

Approaches from superhigh-spin molecules to organic ferromagnets

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Abstract. There are two steps of strategy in the molecular design of organic ferromagnets: the construction of high-spin organic molecules and the introduction of spin-aligning mechanisms into the assemblies of the open-shell molecules. The former approach requires the knowledge of how to endow organic molecules with many half-filled orthogonal orbitals. In π -conjugated diradicals, parallel alignment of the two spins can become favored, if the radical centers are placed in phase with the spin polarization of the intervening π -bonds. We have now studied a wide variety of non-Kekulé hydrocarbons and the heteroatom analogues by EPR spectroscopy and magnetic susceptibility/magnetization measurements to find that only a part of them have high-spin ground states. Some of the superhigh-spin molecules from our laboratories will be discussed in some detail. A similar principle can be applied to effect ferromagnetic exchange coupling between high-spin molecules. Design of molecular stacking in crystals, liquid crystals and molecular layers is found to be indispensable.

A. INTRODUCTION

Ions and complexes of transition metals and lanthanoids often have high-spin ground states since they carry singly occupied 3d and 4f atomic orbitals. How can we mimic these high-spin species by means of organic molecules having only 2s and 2p electrons? The occurrence of the half-filled orthogonal orbitals are dictated by symmetry of the molecules and can be achieved for organic molecular systems in two ways: geometrical and topological symmetry. One-centered diradicals, e.g., carbenes and nitrenes are examples of the former. In π -conjugated diradicals, the intervening π -electrons are polarized. Therefore, if the periodicity of the spin polarization is appropriate, namely, the second radical center is placed at the position in phase with the spin polarization of the π -electrons due to the first radical center, the parallel alignment of the two spins should become favored (ref. 1). Schlenk's hydrocarbon **1** has a triplet ground state and is the first representative of such non-Kekulé hydrocarbons (ref. 2). By combining these two facets of molecular symmetry, *m*-phenylenebis(phenylcarbene) **2** with a quintet ground state has been conceived and constructed (ref. 3). These high-spin molecules **1** and **2** can be viewed as being constructed with a pair of the electron spins connected through a ferromagnetic coupling unit (ref. 1,4). We have been successful in obtaining superhigh-spin organic molecules by repeating such a fragment consisting of the spin and the ferromagnetic coupler to form one- or two-dimensional arrays of the ordered spins in oligomers/polymers (Fig. 1).

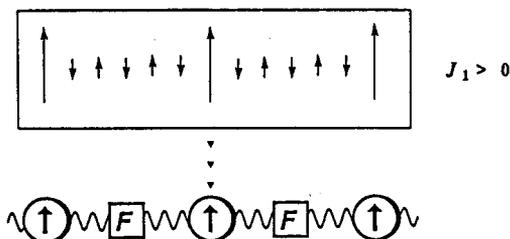
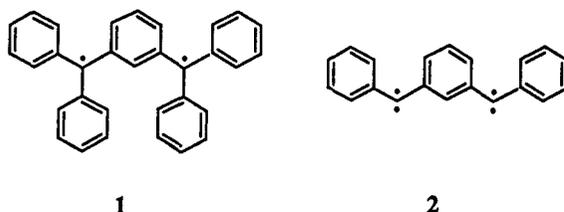


Fig. 1. Schematic presentation of the 1-D array of parallel spins in π -conjugated polyradicals.

Another step of strategy, i.e., introduction of a spin-aligning mechanism into the assemblies of high-spin molecules, is necessary for the establishment of molecular ferromagnetism. Approaches from the studies of crystal structures will be discussed.



B. SEARCH FOR FERROMAGNETIC COUPLING UNITS. CLASSIFICATION OF NON-KEKULE HYDROCARBONS

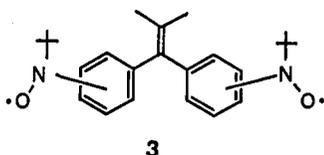
We have studied a variety of non-Kekulé hydrocarbons and their heteroatom analogues, i.e., sets of a pair of spins and a potential ferromagnetic coupling unit, to find the general guiding principle for designing high-spin molecules.

