

## Structure and properties of non-classical polymers II. Band structure and spin densities

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Theoretical investigation of the band structure of three types of nonclassical polymers, namely alternant (one- and two-dimensional), nonalternant and heteroatomic, are carried out. Although polyradicals, these polymers have a considerable delocalization energy which may determine their relative stability.

The spin-density distribution of the alternant type of non-classical polymers corresponds to a ferrimagnetic ground state at 0 K.

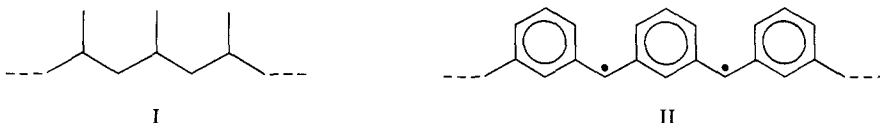
The non-classical polymers represent a new class of organic systems as their band structure and magnetic properties essentially differ from those of common polymers.

**Key words:** Nonclassical polymers—band structure of ~—classification and spin densities of ~

### 1. Introduction

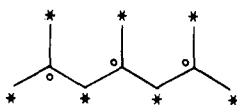
Nonclassical polymers [1] like nonclassical hydrocarbons [2] have a system of conjugation to which no Kekule formula can be attributed. In spite of being polyradicals, they are supposed to be relatively stable due to the considerable delocalization energy [1].

In the first paper [1] the polymers I and II had been considered as models for non-classical polymers



It was shown that their ground states are characterized of maximum spin multiplicity. This is in complete agreement with the formula  $S = \frac{1}{2}(\overset{*}{N} - \overset{0}{r})$  obtained by Ovchinnikov [3] in the treatment of some alternant polyradicals by means of a general Heisenberg Hamiltonian. Here  $\overset{*}{N}$  and  $\overset{0}{r}$  denote the total number of starred and non-starred atoms, respectively.

Using the exact solution of the PPP Hamiltonian Koutecky et al. [4] proved recently that the hydrocarbon,



which may be viewed on a cluster related to polymer I, has a quintuplet ground state  ${}^5A_1$ , i.e. the total spin is  $S = \frac{1}{2}(7 - 3) = 2$ . This result provides strong support for the existence of molecular ferromagnetism in hydrocarbon polyradicals. The latter investigation together with the earlier results obtained in [1, 3, 5] shows that nonclassical polymers may exhibit interesting magnetic properties. Therefore, it is expedient to extend such investigations to different types of polymers in order to support the theory, as well as to attract the attention of the synthetists. Having this in mind, in the present study we extend the treatment from alternant nonclassical polymers to two-dimensional ones as well as to nonalternant and heteroatomic nonclassical polymers.

The band structure of the polymers is obtained by means of a Hückel version of the Bloch method [6]. The method [6] allows also to treat polymers with a finite number of monomeric units; in this case the polymer is thought to be embedded in a cylindrical surface exhibiting at least  $C_N$  symmetry and  $\omega_j = 2j\pi/N$  denotes the argument of the character of the rotation in the irreducible representation  $\Gamma_j$  of this group. For finite  $N$ , each band consists of  $N$  discrete eigenvalues located equidistantly with respect to  $\omega$ .

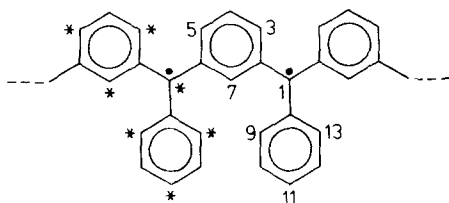
In the case of alternant nonclassical polymers the Alternant Molecular Orbital (AMO) version of the extended Hartree-Fock (EHF) method described in [1, 7, 8] is applied in order to account for the electron correlation. The resulting data are used for a refining of the band structure and the estimation of the spin densities.

A classification of the non-classical polymers has been elaborated which proves to be a helpful means in the investigation of the magnetic properties at finite temperatures being in progress.

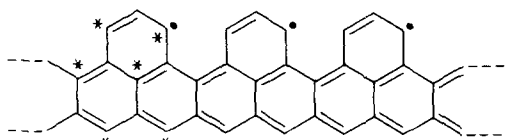
## 2. Alternant nonclassical polymers

An alternant homonuclear system may be represented by two sub-systems of starred and non-starred atoms, respectively, so that every starred atom is connected to non-starred atom and vice versa.

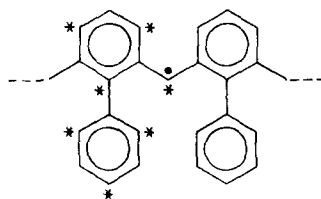
According to the Coulson–Rushbrook theorem [9], an alternant system in which the number of starred atoms,  $S$ , exceeds the number of non-starred atoms,  $R$ , has  $S - R$  non-bonding molecular orbitals (NBMO). Alternant nonclassical systems are, for instance, the polymers III, IV, and V (here and in the following only one of the possible formulae is given).



III



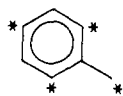
IV



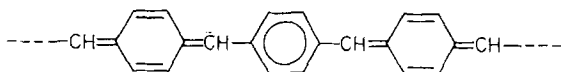
V

In each unit in these polymers there is one starred atom more than non-starred ones. Hence, a polymer consisting of  $N$  units has  $S - R = N$  degenerate NBMO.

