A New Type of Non-Kekulé Diradicals with Triplet Ground States. I. Polymethine Systems

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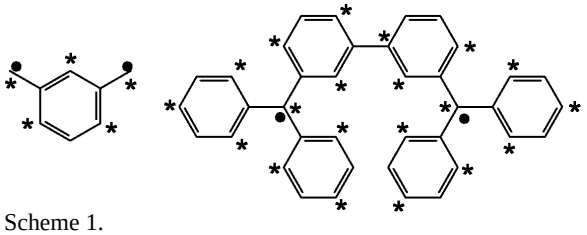
It is shown theoretically that the ground state of a new class of non-Kekulé polymethine molecules can be a triplet state with non-degenerate singly occupied MOs. The investigated polymethine cyanine cations, polymethine oxonol anions, and neutral polymethine merocyanines are derivatives of the stable 2-azaphenalenyl radical whose pentamethine fragment is part of the polymethine chain.

Key words: Non-Kekulé Polymethines, Triplet Diradicals, Polymethines with Low Excitation Energies

Introduction

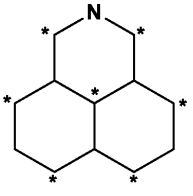
The organic molecular systems with triplet ground state – triplet diradicals – are usually molecules with π-systems featuring degenerate frontier molecule orbitals (MOs), in particular non-bonding MOs (NBMO).

The presence of NBMOs in alternant non-classical (non-Kekulé) radicals and polyradicals is determined by the topology of the molecule, as it follows from the Coulson-Rushbrooke-Longuet-Higgins theorem (CRLH) [1, 2] and the extended CRLH theorem [3, 4]. Examples are the *m*-quinodimethane [5] and the stable Schlenk triplet diradicals [6] shown in Scheme 1.

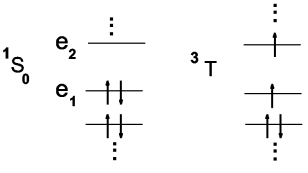


Scheme 1.

According to the extended CRLH theorem, NBMOs are present even if the π-system is non-alternant, and if the π-centers belonging to the non-starred subset $\{R^{\circ}\}$ are heteroatomic [3, 4]. A very important example of a stable monoradical with one NBMO is 2-azaphenalenyl radical which has been synthesized by Rubin *et al.* [7] (Scheme 2).



Scheme 2.



Scheme 3.

In the one-electron approximation the condition for the existence of a triplet ground state in a molecule is (see Scheme 3):

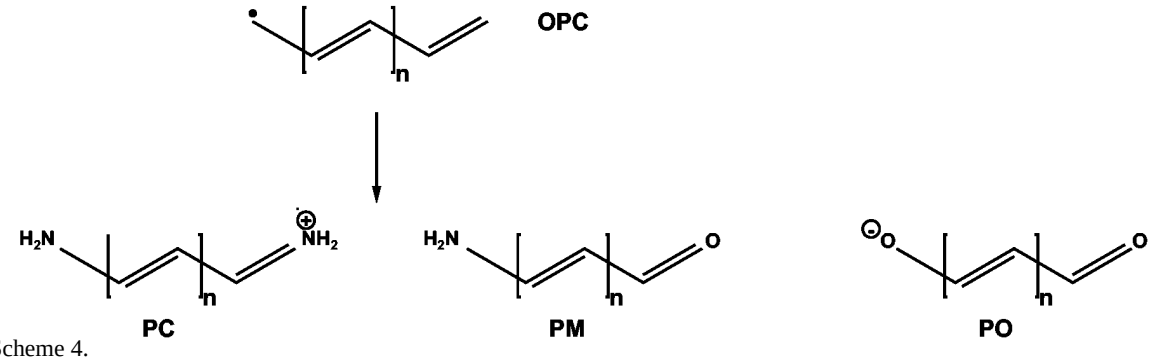
$$E(S) - E(T) = \Delta E_{ST} > 0$$

$$E(S) - E(T) = e_1 - e_2 + I_{11} - I_{12} - K_{12} = \Delta e + I_{11} - I_{12} - K_{12} > 0$$

or

$$\Delta e - I_{12} > I_{11} - K_{12} \qquad (1)$$

In eq. (1), I_{ik} and K_{lm} are two-electron Coulomb and exchange integrals, respectively. For the singlet-triplet



