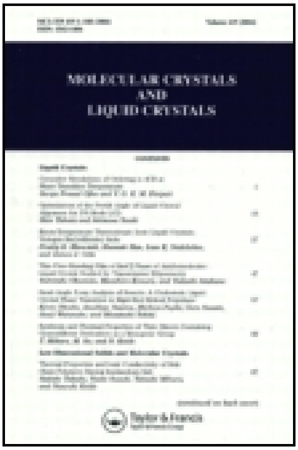

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Organic Open-Shell Systems with Indirect Magnetic Interaction Caused by the Topology of the Elementary Units

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Organic Open-Shell Systems with Indirect Magnetic Interaction Caused by the Topology of the Elementary Units

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The magnetic properties of a class of 1-D π-systems having a frontier half-filled band (HFB) of degenerate non-bonding MOs (NBMOs) localized within the elementary units (EU) have been studied theoretically. The localization of the MOs, determined by the topology of the π-fragments which form the EUs is explained by means of the extended Coulson-Rushbrooke-Longuet-Higgins theorem. The perfect localization and non-overlapping of the NBMOs results in vanishing of the direct (Hund-) and the kinetic exchange interaction between the unpaired electrons. The indirect exchange of the unpaired electrons (spin polarization exchange) occurs via the delocalized π-electrons in the filled energy bands.

Keywords: polymers; indirect magnetic interaction; topology

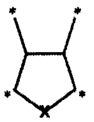
INTRODUCTION

The indirect magnetic exchange interaction is responsible for the magnetic ordering in many crystals with paramagnetic metal ions. This wide-spread and well investigated phenomenon within inorganic materials[1,2] is not investigated in the field of purely organic systems. The investigations of purely organic one-dimensional (1-D) systems sofar have been focused mainly on polymers with continual π-systems of conjugation with intramolecular direct magnetic interaction.[3-5] Mitani et al.[6] have shown by an *ab initio* crystal orbital study that the ferromagnetic interaction between neighbouring monomer units in methylene radical-substituted poly(phenylenemethylene)s arises from the spin polarization. In a recent paper[7] (see also refs. 8, 9), the concept of indirect exchange was generalized for some classes of polyradicals and 1-D organic open-shell π-systems. Synthesizing the high-spin polyradicals poly(*para*-ethinylphenyl)hydro-galvinoxyl, Nishide et al.[10] have proved experimentally the possibility of the indirect coupling between the unpaired electrons in purely organic systems (see also the recent paper of Minato and Lathi[11]).

The indirect exchange interaction suggested in the first communication,[7] is determined by the symmetry of the π-fragments which form the elementary units (EUs). The purpose of the present paper is the investigation of different classes of 1-D polymers for which the localization of the orbitals giving rise to indirect exchange is determined by the topology of the EUs. The topology is explained by means of the extention[12,13] of the Coulson-Rushbrooke-Longuet-Higgins theorem (CRLH).[14-16] Only the indirect exchange interaction of localized π-electrons through delocalized π-electrons in the filled energy bands is considered in this paper.

THE GENERALIZED CRLH THEOREM: MODELS OF POLYRADICALS AND POLYMERS WITH INDIRECT SPIN EXCHANGE

In the case of alternant π-electron systems, the role of the NBMOs for the existence of high-spin states has been demonstrated in the papers of Coulson, Rushbrooke and Longuet-Higgins.[14-16] An alternant system has $N = S^* - R$ NBMOs, where S^* and R are the number of the starred and unstarred π-centers, respectively. The CRLH theorem has been generalized in refs. 12 and 13. Within the CRLH theorem, one always considers two subsets of homonuclear nonbonded π-centers: the subset of starred and the subset of unstarred π-centers. In the generalized theorem,[12,13] only one subset of nonbonded π-centers is responsible for the appearance of NBMOs. It has been shown[12] that a system with M π-centers and a maximum set of R* homonuclear disjoint π-centers must have at least N = 2R* - M NBMOs. The NBMOs are present even if the π-system is a nonalternant one and if the π-centers belonging to the disjoint subset are heteroatomic. Representative examples are the heteronuclear nonalternant systems:



X = O, S, NR

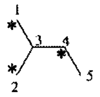
N = 2 x 4* - 7 = 1 NBMO

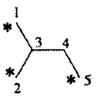
investigated by Berson et al. (see the recent papers, refs. 17, 18, and references given therein).

