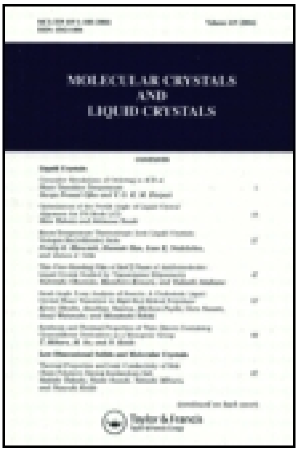

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Design and Demonstration of Ferromagnetic Exchange Interactions in Organic Molecules

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DESIGN AND DEMONSTRATION OF FERROMAGNETIC EXCHANGE INTERACTIONS IN ORGANIC MOLECULES

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Abstract Strategy of how to endow organic molecules with many half-filled orthogonal orbitals has been studied systematically. In principle, parallel alignment of the two spins can become favored in π-conjugated diradicals, if the radical centers are placed in phase with the spin polarization of the intervening π-bonds. Studies of a wide variety of non-Kekulé hydrocarbons and the heteroatom analogues by EPR spectroscopy and magnetic susceptibility/magnetization measurements have revealed, however, that only a part of them related in connectivity to trimethylenemethane have high-spin ground states. Some super-high-spin polycarbenes, polynitrenes and persistent trinitroxides from these laboratories will be discussed in some detail.

INTRODUCTION

Operationally there are two approaches toward the establishment of macroscopic spins (Figure 1a) for molecular based magnetic materials. The first is the exploration of persistent free radicals (S = 1/2) that have ferromagnetic interradical exchange coupling (J_2) in the crystalline state (Figure 1b). Secondly, several S = 1/2 spins may be assembled into high-spin molecules (S >> 1/2 and the exchange coupling between the adjacent spins within the molecule of J_1)(Figure 1c). The latter approach has the possibility of realizing higher Curie temperatures (T_C), since T_C is approximately given by Eq.(1)[1] and J_1 can be one or two order of magnitude greater than J_2 as found later in this paper. This approach requires the knowledge of how to align electrons spins in parallel in molecules in which the chemical bonds generally favor the antiparallel alignment of a pair of electrons.[2]

Since ions and complexes of transition metals and lanthanoids often

$$T_C/k = S(S+1)\ 2J_1J_2 \qquad (1)$$

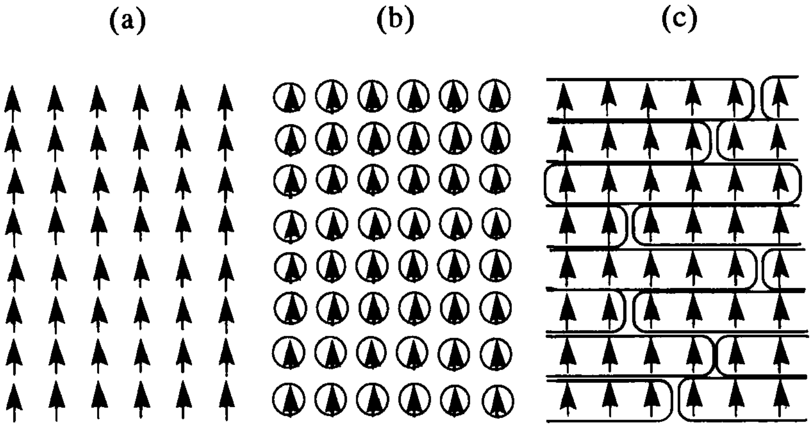
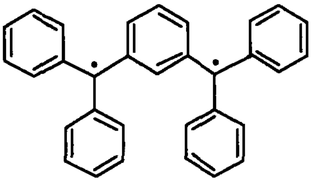


FIGURE 1. Schematic drawing of dissection of a) macroscopic spins into assemblies of b) $S = 1/2$ free radicals and c) $S >> 1/2$ high-spin molecules.

have high-spin ground states due to singly occupied 3d and 4f atomic orbitals, we are encouraged to mimic these high-spin species by means of organic molecules having only 2s and 2p electrons. The occurrence of the half-filled orthogonal orbitals is 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,[3,4] 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. Schlenk's hydrocarbon **1** with a triplet ground state is the first representative of such diradicals.[5] By combining these two facets of molecular symmetry, *m*-phenylenebis(phenylcarbene) **2** with a quintet ground state has been conceived and constructed.[6] 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. We have been successful in exploring a number of such coupling units and obtaining super-high-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 and/or polymers.



