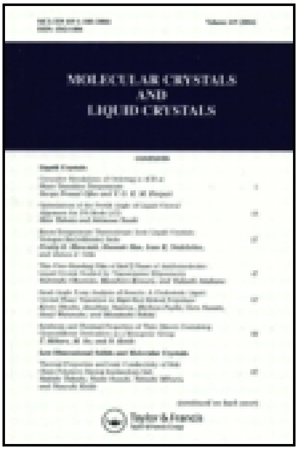

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Photochemical Production of Highly Ordered Spins in Organic Solids

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PHOTOCHEMICAL PRODUCTION OF HIGHLY ORDERED SPINS IN ORGANIC SOLIDS

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Abstract Poly(*m*-phenylenemethynyl)s and the related π-conjugated polymers to which photolabile diazo groups are attached as pendants have been prepared. They were photolyzed and studied in situ by means of ESR spectroscopy and magnetometry on a Faraday magnetic balance equipped with a light guide at cryogenic temperatures. Unprecedentedly high-spin polycarbenes have been characterized.

Keywords: conjugated polymers, poly-(m-phenylenemethynyls), high-spin, polycarbenes, polyradicals, paramagnetic

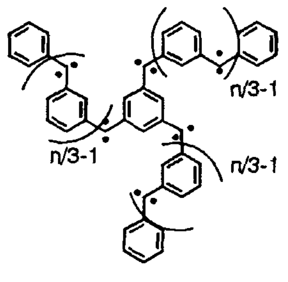
INTRODUCTION

Two electron spins in organic diradicals and radical pairs have a strong tendency to cancel each other by making a chemical bond. Only when the interacting spins are in mutually orthogonal orbitals, a triplet state with parallel spins can be favored. In π-conjugated diradicals, singly occupied non-bonding molecular orbitals satisfy these conditions as in *m*-quinodimethane. By extending such molecular design to π-conjugated polyradicals, highly ordered spins would be established. There are two extreme approaches possible for constructing such super-high-spin polyradicals. One is the production of magnetic polyradicals by photochemical generation of radical centers in precursor polymer samples. The other is photopolymerization of a paramagnetic radical monomer that carries a polymerizable unit other than the radical center.
Some recent results on the basis of the first approach will be discussed.

"STARBURST" POLYCARBENES

Molecular Design

Pseudo-two-dimensional polycarbenes **1** (n = 6, 9) have the highest spin multiplicities ever reported for purely organic molecules.[1] These high spin states originate from their topological symmetry of the π-systems. To expand this structure and realize higher spin multiplicity, we adopted a convergent approach[2] to dendritic "starburst" structure. In this approach, the starting units would give larger units and then these larger units afford the final dendritic macromolecules. The key step to fabricate the units in our system was the secondary-amine-catalyzed trimerization of the ethynyl aryl ketones.[3] Repetition of this reaction would lead to a very large molecule which is a part of the ideal honeycomb-like structure **2**.



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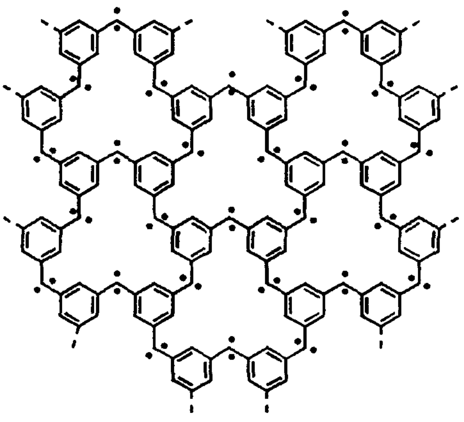