B.1. Isomeric vinylidenebis(phenylnitroxides) 3

The syntheses and analyses of isomeric vinylidenebis(phenylnitroxides) **3** with additional steric protection illustrates such a study (ref. 5). The corresponding dibromo compounds were lithiated with 4 equiv of *tert*-butyllithium and allowed to react with 2 equiv of 2-nitroso-2-methylpropane to give the hydroxyamines, which were then treated with Ag₂O to give **3**. Purification was accomplished by chromatography on silica gel to give analytically pure samples. EPR spectra of **3** in toluene at room temperature consisted of five unperturbed lines ($J > a_N = 11.2$ G, where J stands for the exchange integral between the two nitroxide radicals). The dipolar interaction between the nitroxide radicals was unexpectedly small as revealed by their EPR spectra in frozen matrices: spectral widths as a measure of $2D$ were less than 90 G, but $\Delta m_s = 2$ transitions for the triplet species were clearly observed at $g = 4$. The signals were too small to study the temperature dependence of their intensities. The magnetic susceptibility was measured for powder samples of **3** on a Quantum Design SQUID susceptometer at 1 T in the temperature range 5-300 K. The results are expressed in terms of μ_{eff}/μ_B vs. temperature plots in Fig. 2. The μ_{eff} values approaching $2.45 \mu_B$ at room temperature indicate the near degeneracy of the singlet and

Table 1. Energy gap between the singlet and triplet states in isomeric dinitroxides **5**.

| 5 | $\Delta E_S/T/\text{cm}^{-1}$ | θ/K | GS from VB | GS from MO |
|-------------|-------------------------------|-------------------|------------|-----------------|
| <i>p,p'</i> | 10.6 | -2.0 | $S = 1$ | non-disjoint |
| <i>m,p'</i> | -3.4 | -2.0 | $S = 0$ | disjoint |
| <i>m,m'</i> | -1.8 | -2.1 | $S = 1$ | doubly disjoint |



$$\chi = \frac{2Ng^2\mu_B^2}{k(T - \theta) [3 + \exp(-2J/kT)]} \quad (1)$$

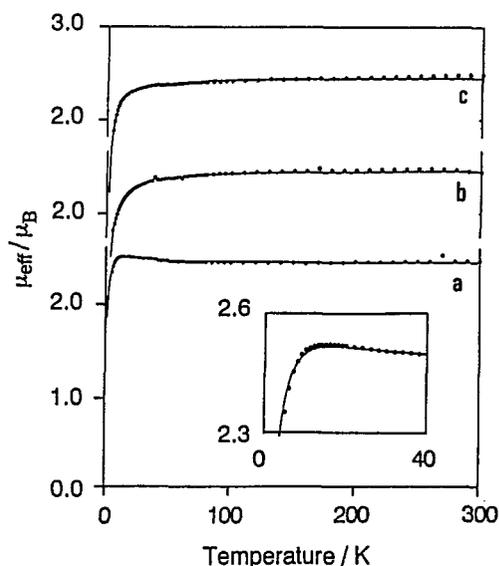


Fig. 2. Temperature dependence of μ_{eff} for isomeric dinitroxides **3**

triplet states for the three isomers. A ground state triplet species should have given a μ_{eff} value of $2.8 \mu_{\text{B}}$. The plots were analyzed in terms of a modified Bleaney-Bowers equation (ref. 6) with a Weiss field θ and purity factor F (eq. 1) and refined by a least-squares method to give the results summarized in Table 1, where ΔE_{S-T} stands for the energy gap between the two states $2J$.

It is concluded from the measurement of the absolute μ_{eff} values and their temperature dependence over wide ranges that, while both dipole-dipole and exchange couplings between the two nitroxide radicals in **3** are unexpectedly weak, the p,p' isomer has a triplet and the m,p' and m,m' isomers have singlet ground states. The conclusions are consistent with Ovchinnikov's VB theory (ref. 7) only partly but fully interpreted in terms of the perturbed MO theory of Borden and Davidson (ref. 8).

