POLYMETHINE-STRUCTURAL PRINCIPLES OF π-CONJUGATED SYSTEMS WITH NON-BONDING MOLECULAR ORBITALS

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To the memory of Professor Oskar E. Polansky

Abstract

It is shown that the open shell homonuclear strepto-polymethines (PMs) are the structural principle of π-conjugated systems having non-bonding molecular orbitals (NBMO). The structure of these systems can be represented as intra- or intermolecular perturbation of one or more PMs.

1. Introduction

The presence of degenerate molecular orbitals (MOs), in particular non-bonding MOs (NBMOs), in a molecular π-system is an important requirement for the existence of high-spin states (Hund's rule). In the case of organic alternant homonuclear π-electron systems, the role of NBMOs for the existence of high-spin states has been demonstrated in the paper of Longuet-Higgins [1].

So far, the experimental and theoretical studies of purely organic high-spin systems have been focused mainly on alternant π-systems with direct (intramolecular) magnetic coupling of

electrons, occupying degenerate delocalized NBMOs [2-4]. Poly(1,3-phenylenemethylene)s and related compounds are typical examples of alternant non-classical (non-Kekule) polymers with a half-filled-band (HFB) of NBMOs.

The open shell strepto-polymethines (SPMs):

$$[\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H-....\overset{2m+1}{C}H_2]^{\bullet}$$
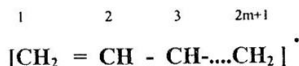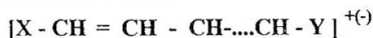
$$m = 0, 1, 2, ...$$

are the simplest π-electron systems having NBMO, as it follows from the Coulson – Rushbrooke – Longuet – Higgins (CRLH) theorem [1, 5, 6] (see Section 2).

The studies in this paper are also targeted at predicting the presence of NBMOs and stem from an idea of Dähne [7, 8] (see also Fabian and Hartman [9]), who shows that the closed shell PMs:

$$[\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H-....\overset{2m+1}{C}H_2]^{+(-)}$$
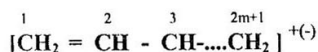
$$m = 0, 1, 2, ...$$

and their α, ω-substituted derivatives

$$[X - CH = CH - CH-....CH - Y]^{+(-)}$$

X, Y –atoms of groups IV, V and VI of the Periodic Table

are structural principles of the organic colorants. Most of the organic colorants contain closed shell polymethine fragments as structural units [7-10]. "The deep color is inherent to the ideal polymethine state" [7].

2. Sufficient Topological Condition for the Occurrence of NBMOs in Organic π-Systems

In the majority of π-electron systems the presence of NBMOs is due to molecular topology. There are three theorems providing sufficient *but not necessary* conditions for the presence of NBMOs in π-electron systems.

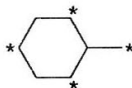### 2a. Coulson-Rushbrooke-Longuet-Higgins theorem (CRLH)
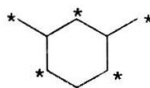
An alternant π-system has:

$$N = S^* - R \tag{1}$$

NBMOs, where {S*} and {R} are the set of the starred and non-starred π-centres, respectively [1, 5, 6]. Typical examples are the open-shell PMs e. g., nonamethine, benzyl radical and *m*-quinodimethane:

$$N = 5^* - 4 = 1 \text{ NBMO}$$

$$N = 4^* - 3 = 1 \text{ NBMO} \qquad N = 5^* - 3 = 2 \text{ NBMOs}$$

2b. Generalized (extended) CRLH theorem

The CRLH theorem has been generalized [11, 12]. In the CRLH theorem one always considers two subsets of homonuclear nonbonded π-centres: the subset of starred and the subset of non-starred π-centres. In the generalized theorem only one subset of nonbonded π-centres is responsible for the appearance of NBMOs. It has been shown [7, 8] that a system with M π-centres and a maximum set of M* homonuclear disjoint π-centres must have at least:

$$N = 2M^* - M \tag{2}$$

NBMOs. A typical example is tetramethylene-ethylene:

CRLH   Extended CRLH

$$3^* - 3^0 = 0 \text{ NBMO} \qquad 2 \times 4^* - 6 = 2 \text{ NBMO}$$

According to the CRLH theorem tetramethylene-ethylene should have no NBMOs. Actually, it has two NBMOs, as it follows from the generalized theorem.

