Structure and Properties of Non-classical Polymers. XV. 1D Polymers Possessing Two Bands with Ferromagnetically Coupled Electrons*

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Dedicated to Professor Achim Mehlhorn on the occasion of his 70th anniversary

The energy spectra and magnetic properties of a new class of non-classical (non-Kekulé) 1D polymers, having two bands with magnetically coupled electrons, have been investigated by many-electron band theory.

Key words: Non-classical 1D Polymers, Molecular Magnets, Polymers with Two Half-filled Bands

Introduction

The so far known purely organic high-spin one-dimensional (1D) polymers with ferromagnetically coupled electrons are usually characterized by *one* half-filled band (HFB) [1, 2]. Herein, a new class of 1D polymers, having two bands in which the electrons are magnetically coupled (ferro- or antiferromagnetically), is investigated theoretically.

The investigations decribed in this paper are an extension of the studies in references [3] and [4], where the structures of a large class of molecules with a triplet ground state have been considered. If the polymers have the same structural principle as the molecules with a triplet ground state described in refs. [3] and [4], their energy spectra should consist of two bands with ferromagnetically coupled electrons.

In this communication only the magnetic properties of systems with such a two-band structure are considered. These systems usually exhibit other types of cooperative phenomena, however, their treatment requires another set of theoretical methods (see [5, 6]). In particular, investigations of the electrical properties (electrical conductivity) of such compounds are in progress.

Structural Principles of the Polymers

π-Systems with NBMOs determined by the molecular topology

There are two classes of π-systems with non-bonding molecular orbitals (NBMO) determined by the molecular topology: homo-nuclear alternant systems, and quasi-alternant systems.

Homo-nuclear alternant radicals

According to the theorem of Coulson, Rushbrooke and Longuet-Higgins (CRLH) [7, 8] a homo-nuclear alternant π-system (hydrocarbon) has at least

$$N = S^{*} - U^{\circ}$$

NBMOs, where $\{S^{*}\}$ and $\{U^{\circ}\}$ are the numbers of the starred and unstarred π-centers, respectively. Examples, representing situations where the CRLH theorem is valid, are the benzyl radical (**Bz**) and the phenalenyl radical (**Ph**) shown in Fig. 1 (here and below only one resonance formula is depicted).

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* Part XIV: ref. [18]

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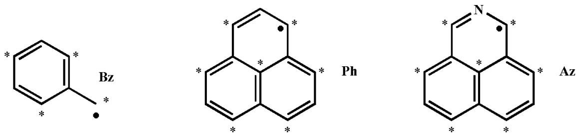


$4^* - 3 = 1$ NBMO $7^* - 6 = 1$ NBMO $14^* - 13 = 1$ NBMO

Fig. 1.

Quasi-alternant radicals

The application of the CRLH theorem is limited to homo-nuclear alternant systems, *i. e.*, alternant radicals. The theorem has been extended (ECRLH) [9, 10]. Radicals for which the ECRLH theorem is valid are designated as quasi-alternant non-classical (non-Kekulé) (QANC) radicals [11]. Within the CRLH theorem one always considers two subsets of homo-nuclear non-bonded π-centers: the subset of starred $\{S^*\}$ and the subset of non-starred $\{U^\circ\}$ ones. According to the ECRLH theorem [9, 10] only one subset of non-bonded (disjoint) π-centers is responsible for the appearance of NBMOs. A system with M π-centers and a maximum set of starred homo-nuclear non-bonded (disjoint) π-centers $\{S^*\}$ must have at least

$$N = 2S^* - M$$

NBMOs.

The NBMOs are present even if the π-system is non-alternant and if the π-centers belonging to the non-starred subset $\{U^\circ\}$ are heteroatomic. A typical example is the stable 2-aza-phenalenyl radical (**Az** in Fig. 1) which has been synthesized and characterized by Rubin and coworkers [12].

The following corollaries rooted in the ECRLH theorem [10] determine the structural principle of the investigated non-Kekulé molecules [3, 4] and polymers.

