

Molecular design of high spin polymers with ferromagnetic coupling among the electrons. Two types of 1-D π -conjugated polymers: Charge transfer and polaronic ferromagnets

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Abstract. Based on Anderson's general theory of magnetism, the sufficient conditions for the existence (arising) of high spin (HS) states with ferromagnetic coupling between the electrons within the half-filled band (HFB) in 1D infinite π -conjugated systems are described here. The structure and magnetic properties of two classes of HS systems are investigated. A). 1D polymers, in which charge transfer triplet biradicals are intrinsic parts of the polymer chain. B). The term dendralene is generalized for a large class of π -conjugated systems. In these systems the polaron (on a reductively or oxidatively doped π -fragment) is strictly localized in one elementary unit. This property, caused by the topology of the π -network, determines the good localization of the Wanniere states in a narrow HFB, and give rise to a HS ground state.

Introduction

An interaction among the magnetic moments can be called ferromagnetic if the interaction tend to align them parallel. In accordance with this definition, the interaction between two electrons in a biradical is ferromagnetic if the ground state is a triplet one. However, bi-or oligo-radical are no ferromagnets. The ferromagnetism is a cooperative phenomenon, i.e., the ferromagnetic properties arise if the number of electrons $N \gg 1$. That is why the theory used for molecular design of organic ferromagnets must be a many-body theory including the electron correlation. This is the basic concept of our consideration.

The progress in the theory of magnetism allows an analysis yielding the *sufficient* (but not *necessary*) conditions for yielding a HS ground state of an infinite regular polymer with ferromagnetic interaction (FM) among the electrons in the half-filled band(s) (HFB).

The conditions, which we determine follow from Anderson's general theory of magnetism (1), and are valid for infinite π -conjugated polymers with translational symmetry, in particular for one-dimensional (1-D) systems. They can be used for the molecular design of HS polymers with ferromagnetic coupling among the electrons in the HFB. The design of two classes: polaronic- and charge transfer (CT) systems, object of our study, are a particular case in this general approach.

The polymers we discuss are model systems. Some of them may not be synthetically available. Nevertheless, they illustrate the principle we are looking for.

Sufficient Condition for Arising of FM Interaction in Infinite 1-D Polymers with π -System of Conjugation

Whangbo-Hubbard condition

Whangbo has derived a condition (2), allowing a simple determination of the relative stability of localized high spin (magnetic) and low spin (non-magnetic) states in the HFB. Let us denote the Coulomb repulsion integrals of two electrons occupying the same Wannier state and adjacent states by U_0 and U_1 , respectively, and the HFB width by $\Delta\varepsilon$. Whangbo's condition reads ($U = U_0 - U_1$ is the renormalized Hubbard integral (3)):

$$\Delta\varepsilon / U < \pi/4 \quad (1)$$

Eq.(1) is similar to those derived by Hubbard (3) considering the dynamic of electrons in a narrow band:

$$\Delta\varepsilon/U < 2/\sqrt{3} \quad (1a)$$

Surprisingly, with one exception (ref.4), the above condition has not been utilized for estimation of the character of the spin state of model polymers. Eq.(1) has the following physical meaning: if the HFB width $\Delta\varepsilon$ is small compared with the one site Coulomb repulsion U , the FM HS state is favoured.

General condition

A condition stronger than the condition of Whangbo follows from the general theory of Anderson (1). A molecular system has high spin multiplicity and FM interaction between the unpaired electrons if the effective exchange integrals J_{eff} in the Heisenberg Hamiltonian:

$$H = -2 \sum_{i \neq j} J_{\text{eff}}(i, j) S_i S_j$$

are positive: $J_{\text{eff}}(i, j) > 0$ (S_i and S_j are the spin operators at site i and j , respectively).

The effective exchange integral J_{eff} , which expresses the spin exchange between the unpaired electrons in the HFB, has three contributions (1,5,6):

Potential (Coulomb) exchange, Kinetic exchange, and Indirect exchange („superexchange“), i.e. J_{eff} can be represented as a sum of three terms (for simplicity the indices i and j are omitted):

$$J_{\text{eff}} = J + J_{\text{kin}} + J_{\text{ind}} \quad (2)$$

In eq.(2):

J - the Coulomb exchange integral between the localized Wannier functions within the i -th and j -th EU's has always a positive value: $J \geq 0$. It favours the ferromagnetic interaction - Hund's rule.

