Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spin Balls and Spin Barbells. Preparation and Magnetic Studies of S = 7/2 Dendritic Heptaradical and Progress Toward Very High Spin Dendrimers[1]

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Version of record first published: 24 Sep 2006.

To cite this article: Andrzej Rajca & Suchada Utamapanya (1993): Spin Balls and Spin Barbells. Preparation and Magnetic Studies of S = 7/2 Dendritic Heptaradical and Progress Toward Very High Spin Dendrimers[1] , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 305-312

To link to this article: http://dx.doi.org/10.1080/10587259308035720

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 305–312
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Printed in the United States of America

SPIN BALLS AND SPIN BARBELLS. PREPARATION AND MAGNETIC STUDIES OF S = 7/2 DENDRITIC HEPTARADICAL AND PROGRESS TOWARD VERY HIGH SPIN DENDRIMERS.[1]

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Abstract 1,3-Connected polyarylmethyl dendritic heptaradical was prepared by the treatment of the heptaether precursor with lithium in THF followed by oxidation of the resultant carboheptaanion using iodine in THF at low temperature. The magnetization studies of heptaradical in frozen THF, which were carried by SQUID at T = 2 - 10 K, indicate the S = 7/2 ground state.

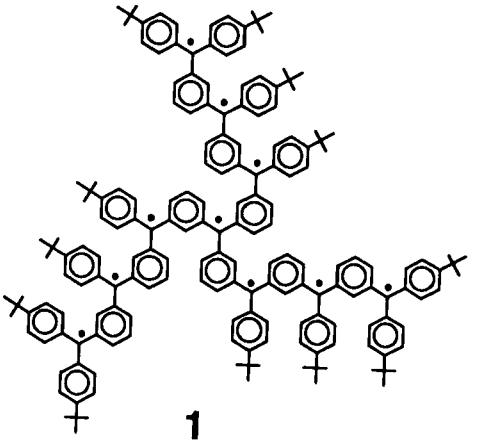
Introduction

Very high spin organic molecules are relevant to the recent subject of organic magnetism.[2-5] While high spin molecules mimic ferromagnetic spin ordering (e.g., exchange interactions) in ferromagnetic solids or films, the magnetism has another important aspect, i.e., magnetic anisotropy.[6] The latter allows for the preferential orientation in space of the magnetization vector (the average direction of the parallel spins) which is a prerequisite for the plethora of magnetic properties. One of the primary sources of the anisotropy in traditional magnets is spin-orbit coupling and the other are the dipolar interactions between the electron spins. The anisotropies derived from the spin-orbit coupling pose a complex quantum mechanical problem and are extremely difficult to evaluate from first principles; they greatly contribute to the intransigence of magnetism with the respect to theory. The dipolar anisotropies can be related to the mesoscopic (multinanometer scale) shape and are readily tractable by theory; they are believed to be in part responsible for the

extraordinary magnetic properties of the nano-structured solids and nanometer-size magnetic particles.[7]

In the carbon-based radicals and carbenes, the spin-orbit coupling is negligible as judged by their g-tensors.[8] For the densities of the unpaired electrons as typically found in organics, the dipolar anisotropy should be significant as long as the shape of the mesoscopic very high spin ($S \gg 10$) molecule (or polymer) is properly controlled (e.g., prolate ellipsoid rather than sphere); therefore, such molecules could provide a unique opportunity for study of magnetism at mesoscopic scale.[9]

We have shown that 1,3-connected polyarylmethyl polyradicals are promising candidates for very high spin organics; the ground states of up to $S = 5$ has been reported.[3]



1

Decaradical **1** and its lower homologues are moderately sterically congested and can be classified as star-branched molecules. We would like to explore the possilibity of preparation of very high spin polyradicals with controlled molecular shape. Hyperbranched (dendritic) structures should provide both maximum efficiency in organic synthesis and control of the molecular shape via steric congestion in three dimensions.[10] We propose that the polyradicals in series I and II would achieve spherical and barbell-like shape, respectively, as suggested by molecular modelling for analogous dendrimers;[11] we refer to them as spin barbells and spin balls (Figure 1).