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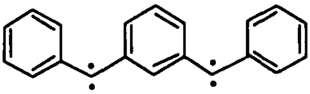


2

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

Kekulé hydrocarbons are expected to have singlet ground states since pairing of all the valence electrons is meant by the presence of a Kekulé canonical structure. At first glance, any non-Kekulé hydrocarbon and its heteroatom analogue seemed to constitute a set of a pair of spins and a potential ferromagnetic coupling unit. However, we have found that only a part of such non-Kekulé systems has a high-spin ground state indeed.

Isomeric vinylidenebis(phenylnitroxides) 3

The syntheses and analyses of isomeric *β,β*-dimethylvinylidenebis(phenylnitroxides) **3** illustrate such a study.[7] The corresponding dibromo compounds were lithiated with 4 equivalents of *tert*-butyllithium and allowed to react with 2 equivalents of 2-methyl-2-nitrosopropane to give the hydroxyamines, which were then treated with Ag_2O 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 ($J_1 > a_N = 11.2$ G). 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.

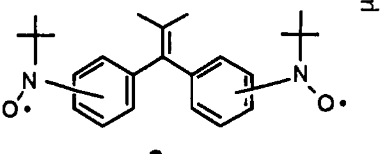
The magnetic susceptibility was measured for powder samples of **3** on a Quantum Design SQUID susceptometer at 1 T in the temperature range 5-300

K. The results are expressed in terms of μ_{eff}/μ_B vs. temperature plots in Figure 2. The μ_{eff} values approaching 2.45 μ_B at room temperature indicate the near degeneracy of the singlet and triplet states for the three isomers. A ground state triplet species should have given a μ_{eff} value of 2.8 μ_B. The plots were analyzed in terms of a modified Bleaney-Bowers equation[8] with a Weiss field θ and purity factor F (Eq. (2)), and refined by a least-squares method to give

Table 1. Energy gap between the singlet and high-spin states in isomeric dinitroxides **3** and dinitrenes **4**

	3		4		
	$\Delta E_{S\text{-}T}$/cm^{-1}	θ/K	$\Delta E_{S\text{-}Q}$/cm^{-1}	GS from VB	GS from MO
p,p'	10.6	-2.0	>>0	S = 1	non-disjoint
m,p'	-3.4	-2.0	-42.0	S = 0	disjoint
m,m'	-1.8	-2.1	-26.2	S = 1	doubly disjoint

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



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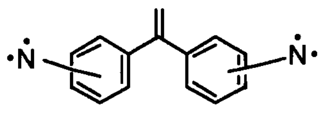

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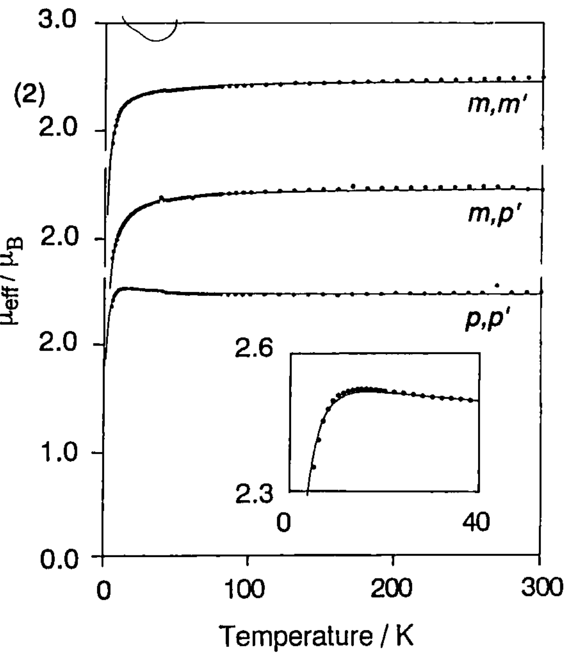


FIGURE 2. Temperature dependence of μ_{eff} for isomeric dinitroxides **3**

the results summarized in Table 1, where $\Delta E_{S\text{-}T}$ 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 rather weak, the *p,p'* isomer has a triplet and the *m,p'* and *m,m'* isomers have singlet ground states. A similar study on the corresponding isomeric dinitrenes **4** has been carried out by means of the temperature dependence of the EPR signal intensities due to the resulting quintet states. Here again it was the *p,p'* isomer that has a quintet ground state; the *m,p'* and *m,m'* isomers were with singlet ground states with thermally accessible quintet states.

