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Structure and properties of non-classical polymers*

IX. Non-alternant polymers**

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Summary. The investigations on alternant non-classical (non-Kekulé) polymers [1, 2] (ANCP) have been extended to a class of quasi-one-dimensional non-alternant non-classical polymers (NANCP).

The energy spectra and the effective spin exchange between the unpaired electrons in the NANCP are investigated theoretically.

As for the ANCP, the energy spectrum of the NANCP is characterized by a wide energy gap in which there is a half-filled band (HFB) of degenerate non-bonding molecular orbitals (NBMO).

The occurrence of a NBMO is a topological property of the considered non-alternant systems, and is explained with an approach which originates from the Sachs theorem.

The effective spin exchange interaction within the HFB of a wide variety of model polymers was calculated. It is shown that the potential (Coulomb) and the indirect exchange interaction (superexchange) are the main components of the effective ferromagnetic interaction. The ground state of the 1D-NANCP is a high-spin one, as in the case of the ANCP.

Key words: High-spin non-alternant polymers – Nature of spin exchange interaction

1 Introduction

In the first communications [1–4] of this series the concept of non-classical polymers (NCP) was introduced: π-systems for which no classical (Kekulé) structure can be written [5]. Theoretical and experimental investigations of homo-nuclear NCP have focused mainly on alternant non-classical polymers (ANCP).

The structural principles and the theory of spin-exchange interaction in ANCP is considered in detail in a number of papers of Klein et al. [6, 7],

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* Dedicated to Professor Jaroslav Koutecky, on occasion of his 70th birthday

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Koutecky et al. [8], and also in [9–13]. Recently the synthesis of high-spin ANCP has been reported [14, 15].

The above-mentioned theoretical [1–13] and experimental [14, 15] studies show that NANCP are among the most promising candidates for high-spin polymers with a possible magnetic ordering. The representatives of a class of high-spin π-systems [16–18] for which the presence of degenerate states is defined by structural principles other than the molecular topology, namely by steric hindrance, are also alternant systems.

In π-electron approximation ANCP are analogs of the high-spin polycarbenes, investigated in the pioneer papers of Itoh [19] and Wasserman [20] (see also [21]), which later were extended in the brilliant syntheses of Iwamura (see [22] and references therein).

In a preliminary paper [23] the theoretical results on ANCP were extended to a class of non-alternant hydrocarbons. It was shown that the basic structural principles of ANCP – the presence of an infinitely narrow band of degenerate non-bonding molecular orbitals (NBMO) is also valid for a class of non-alternant (hydrocarbon) systems. The possibility of a high-spin ground state for non-alternant π-systems has been pointed out by Radhakrishnan [24].

The aim of the present work is to extend the class of NCP to new representatives of non-alternant π-systems – NANCP, respectively, which have a half-filled band (HFB) with degenerate NBMOs. At the same time, the spin exchange in the NBMO band for different model systems is studied in order to propose structures of high-spin NANCPs which may be interesting from a synthetic point of view.

In principle, the idea of high-spin alternant systems (poly-radicals) is given in the papers of Coulson–Rusbrooke–Longuet-Higgins (CRLH) on the theory of alternant hydrocarbons and the theorem for the presence of NBMO in them [25–27][1].

In the next section, an approach will be elaborated which assesses the existence of NBMOs in non-alternant hydrocarbons. The approach is based on an application of the Sachs theorem [29].

2 The occurrence of NBMO in non-alternant hydrocarbons

The presence of degenerate MOs in a molecular system is an important requirement for the existence of high-spin states. In the case of alternant π-systems the role of the NBMOs has been first demonstrated in the cited works of Coulson–Rushbrooke–Longuet-Higgins [25–27]. For such systems, there are:

$$n = N^* - N \tag{1}$$

NBMOs, where N^* and N are the number of the starred and unstarred π-centers, respectively.