A non-classical monomer does not necessarily lead to a non-classical polymer. The type of the polymer is also determined by the topology of the bonds between neighbouring structural units. Thus the typical non-classical benzyl radical forms both, the non-classical polymer II,



and the classical polymer:



### 2.1. One-dimensional alternant non-classical polymers

The structure of the polymers, treated in this subsection, are described above by the formulae III, IV and V. Their characteristic polynomials are given in Appendix

I. For the discussion of the general feature of these systems, polymer III may serve as an example. Its characteristic polynomial reads

$$x(x^2 - 1)^3(x^2 - 4)(x^4 - 8x^2 + 13 - 2 \cos \omega) = 0; \quad (1)$$

the MO energies,  $e_j$ , are related to the roots of the characteristic polynomial  $x_j$ , according to  $x_j = (\alpha - e_j)/\beta$ ; the argument  $\omega = ka$ , where  $k$  denotes the Bloch wave vector;  $\beta < 0$  is the resonance integral for adjacent AO.

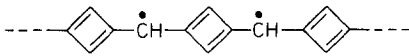
According to Eq. (1), polymer III has 9 infinitely narrow bands: in the bonding region there is a band at  $e_j = 2\beta$  and a three-fold degenerated band at  $e_j = \beta$ ; then there is a non-bonding band at  $e_j = 0$  (containing  $N$  degenerate NBMO), and finally in the antibonding region there are a three-fold degenerated band at  $e_j = -\beta$  and one at  $e_j = -2\beta$ . Besides these, there are two bonding (BMO) and two antibonding (ABMO) bands of the energy:

$$e_j = \pm\beta\sqrt{4 \pm \sqrt{3 + 2 \cos \omega}}. \quad (2)$$

As seen from Appendix I the polymers IV and V have also infinitely narrow bands at  $e_j = 0$  (NBMO); in addition polymer V has two more infinitely narrow bands at  $e_j = \pm\beta$ . All BMO and ABMO bands of these polymers are well separated from the NBMO bands. Thus, all three polymers have the general pattern of valence, NBMO, and conductivity band, depicted schematically in Fig. 1. Since within the applied approximation geometric factors and correlation effects are neglected, the energy gap,  $\Delta E_\infty$ , between the BMO and ABMO bands is determined merely by the molecular topology and equals to:

$$\begin{aligned} \Delta E_\infty(\text{III}) &= \Delta_{\text{top}}(\text{III}) = -2\beta\sqrt{4 - \sqrt{5}} = -2.656\beta \\ \Delta E_\infty(\text{IV}) &= \Delta_{\text{top}}(\text{IV}) = -1.771\beta \\ \Delta E_\infty(\text{V}) &= \Delta_{\text{top}}(\text{V}) = -1.409\beta. \end{aligned} \quad (3)$$

The following polymer



may serve as an example for an alternant non-classical polymer having a zero energy gap. It is easily seen from its characteristic polynomial:

$$x(x^4 - 6x^2 + 4 - 4 \cos \omega) = 0$$

that the valence and conductivity bands have the points  $x = 0$ ,  $\omega = 0$  in common.

The polymers treated here are polyconjugated systems, and may be significantly stabilized by their delocalization energy which may be compared by means of

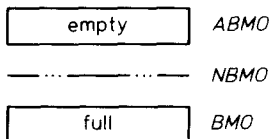


Fig. 1. Scheme of the energy spectrum of alternant non-classical polymers

the specific delocalization energies:

$$\bar{\epsilon} = \frac{1}{mN} \sum_{j=1}^N \sum_i \kappa_{ij} e_{ij} \quad (4)$$

where  $m$  denotes the number of electrons per unit,  $i$  the index of the bands,  $j$  the index of the MO in their bands and  $\kappa_{ij}$  its occupation number.

The specific delocalization energy of polymer III is given by (cf. Eq. (2)):

$$\begin{aligned} \bar{\epsilon}(\text{III}) &= \lim_{N \rightarrow \infty} \left[ \frac{1}{13N} \sum_{i=1}^6 \sum_{j=1}^N 2e_{ij} \right] \\ &= \frac{1}{13} \left\{ 6 + 4 + \frac{2}{\pi} \int_0^\pi \sqrt{4 + \sqrt{3 + 2 \cos \omega}} + \sqrt{4 - \sqrt{3 + 2 \cos \omega}} \right\} d\omega \\ &= \frac{4.301}{\pi} \beta. \end{aligned}$$

For polymers IV and V, respectively, the specific delocalization energies are:

$$\bar{\epsilon}(\text{IV}) = \frac{4.364}{\pi} \beta$$

$$\bar{\epsilon}(\text{V}) = \frac{4.317}{\pi} \beta.$$

The three polymers have a considerable specific delocalization energy in comparison with some well-known systems (polyenes [10] without bond-length alternation:  $4/\pi\beta$ ; diphenylmethyl radical [11]:  $4.181/\pi\beta$ ; and triphenylmethyl radical [11]:  $4.266/\pi\beta$ ). From this, polymer II, IV, and V are supposed to be relatively stable since their specific delocalization energy exceeds in magnitude even that of the triphenylmethyl radical which is known as a stable chemical system due to its considerable delocalization energy.

