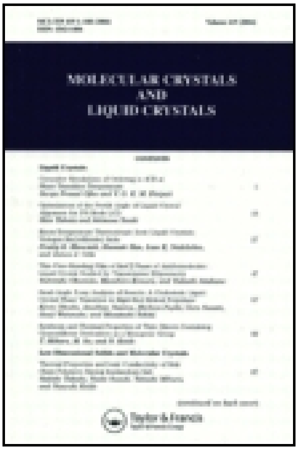

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# Approaches to Superparamagnetic Polycarbenes and Polynitrenes

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# APPROACHES TO SUPERPARAMAGNETIC POLYCARBENES AND POLYNITRENES

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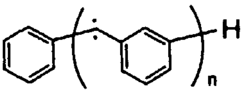
Abstract Poly(m-phenylenemethynyls) and other conjugated polymers to which photolabile diazo or azido groups are attached in every repeating unit have been synthesized. When photolyzed and studied in situ by means of a Faraday balance equipped with a light guide at cryogenic temperatures, the hexa- and nonacarbenes obtained by stepwise synthesis were found to be in $S = 6$ and $9$ ground states, respectively. Attempts to synthesize real polymer samples capable of showing $S = 10^{2\sim3}$ were made. These materials would serve as prototypes for organic opto-magnetic recording devices.

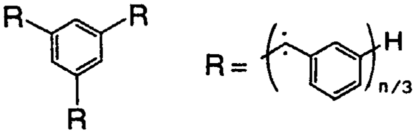
## INTRODUCTION

The large majority of organic molecules have closed-shell electronic structures, i.e., they have a singlet ground state with equal numbers of electrons having $\alpha$ and $\beta$ spin. Most organic compounds are therefore diamagnetic. 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. The assembly of these free radicals are paramagnetic. The alignment of spins in molecular systems becomes an issue when there is an interaction between two doublet centers as in diradicals and radical pairs. The Coulombic repulsion between electrons lifts the zeroth-order degeneracy and gives rise to singlet and triplet states of different total energy for these chemical entities. It is the singlet state which is usually more stabilized, as described by the Heitler-London spin exchange between spins of opposite sign.

Only when the interacting spins are in orthogonal orbitals, the triplet states are favored. The half-filled orthogonal orbitals are dictated by symmetry 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 $\pi$-diradicals, the intervening $\pi$-bonds are polarized and therefore, if periodicity of the spin polarization is appropriate, the parallel alignment of the two spins can become favored. Schlenk hydrocarbon in a triplet ground state is such an example.[1] Poly(m-phenylenecarbenes) **1** are geminate of these two concepts for constructing higher spin organic molecules.[2] We have now extend our previous work in a series of **1**[3] to pseudo-two-dimensional systems as well as to higher polymers. The significance of this strategy and the results will be discussed.



**1**



**2**

## MOLECULAR DESIGN AND SYNTHESES OF THE PRECURSORS

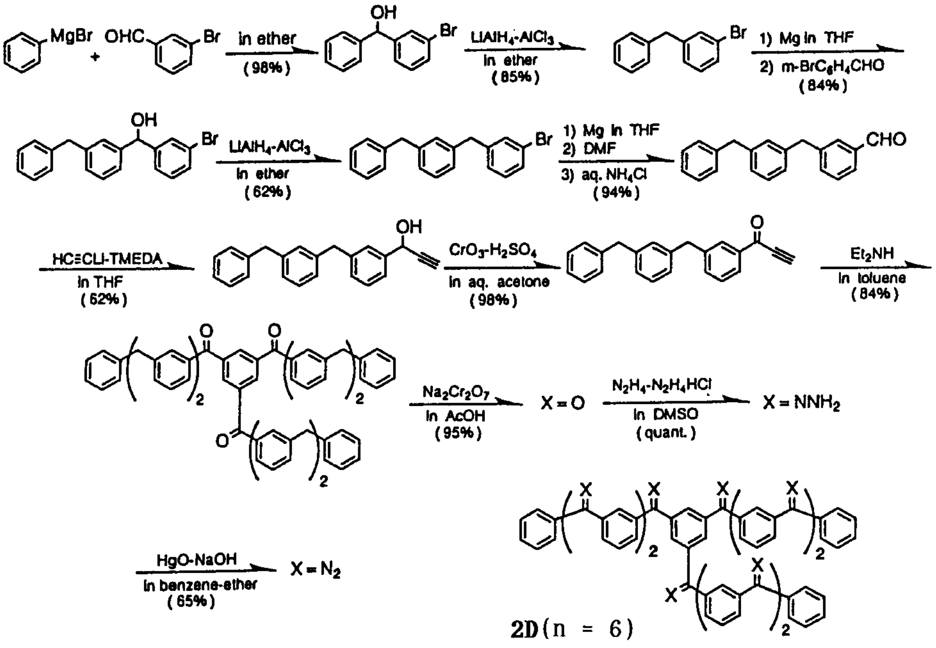
### Pseudo-two-dimensional Hexa- and Nonadiazo Compounds

