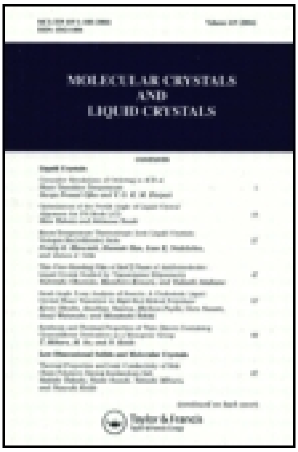

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dendrimeric Hyperbranched Alkylaromatic Polyradicals with Mesoscopic Dimensions and High-Spin Ground States

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Version of record first published: 24 Sep 2006.

To cite this article: Nora Ventosa, Daniel Ruiz, Concepcio Rovira & Jaume Veciana (1993): Dendrimeric Hyperbranched Alkylaromatic Polyradicals with Mesoscopic Dimensions and High-Spin Ground States, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 333-342

To link to this article: http://dx.doi.org/10.1080/10587259308035723

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 333–342
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Printed in the United States of America

DENDRIMERIC HYPERBRANCHED ALKYLAROMATIC POLYRADICALS WITH MESOSCOPIC DIMENSIONS AND HIGH-SPIN GROUND STATES.

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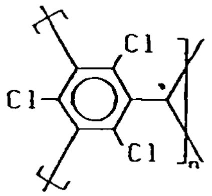
Abstract Molecular design to super high-spin stable organic molecules with dendrimeric character is described. The synthesis of some polyradicals with this characteristics are also reported.

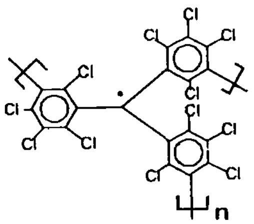
The development of completely organic materials that possess relevant magnetic properties, specially ferromagnetism, is an area of increasing interest that involves several disciplines such as organic synthesis, electronic structure theory, and materials science. If one takes into account the potential usefulness of such kind of materials it is desirable to achieve the magnetic property as an inherent permanent characteristic of a bulk organic material as, for example, a polymer.

One of the general approaches towards ferro- or superparamagnetism in purely organic macromolecules is based on large π-conjugated polyradicals with topologically polarized spins.[1] Recent synthetic efforts towards this new class of organic materials have resulted in several examples of high-spin organic molecules;[2,3] **S=5** is the highest spin multiplicity in organic molecules known to date.[3c,4] The high-spin ground states of these molecules arise, by Hund's rule, from half-filled, multifold near-degenerate, nonbonding, and nondisjoint HOMOs. Most of these molecules, however, lack sufficient stability for practical purposes and in those cases where such instabilities have been overcome, the resulting excited low-spin states are thermally accessible.[5] Until now, such inherent drawbacks have hampered the preparation of large macromolecules possessing both high stabilities and large magnetic moments at room temperatures. We, therefore, focused our attention on persistent high-spin macromolecules having high chemical and thermal stabilities as well as thermally inaccessible excited low-spin states.

There are two prerequisites to realize this objective. First, *stable open-shell building blocks* are required, and second, *ferromagnetic couplings between the spins of these blocks* are necessary. Our choice was the study of polymeric series **I** and **II** which were designed on the basis of the early ideas and polymeric prototypes proposed by Mataga, Itoh, and Ovchinikov.[1]

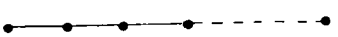


I

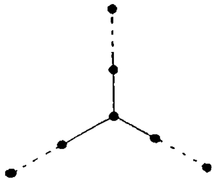


II

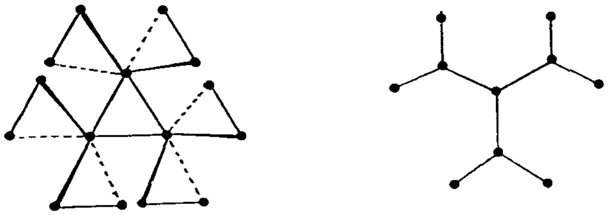
The building blocks of **I** and **II** are polychlorinated triphenylmethyl radicals which show high thermal and chemical stabilities, due to the presence of bulky chlorine atoms around the radical centers.[6] Furthermore, the topology of the radical units in both series permits to expect the presence of ferromagnetic couplings between their radical units, as occurs with others triphenylmethyl polyradicals.[3,7] The strong twisting of the polychlorinated phenyl rings around the radical centers, expected for **I** and **II**, is not a drawback to achieve high spin ground states, as we have previously demonstrated with the synthesis of the two isomers of perchloro-α,α,α',α'-tetraphenyl *m*-xylylene, both with triplet ground states.[8] In addition, the hyperbranched nature of **I** and **II** warrant a highly robust high-spin ground states in both series of polyradicals. In fact, three different molecular and therefore, magnetic interaction topologies can be envisaged for polymeric polyradicals joined by *m*-phenylene units:



Linear topology



Starbranched topology



Hyperbranched topologies

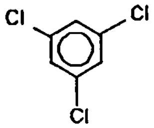
SCHEME I

Linear and starbranched topologies seems to be the less favorable ones in order to obtain robust superhigh-spin ground states, due to the fact that the gaps between their ground and the first excited states must decrease with an increasing number of spin centers; giving rise, under certain circumstances, to the mixing of such states.[5] By contrast, hyperbranched topologies must guarantee a larger energy gap between the ground state and the first excited one, since each spin center is ferromagnetically coupled with at least three other centers.

Finally, **I** and **II** belong to a new type of polymers called dendrimers, starburst or cauliflower polymers. Such kind of compounds have attracted increasing attention due to the expectation that their unique characteristics will impart unusual physico-chemical properties such as fractality, monodispersivity, mesoscopic dimensions, and endoreceptor properties.[9] In addition, this new class of materials demonstrate characteristics, such as supramolecular assemblies, lyotropic liquid crystalline behavior, micellar properties, and behaviors as molecular level ball-bearings in viscous media, which all are related with their supramolecular organization abilities.[9] Since in **I** and **II** the dendrimeric nodes are ferromagnetically coupled, such compounds will have both mesoscopic dimensions and large effective magnetic moments. Due to both facts, quantum-chemical and classical bulk effects could be operative and, therefore, new and exotic magnetic properties could be observed.[10]

In order to obtain polyradical dendrimers **I** and **II** a divergent stepwise synthetic approach was selected.[11] This approach implies five critical stages:

1) **Selection of a initiator core with three reacting sites, such as:**



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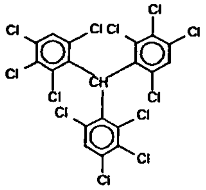
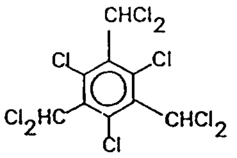


2) **Alkylation of the initiator core with three moles of $CHCl_3$ in order to obtain:**



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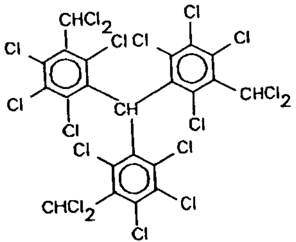
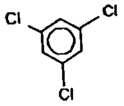


Each introduced $CHCl_2$ groups will act as a branch-junction with a multiplicity of 2 and will be able to act as an alkylating agent in the following step.

3) Subsequent reaction of each of the reactive branch-junction sites with two moles of a reagent. Such reactive molecules will act as branches and will show two or one masked reactive sites, able to be alkylated.



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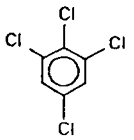
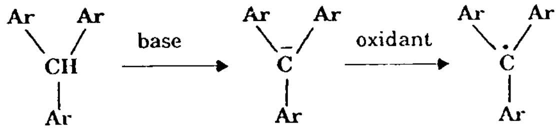