Scheme 4.

gap one obtains (if $\Delta e = 0$):

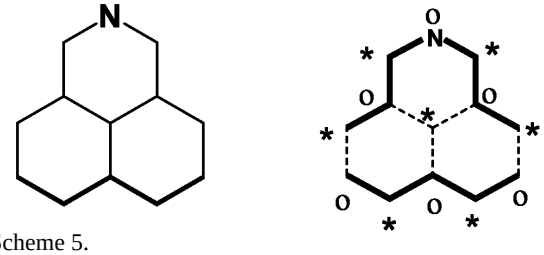
$$E(S) - E(T) = I_{11} - I_{12} + K_{12} \qquad (2)$$

Obviously, eq. (1) is satisfied for molecules with degenerate NBMOs ($\Delta e = 0$, and $I_{12} > I_{11}$). It would also be satisfied for some molecules without degenerate frontier MOs if the energy gap $\Delta e \ll 1$ (if the energy gap tends to zero: $\Delta e \to 0$). A more precise condition for the existence of a triplet ground state in a molecular system must (should) include the electron correlation (see Section 3). Theoretical predictions for molecules without singly occupied degenerate frontier MOs with triplet ground states or very small singlet-triplet gaps are given in the refs. [8–10]. In a recent paper of Wudl *et al.* [11] it has been shown theoretically that the ground state of large polyacenes corresponds to an open-shell singlet diradical. Experimentally produced hydrocarbons with triplet ground states have been investigated in refs. [12–14].

In this paper, which has preliminary character, we consider a ***special*** class of non-Kekulé molecules which can have a triplet ground state, namely polymethine molecules with non-degenerate singly occupied MOs.

Structural Principle of the Investigated Non-Kekulé Polymethine Molecules

The molecules with classical polymethine systems (**PS**) (polymethine dyes) consist of a one-dimensional (1-D) polymethine chain (**OPC**) with an odd number of methine groups linked by atoms of elements of the groups III, V or VI of the Periodic Table in α and ω positions [15–17]. The three main groups of 1-D polymethines (streptopolymethines) are the polymethine-streptocyanine cations (**PC**), the neutral polymethine-streptomerocyanines (**PM**), and



Scheme 5.

the polymethine-streptooxonol anions (**PO**), shown in Scheme 4.

The monoradical **OPC** is the essential structural fragment within the PSs. A characteristic feature of the OPC is the presence of an NBMO, *which follows from the topology of these systems*.

The fundamental idea determining the structural principle of this new class of PSs, namely non-Kekulé polymethines (**NPM**) investigated in the present paper, is related to the polymethine concept of Dähne and Kulpe [18]. In accordance with this conception, the **PC**, **PM** and **PO** follow the "structural principles of unsaturated organic compounds" [18].

In ref. [19] it has been shown that the OPCs exhibit π-conjugated systems with NBMOs. The structure of these systems can be represented by intramolecular or intermolecular perturbations of the 1-D polymethine chain.

As in the case of classical polymethine systems, the NPMs are also derivatives of OPCs. One structural moiety is the pentamethine chain. However, the pentamethine system is for itself a structural fragment within the 2-azaphenalenyl radical possessing a NBMO. This is shown in Scheme 5.

In Fig. 1 the NPMs investigated in this paper are presented.