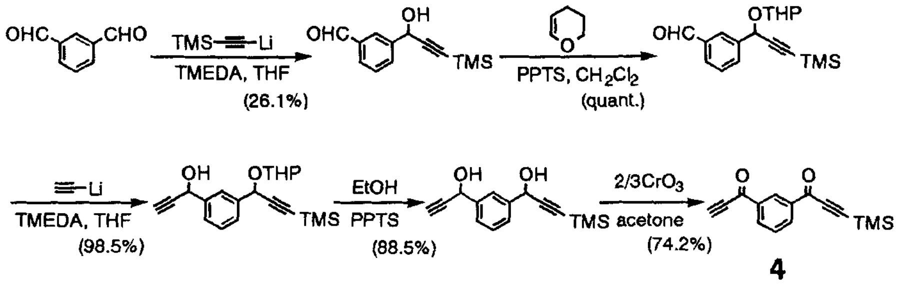
2

Synthesis of the Dodecadiazo Compound

These polyarylcarbenes were synthesized by the photolysis of the corresponding diazo compounds. Two kinds of ethynyl aryl ketones were chosen as starting units. One was ethynyl phenyl ketone **3** and the other was monotrimethylsilyl-protected *m*-phenylenebis(ethynyl)ketone **4**. Preparative route of these ketones is summarized in scheme 1.

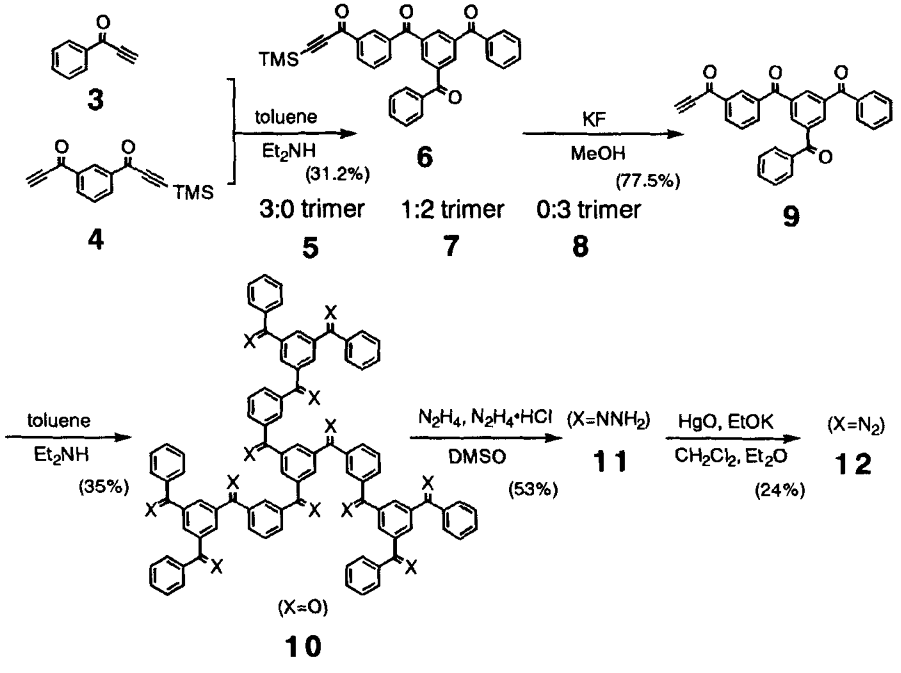
Cross-trimerization of these units afforded a mixture of four sorts of trimers: trimer **5** from three moles of **3**, 2:1-trimer **6**, 1:2-trimer **7**, and trimer **8** from three moles of **4**.

SCHEME 1



These trimers could be separated by gel permeation chromatography (GPC). The trimer **6** was the required fraction in the subsequent reactions.