Taking into account the electron interaction, the energy of a fixed state of the polymers depends on the spin configuration in the NBMO and on the total spin,  $S$ , of the system. If there are  $p$  electrons with  $\alpha$  spin ( $\uparrow$ ) and  $q = N - p$  electrons with  $\beta$  spin ( $\downarrow$ ) occupying the NBMO's (see Fig. 2), one obtains for  $S$  the following expression:

$$S = \frac{1}{2} |p(\alpha) - q(\beta)| = \frac{1}{2} |2p - N| = \frac{N}{2} |1 - 2p/N|. \quad (5)$$

Applying the AMO variant of the Extended Hartree-Fock method [7, 8] (AMO-EHF) described in [1], the ground state energy per electron of a non-classical polymer is given by the following expression (obtained by inserting Eq. (23) into Eq. (22) in [1]):

$$\epsilon = \frac{\gamma}{4} - \frac{\gamma}{m} \left\{ \sum_r^0 (\delta_r^\alpha)^2 + \sum_s^* (\delta_s^\alpha + 2d_s^\alpha)^2 \right\} - \frac{1}{2mN} \sum_\sigma \sum_k |\epsilon_{k\sigma}|. \quad (6)$$

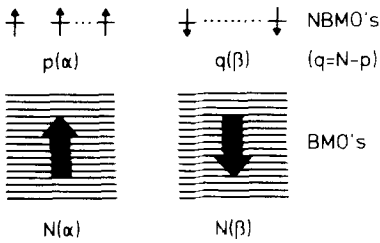


Fig. 2. Scheme of spin distribution of the occupied MO's of alternant non-classical polymers

Therein  $\varepsilon_{j\sigma}$  is the orbital energies depending upon the spin ( $\sigma = \alpha, \beta$ );  $\delta_r^\alpha = -\delta_r^\beta$  and  $\delta_s^\alpha = -\delta_s^\beta$  are the correlation corrections;  $\gamma$  denotes the one center Coulomb integral of the carbon atom; the quantities,  $d_s^\alpha$ , depend on the spin configuration in the NBMO band (Fig. 2) and are equal to [1]:

$$d_s^\alpha = \frac{1}{2N} \sum_{j=1}^p c_{sj}^2 - \frac{1}{2N} \sum_{j=p+1}^N c_{sj}^2 \quad (7)$$

$$d_s^\beta = -d_s^\alpha$$

where  $c_{sj}$  denotes the non-zero NBMO coefficients for the AO of the starred atoms and  $c_{rj} = 0$  for non-starred ones. In Eqs. (6) and (7) and further on  $s$  and  $r$  are the indices of the starred and non-starred atoms, respectively.

In the Hartree-Fock (HF) approximation the correlation corrections vanish ( $\delta_s^\sigma = \delta_r^\sigma = 0$ ); hence, the orbitals energies,  $\varepsilon_{j\sigma}$ , do not depend on the spin and are equal to the energies,  $e_j$ , i.e.:  $\varepsilon_{j\alpha} = \varepsilon_{j\beta} = e_j$ . Thus, Eq. (6) takes the following form:

$$\varepsilon = \frac{-1}{mN} \sum_i \sum_j |e_{ij}| + \frac{\gamma}{4} - \frac{4\gamma}{m} \sum_s (d_s^\alpha)^2 \quad (6a)$$

According to the above equality the energy of an arbitrary alternant non-classical polymer reaches its minimum at the maximum of  $d_s^\alpha$ . This corresponds to a ground state configuration with maximum spin multiplicity:  $S = N/2$ ; as seen from Eq. (5) this implies  $p(\alpha) = N$ , and  $q(\beta) = 0$ . In this case, where  $q_s$  (NBMO) is the contribution of all NBMO to the atomic electron charges Eq. (7) takes the form:

$$2d_s^\alpha = \sum_{j=1}^N c_{sj}^2 = q_s(\text{NBMO}) \quad (8)$$

The validity of the above conclusion, minimum ground state energy corresponding to maximum multiplicity, is also maintained within the AMO-EHF-treatment where electron correlations are taken into account ( $\delta_s^\sigma \neq 0$ ,  $\delta_r^\sigma \neq 0$ ). This can be verified by minimizing the ground state energy corresponding to Eq. (6). Within this approach the energy gap is determined not merely by the topological factor

$\Delta_{\text{top}}$ , but also by a correlation factor,  $\Delta_{\text{corr}}$ , as well [12, 13]:

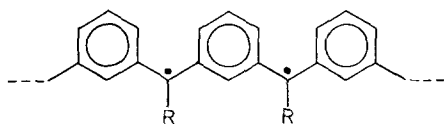
$$\Delta E = \sqrt{\Delta_{\text{top}}^2 + \Delta_{\text{corr}}^2}$$

The orbital energies of the polymers treated are not materially affected by the electron correlations such that the band pattern is qualitatively maintained as given in Fig. 1. The degeneracy of the NBMO's is not removed which has essential consequences for the magnetic properties of these polymers. The energy gap is slightly widened, i.e.:  $\Delta E_{\infty} \approx \Delta_{\text{top}}$ . Thus, in the case of polymer III, using the approach [13] and the values  $\beta = -2, 4 \text{ eV}$ ,  $\gamma = 5, 4 \text{ eV}$  [1, 12], one obtains  $\Delta_{\text{corr}} = 1197 \text{ eV}$  and according to Eq. (3)  $\Delta_{\text{top}} = 6.3744 \text{ eV}$ . From this the energy gap amounts  $\Delta E_{\infty}(\text{III}) = 6.486 \text{ eV}$ .