The conclusions are consistent with Ovchinnikov's VB theory[9] only partly but fully interpreted in terms of the perturbational MO theory of Borden and Davidson.[10]

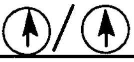
Summary of ferro- and antiferromagnetic coupling units

Similar studies by means of EPR fine structures and magnetic susceptibility and/or magnetization have been carried out on some other non-Kekulé systems. All the experimental results having positive and negative J/cm^{-1} values are collected in Tables 2 and 3, respectively. Here, + and - signs correspond to the ferro- and antiferromagnetic interactions, respectively.

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. The 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 further 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 appear to be two reasons for this success.[11] 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 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. (2)).

In Table 3 are summarized antiferromagnetic coupling units that were found to favor the ground singlet states. Since the high-spin excited states are often low-lying, the magnitude of the energy gaps are determined rather straightforwardly by populating them thermally and studying their Boltzmann

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



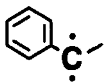
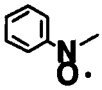
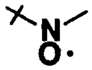
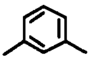
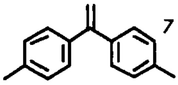
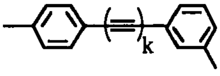
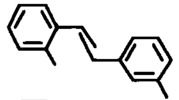
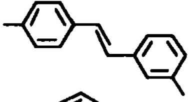
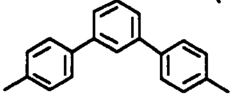
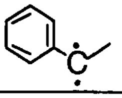
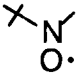
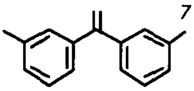
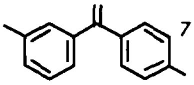
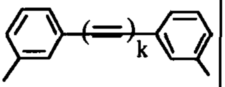
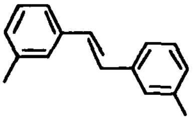
J/cm⁻¹		$-\dot{N}\cdot$		
	≫ 100[6]	≫100[6b]	167	≫ 100[11]
 [7]		≫10		5.3
F* 	≫ 100[12] k = 0	≫100[13,14] k = 0, 1, 2		
		≫100		≫100[15]
	≫ 100[16]	≫100		
				3.7[17]

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

- J/cm^{-1}		—N•	
 [7]		4.4	0.9
AF*  [7]		7.0	1.7
	(20, 45 (k=0))[12] 12 (k=1)[13] 6.0 (k=2)		
	10[16]		6.5[15]

distribution. Note again that the absolute values for the nitroxides are smaller than those for the carbenes and nitrenes.

Strategy for designing high-spin oligo- and polyradicals

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

1) Oligomers and polymers **5 - 10** that have a repeating unit consisting of spins (*X*) and a ferromagnetic coupling unit in one-dimensional array would be high spin species.

2)Composite oligo- and polyradicals such as **11 - 13** 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 triarylmethyl radicals are preferred as spin sources for thermodynamically stable super-high-spin oligo- and polyradicals, since magnitude of the exchange coupling between the neighboring

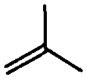
radicals, since magnitude of the exchange coupling between the neighboring centers are large.

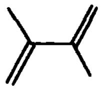
4) Nitroxides are kinetically favored as spin sources, but since the exchange coupling between the neighboring nitroxides is weaker, contamination of the lower spin states in the polyradicals may not be avoided at ambient temperature.

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.[10,18] For example, *p,p*-**3** can be readily seen as a phenylogue of TMM.[7]

6) The antiferromagnetic coupling units in Table 3 are related by connectivity either to tetramethyleneethane (TME) or pentamethylenepropane (PMP).[7] While a number of theoretical studies favor singlet ground states of TME, a limited number of EPR studies had revealed the linear Curie relationship from which the ground triplet states was suggested.[18,19] The present study suggests the singlet ground states of TME and PMP.

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.