A more general approach for predicting the number of NBMOs in alternant systems deals with the Kekulé-structures. In Ref. [27] Longuet-Higgins has

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[1] In a forthcoming paper, a general extension of the CRLH theorem is to be published [28]. This extended theorem [28] expresses the structural principles of unsaturated organic molecules (Hückel systems) with NBMOs

pointed out that a conjugated alternant homonuclear system of M π-centers possesses at least:

$$n = M - 2D \tag{2}$$

NBMOs, where D is the greatest number of double bonds in any resonance (Kekulé) structure. The CRLH theorem is proven only for alternant homonuclear systems. Both methods according to Eq. (1) [25, 26] and Eq. (2) [27], respectively, yield a lower limit for the number of NBMOs in alternant systems.

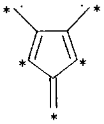
The CRLH theorem has been generalized [30, 31] for some non-alternant and heteroatomic systems with π-conjugation as well. Within the CRLH theorem one always considers two subsets of homonuclear non-bonded π-centers: the subset of the starred and the subset of the unstarred π-centers. In the generalized theorem [31] only one subset of nonbonded π-centers is responsible for the appearance of NBMOs. It was shown [31] that a conjugated system with M π-centers and a maximal set of M^* homonuclear disjoint π-centers must have at least:

$$n = 2M^* - M \tag{3}$$

NBMOs.

The NBMOs are present even if the π-centers not belonging to the disjoint subset are heteroatomic.

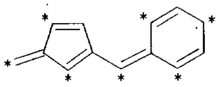
Representative examples are the biradical **1**



1

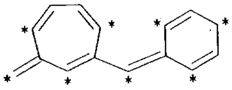
$$n = 2 \cdot 5^* - 8 = 2 \text{ NBMOs}$$

or the monoradicals **2** and **3**



2

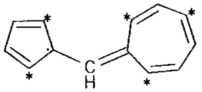
$$n = 2 \cdot 7^* - 13 = 1 \text{ NBMO}$$



3

$$n = 2 \cdot 8^* - 15 = 1 \text{ NBMO}$$

The extended theorem [30, 31] provides only a *sufficient*, but not a *necessary* condition for the presence of NBMOs in Hückel systems. The same assertion is valid for the CRLH theorem [25–27]. The extended theorem does not cover all possible π-systems with NBMO either. There exist many non-alternant π-systems having NBMOs, for which Eq. (3) is not fulfilled. With the non-classical non-alternant system **4**



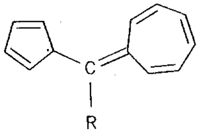
4

$2M^* - M = 12 - 13 = -1$, but the system has 1NBMO.

This is seen from the characteristical polynomial (see Eq. (4)):

$$x[x^{12} - 14x^{10} + 74x^8 + 2x^7 - 184x^6 - 14x^5 + 217x^4 + 26x^3 - 105x^2 - 10x + 16] = 0$$

which has one root $x = 0$, i.e. there is 1 NBMO. The above example **4** is taken from a large group of non-classical (non-Kekulé) π-systems **5**:

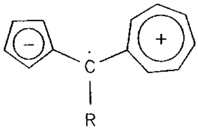


5

5a: R = –H; **5b**: R = –C_6H_5; **5c**: R = –CH=CH_2

where R is an arbitrary alternant system, with an even number of π-centers such as phenyl (**5b**) or vinyl (**5c**).

The charge density distribution of **5** corresponds to the ionic structure:



The sums of π-electron charges of the five- and the seven-membered rings in **5a** (calculated by means of PPP method) are:

$$Q_5 = 5.304, \qquad Q_7 = 6.737, \text{ respectively.}$$

5a is an iso-electronic non-alternant analog of the tri-phenylmethyl radical (and its ions). The results of the synthesis and spectral properties of **5a** will be reported separately [32].