At the end of this subsection we discuss the effect of substituents on the band structure of alternant non-classical polymers. The Coulson-Rushbrooke theorem [9] is based on the equivalence of the Coulomb integrals of the different sites. In a real polymer, however, the  $\sigma$ -core affects the Coulomb integrals of the  $2p\pi$  AO. As a result, the degeneracy of the NBMO is removed. The widening of the NBMO band depends on the art of the substituents but it remains narrow what so ever.

Maximal effects may be anticipated for the replacement of a carbon atom by a hetero atom; such a case is realised in polymer XII, treated in Sect. 4. The perturbation might also be considerable when the substituent ( $-\text{Cl}$ ,  $-\text{CHO}$ ,  $-\text{NO}_2$ , etc.) contributes  $\pi$ -electrons to the system of conjugation.

Medium effects may be anticipated when some hydrogen atoms are substituted by alkyl groups which do not extend the  $\pi$ -electron conjugation; this situation is illustrated by the following example:



VI

The parent compound of this polymer ( $\text{VI}^*$ ,  $R = \text{H}$ ) was treated in [1]; the band structure displays an infinitely narrow NBMO band in the middle of the energy gap,  $\Delta E_{\infty} = -2\beta$ . In the case  $R = \text{alkyl}$ , we denote by  $\alpha = \alpha_0 + h\beta = h\beta$  the Coulomb integral of the exocyclic carbon atom to which the substituent  $R$  is attached. Thus the characteristic polynomial for polymer VI reads:

$$(x^2 - 1)[x(x^4 - 7x^2 + 10 - 2 \cos \omega) + h(x^4 - 5x^2 + 4)] = 0.$$

The NBMO band of  $\text{VI}^*$  is replaced by a narrow band, which is slightly shifted to negative, (positive) energies for  $h > 0$  ( $h < 0$ ). For  $R = \text{methyl}$  ( $h = -0, 4$ ), the NBMO split into a band of MO energies within the interval:

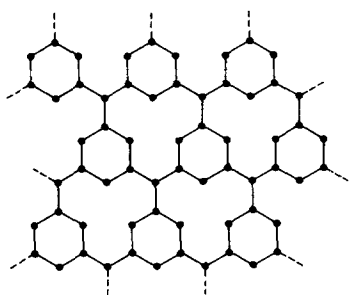
$$0.132 \beta \geq e_k \geq 0.197 \beta.$$

The energy gap between the highest fully filled and the lowest empty band is not affected noticeably by the variation of the parameter  $h$ .

## 2.2. Two-dimensional alternant non-classical polymers

In the case of two-dimensional polymers there are two independent variables  $\omega_1$  and  $\omega_2$ ; if there are  $N_1$  and  $N_2$  elementary units respectively in the two directions of translational symmetry we have  $\omega_{1j} = 2j\pi/N_1$  and  $\omega_{2k} = 2k\pi/N_2$ . Taking this into account, the treatment of one-dimensional polymers is easily extended to two-dimensional systems.

The band structure of two-dimensional alternant non-classical polymers is characterized by a large energy gap and degenerate NBMO band in its middle. For the hydrocarbon VII, proposed by Mataga, the characteristic polynomial is given in Appendix I. The energy gap amounts to  $\Delta E_\infty = -2\beta$  and the NBMO lies in its middle.



VII

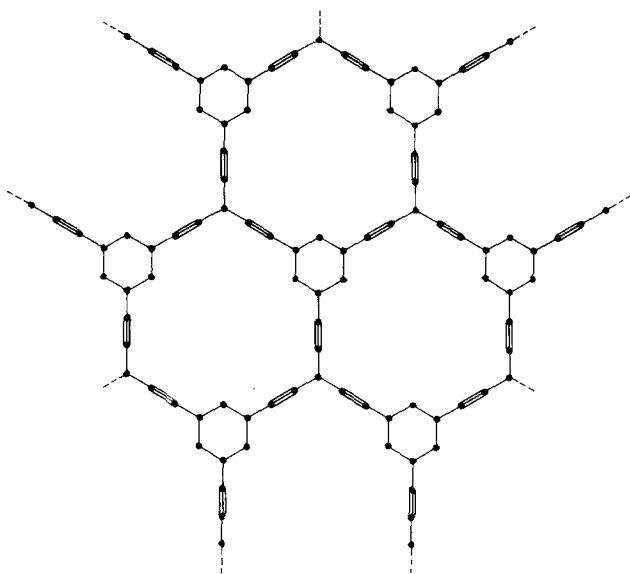
The polymers II and VII have the same monomeric unit, namely benzyl, but VII has a greater delocalization energy per electron than II. The comparison of their values with that of triphenyl radical reveals:

triphenylmethyl- radical	polymer II	Mataga polymer VII
$\bar{\epsilon} = \frac{4.266}{\pi} \beta$	$\bar{\epsilon} = \frac{4.172}{\pi} \beta$	$\bar{\epsilon} = \frac{4.398}{\pi} \beta$

The greater delocalization energy of the two-dimensional polymers suggests their higher relative stability.

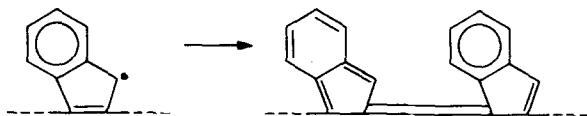
The Mataga polymer, VII, is free of steric hindrance of the hydrogen atoms. This is eluded in the case of the polymer represented on the next page which has a similar band structure as well as an energy gap  $\Delta E_\infty = -2\beta$ .