TMM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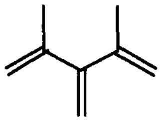
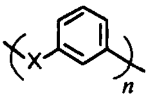

PMP



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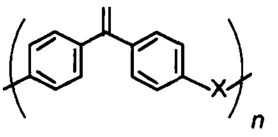

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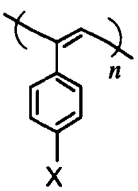

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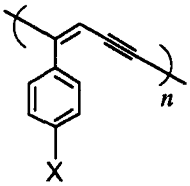

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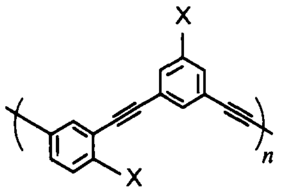

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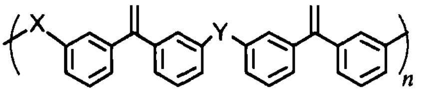

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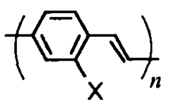

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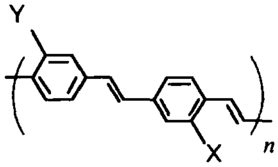

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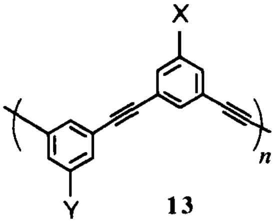


13

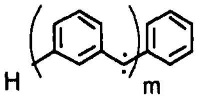
HIGHLIGHTS OF HIGH-SPIN OLIGO- AND POLYRADICALS

A branched-chain hexa- and nonacarbenes **15** in tridecet and nonadecet ground states

Previously we reported the synthesis and characterization of one-dimensional high-spin oligocarbenes **14**.[20] Purely one-dimensional magnetic systems cannot order at any finite temperature. 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 **14** as in crystals or by increasing the dimension of the molecule itself. We have introduced a branched-chain pseudo-two-dimensional structures **15** to seek the latter possibility, although the two-dimensional honeycomb-like π-system would be ideal.[21]

One of the key steps in the synthetic route employed for the precursor is a *sec*-amine-catalyzed trimerization of the ethynyl aryl ketones to give 1,3,5-tris(substituted aroyl)benzenes. When the amine was used in excess, the enaminoketones were formed at the expense of the triketones, suggesting that the enamines must be the intermediate of the cyclization reaction. Otherwise, these reactions appear to be applicable also to the higher analogues of

15. An Oxford Faraday balance was installed with a quartz light guide through which the UV light (480 > λ > 400 nm) was introduced into ca. 80 mg of **15** in 25 ml of 2-methyltetrahydrofuran (MTHF) in a quartz sample basket suspended in the superconducting solenoid ($\leq$ 7 T). The magnetic measurements on **15** 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



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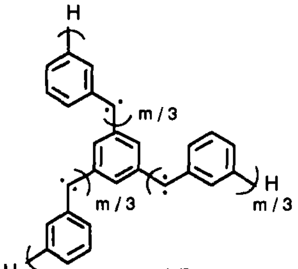

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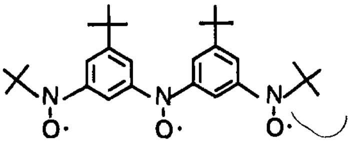

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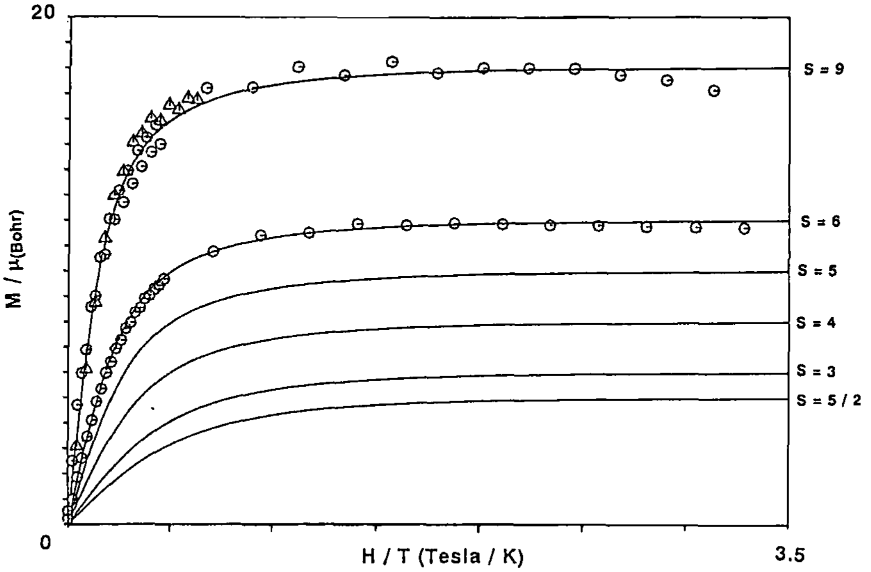


