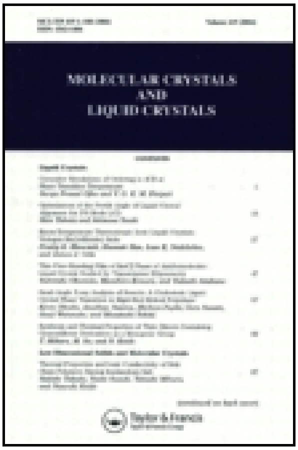

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A NEW CLASS OF NARROW-BAND ORGANIC POLYMERS WITH A FERROMAGNETIC GROUND STATE

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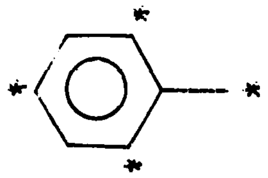
Abstract A new topological method predicting the number of nonbonding molecular orbitals (NBMO's) in organic molecules is elaborated. The method is a generalization of the Longuet-Higgins theorem and extends significantly the number of non-classical (non-Kekule) π -electron systems to alternant and non-alternant hydrocarbons and their heteroanalogues. The polymers of this type possess a band of degenerate NBMO's. A study of the spin correlation in the degenerate band shows that this group of nonclassical systems represents a new class of high-spin polymers, some of which probably with a ferromagnetic ground state.

INTRODUCTION

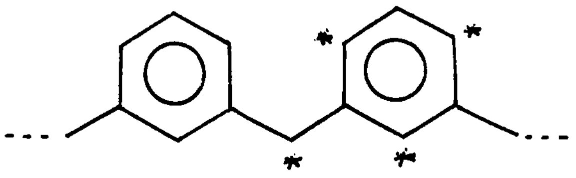
Recent experimental evidence for the existence of organic magnetism has been provided by the investigations of Miller et al.[1,2] on organic molecular systems containing metal atoms, and by the studies of Korshak and Ovchinnikov[3,4] on the synthesis of organic polymers with nitroxide radicals. Another area of active research has been based on the theoretical models of McConnell-Breslow[5-8] (see also the work of Buchachenko[9]) and the models of alternant non-classical (non-Kekule) polymers[10-17] (ANCP's).

The main idea determining the structural principle of ANCP's is connected to the theorem of Coulson-Rushbrooke-Longuet-Higgins (CRLH)[18-20]. According to this theorem, an alternant hydrocarbon (AH) containing s non-neighbouring starred atoms and r non-neighbouring non-starred atoms ($s > r$) possesses $s - r$ nonbonding MO's (NBMO's).

A classical example is the benzyl radical, for which $s - r = 4 - 3 = 1$



Polymer **1** , which is a typical example of an ANCP



1

has 4N starred atoms and 3N non-starred atoms, hence it has a band of N degenerate NBMO's (N is the number of units).

In π -electron approximation, ANCP's are isoelectronic to the high-spin carbenes studied by Itoh[21,22], Wasserman[23], Iwamura[24], Teki et al.[25,26], Sugawara et al.[27-29] (see also[30]).

The CRLH theorem is proved only for homonuclear systems. It provides sufficient , but not necessary, conditions for the presence of NBMO's in π -electron systems. With the present work, the studies on homonuclear ANCP's are extended to a wide class of alternant and nonalternant systems, as well as their heteroanalogues. For the purpose we utilize a generalization of the CRLH theorem. The latter is the basis of a structural principle of a new class of nonclassical polymers, denoted further on for short as QANCP's (Quasi ANCP's).

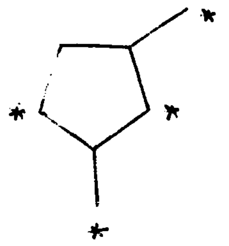
STRUCTURAL PRINCIPLE OF QANCP'S

The structural principle of QANCP's is based on a theorem which gives new, rather general conditions for the presence of NBMO's. Since the proof of the theorem is given in [31,32], we shall only formulate it here.

