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Band Structure of Nonclassical Polymers

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It is shown that fully conjugated alternant nonclassical polymers are comparatively stable systems as a result of the considerable delocalisation energy.

The energy characteristics of the polymers are strongly determined by the electron spin distribution of the degenerate nonbonding molecular orbitals; the full spin configuration, $S > 0$, is favoured. The spin densities depend on the electron correlation and alternate; this corresponds to a ferrimagnetic state of the polymer at 0°K.

Key words: Nonclassical polymers – Band structure of ~ – Ferrimagnetic state of ~.

1. Introduction

According to Dewar [1], nonclassical hydrocarbons are those, to which no classical structure (Kekulé structure) can be associated. Thus, radicals and polyradicals are nonclassical hydrocarbons. Usually they are less stable than hydrocarbons with closed shell electronic structure, but their stability varies in a wide range [2, 3]. An estimation of the significance of the conjugation for the stability of radicals one may gain from a comparison of the properties of Ziegler's radical,

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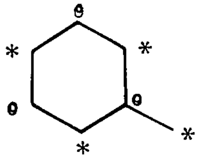
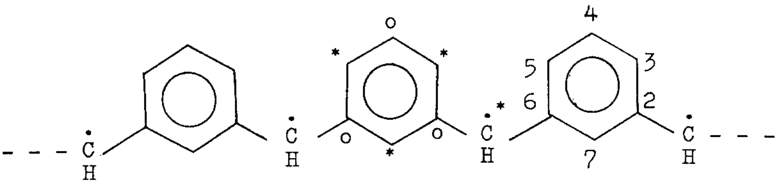
tetra-phenyl-allylradical [4] with those of Koelsch's radical, α,γ-bisphenylene-β-phenyl-allylradical [5]: e.g. the first one exhibits the usual sensitivity of radicals against oxygen, while the second one does not undergo a reaction if kept under air. Assuming that the delocalization of π-electrons may be responsible for the stability, one could expect that nonclassical, but fully conjugated, polymers might be stable at room temperature or below. Such a behaviour would be very interesting; moreover, systems of this type, perhaps, exhibit some unusual magnetic and electric properties. So, it seems to be worthwhile to investigate some systems of this kind.

An alternant hydrocarbon with r starred and s non-starred carbon atoms is a nonclassical system; according to the theorem of Coulson and Rushbrooke [6] it has at least $|r-s|$ degenerate non-bonding molecular orbitals (NBMO). As an example may serve the benzylradical, where $r-s=4-3=1$.



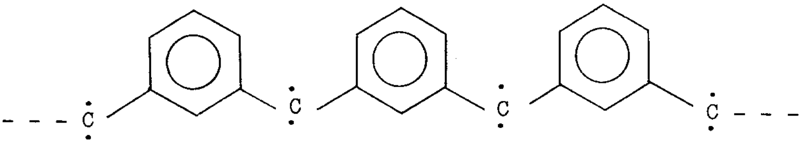
$$r=|\{*\}|=4$$
$$s=|\{*\}|=3$$

Taking this molecule as a monomer unit and linking the exocyclic carbon to the meso-position of the following unit, polymer I is constructed. It has $4N$ starred and $3N$ non-starred carbon atoms, where N denotes the number of the elementary units; hence, it has N NBMOs too.



I

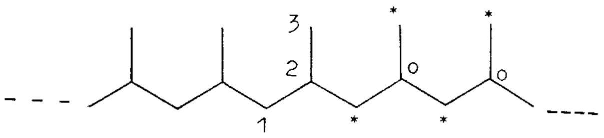
A very similar polymer, *II*, has been investigated by Mataga [7]. There again a great number of NBMOs has to be considered. It is assumed that they arise from those AOs which are not involved in bonds; according to the structure of *II* half of these AOs are σ-AOs, the other half are π-AOs. Occupying the NBMOs with electrons of one and the same spin, a ferromagnetic state results [7].



II

Since the polymers I and II are π-isoelectronic, a ferromagnetic state should be expected also for polymer I. But, as pointed out by Buchachenko [8], in high-polymeric conjugated systems ferrimagnetic states cannot be excluded.

There are no investigations on the band structure of nonclassical polymers except a work [9], where the simplest model of an alternant nonclassical polymer, *III*, has been treated.



III

The spin density distribution of this model polymer has been investigated by Ovchinnikov and Cheranovsky [10].

2. Band-Structure in One-Electron Approximation

For the polymer *III* which consists of N elementary units, the Bloch functions satisfying the Born–Karman conditions are expressed by

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{\mu=0}^{N-1} \sum_{r}^{3} a_{rk}\, e^{i\mu\omega_k} |r, \mu\rangle \tag{1}$$

where $|r, \mu\rangle$ denotes the orthogonalized AO on center r in the elementary unit μ. By means of the methods described in [11], the characteristic polynomial is obtained as follows:

$$x(x^2 - 3 + 2\cos\omega_k) = 0,$$

$$x = (\alpha - e)/\beta,$$

where $\alpha = 0$ marks the origin of the energy scale. Its roots determine the MO energies:

$$\begin{aligned} e_k &= \pm\beta\sqrt{3 + 2\cos\omega_k} \\ \omega_k &= \frac{2\pi}{N} k \\ k &= 1, 2, \ldots, N. \end{aligned} \tag{2}$$