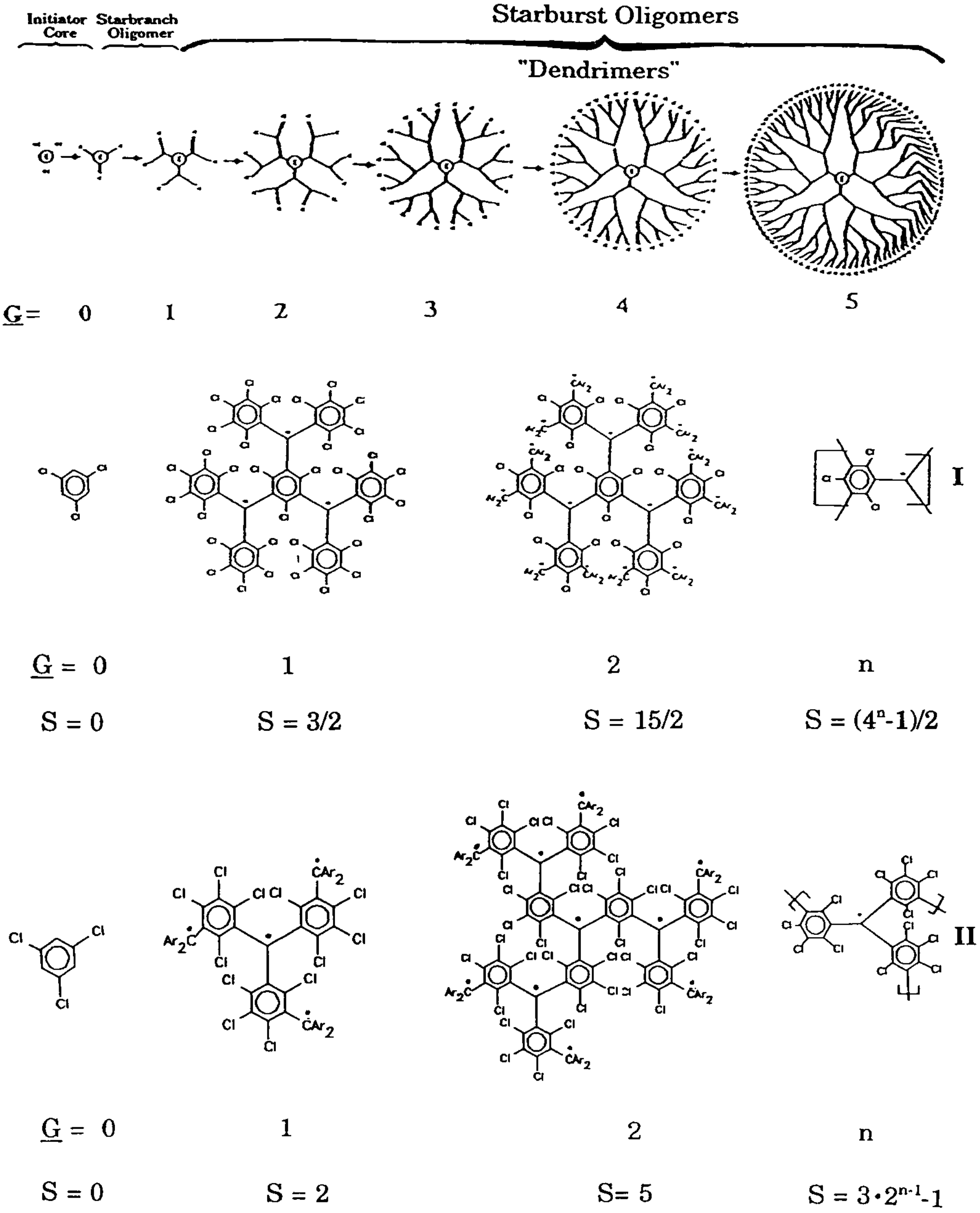
4) Generation of the radical character on each methylic carbon



5) The recurrence of the previous four steps n times in order to prepare the nth generation.

$$\begin{tikzcd} \mathrm{CORE} \arrow[r, "{\substack{1)\ CHCl_3 \\ 2)\ C_6H_3Cl_3}}"'] & D_1 \arrow[r, "{\substack{1)\ CHCl_3 \\ 2)\ C_6H_3Cl_3}}"'] \arrow[d] & D_2 \arrow[r, dashed] \arrow[d] & D_n \arrow[d] \\ & R_1 & R_2 & R_n \end{tikzcd}$$

The different radical generations (R_i) of series **I** and **II** that could be obtained with this synthetic approach, as well as the expected spin multiplicity of their ground states, are represented in Scheme II.

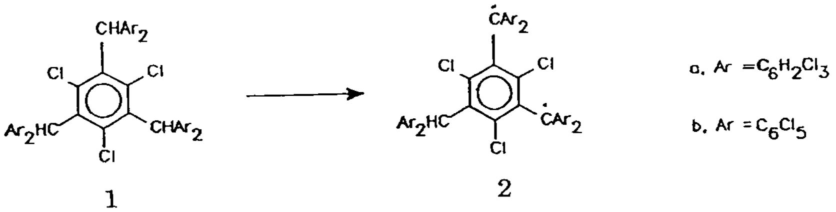


SCHEME II

In the present paper we briefly summarize the results concerning with the synthesis and the most relevant properties of the first generations of polyradical series **I** and **II**.

POLYRADICAL DENDRIMERS OF THE SERIES I

FIRST GENERATION. Using the reactions outlined in Scheme II the polytriarylmethane **1a** was obtained with a high yield . From **1a** only the corresponding dicarbanion was generated, while the tricarbanion derivative was solely generated in a very small proportion. Oxidation of this anionic mixture yielded the biradical **2a**, slightly contaminated by the corresponding triradical, as ascertained by cyclic voltammetry.

