DESIGN AND CONSTRUCTION OF ORGANIC MAGNETIC MATERIALS. APPROACHES FROM HIGH-SPIN POLYMERS

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ABSTRACT

Molecular design of how to align many electron spins in parallel to one another, i.e., in a ferromagnetic fashion, is discussed on the basis of the topological symmetry of π-conjugated molecular frameworks. Typical examples of well-defined high-spin ($S = 4$ and 5) poly(m-phenylenecarbene) are first given. The synthesis and characterization of high-spin poly(acetylenes) and poly(diacetylenes) carrying pendant radicals, carbenes and nitrenes are then discussed. These efforts lead up to the establishment of the paramagnetism of very high-spin species. Interaction leading to the ferromagnetic ordering of the high-spin molecules is needed to realize macroscopic spins. McConnell's theories predicting such possibilities between a pair of organic free radicals with and without donor/acceptor interactions have been demonstrated to be operative in effecting long-range order. Some primitive organic magnetic materials reported in the literature will be reviewed. Lastly, a potential use of these organic magnetic materials generated by photochemical reactions is discussed.

INTRODUCTION

Magnets are made of some metals, alloys, metal/metal compounds, metal oxides, and other metal complexes of the transition and lanthanoid elements. Strong magnetism has never been found in organic materials. Isn't it intrinsically possible to prepare magnets from organic polymers or plastics? In order to answer this question affirmatively, we have to establish molecular design of how to obtain unprecedented macroscopic spins of long-range order in organic molecules and molecular solids.

The large majority of organic molecules have closed-shell electronic structure, i.e., they have a singlet ground state with equal numbers of electrons having alpha and beta spin. Most organic compounds are therefore good electric insulators and magnetically inactive. Strictly speaking, they are diamagnetic, i.e., they are weakly repelled out of the external magnetic field. There are some organic molecules that have open-shell structures where not all electrons are paired. Many of these molecules have one unpaired electron and therefore a doublet ground state. These free radicals show paramagnetic properties. Once two doublet centers are introduced as in diradicals and radical pairs, the alignment of the spins becomes an issue. The Coulombic repulsion between the electrons lifts the zeroth-order degeneracy and gives rise to singlet and triplet states of different total energy for these chemical entities. Chemists already know the conditions for having the ground triplet states and the importance of the singlet/triplet radical pairs in free radical reactions. These should serve as a good starting point for exploiting strong magnetic properties out of organic molecular systems. However, little is known on molecular entities that have more than two unpaired electrons, i.e., the quantum number (S) of the spin angular momentum equal to or greater than 3/2. This is due firstly to the high bonding energy of the K- and L-shell valence electrons in typical organic molecules that leads to their closed-shell electronic structure. There is a large energy gap between the valence and conduction bands making most organic compounds good electric insulators. Secondly, geometrical symmetry of organic molecules is not necessarily high and therefore there are not very many degenerate orbitals. In contrast, high-spin states are the rule rather than the exceptions in transition and lanthanoid metal salts and complexes. The 3d and 4f atomic orbitals in these metal atoms are originally five and seven times degenerate, respectively. Even when the degeneracy is lifted by a set of ligands of lower symmetry, they are still high-spin as long as the ligand field is not very strong.

The same is true for spin alignment in organic molecular assemblies. In crystals, liquid crystals, membranes, and other organized systems, of persistent organic radicals, the unpaired electrons have a stong tendency to behave as randomly oriented spins or the spins align antiparallel next to another. After all, the theory of chemical bonds by Heitler and London dictates the stablization of the antiparallel alignemt of two spins in two approaching orbitals with increasing overlap. Very few examples are known to date in which the electron spins of the neighboring molecules are aligned in parallel. Molecular solids in which more than two unpaired electrons are aligned in parallel among neighboring molecules should be taken into consideration.

SPIN ALIGNMENT WITHIN A MOLECULE AND AMONG MOLECULES. CONCEPTUAL FRAMEWORK OF ORGANIC MOLECULAR MAGNETS

Strong magnetic properties could result from a large assembly of the electron spins. The latter is, however, the necessary but not sufficient conditions for establishing the former. Co-operative phenomena or long-range orders, namely ferro- and ferrimagnetic coupling, have to be introduced among the electron spins for constructing macroscopic spins in molecular systems. Otherwise, the spins would end up in random orientation showing macroscopic paramagnetism, since the energy of interaction of the individual spin with the external magnetic field and that of dipolar interaction between the spins are smaller than the thermal energy kT under conventional experimental conditions of $T > 0$ K.

There appear to be two basic approaches to realization of strong molecular magnets [1]. These principles can be sought either within a molecule or between molecules (Figure 1). Approach A-1 will be emphasized in the following discussion.

A. Ferromagnetic ordering of the electron spins.
A-1. Construction of high-spin molecules exhibiting superparamagnetism. Since the magnetization is proportional to the size of the magnetic moment, it is desirable to have the magnetic moment as high as possible.
A-2. Design of molecular stacking leading to the ferromagnetic interaction between open-shell molecules. This is necessary not only for the realization of organic ferromagnets even from an assembly of doublet molecules but also for establishing long-range order between high-spin molecules (A-3 in Figure 1). Ferromagnetism in α-iron and chromium dioxide would serve as original models for this approach. In α-iron, for example, a microcrystalline particle of radius 20 Å contains ca. 5,000 spins and is considered to form a single domain structure.

B. Simulation of ferrimagnets. This approach starts by accepting the trend of Mother Nature: a strong tendency of two electrons in two overlapping orbitals aligning antiparallel to another. When two magnetic moments of equal strength are taken into account, this leads of course to antiferromagnetic interaction and eventual formation of a covalent bond. But what if two spins of unequal size are aligned alternately? The neighboring two spins cancell each other out, but only partly. The residual moments are in parallel to make macroscopic spins.
B-1. Construction of high-spin molecules having ferrimagnetic intramolecular coupling.
B-2. Alternate stacking of the molecules with different spins. Strong magnetism in ferrites is a prototype of this category.

DESIGN OF HIGH-SPIN ORGANIC MOLECULES THAT HAVE MANY SINGLY OCCUPIED ORBITALS

The question of how to design high-spin organic molecules reduces to the problem of how to arrange many singly occupied orbitals in a molecule. A straightforward answer to the above question would be given by consideration of topological symmetry of conjugated molecules. There are a series of alternant hydrocarbons called