The new types of polymethines under consideration are non-Kekulé π-electron systems, because no classi-

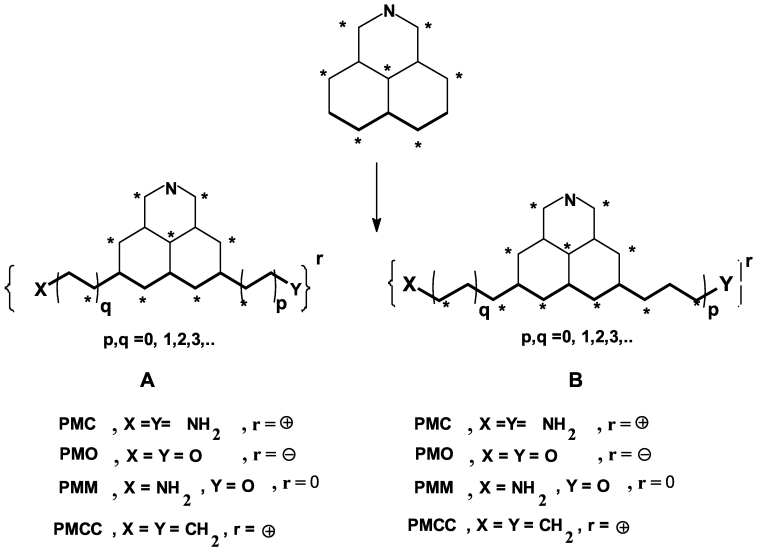
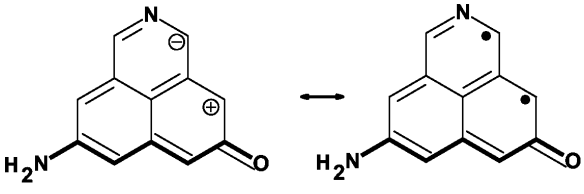


Fig. 1. Investigated NPM molecules.



Scheme 6.

cal (no Kekulé) formula can be attributed to the molecules as illustrated in Scheme 6.

The NBMO in these NPMs is strictly localized within the 2-azaphenalenyl fragment. This important structural feature follows from the consideration given below. In the case of homonuclear alternate radicals $\mathbf{R}^\bullet$ the same result was obtained by Dewar [20].

Let us consider a monoradical $\mathbf{R}^\bullet$ for which the CRLH theorem or the ECRLH theorem [1–4] is valid, *i. e.*, $\mathbf{R}^\bullet$ has one or more NBMOs and is linked to one (or more) subunit(s) **M**:

$$\mathbf{R}^\bullet - \mathbf{M}$$

The subunit (fragment) **M** can be a closed-shell or an open-shell π-system. We denote by Φ_r and by Φ_m the MOs of the separate (non-interacting) fragments $\mathbf{R}^\bullet$ and **M**:

$$\Phi_\mathrm{r} = \sum_\mu \mathrm{C}_{\mathrm{r}\mu}\varphi_\mu\,, \quad \Phi_\mathrm{m} = \sum_\nu \mathrm{C}_{\mathrm{m}\nu}\varphi_\nu$$

and by Φ_n the corresponding NBMO (with $\langle\Phi_\mathrm{n}|\mathbf{H}|\Phi_\mathrm{n}\rangle = \mathrm{E(NBMO)}$. According to refs. [1–4] the NBMO of the radical fragment contains AOs only of the starred basis set $\{R^*\}$:

$$\Phi_\mathrm{n} = \sum_\mu \mathrm{C}^*{}_{\mathrm{n}\mu}\varphi_\mu$$

In LCMO representation the wave function of the polymethine molecule $\mathbf{R}^\bullet - \mathbf{M}$ is given by:

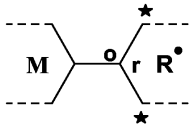
$$\Psi = \mathrm{A}\sum_\mathrm{r} \mathrm{A}_\mathrm{r}\Phi_\mathrm{r} + \mathrm{B}\sum_\mathrm{m} \mathrm{A}_\mathrm{m}\Phi_\mathrm{m} + \mathrm{C}\Phi_\mathrm{n}$$