Beside the N bonding MOs (BMO) and the N antibonding MOs (ABMO), given by Eq. (2), there are N degenerate NBMOs with energy

$$e_l = 0 \qquad (l = 1, 2, \ldots, N).$$

The NBMOs do not contribute to the delocalisation energy per electron; hence, it amounts to

$$\bar{\varepsilon} = E/3N = 2/3N \sum_k e_k \xrightarrow{N\to\infty} 2\beta/3\pi \int_0^{\pi} \sqrt{3 + 2\cos\omega}\, d\omega = \frac{3.514}{\pi}\beta.$$

In the case of polyenes without bond alternation [12], the delocalization energy per electron is equal to

$$\bar{\varepsilon} = 4\beta/\pi.$$

From the secular equations and Eq. (2) are obtained the coefficients of the MOs:

(*a*) BMOs:

$$a_{1k}^2=\frac{1+\cos\omega_k}{3+2\cos\omega_k}$$

$$a_{2k}^2=\tfrac{1}{2} \tag{3}$$

$$a_{3k}^2=\frac{1}{2}\cdot\frac{1}{3+2\cos\omega_k}.$$

(*b*) NBMOs:

$$b_{1k}=\sqrt{2}\,a_{3k}$$

$$b_{2k}=0 \tag{3a}$$

$$b_{3k}=-\sqrt{2}\,a_{1k}$$

$$(l\equiv k=1,2,\ldots,N).$$

Using the same method [11] as above we obtain for polymer *I* the following characteristic polynomial:

$$x(x^2-1)(x^4-7x^2+10-2\cos\omega_k)=0.$$

Polymer *I* has three infinitely narrow bands at $e_k=\beta$, 0, and $-\beta$, respectively. Beside that, two bonding and two antibonding bands appear which have the energy:

$$e_k=\pm\beta\sqrt{\tfrac{7}{2}+\tfrac{1}{2}\sqrt{9+8\cos\omega_k}}$$

$$e_k=\pm\beta\sqrt{\tfrac{7}{2}-\tfrac{1}{2}\sqrt{9+8\cos\omega_k}} \tag{4}$$

$$(k=1,2,\ldots,N).$$

They range from 2.358β to 2β and from 1.732β to 1.199β.

For the coefficients of the NBMOs we obtain:

$$c_{1k}^2=\frac{2}{5-\cos\omega_k}$$

$$c_{3k}^2=(-c_{5k})^2=\frac{1-\cos\omega_k}{5-\cos\omega_k} \tag{5}$$

$$c_{7k}^2=\frac{1+\cos\omega_k}{5-\cos\omega_k}.$$

From Eqs. (4) the delocalization energy per electron is obtained as follows:

$$\bar{\varepsilon} = 2\beta/7\left\{1 + 1/\sqrt{2}\pi \int_0^\pi \sqrt{7+\sqrt{9+8\cos\omega}}\, d\omega \right.$$
$$\left. + 1/\sqrt{2}\pi \int_0^\pi \sqrt{7-\sqrt{9+8\cos\omega\, d\omega}}\right\}$$
$$= \frac{4.172\beta}{\pi}.$$

So, energetically polymer *I* is slightly more stabilized than the polyene, where $\bar{\varepsilon} = 4\beta/\pi$.

Both polymers *I* and *II*, have a considerable energy gap of exactly $-\beta$, determined by the molecular topology (Δ_{top}) [15, 16]

$$\Delta E_\infty(I) = \Delta E_\infty(III) = -\beta = \Delta_{top}. \tag{6}$$

3. Alternant Molecular Orbital Method

The DODS-method (Different Orbitals for Different Spins) is very suitable for systems with unfilled shells [13]. Such systems are the treated nonclassical polymers. In the present study, as in the case of one-dimensional polymers with closed shell [14–16], the Alternant Molecular Orbital (AMO) [17, 18], a variant of UHF method [19], is used. The formalism developed for the simplest model, *III*, of a nonclassical polymer can be directly generalised and applied to any other alternant nonclassical system.

Let us denote by $\varphi_{k\sigma}$, $1 \leq k \leq N$, $\sigma \in \alpha, \beta$, the spin orbital k belonging to the bonding band of *III* and by χ the spin orbital of the NBMOs of *III*; due to DODS, the space factor of $\varphi_{k\alpha}$ and $\varphi_{k\beta}$ being different. Assuming an electron configuration as shown in Fig. 1, i.e. the bonding band is fully occupied and there are p NBMOs occupied by electrons with spin α and $q = N - p$ NBMOs occupied by electrons of spin β, the wave function of *III* is represented by

$$= \frac{1}{\sqrt{(3N)!}} \det \|\varphi_{1\alpha}\varphi_{2\alpha} \cdots \varphi_{N\alpha}\varphi_{1\beta}\varphi_{2\beta} \cdots \varphi_{N\beta}$$
$$\cdot \chi_{1\alpha}\chi_{2\alpha} \cdots \chi_{p\alpha}\chi_{(p+1)\beta} \cdots \chi_{N\beta}\|. \tag{7}$$