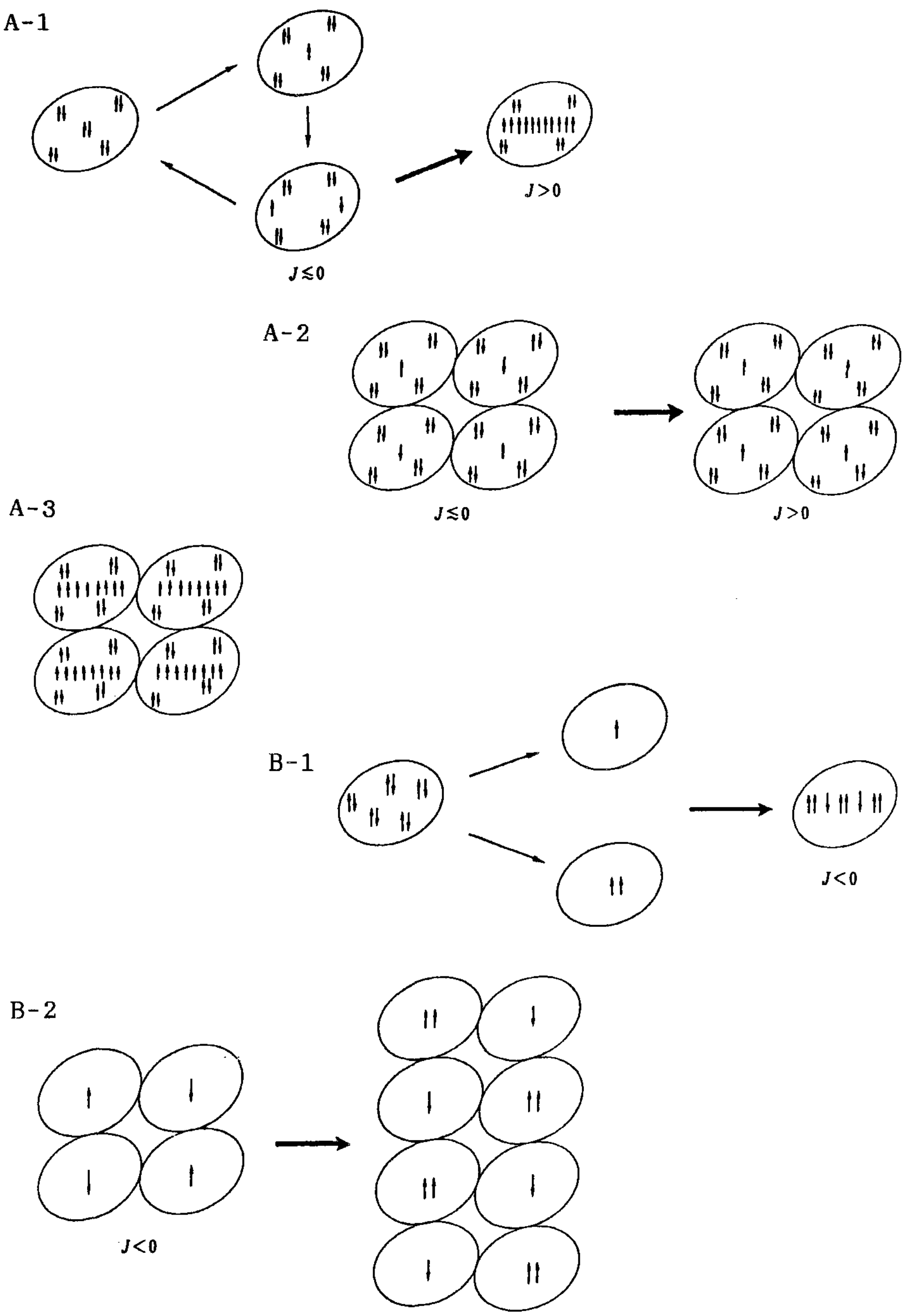


Figure 1. Conceptual sketches for approaches toward strong molecular magnets. Arrows and ellipsoids stand for the electron spins and molecular boundaries, respectively. Thick arrows show where careful molecular design is necessary (paired spins are often left out).

non-Kekule molecules for which we cannot write enough number of bonds and therefore can have degenerate half-filled orbitals in spite of the lower geometrical symmetry of the molecules.

Longuet-Higgins proposed that an alternant hydrocarbon (AH) has at least N - 2T singly occupied non-bonding molecular orbitals (NBMO) where N is the number of carbon atoms in the AH and T is the maximum number of double bonds occurring in any resonance structure [2]. Let us take for example three isomeric benzoquinodimethanes (**1**) in which the numbers of NBMO's are 8 - 8 = 0, 8 - 6 = 2, and 8 - 8 = 0, respectively. Therefore o-and p-isomers (**o-1** and **p-1**, respectively) are predicted to have closed-shell electronic structures with singlet ground states. The prediction is in good agreement with our chemical intuition that classical Kekule structures can be written for these two isomers and with their H-1 NMR spectra successfully observed.

The m-isomer (**m-1**) is predicted to have two degenerate NBMO for which the seventh and eighth electrons are supplied after three bonding MO's are filled with six electrons in accordance with Pauli's exclusion principle. According to Hund's rule, the last two electrons should be accommodated one each to the two degenerate NBMO's. Although in the C_{2v} point group and without any axis higher than two-fold symmetry, **m-1** is therefore predicted to be in a triplet ground state as suggested by its non-Kekule structure. A more quantitative evaluation was put forward by Baudet who estimated by SCF-CI calculations the triplet state being more stable than the singlet by 0.34 eV (7.8 kcal/mol).

Valence-bond theories have been developed by Ovchinnikov [3] and Klein [4] using the expansion of the Heisenberg Hamiltonian: $\mathcal{H} = -2J\mathbf{s}_1 \cdot \mathbf{s}_2$, where $\mathbf{s}_1$ and $\mathbf{s}_2$ are spin operators. According to these theories, the carbon atoms in alternant hydrocarbons are starred in such a way that the stars are created as many as possible and no two stars come next to each

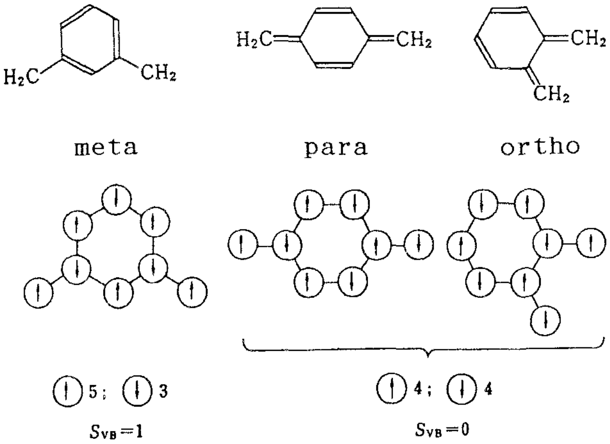


Figure 2. Gamma graphs of the isomeric benzoquinodimethanes **1**.

other. When the numbers of the starred and unstarred atoms are n^* and n, S of the AH is given by Eq. 1:

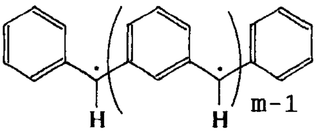
$$S = (n^* - n)/2 \qquad (1)$$

m-Benzoquinodimethane is predicted to be S = 1 since $n^* = 5$ and n = 3. For **o-1** and **p-1**, $n^* = n = 4$ and therefore S = 0. The gamma graphs of the isomeric benzoquinodimethanes (**1**) are collected in Figure 2. Once an up-spin is placed at one benzylic position of starred carbon atom, spin polarization places down-spins at unstarred carbon atoms, ending in the other radical centers with up-spin in the m- and down-spins in the o- and p-isomers, respectively.

Poly(m-phenylenecarbenes)

Polyradicals **2** consisting of m diphenylmethyl units connected at m-positions would have S = m/2 and spin multiplicities of (m + 1). The exchange interactions between the radical centers in **2** are estimated to be 0.2055 and 0.0012 eV for the first and second neighbors, respectively [5].