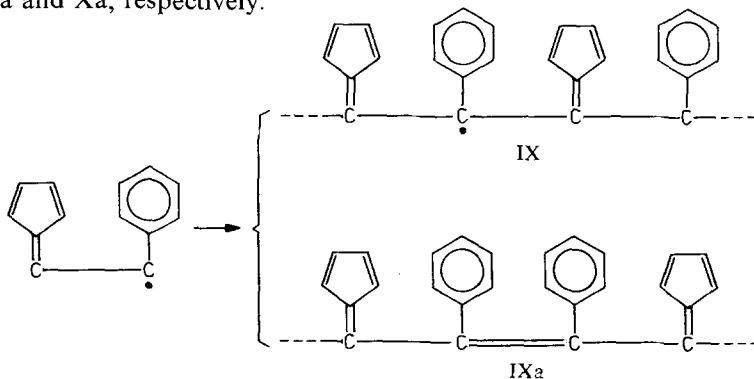


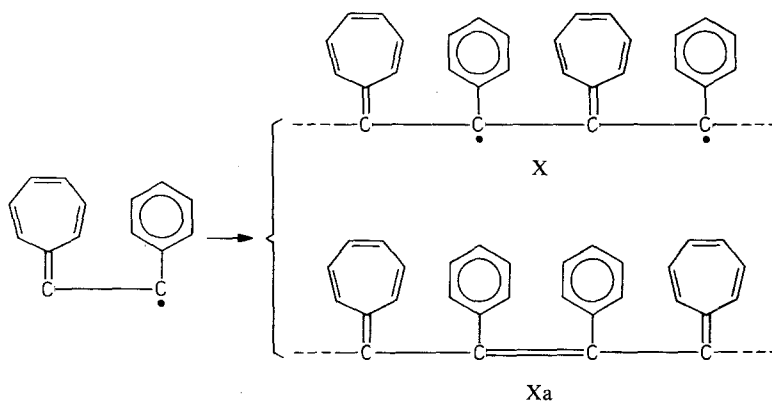
### 3. Non-alternant non-classical polymers

The necessary and sufficient condition for alternant systems is that it does not contain odd membered rings. For the construction of non-alternant polymer systems, the presence of an odd membered ring in the monomeric unit is necessary. In order to obtain a non-classical non-alternant polymer (NANCP) it is not sufficient to choose a non-alternant radical for the monomeric unit, but it is also necessary to prevent the unpaired electrons of neighboring units from forming a pair as shown by the following example:

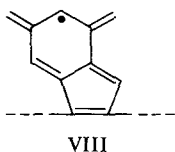


Such a switching is avoided in the case of polymers IX and X. But when one tries to synthesize these polymers by successive additions of monomeric units a head to head, tail to tail alignment may occur corresponding to the polymers IXa and Xa, respectively.

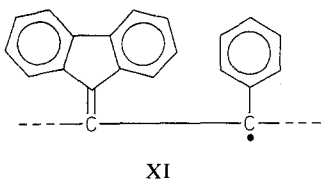




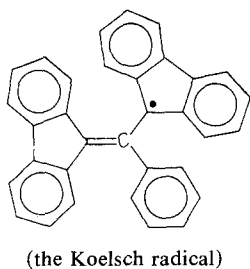
However, the aforementioned difficulties cannot occur in the case of polymer VIII.



Beside the polymers IX and X that polymer XI is another typical member of NANCP.



This polymer contains structural elements of the Koelsch radical [15], which is stable towards oxygen at room temperature.



The characteristic polynomials of all these polymers are given in Appendix I. Since the Coulson-Rushbrooke theorem [9] cannot be applied, no conclusion can be drawn about the occurrence of a NBMO band, which is typical for alternant non-classical polymers.

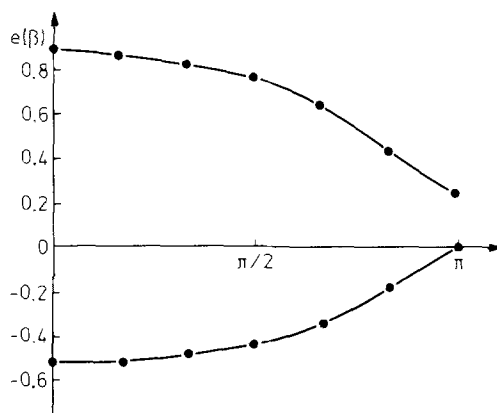
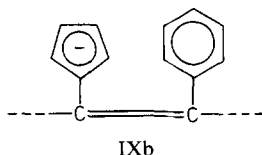


Fig. 3. Energy of the frontier bands of polymer IX

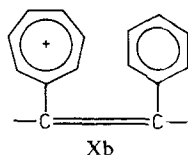
The polymer IX has 7 BMO- and 6 ABMO bands. The frontier bands are shown in Fig. 3. The highest BMO band is half-filled and has a width of about  $0.5\beta$  (1.2 eV).

If the HMO approximation provides a realistic description of the band structure of polymer IX, a metallic state should be anticipated.

However, the polymer IX could be stabilized under certain conditions, by accepting one electron per unit, thus forming the structure IXb; in this case the energy gap is reduced to:  $\Delta E_{\infty}(\text{IXb}) = -0.254\beta$ .