The average π-electron energy per electron of the tri-phenylmethyl radical (planar) is $\varepsilon = 1.358\ \beta$ [33], while that of the iso-electronic radical **5a** (planar) is $\varepsilon = 1.336\ \beta$. With a value of the dihedral angles $\theta = 30°$ (see Fig. 2), ε(tri-phenylmethyl) = $1.339\ \beta$, and ε (**5a**) = $1.316\ \beta$. That means that **5a** should be somewhat less stable than the triphenylmethyl radical.

This is even valid if the five- and seven-membered rings are stabilized by condensed benzene units, as in the case with Koelsch's radical [34], which is stable towards oxygen at room temperature.

In all π-systems of type **5**, $2M^* - M = -1$, but all of them have 1 NBMO. Other nonalternant non-classical systems which have 1 NBMO are shown in Fig. 1. These examples illustrate the vast number of non-classical non-alternant π-systems which represent a new class of polyradicals some of which probably with a high-spin ground state.

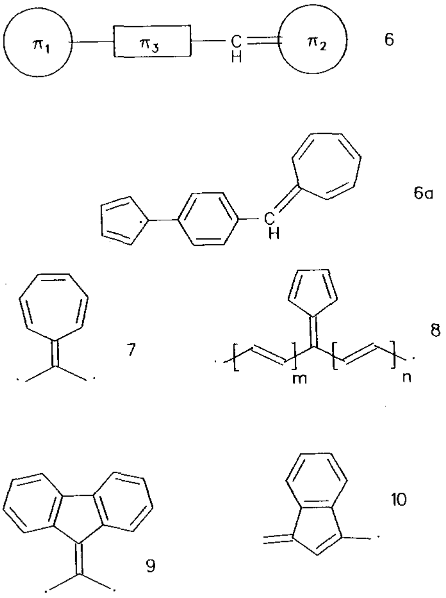


Fig. 1. Examples for non-alternant radicals **6–10** possess one NBMO. For all π-systems only one resonance formula is depicted. In the species **6** π_1 and π_2 are odd-membered rings with different number of π-centers; π_3 is an arbitrary even Kekulé homonuclear π-system. In a very recent work the radical **8** (with $n = m = 0$) has been theoretically investigated by Dowd et al. [53]

For finding the existence of NBMOs in a molecular system one can use the polynomial representation which allows in many cases quantitative conclusions on the energy spectrum of the studied systems [35, 36].

Let us consider a conjugated hydrocarbon with N π-centers and a characteristic polynomial [37, 38]

$$P_N(x) = \det|\boldsymbol{x} \cdot \boldsymbol{I} - \boldsymbol{A}| = \sum_{n=0}^{N} a_n x^{N-n} \tag{4}$$

where $\boldsymbol{A}$ is the Hückel matrix, and $\boldsymbol{I}$ is the unity matrix. The MO energies e and the roots x are related by the expression: $x = (\alpha - e)/\beta$ (α and β are the Coulomb- and the resonance integrals in the Hückel method, respectively; we choose the energy reference level $e_0 = \alpha = 0$). In Eq. (4) $a_N = 0$ corresponds to root $x = 0$ and $e = e(\text{NBMO}) = 0$.

If a given Hückel system has at least one NBMO then the free term in the characteristic polynomial (4) $a_N = 0$, and vice versa. Or, in a general form:

The condition:

$$a_N = 0 \tag{5}$$

is necessary and sufficient for the existence of at least one NBMO in a Hückel system.

The value of a_N ($a_N = 0$ or $a_N \neq 0$) in the characteristic polynomial (4) can be determined easily by means of the Sachs theorem [29]. According to this theorem the coefficient a_N in the characteristic polynomial can be calculated by means of the graph-combinatorical method:

$$a_N = \sum_{s \in S_N} (-1)^{c(s)} \cdot 2^{r(s)} \tag{6}$$

where:

S_N – is the set of all Sachs subgraphs of N vertices,

$c(s)$ – is the number of components (connected parts) in the Sachs sub-graphs,

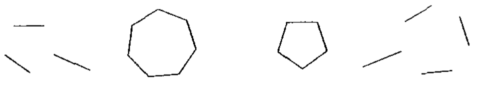
$r(s)$ – is the number of simple rings [alternant (with even number of π-centers) or non-alternant (with odd number of π-centers)].