Corollaries of the ECRLH theorem

Corollary I: Let us consider a π-system consisting of a radical subunit $\mathbf{R}^\bullet$, for which the CRLH or the ECRLH theorem is valid, linked by one arbitrary closed-shell molecule $\mathbf{M}$ or radical $\mathbf{L}^\bullet$. This results in the following two cases:

Systems $\mathbf{R}^\bullet - \mathbf{M}$

If the π-center $\boldsymbol{r}$ of $\mathbf{R}^\bullet$, which is connected with a π-center $\mathbf{m}$ of $\mathbf{M}$, belongs to the set of the non-starred atoms $\{U^\circ\}$ (the MO coefficient $C^\circ{}_r = 0$), then all NBMO coefficients in the fragment $\mathbf{M}$ are equal to zero, *i. e.*, the NBMO coefficients are non-zero only for the starred π-centers in $\mathbf{R}^\bullet$, and the NBMO is strictly localized within the subunit (radical) $\mathbf{R}^\bullet$ (the proof is given in the Appendix). An example with a substituted benzyl radical (**I**) is shown in Fig. 2.

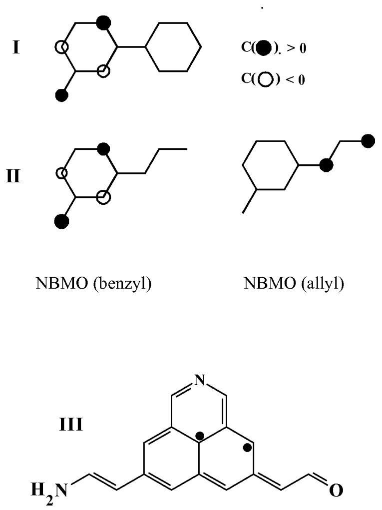


Fig. 2. I) Localization of the NBMOs within the benzyl radical ($\mathbf{R}^\bullet$); II) localization of the NBMOs within the benzyl radical and allyl radical, respectively (in the case of an allyl-substituted benzyl radical); III) localization of the NBMOs within the **Az** fragment in the triplet diradical as investigated in refs. [3, 4].

Systems $\mathbf{R}^\bullet - \mathbf{L}^\bullet$

Here, we consider two alternatives for $\mathbf{L}^\bullet$:

i) $\mathbf{L}^\bullet$ is a homo-nuclear alternant radical

If the π-center $\boldsymbol{r}$ of $\mathbf{R}^\bullet$, which is connected with a π-center $\mathbf{s}$ of $\mathbf{L}^\bullet$, belongs to the set of the starred atoms $\{S^*\}$ then the system has two NBMOs. One of the NBMOs is localized in the subunit $\mathbf{R}^\bullet$, and the other one is localized within the subunit $\mathbf{L}^\bullet$. An example is the allyl-substituted benzyl radical (**II**) shown in Fig. 2.

ii) $\mathbf{L}^\bullet$ is a hetero-nuclear (no QANC) radical, for instance the Weitz-type radical shown in Fig. 3.

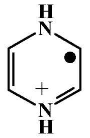


Fig. 3.

The Corollary I could also be applied to some polymers like

$$\ldots \mathbf{M} - \mathbf{R}^\bullet - \mathbf{M} - \mathbf{R}^\bullet \ldots \text{ and}$$

$$\ldots \mathbf{L}^\bullet - \mathbf{R}^\bullet - \mathbf{L}^\bullet - \mathbf{R}^\bullet \ldots \text{(see Appendix).}$$

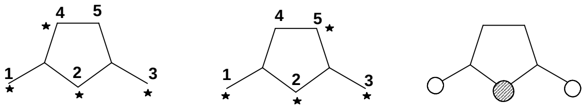


Fig. 4. Localization of the NBMOs within the pentadienyl fragment.

Corollary II: If an alternant or quasi-alternant conjugated π-system has various maximum disjoint sets $\mathbf{P_s}$ (s $= 1,2,\ldots,q$), then the NBMOs are composed only of the AOs of their intersection $\mathbf{P_1} \cap \mathbf{P_2} \cap \ldots \cap \mathbf{P_q}$. A typical example is presented in Fig. 4. In the case of the non-alternant hydrocarbon, shown in Fig. 4, there are two disjoint sets of cardinality 4, containing atoms 1, 2, 3, 4 and 1, 2, 3, 5, respectively. It follows from Corollary II, that the NBMO coefficients are nonzero only for π-sites 1, 2 and 3 in the pentadienyl radical fragment.