Theorem I:

From the N atoms of a given conjugated system let us select a subset T of homonuclear π-centers, which are not bonded by covalent bonds. Since the atoms of any pair t,t' $\in$ T are nonbonded, such a set is called nonbonded. Every Hückel graph is characterized by at least one nonbonded set T with a maximum number of π-centers N_t. The π-centers not belonging to the set T may also be heteronuclear. If for a given Hückel system $2N_t > N$ is fulfilled, then its energy spectrum displays at least $2N_t - N$ NBMO's.

As a first illustration, let us consider the nonalternant nonclassical hydrocarbon 2 and its heteroatomic analogue 2a



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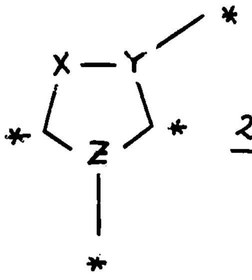


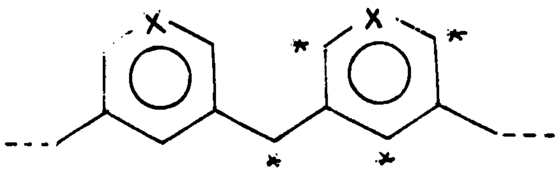
2a

The T-set atoms (vertices) in its Hückel graph are starred. Each system has one NBMO, since $2N_t - N = 2.4 - 7 = 1$.

The theorem is also valid for polymers, for which the condition $2N_t > N$ holds for every unit.

Corollary The coefficients in the LCAO-MO representation of the NBMO's can be non-zero only for the atomic orbitals of the maximum nonbonded set.

Polymers 3,4 and 5 are examples, for which the Theorem holds.



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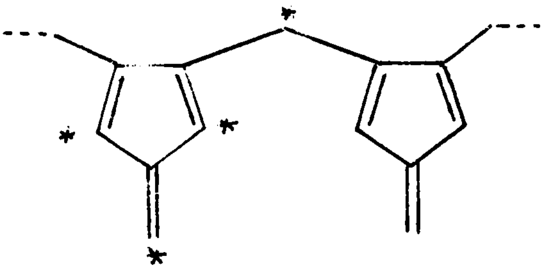
X = N, $\overset{+}{O}$, etc.



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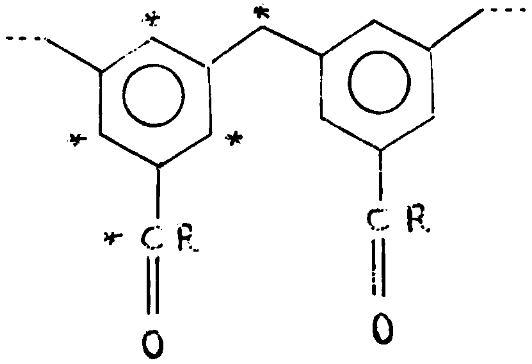


5

R = H, CH_3 or an arbitrary even alternant system.

The above examples illustrate the huge number of heteroatomic analogues and derivatives of alternant and nonalternant hydrocarbons, for which the Theorem holds.

ENERGY CHARACTERIZATION OF QANCP'S AND SPIN EXCHANGE INTERACTIONS

As in previous papers[13,15], the investigations of the band structure were carried out within the tight-binding approximation, a Hückel version of the Bloch method [33].

All studied polymers: 3 - 5 are characterized by a wide gap in which the NBMO band is situated. Since the Pairs-theorem of Coulson-Rushbrooke[18] is violated, the bands of the bonding MO's (BMO's) and antibonding MO's (ABMO's) are not symmetrical relative to the NBMO's, as with AH's (see Fig. 1).