The NBMOs are present even if the π-system is nonalternant and if the π-centres belonging to the disjoint subset are heteroatomic. Representative examples are the heteronuclear nonalternant systems:
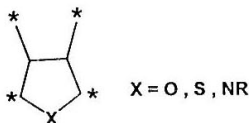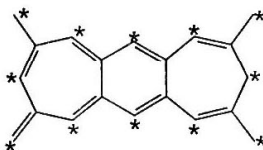
$$N = 2 \times 4^* - 7 = 1 \text{ NBMO}$$

investigated in the papers of Berson et al. (see [13, 14] and the references therein), the triaza-analogous of the benzyl radical:
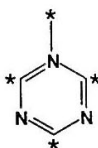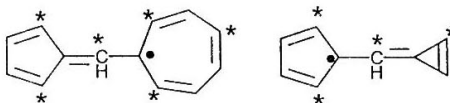

$$2 \times 4^* - 7 = 1 \text{ NBMO}$$

or the tetraradical with 4 NBMOs:

$$2 \times 12^* - 20 = 4 \text{ NBMOs}$$

The CRLH- and the extended theorems provide only sufficient, but not a necessary condition for the presence of NBMOs in a Hückel system. There exist many π-systems having NBMOs for which eq. (2) is not fulfilled. For the non-classical (non-Kekule) non-alternant systems:

1   **2**

is $2M^* - M = -1$, but the systems have one NBMO. The presence of a NBMO follows from the theorem of Sachs [15] (see also [16-20]).

2c. Sachs's theorem

Let us consider a conjugated hydrocarbon with N π-centres and characteristic polynomial [15-20]:

$$P_N(x) = \det | x.\mathbf{I} - \mathbf{A} | = \sum_{n=0}^{N} a_n x^{N-n} \tag{3}$$

where $\mathbf{A}$ is the Hückel matrix, and $\mathbf{I}$ is the unity matrix.

If a Hückel system has at least one NBMO, then the free term in the characteristic polynomial (3) $a_N = 0$, and vice versa. In the general form the condition:

$$a_N = 0 \tag{4}$$

is necessary and sufficient for the existence of at least one NBMO in a Hückel system. The value of a_N in the polynomial (3) can be determined by means of the Sachs's theorem [17] (see also [18,19]). In accordance with the theorem, the coefficient a_N in eq. (4) can be calculated by means of the equation:

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

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 subgraphs;

$r(s)$ is the number of simple rings (with even or with odd number of π-centres).

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

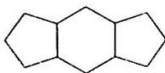In accordance with eq. (5), the condition (4) for the existence of a NBMO reads:

$$a_N = \sum_{s \in S_N} (-1)^{c(s)} \cdot 2^{r(s)} = 0 \tag{6}$$

For structure 1 or similar systems with different odd-numbered rings there is a set of two subgraphs: S_1 and S_2. However, S_1 and S_2 are of different parity, so that the two terms in eq. (6) cancel each other:

$$S_1 \rightarrow c(s_1) = 4 \qquad\qquad S_2 \rightarrow c(s_2) = 5$$
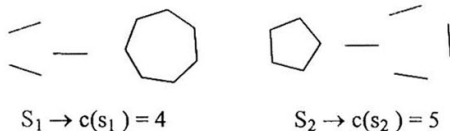
$a_N = (-1)^4 \, 2 + (-1)^5 \, 2 = 0$, and **1** has one NBMO.

The existence of a NBMO in s-indacene

can also be explained with the theorem of Sachs [16].