Let us now replace each doublet radical center in **2** with a triplet carbene to form polycarbenes **3**. The system was originally conceived and proposed by Mataga as early as in 1968 as a model for one-dimensional organic ferromagnets [6]. The dicoordinated carbon atom in diphenylcarbene carries a more or



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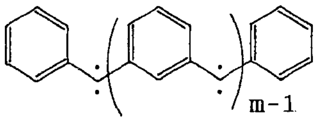

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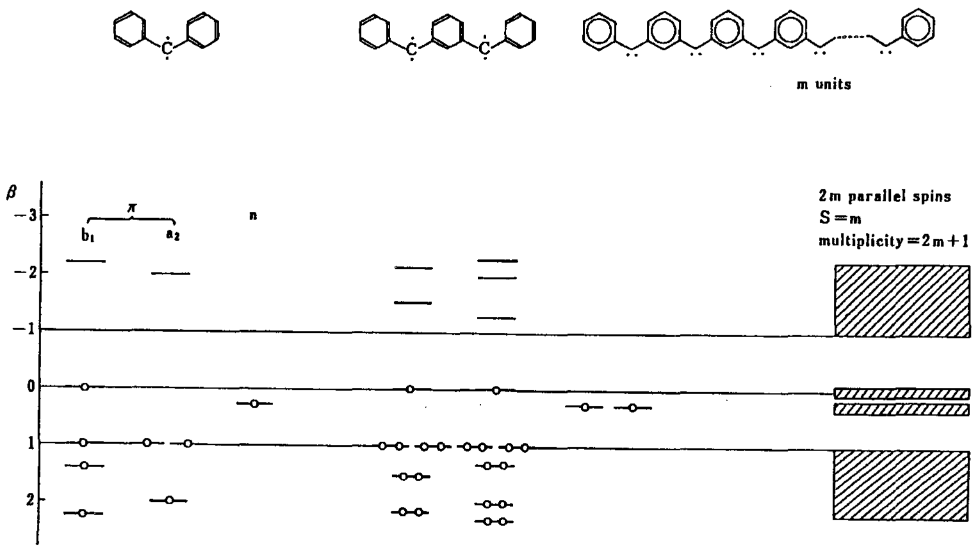


Figure 3. Hückel molecular orbital pictures of poly(m-phenylenecarbenes) **3**.

less localized n-spin in the sp^2-hybridized in-plane orbital and another delocalied π-spin in the p_z orbital. The duality is very much reminiscent of the sd interaction of the electron spins in magnetic transition metals. In the latter,the localized spins of high 3d character at the lattice centers are aligned via strong exchange coupling with the conduction electrons of high 4s character.

As the chain is elongated, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) remain unperturbed at the energy levels of β and $-\beta$, respectively. The energy gap between the valence band and the conduction band of the polymer remains constant with 2β, with 2m parallel spins in the impurity band (= NB levels)(Figure 3). The effective exchange energy between the carbenic centers are estimated by a theoretical study based on the periodic Kondo-Hubbard model to be ca. 0.2 eV (Nasu, 1986).

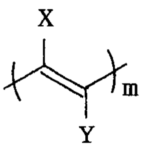
We have learned by our experience that **3** has some more merits than **2**. First, whereas it is rather difficult to generate the latter systematically, a series of the former can find the corresponding diazo compounds as suitable precursors from which they are produced by photolysis at cryogenic temperature. Second, the EPR fine structures of **3** are usually an order of magnitude wide-spread than those of **2**, making the analysis of the exchange interaction easier.

Tyutyulkov analyzed the cross-conjugted systems like **2** theoretically using the Coulson-Rushbrooke theorem and Wannier transformation of the Bloch MO [7]. His results hold multiple significance. First it was suggested by taking into account the interchain interaction of the quasi-one-dimensional polymer that critical temperature T_c in these systems may reach 10^2 - 10^3 K For a second, the radical centers of hydrocarbons **2** can be replaced by heteroatom-centered stable radicals such as nitroxyls. Their band structure is again characterized by a wide energy gap, in the middle of which there is a band of nearly degenerate quantum states.

Poly(acetylenes) and Other Conjugated Polymers

A series of **3** gave rise to novel high-spin organic molecules and served as good models for one-dimensional organic ferromagnets. In order to extend the system further and construct macroscopic spins of practical use, namely, to achieve organic superparamagnets or ferromagnets, however, it became clearer that **3** is far from ideal. It was deemed more practical and promising to introduce new structures in which the radical or carbene centers are attached to the fully conjugated main chains as pendants. In this way, one might be able to construct molecules that have hundreds of parallel spins rather straightforwardly [8].

Poly(acetylenes)(**4**), poly(diacetylenes)(**5**), poly(phenylenes)(**6**), poly(phenylenevinylenes)(**7**) and so on have been proposed as the main chains. The new molecular design that has to be developed concerns now with the question where to place the open-shell centers on the pendants in the side chains of the polymers. As a model for dimer units of poly(diphenyldiacetylenes)(**5b**), isomeric stilbene derivatives (**8**) carrying the



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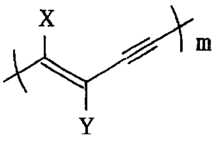

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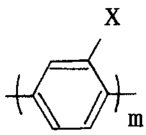

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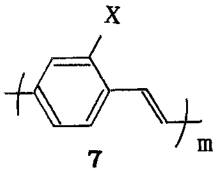
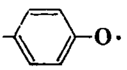
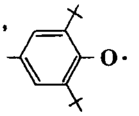


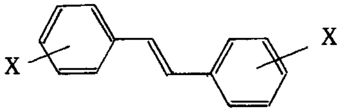
7

b: X=Y=Ph
c: X=H, Y=Ph
d: X=H,
Y=



d': X=H,
Y=



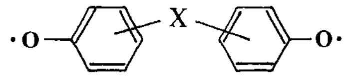


8(X=$\dot{\underset{\cdot}{C}}$Ph), **8a**(X=$CN_2$Ph)

phenylmethynyl groups were taken into account. According to Eq. 1, n = n* in **m,m'-8** and they differ by two in **m,p'-8**. Therefore, the former is predicted to have a singlet ground state. The interaction of the two radical centers in expected to be ferromagnetic in the latter and should lead to a high-spin ground state; a quintet state rather than a triplet since the spins in the n-orbitals at the carbenic centers are added.

When the monophenyl-substituted polymers, e.g., **4c** and **5c**, are taken into account, radical centers are predicted to be placed at the same position of every phenyl ring: all para- or all meta-positions. This is a very fortunate message to synthetic chemists in that regiostereoregular homopolymerization of phenylacetylenes, phenyldiacetylenes and so on can be

Table 1
Coupling of two phenoxyl radicals by various coupling spacers



X	S-T gap[a] m,p'-	m,m'-	p,p'-
none	12.5	-0.6	<<0[b]
CH=CH	6.5	1.4	<<0
CH=CH-CH=CH	6.0		<<0
C=C-C=C	2.7	0.8	<<0
p-C_6H_4	1.8	1.8	<<0
m-C_6H_4	- 0.2	2.3	2.3
C=O	1.9	0.7	0.8
O	2.8	-0.1	-4.5
NH	4.2	0.3	-10.3

a) AM1-CI triplet-singlet energy gaps in kcal/mol. The triplet is the GS where the gap is positive.
b) Kekule structures can be drawn.

employed for the construction of the desired polymers. The polymer carrying p-phenoxyl radicals **4d** is already on a short list of high-spin polymers predicted by Ovchinnikov [3]. Lahti performed a computational modeling of a pair of phenoxyls using the AM-1 semiempirical MO method with configurational interaction [10]. His results are collected in Table 1. The singly occupied MO's are no longer NBMO's due to heteroatom substitution. However, when certain conditions are fulfilled, as discussed by Tyutyulkov, the theorem can be generalized for some classes of non-classical heteronuclear systems.

