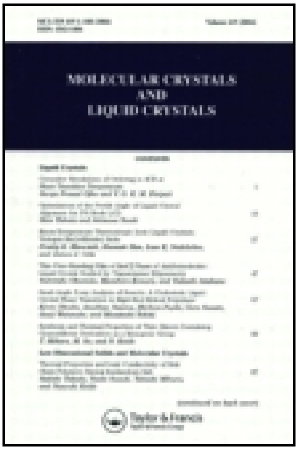

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STABLE TRIPLETS AND QUARTETS FROM CARBON CENTERED POLYRADICALS

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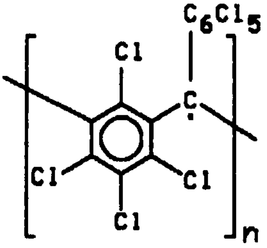
Abstract Several Mono-, di-, and triradicals stable at ambient conditions have been isolated as pure solids. Diradicals 7, 10 and triradical 11 exist in several stereoisomeric forms due to restricted rotation of aryl groups. Diradical 7 ($R=C_6Cl_5$) has been obtained as a 60:40 equilibrated mixture of the meso form (C_s symmetry) and the enantiomeric pair (C_2 symmetry) . Both diastereoisomers have been separated and the rates of convertions between each other at different temperatures have been measured. For the triradical 11 ($R=C_6Cl_5$) two diastereoisomers with C_2 and D_3 symmetries have also been separated , having a diastereoisomeric ratio of 80:20. The magnetic properties of polyradicals have been studied by e.s.r. and magnetic susceptibility measurements. Triplet and quartet ground states have been found, respectively for diradicals and triradicals irrespective of their symmetries.

INTRODUCTION

Current research on magnetic organic materials is aimed towards the development of organic ferromagnets. Among several models for designing such materials,[1] one is based on the so-called "topological degeneration"[2,3] and consists of non-disjoint alternant hydrocarbons (AH) with singly occupied non-bonding molecular orbitals, for which theory predicts a ground open-shell spin states with the highest multiplicities.[2] Up to now, only a very few and unstable species had been tested within this model.[2]

Our attention is directed to obtain such non-disjoint AH's as stable solids, being our final objective the polymeric materials 1 and/or 2. Several years ago ,Mataga and Ovchinnikov,[3] proposed two polymers analogous to 1 and 2 in order to achieve organic ferromagnets.

However, the high unstabilities and synthetical unaccesibilities of their proposals make them a difficult task.



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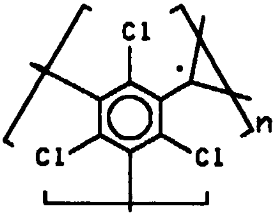


2

On the conrtary, highly chlorinated di- and triarylmethyl radicals posses high persistence and chemical stability. In addition, these materials can be prepared through controlled reactions.[4]