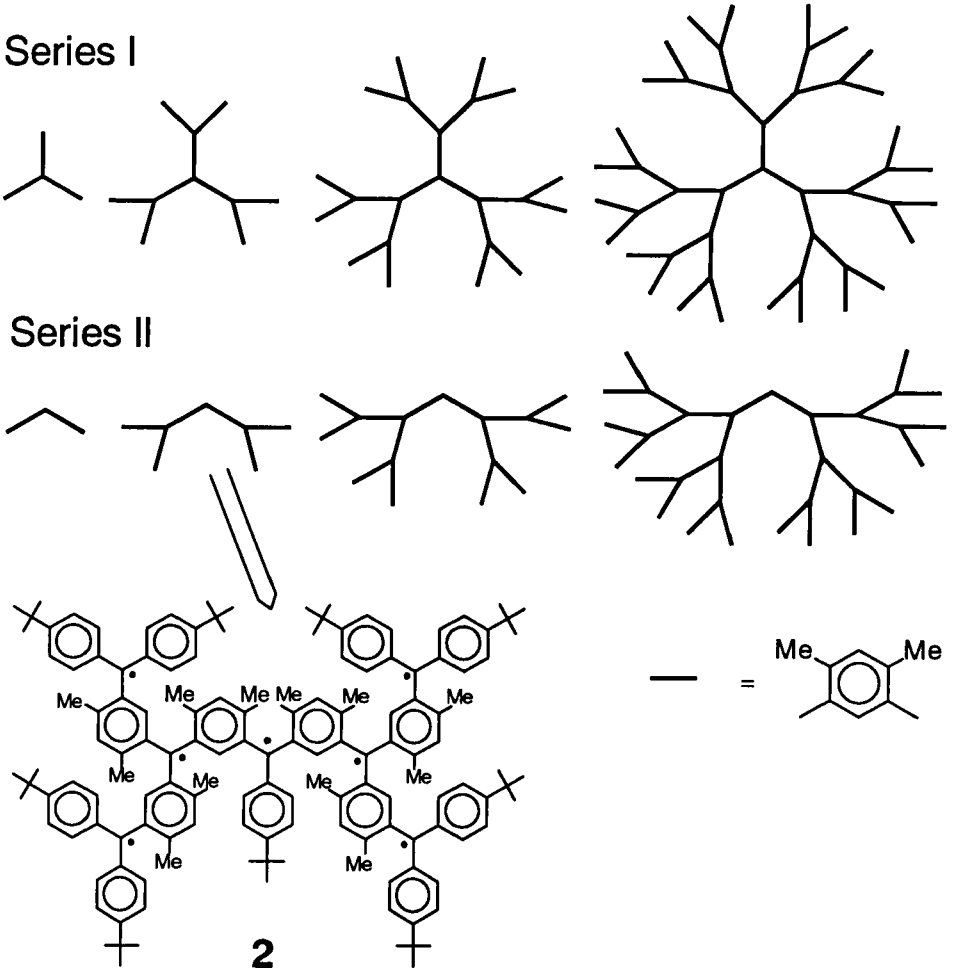
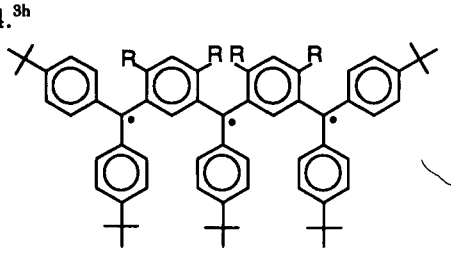


Figure 1. Spin balls (Series I polyradicals with 4, 10, 22, and 46 unpaired electrons) and spin barbells (Series II polyradicals with 3, 7, 15, and 31 unpaired electrons). The "bars" correspond to 4,6-dimethyl-1,3-phenylene linkers between the triarylmethyl sites. The triarylmethyl sites possess unpaired electrons (for polyradicals) or $-OCH_3$ (for polyether precursors). The second polyradical in Series II corresponds to heptaradical **2**. The third and fourth polyether precursors in Series II are labeled in the text as **5** and **6**.

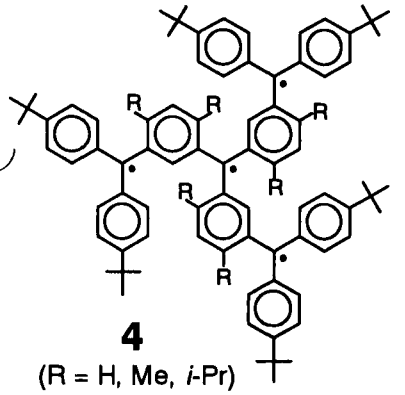
In this paper, we wish to report on preparation and studies of π-conjugated S = 7/2 heptaradical **2** and our progress toward the higher homologues with 15 and 31 unpaired electrons.

Sterically Hindered Tri- and Tetraradicals

Controlling the molecular shape by steric congestion in three dimensions implies that the π-conjugated systems of the polyradicals are significantly twisted out of plane. Consequently, the π-overlap is greatly reduced and the question is whether the ferromagnetic coupling is sufficiently large to have the high spin ground state preferred by large margin. In order to answer these questions we have studied a series of tri- and tetraradicals **3** and **4**.[3h]



3
(R = H, Me, *i*-Pr)



4
(R = H, Me, *i*-Pr)

We have found that all tri- and tetraradicals possess high spin ground states. The most sterically hindered tri- and tetraradicals (R = *i*-Pr) are stable solids at ambient temperature; the absence of the thermal population of their low spin excited states is verified by the magnetic measurements. Therefore, even in the most distorted out-of-plane tri- and tetraradicals (R = *i*-Pr), the high spin ground state is preferred by significantly more than 1 Kcal/mol.