According to Wegner, substituted 1,3-butadiynes undergo topochemically controlled polymerization when the molecules stack side by side and least atomic motions are necessary to effect polymerization [11]. Operationally there are four modes conceivable for the polymerization in crystals of a mono-substituted phenyldiacetylene **9** carrying a radical center at the m- or p-position of the phenyl ring: 1,1'/4',4'' and 1,4' polymerization in parallel and antiparallel stacks as shown in Figure 4a-d. Only types a and d in this Figure are expected to lead to ferromagnetic coupling between the radical centers.

It is not straightforward to obtain conjugated polymers with high content in pendant radicals; either chemical introduction of radicals into polymers is inefficient or radical centers cannot be kept intact during polymerization. A

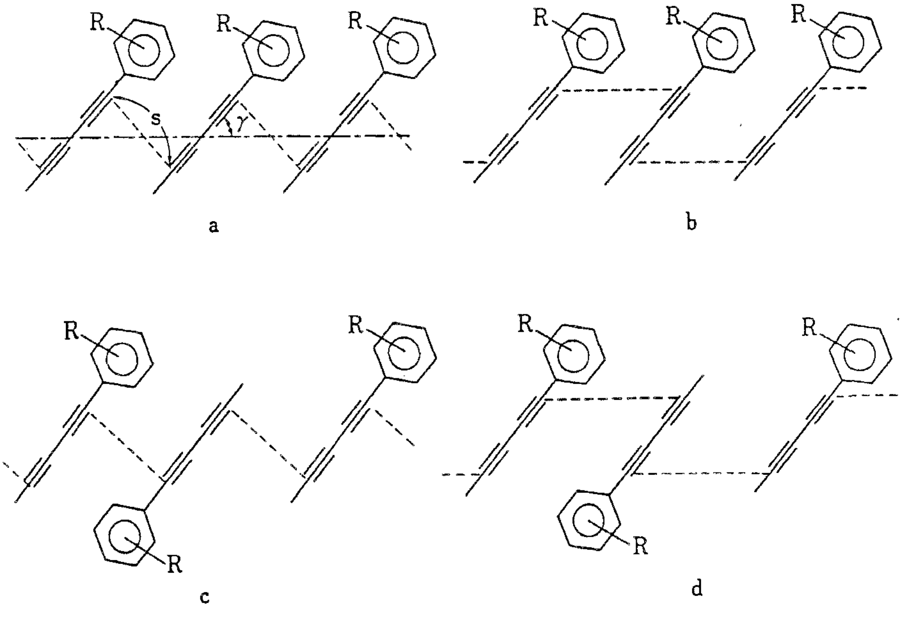


Figure 4. Schematic drawing showing the molecular packing and topochemical polymerization of diacetylenes **9** in crystals. The polymerization in the solid state is said to occur smoothly when $s = 2.4 \sim 4.0$ Å and $\gamma = 45^\circ$ [12].

possible way out for this problem has been proposed by Fukutome: doping of the closed shell cross-conjugated polymers to generate the open-shell centers. The polaronic interaction in these systems is discussed [9].

GENERATION AND CHARACTERIZATION OF HIGH-SPIN ORGANIC MOLECULES

Cross-conjugated Poly(m-phenylenecarbenes) 3

Encouraged by the experimental finding [13] that the dicarbene (**3**(m = 2)) had a ground quintet state, i.e., all four spins were ferromagnetically coupled, Iwamura and Itoh have set out for a project directed toward the construction of higher series of polycarbenes **3** [14].

All the polycarbenes were generated by photolysis at cryogenic temperature of the corresponding polydiazo compounds, e.g., **3a** which in turn were obtained through a series of standard synthetic reactions. Pentadiazo compound **3a**(m = 5) was doped in a single crystal of 1,3-dibenzoylbenzene and photolyzed with the 405-nm mercury line in an EPR cavity at 77 K to give **3**(m = 5) oriented with respect to the direction of an external magnetic field. When the z principal axis is oriented parallel to the external magnetic field, the system with S = 5 should generate eleven spin sublevels. Under a high-field approximation, ten allowed transitions ($\Delta M_S = \pm 1$) are expected to appear in ratios of 1:3:5:7:9:9:7:5:3:1. That is exactly what was observed (Figure 5). The resonance fields and signal intensities were well-reproduced by the exact diagonalization of the spin Hamiltonian with g = 2.003, D = -0.0168 and E = +0.0036 cm^{-1}, and S = 5, confirming **3**(m = 5) to be in the undecet state. Temperature dependence of the total signal intensity in the range 5 - 77 K showed that the observed nonet state is the ground state, while the other states are located at least 300 cm^{-1} above the ground state.

Magnetization of a sample of **3**(m = 4) dispersed in a benzophenone host was determined on a Faraday balance in the range 0-5 T at 2.1 and 4.2 K [15]. The data are plotted in Figure 6 together with those of typical paramagnetic transition metal salts [16]. The observed values follow the curves given by a Brillouin function with various J = S values. For iron alum, there are five singly occupied 3d atomic orbitals and therefore J = S = 5/2. In good agreement with this, the saturation value of the magnetization (M_S) is 5 M_B. For gadolinium sulfate octahydrate, there are seven singly occupied 4f orbitals, J = S = 7/2, and M_S = 7 M_B. These two M_S values are maxima for 3d transition metals and 4f lanthanides, respectively. The data for **3**(m = 4) agree nicely with the theoretical Brillouin function in which J = S = 4. The M_S value of a hydrocarbon surpassed for the first time those of transition metal ions. It should be noted that the magnetization value of **3** can still be increased in principle as well as in practice by increasing the number of the repeating units m. The higher homologs of the series are expected to behave at least as organic molecular superparamagnets.

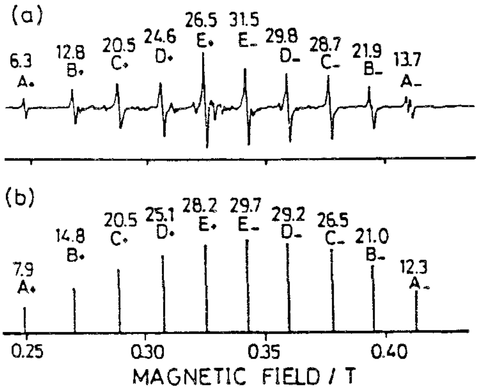


Figure 5. (a) An X-band (9438.9 MHz) EPR spectrum observed after photolysis of a mixed crystal of 1,3-dibenzoylbenzene with **3a**(m = 5) at 50 K in an ESR cavity. The external magnetic field is along the b axis of the former crystal (Pbca space group). (b) Theoretical lines expected of S = 5. The numbers above each line represent the relative signal intensities.

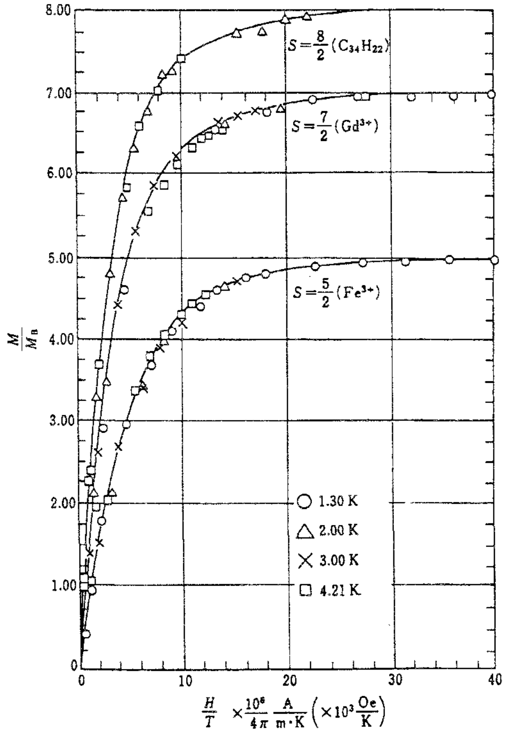


Figure 6. Magnetization curves for paramagnetic species with various J = S values. The magnetic moment of **3**(m = 4) is compared with those of transition metal and lanthanide ions here represented by $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$, respectively.