J_{kin} - a negative component which favours the antiferromagnetic interaction, equal to:

$$J_{\text{kin}} = -2t^2 / U \sim -\Delta\varepsilon^2 / 2U \quad (3)$$

t - is the transfer (resonance) integral between adjacent Wannier functions (WF). The wide-

ning of the HFB, $\Delta\varepsilon$, as seen from the formula (3), results in an increase of the kinetic exchange, and in many cases $J_{\text{eff}} < 0$, i.e. the state is a low spin one. Low values of J_{kin} can be achieved if the Wannier orbitals are well localized within the EU. In such case, the Coulomb repulsion U is strong, and the transfer parameter t has a small value.

J_{ind} - expresses the indirect exchange of the electrons in the HFB via delocalized π -electrons in the filled energy bands. The sign of J_{ind} is determined by the structure of the EU and the interaction between the EU's. Except for some special cases (7), J_{ind} is usually of low value. Summarizing the above theoretical results on HS systems with FM interaction between the electrons, we can draw the following conclusions:

- (i) - these are systems with narrow HFB
- (ii) - the second condition providing a low value of the antiferromagnetic contribution is the good localization of the WF, resulting in weak overlap, respectively, a low value of the hopping integral t .

In other words, the condition providing a stabilization of the localized HS ferromagnetic state in relation to the low spin state reads:

$$J > J_{\text{kin}} + J_{\text{ind}} \quad (4)$$

or if we neglect the indirect interaction :

$$J > J_{\text{kin}} = 2t^2/U \quad (4a)$$

The results from theoretical investigations on several classes of HS systems with different mechanism governing the FM interaction show that the condition (4) is satisfied. These systems are (see the reviews of Miller (9), Iwamura (10) and Dougherty (11) and the references therein):

- i) π - systems with degenerate quantum states. The ferromagnetic properties of these systems are a consequence of the topology of their network. The occurrence of degenerate MO's in such systems can be predicted easily by the theorem of Coulson-Rushbrooke-Longuet-Higgins and its extended version (8). The largest group of high spin systems (and the best studied ones) belongs to this class (10).
- ii) Polaronic high-spin systems:
 - a) Fukutome ferromagnets (12)
 - b) Poly-radical ions of radialenes and dendralenes (4).
- iii) High-spin systems with indirect exchange interaction (7).
- iv) Polyaryl systems in which the rings are orthogonal and they are oxidized to radical cations or reduced to radical anions (13).

Structural Principles of two Types: Polaronic- and CT- HS Polymers.

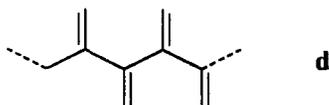
We shall consider two models of HS systems: polaronic- and CT- polymers, for which the condition (4) for appearance of FM HS ground state is satisfied:

A. Appearance of a narrow HFB within the energy gap of a dendralene chain, as a result of doping with electrons or holes.

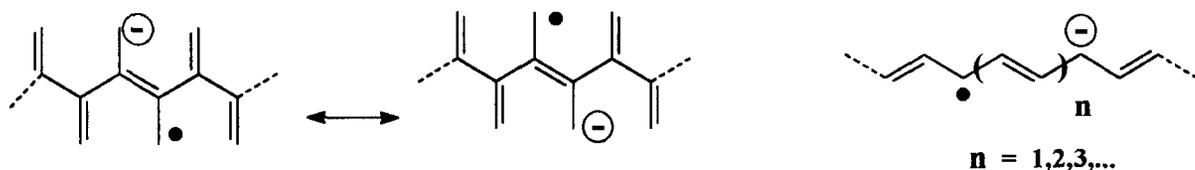
B. Systems, in which triplet CT biradicals are intrinsic parts of the polymer chain (polymers arising by linking of CT triplet biradicals).

Model A.

In a recent paper (4) we have shown that there exists a class of 1-D π -systems, namely the dendralenes and alternant radialenes (14) :

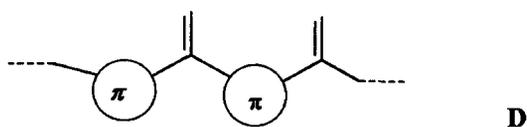


in which the polaron (at reductively or oxidatively doping), in contrast to polyacetylene, is localized in one elementary unit (4).