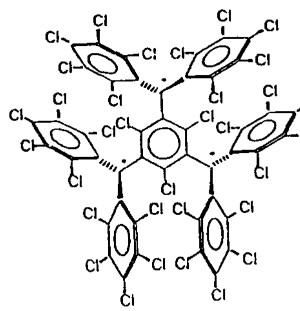


Biradical **2a** was isolated as a stable deep red crystalline powder and it showed the characteristic ESR fine structure of a mixture of three isomeric triplets.[8] The total intensity of the broad and intense absorption, observed at the half-field region ($\Delta M_s = \pm 2$ transition), followed the Curie law, over the temperature range 120-200K. This result suggests that the triplet species responsible for this absorption are the ground states.

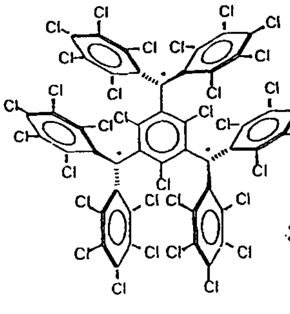
The higher acidity of methylenic protons of polytriarylmethane **1b**, compared with those of **1a**, permitted the selective generation of its dicarbanion and tricarbanion derivatives. From these polyanions, the corresponding biradical **2b** and triradical **3** derivatives were obtained.[12]

Triradical **3** is the first radical generation in the dendrimeric series I. This triradical exists in two interconvertible pairs of enantiomers with C_2 and D_3 symmetries which are isolable (HPLC) as stable solids. They show outstanding stabilities and in solid state do not show **any sign of decomposition up to 250°C**, even in air.

Both isomers display in frozen solutions ESR fine structures corresponding to quartet species (Fig.1). ***3D3*** has a *null* $|E|/hc$ zero field splitting parameter, as expected from its three-fold symmetry, whereas **3C_2** has a *no null* parameter, in accordance with its lower symmetry.



3 (*M, M, P*)
C_2 Symmetry



3 (*M, M, M*)
D_3 Symmetry

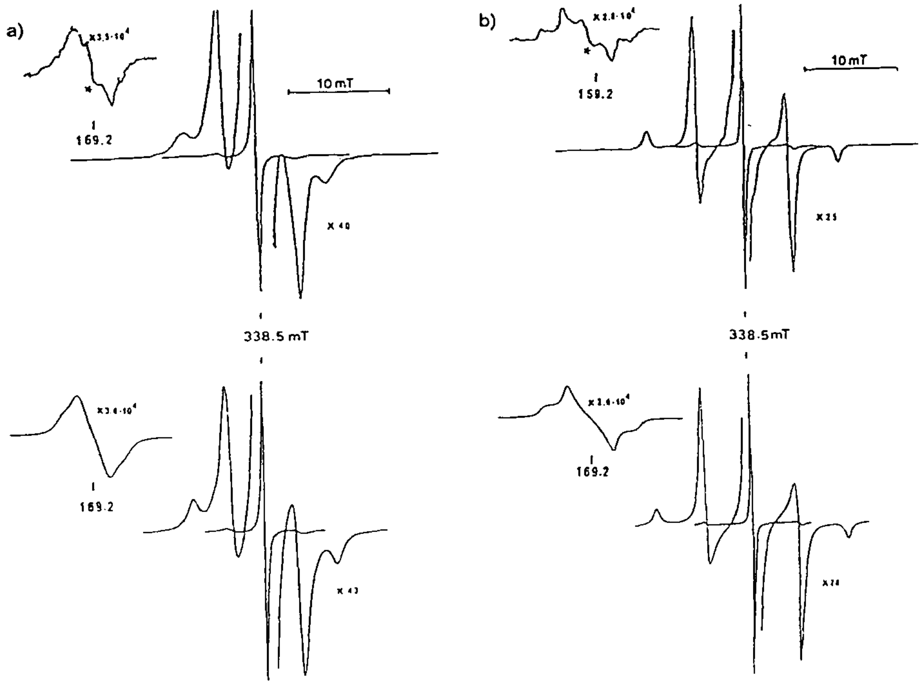


FIGURE 1 Top: Experimental ESR first derivative spectra at 143 K in glassy toluene of pure samples of (a) C_2-**3** and (b) D_3-**3**. Inserts show the observed signals corresponding to $\Delta m_s = \pm 2$ forbidden transitions. Bottom: Simulated spectra for randomly oriented species with (a) $|D|/hc = 0.00363\ \mathrm{cm}^{-1}$, $|E|/hc = 0.00009\ \mathrm{cm}^{-1}$, $g_{xx} = g_{yy} = 2.0029$, $g_{zz} = 2.0012$ and lorentzian line-width (L.l-w) of 0.80 mT and (b) $|D|/hc = -0.00501\ \mathrm{cm}^{-1}$, $|E|/hc = 0\ \mathrm{cm}^{-1}$, $g_{xx} = g_{yy} = g_{zz} = 2.0024$ and L.l-w of 0.42 mT. Inserts show the simulated signals due to $\Delta m_s = \pm 2$ transitions.