On the other hand, a sample of **3**(m = 4) in MTHF glass gave an inverse chi vs. T plots that showed a negative Weiss temperature of -22 K. The nonet species appears to to feel the antiferromagnetic molecular field at temperatures lower than 65 K. This observation suggests that molecular clusters of **3a**(m = 4) must have been formed during the preparation of the glassy sample in spite of rather low concentration of the diazo precursor and that the magnetic coupling in the clusters is antiferromagnetic as usually the case in molecular solids.

Polyacetylenes and Other Polymers Having Pendant Radicals

Model experiments on high-spin polymers: In order to test the guiding principles obtained theoretically for solving the question of where to place the radical centers in the side chains of **4**, **5**, **6** and **7** for aligning the electron spins, some experiments have been performed on model oligomers.

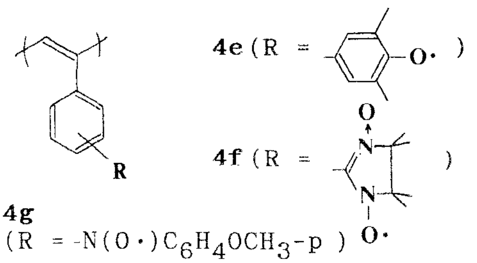
The isomeric stilbene dicarbenes (**8**) were generated in 2-MTHF matrices in an EPR cavity at 16 K [17]. The spectra obtained by the photolysis of the diazo compounds (**8a**), precursors to **m,p'-8** and **m,m'-8**, at 16 K exhibited conspicuous signals at ca. 250 mT characteristic of quintet species. They showed a contrasting temperature dependence; whereas the signal intensity due to **m,p'-8** decreased linearly with the reciprocal of temperature as dictated by Curie law, that of **m,m'-8** increased first and reached a maximum at 50 K and then decreased again. These results strongly suggest that **m,p'-8** has a quintet ground state, while that of **m,m'-8** is populated thermally but lies ca. 200 cal/mol (70 cm^{-1}) above the ground state. The two remote triplet diphenylcarbene moieties linked together through a carbon-carbon double bond are concluded to have sufficient interaction to form a ground quintet state in **m,p'-8** as predicted by theory. Similarly, when diphenyldiacetylenes having nitreno groups at the m,p' and m,m' positions (**9**) were generated, only the former showed the ground quintet state [18].

It is thus established experimentally that the regiostereoregular polymers **4b** and **5b** with the radical centers all at the m positions of the phenyls on one side of the main chain and all at the p positions of those on the other side of the main chain would be high-spin.

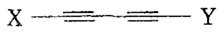
Poly(phenylacetylenes)(**4c**): Olefin-metathesis-type catalysts [19] and rhodium(I) catalysts [20] are effectively used for polymerization of substituted acetylenes. However, many persistent radicals and typical nitrogen-containing functional groups serve as good poisons for these catalysts. Therefore, either radical centers must be introduced after construction of the polymer skeletons or the catalysts have to be modified so that the Lewis acidity of the catalytic center may be reduced and yet the activity may be retained. Important polyacetylenes **4** studied so far are summarized in Table 2.
1) It is difficult to obtain samples with high phenoxyl radical contents, although the radical centers are sterically protected. It appears that, since the spin delocalization is

Table 2
Some representative poly(phenylacetylenes)(**4c**)
carrying pendant free radicals

	average molecular weight M_w	spin concentration spins/g
4d'	1×10^4	2.5×10^{20}
4e	4×10^4	4.4×10^{19}
m-4f	1.5×10^5	2.3×10^{21}
p-4f	———	2.4×10^{21}
4g	7×10^4	2.3×10^{20}



4g
(R = -N(O·)$C_6H_4OCH_3$-p)



9($X=Y=C_6H_4\dot{N}\cdot$)
10h($X=H, Y=C_6H_3$(m-t-BuNOH)(p-Cl))
10i($X=H, Y=C_6H_3$(m-t-BuNO·)(p-Cl))
10j($X=H, Y=C_6H_4$(p-CN_2H))
10k($X=H, Y=C_6H_4$(p-CN_2Ph))

considerable in **4d'** and **4e**, the radicals must be kinetically less stable at the ring and chain carbons where there are no steric protection.

2) The green to dark blue homopolymers carrying 2-(m- and p-ethynylphenyl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxides **4f** contained almost theoretical amounts of the nitroxyls, but the $1/\chi$ vs. temperature plots gave straight lines characteristic of $S = 1/2$ slope with very weak antiferromagnetic coupling. The magnetization vs. magnetic field strength data on the two isomeric samples at 1.8 K deviated slightly downward from the Brillouin functions with $S = 1/2$, revealing again the presence of antiferromagnetic coupling between the unpaired electrons. The expected ferromagnetic coupling among the radical centers in the side chains through the conjugated main chain was not operative in these polymers. In Ullman's nitronyl nitroxyls in **4f** [21], one unpaired electron is delocalized on the two equivalent N-O groups. However, as approximated by allyl radicals with three pi electrons or pentadienyl systems with seven pi electrons, there is a node at carbon-2 in the singly occupied molecular orbital. The spin density at that carbon atom which is attached to the phenyl ring is very small in size and negative in sign. Therefore, the disappointing results may be due to lower delocalization of the electron spins from the side chains into the main chain. Some steric congestion and conformational deformation must also be contributing to the lower exchange interaction through the main chain since the main chain and side chains cannot assume planar conformation; the effective conjugation length must be very short.

3) A polymer of p-bromophenylacetylene cross-linked with m-phenylenebis(acetylene) was lithiated and reacted with 2-methyl-2-nitrosopropane dimer to give insoluble cross-linked polymer [22]. Whereas the sample appeared to be a normal

paramagnet at cryogenic temperatures, it showed saturation magnetization at 100 K characteristic of high-spin species. 4) Much yet remains to be done as regards the choice of the pendant radicals. The ring-opening metathesis polymerization of cyclooctatetraenes [23] has not yet been applied to the construction of high-spin polyacetylenes.

Poly(phenyldiacetylenes)(**5c**): There appear to be two practical limitations in the preparation of high-spin polydiacetylenes based on the above molecular design and model experiments. First, since this polymerization is effected by heat or irradiation (including high-energy radiation to visible light) in the solid state and topochemically controlled [11,12], not all diacetylenes are amenable to the reaction. Second, since the polymers are very insoluble in ordinary organic solvents, radical centers have to be introduced in advance.