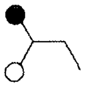
As a result of the generalized CRLH theorem, the following corollaries can be drawn:[12]

Corollary I: If the conjugated π-system has various disjoint sets R_k, k = 1,2,...p, then the NBMOs are composed only of their intersection $R_1 \cap R_2 \cap ... \cap R_p$.

As a result of corollary I, the set of the AOs from which the NBMOs are composed may be obtained. In the case of the radical







there are two maximum disjoint sets comprising positions 1,2,4 and 1,2,5. It follows from Corollary I that the NBMO coefficients are nonzero only for the π-sites 1 and 2.

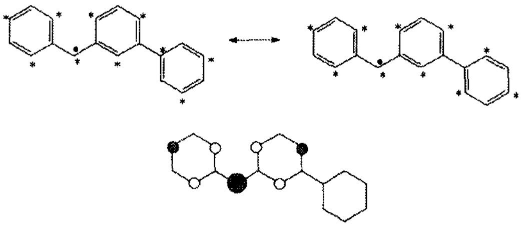
In the case of the nonalternant hydrocarbon with the following structure, there are three various disjoint sets of cardinality 5, and therefore the NBMO coefficients are different of zero as in the pentadienyl radical:

As a result of Corollary I, it follows the Corollary II which determines the structural principle of open-shell π-systems: diradicals, polyradicals and polymers with perfect localized and non-overlapping MOs which cause the indirect exchange interaction.

Corollary II: Let us consider a system consisting of a mono-radical subunit **R**$^{\bullet}$ for which the generalized CRLH theorem is valid, linked with an even alternant closed-shell unit **M**: **R**$^{\bullet}$ - **M**.

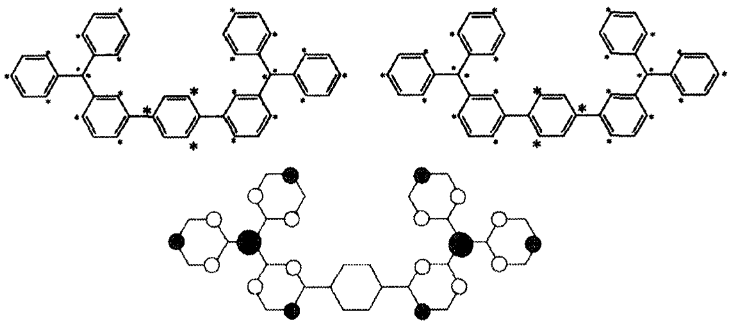
*If the π-center r of **R** (which is connected with the π-center **m** of **M**) belongs to the set of nonstarred ones (the MO coefficient $C_r = 0$), then all the NBMO coefficients in the fragment **M** are zero, i.e., the NBMO coefficients are nonzero only for the starred π-centers in **R**.*

An even π-system with q^* starred and q^0 nonstarred ($q^* = q^0$) π-centers has two maximum disjoint subsets.[12,13] Because there are two maximum disjoint sets in **M**, comprising **m** so that in the first subset **m** is starred and in the second subset **m** is unstarred, it follows from Corollary I that all NBMO coefficients in the fragment **M** are zero, i.e., the NBMO coefficients are nonzero only for π-centers in **R**. An example is the system

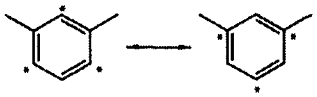


Obviously, Corollary II is also valid for systems consisting of two mono-radical subunits $\mathbf{R}^{\bullet}_1$ and $\mathbf{R}^{\bullet}_2$, for which the generalized CRLH theorem is valid, connected with an even alternant closed-shell subunit M: $\mathbf{R}^{\bullet}_1 - \mathbf{M} - \mathbf{R}^{\bullet}_2$

In the case of the diradical



or in the meta position linked triphenylmethyl radicals



there are two maximum disjoint sets in the central benzene ring. It follows from Corollary I that the NBMO coefficients are nonzero only for the starred π-sites in both triphenylmethyl radicals.