If the π-center **r** of $\mathbf{R}^\bullet$, which is connected to the π-centers m of **M**, belongs to the set of the non-starred atoms $\{\mathrm{R}^\circ\}$ (the MO coefficients are $\mathrm{C}_\mathrm{r}\mu = 0$, Scheme 7), then the matrix elements of the one-electron Hamiltonian **H** are given by

$$\langle\Phi_{\mathrm{r(m)}}|\mathbf{H}|\Phi_\mathrm{n}\rangle = 0$$

and the energy matrix of the molecule $\mathbf{R}^\bullet - \mathbf{M}$ has the following block form:

$$\mathbf{E} = \begin{vmatrix} \langle\Phi_\mathrm{r}|\mathbf{H}|\Phi_\mathrm{r}\rangle & \langle\Phi_\mathrm{r}|\mathbf{H}|\Phi_\mathrm{m}\rangle & [0] \\ \langle\Phi_\mathrm{m}|\mathbf{H}|\Phi_\mathrm{r}\rangle & \langle\Phi_\mathrm{m}|\mathbf{H}|\Phi_\mathrm{m}\rangle & [0] \\ [0] & [0] & \langle\mathrm{NB}|\mathbf{H}|\mathrm{NB}\rangle \end{vmatrix}$$



Scheme 7.

This means that the NBMO is strictly localized within the radical fragment $\mathbf{R}^\bullet$. The subsystem **M** includes all

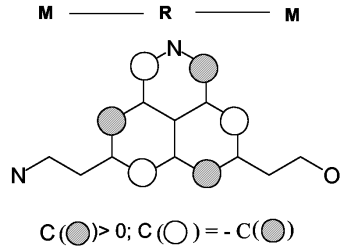


Fig. 2. Localization of the NMBO wave function within the 2-azaphenalenyl fragment of the polymethine **A-PMM** (**p** = **q** = **1**) (see Fig. 1).

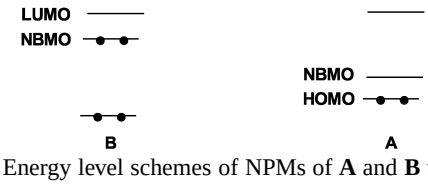
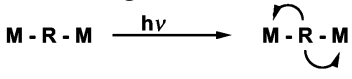


Fig. 3. Energy level schemes of NPMs of **A** and **B** type (see Fig. 1).

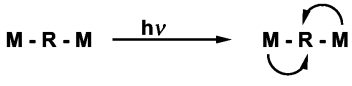
coefficients $C_{m\nu}(\mathbf{M}) = 0$. Obviously, the above considerations are valid also for NPMs, *i. e.*, for $\mathbf{M} - \mathbf{R}^{\bullet} - \mathbf{M}$ systems. This is illustrated in Fig. 2 for the structure **A-PMM** (**p** = **q** = 1) shown in Fig. 1.

In the case of the NPMs of type **B** (the number of the π-centers N in fragments **M** is even, N = 2n, see Fig. 1) the NBMO is occupied, *i. e.*, the NBMO is the HOMO. For NPMs of type **A** (the number of the π-centers N in **M** is odd, N = 2n + 1, see Fig. 1) the NBMO is vacant, *i. e.*, the NBMO is the LUMO (see Fig. 3).