The polymer X has 7 BMO and 8 ABMO bands. The lowest ABMO band is half-filled. From an energetic viewpoint a more favourable structure, Xb can be achieved by losing one electron per unit. Hereby, the energy gap amounts to:  $\Delta E_{\infty}(\text{Xb}) = -0.445\beta$ .



The polymer VIII contain ring with an odd number of atoms, hence, the Coulson-Rushbrooke theorem [9] does not hold. Still, NBMO's appear due to the factors discussed in [16] (see the characteristic polynomial for polymer VIII given in Appendix I).

In Table 1 the specific delocalization energies of the polymers VIII to XI and those of their monomeric units are given. Polymer XI has the largest specific

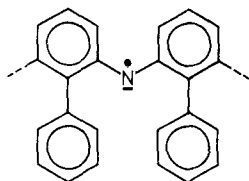
**Table 1.** Specific electron delocalisation energies of polymers VIII to XI, of their monomeric units, and of the Koelsch radical [15] (in  $\beta$  units)

	Polymer	Monomeric units
VIII	$4.297/\pi$	$3.965/\pi$
IX	$4.402/\pi$	$4.351/\pi$
X	$4.241/\pi$	$4.093/\pi$
XI	$4.473/\pi$	$4.310/\pi$
Koelsch radical		$4.386/\pi$

delocalization energy, comparable with that of Koelsch's radical, quoted also in Table 1. Since this radical is very stable [15], a considerable stability of polymer XI may be also expected. Thus, polymer XI offers possibly a real chance for the synthesis of a non-classical polymer.

#### 4. Nonclassical polymers with heteroatoms

The replacement of a carbon atom or a CH-group in a non-classical polymeric hydrocarbon by a heteroatom, e.g. N, results in the formation of a nonclassical heteropolymer. Thus, polymer XII is derived from polymer V.



XII

The nitrogen atom in XVII forms two  $\sigma$ -bonds, a lone pair, and contributes one electron to the  $\pi$ -system of conjugation. The Coulson-Rushbrooke theorem [9] does not apply to heteroatomic polymers. Therefore, as in the case of class 1 of nonalternant nonclassical polymers, a NBMO-band does not appear necessarily. And, indeed, polymer XII has no NBMO band as follows from its characteristic polynomial, given in Appendix I. We assume [17]  $h = 1$  for the Coulombic parameter of the nitrogen: It consists of 7 BMO- and 6 ABMO bands; as in the case of polymer V there occur 1 BMO and 1 ABMO which are infinitely narrow and are located at  $\pm\beta$ , respectively. The highest BMO band, occupied by only half of the electrons, is almost degenerate and ranges as follows:

$$0.319\beta \leq e_{7j} \leq 0.311\beta.$$

The energy gap between the highest fully occupied and the lowest empty band has the magnitude:

$$\Delta E_{\infty}(\text{XII}) = e_8(\omega_j = \pi) - e_6(\omega_j = \pi) = -1.409\beta.$$

### 5. Spin densities of alternant nonclassical polymers

In this discussion of the band structure of alternant non-classical polymers we have made use of the AMO version of the EHF method [6, 7] in order to refine the band structure with special regard to the energy gap. As pointed out in [18, 19], the AMO's are closely related to the Spin Density Waves (SDW), which may be well adopted for alternant non-classical polymers [1], where, as a consequence of the Coulson-Rushbrooke theorem [9], no charge alternations occur within the HF approximation. However, the AMO (SDW) formalism used in [1] cannot be applied without certain modifications to nonalternant and/or heteroatomic polymers which usually possess a very pronounced structure of net atomic charges. Therefore, we restrict our considerations here to alternant non-classical polymers.

Within the AMO-EHF (SDW) method the spin densities at starred and non-starred atoms,  $\rho_r$  and  $\rho_s$ , respectively, are expressed [1] as follows:

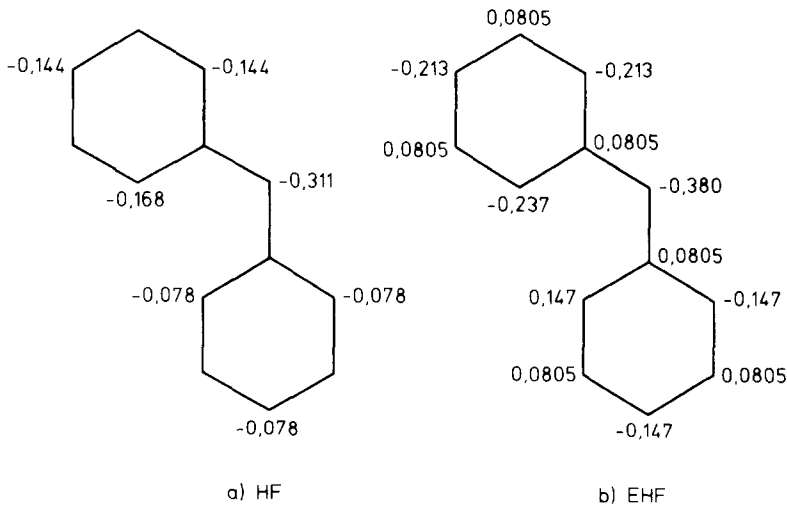
$$\begin{aligned}\rho_s &= q_s^\alpha - q_s^\beta = 2d_s^\alpha + 2\delta_s^\alpha \\ \rho_r &= q_r^\alpha - q_r^\beta = 2\delta_r^\alpha\end{aligned}\quad (10)$$

where  $\delta_s^\alpha$  and  $\delta_r^\alpha$  are the correlation corrections already used in Eq. (6).

