Monatshefte für Chemie 136, 1573–1578 (2005)
DOI 10.1007/s00706-005-0343-6

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Structure and Energy Spectra of a Class of Non-*Kekule* Polymethine Dyes: A Theoretical Study

Nikolai Tyutyulkov[1,2], **Nedko Drebov**[2], and **Fritz Dietz**[1,*]

[1] Universität Leipzig, Wilhelm-Ostwald-Institut für Physikalische
und Theoretische Chemie, D-04103 Leipzig, Deutschland
[2] University of Sofia, Faculty of Chemistry, Chair of Physical Chemistry,
BG-1126, Sofia, Bulgaria

Received November 15, 2004; accepted December 21, 2004

Summary. It is shown that the extended *Coulson-Rushbrooke-Longuet-Higgins* theorem is the structural principle of a class of 1-D polymethine systems with nonbonding MOs and a small HOMO-LUMO gap. From this point of view the structural and spectroscopic properties of a class of pyridocyanine dyes earlier investigated can be interpreted.

Keywords. Polymethine dyes; Energy spectra; Molecular structure; Topology.

Introduction

The extensive search of polymethine systems with long-wavelength absorption maxima is determined by their multilateral applications. In the excellent papers of *Dähne* [1] and *Fabian* and *Hartmann* [2, 3] it is shown that "pathological" molecules [3] as **1** (Fig. 1) are an essentially new class of polymethine systems which should show remarkably long-wavelength absorption in contrast to the well known iso-π-electronic pyridocyanine molecules **2a** and **3a** (see Fig. 1) [3]. Numerical results [2, 3] for some examples show that the molecules of type **1** have one nonbonding MO (NBMO) which determines the low HOMO-LUMO gap. However, in these papers [2, 3] no explanation is given why the NBMOs arise in these π-systems. The consideration of this problem determines the aim of the present work. Based on this study a considerable extension of the group of polymethine systems with low excitation energies and long-wavelength absorption up to the NIR spectral region can be expected.

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[*] Corresponding author. E-mail: dietz@quant1.chemie.uni-leipzig.de

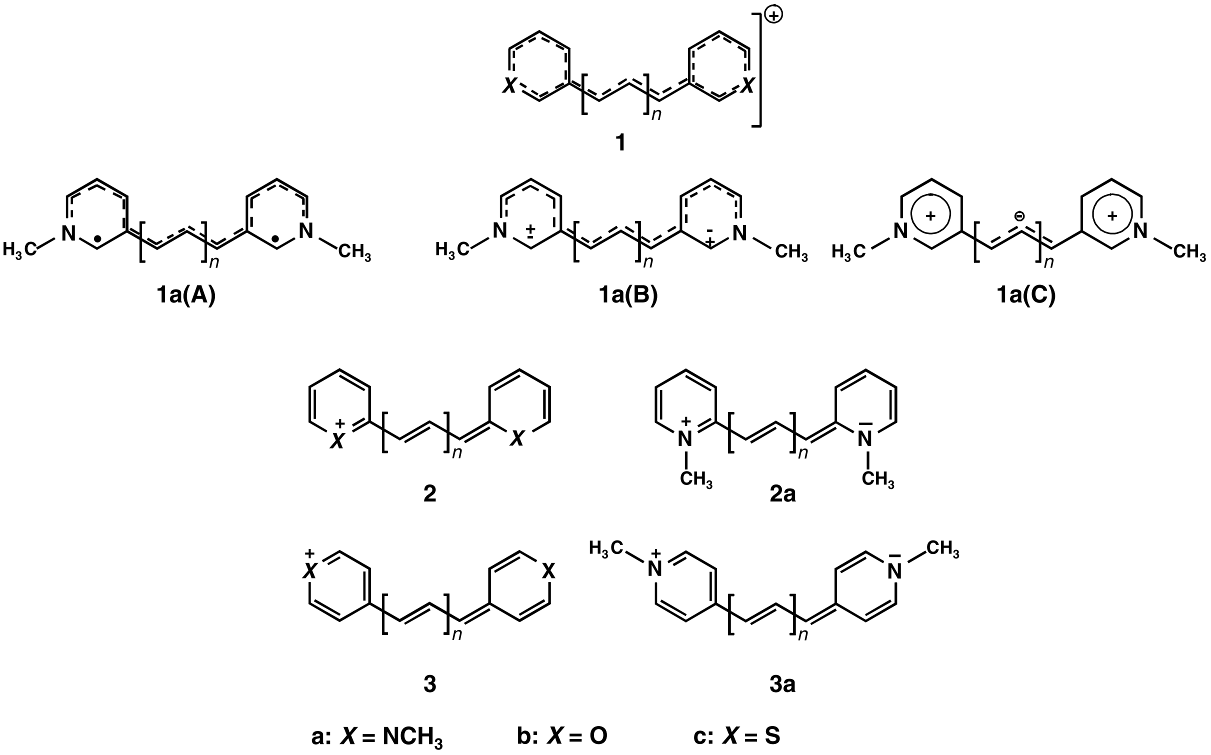


Fig. 1. Iso-π-electronic polymethines **1–3** and the corresponding isomeric pyridocyanines **1a–3a**