B.2. Summaries of ferro- and antiferromagnetic coupling units

Similar studies by means of EPR fine structures and magnetic susceptibility/magnetization have been carried out on various non-Kekulé systems. The results are collected in Tables 2 and 3 depending respectively on the positive or negative J/cm^{-1} values obtained experimentally from the energy gaps; the + and - signs correspond to the ferro- and antiferromagnetic interactions, respectively.

Table 2. Ferromagnetic coupling units and the magnitude of the coupling

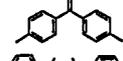
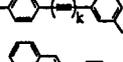
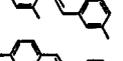
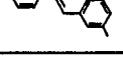
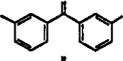
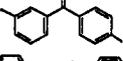
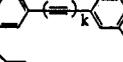
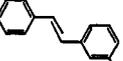
| J/cm^{-1} | \uparrow / \uparrow | | |
|---|---|------------------------|---|
| |  | $-\dot{\text{N}}\cdot$ |  |
|  | $\gg 100$ | $\gg 100$ | $\gg 100$ |
|  | $\gg 100$ | $\gg 100$ | $\gg 100$ |
|  | $\gg 100$ | $\gg 100$ | $\gg 100$ |
|  | $\gg 100$ | $\gg 100$ | $\gg 100$ |
|  | $\gg 100$ | $\gg 100$ | $\gg 100$ |

Table 3. Antiferromagnetic coupling units and the magnitude of the coupling

| $-J/\text{cm}^{-1}$ | \uparrow / \downarrow | | |
|---|---|------------------------|---|
| |  | $-\dot{\text{N}}\cdot$ |  |
|  | | 4.4 | 0.9 |
|  | | 7.0 | 1.7 |
|  | (20, 45 (k=0)) | 12 (k=1) | 6.0 (k=2) |
|  | 10 | | 6.5 |

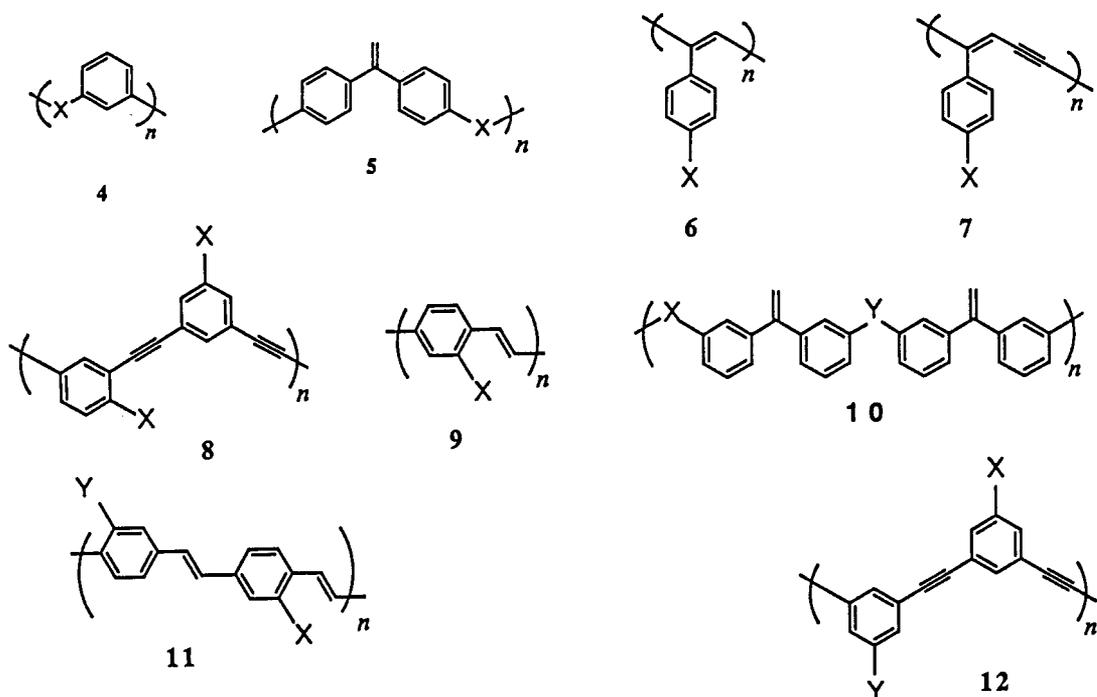
Since the $2p$ -atomic orbital of more electronegative heteroatoms is lower in energy, the degeneracy of non-bonding MO's of alternant hydrocarbons will be lifted by introduction of a heteroatom radical center. Results in Tables 2 and 3 show that the perturbation due to the introduction of heteroatoms is smaller than expected and the topological consideration developed for alternant hydrocarbons can be applied to heteroatom-perturbed conjugated systems. The numerical values in Table 2 are classified into two groups. For carbenes and nitrenes as the spin sources, the ground states are high-spin and the energy gaps between these states and the first excited lower-spin states are large. Since the latter states cannot be populated thermally up until the temperature at which they start to disappear by chemical reactions, only the lower limits of the J values are obtained. When the nitroxides are employed as spin sources, the excited lower-spin states can often be populated thermally. There are two reasons for this success. Firstly, the nitroxides are persistent and allow the range of the experiments from cryogenic up to ambient temperatures. The second is the higher localization of the spin density at the nitroxide radicals and the consequent lower distribution of the spins on the phenylene ring. Since the effective exchange interaction between the two terminal radicals is governed by the polarization of the intervening π -electrons, transmission of the topological relationship becomes less effective by the lower spin density on the ring. The consequent population of the readily accessible excited states serves allowed us to obtain for the first time the quantitative information on the energy gaps between the high-spin ground and low-spin excited states by means of Bleaney-Bowers type equations (e.g., eq. 1).