Numerical Methods of Investigation

Energy spectra

If the MOs of the 1D system have the form of Bloch running waves

$$\Psi(\kappa) = N^{-1/2}\sum_{\mu}\sum_{r} C_r(k)\exp(-ik\mu)|r,\mu\rangle \qquad (1)$$

($k \in [-\pi,\pi]$ is the wave vector, μ denotes the number of the elementary units (EU) and $|r,\mu\rangle$ is the r-th AO within the μ-th EU), in the Hückel-Hubbard version of the Bloch method the MO energies $e(k)$ are eigenvalues of the energy matrix [13]

$$E(k) = E_0 + V\exp(ik) + V^{+}\exp(-ik) \qquad (2)$$

where E_0 is the energy matrix of the EU, V is the interaction matrix between neighboring EUs (μ-th and $\mu+1$-th), and V^{+} is the transposed matrix.

Spin-exchange interaction in the half-filled band

In accordance with Anderson's theory of magnetism [14] it has been shown (see ref. [15] and references given therein) that the effective exchange integral, J_{eff}, in the Heisenberg-Dirac-Van Fleck Hamiltonian (i and j denoting the EUs)

$$H = -2\sum_{i,j} J_{\mathrm{eff}}(i,j)S_iS_j = -2\sum_{i,j} J_{\mathrm{eff}}(\tau)S_iS_j \qquad (3)$$

can be expressed as a sum of three contributions

$$J_{\mathrm{eff}} = J + J_{\mathrm{kin}} + J_{\mathrm{ind}} \qquad (4)$$

J is the direct (Coulomb, Hund) exchange integral between the Wannier states localized at the i-th and j-th sites.

J_{kin} ($J_{\mathrm{kin}} < 0$) is the kinetic exchange parameter representing the anti-ferromagnetic contribution to the spin exchange

$$J_{\mathrm{kin}} = -\Delta\varepsilon^2/2U = -\Delta\varepsilon^2/2(U_0 - U_1) \qquad (5)$$

where $\Delta\varepsilon$ is the NBMO band width and U is the renormalized Hubbard parameter [16]. U_0 and U_1 are the Coulomb repulsion integrals of two electrons residing in the same Wannier state and occupying adjacent Wannier states ($\tau = 1$), respectively.

The term J_{ind} expresses the indirect exchange (superexchange) *via* delocalized π-electrons in the filled energy bands. The sign of J_{ind} is determined by the structure and the interaction between the EUs. The terms can be calculated using a formalism described in ref. [17].

The calculations have been carried out using a standard set of parameters [15, 16]. The exchange parameter in Eq. 4 was calculated by means of the screened Mataga-Nishimoto potential [19] for the two-center Coulomb atomic integrals

$$\gamma_{rs}(M) = e^2/(a + DR_{rs}) \qquad (6)$$

where D is the screening constant.

The results obtained by means of the Ohno potential [20] do not differ substantially from the results calculated using the Mataga-Nishimoto approximation.

Objects of Investigations

We paid our attention to different types of polymers, having two half-filled bands with magnetically coupled electrons, as described below.

Polymers of type I

To this first group belong polymers with the general formula shown in Fig. 5. The localization of the NBMOs within the polymers of type I is also given in Fig. 5. If $\mathbf{Y}$ is a closed-shell system, then only an indirect magnetic interaction arises between electrons of the NBMOs localized strictly within the $\mathbf{Az}$ radicals (see Corollary I). Polymers of this type with different closed-shell subunits $\mathbf{Y}$ have been investigated in more detail in refs. [18, 21]. Here, only one new example is given.

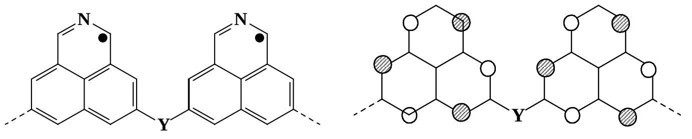


Fig. 5.

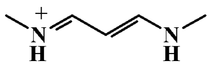


Fig. 6.