The observed high-spin states for the isomers of triradical **3**, as well as those for diradical **2b**, were shown to be the ground states by susceptibility, magnetization and ESR measurements.[11]

Triradicals **3**-C_2 and **3**-D_3 are interconverting in solution and at a sufficiently high temperatures they are in equilibrium. We have determined the equilibrium constants of the **3**-C_2 /**3**-D_3 interconversion process at several temperatures and in different solvents. The most remarkable result of this study is the linear relationship existing between the equilibrium thermodynamic parameters ΔH and ΔS. Such a result is ascribed to the different exoreceptor properties of both isomers. In particular, to the higher efficiency showed by the D_3 isomer to interact with the solvents. This behavior is explained by the distinct solvent accessible surfaces showed by both isomers which, in turn, are due to the different texture or roughness of their surfaces; i.e., to their distinct fractal dimensions (Fig. 2).[13] The distinct fractal character showed by the isomers of **3** reveals, for the first time, that even the first generation of the series **I** have one of the typical characteristics of starburst dendrimers.

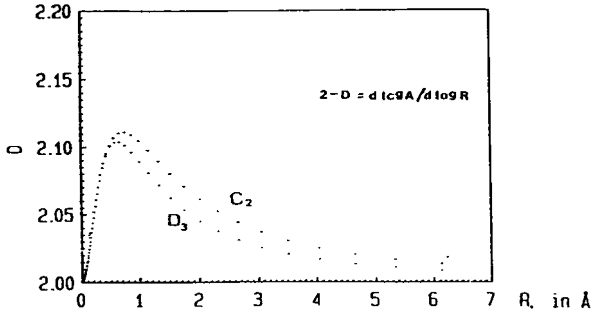


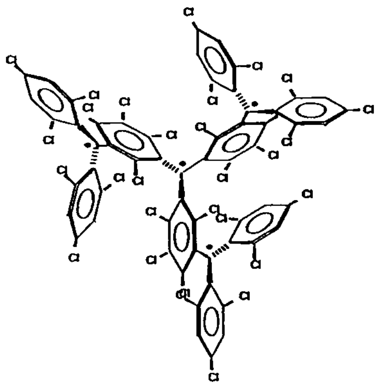
FIGURE 2. Fractal dimensions (D) of **3**-D_3 and **3**-C_2 isomers vrs. probe radii of solvent (R)[14]

Other characteristics of starburst dendrimers, such as the spheroidal shapes, are also manifested in both isomers of triradical **3**. Thus, these shapes are responsible of the extremely high tumbling rates observed by ESR spectroscopy in diluted solid solutions of both quartets even at 150 K.

SECOND GENERATION. The second hydrocarbon generation for series I (D_2, Scheme I) has been obtained following the divergent stepwise synthesis previously mentioned. However, such a compound was obtained with some structural defects in its external tier that avoid the preparation of a pure sample of the second polyradical generation (R_2, Scheme II). This result indicates that the typical limit generation of starburst dendrimers is reached in this earlier generation. The cause of such defects are the bulkiness of terminal groups (pentachlorophenyl groups), as well as the small accessible surface area per terminal group available in this hyperbranched topology. In order to minimize such an overcrowding we have started the synthesis of polyradical dendrimers of the series II which must have lesser ramifications.

POLYRADICAL DENDRIMERS OF THE SERIES II

FIRST GENERATION Up to now we have only obtained the first polyradical generation, within the series II: the tetraradical **4**. This polyradical shows a ESR fine structures corresponding to several high-spin molecules. Due to the structural defects of this molecule and to the large number of isomers that are expected for this tetraradical -twelve enantiomeric pairs differing in the helicity of the four propellers; in Figure 3 is shown one of these stereoisomers- the interpretation of the resulting ESR spectrum is not direct. Further magnetic studies are in progress in order to fully characterize and determine the nature of the ground state of this polyradical.



4 ***P,M,M,M***

FIGURE 3

ACKNOWLEDGMENTS. This work was supported by C.I.C.y T. (Grant MAT91-0553), and C.I.R.I.T (Grant to N. Ventosa).

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