In Table 3 are summarized antiferromagnetic coupling units that were found to favor the ground singlet states. Since the high-spin first excited states are often low-lying, the magnitude of the energy gaps are determined rather straightforwardly by populating them thermally and studying their Boltzmann distribution. Note again that the absolute values for the nitroxides are smaller than those for the carbenes and nitrenes.

B.3. Strategy for designing high-spin oligo/polyradicals

We note a number of important trends that would serve as guiding principles for designing high-spin oligo/polyradicals. They are summarized as follows.

- 1) If one wishes to construct high-spin oligo/polyradicals by repeating such a fragment consisting of the spin and the ferromagnetic coupler to form one-dimensional arrays of the ordered spins (Figure 1), oligomers/polymers **4** - **9** in which X is the radical center are predicted to be promising candidates.
- 2) Composite oligo/polyradicals such as **10** - **12** will be high-spin when the spin quantum numbers S of X and Y are different. The adjacent spins tend to cancel each other out but only partly to give residual spins as in ferrimagnets.
- 3) Carbenes, nitrenes and probably diphenylmethyl radicals are preferred as spin sources for thermodynamically stable superhigh-spin oligo/polyradicals, since magnitude of the exchange coupling between the neighboring centers are large.
- 4) Nitroxides are kinetically favored as spin sources, but since the exchange coupling between the neighboring nitroxides is weaker, contamination of the lower spin states in the polyradicals cannot be avoided at ambient temperature.
- 5) The ferromagnetic coupling units in Table 2 are related by connectivity to trimethylenemethane (TMM) which has been established to have a ground triplet state (ref. 8). For example, *p,p*-**3** can readily be seen as a phenylogue of TMM (ref. 5).
- 6) The antiferromagnetic coupling units in Table 3 are related by connectivity either to tetramethylethane (TME) or pentamethylenepropane (PMP)(ref. 5). While a number of theoretical studies favor singlet ground states of these diradicals, a limited number of EPR studies had revealed the linear Curie relationship from which the ground triplet states was hinted (ref. 8, 9). The present study suggests the singlet ground states of TME and PMP (ref. 5).
- 7) Other potentially ferromagnetic coupling units may be introduced if they are related in connectivity to TMM. Similarly, new antiferromagnetic coupling units may be found if they have the topology similar to TME or PMP.