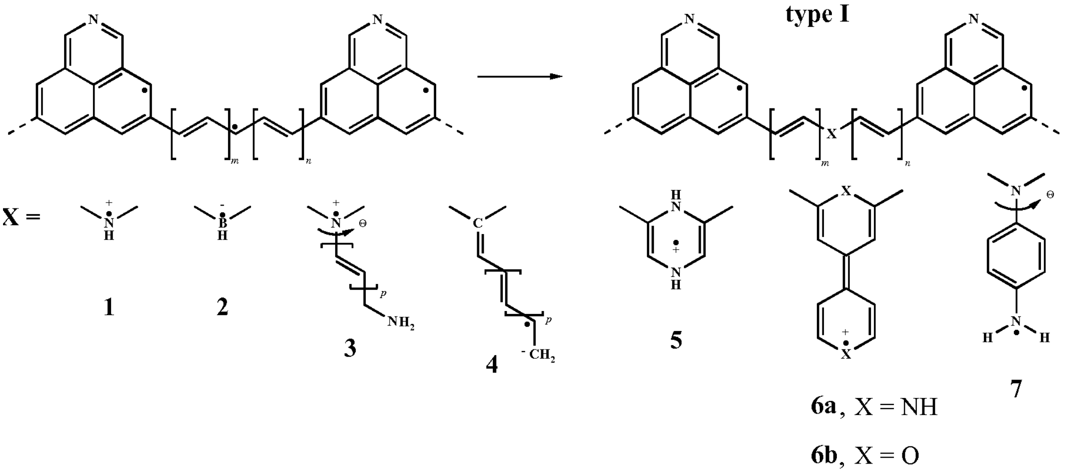


Fig. 7. Investigated polymers of type I. Weitz (**X** = **6a**,**b**) [21, 22], Wurster (**X** = **7**) radicals [22, 23]. For the stable radicals **X** = **3**, see refs. [22, 24], and for **X** = **4**, see refs. [25, 26].

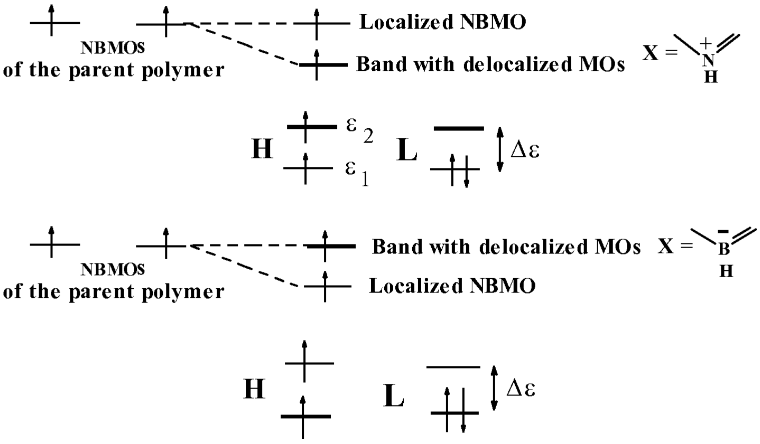
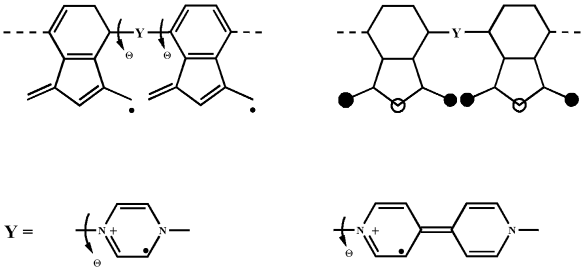


Fig. 8. Frontier bands of the polymers **1** and **2** with $m = n = 0$ (see Fig. 7). **H** and **L** denote the high- and low-spin states.

If **Y** is, *e. g.*, the trimethine cyanine unit (Fig. 6), then the indirect exchange parameter is $J_{\text{ind}} = -2.7$ meV.

The investigated polymers for which **Y** is an open-shell π-electron system are shown in Fig. 7. The polymers of this type can be considered as derivatives of the parent polymer I (Fig. 7). An arbitrary perturbation, *e. g.*, substitution of one CH group by another atom or atomic group **X**, is connected with a splitting of the degenerated NBMO bands. The degree of perturbation depends on the character of **X**.

