Drawbacks Arising from the High Steric Congestion in the Synthesis of New Dendritic Polyalkylaromatic Polyradicals

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The synthesis of the highly strained tris(α,α-bis(pentachlorophenyl)-2,4,5,6-tetrachlorotolyl)methane (**8**), which is the precursor of the first generation of the polyradical series III, has been achieved by exhaustive chlorination of compound **11**. Stepwise divergent synthesis, by successive Friedel−Crafts reactions, of the precursors of dendritic series II and III was not possible since the limit generation was reached in the earlier synthetic steps due to high steric congestion. Several polyradical mixtures derived from **8** have also been prepared, being stable under ambient conditions. The formation, electrochemistry, and magnetic properties of these polyradical species are discussed. The steric hindrance of highly chlorinated hydrocarbon **8** prevents the formation of tetraradical **15**.

Introduction

The development of magnetic materials with mesoscopic size is an area of increasing interest due to the new and exotic properties expected for such compounds, taking into account that nanometer size structures can manifest quantum-mechanics effects at the macroscopic scale.[1] The potential use of such compounds requires specific chemical and structural characteristics such as a high stability, uniformity, and a well defined size. These compounds, however, conflict with the realization that "engineering down" approaches are unpractical. Hence, with the possibility of "engineering up" from an initiator core, large and complex molecules have become an increasingly attractive prospect.

Dendrimers,[2] also called cascade molecules or cauliflower compounds,[3] are step growth macromolecules with symmetrical three-dimensional structures with a sharply defined size. These compounds show unusually interesting properties such as fractality, monodispersivity, mesoscopic dimensions, and endoreceptor properties, being suggested as units for the construction of three-dimensional devices on a molecular level (nanotechnology).[2] On the other hand, purely organic magnetic materials are current topics of great interest, one of the general successful approaches being those based on π-conjugated polyradicals with topologically polarized π spins.[4] Thus, combination of the last type of polyradicals with a dendritic nature seems a proper way to achieve mesoscopic organic magnetic materials.

Following this approach, we started the study of three different series of polyradical dendrimers, differing in the initiator core (Chart 1). All are based on highly chlorinated 1,3-connected polyarylmethyl radical centers for which theory predicts ferromagnetic couplings between the neighboring spins and, therefore, high-spin ground states for the resulting dendrimers. Moreover, due to their hyperbranched topologies, they must have large energy gaps between the ground states and the first excited ones. High thermal and chemical stability are indeed expected for all the members of these series due to the great steric hindrance produced by the chlorine atoms in the ortho positions that proved to be very effective in the stabilization of a wide number of similar mono- and biradicals.[5] The series of dendrimer polymers I differs from series II and III in the nature, size, and/or multiplicity (or branching) of their central core unit, N_c, and the three series differ in their branching-juncture multiplicities, N_b. Thus, the series I has a hyperbranched topology with $N_c = 3$ and $N_b = 4$, and the series II has $N_c = 6$ and $N_b = 4$ while the series III has a lower level of branching with $N_c = 3$ and $N_b = 2$ and the topology of a three-coordinated Caley tree.

Up to now, we have obtained the first polyradical generation of the series I which, as predicted, is a robust quartet that displays a high stability and show typical starbust dendrimeric characteristics such as a fractal character and a spheroidal shape.[6,7] Nevertheless, the second generation of this dendritic series revealed a drop

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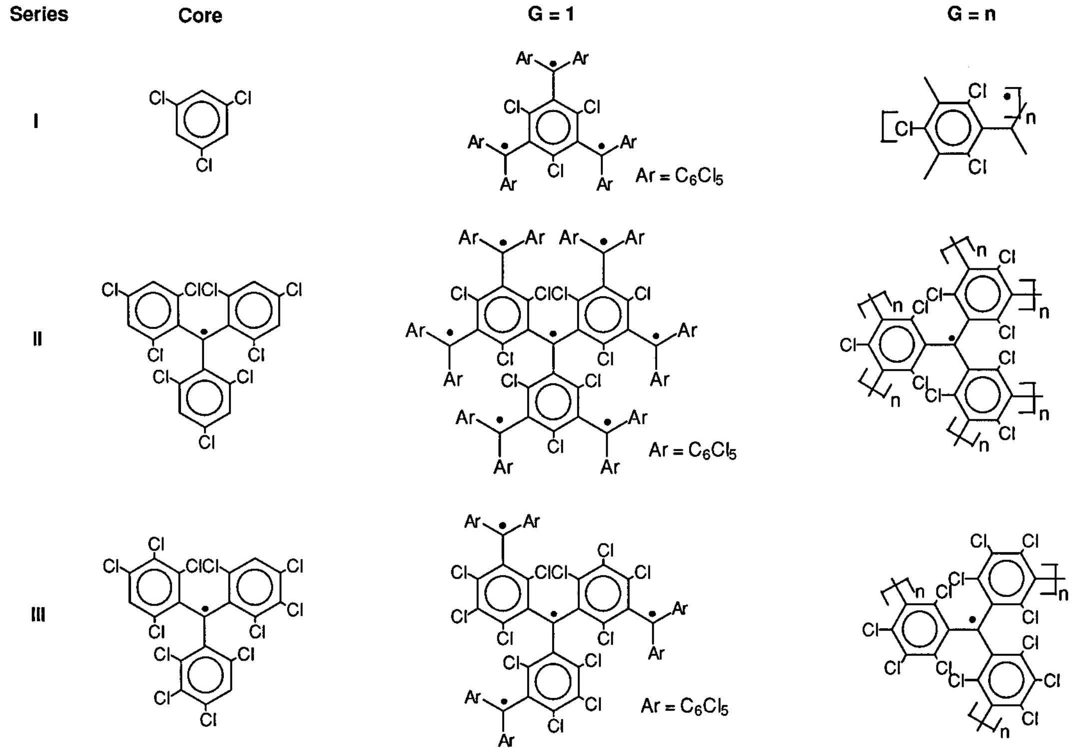
Chart 1



of the effective *S* value.[7] Such a drop has also been observed by Rajca et al. in analogous dendritic polyradicals with up to 7, 15, and 31 sites for ferromagnetically coupled electrons that surprisingly show spin averages of 3, 7/2, and 5/2, respectively. The authors have attributed tentatively this phenomena to the presence of defects in these π conjugated systems that interrupt the ferromagnetic coupling to the extent that some parts of the polyradicals become effectively uncoupled.[8]