C. HIGHLIGHTS OF HIGH-SPIN OLIGO/POLYRADICALS

C.1. A branched-chain hexa- and nonacarbenes **14** in tridecet and nonadecet ground states

Previously we reported the synthesis and characterization of one-dimensional high-spin oligocarbenes **13** (ref. 11). One-dimensional alignment of the parallel spins in infinite systems is stable only at 0 K. Entropy favors the population of the lower spin states. In order to realize the long-range order at finite temperatures, an increase in the dimension of the aligned spins is imperative. This can be achieved either by imposing the proper stacking orientation and therefore magnetic interaction between the molecular chains of **13** as in crystals or by increasing the dimension of the molecule itself. We have introduced a branched-chain pseudo-two-dimensional structures **14** to achieve the latter possibility, although the two-

dimensional honeycomb-like π -system would be ideal. One of the key steps in the synthetic route employed for the precursor is the *sec*-amine-catalyzed trimerization of the ethynyl aryl ketones to give 1,3,5-tris(substituted aryl)benzenes, a method also applicable to the higher analogues of **14**. An Oxford Faraday balance was installed with a quartz light guide through which the UV light ($480 > \lambda > 400$ nm) was introduced into ca. 80 μ g of **14** in 25 μ l of 2-methyltetrahydrofuran (MTHF) in a quartz sample basket suspended in the superconducting solenoid (< 7 T). The magnetic measurements on **14** thus produced at ca. 2 K were carried out *in situ*. The plots of the magnetization vs. the applied magnetic field strength at 2.1, 4.8, and 10.0 K were analyzed in terms of the Brillouin function to give $S = 6.0$ for $m = 6$ and $S = 9.0$ for $m = 9$, the highest spins ever reported for purely organic molecules (Fig. 3)(ref. 12).

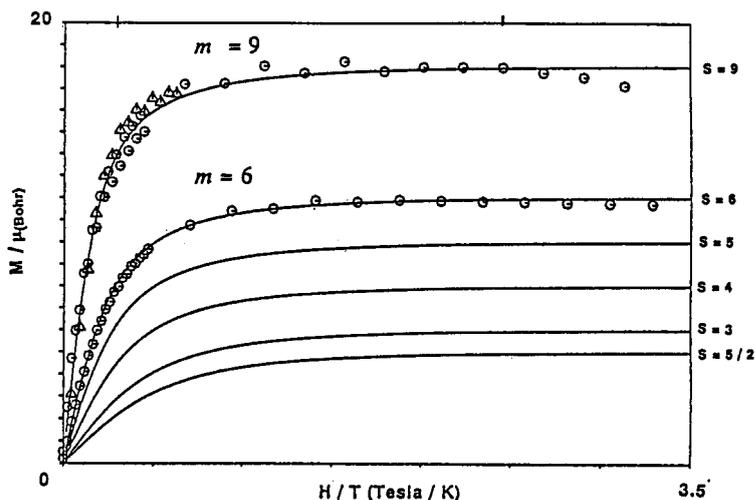
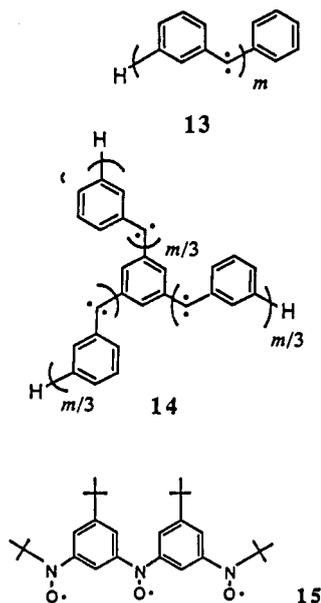


Fig. 3. Temperature and field dependence of the magnetization for hexa- and nonacarbenes **14** and the theoretical magnetization curves for several paramagnetic species.

The magnitude of the effective magnetic moment for a sample with concentration of 6.7 mM or higher was smaller by 15 % at 1.9 K than that at 20 K. A similar behavior was observed for partially photolyzed neat samples. The exchange interaction between the tridecet molecules in fortuitously formed clusters is suggested to be antiferromagnetic. Additional designs of molecular stacking should be made for establishing the order extending among the high-spin molecules (see D.1.).