The components of a Sachs subgraph are either simple rings or two vertices connected by an edge (——).

In accordance with Eq. (6), Eq. (5) for the existence of a NBMO reads:

$$a_N = \sum_{s \in S_N} (-1)^{c(s)} \cdot 2^{r(s)} = 0 \tag{5a}$$

For **4** or similar systems with different odd-numbered rings there is a set of two subgraphs: s_1 and s_2, however $c(s_1)$ and $c(s_2)$ are of different parity, so that the two terms in a_N (see Eq. (5a)) cancel each other:

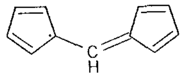


$s_1, c(s_1) = 4$ $s_2, c(s_2) = 5$

$a_N = (-1)^4 \cdot 2 + (-1)^5 \cdot 2 = 0$, and **4** has 1 NBMO.

It is emphasized that the absence of a Kekulé formula in a homonuclear π-system is not a sufficient condition for the appearance of a NBMO.

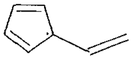
For systems with identical odd membered rings, such as:

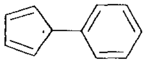


$c(s_1)$ and $c(s_2)$ are of the same parity:

$s_1, c(s_1) = 4$ $s_2, c(s_2) = 4$

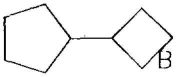
and $a_N = 4 \neq 0$, i.e. there is no NBMO. It is easily seen, that for the non-alternant systems





the a_N terms are: $a_N = 8$ and $a_N = 2$, respectively, hence in the above hydrocarbons there are no NBMOs.

NBMOs can also arise for systems, for which the presence of NBMOs results from the symmetry of the systems. A typical example is the hydrocarbon:



In the characteristic polynomial of the above hydrocarbon

$$P_9(x) = x^9 - (9 + b^2)x^7 + (25 - 2b + 7b^2)x^5 + 2x^4 - (24 - 10b + 13b^2)x^3 - (6 + 2b^2)x^2 + (6 - 10b + 6b^2)x + 2 - 4b + 2b^2$$

the term a_N read:

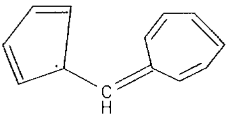
$$a_N = 2 - 4b + 2b^2$$

where b denotes the resonance integral of the bond **B** in the above formula.

If the hydrocarbon belongs to the symmetry group C_{2h}, $b = 1$ and $a_N = 0$, hence the hydrocarbon has 1 NBMO.

If the symmetry is C_{1h}, $b = 1$, $a_N = 0$ and the hydrocarbon has no NBMO.

On changing the symmetry of an arbitrary system, for which Eq. (5a) is valid as a result of the Sachs theorem, the occurrence of a NBMO does not change, since it is determined solely by the topology of the systems. For example, the geometric deformation of the monoradical **4**

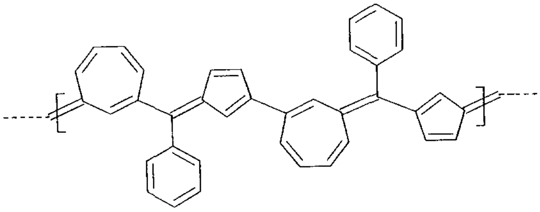


does not change the presence of a NBMO.

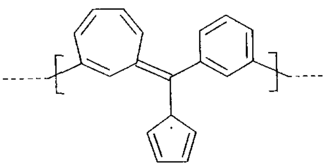
The above results can be extended in a straightforward fashion to some one-dimensional systems representing models of NANCP.

A non-classical non-alternant monomer does not necessarily lead to a NANCP. The type of the polymer is also determined by the topology of the bonds connecting the neighbouring structural units (monomers). The typical non-classical monoradical **5b** form both:

i) the classical polymer (by doubling of the unit cell):



ii) the NANCP *A* (see Fig. 2):



A

If Eq. (5a) holds for each unit cell as well as for the polymer, then for such 1D-NANCP the number of NBMOs is proportional to the number of unit cells.