In the ground state characterized by maximum multiplicity, all the electron spins are parallel ( $S = N/2$ ) and, hence, from Eqs. (8) and (10) one obtains

$$\begin{aligned}\rho_s &= q_s(\text{NBMO}) + 2\delta_s^\alpha \\ \rho_r &= 2\delta_r^\alpha.\end{aligned}\quad (11)$$

Within the HF approximation, the correlation corrections,  $\delta_s^\alpha$  and  $\delta_r^\alpha$ , vanish. Hence, the spin densities are equal to the contributions of the NBMO to the



**Fig. 4.** Distribution of spin density in the elementary unit of polymer I at  $p/N=0$ : a) in HF approximation; b) in EHF-AMO approximation

atomic electron charges, i.e. zero for the non-starred atoms. Their values for polymer III are shown in Fig. 4a; they are calculated from the NBMO coefficients as follows:

$$\begin{aligned}c_{1,j}^2 &= 4(c_{11,j})^2 = 4Q(\omega_j) \\c_{3,j}^2 &= (-c_{5,j})^2 = 2(1 - \cos \omega_j)Q(\omega_j) \\c_{7,j}^2 &= 2(1 + \cos \omega_j)Q(\omega_j) \\c_{9,j}^2 &= c_{13,j}^2 = 1/4(-c_{1,j})^2 = Q(\omega_j)\end{aligned}$$

where  $Q(\omega) = (13 + 12 \cos \omega)^{-1}$ .

In the case of  $N \rightarrow \infty$ , the charge densities are obtained by means of integrating the above expressions:

$$q_s(\text{NBMO}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} c_s^2(\omega) d\omega.$$

Taking into account Eq. (11), we obtain the total atomic spin-densities per unit of the ground state:

$$\rho^* = \sum_s^* \rho_s = 1 + 2 \sum_s^* \delta_s^\alpha \quad (12)$$

$$\rho = \sum_r \rho_r = 2 \sum_r \delta_r^\alpha = -2 \sum_s^* \delta_s^\alpha$$

wherein the condition [1]

$$\sum_s^* \delta_s^\alpha + \sum_r \delta_r^\alpha = 0 \quad (13)$$

is used. Eq. (12) implies that the total spin densities per unit at atoms belonging to different subsystems-starred and non-starred differ in magnitude and sign, i.e.  $\rho^* \neq \rho$ .

The two subsystems form two spin sublattices. Eq. (12), i.e.,  $\rho^* \neq \rho$ , correspond to a ferrimagnetic ground state of non-zero total spin ( $0 < S < N/2$ ) since the sublattices display antiparallel spins of different magnitude. The correlation corrections,  $\delta_s^\sigma$  and  $\delta_r^\sigma$ , and consequently the quantities  $\rho^*$  and  $\rho$  are calculated for polymers I, II and III. The result  $\rho^* \neq \rho^0$  not changed qualitatively; thus, these polymers have a ferrimagnetic ground state.

The correlation corrections,  $\delta_s^\sigma$  and  $\delta_r^\sigma$ , are different at different atoms. As discussed in [1], they are obtained by solving a system of  $(m - 1)$  coupled integral equations, where  $m$  denotes the number of AO per unit. The mean values of the correlation corrections for each subsystem of atoms:

$$\bar{\delta}^\sigma = \frac{1}{S} \sum_s^* \delta_s^\sigma$$

$$\delta^\sigma = \frac{1}{R} \sum_r \delta_r^\sigma$$

$$\sigma \in \alpha, \beta$$

are obtained quite easily [1]. The above relations and condition (13) yield the following equalities for the mean correlation corrections:

$$\delta^{*\sigma} = (R/S) \cdot \delta^\sigma$$

where  $S$  and  $R$  denote the number of starred- and non-starred atoms per unit, respectively. From this, the atomic spin densities (11) take the form:

$$\rho_s = q_s(\text{NBMO}) + 2\delta^{*\alpha}$$

$$\rho_r = 2\delta^\alpha$$

and for the total spin densities (12), we obtain:

$$\rho^* = 1 + 2R\delta^{*\alpha} \tag{14}$$

$$\rho = 2S\delta^\alpha.$$

The mean spin densities, calculated for polymer I, are shown in Fig. 4b.

The total spin densities calculated either according to Eq. (12) or by using the mean values of the correlation corrections do not differ substantially. In the case of polymer I, for instance, they read:

$$\rho^* = 1 + 2 \sum_s^* \delta_s^{*\alpha} = 1.375$$

$$\rho = 1 + 2s\delta^\alpha = 1.484.$$

The use of the mean values in the calculation of the spin densities is reasonable since the correlation corrections are obtained without any projection of the wave function [1], i.e., the magnitudes  $\delta_s^\sigma$  and  $\delta_r^\sigma$  obtained from  $(m-1)$  coupled integral equations (Eq. (18) in [1]) are not fully correct. Their calculation is rather lengthy. In contrast to that, as seen from Eqs. (19) and (20) of [1], the mean values  $\delta^*$  and  $\delta$  are obtained from a single integral equation. Since the spin densities do not differ substantially either the one or the other set of correlation corrections are used it seems to be reasonable to use the mean values.