SCHEME 2

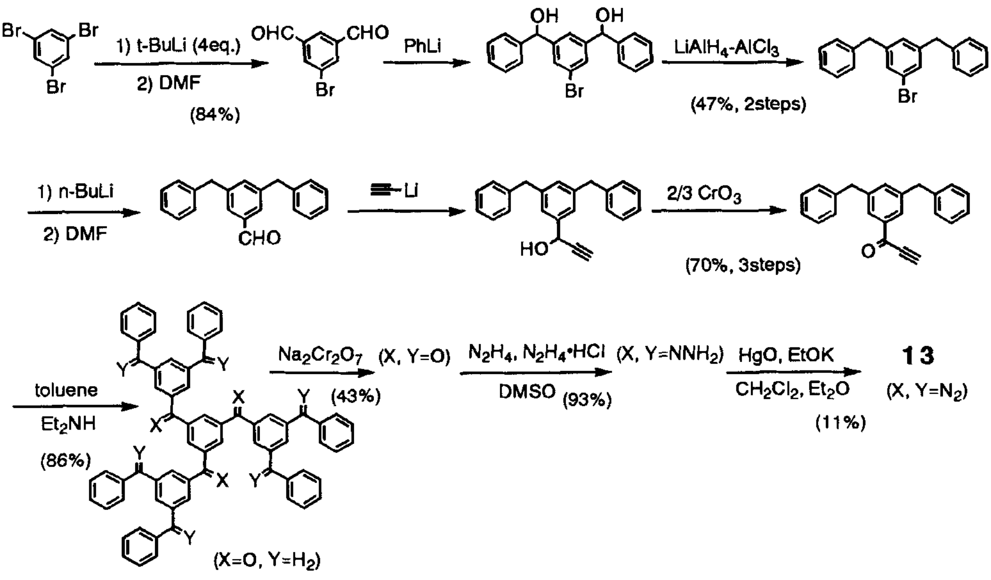


After removal of the protecting group, the trimerization reaction of **9** was carried out for the second time to afford dodecaketone **10**. Thus the construction of the skeleton of dodecacarbene was completed. ^{1}H and ^{13}C NMR, IR and FAB mass spectra were all consistent with structure **10**. Dodecahydrazone **11** was derived from **10** in a usual way and oxidized with HgO to dodecadiazo compound **12**, which was purified through a column of neutral alumina (ICN, activity IV) with a mixture of hexane and benzene. IR (2036 cm^{-1}) and UV-vis (CH_2Cl_2 : λ_{max} (ε) 292 (362000), 520 nm (1660))[4] (scheme 2).

Synthesis of Nonadiazo Compound

Another "starburst" polycarbene was studied. The synthesis of this nonadiazo compound **13** is summarized in scheme 3. There were no separating steps involved in this route. IR and UV-vis spectra of **13** were as follows: IR (2037 cm^{-1}) and UV-vis (CH_2Cl_2 : λ_{max} (ε) 289 (187000), 516 nm (954)).[4]

SCHEME 3



ESR Study and Magnetic Measurement of the Photochemically Generated Polycarbenes

Photolysis of **12** and **13** were carried out in MTHF glasses at 9 K with a Xe lamp (400 nm < λ < 480 nm obtained by combination of a Kenko

B-390 band-path filter and an OCLI B cold mirror) in an X-band ESR cavity of a Bruker ESP 300 spectrometer equipped with an Air Products LTD-3-110 cryogenic temperature controller. The ESR signals observed in situ were single lines centered at *ca.* 335 mT with a line width of 10 mT; signals attributable to triplet carbenes and quintet dicarbenes were very weak if not undetected (Figure 1). The signals obeyed the Curie-Weiss laws in the temperature range 10-50 K, with no change of the signal shape due to a thermally populated low spin state.

When the weak light (*ca.* 1/10 quantity of light) intensity was used in the photolysis of **12**, signals attributable to triplet carbenes and quintet dicarbenes were obtained in the initial stage of the photolysis, which gradually became weaker and finally undetectable as compared to the center signal attributable to the high-spin state.