FIGURE 3. Temperature and field dependence of the magnetization for hexa- and nonacarbenes **15** and the theoretical magnetization curves for several paramagnetic species.

molecules (Fig. 3).[21,22]

There are several keys to this success of the characterization of **1 5** by means of the magnetization measurement: 1) precursor polydiazo compounds were obtained in >99 % pure states, 2) photochemical reactions are typically very efficient, 3) side reactions and possible over-irradiation were avoided by using a low-energy band-path-filtered light of 400~480 nm, 4) the magnetic measurements on the photochemically generated polycarbenes were performed in a Faraday balance in situ, and 5) the background data due to dia- and any paramagnetic contributions were subtracted very precisely.

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.

Determination of the energy gap between the ground and excited states in trinitroxide **1 6**

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.[11] EPR spectra of **1 6** 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 **1 6** 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 (Figure 4). 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: $H = -2J(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3)$, 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 temperature dependence of the molar susceptibility is given by an equation describing the Boltzmann distribution of the spins among these energy levels. 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, **1 6** with a quartet state is in an antiferromagnetic Weiss field in microcrystalline solids.

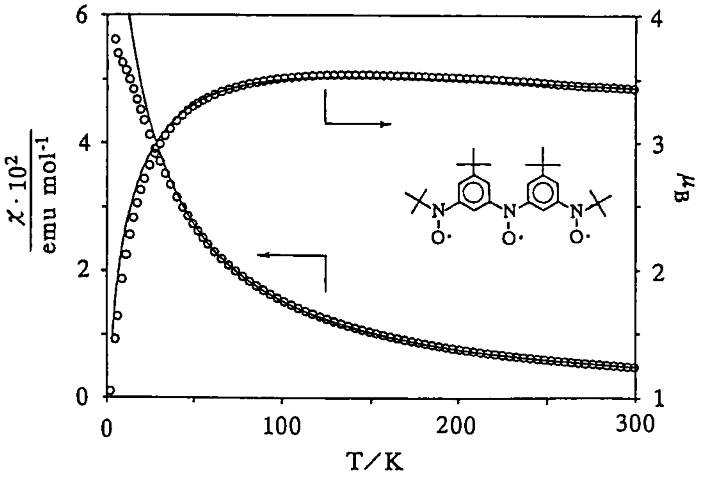


FIGURE 4. Temperature and dependence of the magnetic susceptibility and effective magnetic moments for trinitroxide **1 6**.

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 and/or polymers, unprecedentedly high-spin organic molecules have been constructed. However, linear **5** and **6** have 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., **7** - **10**, has therefore been sought. This strategy is expected to be superior to **5** and **6** 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) **7**[23] and poly(phenyldiacetylenes) **8**[24] carrying a radical center on each phenyl ring have been sought without much success. The negative results are ascribed to the nitroxide radicals used for X's that have more localized spins and consequent weaker exchange coupling between the neighboring sites. We have therefore employed poly[*m*-(nitrenophenyl)ethynylenes] **9**($X = \dot{\mathrm{N}}\cdot$) and **13**($X = Y = \dot{\mathrm{N}}\cdot$) in which the π-spins on the nitrene centers are expected to delocalize more extensively and couple more strongly with those at the neighboring sites. Specifically, the magnetic properties of dimers **17**, trimers **18**, and a pentamer **19** representing the various substructures in **9** and **13** have been studied.[14] The corresponding oligoazides (10^{-3} M in MTHF) were photolyzed (λ> 300 nm) at 6 K and their X-band EPR spectra were obtained. For example, **17a** showed characteristic fine structures of quintet dinitrenes (Figure 5). From a set of the highest-field Z transition ($m_S = -2 \rightarrow -1$) and next highest-field Y transition ($m_S = 1 \rightarrow 2$), zero-field splitting parameters were calculated on the basis of a third-order