Due to the promising properties of these polyradical dendrimers our aim was focused to the design of alternative molecular topologies, those of the series II and III, that overcome such steric congestions. Polychlorotriphenylmethyl polyradicals are usually synthesized following three successive steps: (1) obtaining the polytriphenylmethane precursors, (2) generation of the corresponding polycarbanions by acid–base reactions, and (3) oxidation of such polycarbanions to the corresponding polyradicals. One of the main drawbacks lies in the difficulty in growing well-characterized polytriphenylmethane precursors (step 1). Due to the large number of bulky chlorine atoms, the limit generation in the precursors of series of polyradicals can be achieved only at early generations. The limit generation is a self-limiting step characterized by the presence of high steric congestion and over which it is very difficult to continue growing new generations without structural defects. Concerning the synthesis of the polyradicals, the limiting step is the generation of the polycarbanions. The presence of large steric congestions increase the probability of formation of carbanions with defects arising from negative charges missing specially in those centers that are more shielded. Since the central core unit of series II and III is larger than that of series I, it seemed promising to move toward these two new series in order to decrease the hindrance and, as a result, to obtain higher generations of stable polyradical series.

We now report the results concerning the synthesis of the polytriphenylmethanes precursors of the first generation of series II and III as well as the synthesis and the most relevant properties of the polyradicals that belong to the first generation of series III. Unexpectedly, the topologies of these new polyradicals not only do not decrease but even increase the steric congestions and affect the formation of these new radicals.

Results and Discussion

Synthesis and Characterization of the Precursor Polytriarylmethanes. The synthetic approach was based on the divergent dendrimeric growth methodology.[2,3] The first step is the functionalization of the initiator core of the series II, i.e., of tris(2,4,6-trichlorophenyl)methane (**1**),[9] by the introduction of new branch junction elements ($CHCl_2$ groups) in each *meta* position of the phenyl rings. Thus, compound **2** was obtained in high yield by a Friedel–Crafts alkylation of **1** with chloroform. Each introduced $CHCl_2$ group is a potential alkylating agent, with a branching multiplicity of 2, which can be used for the construction of the next generation of this series of compounds (Scheme 1). To obtain the precursor of the polyradical of the first generation, reaction of **2** with pentachlorobenzene is required. To continue toward the precursor of the next member of series II, compound **3**, three consecutive Friedel–Crafts reactions must be accomplished: first that of **2** with 1,3,5-trichlorobenzene, second the reaction of the obtained compound **4** with $CHCl_3$, and finally the resulting compound with pentachlorobenzene.

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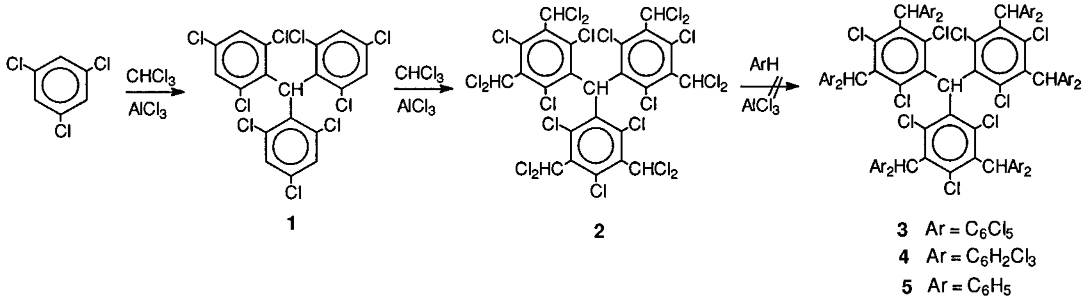
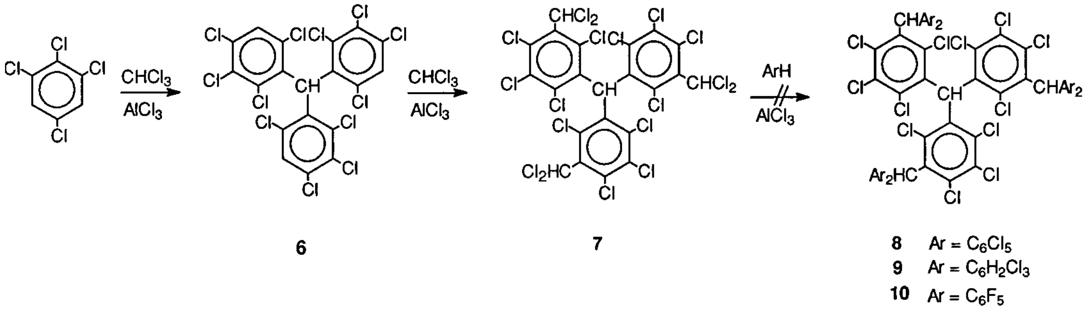
Scheme 1



Scheme 2



Unfortunately, the reaction of **2** with pentachlorobenzene or 1,3,5-trichlorobenzene via an acid-catalyzed Friedel−Crafts reaction failed along different experimental conditions tested. To all appearances, the propeller-like conformation of triarylmethane units and the high effective volume of chlorine atoms originate a high shielding in the earlier dendrimeric generations that prevents this highly disfavored reaction to proceed in the desired way.[10] We, therefore, tried the reaction of **2** with benzene provided that benzene has not such bulky substituents and, consequently, displays a smaller van der Waals volume as well as an enhanced reactivity with respect to chlorinated analogues. Unfortunately, all attempts to isolate the condensation compound **5** were once more unsuccessful since in all reactions tested we obtained a complex mixture of products. The results suggest that the limit generation had been reached in the first synthetic step, due to the steric hindrance, and furthermore that the reactive intermediates formed undergo further reactions such as dealkylations or hydride additions, which are typical of reversible Friedel−Crafts reactions.[11] Therefore, to avoid such big steric hindrance problems we turned our attention toward a new series of highly chlorinated hydrocarbons, the precursors of series III (Chart 1). The nature of the structural components in this series was maintained as in series II, although, the multiplicity of the core and branches was strongly decreased. As a starting precursor, acting as the initiator core of the series III, we chose tris(2,3,4,6-tetrachlorophenyl)methane (**6**), which only contains three reacting sites instead of the six of compound **1**, the precursor of the initiator core of series II. Polytriphenylmethane compounds obtained from this compound by successive Friedel−Crafts reactions were intended to act as the precursors of dendrimeric polyradicals of series III.