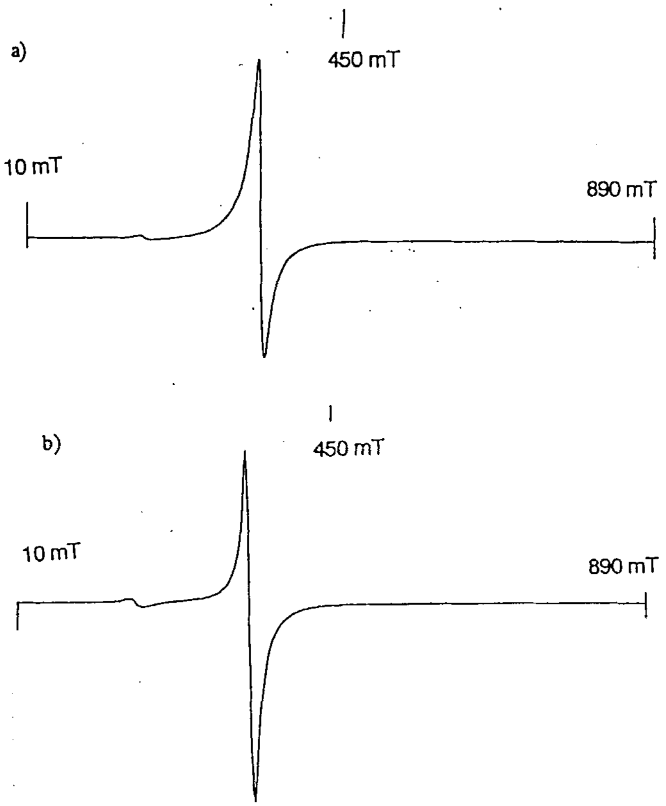


FIGURE 1 ESR spectra of the photoproducts of a) **12** and b) **13**.

Magnetic measurements were carried out on an Oxford Faraday balance installed with a quartz light guide for irradiation of the precursor samples. UV-vis light (400 nm < λ < 480 nm from a Xe lamp) was introduced into *ca*. 0.006 mg of **12** in 100 μL of MTHF in a quartz sample basket suspended in the superconducting solenoid and cooled at ca. 2 K. The field dependence of magnetization of the photoproduct was determined in situ at 2.1, 4.2, and 9.1 K. The paramagnetic contribution was obtained by subtracting the corresponding values obtained before irradiation. It is the advantage of this method that the effect of any paramagnetic impurities can be canceled by this treatment. The plots of the magnetization vs. the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function.

While such a treatment of the observed data gave S = 9 for **1** (n = 9) (see Figure 2),[1] the magnetization data for the photoproduct of **12** did

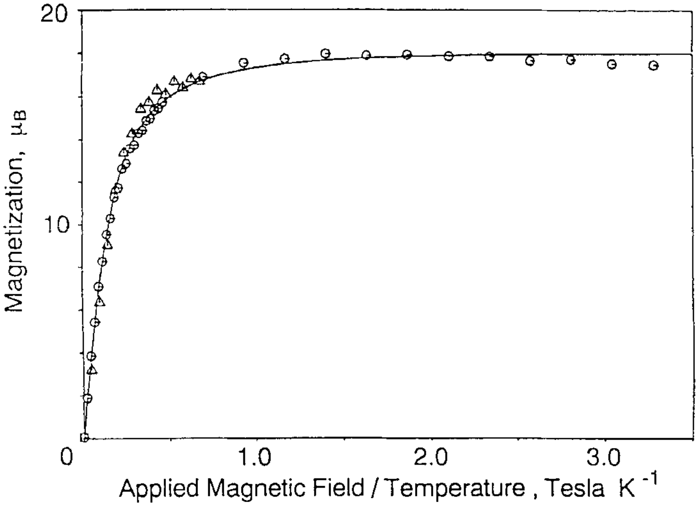


FIGURE 2 Magnetization curve for **1** (n = 9) with S = 9 in MTHF glasses at 2.1 K (o) and 10.0 K (Δ).[1]

not satisfy the Brillouin function with S = 12 or any other single spin quantum number S (Figure 3). As H/T was increased, the magnetization rose rapidly but leveled off rather slowly. The results are most reasonably interpreted in terms of the presence of various species with different S values; the sharp rise and slow saturation of the magnetization correspond to the species with high and low S values respectively.

Therefore the observed data in Figure 3 should in principle be simulated by a sum of the several theoretical curves with different spin quantum numbers. Furthermore, the data obtained at three different temperatures do not agree with one another. Since the magnetization is attenuated at lower temperature, the presence of antiferromagnetic interaction among the ordered spins is suggested. When the sample concentration as low as 0.1 mM is taken into account, the observed antiferromagnetic interaction is assigned to an interbranch interaction within a molecule rather than between molecules. Efforts are in progress to obtain a homogeneous dodecacarbene sample.