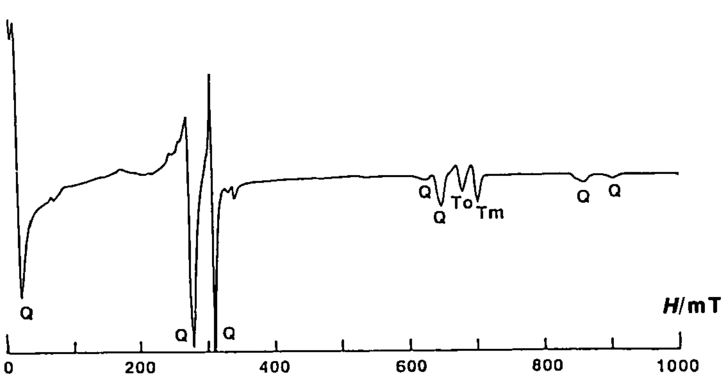
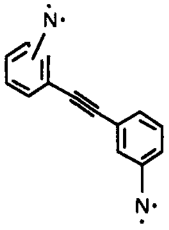
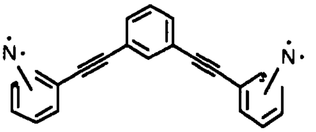


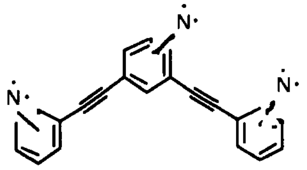
FIGURE 5. X-band EPR fine structures due to **17a** at 8 K.



17a: *o,m'*
17b: *m,m'*
17c: *m,p'*



17d: *o,o''*
17e: *p,p''*
17f: *o,p''*
17g: *m,p''*
17h: *m,m''*



18a: *p,m',p''*
18b: *m,p',m''*

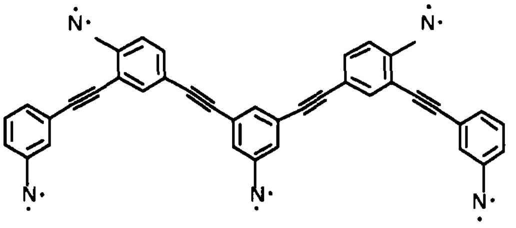


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Table 4. Zero Field Splitting Parameters for the Quintet Dinitrenes **17**

	D/hc/cm^{-1}	E/hc/cm^{-1}		D/hc/cm^{-1}	E/hc/cm^{-1}
17a[a]	0.1630	0.0148	**17e**	0.1488	0.0055
	0.1758	0.0065	**17f**	0.1510	0.0116
17b	0.169	0.040	**17g**	0.1508	0.0104
17c	0.1575	0.020			
17d[a,b]	0.1620	0.0077			
	0.1577	0.0137			
	0.1622	0.0125			
	0.1575	0.0089			

a) two sets of D/E values due to the presence of two conformers.
b) two combinations are possible.

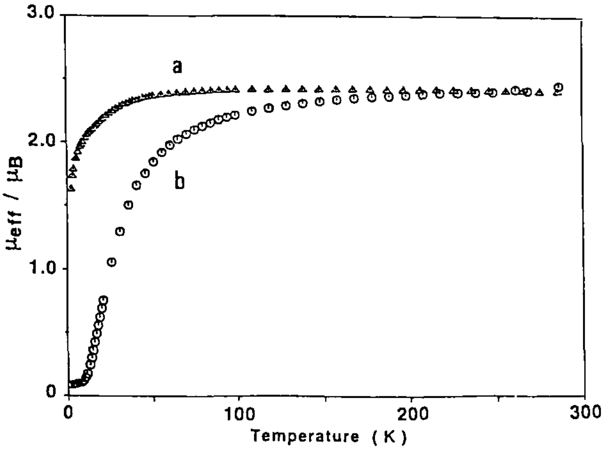
perturbation method.[25]

Plots of the signal intensities vs. temperature for quintet dinitrenes **17a** and **17c** - **17f** followed the Curie law in the range of 6 - 80 K, and no thermally populated signals were detected. The two triplet units are concluded to interact ferromagnetically in these dinitrenes. On the other hand, when two terminal nitrenes were both meta (**17h**) to the respective ethynylene bridge, 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 **9** into magnetically independent parts. Antiferro- and ferromagnetic interac-tions in **17b** and **17c** have already been included in Tables 2 and 3. In **17g**, signals due to a quintet state were observed as a thermally accessible excited state having a maximum intensity at 8 K. The quintet is estimated to be less stable than the ground state by 27 cal/mol from a model of two weakly interacting triplet. From these results, polymer **9** 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 (**17h**) to the respective ethynylene bridges, they are 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 **9** into magnetically independent parts.