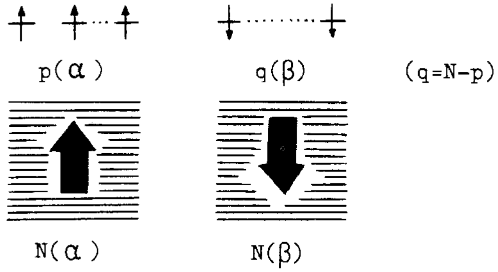


Fig. 1. Scheme of spin distribution on the occupied MOs of polymer *III*

If the BMOs are denoted by $|k\rangle$, and the ABMOs by $|\bar{k}\rangle$, according to the AMO method [14, 17, 18], the orbitals for different spins receive the form:

$$\begin{aligned}
&|k_\alpha\rangle = \sin\theta_{k\alpha}|k\rangle + \cos\theta_{k\alpha}|\bar{k}\rangle\\
&|k_\beta\rangle = \sin\theta_{k\beta}|k\rangle - \cos\theta_{k\beta}|\bar{k}\rangle\\
&(k = 1, 2, \ldots, N).
\end{aligned}\tag{8}$$

The AMOs are closely related [20] to the Spin Density Waves (SDW) [21].

Taking into account the Bloch representation [1] of the MOs and Eq. (8) for the AMOs, in the case of the electron distribution given in Fig. 1 one obtains for the atomic electron densities the following expressions:

$$\begin{aligned}
q_r^\alpha &= \sum_k^N (a_{rk}\sin\theta_{k\alpha} + \bar{a}_{rk}\cos\theta_{k\alpha})^2 + \sum_l^p b_{rl}^2\\
&= \sum_k^N a_{rk}^2 + \sum_k^N \{(\bar{a}_{rk}^2 - a_{rk}^2)\cos^2\theta_{k\alpha} + a_{rk}\bar{a}_{rk}\sin 2\theta_{k\alpha}\}\\
&\quad + \sum_{l=1}^p b_{rl}^2 + \tfrac{1}{2}\sum_{p+1}^N b_{rl}^2 - \tfrac{1}{2}\sum_{p+1}^N b_{rl}^2\\
&= \tfrac{1}{2}q_r + d_r^\alpha + \delta_r^\alpha,
\end{aligned}\tag{9}$$

where a_{rk}, $\bar{a}_{rk}$, and b_{rk} denote the LCAO coefficients of BMOs, ABMOs, and NBMOs, respectively,

$$\delta_r^\alpha = \sum_k \{(\bar{a}_{rk}^2 - a_{rk}^2)\cos^2\theta_{k\alpha} + \bar{a}_{rk}a_{rk}\sin 2\theta_{k\alpha}\};$$

$$d_r^\alpha = \tfrac{1}{2}\sum_{l=1}^p b_{rl}^2 - \tfrac{1}{2}\sum_{l=p+1}^N b_{rl}^2;$$

$$q_r = 2\sum_k a_{rk}^2 + \sum_{l=1}^N b_{rl}^2;$$

$$q_r^\beta = \tfrac{1}{2}q_r + d_r^\beta + \delta_r^\beta;$$

$$d_r^\beta = -d_r^\alpha.$$

If $(r-s) > 1$, there are $N(r-s)$ NBMOs and the summation limits for l in Eq. (9) have to be changed appropriately. In the following we assume $r - s = 1$.

The above Eqs. (9) are valid for arbitrary systems: for non-alternant systems, as well as for systems with heteroatoms.

If the system is homonuclear and altenant,

$$\overset{*}{\bar{a}}_{rk} = \overset{*}{a}_{rk}, \qquad \bar{a}_{sk} = -a_{sk},$$

and:

$$\begin{aligned}
\overset{*}{q}{}_r^{\alpha} &= \tfrac{1}{2} + d_r^{\alpha} + \sum_k a_{rk}^2 \sin 2\theta_{k\alpha} \\
&= \tfrac{1}{2} + d_r^{\alpha} + \delta_r^{\alpha} \\
\overset{0}{q}{}_s &= \tfrac{1}{2} + d_s^{\alpha} - \delta_s^{\alpha} \\
\overset{0}{q}{}_s^{\beta} &= \tfrac{1}{2} - d_s^{\alpha} - \delta_s^{\beta} \\
\overset{*}{q}{}_r^{\beta} &= \tfrac{1}{2} - d_r^{\alpha} + \delta_r^{\beta}.
\end{aligned} \tag{10}$$

Within the framework of the SDW approximation [14, 20]:

$$\delta_r^{\beta} = -\delta_r^{\alpha}; \qquad \delta_s^{\beta} = -\delta_s^{\alpha}.$$

Similar expressions may be obtained for the bond orders; here they are not presented, since they will not be needed in the framework of the Hubbard's approximation [22], which will be applied now.