The energy spectra of the polymers are characterized by two frontier bands with different symmetry (see Fig. 8): one band of NBMOs localized in the **Az** fragments, and another band of delocalized MOs. The polymers are considered as 1D systems for which the Born-Karman conditions are fulfilled. The atoms within the EUs of the polymers are thought to be embedded in a cylindrical surface exhibiting at least C_{2p} symmetry ($2p$ is the number of the EUs). According to this model the MOs of the band with localized MOs belong to the point group $D_{(2p)d}$, and the MOs



8 **9**

Fig. 9. Investigated polymers of type II.

of the band with delocalized MOs belong to the point group C_{2p}. Here, we consider polymers with **Az** radicals as subunits. The results for 1D systems in which the **Az** radicals are replaced by **Bz** radicals are qualitatively similar.

Polymers of type II

The investigated polymers of this type are shown in Fig. 9.

Numerical Results and Discussion

Polymers of type I

If we consider only the frontier bands (see Fig. 8), then the condition for the existence of a high-spin state in the polymers of type I is as follows

$$E(H) - E(L) = \Delta E_{HL} < 0$$

and

$$\begin{aligned} \Delta E_{HL} &= \varepsilon_1 + \varepsilon_2 + J_{\text{ind}}(1) + J_{\text{eff}}(2) \\ &\quad + J_{\text{eff}}(1,2) - 2\varepsilon_1 - I(1,1) \\ &= \Delta\varepsilon + J_{\text{ind}}(1) + J_{\text{eff}}(2) \\ &\quad + J_{\text{eff}}(1,2) - I(1,1) \\ &< 0 \end{aligned} \tag{7}$$

In Eq. 7, $I(1,1)$ is the Coulomb integral between the electrons occupying the band with delocalized MOs, J_{ind} (1) is the indirect exchange integral between the electrons within the band with localized NBMOs, and J_{eff} (2) is the effective exchange integral between the electrons within the band with delocalized MOs. Because the exchange integral between the electrons of the frontier bands J_{eff} (1,2) = 0 (MOs belonging to the delocalized band and the ones belonging to the localized band have different symmetry), for Eq. 7 one obtains

$$\Delta\varepsilon + J_{\text{ind}}(1) + J_{\text{eff}}(2) < I_{11} \tag{7a}$$

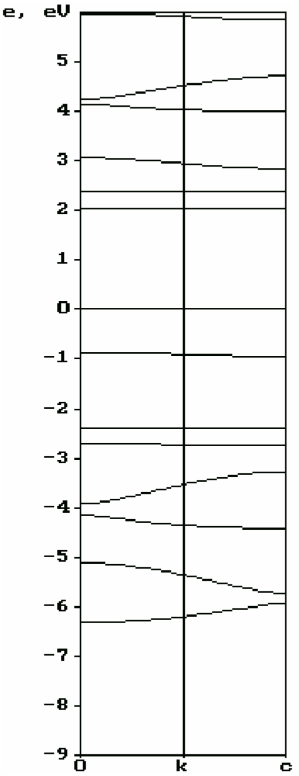


Fig. 10. Energy dispersion of the bands of the polymer **1** with $m = n = 0$.

The condition for the existence of a high-spin state in the polymers of type II is similar. Eq. 7a is fulfilled for all polymers with $m(n,p) \geq 1$.

The band structure of the investigated polymers is characterized by a large gap in which the two frontier HFBs are situated. This is illustrated by the band structure of the polymer **1** shown in Fig. 10.

In Tables 1 – 4 are collected the numerical results for the calculated values of the components of the effective exchange integral between the electrons in the HFBs for the polymers of types **1** – **9**. The presented results are for Wannier states localized at neighboring polymer sites. All radicals (EU) are assumed to have ideal geometry, *i. e.*, all bond lengths are 1.40 Å, and the bond angles are 120° (for the benzene rings) and 108° (for the five-membered rings), respectively. The geometry optimization of the dihedral angles Θ for polymers of the type II (see Fig. 9) have been performed with the semi-empirical AM1 method [26] for a cluster with

Table 1. Calculated values of the components of the effective exchange integral between the electrons in the delocalized HFBs of the polymers **1** and **2** for different values of the structural parameters m and n. In all cases, $J_{\mathrm{kin}} \sim 0$. All values are in meV. $J_{\mathrm{ind}}{}^{*}$ is the indirect exchange parameter for the electrons within the localized HFB.