1-Phenyl-1,3-butadiyne derivatives carrying N-tert-butylhydroxylamino (**10h**) and stable t-butylnitroxyl (**10i**) groups have been prepared [24]. The crystal structure of triclinic **10h** from ether, mp 140 ° C, was determined to show that the molecules are stacked head-to-tail along the a/c diagonal direction as cases c and d in Figure 4. Since the distances between carbons 1 and 4' and 4 and 4' of the neighboring molecules are 4.55 and 4.72 Å, respectively, the polymerization is considered to take place in this direction. The one dimensional columnar stacks are bridged by intermolecular hydrogen bond between two hydroxylamino groups. Mixed crystals of **10h** and **10i** (1:<1) were polymerized in the solid state at 120 C to give black-violet microcrystals with metallic luster that showed a broad ESR signal at ca. 300 mT in addition to a normal signal centered at $g = 2.006$. The magnetization curve of this sample at 4.2 K agreed with the Brillouin function with $S > 1/2$. The $1/\chi$ vs. temperature plots in the 70 - 150 K region showed a Weiss constant of +18.0 K, suggesting the ferromagnetic coupling of the doublet centers. The Curie constant of the linear part of the plots showed that ca. 6 % of the monomer units in the sample was the isolated active nitroxyl.

Solid-state polymerizations of two diacetylene derivatives having p-diazo-methyl and p- -diazobenzyl groups (**10j** and **10k**, respectively) have been performed at 40 ~ 50 ° C to give dark violet polycrystalline samples. The diazo groups are intact under these conditions. When photolyzed in MTHF at cryogenic temperature in an ESR cavity, both **10j** and **10k** gave strong signals due to triplet monocarbenes; $D = 0.4666$ and $E = 0.0210$ cm^{-1} and $D = 0.3795$ and $E = 0.0181$ cm^{-1}, respectively. These signals obeyed Curie law in the temperature range 4.6 - 77 K. The photolyses of the polymer samples were carried out at 4.2 K within the cryostat of a Faraday balance and the magnetic measurements were performed in situ. Both the magnetization curves and $1/\chi$ vs. temperature plots gave $S = 1$ with small negative Weiss constants. Although no crystal structural data are available, the results suggest that the stackings of **10j** and **10k** in crystals may not be in line with the expected topochemical polymerization giving ferromagnetic coupling among the carbene centers [25].

Recently, a 1,3,5-hexatriyne **11** corresponding to diyne **10i** was prepared and allowed to polymerize at 40 °C to give black solid with metallic luster that are insoluble in typical organic solvents and attracted to a magnet at romm temperature. The magnetic susceptibility of the polymer between 4.2 and 300 K fitted nicely with a Curie-Weiss expression at high magnetic field (2 T), but under low magnetic field (0.3 T) the 1/ vs. T relation was more complex. The plot of the magnetization against H is reproduced in Figure 7a and b. These results indicate that the polymer samples contain both isolated and highly ordered spins [26].

Many other diacetylenes carrying free radical substituents remain unpolymerized after being prepared laboriously. Controll of molecular packing in crystals is seriously sought. Introduction of technology of liquid crystals or Langumuir-Blodgett's membranes may be of help.

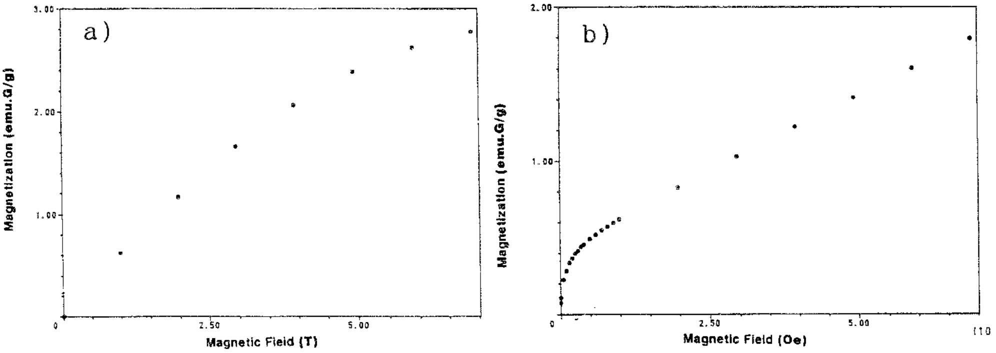


Figure 7. Magnetization curves for poly(triacetylene) due to **11** at a) 4.2 and b) 100 K.

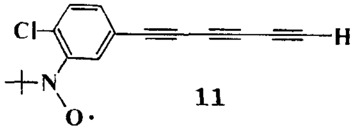
In 1986 Korshak and Ovchinnikov reported black powdery materials obtained by polymerization of a diacetylene carrying a pair of persistent nitroxyl radicals symmetrically (**12**). A part of this sample was described to show ferromagnetic properties (spontaneous magnetization of ca. 0.022 emuG/g)[27]. The results were for some time a subject of considerable interest and controversy. The observed crystal structure does not appear to satisfy the empirical criterion for the topochemical polymerization. Even if the expected poly(diacetylene) skeleton is formed, the structure of the polymer 5(X = Y = TEMPO) is not consistent with the molecular design described previously in two ways. First, radical centers are not conjugated with the main chain to have meaningful exchange coupling; they are too far apart by three saturated carbon atoms. Even if there is one, since the structure is symmetric, the interaction is expected the topological symmetry to be antiferromagnetic. According to the latest report [28], two polymorphs of **12** exhibit normal paramagnetic behavior before and after heat treatment; any ferromagnetic contribution that might be observed at higher temperature is due to a contribution corresponding to 5 ppm Fe contamination. Similarly, a claimed spontaneous magnetization of 88.5 emu G/mol and a coercive field of 455 G due to the thermally treated product of 2,4-hexadiyne-1,6-diyl bis(2,2,5,5-tetramethylpyrrolin-1-oxyl-3-carboxylate)[29] was later questioned [30].

Polymers that may have two-dimensional network structures: Torrance obtained a sample that showed ferromagnetic behavior with a high Curie temperature by a reaction of 1,3,5-triaminobenzene with iodine under rather drastic conditions [31]. A charge-transfer complexes of iodine with an aniline black-type polymer (**13**; a hetero-atom-containing analogue to **13**) may have been responsible for the magnetic property. More recently, Ota and Otani reported resinous materials called COPNA obtained by acid-catalyzed condensation of aromatic aldehyde with electron-rich aromatic hydrocarbons, e.g., pyrene. When treated under hydrogen-abstraction conditions, some of the resulting samples was attracted by a magnet at room temperature (M_w 1700 - 2000, M_s = 0.12 - 0.20 and M_r = 0.35 emuG/g, H_c = 65 - 105 Oe [32]).

Three pyrolytic graphite samples are also reported to have residual magnetization (for example, M_s = 0.5 and M_r = 0.35 emuG/g, H_c = 600 Oe [33]). All these samples seem to have in common extended two-dimensional structure **13** with dangling bonds as radical centers. However, they are problematic in one way or another. Some are not obtained reproducibly and others are difficult to characterize or prepare in quantities. It is extremely necessary to synthesize high-spin polymers systematically and stoichiometrically based on the strict molecular design described in the last section.

DESIGN OF FERROMAGNETIC COUPLING AMONG ORGANIC FREE RADICALS AND HIGH-SPIN MOLECULES IN MOLECULAR ASSEMBLIES

Long-range order of the electron spins in one-dimensional systems is said to be unstable physically and can be achieved only at T = 0 K. However, since real molecular assemblies are usually three-dimensional systems, the interchain interactions, although small, could lead to the generation of long-range magnetic order also at T > 0. This problem has been discussed by Tyutyulkov [7] who estimated the absolute



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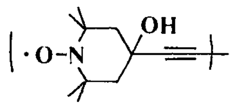

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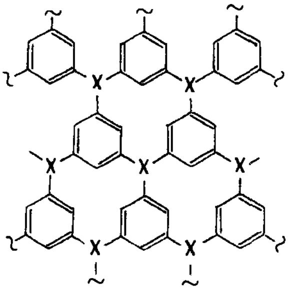

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value of J between two one-dimensional chains of planar polyradicals **2** by using an expression $T_c = 2J/k_B\ln 3 = 21167.4J$ K. For J values in the range 0.16 - 0.20 eV, T_c values in the range 910 - 1190 K have been obtained. Thus intermolecular interactions are extremely important for spin ordering at finite temperatures.