The AMOs, $|k_{\sigma}\rangle$, used for the construction of the wave function like Eq. (7) are obtained from

$$\hat{F}^{\sigma}|k_{\sigma}\rangle = E_{k\sigma}|k_{\sigma}\rangle,$$

where $\hat{F}^{\sigma} = \hat{F} + \hat{f}^{\sigma}$ denotes the UHF operator. The BMOs and the ABMOs are obtained from the operator in the conventional HF method, $\hat{F}$ according to

$$\begin{aligned}
\hat{F}|k\rangle &= e_k|k\rangle \\
\hat{F}|\bar{k}\rangle &= \bar{e}_k|\bar{k}\rangle.
\end{aligned}$$

In the framework of the Hubbard's approximation [22], the nonvanishing elements of the matrix representation of $\hat{F}^{\sigma}$ have the following forms [14]:

$$\begin{aligned}
F_{rr}^{\sigma} &= F_{rr} + \gamma_r d_r^{\bar{\sigma}} + \gamma_r \delta_r^{\bar{\sigma}} \\
F_{rs}^{\sigma} &= \beta \, (r \text{ and } s \text{ are neighbours}),
\end{aligned} \tag{11}$$

where γ denotes the one-center Coulomb integrals.

From the secular equations the AMO energies are given by (see [14])

$$\begin{aligned}
E_{k\sigma} &= \tfrac{1}{2}(\langle\bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle + \langle k|\hat{f}^{\sigma}|k\rangle) \pm \varepsilon_{k\sigma}, \\
\varepsilon_{k\sigma} &= \{\tfrac{1}{4}(\bar{e}_k - e_k + \langle\bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle - \langle k|\hat{f}^{\sigma}|k\rangle)^2 \\
&\quad + \langle k|\hat{f}^{\sigma}|\bar{k}\rangle^2\}^{1/2} \\
&\sigma \in \alpha, \beta,
\end{aligned} \tag{12}$$

and one also obtains

$$\begin{aligned}\sin 2\theta_{k\alpha} &= -\frac{\langle k|\hat{f}^{\sigma}|\bar{k}\rangle}{\varepsilon_{k\alpha}}\\ \sin 2\theta_{k\beta} &= \frac{\langle k|\hat{f}^{\sigma}|\bar{k}\rangle}{\varepsilon_{k\beta}}.\end{aligned} \tag{13}$$

From Eq. (11) we obtain the matrix elements figuring in Eqs. (12–13):

$$\begin{aligned}\langle k|\hat{f}^{\sigma}|\bar{k}\rangle &= \gamma\left\{\sum_{r}^{*} a_{rk}^{2}(d_{r}^{\bar{\sigma}}+\delta_{r}^{\bar{\sigma}})-\sum_{s}^{0} a_{sk}^{2}\delta_{s}^{\bar{\sigma}}\right\}\\ \langle k|\hat{f}^{\sigma}|k\rangle &= \langle \bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle\\ &= \gamma\left\{\sum_{r}^{*} a_{rk}^{2}(d_{r}^{\bar{\sigma}}+\delta_{r}^{\bar{\sigma}})+\sum_{s}^{0} a_{sk}^{2}\delta_{s}^{\bar{\sigma}}\right\}.\end{aligned} \tag{14}$$

In the above expressions the index r marks the starred AOs and s the non-starred AOs.

Applied to polymer *III*, Eqs. (14) have the form:

$$\begin{aligned}\langle k|\hat{f}^{\sigma}|\bar{k}\rangle &= \gamma\{a_{1k}^{2}(d_{1}^{\bar{\sigma}}+\delta_{1}^{\bar{\sigma}})-a_{2k}^{2}\delta_{2}^{\bar{\sigma}}+a_{3k}^{2}(d_{3}^{\bar{\sigma}}+\delta_{3}^{\bar{\sigma}})\}\\ \langle k|\hat{f}^{\sigma}|k\rangle &= \langle \bar{k}|\hat{f}^{\sigma}|\bar{k}\rangle\\ &= \gamma\{(d_{1}^{\bar{\sigma}}+\delta_{1}^{\bar{\sigma}})a_{1k}^{2}+a_{2k}^{2}\delta_{2}^{\bar{\sigma}}+a_{3k}^{2}(d_{3}^{\bar{\sigma}}+\delta_{3}^{\bar{\sigma}})\}.\end{aligned} \tag{15}$$

Admitting the conditions:

$$\begin{aligned}&\sum_{r} a_{rk}^{2}+\sum_{s} a_{sk}^{2}=1\\ &\sum_{r}\delta_{r}^{\sigma}-\sum_{s}\delta_{s}^{\sigma}=0\end{aligned} \tag{16}$$

it appears that:

$$\begin{aligned}\langle k|\hat{f}^{\sigma}|\bar{k}\rangle &= \Delta_{\sigma}(\omega_{k})\\ &= \gamma\{(\delta_{1}^{\bar{\sigma}}+\delta_{3}^{\bar{\sigma}})+a_{1}^{2}(d_{1}^{\bar{\sigma}}-\delta_{3}^{\bar{\sigma}})+a_{3k}^{2}(d_{3}^{\bar{\sigma}}-\delta_{1}^{\bar{\sigma}})\}.\end{aligned} \tag{15a}$$

