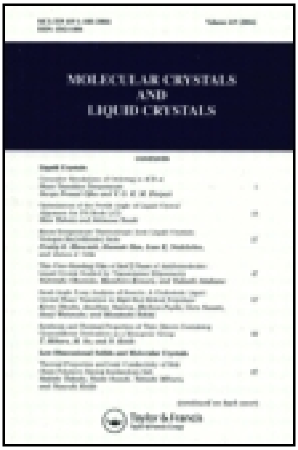

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Is the Orthogonality of Partially Filled Orbitals in a Regular Chain a Proper Strategy Towards High Spin Molecules?

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IS THE ORTHOGONALITY OF PARTIALLY FILLED ORBITALS IN A REGULAR CHAIN A PROPER STRATEGY TOWARDS HIGH SPIN MOLECULES?

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Abstract The Hartree-Fock band theory predicts that the FM state would be energetically favored over the AF and M states at the limit case where the overlap between the interacting semiocuped orbitals is really zero (orthogonality). In order to test experimentally this strategy towards organic high spin molecules, we addressed ourselves to salts of polyradical-cations 1.

Mono- and di- radical-cation generated from perchlorobiphenyl/SbF$_5$ have been studied at several temperatures with UV-Vis and ESR spectroscopies. The spectral data agree with a D_{2d} ground-state triplet with two localized electrons, each one placed (and delocalized) only on one phenyl moiety.

INTRODUCTION

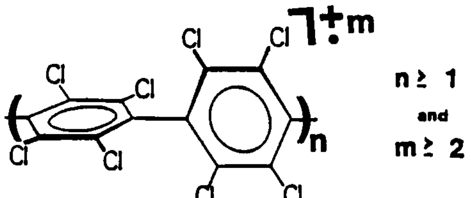
The search for ferromagnetic organic compounds (molecular solids or polymers) is an area of increasing interest. Ferromagnetism is a macroscopic property which requires a spin alignment throughout the solid. Therefore, the existence of ferromagnetic couplings among open-shell molecules (in molecular solids) or constituent units (in polymeric chains or networks) is a necessary prerequisite for this property. Three well-theoretically founded approaches are being followed in order to achieve these ferromagnetic couplings among the repetitive units: (1) Strong configurational admixing with spin conservation of a virtual excited state with the ground state,[1] (2) Heitler-London spin exchange between positive and negative spin densities,[2] and (3) The so-called "topological degeneration" approach which consists on large non-disjoint alternant hydrocarbons with partially occupied degenerate non-bonding molecular orbitals.[3]

Miller and co-workers have recently demonstrated that bulk ferromagnetism is achievable in molecular solids.[4] Nevertheless, extensive experimental and theoretical studies are still required in order to get a deeper understanding and even to control the cooperative phenomena in organic solids. Those concerning with the different mechanism for the stabilization of ferromagnetic couplings would be particulary promising.

Whangbo has described within the Hartree-Fock band theory the problem of the relative stabilization of metallic (M) versus magnetic insulating (ferromagnetic, FM, and antiferromagnetic, AF) states in a regular chain with one (or more) partially filled band (s)[5]. Essentially this problem is reduced on how well electron-electron repulsions are screened by the bonding interactions between the repeat units. So, when the resulting band wide, W, of a chain of half-filled interacting orbitals is smaller than on-site electron-electron repulsion term, V, (i.e., $W<V$) the insulating FM and AF states are energetically favoured over the M state. At the limit case where the overlap between the interacting orbitals is really zero, and hence $W=0$, the preferred state would be the FM where the electrons would be ferromagnetically coupled and localized on each repeat unit.[6] This stabilization turns out to be quite analogous to that predicted for twisted ethylene (D_{2d}) where the triplet would be the ground state .[7]

To our knowledge this approach to FM coupling stabilization has not been experimentally tested in organic compounds. Thus, we addresed ourselves to di- and poly radical-cations <u>1</u> with the conviction that neighbour rings would be canted perpendicular to one another due to the bulky <u>ortho</u>-chlorines, as is indeed observed for perchlorobiphenyl (cant angle ca. 87º).[8]

<u>SCHEME I</u>



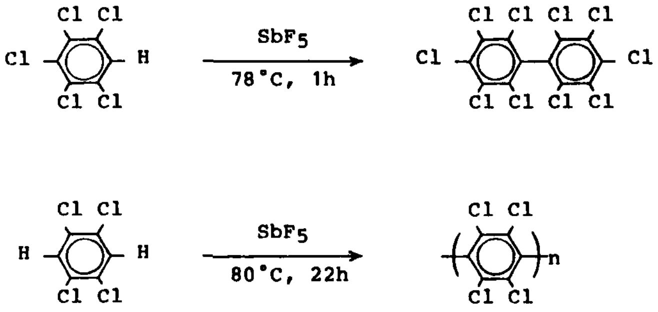
<u>1</u>

RESULTS AND DISCUSION

Synthesis

Dehydrocoupling (Scholl) reactions, using SbF_5 as the Lewis acid catalyst-oxidant agent, were carried out with pentachlorobenzene and 1,2,4,5-tetrachlorobenzene yielding perchlorobiphenyl 2 and poly(p-perchlorophenylene) 3 (degree of polymerization, ≤55), respectively.