2d. Other Criteria for the Occurrence of NBMOs: Systems, for which the presence of NBMO results from the symmetry

In some cases the occurrence of NMBOs can result not from molecular topology but from other factors, such as symmetry. Sometimes, it may happen incidentally.
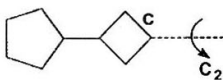
3

The characteristic polynomial of the above hydrocarbon **3** reads:

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

where $c = \beta_c/\beta_0$ denotes the ratio of the resonance integral of the bond **c** and the standard one. If the hydrocarbon belongs to the symmetry group C_{2v} ($c = 1$), and $a_N = 0$, then the hydrocarbon has 1 NBMO.

3. Method of Investigation and Derivation of the Fundamental Relations
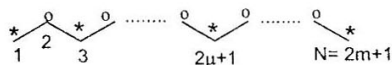
3a. Intramolecular Perturbation in Polymethines

Let us denote by

$$|NB> = \sum_{\mu}^{\cdot} C_{\mu} |\mu>$$
(7)

the NBMO (according to [1,5,6,12] the NBMO contains AOs only of the starred set), and by

$$|k> = \sum_{\mu}^{\cdot} A_{k\mu} |\mu> + \sum_{\nu} B_{k\nu} |\nu>$$

the other MOs of a PM with 2m-1 AOs:

The MO energies of the PM are equal to:

$$E_k = <k|H_o|k>, \quad E_o = <NB|H_o|NB>$$

If we denote by $|i>$ the wave function of the polymethine, in LCMO representation:

$$|i> = \sum_k D_{ik} |k> + d |NB>$$

the energy matrix has a block form:

$$\varepsilon_o = \begin{vmatrix} E_o & [0] \\ \\ [0] & D \end{vmatrix}$$

where **D** is a diagonal matrix with matrix elements $\{E_k\}$.

Let us consider a perturbed PM arising by linking of two (or more) π-centres: σ-th and ρ-th, belonging to different subsets, starred and non-starred, respectively (see Fig. 1):

$$\overset{o}{\sigma}\text{——}\overset{\star}{\rho}$$

If the Hamiltonian of the perturbed PM is $H = H_o + h$, then the matrix elements:

$$<NB|h|NB> = C_\sigma C_\rho \beta_{\sigma\rho} \quad = 0$$

$$<NB|h|k> = \Sigma C_\sigma \beta_\sigma$$

$$|k> = \sum_\mu C_\sigma A_{k\mu} <\sigma|h |\mu> + \sum_\nu C_\sigma B_{k\nu} <\sigma|h |\mu> = 0$$

vanish, because $C_\sigma = 0$. Hence, the NBMO also does not interact with the other MOs, i. e. the perturbed system has at least one NBMO.

Examples of systems with NBMOs arising from intramolecular perturbation in different polymethine chains are collected in Fig.1.
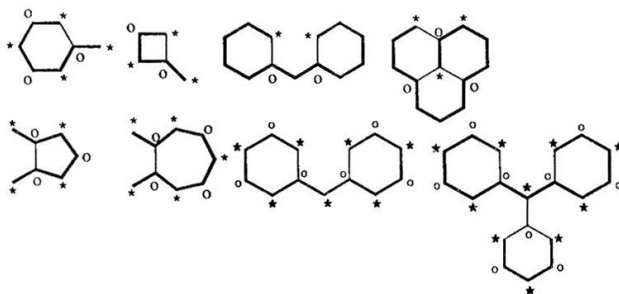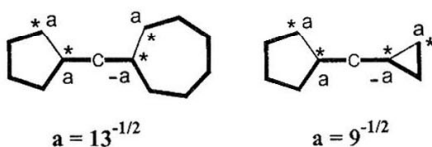
Fig. 1. Systems with NBMOs arising from intramolecular perturbation in
polymethine chains.

Special cases are the π-electron systems

$$a = 13^{-1/2} \qquad\qquad a = 9^{-1/2}$$

In these cases the matrix element <NB|h|NB> vanishes, because there are two terms with
opposite sign.