In the limit of $N \to \infty$, in the case of polymer *III*, for the correlation corrections δ are obtained the following equations:

$$\begin{aligned}\delta_{1}^{\alpha} &= -\frac{1}{2\pi}\int_{0}^{2\pi} a_{1}^{2}(\omega)\frac{\Delta_{\alpha}(\omega)}{\varepsilon_{\alpha}(\omega)}\,d\omega\\ \delta_{3}^{\alpha} &= -\frac{1}{2\pi}\int_{0}^{2\pi} a_{3}^{2}(\omega)\frac{\Delta_{\alpha}(\omega)}{\varepsilon_{\alpha}(\omega)}\,d\omega\\ \varepsilon_{\alpha}(\omega) &= [(3+2\cos\omega)^{2}\beta^{2}+\Delta_{\alpha}^{2}(\omega)]^{1/2}.\end{aligned} \tag{17}$$

In general, for any alternant nonclassical system, constructed, from elementary units each containing m AOs, one obtains $(m-1)$ linearly independent δ_{i}^{σ}'s which satisfy the equations:

$$\begin{aligned} &\delta_i^\alpha = -\frac{1}{2\pi}\int_0^{2\pi} a_i^2(\omega)\,\frac{\Delta_\alpha(\omega)}{\varepsilon_\alpha(\omega)}\,d\omega \\ &i = 1, 2, \dots, (m-1), \end{aligned} \tag{18}$$

where $\varepsilon_\alpha(\omega)$ and $\Delta_\alpha(\omega)$ are determined by Eqs. (12) and (14), respectively. Due to the SDW formalism

$$\delta_i^\beta = -\delta_i^\alpha.$$

In Eqs. (18) one has to integrate over all the bands of the BMOs.

This work could be considerably simplified if one approximates the correlation corrections as follows:

$$\begin{aligned} \delta_r^\alpha &= -\delta_r^\beta = \overset{*}{\delta} \\ \delta_s^\alpha &= -\delta_s^\beta = \overset{0}{\delta}. \end{aligned} \tag{19}$$

Obviously, $\overset{*}{\delta}$ ($\overset{0}{\delta}$) is at best understood as the mean values of the δ_r's (δ_s's) and, hence, one obtains:

$$\begin{aligned} \overset{*}{\delta} &= 1/r \overset{*}{\sum_r} \delta_r = \frac{1}{2\pi r}\overset{*}{\sum_r}\int_0^{2\pi} a_r^2(\omega)\sin 2\theta(\omega)\,d\omega \\ &= \frac{1}{4\pi r}\int_0^{2\pi}\sin 2\theta(\omega)\,d\omega \\ \overset{0}{\delta} &= 1/s \overset{0}{\sum_s} \delta_s = \frac{-1}{2\pi s}\overset{0}{\sum_s}\int_0^{2\pi} a_s^2(\omega)\sin 2\theta(\omega)\,d\omega \\ &= \frac{-1}{4\pi s}\int_0^{2\pi}\sin 2\theta(\omega)\,d\omega, \end{aligned} \tag{20}$$

where r and s denote the number of starred and nonstarred atoms in the elementary unit, respectively.

From Eq. (20) it follows immediately that

$$\overset{0}{\delta} = (r/s)\overset{*}{\delta}.$$

Thus, Eqs. (18) are reduced to the equation:

$$\overset{*}{\delta} = \tfrac{1}{4}\pi r\int_0^{2\pi}\sin 2\theta(\omega)\,d\omega = \tfrac{1}{4}\pi r\int_0^{2\pi}\frac{\Delta_\alpha(\omega)}{\varepsilon_\alpha(\omega)}\,d\omega \tag{21}$$

where (see Eq. (14)):

$$\Delta(\omega_k)=\gamma\left\{\overset{*}{\delta}\sum_r a_r^2(\omega_k)+\overset{0}{\delta}\sum_s a_s^2(\omega_k)+\sum_r a_r^2(\omega_k)d_r^\alpha\right\}$$

$$=\gamma\left\{\tfrac{1}{2}(\overset{*}{\delta}+\overset{0}{\delta})+\sum_r a_r^2(\omega_k)d_r^\alpha\right\}$$

$$=\frac{r+s}{2s}\overset{*}{\delta}+\sum_r a_r^2(\omega_k)d_r^\alpha .$$

For the mean energy of an electron, i.e. the energy per electron, the following expression is obtained:

$$\begin{aligned}\varepsilon &= 1/mN\left\langle\Phi\left|\sum_i \hat{h}(i)+\sum_{i<j}\frac{e^2}{r_{ij}}\right|\Phi\right\rangle\\ &=1/2mN\sum_\sigma\sum_{k(l)}\langle k(l)_\sigma|\hat{h}+\hat{F}^\sigma|k(l)_\sigma\rangle\\ &=1/2mN\sum_\sigma\sum_{k(l)}\langle k(l)_\sigma|2\hat{F}^\sigma-\hat{R}|k(l)_\sigma\rangle\\ &=-1/2mN\sum_\sigma\sum_k|\varepsilon_{k\sigma}|-E_{\text{el}}=\varepsilon_\alpha+\varepsilon_\beta-E_{\text{el}}.\end{aligned}\tag{22}$$

In the above equation E_{el} stands for the electron interaction energy per electron, which is given by:

$$\begin{aligned}E_{\text{el}}&=1/2mN\left\{\sum_\sigma\sum_k\langle k_\sigma|\hat{R}|k_\sigma\rangle+\sum_l\langle l|\hat{R}|l\rangle\right\}\\ &=\gamma/4-\gamma/m\left\{\sum_r(\delta_r^\alpha+2d_r^\alpha)^2+\sum_s(\delta_s^\alpha)^2\right\}\end{aligned}\tag{23}$$

where the operator of the electron interaction is denoted by $\hat{R}=\hat{F}^\sigma-\hat{h}$.