The spin alignment in **1** is after all one-dimensional. In order to realize the long-range order at finite temperature, it is imperative to increase the dimension of **1**. This could in principle be achieved either by imposing proper magnetic interaction between the molecular chains of **1** as in crystals or by increasing the dimension of the high-spin molecules themselves. The prototypes of the first approach by controlling the stacking orientation of diphenylcarbene derivatives have been reported.[4] We have now introduced the pseudo-two-dimensional structure **2** as a second possibility.

The synthetic scheme employed for the precursor **2D**(n = 6) is outlined in Scheme I. One of the key steps in this reaction sequence is the secondary amine-catalyzed trimerization of the ethynyl aryl ketones to give 1,3,5-tris(substituted aroyl)benzenes.

**2D**(n = 9) has been obtained similarly. Both polydiazo compounds **2D** were purified at 0 C through a column of neutral alumina (activity IV) with a mixture of hexane and benzene. IR(2060 $cm^{-1}$) and NMR data were fully in line with the structures.

**Scheme I**

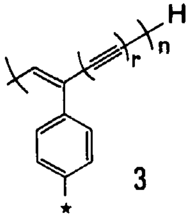


**2D**(n = 6)

### Poly(p-ethynyldiphenylcarbene) and Poly[1-(p-nitrenophenyl)-1,3-butadiyne)

Both structures **1** and **2** require stepwise syntheses. In order to prepare molecules in which many thousands of electron spins are aligned in parallel, it is advisable to take advantage of the conjugated polymers,[5] e.g., poly(phenylacetylenes), poly(phenyldiacetylenes), poly(phenylenevinylenes), etc. that are popular in conducting polymers and non-linear optical materials. The problem now reduces to the question of where to place the triplet carbene or nitrene centers on the side chains as pendants. Theoretical[6] as well as experimental[7] studies on the prototypes have revealed that the triplet centers on the p-positions of the pendant phenyl rings (**3**) would couple in a ferromagnetic fashion via the polarization of the conjugated main chains.

A series of 1-(p-substituted phenyl)-1,3-butadiynes **4P** were prepared. Some of the crystalline samples of the diacetylenes underwent spontaneous solid-state polymerization[8] at slightly elevated temperatures to give dark-violet colored insoluble polymers which were then photolyzed at cryogenic temperatures to generate the triplet carbene or nitrene centers.



**3**

**4P** R = PhCN$_2$, N$_3$

ESR SPECTROSCOPIC STUDIES AND MAGNETIC MEASUREMENTS OF THE PHOTOCHEMICALLY GENERATED POLYCARBENES AND POLYNITRENES

Photolysis of **2D** in MTHF glasses at 10 K in an X-band ESR cavity resulted in the appearance of strong and complex ESR signals centered at ca. 3300 G and characteristic of high-spin states; signals attributable to triplet carbenes and quintet dicarbenes were very weak.