3b. Intermolecular Perturbation in Polymethines

Essentially, the structural principle of this kind of π-systems, arising from intermolecular
perturbation, follow from the theorem of Dewar [21,22] (Chapter VI, p. 228/229 in ref. [21]).
Let us consider a system **RS** formed by the 'union' of fragments **R** and **S**. The theorem of
Dewar reads [21]:

"If **RS** is formed by union of **R** with **S** in such a way that the coefficients of one MO Φ_μ of **R**
vanish at all points of union with **S**, then Φ_μ survives unchanged in **RS**".

If Φ_μ of **R** is a NBMO, it survives unchanged in RS. Some examples are shown in Fig. 2.
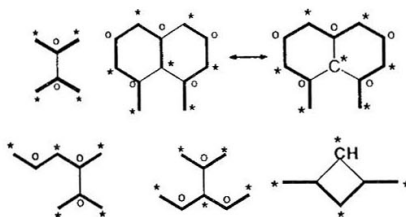
Fig. 2. Systems with NBMOs arising from intermolecular perturbation.

When the presence of NBMOs is not due to molecular topology (as in **3**), the discussion in Sections *3a* and *3b* is not valid, since eq. (7) does not hold.

3c. Derivatives of Polymethine Systems with NBMOs

The following corollaries rooted in the generalized CLHR theorem [12] extend substantially the set of π-systems with polymethine structural principle possessing NMBOs.

Corollary I

If the π-conjugated system has various maximal disjoint sets, R_k, $k = 1, 2,...K$, then the NBMOs are composed only of the AOs of their intersection

$$R_1 \cap R_2 \cap ......\cap R_k.$$

The Hückel graph:
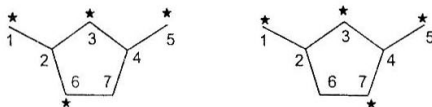
has two maximal disjoint subsets of cardinality 4. Thus the NBMO is composed of AOs of centers 1, 3 and 5.

Corollary II

Let us consider a system consisting of a subunit **R**, for which the extended CRLH theorem is valid (i. e., **R** has one or more NBMOs) and which is linked with an even π-alternant closed-shell subunit **M**:

$$\textbf{R} ...... \textbf{M}.$$

If the π-centre(s) r of R which is (are) connected to the π-center(s) m of M, belong to the set of the non-starred atoms $\{R\}$ (the MO coefficients $C_r = 0$), then all NBMO coefficients in the fragment M are zero, i. e., the NBMO coefficients are nonzero only for the starred π-centres in R, and the NBMOs are strictly localized within the subunit R.

If an even π-system has q^* stared and $q^o = q^*$ non-starred π-centres, there are two maximum disjoint sets in M, comprising m. In the first subset m is starred and in the second subset m is non-starred. Hence, it follows from *Corollary* I that all NBMO coefficients in the fragment M are zero [23].

The above speculations lead directly to the following conclusion:

If the π-centre(s) of a polymethine subsystem R with coefficient(s) in the NBMO(s) $C_r = 0$ is/are linked to a π-subsystem of M type, the NBMO(s) survive(s) in the united system. This is illustrated by the examples shown in Fig. 3.
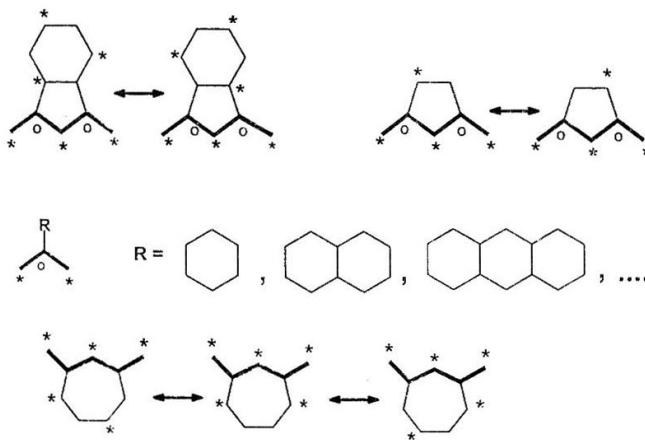

Fig. 3. Systems with NBMOs due to localization of the NMBO within the polymethine fragment.

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