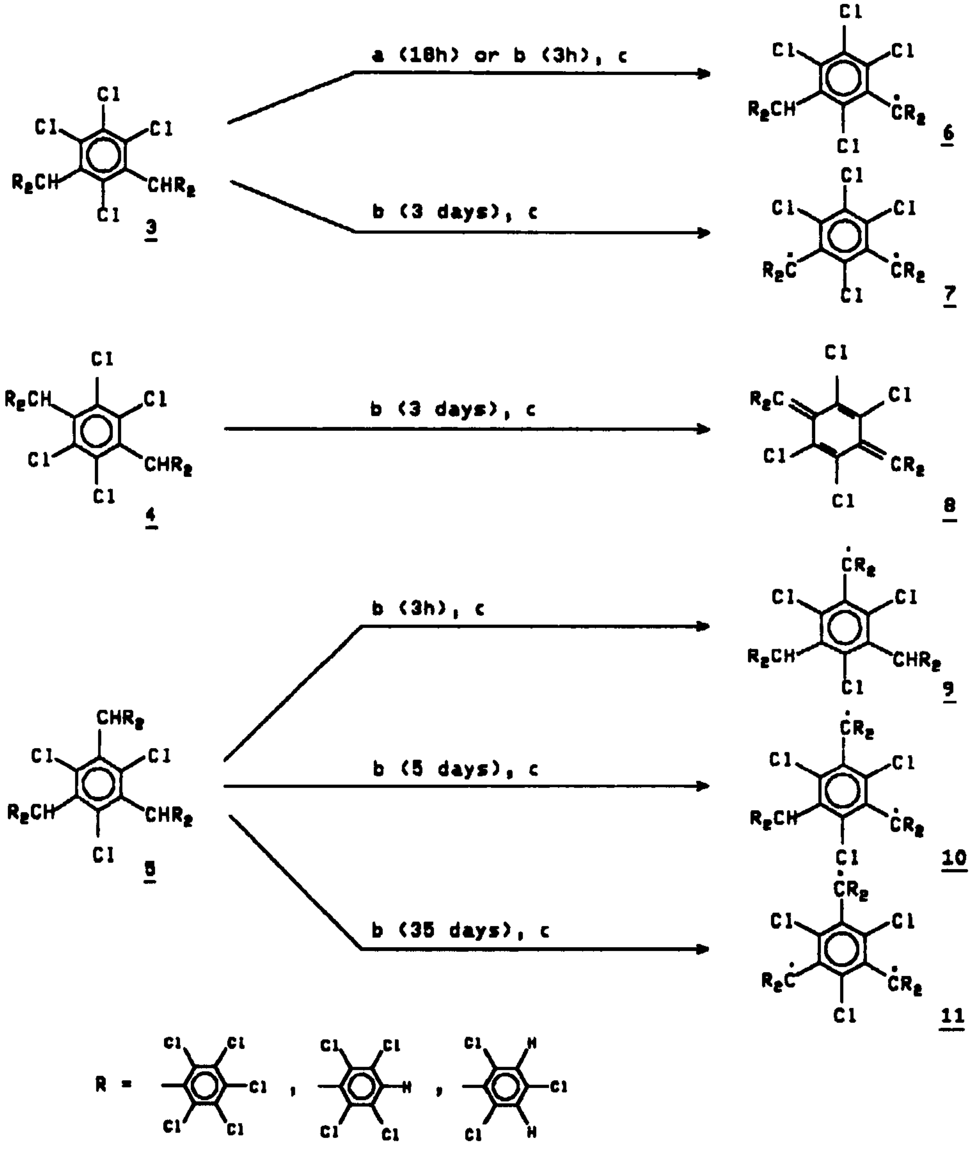
In order to test the feasibility of our final objective, we have prepared several non-disjoint AH's as model compounds (see Scheme 1) and studied their physical, chemical, and structural properties both in solution and in the solid state.[5]

Perchlorotriphenylmethyl radical has a propeller-like conformation with a high congestion of *ortho*-chlorine atoms which gives rise to a resolvable pair of enantiomers differing only in the sense of their helicities.[4,6] Consequently, several stereoisomeric propeller forms were also expected for the polyradical model compounds, due to the restricted rotation of their aryl groups. Until now the effect of such isomerism in high spin molecules has never been assessed, basically because their intrinsic unstability. Only in very few cases, indirect evidences of such isomerism has been given.[7] In the present paper, we report for the first time the separation of non-disjoint AH stereoisomers and the influence of their symmetries on the magnetic properties.

SYNTHESIS AND RELEVANT PROPERTIES

Polyradicals 6-11 were prepared from the corresponding polyarylmethanes 3-5 in a "one pot" reaction by treatment with an appropriate base

Scheme 1

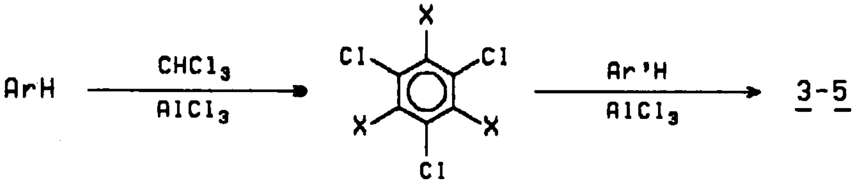


"one-pot" reaction: a, $NaNH_2$-18 crown-6/THF; b, exc. nBu_4NOH/THF and c, exc. p-chloranil and further oxidation of the resulting mono-, di- and tricarbanions (Scheme 1).[7]

Polyradicals 6-11 were isolated as a deep red solids being completely stables at ambient conditions. For most of them a very slow decomposition have been observed in solution.