4. Energy Characteristics of the Polymers

The energy of the system depends strongly on the multiplicity of the system, i.e. on the S_z-projection of the total spin upon the z-axis; $S_z=\frac{1}{2}|p(\alpha)-q(\beta)|$ (see Fig. 1). Since the BMOs are occupied by equal number of electrons with spin α and spin β, the total projection S_z is determined by the spin population of the NBMOs, hence, one obtains (see Fig. 1):

$$S_z=\tfrac{1}{2}|p(\alpha)-q(\beta)|=\tfrac{1}{2}|2p-N|=N/2|2p/N-1|.$$

Table 1 illustrates the dependence of the ground state energy of polymer *III* on the parameter p/N. Minimal values of the ground state energy are achieved for $p/N=0$ or 1. The same results are obtained for polymer *I*.

Both results convey Hund's rule for maximum multiplicity, essentially used in Mataga's work [7], and also concur with the results of Ovchinnikov [23], where it is qualitatively shown that $S>0$.

Table 1. Values of d_r, the correlation correction δ_r and the ground state energy (of polymer *III*) estimated by means of Eq. (22) depending on p/N. The results are obtained for $\beta = -2.4$ eV and $\gamma = 5.4$ eV; the same parameters are used in the band structure-investigations of polyenes and alternant hydrocarbons with closed shell [15–16]

p/N	d_1^α	d_3^α	δ_1^α	δ_3^α	$-\varepsilon_\sigma$(eV)[a]	$-\varepsilon$ (eV)
0	−0.224	−0.276	−0.079	−0.081	4.252	2.752
0.1	−0.203	−0.197	−0.068	−0.072	4.186	2.271
0.2	−0.179	−0.121	−0.054	−0.056	4.121	1.885
0.3	−0.145	−0.055	−0.038	−0.036	4.069	1.605
0.4	−0.089	−0.011	−0.020	−0.017	4.036	1.416
0.5	0.0	0.0	0.0	0.0	4.026	1.342
0.6	0.089	0.011	0.020	0.017	4.036	1.416
...	...					
1.0	0.224	0.276	0.079	0.081	4.252	2.752

[a] $\sigma \in \alpha, \beta$

The orbital energies of both polymers *I* and *III* do not depend essentially on the correlation corrections which are comparatively small; this fact is illustrated in Fig. 2. When $p/N = 1/2$, then $\delta_r = 0$, hence, $\varepsilon_\sigma(\omega_k) = e(\omega_k)$.

In the case of polymer III, at $p/N = 0$, the energy gap amounts to (see Eq. (6)):

$$\Delta E_\infty^\sigma = \sqrt{\beta^2 + \Delta_\sigma^2(\pi)} = \sqrt{\Delta_{\text{top}}^2 + \Delta_{\text{corr}}^2} = 2.78 \text{ eV},$$

where $\beta = -2.4$ eV, $\gamma = 5.4$ eV [15–16].

For polymer *I* the contribution of the correlation corrections to the degenerate BMOs ($e_k = \beta$) is negligibly small for $p/N = 0$:

$$E_\sigma(\pi) = \pm\sqrt{\beta^2 + 0.059^2\gamma^2} \simeq \pm\beta.$$

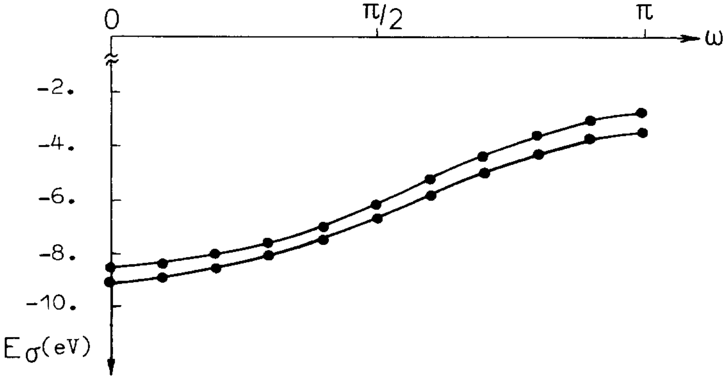


Fig. 2. Energy of the BMO $\varepsilon_\sigma(\sigma \in \alpha, \beta)$ of polymer *III* upon ω at: (1) $p/N = 0$; (2) $p/N = 0.5$; $\beta = -2.4$ eV; $\gamma = 5.4$ eV