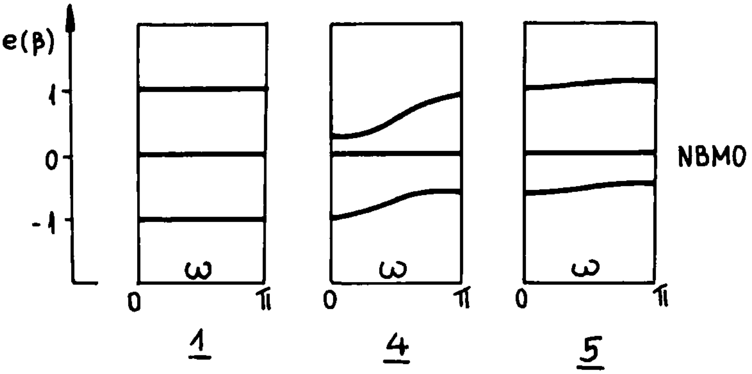
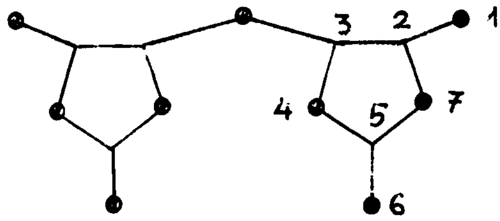


FIGURE 1. Energy dispersion relation of the frontier bands for polymers 1, 4 and 5. (With polymer 5 the following parametrization was used: $\alpha_0=\alpha+1.5\beta$, $\beta_{CO}=1.4\beta$.

QANCP's are polyconjugated systems. For some of them the delocalization energy may lead to a significant stabilization of the polymer. Let $\mathcal{E}$ denote the specific (per electron) delocalization energy. With polymer 3, taking $\alpha_0 = \alpha + \beta$, $\beta_{CN} = \beta$, one obtains : $\mathcal{E} = 1.498\beta$. The monomer specific delocalization energy of 3 , calculated

ELECTRON AND SPIN DENSITIES

QANCP'S are non-alternant systems. However,as with odd AH's (corollary 1 of Theorem I), their NBMO's contain only starred AO's (subset T). Consequently, the electron densities are non-zero only for starred AO's. Qualitatively, this is illustrated in the following scheme, where ● denote the π - centers of polymer **4** with non-zero electron densities .



The analogy between the two types of polymers: QANCP's and ANCP's, regarding the electron densities pertaining to the NBMO band, may be generalized also for the spin densities ρ_r:

$$\rho_r = \begin{cases} 0 & \text{- for non-starred atoms} \\ q_r & \text{- for starred atoms} \end{cases}$$

q_r are the charges calculated using the NBMO coefficients on condition that all NBMO's are occupied with electrons of parallel spins, i.e. S = N/2 . For example, for polymer **4**

$$q_1 = q_4 = q_7 = 1/\pi \int_0^{\pi} \frac{d\omega}{5 + 2\cos\omega} = 0.2182$$

$$q_6 = 1 - 3q_1 = 0.3\ 53$$

with the same parameters is $\mathcal{E} = 1.416\beta$. For comparison, the specific delocalization energy for the relatively stable triphenylmethyl radical[34] is $\mathcal{E} = 1.358\beta$. Consequently, the specific delocalization energy gained on "formation" of polymer 3 amounts to $\Delta\mathcal{E} = 0.082\beta$. Assuming the thermochemical value of β to be 80 kJ/m [35], the total delocalization energy gained on formation of polymer 3 is $\Delta E = 45.9$ kJ/m.

In the Hückel approximation, in which the CRLH- and the generalized theorem are derived, according to Hund's rule, the ground state of a polymer with N NBMO's has maximum multiplicity,i.e. the total spin equals[36]:

$$S = 1/2\ N\ (\text{NBMO's}) \tag{1}$$

In the case of ANCP's, $S = (s - r)/2$. This result follows from the considerations of Ovchinnikov[11], made more precise by Klein[12,37] and others[13]. For QANCP's, which are heteroanalogues of AH's, e.g. for polymers 3 and 5, the results of [12,13,36,37] can be directly generalized,i.e. for them equation (1) is valid. For non-alternant hydrocarbons and their heteroanalogues, for which Theorem I holds, eq.(1) is also valid. However, the generalization of the results in [11,12,36] in this case is not trivial and requires special investigation.