The excitation of NPM molecules is associated with a substantial charge-transfer from the 2-azaphenalenyl fragment $\mathbf{R}^{\bullet}$ to the fragments **M** for NPMs of type **B**,



and from the fragments **M** to the 2-azaphenalenyl fragment $\mathbf{R}^{\bullet}$ for NPMs of type **A**,



In the ground state the total spin density of the 2-azaphenalenyl fragment of type **A**, **PMC** (**p** = **q** = **1**, see Fig. 1) is equal to (PPP method [21, 22]):

$$Q = \sum_i q_i = 12.264,$$

and in the excited state (HOMO-NBMO transition):

$$Q^* = \sum_i q^*_i = 12.948.$$

Table 1. Values of the energy differences, $\Delta\varepsilon$(S) (CISD correction of the closed-shell singlet energy), and $\Delta\varepsilon(T) = {}^3E - E_0$ (triplet energy minus closed-shell singlet energy) of **PMC**, **PMO**, **PMCC**, and **PMCA**, type **B** molecules (**p** = **q** = 1, see Fig. 1 and Scheme 9), calculated by means of the PPP-CI method [20 – 22]. Two-center atomic Coulomb repulsion integrals were calculated with the approximations of Mataga-Nishimoto (M) [24], and Ohno (O) [25], respectively. $\Delta\varepsilon_{calc}$ and $\Delta\varepsilon_{exp}$ are the calculated (PPP method) and the experimental excitation energies (of the longest-wavelength singlet-singlet transition) of the streptopolymethine cyanine and streptopolymethine oxonol, respectively, with 11 methine groups. All values are in eV.

NPM	$\Delta\varepsilon$(S)	$\Delta\varepsilon$(T)	$\Delta\varepsilon_{calc}$	$\Delta\varepsilon_{exp}$
PMC (M)	−0.55	0.62	1.34	1.69 [30]
PMC (O)	−0.38	1.09	1.60	
PMO (M)	−0.75	−1.00	1.60	1.83 [31]
PMO (O)	−0.65	−0.79		
PMCC (M)	−0.37	0.85	1.55	
PMCA (M)	−0.45	0.95	1.55	

Methods of Investigations

Because the structural principles of the investigated non-Kekulé polymethine molecules (NPMs) were introduced as a π-electron model, the first numerical results have been obtained in π-electron approximation with the Pariser-Parr-Pople (PPP) method [21 – 23]. For our calculations, the configuration interaction includes all the singly and doubly excited configurations in the (5|5) active space. The calculations were carried out using standard parametrization of the resonance integrals [23]. The two-center atomic Coulomb repulsion integrals were estimated using the Mataga-Nishimoto approximation [24] and the Ohno approximation [25], respectively.

Numerical results were obtained also with the semi-empirical AM1-CI method [26 – 28] (see Table 3, AM1-CI/CAS(m,m) method [27], considering all the excited configurations within the subspace of **m** occupied MOs and **m** unoccupied MOs, m = 5 in the case of **PMM** systems, and m = 6 for **PMO** and **PMC** systems, respectively).

Ab initio [29] geometry optimizations and CI calculations were carried out using the 6-31G* standard basis set. The CI includes singly and doubly substituted configurations (frozen-core (CISD)).

Numerical Results and Discussion

In Tables 1 – 3 are presented the calculated values of the energy differences, $\Delta\varepsilon$(S), as CISD corrections of the closed-shell singlet energy, and $\Delta\varepsilon(T) = {}^3E - E_0$, the triplet energy minus the closed-shell singlet energy,

Table 2. Values (in eV) of the energy differences, $\Delta\varepsilon$(S) and $\Delta\varepsilon$(T), for the **PMM**, type **B** molecules, with different values of **p** and **q** (see Fig. 1), calculated by means of the PPP-CI method [20 – 22] (see the text in Table 1). Two-center atomic Coulomb repulsion integrals were calculated with the approximations of Mataga-Nishimoto (M) [24] and Ohno (O) [25], respectively.

p	**q**	Method	$\Delta\varepsilon$(S)	$\Delta\varepsilon$(T)
1	1	M	−1.30	−1.50
1	1	O	−1.22	−1.36
0	1	M	−1.39	−1.56
0	1	O	1.28	−1.45
2	1	M	−0.85	−1.50
2	1	O	−0.79	−1.32
3	1	M	−1.41	−1.45
3	1	O	−1.21	−1.32

Table 3. Calculated values (in eV) of the energy differences, $\Delta\varepsilon$(S) and $\Delta\varepsilon$(T) (see Scheme 9) and the singlet-triplet splitting energies, ΔE_{ST}, of the **PMO** and **PMM**, type **A** molecules, with different polymethine chain length (p, q, see Fig. 1). The results are obtained by means of the AM1-CI method.