SCHEME 2



2 (93 %)

3 (86 %)
n ≤ 55

The appearance of the UV spectra of polymer 3 is very close to those of C_6Cl_6 and 2;[9] consisting of a structurated medium-intensity secondary band and an intense primary band without the presence of any intense conjugation band around 300 nm. Consequently, in 2 a complete inhibition of resonance between the phenylene moieties occurs due to steric interactions among the four o-chlorines causing the rings to be perpendicular to each other and, therefore, spectroscopically independents.

Radical-cations generation

Treatment of 2 with SbF_5 under Ar atmosphere afforded a deep blue ESR active solution due to radical-cations formation. These species are completely stable in this oxidant media even at high temperatures. Thus, quenching (in aq HCl) the SbF_5 solution after heating at 80 ºC during 15 days afforded 2.

Two different radical species are formed during oxidation of 2, as ascertained from ESR studies. Thus, during the course of the oxidation two distinct signals are simultaneously developed (Figure 1): an asymmetrical central line (marked with Δ) and four broad lines (marked with ▲) characteristic of a triplet. The intensity of central line, relative to those of the triplet ones, is almost reduced to zero by sample dilution with pure SbF_5 and, furthermore, the saturation behaviour of central line, when incident microwave power is changed, is different (saturates faster) to that observed for the triplet lines.

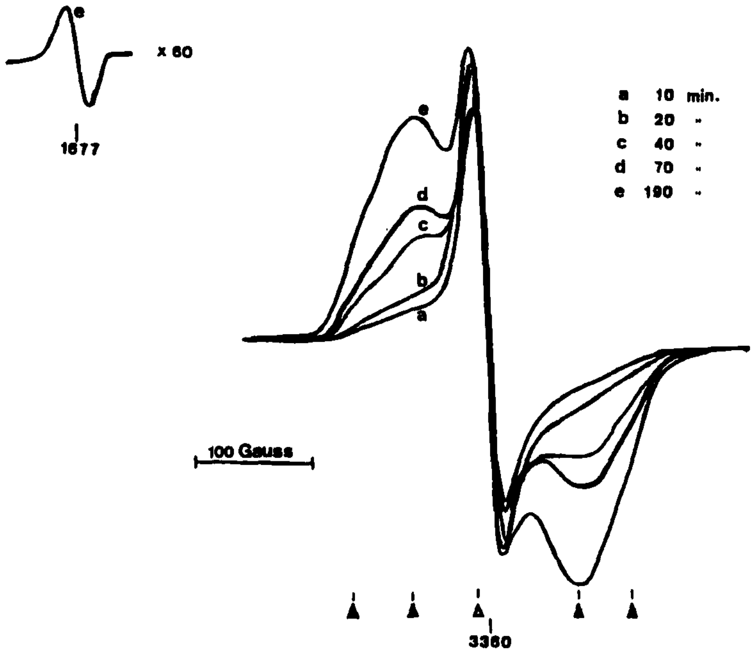
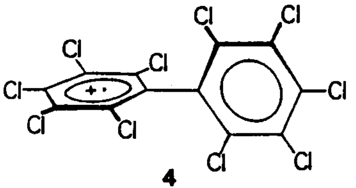


FIGURE 1. Evolution with time of the ESR absorptions in the oxidation of 1 with SbF_5 at 80 ºC. The spectra where registered in glass SbF_5 (at -130 ºC) after quenching the oxidation by freezing.

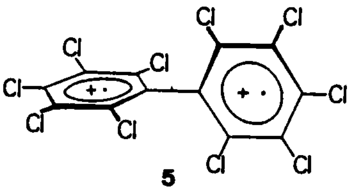
Such results clearly demonstrate that a two-step oxidation of 2 takes place producing a radical-cation and a doubled-charged triplet.

ESR and UV-Visible characterization

The average g-value, 2.0131, of radical-cation is very close to that previously reported for radical-cation of hexachlorobenzene, g= 2.0156,[10] permitting therefore to assign this absorption to 4. The slight asymmetry observed for this signal has been tentatively adscribed to an anisotropic g-tensor (Lineshape has been simulated with $g_{\parallel}=2.0019$, $g_{\perp}=2.0187$ and lorentzian half-width at half-heigth, W_0= 15 Gauss).