Figure 2 depicts the model NANCPs for which the energy spectrum and the spin-exchange interaction in the half-filled band (HFB) were calculated.

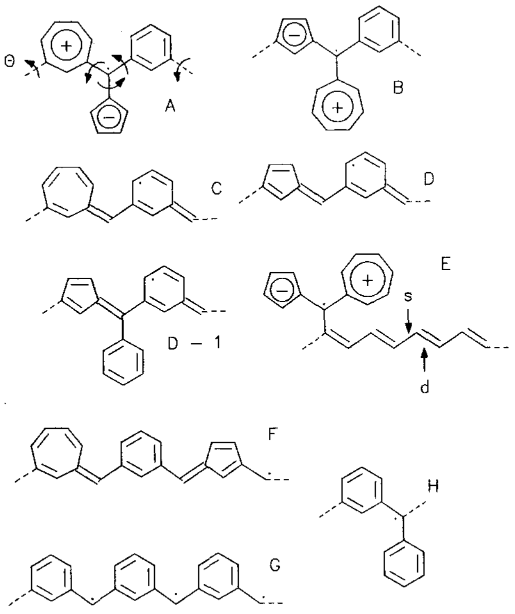


Fig. 2. Unit cells of the studied NANCP $A - H$ for which the energy spectra and spin exchange interaction in the HFB were calculated. As with the non-alternant radicals shown in Fig. 1 only one resonance formula is indicated. The torsion angles θ are depicted only in the formula **A**

3 Methods of investigation

As in the previous communications [2–4] the studied NANCP were considered as 1D-systems, for which the Born–Karman conditions are satisfied. The energy spectrum was determined in the tight binding approximation – a Hückel version of the Bloch method.

If we juxtapose to the polymer a Bloch wavefunction with a wave vector $k \in [-\pi, \pi]$, then the MO energies $e(k)$ are eigenvalues of the energy matrix [35, 39]:

$$\boldsymbol{H}(k) = \boldsymbol{H} + \boldsymbol{V}\exp(ik) + \boldsymbol{V}^{+}\exp(-ik)$$

where $\boldsymbol{H}$ is the energy matrix of the unit cell, $\boldsymbol{V}$ is the matrix representing the interaction between the jth and the $(j+1)$th unit cell of the 1D-polymer, and $\boldsymbol{V}^{+}$ is the transpose of $\boldsymbol{V}$.

The band structure was calculated using a standard value of the resonance integral $\beta = -2.4\,\text{eV}$ [2–4].

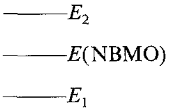
The Wannier functions of the investigated NANCP are well localized on the unit cell. This is seen from Table 1, where the calculated values of the norm of localization L of the Wannier state are presented (see Appendix I). Because of the good localization, the Wannier functions are appropriate for the study of the spin correlation within the HFB.

The term J_{eff} in the Heisenberg Hamiltonian:

$$\boldsymbol{H}_{eff} = -2\sum_{j\neq 1} J_{eff}(j, l)\boldsymbol{S}_j\boldsymbol{S}_l \tag{7}$$

is the effective exchange integral between Wannier functions localized upon the jth and lth unit cell. The value of J_{eff} depends upon the relative distance between

Table 1. Frontier MO energies: E_1 (occupied top), E_2 (vacant bottom), and the average π-electron energy per electron ε (see Eq. (13)), of the investigated model polymers (all entries are in β units). The bond lengths and the resonance integrals, respectively, are assumed to be identical ($\beta = \beta_0$). In accordance with [53] the dihedral angles θ are chosen to be equal to 30° [$\beta(\theta) = \beta_0 \cdot \cos\theta$]. L is the localization norm of the Wannier functions (see Appendix I)