C.2. Determination of the energy gap between the ground and excited states in trinitroxide **15**

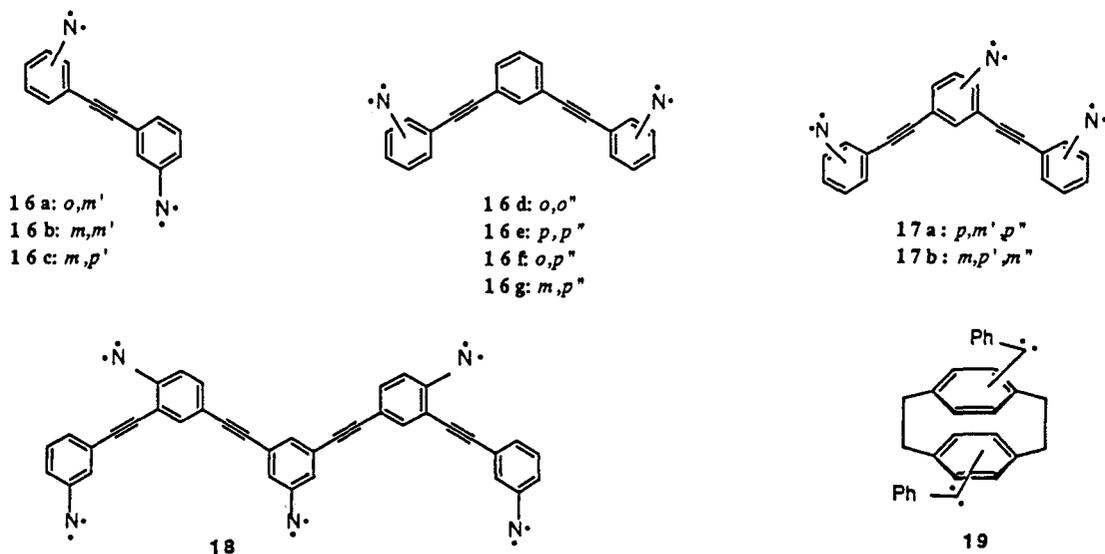
Magnitude of the ferromagnetic coupling through the *m*-phenylene unit has been determined for the first time by taking advantage of the attenuating effect of the nitroxide radicals (ref. 13). EPR spectra of **15** in a toluene glass at 4.2 K showed a fine structure characteristic of randomly oriented species in a quartet state ($D/hc = 0.0087$ cm^{-1} and $E/hc < 0.0003$ cm^{-1}). The signal intensity decreased as the temperature was increased in the range 4.2 - 30 K in good agreement with a Curie law within the experimental error. Thus whereas the quartet was concluded to be either a ground state or is degenerate with lower spin states, it was not possible to determine from these experiments how close the thermally accessible lower spin states lie above the ground quartet state.

Magnetic measurements were carried out on a Faraday balance in the range 2 - 300 K. As the temperature was increased, the moment of **15** increased from 1.05 μ_B at 2 K, reached a maximum of 3.53 μ_B at ca. 140 K, and gradually decreased to 3.43 μ_B at 300 K. The latter decrease is due to the thermal population of the spins from a quartet ground state to excited doublet ones. The suppression at lower temperature is due to intermolecular antiferromagnetic coupling. The magnetic interaction in the linear triradical system can be described by the spin Hamiltonian: $H = -2J(S_1S_2 + S_2S_3)$, which assumes an isotropic exchange interaction and neglects intramolecular coupling J' between the terminal radicals. The eigenvalues of this Hamiltonian are: $E_1 = 2J(S = 1/2)$, $E_2 = 0$ ($S = 1/2$), and $E_3 = -J(S = 3/2)$. The molar susceptibility is given by the equation similar to eq. 1. Best fit parameters were $\theta = -19 \pm 2$ K and $J/k = 240 \pm 20$ K; the energy gap between the quartet and the lower excited doublet states was estimated to be 240 K = 167 cm^{-1} = 480 cal/mol. While the intramolecular exchange coupling is strongly ferromagnetic, **15** in a quartet state is in an antiferromagnetic Weiss field in microcrystalline solids (ref. 13).