Triphenylmethane **6** was synthesized by a Lewis acid-catalyzed condensation of 1,2,3,5-tetrachlorobenzene with chloroform. Once we synthesized the initiator core, we moved toward the synthesis of the first generation of series III using a two-stage reaction. First, **6** was alkylated with chloroform, yielding the triarylmethane **7** that has three branch junction elements (Scheme 2). However, as in the previous series, the second step, i.e., the subsequent Friedel−Crafts reaction of **7** with pentachlorobenzene and 1,3,5-trichlorobenzene, failed. Both reactions were further attempted by varying the key reaction parameters such as the ratios between aryl, catalyst, and alkylating agent and the reaction temperature and time. In all conditions assayed, complex mixtures of products were obtained in which it was not possible to identify the desired compounds by spectroscopic techniques. The same discouraging results were obtained in the reaction of **7** with pentafluorobenzene, despite the smaller volume of the aromatic substrate and the fact that pentafluorobenzene gives Friedel−Crafts reactions with chloroform and dichloromethane in high yields.[12]

Finally, reaction of **7** with benzene was successful since it gave the polytriphenylmethane **11** (Scheme 3) in variable yields depending upon the reaction conditions (Table 1). In fact, extreme conditions such as a high temperature (reflux) and large excess of benzene and the Lewis acid, $AlCl_3$, with respect to the alkylating agent **7**, molar ratios larger than 60:1 and 3:1, were required to achieve high yields (80%).

The results demonstrate that **7** can act as an alkylating agent, although it did not react with polyhalogenated benzenes. This lack of reactivity could be ascribed to the enhancement of the steric hindrance of the reaction intermediates and also to the electronic deactivation that precludes the desired reactions. It should be noticed that the optimum reaction conditions to obtain **11** were also used in the previous attempted reactions of **7** with polyhalogenated benzenes reaching to the same previous disappointing results. To sum up, although it is well-

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(10) The large steric hindrance and the negative inductive effects produced by the chlorine atoms in both the substrate and the alkylating agent make it necessary to use extreme reaction conditions, such as an excess of the Lewis acid, high temperatures, long times, and to carry out the reaction in absence of solvent.

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Scheme 3

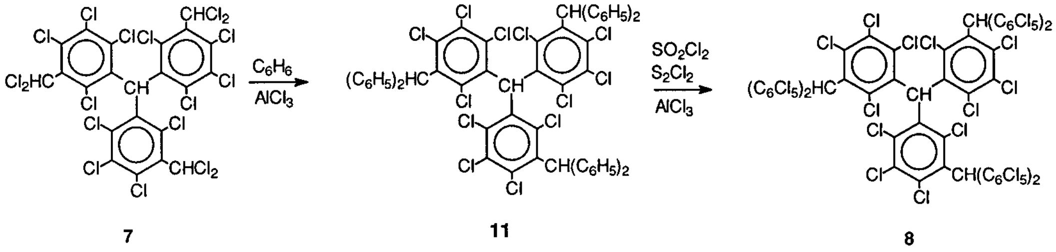

Table 1. Different Reaction Conditions for the Synthesis of 11[a]

C_6H_6/**6**[b]	$AlCl_3$/**6**[b]	time (h)	yield (%)
41	7	0.5	30
200	7	0.5	88
400	7	0.5	89
1200	7	0.5	85
1200	0.3	0.5	*c*
1200	1	0.5	27
1200	14	0.5	*d*
1200	7	2.5	65
1200	7	3.5	62
1200	7	6.5	68

[a] All the experiments were performed using the same amount of the alkylating agent **6** and reflux temperature. [b] Molar ratio. [c] Starting material recovered. [d] Complex mixture containing carbonilic compounds.

known that asymmetrical branching, such as that of series III, should lead to a classical relationship between density and molecular mass, the results presented here show that, despite topology changes, the limit generation was reached at the first steps.

As the last attempt to synthesize the polytriarylmethane **8**, the precursor of the second generation of series III, we performed an exhaustive perchlorination of **11** using the BMC reagent.[13] This reagent is a powerful chlorinating agent that was extensively used in the perchlorination of a great number of triarylmethanes.[14] However, this was the first time in which such a chlorinating agent has been used with a molecule such as **11** with a large structural complexity. Indeed, reaction of **11** with the BMC reagent eventually yielded the highly chlorinated compound **8**. IR analysis showed a complete disappearance of the stretching bands corresponding to the stretching C_{arom}−H bonds, and a similar behavior was observed for the corresponding ^{1}H NMR signals. The elemental analysis agrees with the spectroscopic studies confirming that the chlorination was smoothly completed without any fragmentation yielding the dendrimer **8** which contains 42 Cl atoms. By FAB mass spectroscopy, using positive and negative ions and various matrixes, we did not observe with **8** any significant parent peak. Nevertheless, by MALDI/TOF technique in negative mode and using 2,5-dihydroxybenzoic acid as a laser absorbing matrix, the molecular peak is seen with a series of consecutive losses of 35 units corresponding to the loss of chlorine atom from the parent peak.

Characterization of the rest of synthesized compounds was achieved by ^{1}H NMR, IR and UV−vis spectroscopies as well as by elemental analysis and thermal analysis. Due to the presence of bulky chlorine atoms, the aromatic rings in **6**, **8**, and **11** as well as the $CHCl_2$ groups in **2** and **7** have highly restricted rotations, giving rise to a large number of atropoisomers with different populations. For this reason, ^{1}H NMR spectra of all these compounds consist of multiplets on account of the non equivalence of protons belonging to different atropoisomers. All the reported compounds are moderately soluble in typical organic solvents such as CH_2Cl_2, $CHCl_3$, C_6H_6, and THF. Amazingly, the solubility increases with increasing the molecular weight, a general trend that was previously observed by Neenan et al. in a different series of 1,3,5-phenylene-based hydrocarbon dendrimers.[15] Another relevant characteristic of these branched molecules is the tendency to entrap solvent when crystallized in a wide variety of solvents such as C_6H_6, n-C_6H_{14}, $CHCl_3$, and CCl_4. This makes necessary a thermal treatment of the compounds under vacuum in order to perform their complete characterization. Inclusion compounds of triphenylmethane with benzene in a 1:1 ratio were reported earlier.[16] More recently we reported the affinity of the perchlorotriphenylmethyl radical and some of its radical derivatives to form inclusion compounds with cyclic small molecules.[17] X-ray structures of the chlatrates showed that guest molecules were placed into channels in the structure with a host/guest ratio of 1:1.[17] Obtaining a single crystal of the compounds studied here has proven to be very difficult due to the great number of isomers. Unfortunately, this fact precludes a complete study of the inclusion compounds formed.