Polymer	E_1	E_2	ε^a	L
A	0.618	−0.420	1.333	0.973
B	0.521	−0.445	1.332	0.973
C	0.213	−0.465	1.298	0.512
D	0.655	−0.259	1.294	0.604
D – 1	0.648	−0.232	1.333	0.717
E^b	0.237	−0.217	1.301	0.807
F	0.201	−0.228	1.291	0.514
G	1.0	−1.0	1.288	0.737
H	1.0	−1.0	1.341	0.792

[a] The average π-electron energy of infinite polyacetylene without bond length alternation is [52] $\varepsilon = 4/\pi\beta = 1.273\,\beta$

[b] For polymer ***E*** the bond length alternation within the polyene chain is assumed to be (see Fig. 2): $s = \beta_s/\beta_0 = 0.967$ and $d = \beta_d/\beta_0 = 1.034$ [47]

the unit cells:

$$J_{eff}(j, l) = J_{eff}(|j - l|) = J_{eff}(q) \tag{8}$$

For simplicity, the dimensionless distance parameter q is omitted in the following formulas.

Based on the results of Anderson [40] it was shown [23, 41, 42] that the effective exchange integral J_{eff} in the Heisenberg Hamiltonian (7) can be represented as a sum of three components (terms):

$$J_{eff} = J + J_{kin} + J_{ind} \tag{9}$$

The terms in Eq. (9) have the following meaning:

J – is the direct (potential) exchange integral between adjacent Wannier states.

The antiferromagnetic contributions are given by the kinetic exchange parameter:

$$J_{kin} = -2t^2/(U_0 - U_1 - 2J) \tag{10}$$

where:

U_0 – is the Coulomb repulsion integral of two electrons occupying the same Wannier state, and U_1 is the Coulomb integral of two electrons residing at adjacent Wannier states;

t – is the transfer parameter calculated with Wannier functions.

If the renormalized Hubbard integral $U = U_0 - U_1 \gg J$, Eq. (10) transforms into the form:

$$J_{kin} = -2t^2/U \tag{10a}$$

which is familiar in the VB-theory of magnetism [43, 44] (see also [45]).

The term J_{ind} describes the spin coupling (indirect exchange) caused by spin polarization within the whole system of π-conjugation. The term J_{ind} is calculated within a formalism given in [46, 47].

The Coulomb integrals (U_0 and U_1) were calculated within two different approximations for the atomic Coulomb repulsion integrals:

i)
$$\gamma_{\mu\nu} = e^2/(e^2/\gamma + D \cdot R_{\mu\nu}) \tag{11}$$

for different values of the screening constant D. If $D = 1$, Eq. (11) is identical with the Mataga–Nishimoto approximation [48].

ii) Hubbard approximation [49]:

$$\gamma_{\mu\nu} = \delta_{\mu\nu} \cdot \gamma \tag{12}$$

With the Hubbard approximation only one center Coulomb atomic integrals γ are preserved.

4 Numerical results and discussion

4.1 Band structure

All polymers studied herein are characterized by a wide energy gap. The band of degenerate NBMOs is situated within the gap. Table 1 shows the energies of the frontier MOs, which determine the width of the band gap of the investigated NANCP.

In all cases the number of bonding MO bands is equal to $(M - 1)/2$, where $M = 2m + 1$ is the number of π-centers in the unit cell. This means that the degenerate NBMO band is half-filled; each unit cell contributes with one π-electron to the degenerate NBMO band.

The presence of a band with degenerate NBMOs at the NANCP as well as at ANCP [2–4] is a topological property of these π-electron systems. This is a very important feature because the change of the geometry (for instance, as a result of the Jahn–Teller distortion), does not lead to a splitting of the NBMO band.

As a result of the σ–π interaction the degeneracy of the NBMO band is removed, but it always remains narrow. This is illustrated by the following example.