Corollary II is also valid for 1-D π-systems $.....\mathbf{R}^{\bullet} - \mathbf{M} - \mathbf{R}^{\bullet} - \mathbf{M} -....$, if this Corollary is valid for each EU. In these polymers, the NBMOs are perfect localized within the fragments $\mathbf{R}^{\bullet}$.

METHODS OF INVESTIGATION

The methods used in this paper are described in more detail in ref. 7. Here, it is given only a short survey.

Energy spectra

The polymers are presumed to be 1-D systems for which the Born-von Karman conditions are fulfilled. In the Hückel-Hubbard version[19] of the Bloch method, the MO energies $e(\boldsymbol{k})$ are obtained by the numerical diagonalization of the matrix[20]

$$\boldsymbol{E}(\boldsymbol{k}) = \boldsymbol{E_0} + \boldsymbol{V}\exp(\mathrm{i}\boldsymbol{k}) + \boldsymbol{V^+}\exp(-\mathrm{i}\boldsymbol{k}), \qquad (1)$$

where $\boldsymbol{E_0}$ is the energy matrix of the EU, $\boldsymbol{V}$ is the interaction matrix between neighbouring EUs (μ-th and ($\mu+1$)-th), and $\boldsymbol{V^+}$ is the transposed matrix. The localized partially occupied MOs (LPOMOs), whose energies are also eigenvalues of $\boldsymbol{E}(\boldsymbol{k})$, are degenerate and localized within the radical fragments $\mathbf{R}^{\bullet}$. They do not depend on the wave vector $\boldsymbol{k}$, and in fact, they coincide with the Wannier functions.

Indirect exchange interaction in polymers with LPOMOs

Let us denote by $J_{\mathrm{eff}}\,(\sigma,\rho)$ the effective exchange integral in the Heisenberg Hamiltonian:

$$\mathbf{H} = -\sum J_{\mathrm{eff}}(\sigma-\rho)\mathbf{S}_\sigma\mathbf{S}_\rho = -\sum J_{\mathrm{eff}}(\tau)\mathbf{S}_\sigma\mathbf{S}_\rho \qquad (2)$$

between the EUs σ and ρ ($\tau=\sigma-\rho$ is the relative distance between the EUs) upon which the Wannier functions are localized. Based on the results of Anderson[21] it has been shown [22] that J_{eff} can be expressed as a sum of three contributions (in the following, the dimensionless distance parameter τ is omitted for simplicity):

$$J_{\mathrm{eff}} = J - J_{\mathrm{kin}} + J_{\mathrm{ind}} = J - 2t^2/U + J_{\mathrm{ind}} \qquad (3)$$

For the considered polymers, Hund's rule cannot be used to predict the character of the exchange interaction between the electrons occupying degenerate states. Because the Wannier states (LPOMOs) are localized on non-overlapping AO sets, the Coulomb exchange integral J is vanishing. The transfer parameter t and the kinetic exchange integral J_{kin} are also equal to zero

($t = J_{kin} = 0$). Therefore, the indirect exchange J_{ind} of the unpaired electrons (spin polarization exchange) is the only component of the effective exchange integral ($J_{eff} = J_{ind}$), and occurs via the delocalized π-electrons in the filled energy bands. The sign of the effective exchange integral J_{eff} determines the character of the exchange interaction: $J_{eff} > 0 \Rightarrow$ ferromagnetic, and $J_{eff} < 0 \Rightarrow$ antiferromagnetic. The term J_{ind} is calculated using a formalism described in refs. 7-9.

Parametrization

The exchange parameter J_{ind} was calculated using the screened Mataga-Nishimoto approximation[23] for the two-center atomic Coulomb integrals γ_{rs} ($a=e^2/\gamma$):

$$\gamma_{rs} = e^2/(a+DR_{sr}) \qquad (4)$$

for different values of the screening constant D. The values of J_{ind} do not depend qualitatively on the screening parameter D. Therefore, all the data given in this paper were obtained using D = 3.