Such interactions in the molecular aggregates of some members of the series **3** has been found, however, to be antiferromagnetic. Exchange coupling among neighboring free radicals or high-spin molecules is usually very small and antiferromagnetic at best in organic solids. This is more the rule rather than the exception. Actually there are only a handful of examples known in the literature in which ferromagnetic interaction has been observed in organic free radicals in well-defined crystals. Strategies leading to stabilization of ferromagnetic intermolecular coupling are highly needed[34].

Two theories have been introduced in the sixties on how to align electron spins in parallel between open-shell molecules [35].

McConnell's Heitler-London Spin Exchange Model Between Spin Densities of Opposite Sign on Radicals A and B

The first theory is based on Heitler-London spin exchange between positive spin density on radical A and negative spin density on radical B. The effective exchange interaction between A and B can be ferromagnetic when the product of spin densities ρ_i and ρ_j at two interacting sites i and j on different radical molecules A and B is negative. This theory is equivalent to a through-space version of spin polarization due to topological symmetry when the original valence bond theory discussed in a previous section and shown in Figure 2 is considered as through-bond interaction.

Let us now pay attention to one representative case; the superimposable stacking of the two benzene rings one from each triplet diphenylcarbene molecule. These are considered to represent idealized modes of dimeric interaction of the aromatic ring parts of the open-shell molecules in ordered molecular assemblies like crystals, liquid crystals and membranes.

The spin distribution in diphenylcarbene is basically of benzyl radical-type. When the theory is applied to the idealized dimeric interaction modes, the signs of $\rho_i\rho_j$ at each interacting site between the two benzene rings are all negative in the ortho (60°-rotated from the superimposable stacking) and para (180° rotation) stacking patterns and all positive in the gem (superimposable stacking) and meta (120°-rotated configuration)(Figure 8). Therefore, the ortho and para overlaps are predicted to give the qunitet ground state, while the gem and meta would lead to the ground singlet state.

Izuoka et al. took advantage of the [2.2]paracyclophane keleton in order to disclose the effect of orientation of the stacking from the experimental point of view [36]. Among the three isomers of bis(phenylmethylenyl)[2.2]paracyclophanes (**14**), pseudoortho- and pseudopara isomers (**o-14** and **p-14**, respectively) satisfy the McConnell's condition to give the quintet ground states. They were produced by photolyses of the corresponding bis(α-diazobenzyl)[2.2.]paracyclophanes (**14a**) in 2-MTHF at cryogenic temperatures, and their ESR fine structures were studied.

For example, when a solid solution of **o-14a** in 2-MTHF was irradiated with Pyrex-filtered light in an ESR cavity at 11 K, a set of intense ESR signals were obtained that resembled as a whole that of m-phenylenebis(phenylmethylene) **3**(m = 2) in the quintet ground state. The resonance positions and intensities of the signals are reproduced well by a second-order perturbation calculation as a quintet species (Q) with zero-field splitting parameters D = 0.0624 cm^{-1} and E = 0.0190 cm^{-1}. The signal intensities of the quintet were found to obey Curie law in the temperature range 11 - 50 K, showing that the **o-14** has a quintet ground state. At temperatures higher than 20 K, a new signal appeared at 104.0 mT. The intensity of this signal increased as the temperature was elevated and reached a maximum at 55 K. The signal decayed irreversibly at temperatures higher than 50 K. The thermal behavior is characteristic of a thermally populated triplet (T). By assuming the Boltzman distribution of electron spins among the three states, the signal intensity for T vs. temperature relation gave ΔE_{QT} = 61 cm^{-1} (= 175 cal mol^{-1}) and J was calculated to be +16 cm^{-1}.

In the case of the pseudometa isomer (**m-14**), signals due to a quintet state was not observed. Instead, a set of signals due to the thermally populated triplet T_T grew in at 25 K. The

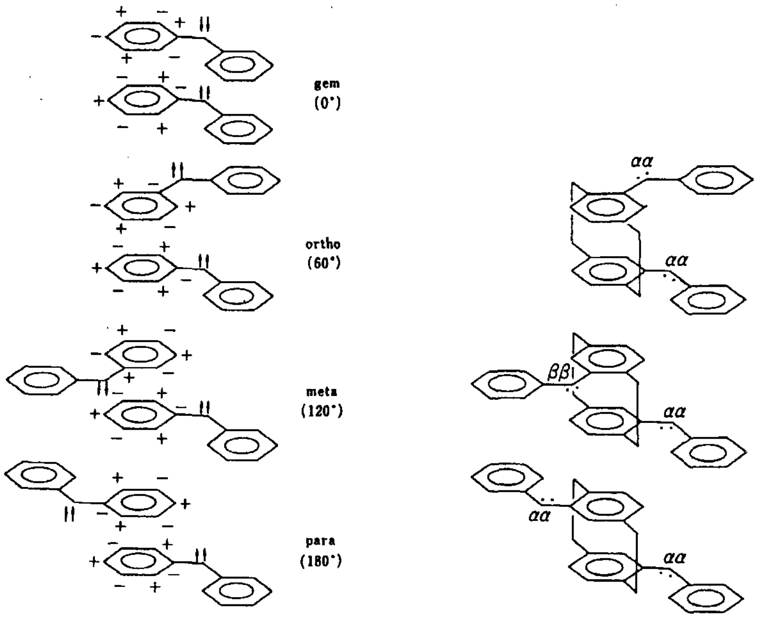

Figure 8. Idealized stacking modes of two diphenylcarbene molecules. Two benzene rings one each from the two carbene molecules are always in superimposable disposition. The corresponding model dimers **14** are also shown.

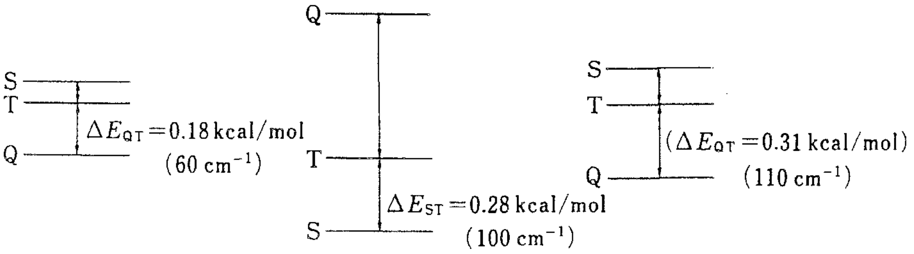

Figure 9. The observed order of states for the isomeric [2.2]-paracyclophanedicarbenes **14** that is in good agreement with the McConnell's first theory.

temperature dependence data were analyzed to conclude that **m-14** has a singlet ground state with a triplet populated thermally with ΔE_{ST} = 98 cm^{-1} (= 280 cal/mol).