5. Electron Interaction Energy in the NBMO Band

The mean interaction energy of the electrons in the NBMOs with themselves is given by the formula (in the case of polymer *III*):

$$\begin{aligned} E_{\mathrm{el}}(\mathrm{NBMO}) &= 1/N\left\langle \det(\mathrm{NBMO}) \sum_{i<j} \frac{e^2}{r_{ij}} \det(\mathrm{NBMO}) \right\rangle \\ &= \gamma q_1(p)[q_1 - q_1(p)] + \gamma q_3(p)[q_3 - q_3(p)] \\ &= \gamma q_1(p)[0.388 - q_1(p)] + \gamma q_3(p)[0.612 - q_3(p)] \\ &= \gamma[\tfrac{1}{4}(q_1^2 + q_3^2) - d_1^2 - d_3^2], \end{aligned} \tag{24}$$

which may be generalized for an arbitrary alternant nonclassical system:

$$E_{\mathrm{el}}(\mathrm{NBMO}) = \overset{*}{\sum_r} \overset{*}{q}_r(p)[\overset{*}{q}_r - \overset{*}{q}_r(p)] = \gamma/4 \overset{*}{\sum_r} \overset{*}{q}{}_r^2 - \gamma \overset{*}{\sum_r} \overset{*}{d}{}_r^2. \tag{25}$$

In the above expressions, correct in the Hubbard's approximation, the following denotations are used:

$$q_r(p) = \sum_{l=1}^{p} b_{rl}^2 = d_r + \tfrac{1}{2} \sum_{1}^{N} b_{rl}^2 = d_r + \tfrac{1}{2} q_r$$

$$\det(\mathrm{NBMO}) = 1/\sqrt{N!}\,|\chi_{1\alpha}\chi_{2\alpha} \cdots \chi_{p\alpha}\chi_{(p+1)\beta} \cdots \chi_{N\beta}|.$$

Expression (24) has its maximum, i.e. the electron interaction is strongest, at $p/N = \frac{1}{2}$ (this means $S_z = 0$), and vanishes at $p/N = 0$ or 1.

6. Spin Densities

The electron correlation taken into account influences the spin density distribution

$$\rho_r = q_r^\alpha - q_r^\beta.$$

From Eqs. (9)–(10) we obtain:

$$\rho_r = d_r^\alpha + \delta_r^\alpha - d_r^\beta - \delta_r^\beta = 2d_r^\alpha + 2\delta_r^\alpha. \tag{26}$$

Table 2 shows the dependence of the spin densities at different values of p/N. For $p/N = 1$ (all the electrons in the NBMOs have spin α) one obtains

$$\begin{aligned} &\rho_1 + \rho_3 = 1 + 2(\delta_1^\alpha + \delta_3^\alpha) \\ &\delta_2 = -2(\delta_1^\alpha + \delta_3^\alpha). \end{aligned} \tag{27}$$

The above equations, generalised for an arbitrary alternant nonclassical system in the ground state, when $p/N = 1$, take the form ($r - s = 1$):

$$\begin{aligned} &\overset{*}{\rho} = \overset{*}{\sum_r} \overset{*}{\rho}_r = 1 + 2 \overset{*}{\sum_r} \overset{*}{\delta}{}_r^\alpha \\ &\overset{0}{\rho} = \overset{0}{\sum_s} \overset{0}{\rho}_s = -2 \overset{0}{\sum_s} \overset{0}{\delta}{}_s^\alpha. \end{aligned} \tag{28}$$

Table 2. Dependency of the spin densities ρ_r of polymer *III* (see Eqs. (27), (28) and Table 1) on the parameter p/N. $\beta = -2.4$ eV; $\gamma = 5.4$ eV

p/N	ρ_1	ρ_2	ρ_3
0.0	−0.606	0.320	−0.714
0.1	−0.542	0.280	−0.538
0.2	−0.466	0.216	−0.354
0.3	−0.366	0.148	−0.182
0.4	−0.218	0.074	−0.056
0.5	0.0	0.0	0.0
0.6	0.218	−0.074	0.056
. . .	. . .		
1.0	0.606	−0.320	0.714

In the Hartree–Fock approximation $\delta_s^\alpha = \delta_s^\beta = 0$ for all nonclassical systems, the spin densities at the nonstarred atoms being zero:

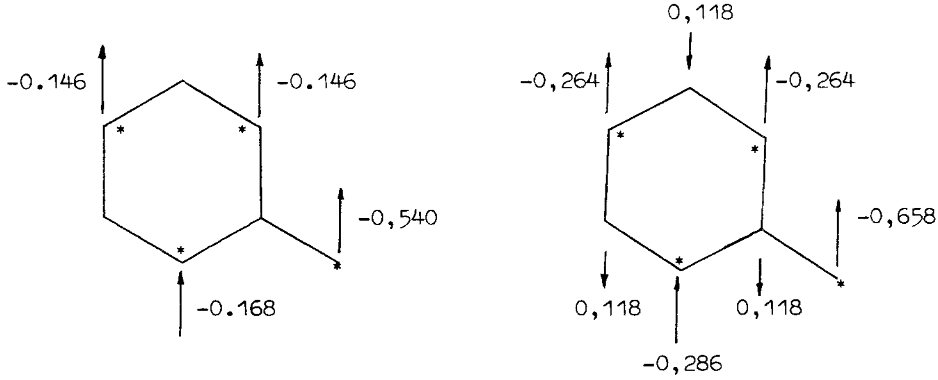
$$\overset{0}{\rho}(\mathrm{HF}) = 0. \tag{29}$$

7. Conclusion

As illustrated by Table 2, the spin densities alternate upon the centres of an elementary unit. The same result is obtained for polymer *III* by Ovchinnikov [10], too. In the case of polymer *I* the alternation of the spin density is shown in Fig. 3.