Theoretical Background

There are two types of non-*Kekule* radicals (topological diradicals) which possess NBMOs:

i) homonuclear alternant non-*Kekule* π-systems, and
ii) quasi-alternant non-*Kekule* π-systems.

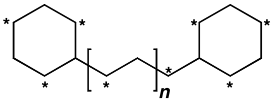
Homonuclear Alternant Non-Kekule π-Systems

The fundamental idea determining the structural principle of the alternant non-classical (non-*Kekule*) radicals and polyradicals with NBMOs follows from the *Coulson-Rushbrooke-Longuet-Higgins* (*CRLH*) theorem [4–6]. According to this theorem a homonuclear alternant π-system (hydrocarbon) has at least N (Eq. (1)) NBMOs, where S^* and R° are the number of the starred and unstarred π-centers.

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

In such systems for which the *CRLH* theorem is valid every unstarred C atom is connected with one or two starred C atoms and *vice versa*. A typical example is the monodiradical **4** shown in Scheme 1 which has 1 NBMO (Eq. (2)).

$$N = S^* - R^\circ = (n+7) - (n+6) = 1 \text{ NBMO} \tag{2}$$



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Scheme 1

Quasi-Alternant Non-Kekule π*-Systems*

The application of the *CRLH* theorem is limited *only* to homonuclear alternant π-electron systems, i.e., alternant hydrocarbons (AH). The theorem provides a sufficient but not necessary condition for the presence of NBMOs in the π-electron systems.

The theorem has been extended [7–9]. The extended *Coulson-Rushbrooke-Longuet-Higgins* theorem (*ECRLH*) is applicable to a more comprehensive set of π-systems which possess NBMOs. Molecules for which the *ECRLH* theorem is valid are designated as quasi-alternant non-classical (non-*Kekule*) (QANC) π-systems [9].

Within the *CRLH* theorem one always considers two subsets of homonuclear nonbonded π-centers: the subset of starred $\{S^*\}$ and the subset of unstarred $\{R^\circ\}$ ones. According to the *ECRLH* theorem [7, 8] only one subset of nonbonded (disjoint) π-centers is responsible for the appearance of NBMOs. A system with M π-centers and a maximum set of starred homonuclear nonbonded (disjoint) π-centers $\{S^*\}$ must have at least N (Eq. (3)) NBMOs.

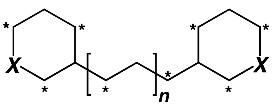
$$N = 2S^* - M \tag{3}$$

The NBMOs are present even if the π-system is non-alternant and if the π-centers belonging to the nonstarred subset $\{R^\circ\}$ are heteroatomic.

Application of the *ECRLH* Theorem

The polymethines **5** to **7** (Scheme 2, here, only the molecular topology is depicted) arising by substitution of non-starred methine groups in the parent hydrocarbon **4** with $X = \mathrm{N}Me$, O or S, are typical examples of QANC polymethines. All these molecules have 1 NBMO as it follows from Eq. (3) (see Eq. (4))

$$N = 2S^* - M = 2(n+7) - (13+2n) = 1 \text{ NBMO} \tag{4}$$



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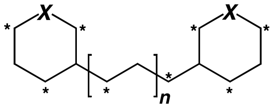

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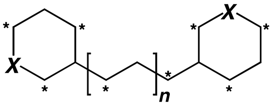

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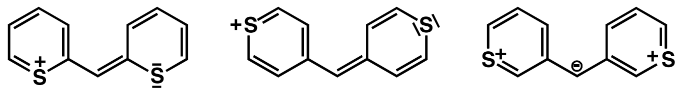
Scheme 2



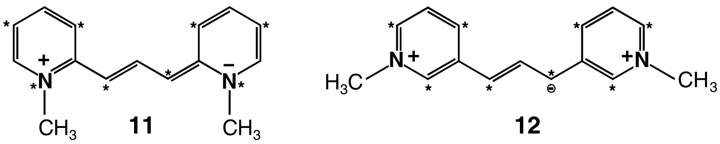
8 **9** **10**

$\Delta E = 2.40$ eV ($\lambda_{max} = 517$ nm)