Synthesis and Characterization of the Polyradicals. The synthesis of the polyradical species **12**−**15** was undertaken by treatment of the polyarylmethane **8** with a solution of aqueous n-$Bu_4N^+OH^-$ by using different substrate/base ratios and reaction times in THF followed by oxidation of the resulting polycarbanions with p-chloranil.

Our previous experience with the radicals of series I was that controlling the excess of the base and/or reaction times in the first step allows the control of the formation of the corresponding mono-, di-, and tricarbanions and, therefore, of the desired polyradical. Nevertheless, due to the lack of knowledge of the precise experimental conditions required to generate the different carbanionic species from **8**, a preliminary experiment was designed. An aliquot of **8** was treated with an excess of base, and the evolution of the reaction was followed by UV−vis spectroscopy. It can be anticipated that the intensity of the 518 nm band, characteristic of the carbanionic

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Chart 2

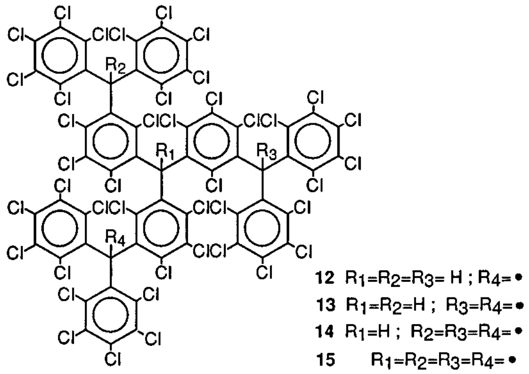

Table 2. Different Reaction Conditions Used for the Generation of the Polyanions Derived from 8

reaction	base/**8**[a]	reaction times (days)
1	1/1	0.2
2	2/1	0.2
3	3/1	0.2
4	100/1	0.3
5	100/1	28

[a] Molar ratio.

species, will increase until a maximum is reached where the formation of the tetracarbanionic species should be assumed. As expected the UV–vis spectra recorded 24 h after the reaction was initiated revealed a relatively high intensity of the 518 nm band, confirming that the first carbanion species can be obtained in short periods of time. From here on the evolution was slower as expected from an increase of the intramolecular Coulombic repulsions on increasing the number of charges. After one month of reaction, the intensity of the band keeps constant for more than two weeks, confirming that the reaction was concluded.

Taking into consideration the above-mentioned experiment, five different reactions using different substrate/base ratios and reaction times were carried out and the resulting carbanionic species were oxidized with an excess of *p*-chloranil. The experimental conditions used in the first step of each of these reactions are summarized in Table 2.

The samples obtained from the experiments 1–5, that will be referred to from now on as samples **A**–**E**, respectively, were isolated as deep red-purple solids, completely stable in ambient conditions after their chromatographic purification. Finally the samples were characterized by electrochemistry, UV–vis and ESR spectroscopies, HPLC, and magnetic measurements.

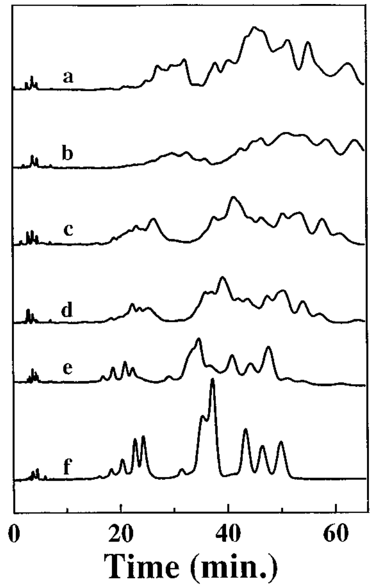

Figure 1. HPLC of polyarylmethane **8** (a), and samples **A** (b), **B** (c), **C** (d), **D** (e), **E** (f) on an ODS column operating at 263 K and using CH_3CN/THF mixtures as eluent (55/45).

UV–vis spectra and HPLC experiments give qualitative evidence of the increase of the radical character of the samples when increasing the base proportion and the reaction times. Thus, the molar extinction coefficients of the characteristic radical bands at 568 and 389 nm[6] increase progressively up to the last sample (Table 3) as expected from an increase of the number of radical centers in the final products.

On the other hand, the complexity of the chromatograms diminishes from samples **A** to **E** (see Figure 1), as expected by the higher number of atropisomers and the lower energy barriers when the number of Ar_3CH units is larger than the number of $Ar_3C^\bullet$ in a given molecule.[18]

Electrochemistry. Electrochemical studies in CH_2Cl_2 with tetrabutylammonium hexafluorophosphate as supporting electrolyte were done at room temperature. In the cyclic voltammogram (CV) of sample **A** only one reversible wave, characteristic of a monoradical species,

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(18) It has been shown that the different atropisomers of these kind of polyradicals display striking differences in their overall sizes, shapes, and surfaces, allowing these stereoisomers to be chromatographically separated. The interconversion between the stereoisomers of these polyradicals is relatively low due to the bulky *o*-chlorine atoms that hinder the correlated rotation of the aryl groups [see: ref 7 and Ventosa, N.; Ruiz, D.; Tomas, X.; Bieber, A.; André, J.-J.; Rovira, C.; Veciana, J. *J. Am. Chem. Soc.*, submitted.], and, therefore, it can be quenched by lowering the temperature. Nevertheless, the interconversion of the stereogenic Ar_3CH centers in these polyradicals is always faster that that of the stereogenic $Ar_3C^\bullet$ centers [see: Crespo, M. I. Ph.D. Thesis. Institut Químic de Sarriá, 1991, Barcelona, Spain.]. The stereochemical analysis of tetraradical **15**, based on previous considerations given by Mislow et al. [see: Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535 and Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.] and on energy minimizations performed by empirical calculations with the Drieding force-field, predicts 12 different enantiomeric pairs for which different relative abundancies are expected. For the rest of the polyradicals, a larger number of stereoisomers is expected since the presence of Ar_3CH moieties introduces additional stereogenic elements. Thus, 24 different enantiomeric pairs are expected for polyradical **14**.

(19) Zero-field splitting parameters are much lower than those of the quartet of series I as well as its corresponding triplet [see ref 6c]. This fact can be due to the location of the radical centers on two or three electronically isolated external $Ar_3C^\bullet$ units. Nevertheless, the location on neighboring $Ar_3C^\bullet$ units that are electronically connected cannot be excluded since a large torsion of these units, due to the high steric congestion, could lead also to a large decrease of the zero-field splitting.