C.3. Approaches to conjugated linear oligomer/polymers to which radical centers are attached as pendants. Studies on prototypes have amply demonstrated that *m*-phenylene units are most dependable in aligning in parallel doublet and triplet spins as well as polarons at its two ends. By repeating such a fragment consisting of the spin and the ferromagnetic coupler to form one- or two-dimensional arrays of the ordered spins in oligomers/polymers, unprecedentedly high-spin organic molecules have been constructed. However, linear **4** and **5** has a structural disadvantage. Since open-shell center *X* is on the cross-conjugated main-chain, all *X*'s have to be kept intact; otherwise the parallel alignment of all the spins along the chain by means of spin polarization of the π -electrons may be disrupted at the site where *X* is lost by chemical accident. Modification of the skeletal structure where radical centers are placed in their main chains to conjugated linear polymers to which radical centers are attached as pendants, e.g., **6** - **9**, has therefore been sought. This approach is expected to be superior to **4** and **5** in that one radical center may be lost without interfering with the exchange coupling between the two intact neighbors, although the magnitude of the coupling may be somewhat diminished. Poly(phenylacetylenes) **6** (ref. 14) and poly-(phenyl-di-acetylenes) **7** (ref. 15) carrying radical center on each phenyl ring have been sought without much success.

We have therefore taken poly[*m*-(nitrenophenyl)ethynylenes] **8** ($X = N$) into account and studied the magnetic properties of oligomers **16** representing the various substructures in **8** (ref. 16). An X-band EPR spectrum obtained for 10^{-3} M solutions of the nitrenes **16** in MTHF at 6 K showed a set of the highest-field Z transition ($m_s = -2 \rightarrow -1$) and next highest-field Y transition ($m_s = 1 \rightarrow 2$), from which zero-field splitting (zfs) parameters were calculated on the basis of a third-order perturbation method. Plots of the signal intensities vs. temperature for these quintet dinitrenes followed the Curie law in the range of 6 - 80 K, and no thermally populated signals were detected. The two triplet units in these dinitrenes were concluded to interact ferromagnetically. From these results including similar dinitrenes **16b** - **f**, polymer **8** was concluded to be high-spin. Since loss of a nitrene unit meta to the ethynylene bridges has now been found not to disrupt the exchange coupling between the two remote neighbors, such a chemical accident may be acceptable in retaining the intramolecular ferromagnetic exchange coupling along the chain. On the other hand, when two terminal nitrenes were both meta (**16g**) to the respective ethynylene bridges, only a strong signal due to the X,Y transition of a triplet mononitrene was observed at 699 mT. The two nitrene units are concluded to be independent of each other; loss of the triplet center ortho or para to the ethynylene bridges should lead to the separation of the polymer molecule **8** into magnetically independent parts.

Oligonitrenes **17** were generated by photolysis of the corresponding tri- and tetraazido compounds diluted in poly(methyl methacrylate)(ca. 0.2 wt %) and their magnetization was studied. The field dependence of the magnetization at several temperatures in the range 4.2 - 10.5 K were analyzed in terms of the Brillouin function to determine the effective total spin quantum number, *S*. Both *p,m'*, *p',p''* and *m,p',m''*-**17** gave best fits with $S = 2.9 \approx 3$. Similarly, pentanitrene **18** gave a result in which *S* is greater than 4 but not quite as high as theoretical value of 5. Difficulty in effecting a complete photochemical reaction because of masking of the phenyl azide chromophore by that of the polymer skeleton is thought to be responsible for the observed lower *S* value. Once this problem is solved, **8** promises to be a super-high spin polymer.