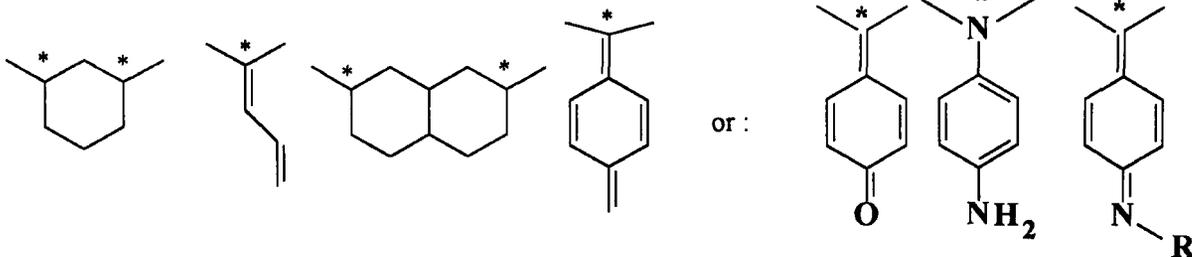


This property, caused by the topology of the π -network - 1,1 linking of the vinylene units, determines the good localization of the Wannier functions, and arising of a HS ground state.

The dendralenes **d** are the simplest examples of a large class of π -conjugated systems, having the same topology, and therefore the same properties - localization of the polaron in one fragment. A general topological model has the form:



where π is an arbitrary even alternant or heteronuclear system *connected at two or one starred π -centers with vinylene groups*, e.g.:

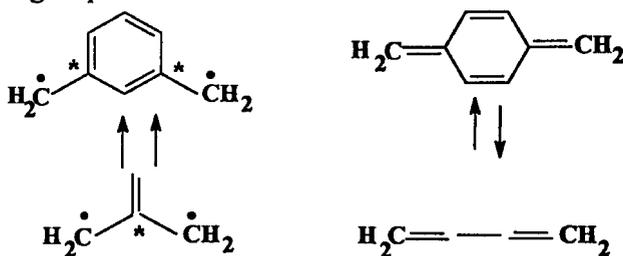


Dendralene **D** can be considered from different point of view. In one 1D π -system the vinylidene unit is such a conjugation barrier as monocyclic (e.g. benzene) or polycyclic even hydrocarbons connected at two starred π -centers with the adjacent structural units:



When two CH_2 groups are linked at *meta*-position in the benzene ring, the two electrons are coupled ferromagnetically. Linking at *para*- or *ortho* positions, on the other hand, give rise to quinoid structures with diamagnetic molecules.

A similiary situation is found by linking of two CH₂ groups at 1,1- or 1,2- positions, respectively, in vinylidene group:



If π is connected at two π -centers with vinylene groups, the linking of two starred π -centers of π is important condition for this class of polymers. This type of connection corresponds to the generalized term of *meta* position in an alternant π -system. In a polycyclic even alternant system two π -centers are in meta position each other if they are separated by $2n+1$ ($n = 0, 1, 2, \dots$) π -centers. The linking of a starred and an non-starred π -center of π with the vinylene groups leads to doubling the elementary unit, for instance:

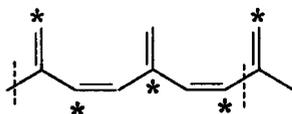


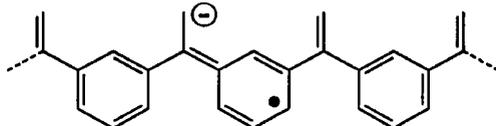
Table 1 Calculated values (in eV) of the contributions to the effective spin exchange (see eq.(2) between the unpaired electrons in the HFB for polymers D-1, D-2 and D-3. The kinetic term of all polymers $J_{kin} < 10^{-3}$ eV. $\Delta\varepsilon$ is the band width of the HFB, and U is the renormalized Hubbard integral (eq.(3)).

Poly mer	$\Delta\varepsilon$	U	J	J_{ind}	J_{eff}
D-1	0.29	2.033	0.432	0.017	0.449
D-2	0.28	1.090	0.295	0.017	0.312
D-3 *	0.09	2.057	0.435	0.078	0.513

* $\Theta = 60^\circ$.