Polymer	m	n	J	J_{ind}	J_{eff}	$J_{\mathrm{ind}}{}^{*}$	D
1	0	0	63	16	79	−8	1
1	0	1	27	9	36	−6	1
1	0	1	36	9	45	−10	5
1	0	1	37	10	47	−10	10[a]
2	0	1	28	9	37	−6	1
2	0	1	39	8	47	−9	10[a]
1	1	1	59	11	70	−6	1
1	1	2	43	9	52	−4	1
1	2	2	25	7	32	−3	1
2	2	2	23	7	30	−3	1
1	3	0	8	5	13	∼ 0	1
2	3	0	8	4	12	∼ 0	1

[a] Dielectric constant of graphite [27].

Table 2. Numerical values for the components of the effective exchange integral between the electrons in the delocalized HFBs of the polymers **3** and **4** for different values of the parameters m, n, and p. In all cases, $J_{\mathrm{kin}} \sim 0$. All values are in meV. $J_{\mathrm{ind}}{}^{*}$ is the indirect exchange parameter of the electrons within the localized HFB.

Polymer	m	n	p	J	J_{ind}	J_{eff}	$J_{\mathrm{ind}}{}^{*}$
3	0	0	1	11	4	15	2.5
3	0	0	2	27	3	30	4
3	0	0	3	39	2	41	5
3	1	0	1	8	4	12	∼ 0
4	1	1	1	8	2	10	1
4	0	0	2	14	3	17	2

two EUs. The two-center Coulomb atomic integrals for the two types of polymers, I and II, were evaluated using the Mataga-Nishimoto potential [Eq. 6]. Because the results for the various contributions to the effective spin exchange integral J_{eff}, obtained with different values of the screening constant D, are qualitatively identical, in the Tables the results are given only for $D = 1$. Only for comparison, the results with different values of D are given in Table 1.

In Table 1 calculated values of the components for the effective exchange integral between the electrons in the delocalized HFBs of the polymers **1** and **2** (Fig. 7) are summarized. In all cases a strong ferromagnetic exchange interaction can be expected. The main component to J_{eff} is the direct (Coulomb or Hund) exchange while the kinetic contribution is negligible or zero for all the polymers of type I investigated in this paper. The values of J_{eff} are diminished by the indirect exchange parameter for the electrons in the localized HFB. The influence of the extension of the π-electron system of the EU (n, m in Fig. 7) is very weak, and also the screening constants for the calculation of the two-center atomic integrals do not change the results significantly.

Table 3. Calculated values of the components of the effective exchange integral between the electrons in the delocalized HFBs of the polymers **5**, **6**(**a**,**b**) and **7**. In all cases, $J_{\mathrm{kin}} \sim 0$. All values are in meV. $J_{\mathrm{ind}}{}^{*}$ is the indirect exchange parameter for the electrons within the localized HFB.

Polymer	m	n	J	J_{ind}	J_{eff}	$J_{\mathrm{ind}}{}^{*}$
5	1	0	5	2	7	−1
5	1	1	5	3	8	−1
6a	0	0	13	4	17	−1
6b	0	0	12	4	16	−1
7	0	0	14	4	18	−8

Table 4. Calculated values of the components of the effective exchange integral between the electrons in the delocalized HFBs of the polymers (type II) **8** and **9**. All values are in meV. $J_{\mathrm{ind}}{}^{*}$ is the indirect exchange parameter for the electrons within the localized HFB.

Polymer	J	J_{ind}	$-J_{\mathrm{kin}}$	J_{eff}	$J_{\mathrm{ind}}{}^{*}$
8	16	−3	9	4	∼ 0
9	35	−1	6	28	∼ 0

The results for polymers **3** and **4** collected in Table 2 are quite similar to those of polymers **1** and **2**. The indirect exchange integral of the electrons in the localized HFBs for polymers **3** and **4** has positive values. The ferromagnetic exchange interaction within the polymers **5**, **6**, and **7** is rather weak in comparison with those of the polymers **1** – **4**, as it can be seen from the data of Table 3.

Polymers of type II

Because the NBMOs are strictly localized within the pentadienyl fragments, and **Y** is a closed–shell system (Fig. 9), only a weak indirect exchange interaction arises as in the case of polymers I. If, for instance, **Y** (in the structure of Fig. 9) is the *p*-phenylene fragment (Fig. 11), then the indirect exchange parameter is $J_{\mathrm{ind}} = 0.1$ meV.