D. APPROACHES TO FERROMAGNETIC INTERACTION BETWEEN HIGH-SPIN MOLECULES

As seen in **3**, **14** and **15**, the exchange interaction between adjacent high-spin molecules in crystals and other molecular assemblies is usually weak and antiferromagnetic; the electron spins have a strong tendency to align antiparallel next to each other. This characteristic of organic molecules is readily understood by Heitler-London spin exchange between spins of opposite signs. Additional designs of molecular stacking should be made for establishing the spin order extending among the molecules. One of the approaches can be understood by dissecting the π -conjugated diradicals in Figure 1 into two separate molecules (Fig. 4). By ordering the polarized spins in antiparallel at the site of contact between the adjacent molecules, the spins of the two radical centers can effectively be aligned in parallel. A theoretical formulation of this idea was proposed in 1963 (ref. 17) and verified experimentally by employing prototype dimers **19** in 1987 (ref. 18). The necessary stacking orientation of the open-shell molecules has been sought in crystals with partial success. Thus, when a polycrystalline sample of diazodiphenyl-methane carrying the octyloxy chains in the *p,p* position was only partially photolyzed at cryogenic temperature and studied by EPR and susceptometer/magnetometer *in situ*, the orientation of the triplet carbenes generated side by side is governed by that in the precursor crystals. As a result, the carbenes generated in aggregates were found to couple ferromagnetically to give effective $S = 4$ at 2.1 K (ref. 19).

$$\chi_g = \frac{Ng^2\mu_B^2}{4kT} \left(\frac{1+5.798X+16.903X^2+29.377X^3+29.833X^4+14.037X^5}{1+2.798X+7.0087X^2+8.654X^3+4.574X^4} \right)^{\frac{2}{3}} \quad (2)$$

$$X = J/2kT$$

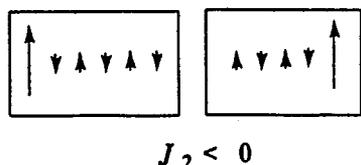


Fig. 4. Schematic presentation of the spin alignment between radical molecules.

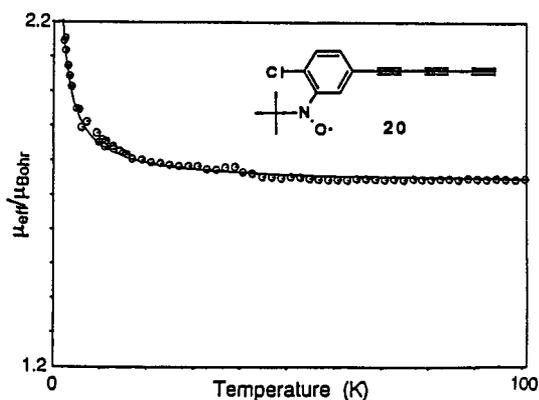


Fig. 5. Temperature dependence of μ_{eff} for a crystalline sample of triacetylenic nitroxide **20**.

We recently found that the temperature dependence of the paramagnetic susceptibility and effective magnetic moment of triclinic crystals of 1-[4-chloro-3-(*N-tert*-butyl)oxyamino]phenyl]-1,3,5-hexatriyne **20** was fitted to a Curie-Weiss law with $\theta = +2.5$ K and a 1-D Heisenberg ferromagnet (eq. 2) in which $g = 2.0059$ and $J/k = +1.3(1)$ K (optimized) (Fig. 5). Since the crystals underwent polymerization/decomposition at ambient temperature, it was not possible to obtain diffraction data good enough to solve its crystal structure. By analogy with that of a similar 1,3-butadiyne (ref. 15), it is understandable that there is in the crystals of **20** a direction in which an effective interradsical distance is shorter than in the other directions. Exploratory work on the topochemical solid-state polymerization of such acetylenic compounds is of great interest (ref. 20).

E. CONCLUSION

While we have been able to establish molecular design of superhigh-spin molecules, they cannot become ferromagnets by themselves. The long-range order of spins extending among such molecules is necessary for the development of ferromagnetism. Some approaches toward this goal by the control of molecular stacking are promising. An assembly of superhigh-spin molecules may acquire magnetocrystalline or shape anisotropy and the relaxation time for reorientation of a principal axis of the magnetization become longer than the measuring time. Then they will have a chance of developing residual magnetization at temperatures lower than the blocking temperature. Aside from ferromagnetism, these residual magnetization can be used as magnetic memory as well. Our studies have shown that the purely organic magnetic materials of this kind may be obtained by uv-irradiation of diamagnetic or weakly paramagnetic polymeric solids.

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