All these results suggest to consider a nonclassical alternant polymer as divided into sub-lattices, one for the starred and the other for the nonstarred atoms (Fig. 4). Each of these sub-lattices are populated with electrons of parallel spins, but opposite between the sub-lattices. Thus, it results that $S_z > 0$ for the polymer.

Consequently, the one-dimensional nonclassical polymers investigated have a ferrimagnetic ground state.



(a) (b)

Fig. 3a, b. Distribution of the spin density in the elementary unit of polymer *I* at $p/N = 0$. **a** In HF approximation; **b** in AMO approximation

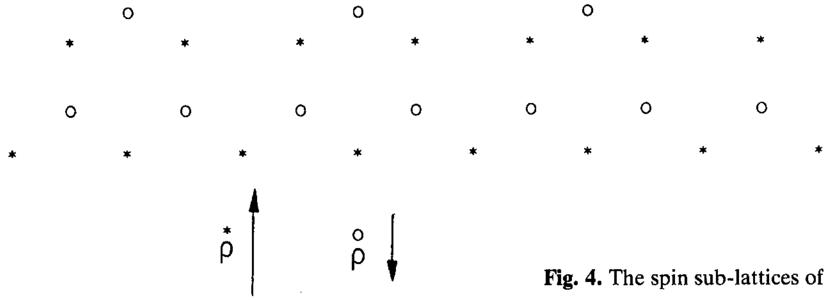


Fig. 4. The spin sub-lattices of polymer *I*

This result is valid at $T = 0°K$. The magnetic properties of the treated systems will depend on the temperature behaviour of the spin population. A statistical treatment of this problem is under investigation.

The numerical data collected in Table 1 and 2 may change slightly in case of spin projection of the wave functions, but no essential qualitative change has to be expected.

Thus, the results obtained may be generalized, probably, to the conclusion that fully conjugated alternant nonclassical polymers (i.e. polyradicals) gain enough energy from the delocalisation of the π-electrons to exhibit energetic stability.

References

1. Dewar, M. J.: The MO theory of organic chemistry. New York: McGraw-Hill 1969
2. Buchachenko, A. L.: Stable radicals. New York: Consultant Bureau 1965
3. Forrester, A. R., Hay, J. M., Thomson, R. H.: Organic chemistry of stable free radicals. London and New York: Academic Press 1968
4. Ziegler, K., Ochs, C.: Berichte deutsche Chem. Ges. **55**, 2257 (1922); Ziegler, K.: Annalen Chemie **434**, 34 (1923)
5. Koelsch, C. F.: J. Am. Chem. Soc. **79**, 4439 (1957)
6. Coulson, C. A., Rushbrooke, G. S.: Proc. Cambridge Phil. Soc. **36**, 193 (1940)
7. Mataga, N.: Theoret. Chim. Acta (Berl.) **10**, 372 (1968)
8. Buchachenko, A. L.: Compt. Rend. Acad. Sci. USSR (Dokladi) **244**, 1146 (1979)
9. Tyutyulkov, N., Bangov, I.: Compt. Rend. Acad. Bulg. Sci. **27**, 1417 (1974)
10. Ovchinnikov, A. A., Cheranovski, V. O.: Theoret. Exp. Chem. (USSR) **17**, 10 (1981)
11. Polansky, O. E., Tyutyulkov, N. N.: Match. **3**, 149 (1977)
12. Coulson, C. A.: Proc. Roy. Soc. **A169**, 413 (1939)
13. Harriman, J. E.: Theoretical foundation of electron spin resonance. New York: Academic Press 1978
14. Tyutyulkov, N.: Int. J. Quantum Chem. **13**, 443 (1978)
15. Tyutyulkov, N., Kanev, I., Polansky, O., Fabian, J.: Theoret. Chim. Acta (Berl.) **46**, 191 (1977)
16. Tyutyulkov, N., Polansky, O., Fabian, J.: Z. Naturforsch. **30a**, 1308 (1975)
17. Lödwin, P.-O.: Phys. Rev. **97**, 1509 (1955)
18. Pauncz, R.: AMO Method. Philadelphia: Saunders 1967
19. Mayer, I.: in Advances in Quantum Chemistry **12**, 190 (1980)
20. Calais, J.-L.: in Lectures Notes in Physics, Vol. **113**: Recent advances in the quantum theory of polymers, p. 169. Berlin: Springer 1980
21. Overhauser, A. W.: Phys. Rev. Letters **4**, 462 (1960); Phys. Rev. **167**, 691 (1968)
22. Hubbard, J.: Proc. Roy. Soc. **A276**, 238 (1963)
23. Ovchinnikov, A. A.: Theoret. Chim. Acta (Berl.) **47**, 297 (1978)

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