Radical precursors 3-5 were synthesized by the general two-step Friedel-Crafts sequence outlined in Scheme 2.[7]

Scheme 2



X= Cl, $CHCl_2$

ArH= 1,2,4,5-; 1,3,4,5-tetrachlorobenzene or 1,3,5-trichlorobenzene.

Ar'H= pentachlorobenzene; 1,2,4,5-tetrachlorobenzene or 1,3,5-trichlorobenzene.

As it was expected, polyradicals 6-11 exist in solution in several stereoisomeric forms due to the different propeller helicity of triphenylmethyl (or triphenylmethane) moieties. Such stereoisomers are mutually interconverting with different energy barriers depending on the nature of the stereogenic center. Thus, triphenylmethyl moieties have always larger energy barriers than triphenylmethane ones therefore permitting the resolution of their stereoisomers by liquid chromatography. A point worth noticing is that the crystallization of polyradicals always yields only one stereoisomer, while a rapid solvent evaporation afford amorphous solids with stereoisomeric compositions similar to those observed in the equilibrated solutions.

As a representative examples of the chemical and physical properties of polyradicals 6-11 we present here two cases, the diradical 7 (R= C_6Cl_5) and triradical 11 (R= C_6Cl_5).

Diradical 7 case

Two diastereoisomers, 7a and 7b have been completely resolved by HPLC. They have identical electronic absorption spectra as ascertained by UV-visible diode array detection of both chromatographic peaks and by quantitative UV-visible spectra of 7 in both crystalline and amorphous solid state. Both diastereoisomers show slight hypsochromic shifts in their absorption maxima with respect to the monoradical 4 (R= C_6Cl_5), and their molar absortivities are twice to those observed for the monoradical 4. These results are in agreement with qualitative theoretical considerations.

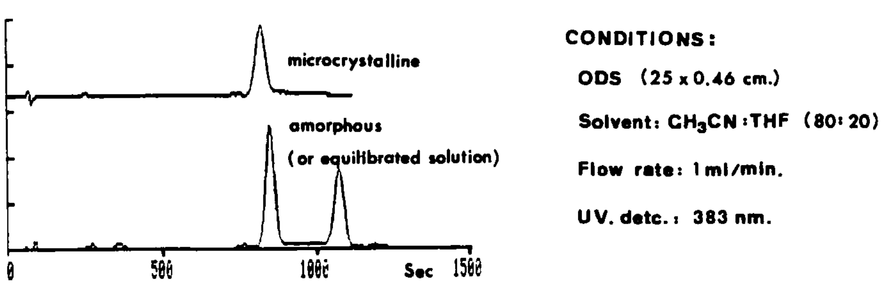
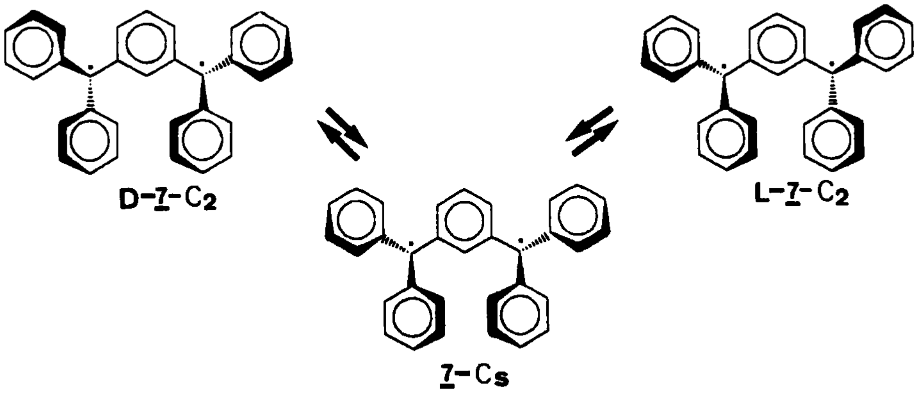


Figure 1. Chromatographic separation of diradical 7. a) microcrystalline sample and b) amorphous sample.