Oligonitrenes **18** and **19** 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''* and *m,p',m''*-**18** gave best fits with $S = 2.9 = 3$. Similarly, pentanitrene **19** 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, **9** promises to be a super-high-spin polymer.

EXCEPTIONS

We have witnessed a number of examples in which the *m*-phenylene unit serves as a robust ferromagnetic coupler. In order to stabilize the radical centers kinetically, we introduced methoxy groups into this coupling unit.[26] 2,4-Dimethoxy-*m*-phenylenbis(*N*-*tert*-butylnitroxide) (**20**) thus designed showed, in a frozen toluene matrix, X-band EPR fine structures characteristic of triplet dinitroxides: $D/hc = 0.0179\ cm^{-1}$ and $E/hc = 0.0008\ cm^{-1}$. A $\Delta m_s = 2$ transition was observed at 1692 mT. Deviation of the temperature dependence of the signal intensities from a Curie law was not appreciable. The μ_{eff} obtained on a Faraday balance showed a limiting value of 2.45 μ_B at higher temperature, a value consistent with degenerate singlet and triplet states. As the temperature was decreased, the μ_{eff} value for a sample in PVC film (2 mol%) remained constant in the range 45~300 K and decreased slightly at the lower temperature (Figure 6). The results are interpreted in terms of nearly degenerate triplet and singlet states: the χ values were simulated by a Bleaney-Bowers equation (Eq. (2)) in which $2J = -7.0\ k_BK = -4.9\ cm^{-1}$. The observed triplet lies slightly above the ground singlet state.



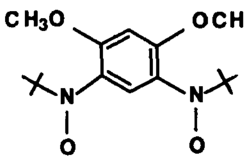


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FIGURE 6. Temperature dependence of μ_{eff} values of **20** in (a) PVC films and (b) in neat crystals.

Similar μ_{eff} vs. temperature plots for a microcrystalline sample of **20** are dominated by an antiferromagnetic interaction; as the temperature was lowered, μ_{eff} started to decrease appreciably at ca. 50 K, and then decreased more sharply (Figure 10). The data were interpreted in terms of a singlet/triplet model in which $2J = -73.8\ k_BK = 51.3\ cm^{-1}$; the ground state is decidedly a singlet.

It is often the case that μ_{eff} values of free radicals in neat crystals decrease at lower temperatures because of antiferromagnetic interradical exchange coupling. Diamagnetic dimers are sometimes formed in the extreme.

An X-ray crystal structure analysis has been performed on a monoclinic single crystal of **20** to show that the *tert*-butylnitroxide moieties are considerably out of the *m*-phenylene plane (by 65.1 ° and 75.3 °) and in *syn* conformation.[26] There is no interradical distance shorter than 7.04 Å between the neighboring molecules; the formation of a dimer is not suggested. It is highly likely that the strong antiferromagnetic coupling is intramolecular. Lower π-spin polarization on the *m*-phenylene ring and a possible antiferromagnetic through-space interaction between the spins rather localized on the nitroxide radicals at a distance of 5.74 Å (between the two middle points of the N-O bonds) may be responsible for the non-ferromagnetic coupling in **20**. In toluene and PVC solid solutions, **20** is presumed to take another conformation, e.g., more planar or *anti* form in which such antiferromagnetic coupling is less effective.

In short, the 4,6-dimethoxy-*m*-phenylene unit in **20** is not a ferromagnetic coupling unit but the two nitroxide groups are coupled in an antiferromagnetic fashion strongly in crystals and weakly in solid solutions. Some care should be taken in the proper choice of a combination of spins and ferromagnetic couplers for designing high-spin polymers.

CONCLUSION

While we have been able to establish molecular design of super-high-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 super-high-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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