(20) Experimental magnetization data, *M*, were fitted to eq 1,

$$\frac{M}{N_A \mu_B} = \sum_{i=1}^{n} f_i g_i S_i B_{S_i}(\chi_i) \qquad (1)$$

where $B_{S_i}(\chi_i)$ is the Brillouin function for a paramagnetic species, i, with g_i and an effective spin number of S_i which is present with a molar fraction of f_i in the mixture of *n* paramagnetic species. The Brillouin function is given by eq 2,

$$B_{S_i}(\chi_i) = \frac{1}{S_i}\left[\frac{2S_i+1}{2}\cot gh\left(\frac{2S_i+1}{2}\chi_i\right) - \frac{1}{2}\cot gh\left(\frac{1}{2}\chi_i\right)\right] \qquad (2)$$

being the argument, χ_i, of this function as:

$$\chi_i = \frac{g_i \mu_B H}{k T_{\mathrm{eff}}} \qquad (3)$$

where T_{eff} is the effective temperature, $T_{\mathrm{eff}} = T - \theta$, which takes into account in a first approximation the averaged weak intermolecular magnetic interactions between the species. For a rigorous treatment of such intermolecular interactions, a generalization of the molecular mean-field treatment is required; see ref 6c.

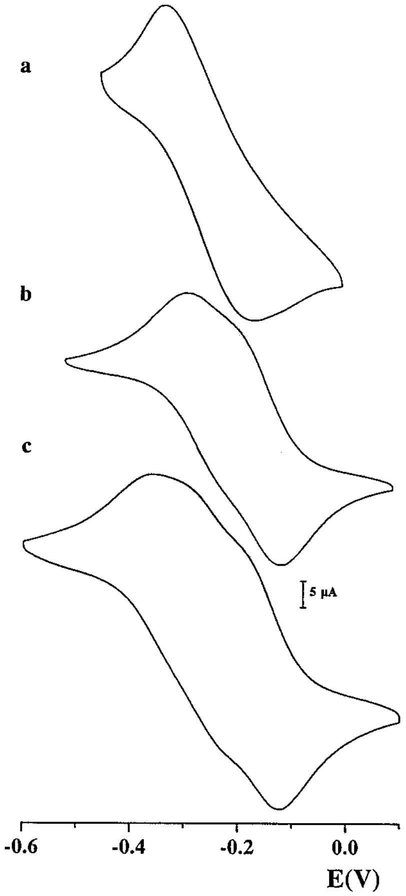

Figure 2. Cyclic voltammograms of samples **A** (a), **C** (b), **E** (c) in CH_2Cl_2, with 0.1 M $Bu_4N^+PF^{6-}$, Pt wire (working and auxiliary), and Ag/AgCl (reference) electrodes.

Table 3. Molar Extinction Coefficients (in L cm^{-1} mol^{-1}) of the Two Characteristic Radical Absorption Maxima for Samples A−E

sample	band, $\lambda = 568$ nm	band, $\lambda = 389$ nm
A	800	22000
B	1800	48000
C	2600	68000
D	3300	77500
E	4450	102500

was observed at $E_{1/2} = -0.18$ V (vs the standard Ag/AgCl electrode). CV's of the rest of samples revealed a qualitative increase of the number of electrochemical processes as expected from the successive replacement of the Ar_3-CH by $Ar_3C^{\bullet}$ units. However, while the analogous polyradical series derived from the first generation of series I show well-defined stepwise one-electron reduction processes, the present series of polyradicals display CV's where the different waves can only be differentiated as a shoulders due to the small peak-to-peak separations (60−80 mV or even smaller). Representative voltammetries of samples **A**, **C**, and **E** are depicted in Figure 2.

The complexity of these CV's only allows a qualitative estimation of the nature of polyradical species formed in each experiment. A detailed inspection of the CV of sample **E** revealed that only three reversible waves are present. Quantitative results were obtained by bulk electrolysis experiments. In this way the chronoamperometric limiting currents of samples **A**−**E** were in agreement with the consumption of 0.6, 1.3, 1.5, 1.8, and 2.9 Faraday/mol, respectively.

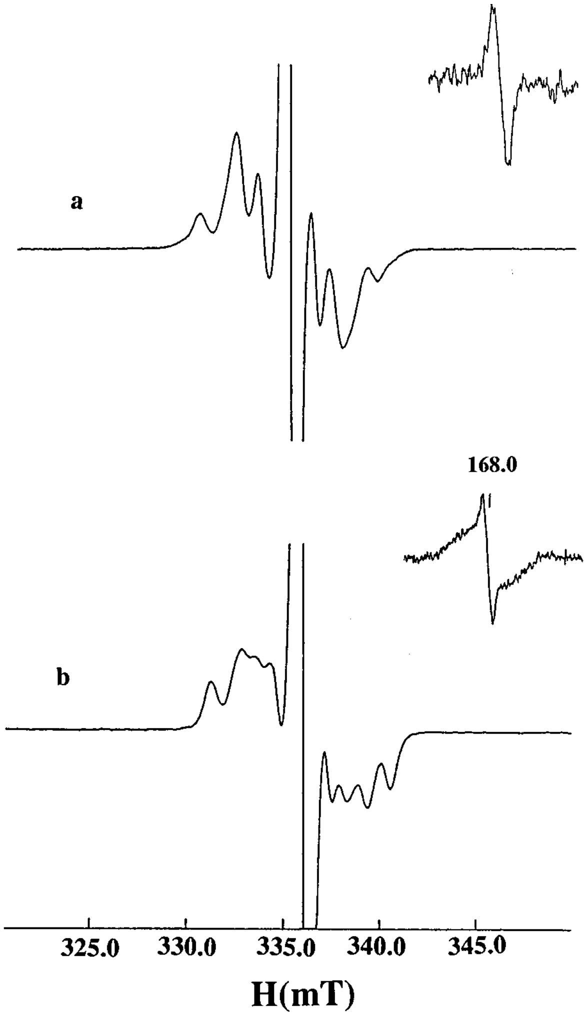

Figure 3. First derivative ESR spectra at 165 K in glassy toluene of samples **D** (a), **E** (b). Insets show the observed signals corresponding to $\Delta M_s = \pm 2$ forbidden transitions.

The increase of the number of waves in the CV's and the number of Faraday/mol consumed in the bulk electrolysis experiments confirm an increase of the radical character of the samples when increasing the substrate/base ratio and reaction times used in their synthesis as well as the formation of mixtures of different polyradicals in each case. It must also be emphasized that the presence of only three reversible waves in the CV, instead of the four waves expected for a tetraradical, and the consumption of 2.9 Faraday/mol of sample **E** seem to point out that we only have been able to synthesize up to the triradical species **14** and not to the desired tetraradical **15**. Such results were confirmed later on by magnetic measurements.