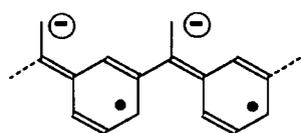
The above structures constitute the basic theoretical models of a new class of HS π -polymers with distinct (clear) expressed FM interaction between the electrons within the HFB. For all polymers D, the band width of the HFB $\Delta\varepsilon < 0.4$ eV, the WF are very good locali-zed, and the kinetic exchange $J_{kin} \sim 0$, i.e., all the polymers satisfy the condition, eq. (4) (see Table 1).

The good localization of the WF is a topological property of the polymers. A polaron for example of the polymer D-1 :

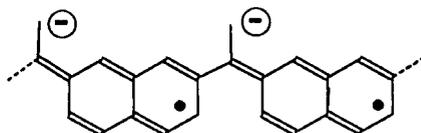


is localized in one EU. A structural relaxation corresponding to a polaron delocalized to more than one EU is not possible. For such a polaron there is no corresponding valence formula.

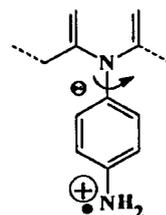
To a fully reduced or oxidized infinite polymer, for instance D-1, D-2, and D-3 one can attribute the structures (here and below only one resonance structure is depicted):



D-1



D-2



D-3

All polymers of type **D** have a large energy gap ΔE between the frontier HOMO -LUMO bands. For instance $\Delta E = 3.0$ eV for polymer **D-1**. The calculations for ΔE were carried out by means of a AMO variant of the EHF method (4). The geometries of the infinite polymers were obtained by means of an extended Su-Schrieffer- Heeger method , described in (15).

If the dendralenes **D** are homonuclear alternant systems, then , as in the case of **d** dendralene, the magnetic characteristics of **D**⁺ (HOMO band is the HFB) and **D**⁻ polymers (LUMO band is the HFB) are identical (see 4).

Table 1 collects the results of the calculated contributions of the effective exchange integral J_{eff} (see eq. (2)) for the three model polymers: **D-1** , **D-2** and **D-3**.

The calculations were carried out using a standard set of parameters (4,8). Within the calculation of the Coulomb (U_0 and U_1) and exchange integrals (J) with WF, the two center atomic Coulomb integrals are calculated using Mataga-Nishimoto approximation (16).

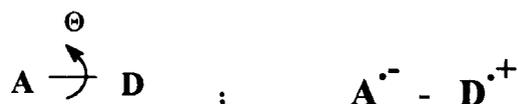
The numerical results for the spin exchange in the HFB of the polymers **D-1**, **D-2** and **D-3** show that the polymers have a HS ground state. The direct Coulomb interaction is the main contribution to the spin exchange. The role of the indirect exchange interaction is small and the kinetic term $J_{\text{kin}} \sim 0$.

Model B.

In 1963, the first theoretical model of forming organic ferromagnets with *intermolecular* CT mechanism was proposed by McConnell (17 ; see also ref.18). He has considered a linear **D**⁺· **A**⁻· chain, where **D**⁺· and **A**⁻· are a cation radical of donor **D** and anion radical of acceptor **A**, respectively. This concept was developed by Breslow (19) and Miller and Epstein (20).

A model for an *intramolecular* CT system with triplet ground state is given in the paper of Breslow (21). Several examples for derivatives of the *antiaromatic* benzene dication with multiple donor substituents are stable and may have a triplet ground state. In this study we consider ladder type polymers with mutual π -system of conjugation, including antiaromatic cyclopentadienyl cations (CPC) or cycloheptatrienide anions (CHA) as fragments in the 1D chain.

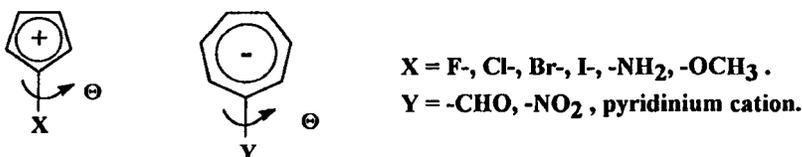
The structural principle of the CT triplet diradicals follows from Mulliken's idea of the CT molecular systems (ref. 22). The models of these CT diradicals consist of an acceptor (**A**) and a donor (**D**) which are π -systems covalently bonded by means of a σ bond



If the donor's ionisation potential is of low value whereas the acceptor's electron affinity is high, then the singlet-triplet splitting ($\Delta = E_T - E_S$) may have not only low, but even negative value, i.e. the ground state of the system is a triplet one.