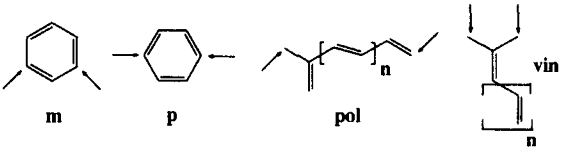
A standard value of the one-center Coulomb integral $\gamma = 10.84$ eV was used.[7-9] The geometry of the polymers (bond lengths and dihedral angles Θ) was estimated by means of the quantum-chemical AM1 method[24] (SPARTAN Program System[25]) for a biradical $\mathbf{R}^{\bullet}$ - $\mathbf{M}$ - $\mathbf{R}^{\bullet}$. The resonance integrals were calculated using Mulliken's formula:[26] $\beta(R) = \beta_0(R_0)\, S(R)/S(R_0)$, with $\beta_0(R_0) = \beta_0(1.4\text{Å}) = -2.4$ eV.[3-5] The dependence of the resonance integrals on the dihedral angle Θ is atopted as $\beta(\Theta) = \beta \cos\Theta$.

NUMERICAL RESULTS AND DISCUSSION

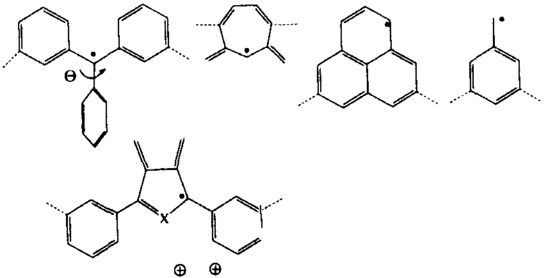
The indirect exchange interaction in polymers depends on the following factors:

- the structure of the radical fragment $\mathbf{R}^{\bullet}$,
- the structure of the coupling unit **M**. For a definite coupler, the nature (ferro- or antiferromagnetic), and the magnitude of the interaction depend on the coupling topology (e.g., *meta*-phenylene or *para*-phenylene as coupler),
- the distance between neighbouring radical fragments.

The following couplers **M**



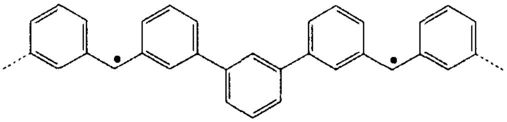
and radical fragments **R**



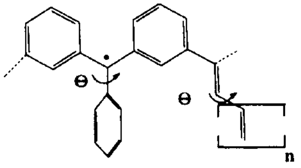
$X = CH, \overset{\oplus}{N}H, \overset{\oplus}{S}$.

were used for the model polymers investigated.

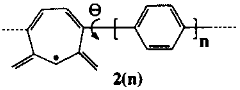
In all cases of model polymers with radical fragments coupled through the *meta*-phenylene unit (**m**), the indirect interaction parameter J_{ind} is practically zero ($J_{ind} < 10^{-4}$ eV), e.g.,



Following are given the numerical results for the indirect exchange interaction of the polymers **1**(**n**) and **2**(**n**):



1(n)



2(n)

n	ΔE [eV]	J_{ind} [meV]
0	2.762	0.8
1	1.846	2.0
2	1.554	2.8
12	0.506	10.1

n	J_{ind} [meV]
0	- 8.8
1	- 4.3
1*	0
2	- 0.7
3	~ 0

* $\Theta = 90°$

Contrary to the *meta* phenylene (**m**) unit, the *para*-phenylene (**p**) and the vinylidene (polyenylidene) (**vin**) fragments are effective couplers. However, the sign of J_{ind}, i.e., the nature of the magnetic interaction (ferro- or anti-ferromagnetic) is different.

The effective exchange parameter $J_{ind}(\tau)$ decreases rapidly with the distance τ between the radical fragments (see eqs. 2 and 3). At $\tau \geq 2$, $J_{ind}(\tau) < 10^{-3}$ eV for all the model polymers. On this account, the results for J_{ind} given above were calculated for $\tau = 1$ (adjacent EUs).

In the case of the polyenylidene fragment (**vin**) as coupling unit in polymer **1**(**n**), J_{ind} increases with increasing the polyenylidene chain length. There are a general relationship between the width of the energy gap EG (ΔE) of the polymer and the magnitude of the indirect exchange interaction (J_{ind}). With decreasing EG, the indirect exchange integral $|J_{ind}|$ increases.

The extention of the EU is connected with a decrease of $|J_{ind}|$ due to the large distance between the radical fragments. If the radical centers are coupled through a polyene chain (**pol**), the indirect exchange parameter is vanishingly small ($J_{ind} < 10^{-3}$ eV) at $n \geq 1$.

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