## 6. Discussion

The magnetism and conductivity of non-classical polymers are of great interest. The theoretical treatment of the conductivity of non-classical polymers lies beyond the aims of the present paper and will be the subject of a future study.

The real polymers, if synthesized, will be three-dimensional ones. Unless strong valence interactions between the chains and the planes, respectively, form  $\sigma$ -bonds, the polymers will exist as quasi-one-dimensional or quasi-two-dimensional (of graphite type) systems. All the results obtained are qualitatively reliable if

the interaction between chains or planes remains weak-non-valent. In this case the restrictions imposed by the theorems [20, 21] which rule out spontaneous magnetization in one and two dimensions fail. Still, the problem whether the discussed results will be of practical interest for the polymer chemistry remains open, since it is hard to estimate the lifetime of non-classical polymers. However, due to the considerable delocalization energy they may be even more stable than the triphenylmethyl radical.

It is not easy to predict the effect of interchain or interplane interaction within the materials, if synthesized. These interactions may drastically change the electric and magnetic properties in some cases. Nevertheless, the chemistry of radicals has provided some rather surprising results as, e.g., it was in the case of the Koelsch radical [15].

On account of the above considerations, one may expect that the non-classical polymers represent some organic material exhibiting attractive physical properties.

### Appendix I

Here we give the characteristic polynomials for some of the polymers.

Polymer II:

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

Polymer III:

$$x(x^2 - 1)^3(x^2 - 4)(x^4 - 8x^2 + 13 - 2 \cos \omega) = 0.$$

Polymer IV:

$$x[x^{10} - 14x^8 + (68 - 4 \cos \omega)x^6 - (144 - 22 \cos \omega)x^4 + (131 - 32 \cos \omega + 4 \cos^2 \omega)x^2 - (40 - 12 \cos \omega + 4 \cos^2 \omega)] = 0.$$

Polymer V:

$$x(x^2 - 1)[x^{10} - 14x^8 + (70 - 2 \cos \omega)x^6 - (154 - 12 \cos \omega)x^4 + (147 - 16 \cos \omega)x^2 - 46 + 2 \cos \omega] = 0.$$

Polymer VII:

$$x(x^2 - 1)[x^4 - 8x^2 + 13 - 2 \cos \omega_1 - 2 \cos \omega_2 - 2 \cos(\omega_1 - \omega_2)] = 0.$$

Polymer VIII:

$$x[x^{10} - (13 + 2 \cos \omega)x^8 + (58 + 18 \cos \omega)x^6 + 2(1 + \cos \omega)x^5 - (106 + 48 \cos \omega)x^4 - 10(1 + \cos \omega)x^3 + (70 + 42 \cos \omega)x^2 + 12(1 + \cos \omega)x - 6(1 + \cos \omega)] = 0.$$



Polymer IX:

$$\begin{aligned} & x^{13} - (15 + 2 \cos \omega)x^{11} + (85 + 22 \cos \omega)x^9 + 2x^8 - (230 - 88 \cos \omega)x^7 \\ & - (18 + 4 \cos \omega)x^6 + (311 + 158 \cos \omega)x^5 + (50 + 24 \cos \omega)x^4 \\ & - (199 + 130 \cos \omega)x^3 - (50 + 36 \cos \omega)x^2 + (47 + 40 \cos \omega)x \\ & + 16(1 + \cos \omega) = 0. \end{aligned}$$

Polymer X:

$$\begin{aligned} & x^{15} - (17 + 2 \cos \omega)x^{13} + (144 + 26 \cos \omega)x^{11} - (387 + 130 \cos \omega)x^9 \\ & + 2x^8 + (711 + 316 \cos \omega)x^7 - (18 + 4 \cos \omega)x^6 + (701 + 392 \cos \omega)x^5 \\ & + (50 + 24 \cos \omega)x^4 + (342 + 238 \cos \omega)x^3 - (50 + 36 \cos \omega)x^2 \\ & - (63 + 56 \cos \omega)x + 16(1 + \cos \omega) = 0. \end{aligned}$$

Polymer XI:

$$\begin{aligned} & (x^2 - 1)^2(x^4 - x^3 - 5x^2 + 3x + 4)[x^{13} + x^{12} - (17 + 2 \cos \omega)x^{11} \\ & - (15 + 2 \cos \omega)x^{10} + (110 + 26 \cos \omega)x^9 + (84 + 22 \cos \omega)x^8 \\ & - (342 + 122 \cos \omega)x^7 - (218 + 86 \cos \omega)x^6 + (533 + 254 \cos \omega)x^5 \\ & + (263 + 142 \cos \omega)x^4 - (393 + 236 \cos \omega)x^3 - (127 + 92 \cos \omega)x^2 \\ & - (108 + 80 \cos \omega)x + 16(1 + \cos \omega)] = 0. \end{aligned}$$

Polymer XIII:

$$\begin{aligned} & x(x^2 - 1)[x^{10} - 14x^8 + (70 - 2 \cos \omega)x^6 - (154 + 12 \cos \omega)x^4 \\ & + (147 - 16 \cos \omega)x^2 - 46 + 2 \cos \omega] \\ & + h(x^2 - 1)(x^{10} - 12x^8 + 50x^6 - 88x^4 + 65x^2 - 16) = 0. \end{aligned}$$

In the last expression  $h$  is the parameter for the Coulomb integral of the nitrogen atom according to  $\alpha_N = \alpha + h\beta$ .

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