Magnetic Properties. X-band ESR spectra of samples **A**−**E** in frozen toluene matrix consists of the superimposition of two types of lines: a symmetric broad central line and a few symmetrical lines besides the central one that increases in complexity on going from sample **A** to sample **E** (see Figure 3). The central line is due to monoradical species and polyradical species with very small spin−spin dipolar interactions, whereas the other set of symmetrical lines are attributed to polyradical species with larger dipolar interactions.

Due to the complexity of those signals, any assignment to a specific species cannot be performed, showing only that samples consist of complex mixtures of polyradicals. The only data that can be qualitatively extracted from the ESR spectra is that the zero-field splitting parameters of polyradical species are small, indicating weak

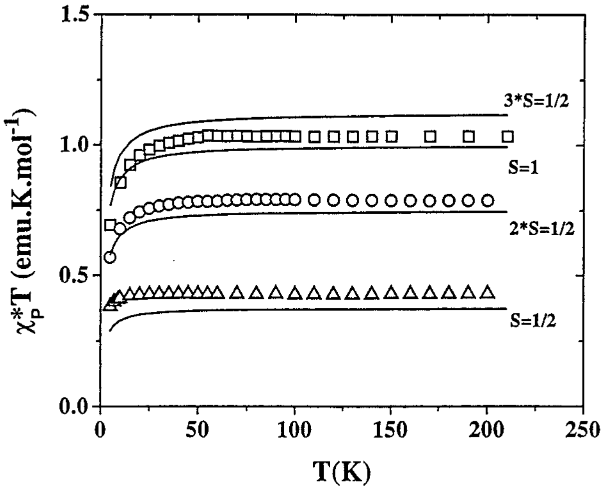

Figure 4. Temperature dependence of the product χT for samples **B** (Δ), **C** (○), and **E** (□). Continuous lines are the magnetic behaviors expected for pure paramagnetic systems with weak antiferromagnetic intermolecular ($\theta = 2$ K) having the indicated spin values.

spin−spin dipolar interactions between the unpaired electrons.[19] Only samples **D** and **E** display significant signals in the $g \approx 4$ region (see insets of Figure 5) corresponding to forbidden $\Delta M_S = \pm 2$ transitions, indicating the presence of a larger proportion of high-spin species.

The magnetic susceptibility was measured in the temperature range 2−250 K for samples **A**−**E**. The χT vs T plots of such samples give straight lines down to 30 K where small downward deviations, due to the presence of weak intermolecular antiferromagnetic interactions, are observed (see Figure 4). The magnetic effective moments found for samples **A**−**E** at room temperature were 0.23, 0.45, 0.62, 0.80, and 1.15 emu K mol^{-1}, respectively, showing that the samples are in fact mixtures of radical species with different effective spin numbers S.

Magnetization measurements of samples **A**−**E** were performed at 1.8 K and 3 K as a function of the external magnetic field. The plots of the magnetization per mol ($M/N\mu_B$) versus the ratio of the magnetic field over the absolute temperature for the most representative samples are shown in Figure 5.

To determine the average effective spin numbers and, therefore, the composition of each sample the $M/N\mu_\beta$ vs H/T data were fitted to a magnetic model considering the possible presence of mixtures of the precursor **8**, the monoradical **12** ($S = 1/2$), and a triplet ($S = 1$) and a quartet ($S = 3/2$) as well as a biradical ($2\cdot S = 1/2$) and triradical ($3\cdot S = 1/2$) species, both with magnetically independent radical centers.[20] Such a combination of species makes sense provided that two possible pathways are expected for the reaction of **8** with the base. The first pathway initially assumes the succesive generation of the external Ar_3C^- units and finally of the central Ar_3C^- one. This pathway is the most likely since it minimizes intramolecular Coulombic repulsions among the negative charges of the Ar_3C^- units and will provide mixtures of monoradical ($S = 1/2$), biradical ($2\cdot S = 1/2$), and triradical ($3\cdot S = 1/2$) species. The second pathway assumes the formation of the central Ar_3C^- and external Ar_3C^- units simultaneously to obtain, after oxidation, mixtures of triplet and quartet species. The main drawback of the fitting of $M/N\mu_\beta$ vs H/T data to a proper magnetic model for mixtures of species with different S values relies on the large number of parameters to be adjusted. Therefore, to improve the accuracy of the method, we imposed that the possible solutions should also agree with the values previously obtained in the chronoamperometric experiments and in the magnetic susceptibility measurements.

From the results of the fitting shown in Table 4, two main conclusions can be extracted: (1) Despite the large excess of base and the long reaction times used, the tetraradical species **15** remains elusive since sample **E** is mostly formed by the triradical species **14**. (2) The control of the formation of a specific polyradical is not possible by changing the substrate/base ratio and the reaction times since complex mixtures of polyradicals were always obtained. Such results suggest that the high steric congestion of polyarylmethane **8** hinders that the reagent (base) at all the reactive centers (acidic protons) of **8**, thus precluding the formation of tetraradical **15**.

Conclusions

The high steric congestion in the dendritic series II and III originates that the limit generation is reached in early synthetic steps. Such a situation prevents us from obtaining the precursor of the first generation of series II. By contrast, thanks to the lower branching degree of series III, we have been able to synthesize the highly chlorinated hydrocarbon **8**, the precursor of the first generation of series III. However, the large overcrowding present in this dendritic series and the strong experimental conditions required in obtaining **8** made futile any effort to produce higher generations of series III without structural defects.

It has also been shown that the steric congestion does not only affect the synthesis of the highly chlorinated hydrocarbon precursors but also the preparation of the polyradicals series derived from **8**. Despite the large excess of base and the long reaction times used in the synthesis of such polyradicals, the preparation of the first target compound, the tetraradical species **15** is elusive. In addition, it is very difficult to control the formation of a pure polyradical, always obtaining mixtures of different species.

Experimental Section

All solvents were reagent grade from SDS and were used as received unless otherwise indicated. All reagents, organic and inorganic, were of high purity grade and obtained from E. Merck, Fluka Chemie, and Aldrich Chemical Co. The Friedel−Crafts condensations were carried out in a glass pressure reactor. Elemental analyses were obtained in the Servei de Microanalisi del CID (CSIC), Barcelona. NMR spectra were recorded on a Bruker AC-400 and on a Bruker 250. The MALDI mass spectrum was recorded using a KRATOS MALDI spectrometer in Linear High Power negative mode.