4



5

Zero-field splitting parameters of the double-charged triplet, $|D/hc|$= 0.013 cm^{-1} and $|E/hc| \leq$ 0.002 cm^{-1} ($g_{xy}=g_z=2.0157$) have been determined by a simulation procedure (Figure 2b). As occurs for triplet molecules dissolved in a host-matrix with a markedly dissimilar geometry, the linewidth of triplet/SbF_5 spectrum is very broad. So, it appears likely that a range of solute-solvent configurations is tolerated with the various configurations displaying a distribution of D values with a mean of 0.013 cm^{-1}. Such mean value is well below to that of the triplet hexachlorobenzene dication, $|D/hc|$=0.1012 cm^{-1},[10] indicating that the two electrons are on average further apart than in $C_6Cl_5^{+2}$. From the relationship , $D' = 2.79 \times 10^4/r^3$ where D' is in Gauss and r in Å, it is possible to estimate the average interspin distance of the triplet, $r_{1,2} \approx 5.9 \pm 0.3$ Å. Such distance is somewhat larger than that between the centers of two phenyl rings, 4.2 Å, suggesting that each electron is delocalized on the carbon and chlorine atoms of only one phenyl moiety, as in 5. The negligible E value agrees with an axial symmetry (D_2 or D_{2d}) as is expected from the large repulsions between o-chlorine atoms.

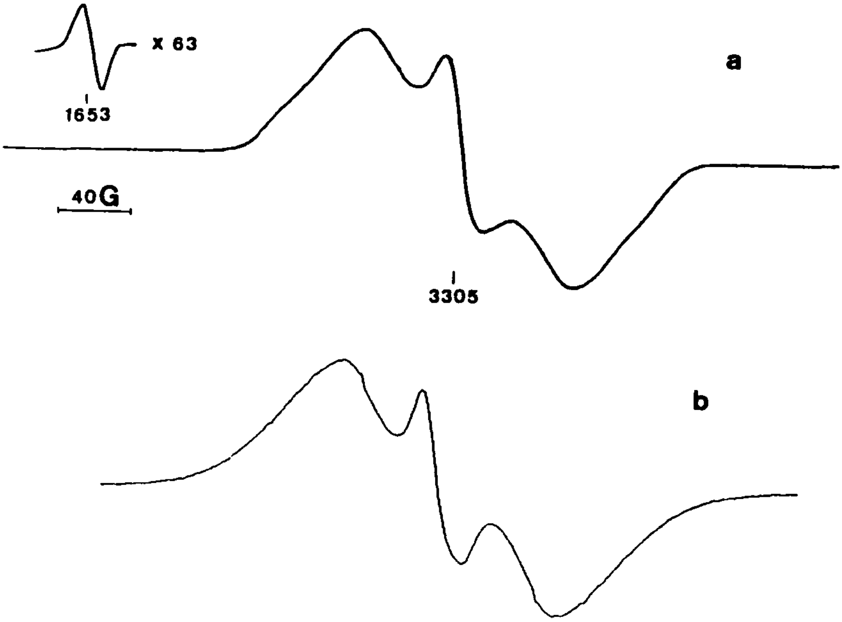


FIGURE 2. a) Observed ESR spectrum of 5 in glass SbF_5 (at -130 ºC). b) Sum of simulated spectra of randomly oriented species: 1) triplets (95%) with D'=135 Gauss, E'=0, g=2.0157, and W_0=42 Gauss and 2) radicals (5%) with $g_{\parallel}$=2.0019, $g_{\perp}$=2.0187, and W_0=15 Gauss.

The UV-visible spectra of radical-cation 4 and triplet 5 in SbF_5 solution at r.t. show absorption maxima at 247, 275, 335, 555 and 600 nm. A point worth noticing is that triplet 5 does not show any additional absorption neither significant band shift with respect to radical-cation 4. Therefore, the two radical-cation substuctures of 5 are not in conjugation with one another in a classical π sense , in spite themselves are classically delocalized. Accordingly, triplet 5 belongs to point group D_{2d} with both phenyl groups orthogonally disposed.

The Curie-Weiss plot of the intensity of the Δm_s=2 line vs 1/T over the range 139-233K gives a straight line (r= 0.997). Such result agrees with a ground-state triplet for 5.

Expansion of the above described results to extended systems, such as perchloroterphenyl, perchloroquaterphenyl and poly(p-perchlorophenylene) 3, is in progress.

CONCLUDING REMARKS

These preliminary results show that orthogonality of partially filled orbitals in a regular chain is a promising strategy in order to achieve ferromagnetic couplings, in agreement with theoretical expectations. So, extension of this strategy to other series of organic compounds, specially to neutral polyradicals, is encouraged.

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