The characteristic polynomial of the polymer **D** (see Fig. 2) reads:

$$x^{13} - 15x^{11} + 84x^9 + 2x^8 - 219x^7 - 16x^6 + (271 - 2\cos k)x^5 + (36 + 2\cos k)x^4$$
$$- (141 - 4\cos k)x^3 - (24 + 2\cos k)x^2 + (18 - 2\cos k)x = 0$$

Replacing the hydrogen of an exocyclic methine group by an alkyl substituent, changes the Coulomb integral of the exocyclic C-atom. If we denote by $\alpha = \alpha_0 + h\beta$ the Coulomb integral of the latter (i.e. if we assume the inductive model of the $\sigma-\pi$ interaction [50, 51]), the characteristic polynomial of the polymer has the form:

$$\begin{aligned} x^{13} &+ hx^{12} - 15x^{11} - 13hx^{10} + 84x^9 + (2+64h)x^8 - (219+2h)x^7 \\ &- (16+135h)x^6 + (271 - 2\cos k - 14\,h)x^5 \\ &+ (36 + 2\cos k + 137h)x^4 - (141 - 4\cos k + 26h)x^3 \\ &- (24 + 2\cos k + 56h)x^2 + (18 - 2\cos k - 14h)x + 4h = 0 \end{aligned}$$

$h = -0.4$ for the methyl group [51], and the NBMOs split into a band of MO energies within the interval:

$$-0.155\,\beta < e(k) < -0.114\,\beta$$

By means of a perturbation approach the MO energies of the half-filled band lie in the interval:

$$2h/(11 - 7h)\beta < e(k) < 2h/(7 - 7h)\beta$$

Table 1 also provides the values of the average π-electron energy ε per electron, calculated according to the formula:

$$\varepsilon = 2/\pi M \int_0^{\pi} \sum_i e_i(k)\,dk \tag{13}$$

where $e_i(k)$ are the MO energies (see Eq. (6)) of the ith band of bonding MOs.

From the data in Table 1 it can be seen that the average π-electron energy per electron ε is greater for all polymers than those of polyacetylene (with equal bond lengths) which is $\varepsilon = 4/\pi\beta = 1.273\,\beta$ [51].

4.2 Spin exchange interaction within the HFB of NANCP

The calculation of the effective exchange integrals J_{eff}, which express the effective spin exchange between the unpaired electrons in the HFB (Eq. (9)) were carried out with a standard value for the resonance integral $\beta = -2.4$ eV [2–4]. In order to estimate the influence of the atomic Coulomb integrals on the spin correlation in the investigated polymers, calculations have been performed with different approximations for the atomic Coulomb integrals (see Eqs. (11)–(12)). No qualitative changes of J_{eff} were observed for the different approximations. This conclusion can be drawn from the numerical results in Table 2. Therefore, Table 3 gives only the results with one approximation for the Coulomb integrals, namely within Mataga–Nishimoto formula (Eq. (11)) with: $\gamma = 10.84$ eV, and $D = 1$.

The components of the effective exchange integral $J_{eff}(q)$ decrease rapidly with the distance between the unit cells. For all investigated NANCP $J_{eff}(q > 2) < 10^{-3}$ eV. This can be seen, for instance, from the results for polymer ***D* — *1***, represented in Table 4. Hence, Table 3 collects only the results calculated with $q = 1$.

The following conclusions can be made from the numerical results in Table 3. All NANCP exhibit a net spin exchange of ferromagnetic nature: $J_{eff} > 0$. For all polymers the hopping integral (transfer parameter) t between neighboring Wannier states $t \sim 0$, and $J_{kin} \sim 0$, respectively. The magnetic exchange interac-