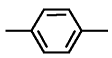


Fig. 11.

A somewhat different result was obtained for the two polymers of type II with an open-shell fragment **Y** in polymers **8** and **9** represented in Fig. 9. The data are summarized in Table 4. The values of J_{eff} are reduced by negative values of J_{ind} and J_{kin} while the indirect exchange parameter for the electrons within the localized HFB is zero. Therefore, the ferromagnetic properties of these polymers are only weakly marked.

Altogether, the numerical results documented in Tables 1 – 4 are determined by the conditions which are discussed above.

Conclusions

Two types of polymers possessing two half-filled bands (HFBs) with ferromagnetically coupled electrons have been investigated by means of many-electron band theory. The structural principle of the polymers is determined by two corollaries rooted in the extended Coulson-Longuet-Higgins theorem. These two HFBs belong to different symmetry groups. One of the HFBs is composed of NBMOs which are strictly localized within one subunit of the elementary units (EUs) of the polymer types I and II and thus leads only to a small indirect exchange interaction. The NBMOs of the second HFB are delocalized. In both types of polymers, the effective exchange integral corresponds to a strong ferromagnetic interaction between the electrons within the delocalized band. In this paper, only cooperative magnetic properties are considered. The electrical (conduction) properties determined by the energy spectra of the polymers are of peculiar interest. Investigations of this problem are in progress.

Appendix

We denote by Φ_r and Φ_m the MOs of the separate non-interacting radical $\mathbf{R}^\bullet$, and the closed-shell subunit **M**

$$\Phi_r = \sum_r C_r \phi_r, \quad \Phi_m = \sum_m C_m \phi_m$$

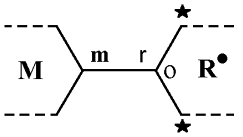
and by

$$Nb = \sum_r C^*{}_r\, \varphi^*{}_r$$

the corresponding NBMO of the radical. In LCMO representation the wave function of the system $\mathbf{R}^\bullet - \mathbf{M}$ is given by

$$\psi = ANb + \sum_r A_r \Phi_r + \sum_m A_m \Phi_m$$

If the π-centers **r** of $\mathbf{R}^\bullet$, which are bonded to the π-centers **m** of **M**, belong to the set of the non-starred atoms $\{U^\circ\}$ where the MO coefficients $C_r = 0$



then all matrix elements of the one-electron Hamiltonian are

$$\langle \Phi_{m(r)} | H | Nb \rangle = 0$$

and the energy matrix for the system $\mathbf{R}^\bullet - \mathbf{M}$ has the following block form

$$\mathbf{E_0} = \begin{pmatrix} \langle \mathbf{NB}|\mathbf{H}|\mathbf{NB} \rangle & [\mathbf{0}] & [\mathbf{0}] \\ [\mathbf{0}] & \langle \boldsymbol{\Phi}_\mathbf{r}|\mathbf{H}|\boldsymbol{\Phi}_\mathbf{r} \rangle & \langle \boldsymbol{\Phi}_\mathbf{r}|\mathbf{H}|\boldsymbol{\Phi}_\mathbf{m} \rangle \\ [\mathbf{0}] & \langle \boldsymbol{\Phi}_\mathbf{m}|\mathbf{H}|\boldsymbol{\Phi}_\mathbf{r} \rangle & \langle \boldsymbol{\Phi}_\mathbf{m}|\mathbf{H}|\boldsymbol{\Phi}_\mathbf{m} \rangle \end{pmatrix}$$

The *Corollary I* is also valid for polymers of types

$\ldots \mathbf{M} - \mathbf{R}^\bullet - \mathbf{M} - \mathbf{R}^\bullet \ldots$ and $\ldots \mathbf{L}^\bullet - \mathbf{R}^\bullet - \mathbf{L}^\bullet - \mathbf{R}^\bullet \ldots$

Because the NBMOs of $\mathbf{R}^\bullet$ of the μ-th EU do not interact with the MOs of **M** (and $\mathbf{L}^\bullet$, respectively) of the neighboring EUs in the matrices V and V^+ in Eq. 2, then

$$\langle \Phi_m | H | Nb \rangle = 0$$

i. e., the NBMOs are localized in the radicals $\mathbf{R}^\bullet$.

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