As with ANCP's, the Wannier functions of QANCP's are well localized on the units. For example, this is seen from Table 1, where the coefficients a_1 for polymer 4 are presented (see the numbering of the AO's of polymer 4).

TABLE 1 Coefficients $a_1(\tau) = a_1(\mu - \nu)$ for the NBMO Wannier functions of polymer **4**. μ and ν denote different units.

τ	$a_1(\tau)$	τ	$a_1(\tau)$
0	0.4620	3	-0.0013
1	-0.0485	4	0.0002
2	0.0076	5	$< -10^{-4}$

The good localization of the Wannier functions makes them appropriate (as with ANCP's[38-40])for the study of the spin coupling and the effect of the electron correlation in the polymers in question.

In papers [38,39] it was shown that the effective exchange integral in the Heisenberg Hamiltonian can be evaluated by:

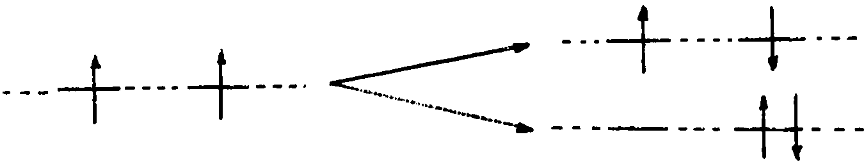
$$J_{eff} = 1/4 \left[E(\pi) - E_0 \right] = J - J_{kin} =$$

$$= J - 2\beta^2 / (U_0 - U_1 - 2J) \qquad (2)$$

In the above expression E_0 is the energy of the ferromagnetically aligned state, $S = N/2$, and

$$E(\omega) = E_0 + 4\left[J - 2\beta^2 / (U_0 - U_1 + 2J\cos\omega) \right] \sin^2(\omega/2) \qquad (3)$$

gives the dispersion law for the elementary excitations to homeopolar and ionic configurations



In the above expressions U_0 is the one-center (Hubbard type) Coulomb repulsion between electrons residing on the same Wannier function , and U_1 - the Coulomb integral between functions centered on adjacent units.

For small values of $2J/(U_0 - U_1)$, expression (2) transforms into the familiar from VB-theory of magnetism expression[41,42] $J_{eff} = J - 2\beta^2/(U_0 - U_1)$ (see also [43]).

The potential exchange J between adjacent Wannier functions is always positive, i.e. it favours the ferromagnetic order. The anti-ferromagnetic contribution depends on the values of , J, U_0 and U_1 . For polymer **4** , the following values (calculated with the approximation given in [40]) for the exchange and Coulomb integrals are obtained: $J = 0.254 eV$, $U_0 = 5.194 eV$, $U_1 = 3.203 eV$ .For these values equation (4) yields

$$J_{eff} = (0.254 - \beta^2/1.483) \text{ eV}$$

This implies that for $|\beta| < 0.613$ eV, which is the physically relevant range for the transfer parameter[39], $J_{eff} > 0$ .Hence polymer **4** exhibits a ferromagnetic alignment at T = 0° K. This conclusion corresponds to the results obtained for a cluster of **4**, composed of two monomer units. Calculations in the PPP-approximation including all doubly excited configurations, show that the energy of the triplet state is by 0.10 eV lower than that of the singlet state.

DISCUSSION

Since QANCP's are one-dimensional systems, ferromagnetic ordering can occur only for T = 0° K [44,45] .

However the actual crystal, for presumably synthesized QANCP's, is envisioned as a 3-dimensional system. Hence, even weak interactions between the separate polymer chains[40], may lead to the stabilization of the macroscopic spin configuration (magnetic ordering) at T > 0° K.

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