Dendritic S = 7/2 Heptaradical

Treatment of the polyether precursor[3i] with lithium in THF for several days gives a red solution of the carboheptaanion; the subsequent oxidation

with 3.5+ equiv of iodine in THF or 2-MeTHF at 180 K for 40 min produces heptaradical **2**. ~0.01 M **2** in THF and 2-MeTHF is used for SQUID measurements.[3a,h] In the normalized plots of magnetization (M/M_{sat}) vs the ratio of the magnetic field and temperature (H/T), the experimental points at T = 2, 5, 10 K are compared to the Brillouin functions, which correspond to the theoretically predicted behavior for a paramagnet of a given spin (S).[12] Most of the experimental points fall between the S = 7/2 and S = 5/2 Brillouin curves. The temperature dependence, which is somewhat less for 2-MeTHF than for THF and, for **2** in THF, is also confirmed by the downward turn of the χT vs T plot at T < 10 K, may be caused by intermolecular antiferromagnetic interactions. The magnetization at T = 10 K and T = 5 K corresponds to approximately S = 3 (Figure 2).

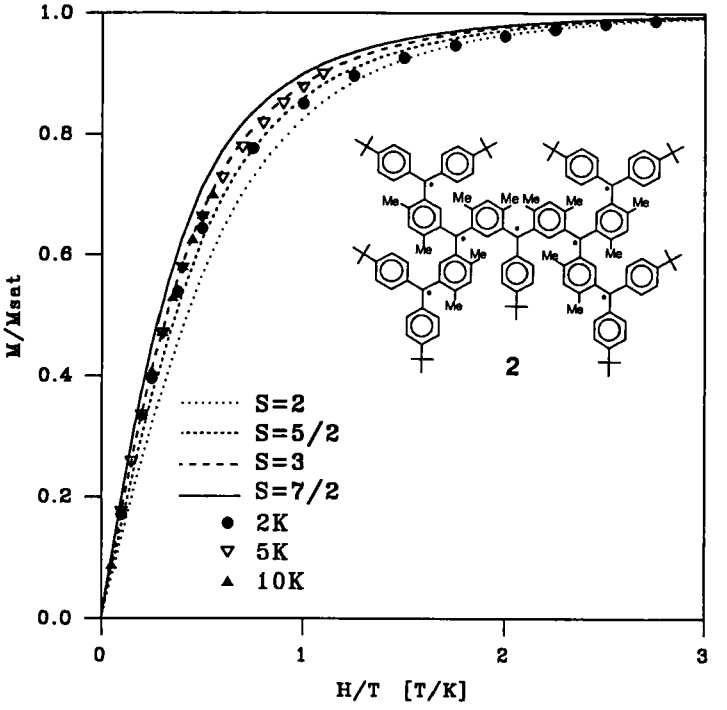


Figure 2. Normalized plots of magnetization vs ratio of magnetic field and temperature (M/M_{sat} vs H/T) at T = 2, 5, 10 K for heptaradical **2** in 2-MeTHF. The curves correspond to the Brillouin functions for S = 2, 5/2, 3, 7/2.

The discrepancy between the experimental and theoretical values of S = 3 and S = 7/2, respectively, may be caused by the presence of small amount of polyradicals with defects (e.g., one unpaired electron missing at one of the triarylmethyl sites) or low spin impurities. We conclude that heptaradical **2** possesses octet ground state (S = 7/2).

Toward Spin Balls and Spin Barbells

The precursors for higher homologues of heptaradical **2** are prepared; i.e., polyethers **5** and **6** (Figure 1). Both polyethers are obtained via convergent routes analogous to those used to obtain the polyether precursors for heptaradical **2** and other polyradicals previously reported.[3] For each compound under 5,000 Daltons, the $(M - OCH_3)^+$ isotopic clusters using FABMS are found in satisfactory agreement with the simulation of natural abundance of isotopes. For, **6** (MW = 8,854.98 Daltons) and the corresponding triarylmethanol only average mass peaks for the $(M - OCH_3)^+$ clusters are obtained.

We are striving to further purify the polyether precursors and to improve the carbanion method for generation of very high spin polyradicals. Also, we are developing the synthetic methods for polyradicals where the moderate number of defects do not render strong ferromagnetic coupling in the molecule; for such polyradicals, very high spins may be achieved even in the presence of defects.

Conclusion

Dendritic high spin ground state (S = 7/2) polyradical was prepared. Dendritic polyradicals with as many as 31 unpaired electrons (S = 31/2) may be feasible.

Acknowledgement

We gratefully acknowledge the National Science Foundation for the support of this research (CHEM-8912762 and CHE-9203918). We thank The

Camille and Henry Dreyfus Foundation for the Teacher-Scholar Award to A.R. We thank Professor Sy-Hwang Liou of the Department of Physics for the access to the SQUID magnetometer.

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