cm^{-1}, and E_T = -0.03433 cm^{-1}. The absolute sign of

the fine structure parameters was determined from relative signal intensities at low temperature.

Figure 6 (b) shows the ESR spectrum observed at 77 K. The new set of the lines labeled by a and b has a pattern characteristic of the four $\Delta M_S = \pm 1$ allowed transitions from a quintet spin sublevels, while another new set of the lines $A_{\pm}$, $B_{\pm}$, and $C_{\pm}$ has a pattern characteristic of those from a septet spin sublevels. Their angular dependence also obeys the prediction from the spin Hamiltonian (1) with S = 2, and 3. The analysis of the spectra yielded as preliminary values $D_Q = +0.047$ cm^{-1} for the quintet state and $|D_S| = 0.067$ cm^{-1} or the septet state. Thus three spin states with S = 1, 2, and 3 were identified.

The temperature dependence observed in the range of 1.7 to 180 K was completely reversible. With increasing temperature, the S = 2 signals, a and b, first appeared at about 10 K and subsequently the S = 3 signals, $A_{\pm}$, $B_{\pm}$, and $C_{\pm}$, appeared and gained their intensity, while the S =1 signals $T_{\pm}$ diminished their intensity. This temperature dependence clearly shows the triplet ground state with the thermally excited quintet and septet states, the septet state being highest.

The weak interaction model also applies to the spin system with non-identical high-spin moieties and it satisfactorily correlates the ESR spectra of the triplet, quintet, and septet states as well as their energy levels. In this case, the exchange energy corresponding to the first term of Eq. (5) becomes $-J^{eff}[S(S+1) - 8]$,[1,23] i.e.,

$-4J^{eff}$ for S = 3 (septet)

$2J^{eff}$ for S = 2 (quintet)

$6J^{eff}$ for S = 1 (triplet).

Since S = 1 is the ground state, J^{eff} is negative (antiferromagnetic) as expected from the experiment for a,a'-BPDE. From the temperature dependence of signal intensity J^{eff} was estimated to be -4 cm^{-1}.

Thus the ground-state triplet is realized as the residual spin due to ferrimagnetic interaction in the model compound of organic ferrimagnets. This high-spin molecule may be regarded as

a counterpart of an inorganic metal complex of Cu^{2+} (S = 1/2) and Mn^{2+} (S = 5/2) reported by Kahn et al.[26] On the other hand, preliminary experiment reveals that 3T4'Q-ether shows the ferromagnetic exchange whereas 3T3'Q-ether gives either exchange depending on its molecular conformation. These findings make it possible to control the high-dimensional spin alignment by the through-bond approach. The existence of such molecules with antiferromagnetic exchange through bridges indicates the possible occurrence of organic ferrimagnetism for properly designed macromolecules.

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REFERENCES

1. K. Itoh, Pure Appl. Chem., 50, 1251 (1978).
2. K. Itoh, Chem. Phys. Lett., 1, 235 (1967).
3. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, J. Am. Chem. Soc., 89, 5076 (1967).
4. Y. Teki, T. Takui, T, Kinoshita, S. Ichikawa, H. Yagi, and K. Itoh, Chem. Phys. Lett., 141, 201 (1987).
5. Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, J. Am. Chem. Soc., 108, 2147 (1986), and references therein.
6. S. Morimoto, K. Itoh, F. Tanaka, and N. Mataga, Preprints of the Symposium on Molecular structure, Tokyo, p. 76 (1968).
7. N. Mataga, Theor. Chim. Acta, 47, 297 (1968).
8. K. Itoh, Bussei, 12, 636 (1971).
9. A. A. Ovchinnikov, Theor. Chim. Acta, 47, 297 (1978).
10. D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Matsen, J. Chem. Phys., 77, 3101 (1982).
11. S. A. Alexander and D. J. Klein, J. Am. Chem. Soc., 110, 3401 (1988).
12. N. Tyutyulkov, P. Schuster, and O. E. Polansky, Theor. Chim. Acta, 63, 291 (1983).
13. C. I. Ivanov, N. Tyutyulkov, G. Olbrich, H. Brenzen, and O. E. Polansky, Theor. Chim. Acta, 73, 27 (1988).
14. N. Nasu, Phys. Rev., B33, 330 (1986).
15. H. Fukutome, A. Takahashi, and M. Ozaki, Chem. Phys. Lett., 133, 34 (1987).
16. Y. Teki, T. Takui, M. Kitano, and K. Itoh, Chem. Phys. Lett., 142, 181 (1987).

17. H. M. McConnell, Proc. R. A. Welch Found. Chem. Res., 23, 114 (1967).
18. R. Breslow,B. Jaun, R. Q. Klutz, and C. Z. Xia, Tetrahedron, 38, 863 (1982); R. Breslow, Pure Appl. Chem., 54, 927 (1982).
19. J. S. Miller, A. J. Epstein, and W. M. Reiff, Chem. Rev., 88, 201 (1988).
20. N. D, Mermin and H, Wagner, Phys. Rev. Lett., 17, 1133 (1966).
21. H. O. Prilchand and H. A. Skinner, Chem. Rev., 55, 745 (1955).
22. P. W. Anderson, Phys. Rev., 115, 2 (1959).
23. Y. Teki, T. Takui, M. Kitano, and K. Itoh, Chem. Phys. Lett., to be published.
24. J. Kanamori, J. CPhys. Chem. Solids, 10, 87 (1959).
25. A. L. Buchachenko, C. R. (Dokl.) Acad. Sci. USSR, 244, 1146 (1979).
26. K. Itoh, T. Takui, Y. Teki, and T. Kinoshita, J. Mol. Electr., 4, 181 (1988).
27. Y. Pei, O. Kahn, J. Sletten, J. Renard, R. Georges, J. Gianduzzo, J. Curely, and Q. Xu, Inorg., Chem., 27, 47 (1988).