Table 2. Calculated values (in eV) of the contributions to the effective spin exchange between the unpaired electrons in the HFB, for polymer *C* (see Fig. 2). In all cases, the transfer parameter between adjacent Wannier states $t(q > 1) = 0$, and the kinetic exchange parameter $J_{kin} = 0$. The results have been obtained with $\beta = -2.4$ eV. The Coulomb integrals are calculated using Eq. (11) (**a**, **b**, **c**) and Eq. (12) (**d**)

a: $\gamma = 10.84$ eV, $D = 1$

b: $\gamma = 10.84$ eV, $D = 2$

c: $\gamma = 7.00$ eV, $D = 1$

d: Hubbard approximation with $\gamma = 7.00$ eV

Parameter set	J	J_{ind}	J_{eff}
a	0.064 (0.070)	0.043 (0.045)	0.107[a] (0.126)[b]
b	0.076 (0.082)	0.050 (0.052)	0.126 (0.134)
c	0.036 (0.039)	0.015 (0.016)	0.051 (0.055)
d	0.060 (0.065)	0.024 (0.025)	0.084 (0.090)

[a] Results obtained for a value of the dihedral angles $\theta = 30°$
[b] Results obtained for a value of the dihedral angles $\theta = 0°$

Table 3. Calculated values (in eV) of the different components of the effective spin-exchange interaction between the unpaired electrons in the HFB of the polymers. The results are obtained with $\beta = -2.4$ eV, Mataga–Nishimoto approximation (Eq. (11)) for the Coulomb integrals (with $\gamma = 10.84$ eV and $D = 1$), and a dihedral angle $\theta = 30°$ (see Table 1). In all cases the transfer parameter $t = 0$, hence the kinetic exchange contribution $J_{kin} = 0$

Polymer	J	J_{ind}	J_{eff}
A	0.010	0.003	0.013
B	0.010	0.004	0.014
C	0.064	0.043	0.107
D	0.053	0.032	0.085
D* − *1	0.040	0.024	0.064
E	0.183	0.081	0.264
F	0.026	0.027	0.053
G	0.174	0.066	0.240
H	0.101	0.042	0.143

Table 4. Calculated values (in eV) of the different parameters and contributions to the effective spin exchange between the unpaired electrons in HFB (see Eqs. (9)–(10)) for polymer ***D* – *1*** for integer values of the dimensionless distance parameter q (see Eq. (8)). The calculations are carried out with the parameters given in Table 3

q	$U(q)$[a]	J	J_{ind}
1	1.565	0.040	0.024
2	0.737	[b]	[b]
3	0.490	[b]	[b]

[a] $U(0) = U_0 = 3.964$ eV
[b] $J < 10^{-3}$ eV

tion in HFB is caused by the dominating effect of the direct (potential) exchange and partly by the indirect exchange.

Table 3 also includes the numerical results for two typical ANCP: ***G*** and ***H***. High-spin oligomers of type ***H*** have already been synthesized [22]. The effective exchange integrals J_{eff} for ***H*** and ***G*** have the same order of magnitude as the investigated NANCPs ***C***, ***D***, ***E***, and ***F***.

Substitution of the H-atom at the methine group of polymers by a phenyl group, as in the case with ***D* – *1*** or ***H***, decreases the π-electron energy (see Table 1). The change of the J_{eff} is not significant.

5 Conclusions

From the quantitative results presented in this paper the following general conclusions can be drawn:

Some classes of non-classical (non Kekulé) non-alternant hydrocarbons, e.g. polyradicals and polymers like the non-classical alternant systems, may exhibit a high-spin ground state with spin coupling of ferromagnetic nature.

Appendix I

Let us denote the Bloch functions of the HFB by:

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

where μ marks the unit cell, r labels the atoms of the cell, and $|\nu\rangle$ is given by the expression:

$$|\nu\rangle = N^{-1/2} \sum_{l} \exp(-ik\nu) \,|1\rangle = \sum_{\mu} \sum_{r} a_r(\mu - \nu) \,|\mu, r\rangle$$

In the limit $N \to \infty$ the orbital coefficients of the Wannier functions in the

AO basis are:

$$a_r(\mu - \nu) = 1/2\pi \int_0^{\pi} \exp i[(\mu - \nu)k]C_r(k)\,dk$$

The norm of localization L is defined as:

$$L = \sum_r |a_r(0)|^2$$

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