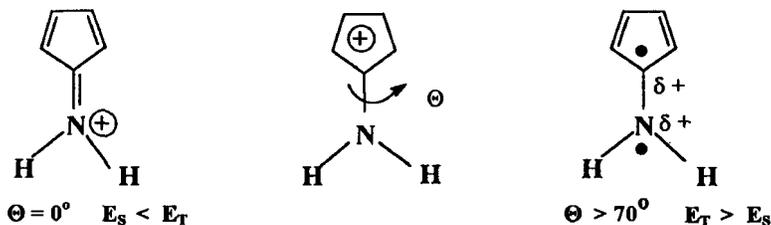
This effect could be enhanced if the dihedral angle Θ between the two fragments **A** and **D** is large. Steric effects, which lead to a decrease of the overlap between the π -orbitals of **A**⁻ and **D**⁺, could be achieved by means of suitable substituents in the donor or/and acceptor fragments (ref. 23,24) . In such a way coupled donor-acceptor systems are the donor-substi-

tuted anti-aromatic CPC or the acceptor-substituted antiaromatic CHA:



Here, we consider only two examples: the amino-CPC and the pyridinium- substituted CHA. (The results of *ab initio* calculations should be published elsewhere). The geometries were optimized by *ab initio* SCF calculations using a 3-21 G basis set. Afterthat, the energies of the different electronic states have been calculated with a CI procedure including all the singly and doubly excited electron configurations- program GAMESS (25).

In the case that the amino group and the CPC ring are coplanar, that means the dihedral angle $\Theta = 0$, the ground state is a singlet one. The singlet-triplet splitting $\Delta = E_T - E_S = 17.9$ kcal/mol. The rotation of the amino group about the C-N bond stabilizes the triplet ground state more than the singlet state. If $\Theta > 70^\circ$, the ground state of the amino -CPC is a triplet one. At $\Theta = 90^\circ$, the singlet-triplet splitting $\Delta = - 9.2$ kcal/mol.

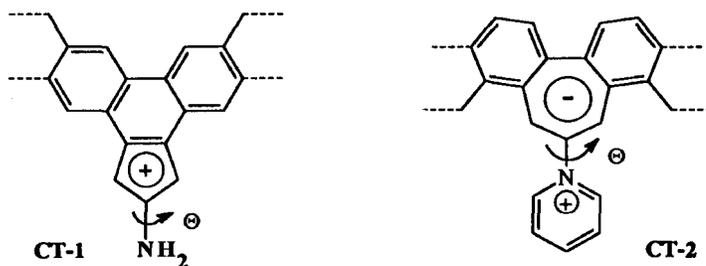


Another way to stabilize the triplet state more than the singlet state is the annelation of benzene rings of the corresponding Jahn-Teller structures.

In the case of the annelation of a benzene ring at the 3,4 positions results the 2-amino indenyl cation. The quantum-chemical calculations (SCF-CI) show that the ground state of the 2-amino indenyl cation is triplet.

Similarly, an acceptor-substituted anti-aromatic CHA could be a building block for polymeric high spin systems. An appropriate substituent (acceptor) is the positively charged pyridinium ring. Here, for the unsubstituted CHA the ground state still is a triplet state, with a singlet-triplet splitting $\Delta = - 4.4$ kcal/mol. Pyridinium substitution and also the structural fixation of the corresponding Jahn-Teller form by benzene annelation at the 3,4 and 5,6 positions increase the singlet-triplet energy difference.

So, the 2-amino indenyl cation and 3,4,5,6 dibenzo CHA are suitable candidates for building blocks of polymeric HS systems with magnetic order. The model polymers CT-1 and CT-2 illustrate this idea:



The calculations of several model polymers of this group show that they have a HS ground state with clear FM coupling between the electrons within the (two) HF bands.

The structural variety of theoretically probable high spin: CT- and dendralene like systems is impressing. This gives rise to hope that some of the synthetically accessible ones will prove to be purely organic ferromagnets.

Acknowledgments

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