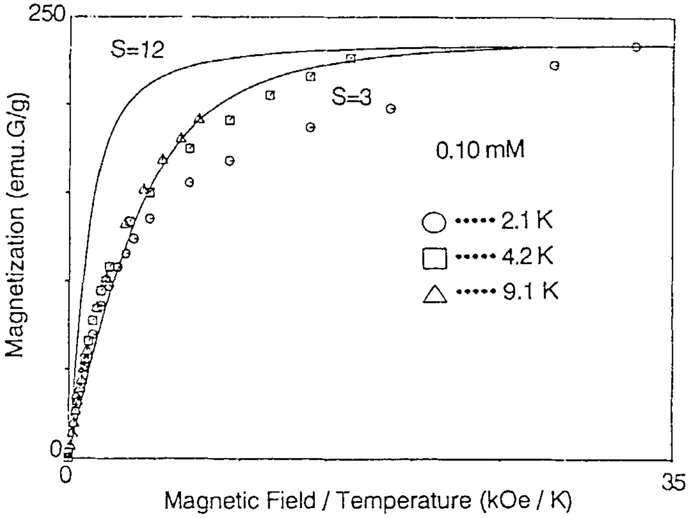


FIGURE 3 Magnetization data for the photoproduct of **12**.

The photoproduct of **13** was measured similarly at 2.1 and 4.0 K. In this case, the observed data agreed with the theoretical curve not for $S = 9$ but nicely for $S = 7$ (Figure 4). The observed S value which is lower than the theoretical one is similar to the case of **12** but seems to differ considerably in two aspects. Firstly, the data for **13** at the two temperatures were mutually consistent and fitted to the same Brillouin function. Secondly, the observed magnetization data were stoichiometric and corresponded to 14 parallel spins or a heptacarbene. The origin of the loss of one carbene center per molecule remains to be investigated. Several measurements were made at different time of irradiation to show that the observed $S = 7$ did not depend on the degree of the photoreaction.

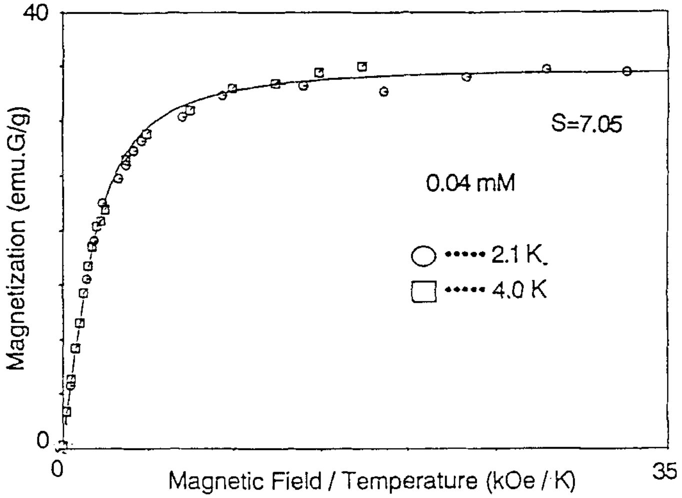


FIGURE 4 Magnetization data for the photoproduct of **13**.

CONCLUSION

We have demonstrated that the molecules having 12~18 electron spins coupled strongly in a ferromagnetic fashion and therefore large magnetic moments can be constructed photochemically. While the "Starburst" skeletal structures are favored from a synthetic point of view of extending the cross-conjugated molecular structure, the triplet carbene centers may not be kept intact when they are accumulated too densely. Interaction between these high-spin oligomers appears to be antiferromagnetic and remains to be overcome before real ferromagnets are realized.

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3. K. Balasubramanian, S. Selvaraj, and P. S. Venkataramani, Synthesis, 1980, 29.
4. The *n*-π^* molar absorption coefficient per one diazo group was 138 supporting that this molecule carries 12 diazo groups.