NPMs	**p**	**q**	$\Delta\varepsilon$(S)	$\Delta\varepsilon$(T)	ΔE_{ST}*
PMO	0	0	−1.22	−0.95	−0.27
PMO	1	1	−1.28	−1.37	0.09
PMO	2	2	−1.04	−1.18	0.14
PMO	3	3	−0.87	−1.05	0.18
PMM	0	0	−1.01	−1.10	0.09
PMM	1	1	−1.09	−1.67	0.58
PMM	2	2	−0.97	−1.53	0.56
PMC	0	0	−1.19	−0.25	−0.94
PMC	1	1	−0.99	0.10	−1.09
PMC	2	2	−0.90	0.06	−0.96
PMC	3	3	−0.60	0.28	−0.88
PMC	4	4	−0.35	0.47	−0.82

* $\Delta E_{ST} = \Delta\varepsilon(S) - \Delta\varepsilon(T)$.

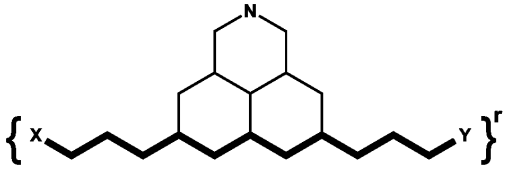
for the investigated molecules. From the data of Table 1 it follows that the ground states of **PMC**, **PMCC**, and **PMCA**, type **B**, ($p(q) \leq 3$, see Fig. 1 and Scheme 9), should be singlets, but a triplet state should be the ground state of **PMO**, about 0.2 eV below the singlet state.

In Table 2 are summarized the CISD corrections of the lowest-lying singlet and triplet states, respectively, of compounds **PMM**, type **B**, with different values of p and q (Scheme 10). For all the **PMM** molecules the triplet states lie below the closed-shell singlet states, *i. e.*, the ground state is clearly the triplet diradical state.

Values of the correlation correction of the singlet and triplet states, respectively, and the singlet-triplet splittings calculated with the AM1-CI method in Table 3 show that the merocyanines (**PMM**) and the

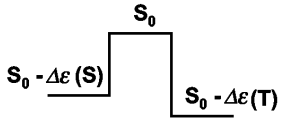
Table 4. Calculated values (*ab initio* method, CISD/6-31G*, in a. u.) of the total energies of the lowest lying singlet (E(S)) and triplet states (E(T)), the singlet-triplet splittings, $\Delta E_{ST} = E(S) - E(T)$ (closed shell singlet state energy – triplet state energy, also in eV) of the **NPM**, type **A** molecules, $\mathbf{p} = \mathbf{q} = 0$ (see Fig. 1).

NPM	E(S)	E(T)	ΔE_{ST}	ΔE_{ST} (eV)
PMO	−662.509569	−662.537272	0.027703	0.75
PMM	−643.197050	−643.251843	0.054793	1.49
PMC	−623.790403	−623.781959	−0.008444	−0.23

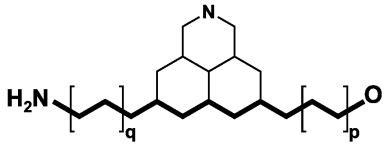


PMC, X = Y = NH_2, r = ⊕ **PMO, X = Y = O, r = ⊙**

PMCC, X = Y = CH_2, r = ⊕ **PMCA, X = Y = CH_2, r = ⊙**



Schemes 8 and 9.