Tris(2,3,4,6-tetrachlorophenyl)methane (6). A mixture of anhydrous chloroform (0.6 mL; 7.4 mmol), aluminum trichloride (3.95 g; 51.5 mmol), and 1,2,3,5-tetrachlorobenzene (13.26 g; 61.4 mmol) was heated at 110 °C with magnetic stirring in a glass pressure vessel during 3.5 h. The mixture was poured into cracked ice/hydrochloric acid and extracted with chloroform. The organic layer was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. Flash chromatography (silica gel, hexane) afforded 4.1 g (84%) of **6** as a spongy white solid: mp 241−243 °C; ^1H NMR (CD_2Cl_2) δ 7.00−7.18 (m, 1H), 7.61−7.75 (m, 3H); IR (KBr): ν 3123, 3072, 2956, 2924, 1560, 1532, 1406, 1363, 1335, 1300, 1237, 1181, 1117, 948, 854, 811, 718, 643, 618, 575, 532 cm^{-1}; UV−vis (C_6H_{12}) λ_{max} nm (log ϵ) 219(4.98), 247(4.48), 279(2.92), 289(3.12), 298(3.12). Anal. Calcd for $C_{19}H_4Cl_{12}$: C, 34.70; H, 0.61; Cl, 64.69. Found: C, 34.61; H, 0.62; Cl, 64.70.

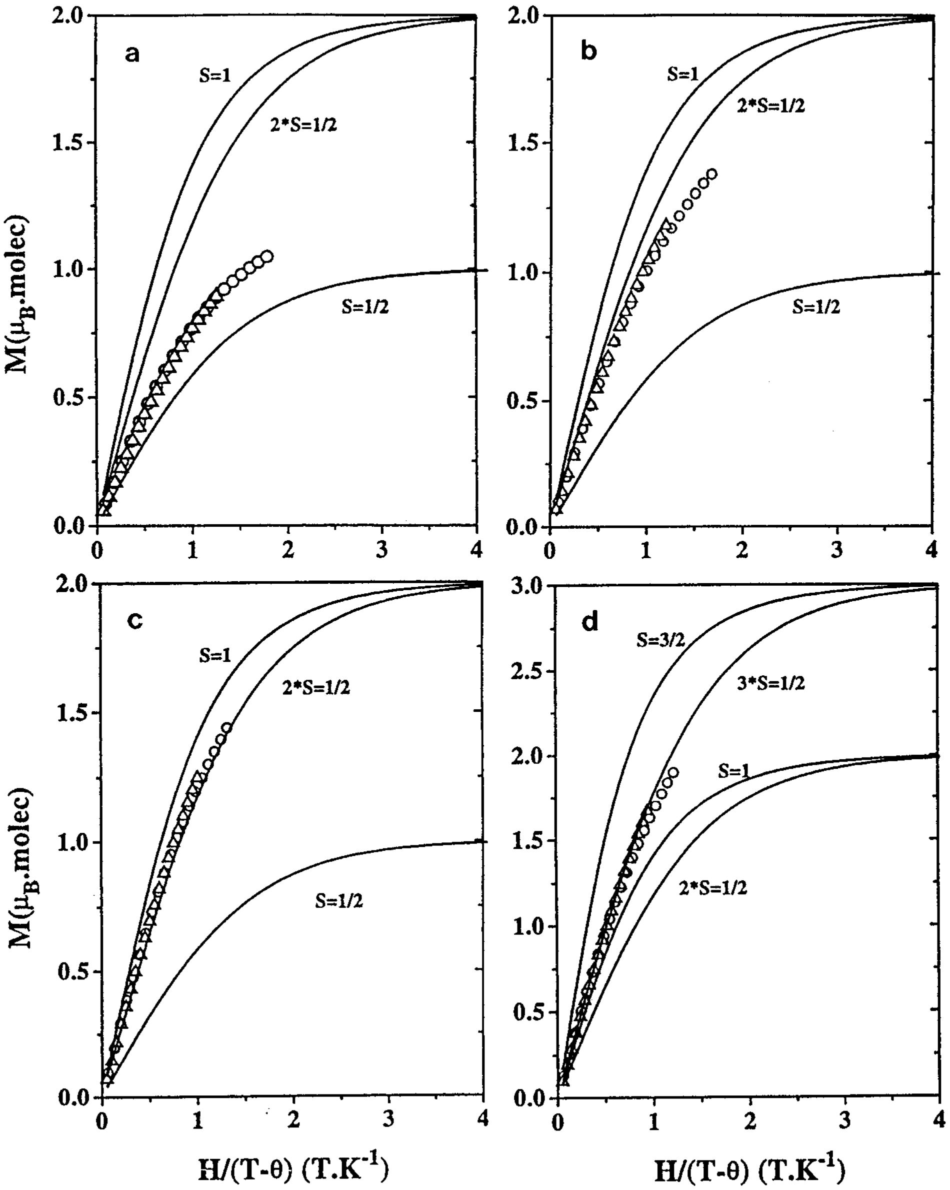

Figure 5. Field strength dependence of the magnetization of samples **B** (a), **C** (b), **D** (c), **E** (d) at (Δ) 1.8, and (○) 3 K. Solid lines are the calculated molar magnetization curves for pure paramagnets in systems with weak antiferromagnetic intermolecular interactions ($\theta = 2$ K) having the indicated spin values.

Table 4. Molar Ratio of the Different Polyradical Species Found from the Fitting of Magnetization Data for Samples I–V

sample	θ (K)	**8** (%)	$S =$ 1/2 (%)	$2{\cdot}S =$ 1/2 (%)	$3{\cdot}S =$ 1/2 (%)	$S =$ 1 (%)	$S =$ 3/2 (%)
A	−0.2	45	50	5	0	0	0
B	−0.6	0	82	18	0	0	0
C	−1.1	0	34	66	0	0	0
D	−2.0	0	12	40	43	5	0
E	−2.3	0	0	0	80	15	5