The zero-field splitting (ZFS) parameters corresponding to diastereoisomers 7a and 7b have been determined by simulation of rigid media ESR spectra of samples with different diastereoisomeric proportions. The ZFS parameters (7a: $|D/hc| = 0.0156\ cm^{-1}$; $|E/hc| = 0.0052\ cm^{-1}$ and 7b: $|D/hc| = 0.0080\ cm^{-1}$; $|E/hc| \leq 0.0003\ cm^{-1}$) are in accordance with the expected symmetries for both diastereoisomers permitting their structural assignations. Thus, a C_s symmetry (meso form) has been assigned to 7a and a C_2 symmetry (DL-form) to 7b (see Scheme 3). Unfortunately, attempts to resolve antipodes of 7b by HPLC on chiral stationary phase -(+)-OT- were be unsuccessful due to the low solubility of 7b. Thus, confirmation of the C_2-symmetry of 7b is at present still pending.

Diastereomerization rates in the range 14-40 ºC have been measured from equilibration experiments of pure 7-C_s. The diastereomerization barrier calculated from these rates, for a two independent two-ring flip mechanisms (Scheme 3), ($\Delta G^{\ddagger}_{298}$= 97±8 kJ mol^{-1}) is smaller than that of the perchlorotriphenylmethyl radical ($\Delta G^{\ddagger}_{298} \geq$ 130 kJ mol^{-1}),[6] indicating that a perturbation between the two radical moieties of 7 takes place.

Scheme 3[8]



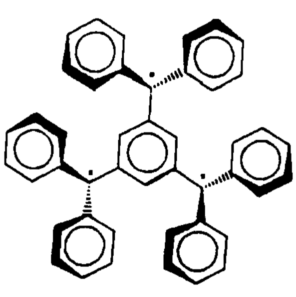
The equilibrium constant in the temperature range studied is K(7-C_s/7-C_2) = 1.5 ± 0.1. The higher stability of 7-C_s is adscribed to its higher disorder (entropic considerations alone would lead to 7-C_s/7-C_2 ratio of 1.0) and to a further stabilization, ΔH= 1.0 kJ mol^{-1}, because of intramolecular Cl-Cl interactions.

The ESR signal intensities of Δm_s= 1 and Δm_s= 2 lines of both diastereoisomers obey the Curie law in the range 105-180 K. Such results are in accordance with triplet ground states for both isomers. The magnetic behavior of pure microcrystalline 7-C_s has also been studied by means of susceptibility measurements performed with an ac susceptometer at zero external field in the temperature range 4.2-25 K and with a Faraday magnetometer from 80 to 300 K. A Curie-Weiss law is obeyed, C= 0.95 emu mol^{-1} and Θ= -1.23 K, which corresponds to μ= 2.72 μ_B and S= 1 system.

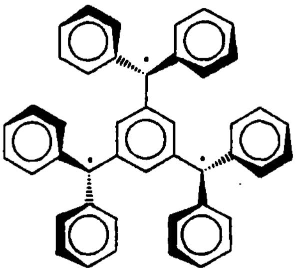
Triradical 11 case

Triradical 11 exits in two diastereoisomeric forms which have been completely resolved by HPLC. The electronic absorption spectra of both diastereoisomers are identical and show similar characteristics as those described for the diradical 7. The observed diastereoisomeric ratio in an equilibrated sample of triradical (80:20) is very close to that expected for a mixture in equilibrium of two pairs of enantiomers with C_2 and D_3 symmetries (according with entropic considerations, the C_2:D_3 ratio would be 75:25). Thus, the tentative structural assignation (Scheme 4) of adscribing a C_2 symmetry to the diastereoisomer which is obtained pure by crystallization is proposed.

Scheme 4[8]



11-C_2



11-D_3

The magnetic behavior of pure microcrystalline 11-C_2 is that of a paramagnetic system (C= 1.89 emu mol^{-1} and Θ= -1.34 K) with μ= 3.89 μ_B and S= 3/2.

CONCLUSIONS

At the first stage of our investigations concerning with the chemical, physical and structural properties of non-disjoint alternant hydrocarbons with high spin multiplicities, two important features are remarked: a) Such species can be obtained as stable solids and b) The ground state multiplicities predicted by current theories are not affected by the different symmetries of the molecules. Based on the results here described, ground states with high multiplicities and with no low-lying excited states are expected for the extended systems 1 and 2.

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8. Chlorine atoms has been omitted for clarity.