Scheme 10.

oxonols (**PMO**), both of type **A**, should have triplet ground states. With an increase of the length of the polymethine chain the singlet-triplet splitting increases and the stability of the triplet ground state is increased.

In Table 4 the values of the total energies of the lowest lying singlet and triplet states are collected, and the singlet-triplet splitting energies of the type **A** polymethine cyanines (**PMC**), polymethine oxonols (**PMO**), and polymethine merocyanines (**PMM**) with $p = q = 0$ (Fig. 1). The ground state of the polymethine cyanine (**PMC**, $p = q = 0$) is a singlet state, but the ground states of the corresponding oxonol (**PMO**) and merocyanine (**PMM**) are clearly triplet states with relatively large singlet-triplet splitting energies.

The relative stability of the singlet and triplet ground states of the considered NPMs was also examined at the DFT level of theory using a B3LYP hybrid functional and a 6-31G* basis set. The results (see Table 5)

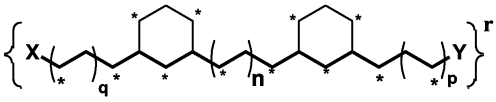
Table 5. Energies (in eV) for the singlet-triplet gaps (between the optimised triplet states and the open-shell singlet states, ΔE(T-OS), and the optimised triplet state and the closed-shell singlet states, ΔE(T-CS)), spin contaminations for the open-shell singlet states ($\langle S^2 \rangle$), and energy differences between open-shell and closed-shell singlet states (ΔE(OS-CS)) obtained with B3LYP functional (6-31G* basis set).

NPM	p	q	ΔE(T-OS)	ΔE(T-CS)	$\langle S^2 \rangle$	ΔE(OS-CS)
PMO	0	0	0.14	0.04	0.63	−0.10
PMO	1	1	−0.15	−0.52	0.98	−0.37
PMM	0	0	−0.06	−0.27	0.75	−0.22
PMM	1	1	−0.38	−0.81	0.93	−0.43
PMC	0	0	0.89	0.89	0.00	0.00
PMC	1	1	0.44	0.44	0.00	0.00

are in perfect agreement with those obtained through the AM1-CI method (Table 3). Additionally, unrestricted broken symmetry B3LYP calculations have also been performed for the singlet states. The ground state of **PMC**s ($\mathbf{p} = \mathbf{q} = 0, 1$) is obtained to be a closed-shell singlet state. It was found that for systems **PMM** there is a low lying open shell singlet state below the closed-shell singlet state. However, the ground state is predicted to be a triplet state. For **PMO** systems the B3LYP calculations show that the ground state is an open-shell singlet ($\mathbf{p} = \mathbf{q} = 0$), but as the number of ethylene units is increased ($p = q = 1$), it becomes a triplet state.

The numerical results obtained with different methods lead to the same qualitative conclusions concerning the character of the ground state of the investigated NPMs: For **PMC**, **PMCC**, and **PMCA** ($\mathbf{p}(\mathbf{q}) < \mathbf{1}$), the ground state is a closed-shell singlet state. With the number of methine groups ($p = q \geq 0$) increasing, the ground state of the **PMO** molecules also becomes a triplet state. The largest $\Delta\varepsilon(T)$ values have been calculated for **PMM** molecule in which the fragments **M** are of donor-acceptor type (see ref. [32]).

Investigations are in progress to develop PM derivatives of other radicals, *e. g.*, substituted diphenylmethyl radicals as shown in Scheme 11, or other alternant or quasialternant systems with NBMO.



X = Y = NH$_2$, r = ⊕
X = Y = O , r = ⊖
X = NH$_2$, Y = O , r = 0
X = Y = CH$_2$, r = ⊕

Scheme 11.

Conclusions

The numerical results presented in this paper characterize potential structures of a new class of non-Kekulé polymethine systems (NPM) possessing very low excitation energies and longest-wavelength absorptions in the visible or NIR spectral region. In some cases the ground state is a triplet state with non-degenerate singly occupied MOs. This new type of PSs is a very large class of π-electron systems of which the results have been given only for NPM systems which are derivatives of the 2-azaphenalenyl radical.