Tris(α,α,2,4,5,6-hexachlorotolyl)methane (7). A solution of compound **6** (0.390 g; 0.6 mmol) in chloroform (25 mL; 310 mmol) containing aluminum trichloride (0.095 g; 0.7 mmol) was refluxed in an argon atmosphere for 3 h. The resulting brown solution was poured into cracked ice/hydrochloric acid. The organic phase was separated and washed with aqueous NaHCO$_3$ and with water. After drying over anhydrous sodium sulfate, the solvent was evaporated and the brown residue flash chromatographed (silica gel, hexane/CHCl$_3$ 3:1). The white spongy solid obtained was recrystallized from benzene, and a clahtrate of **7** with benzene in a 2:1 proportion was isolated (0.545 g, 96%): mp 198–200 °C. Anal. Calcd for C$_{22}$H$_4$Cl$_{18}$·0.5C$_6$H$_6$: C, 34.70; H, 0.61; Cl, 64.69. Found: C, 34.61; H, 0.62; Cl, 64.70. After heating at 100 °C under vacuum. ^{1}H NMR (CD$_2$Cl$_2$) δ 6.96–7.20 (m, 1H), 7.60–7.76 (m, 3H); IR (KBr): ν 3041, 2924, 1532, 1370, 1272, 1251, 1223, 1117, 1033, 963, 921, 871, 810, 773, 715, 673, 636, 615, 536, 478, 447 cm^{-1}; UV–vis (C$_6$H$_{12}$) $\lambda_{\max}$ nm (log ϵ) 230(5.13), 250(4.72), 286(3.25), 298(3.47), 309(3.54). Anal. Calcd for C$_{22}$H$_4$Cl$_{18}$: C, 29.15; H, 0.44; Cl, 70.40. Found: C, 28.92; H, 0.33; Cl, 70.55.

Tris(α,α-diphenyl-2,4,5,6-tetrachlorotolyl)methane (11). A solution of **7** (0.442 g; 0.5 mmol) in anhydrous benzene (17.7 mL; 200 mmol) containing aluminum trichloride (0.463 g; 3.5 mmol) was refluxed in an inert atmosphere during 30 min and then poured into cracked ice/hydrochloric acid. The organic phase was separated and washed with aqueous NaHCO$_3$ and with water. After drying over anhydrous sodium sulfate, the solvent was evaporated and the residue flash chromatographed (silica gel, hexane/CHCl$_3$ 4:1 → 2:1). The resulting main product was recrystallized from hexane and heated at 90 °C under vacuum in order to eliminate the included solvent, yielding **11** as a white solid (0.521 g; 89%): mp 245–247 °C, ^{1}H NMR (CD$_2$Cl$_2$) δ 6.38–6.52 (m, 3H), 6.84–7.25 (m, 32H); IR (KBr): ν 3091, 3063, 3028, 2924, 1950, 1887, 1810, 1754, 1600, 1537, 1495, 1453, 1376, 1348, 1278, 1187, 1159, 1110, 1075, 1033, 921, 837, 816, 747, 719, 698, 621, 600, 572, 501, 473 cm^{-1}; UV–vis (C$_6$H$_{12}$) $\lambda_{\max}$ nm (log ϵ) 252(4.67), 292(3.07), 302(2.99). Anal. Calcd for $C_{58}H_{34}Cl_{12}$: C, 60.24; H, 2.96; Cl, 36.79. Found: C, 60.07; H, 3.27; Cl, 36.58.

Tris(α,α-bis(pentachlorophenyl)-2,4,5,6-tetrachlorotolyl)methane (8). A solution of compound **11** (0.100 g; 0.086 mmol) and S_2Cl_2 (0.022 g;0.16 mmol) in SO_2Cl_2 (3.5 mL; 43.2 mmol) and the resulting dark red solution was refluxed during 3 h. Then the solution was concentrated to about one-third of this initial volume and refluxed an additional 1 h adding, occasionally, small amounts of SO_2Cl_2 in order to keep the volume of the solution constant. Finally, ice was added to the reaction mixture, and then solid $NaHCO_3$ was added until no more gas evolution took place. The resulting mixture was heated on a steam bath, cooled, and finally, acidified with aqueous HCl. The insoluble material was filtered, washed with water and dried. By flash chromatography (silica gel, first hexane, then hexane/chloroform 5:1) and recrystallization from benzene/methanol, compound **8** was obtained (0.086 gr, 45%): mp: 225−227 °C; ^{1}H NMR (CD_2Cl_2) δ 6.5−7.2 (m, 4H); IR (KBr): ν 2924, 1532, 1370, 1342, 1244, 1188, 1117, 1040, 878, 808, 716, 681, 646, 527, 470 cm^{-1}; UV−vis (C_6H_{12}) λ_{max} nm (log ϵ) 223(5.68), 295(3.59), 305(3.51); MS (MALDI-TOF): 2189 (M^-). Anal. Calcd for $C_{58}H_4Cl_{42}$: C, 31.81; H, 0.18; Cl, 68.00. Found: C, 32.04; H, 0.21; Cl, 67.81.

Tris(α,α,α′,α′,2,4,6-heptachloroxylyl)methane (2). A solution of tris(2,4,6-trichlorophenyl)methane (**1**) (0.3 g; 0.5 mmol) in chloroform (25 mL; 280 mmol), containing aluminum trichloride (0.11 g; 0.8 mmol), was refluxed in an argon atmosphere for 21 h. The resulting blue solution was poured into cracked ice/hydrochloric acid, and the organic phase was separated and washed with aqueous $NaHCO_3$ and with water. After drying over anhydrous sodium sulfate, the solvent was evaporated and the residue flash chromatographed (silica gel, hexane/$CHCl_3$ 3:1). Compound **2** eluted first and was recrystallized from benzene yielding a clahtrate with benzene in a 2:1 proportion (0.245 g, 45%): mp 250 °C dec; ^{1}H NMR (CD_2Cl_2) δ 6.92−7.21 (m, 1H), 7.35 (s, 3H), 7.60−7.81 (m, 6H); IR (KBr): 3044, 1532, 1377, 1272, 1223, 1040, 1005, 787, 722, 790, 582, 442 cm^{-1}; UV−vis (C_6H_{12}) λ_{max} nm (log ϵ) 290(3.11), 299(3.28), 309(3.27). Anal. Calcd for $C_{25}H_7Cl_{21}\cdot 0.5\ C_6H_6$: C, 30.83; H, 0.92; Cl, 68.25. Found: C, 30.06; H, 0.98; Cl, 68.36.

Synthesis of the Polyradical Species. Tetrabutylammonium hydroxide (40% in water) was added in the dark to a suspension of **8** in THF, and the resulting mixture was stirred at room temperature. After a specific period of time, an excess of *p*-chloranil was added and the stirring continued an additional 3−4 h. Elimination of the solvent gave a residue which was passed through silica gel (CCl_4) to gave the polyradical sample as a deep-red purple solid which is stable in contact with the atmosphere and at temperatures up to 150 °C. By recrystallization from benzene, polycrystalline samples were obtained. Elemental analyses of all samples are almost identical with the starting precursor and agree with the calculated values.

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