A light guide has been installed in an Oxford Faraday balance. The polycarbenes and polynitrenes were produced photochemically at cryogenic temperatures in a sample basket suspended in the superconducting solenoid (≤7 T) and the magnetic measurements were carried out in situ. The magnetization vs. applied magnetic field strength curve was analyzed in terms of a Brillouin function to give $S = 6$ for **2**($n = 6$), the highest spin ever reported for purely organic molecules (FIGURE 1). **2D**($n = 9$) gave a preliminary magnetization curve which was interpreted in terms of a mixture of $S = 5 \sim 9$. When the sample concentration was high, the presence of antiferromagnetic intermolelcular interaction was revealed by the

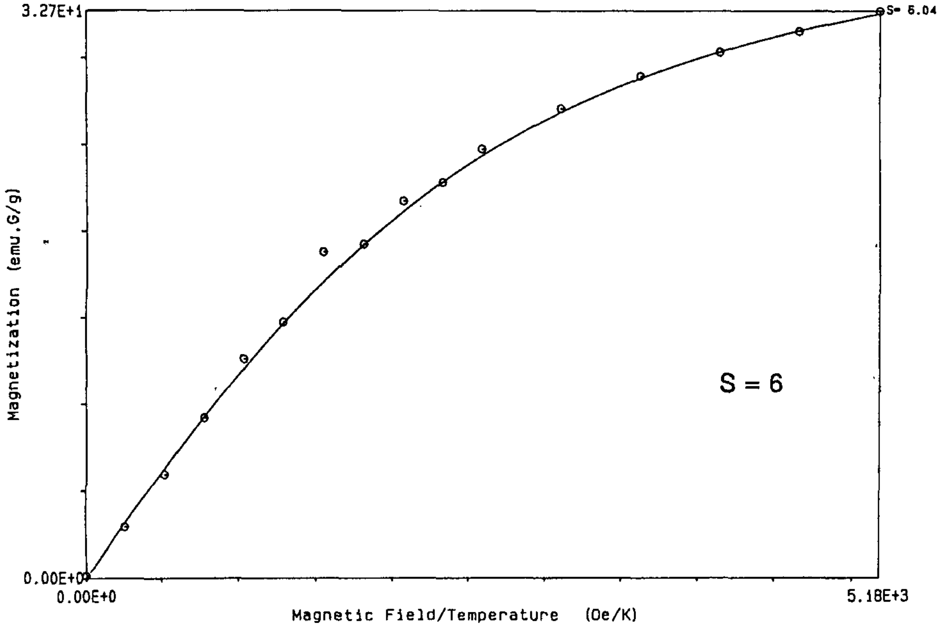


Figure 1 Field dependence of magnetization of **2**(n = 6) at 1.9 K.

apparent lowering of the effective magnetic moment at 1.9 K relative to 10 K. The same was true with the partially photolyzed neat samples of **2D**. The exchange interaction between the high-spin molecules in fortuitously formed clusters of them is suggested to be antiferromagnetic. Similar measurements of the photolysates of polydiazo and polyazido compounds due to **4P** revealed weakly coupled (Weiss temperature of ca. -2 K) independent spins (S = 1). There are two reasons conceivable for the failure to realize very high-spin products: difficulty in completing photochemical reactions as revealed by the Curie constants lower than the theoretical ones and wrong topochemistry of the solid-state polymerizations as suggested by X-ray structure of the monomer crystals.

## CONCLUSION

Approaches to superparamagnetic polycarbenes and nitrenes have been made. Once a molecular assembly of these superhigh-spin molecules acquires magnetocrystalline or shape anisotropy and the relaxation time for the reorientation of the principal axis of the magnetization becomes longer than the measuring time, it will have a chance of developing residual magnetization at the temperatures lower than the blocking temperature. The residual magnetization can be used as magnetic memory. The present study has shown that the purely organic magnetic materials of this kind may be obtained by uv-irradiation of diamagnetic or weakly paramagnetic polymeric solids. The photochemical process gives us an idea of transforming optical signals into magnetic memory just as photoresists are formed by photochemical reactions. Thus these materials serve as a prototype for organic optomagnetic recording devices.

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