All the results are summarized in Figure 9 and serve as the first positive operational test for the McConnell's theory [35]. It is also noted that the orientational mode of stacking of spin-containing benzene rings can be useful in aligning spins parallel or antiparallel between high-spin aromatic molecules. Similar experiments have been performed with the [3.3]paracyclophane isomers to obtain parallel results.

It is thus well established that, if the assemblies of high-spin molecules can be arranged such that the interaction between the spin densities of opposite sign could become most important between the neighboring radicals or carbenes, the polyradicals might obtain longer range magnetic order and exhibit ferromagnetism as bulk properties. The conclusion was supported by inspection of the EPR fine structures and magnetic susceptibilities of a series of partially photolyzed micro-crystals of diazo compounds.

Stimulated by the above model experiments, Yamaguchi et al. carried out APUHF STO-3G calculations for the dimeric interaction of benzyl radicals in the geminal, ortho, meta and para conformations [37]. The results show that the signs of the calculated J_{ab} are positive for the ortho and para and negative for the geminal and meta stackings in good agreement with the McConnell's theory. The signs do not depend on variation of the intermolecular distance R, although the absolute values decrease with R in an exponential manner. The absolute values appear to increase as the basis sets are improved; 218 cm^{-1} for the para overlap at a distance of 3.4 A is modified to 412 and 517 cm^{-1} by using the 4-31G and APUMP4 6-311G** methods, respectively. The signs of J_{ab} can be explained by the extended McConnell model: $J_{ab} = J_{ab}(OO) + J_{ab}(SDP)$, where the first and second terms denote the orbital overlap (OO) and spin density product (SDP), respectively. For example, the OO-term between the singly occupied and singly unoccupied orbitals are not zero for the geminal and meta overlaps, whereas it reduces to zero in the ortho and para overlaps. In other words, the OO-term favors the singlet state for the gem and meta configurations. The SDP-term, on the other hand, plays a dominant role to detrmine the sign of the J_{ab} value for the ortho and para dimers. Similar theoretical treatments have been carried out on the clustering of triplet carbenes and allyl radicals.

Ferromagnetic Coupling in Donor-Acceptor Salts

It is usually the case that, in the alternating stack of charge transfer salts ($...D^+A^-D^+A^-D^+A^-D^+A^-...$), the electron spins generated on the donor (D) and acceptor (A) components are antiferromagnetically coupled. This is as a result of admixing of the wave functions of the closed-shell components to the resultant wave function of the charge-transfer salt (Figure 10 (a)). A second theory of McConnell predicts that, when either D or A has triplet ground state, the electron spins developed on a pair of D and A can have ferromagnetic coupling (Figure 10(b) or (b')). In other words, configurational admixing of a virtual triplet excited state becomes possible with the ground state for a chain of alternatig radical cation donors and radical anion acceptors.

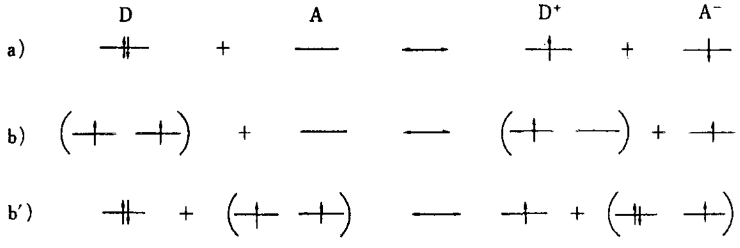

Figure 10. Figurative presentation of the strategies for spin alignment in D/A salts or complexes by application of the spin conservation in different electron configurations of interacting molecular orbitals. a) Typical D/A interaction between two closed-shell D and A, and b and b') McConnell's proposal.

It was Breslow who first paid attention to this theory and set out on the synthesis of aromatic dications that should be readily generated and form stable CT complexes [38]. Miller and Epstein extended the original formulation of of Figure 10 and made it possible to take into account ferrimagnetic stacking interaction in some D/A combinations, e.g., doublet D and triplet A as well. It is also feasible to seek ferromagnetic interaction in a stack of either all donors or all acceptors, as commonly found in electrically conducting radical ion salts. These possibilities are under discussion by Torrance and Wudl as well.

Miller and coworkers studied decamethylferrocene/TCNE salts in some detail [39]. The susceptibility of the polycrystalline samples obeyed the Curie-Weiss expression with θ = +30 K for T > 60 K, suggesting dominant ferromagnetic interactions. Below 60 K a substantial departure from Curie-

Weiss behavior was evident and the data could be fitted by an $S = 1/2$ one-dimensional Heisenberg model with ferromagnetic exchange ($J = + 21\ cm^{-1}$). Below 15 K three-dimensional ordering set in and the magnetisation was no longer linearly proportional to the magnetic field. A spontaneous magnetization up to 1.1×10^4 emuG/mol was observed below the Curie temperature of 4.8 K. Spin alignment between chains is ascribed to the $TCNE^-$ residing in an adjacent chain equally proximal to the Fe(III) as it is the intrachain $TCNE^-$'s.

Since iron(III) in the ferricenium ions is low-spin ($S = 1/2$) and the spins on the acceptor TCNE appear to be contributing to the bulk magnetic properties as well, the D/A salt may be considered as dependable molecular magnetic materials.

Pursuit of finding suitable organic donors and acceptors that possess a rotation axis of order $n > 3$ or have D_{2d} symmetry is in progress [40].

POTENTIALS OF HIGH-SPIN ORGANIC MOLECULES

Once super high-spin molecules are formed as designed, there are two mechanisms possible through which spontaneous magnetization will appear. One is the formation of long-range spin order by favorable interchain interaction. According to Tyutyulkov, while one-dimensional ordering within a molecules is unstable at finite temperature, the order can be stabilized considerably by inter-chain interaction; T_c can become as high as 1000 K. On the other hand, if the superparamgnetic molecules have magnetocrystalline anisotropy and high barrier to paramagnetic relaxation, again spontaneous magnetization will appear at temperatures lower than blocking temperature T_B.

The attempted photochemical route to super high-spin molecules would have some significance as an approach to organic opto-magnetic recording devices. The current optomagnetic recording devices employ vertically magnetized thin films. When digital or analog signals fall on the amorphous magnetic film as a focussed laser beam, that part of the film is warmed instantaneously at temperature higher than the Curie temperature T_c. As a result, the magnetization can be inversed by the effective demagnetization field or by additional application of a weak electric ring current. The signal thus recorded can be read by application of a magnetic Kerr effect. Thus no photochemical effects are involved in the process. Since a number of photoresists are made by use of photochemical processes including diazo compounds followed by Wolff rearrangement, we propose purely photochemical approaches to optomagntic recording devices. There are a couple of molelcular designs possible. One would be the photochemical polymerization of a paramgnetic species in such a way that the regioselectivity of the polymerization reactions satisfy the topological requirement for the ferromagnetic coupling of the radical centers in the newly formed polymer molecules. Second, prior polymerization of the monomer containing appropriate precursor functional group followed by photochemical generation of superhigh-spin molecules. The above example corresponds to the latter case.

CONCLUSION

On the basis of rigorous molecular design guided by theory and model experiments, a number of high-spin organic molecules have been synthesized and spin alignment in molecular assemblies has been advanced with reasonable success. We find the two approaches, i.e., spin alignment within a molecule and among molecules, are complementary to each other in expanding our understanding of chemical bonds and organic moleucles and developing novel organic magnetic materials.

Realization of purely organic ferromagnets remains of multidisciplinary scientific interest. They are not yet usable realities, but it is already possible to state an overall conceptual framework for exploiting the magnetic properties of organic compounds and their potential applications.

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