Acknowledgement

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[1] C. A. Coulson, G. S. Rushbrooke, Proc. Cambridge Phil. Mag. **36**, 193 (1940).
[2] C. A. Coulson, H. C. Longuet-Higgins, Proc. Roy. Soc. London **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447 (1948); **A195**, 188 (1948).
[3] N. Tyutyulkov, O. E. Polansky, Chem. Phys. Lett. **139**, 281 (1987).
[4] S. Karabunarliev, N. Tyutyulkov, Theoret. Chim. Acta **76**, 65 (1989).
[5] M. S. Platz, in W. T. Borden (ed.): Diradicals, p. 195, Wiley, NY (1982).
[6] E. Müller, I. Müller-Rodloff, Liebigs Ann. Chem. **517**, 134 (1935).
[7] S. Zheng, J. Lan, S. I. Khan, Y. Rubin, J. Am. Chem. Soc. **125**, 5786 (2003).
[8] P. Baumgartner, E. Weltin, G. Wagniere, E. Heilbronner, Helv. Chim. Acta **48**, 751 (1965).
[9] R. Hoffmann, J. Am. Chem. Soc. **90**, 1475 (1968).
[10] G. J. Gleicher, D. D. Newkirk, J. C. Arnold, J. Am. Chem. Soc. **95**, 2526 (1973).
[11] M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, F. Wudl, J. Am. Chem. Soc. **126**, 7416 (2004).
[12] J. Michl, J. Kole, J. Am. Chem. Soc. **92**, 4148 (1970).
[13] H. Angliker, E. Rommel, J. Wirz, Chem. Phys. Lett. **87**, 208 (1982).
[14] D. R. McMasters, J. Wirz, J. Am. Chem. Soc. **123**, 238 (2001).
[15] W. König, Ber. Dtsch. Chem. Ges. **55**, 3306 (1922).
[16] W. König, J. Prakt. Chem. **112**, 1 (1926).

[17] N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz, A. Tader, Polymethine Dyes – Structure and Properties, St. Kliment Ochridski University Press, Sofia, Bulgarien (1991).
[18] S. Dähne, S. Kulpe, Structural Principles of Unsaturated Organic Compounds, Akademie-Verlag, Berlin (1977).
[19] N. Tyutyulkov, F. Dietz, A. Tadjer, MATCH (Commun. Mathem. and Computer Chemistry) **53**, 99 (2005).
[20] M. J. S. Dewar, MO Theory of Organic Chemistry, p. 229, McGraw-Hill Book Comp., New York, (1969).
[21] R. Pariser, R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).
[22] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).
[23] J. Fabian, G. Tröger-Naake, J. Prakt. Chem. **318**, 801 (1976).
[24] N. Mataga, K. Nishimoto, Z. Phys. Chem. **13**, 140 (1957).
[25] K. Ohno, Theoret. Chim. Acta **11**, 145 (1964).
[26] J. J. J. Stewart, MOPAC: A General Molecular Orbital Package, (Version 7.2), Quantum Chemistry Program Exchange (1995).
[27] S. Karabunarliev, M. Baumgarten, K. Müllen, J. Phys. Chem. **A 102**, 7029 (1998).
[28] SPARTAN 04, Wavefunction, Inc., Irvine, CA (1997).
[29] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. M. Montgomery (Jr.), T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strani, O. Farkas, D. K. Malick, D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople. Gaussian, Inc., Wallingford, CT (2004).
[30] S. S. Malhotra, M. C. Whiting, J. Chem. Soc. (London) 3812 (1960).
[31] T. S. Sorensen, J. Am. Chem. Soc. **87**, 3673 (1965).
[32] H. Meier, Angew. Chem. **117**, 2536 (2005).