$\Delta E = 2.44$ eV ($\lambda_{max} = 508$ nm)

$\Delta E = 1.51$ eV ($\lambda_{max} = 823$ nm)

Scheme 3



11 **12**

$\Delta E_{calc} = 2.32$ eV ($\lambda_{max} = 534$ nm) $\Delta E_{exp} = 2.16$ eV ($\lambda_{max} = 575$ nm)

$\Delta E_{calc} = 2.01$ eV ($\lambda_{max} = 618$ nm)

Scheme 4

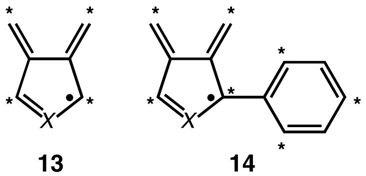
The calculated values of the transition energy, ΔE, for the longest wavelength S_0–S_1 $\pi\pi^*$ transition for the sulphur-containing polymethine systems **8** to **10** are given in Scheme 3 (*PPP* calculation based on AM1 optimized geometries, parameters: $I_S = 20$ eV, $\gamma_{SS} = 9.94$ eV, $\beta_{CS} = 1.9$ eV).

It can be seen that the ΔE values for the system with a NBMO (**10**) is significantly smaller and therefore a longest-wavelength absorption is situated in the NIR region in comparison with the polymethines without a NBMO (**8** and **9**). In a similar relation are the numerical results for the pyridocyanines **11** and **12** given in Scheme 4. The values are taken from Ref. [3].

The polymethines **1** are only a special case of a large class of quasi-alternant non-classical polymethine systems arising from the parent non-classical non-*Kekule* homonuclear monoradical (**4**). The NBMO is present even if the π-system is non-alternant and if the π-centers belonging to the unstarred subset $\{R^\circ\}$ are heteroatomic [7, 8]. Examples for non-alternant heteronuclear monoradicals with a NBMO are the π-systems **13** and **14** (Scheme 5) synthesized by *Berson et al.* [10, 11].

The above QANC radicals can be used as subunits of QANC polymethine molecules. Examples are shown in Scheme 6.

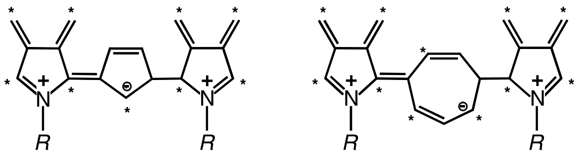
A very important example of a stable neutral monoradical with one NBMO is the aza substituted phenalenyl radical (2-azaphenalenyl radical is shown in Scheme 7)



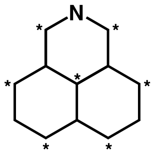
13 **14**

X **= N*R*, O, S**

Scheme 5

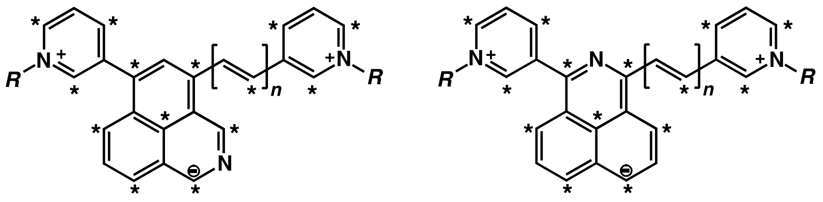


Scheme 6



7* x 2 - 13 = 1 NBMO

Scheme 7



ΔE = 2.05 eV (λ = 604 nm) **ΔE = 1.84 eV (λ = 672 nm)**

Fig. 2. Structures of pyridocyanines with a 2-azaphenalenyl building block

which has been recently synthesized and characterized by *Rubin et al.* [12]. With this radical as a building block polymethine systems of type **1** having one NBMO should be candidates for compounds with extremely long-wavelength absorption. Some examples for corresponding pyridocyanines are given in Fig. 2.

Conclusions

In this paper it is shown that the extended *Coulson-Rushbrooke-Longuet-Higgins* theorem is the basis of a structural principle of a new class of non-classical polymethine systems with one NBMO. Their longest-wavelength absorption maxima should be significantly bathochromic shifted in comparison with the iso-π-electronic molecules without a NBMO. A practical significance of these quasi-alternant non-classical (non-*Kekule*) polymethines is that they should absorb in the near infrared spectral region.

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft.

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