A Class of Non-Kekulé Molecules with Low Excitation Energies

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Dedicated to Professor Dr. Jürgen Fabian on the occasion of his 70th anniversary

A class of non-Kekulé molecular systems with a new structural principle and low excitation energies or with a triplet ground state was investigated theoretically. The systems consist of a non-Kekulé monoradical, possessing a non-bonding molecular orbital linked in a specific way to another monoradical.

Key words: Non-Kekulé Molecules, Triplet Diradicals, Molecular Systems with Low Excitation Energies

Introduction

In this communication we consider a class of non-Kekulé molecules with a new structural principle and with (very) low excitation energies. The structural principle and the peculiarity of the investigated systems are described in detail in the following section.

The investigations presented in the paper are an extension of the studies in lit. [1], in which the same structural principle determines the very low excitation energy of a group of polymethine mono-radicals.

## Structural Principle of the Investigated Molecules

π Systems with NBMOs determined by the molecular topology

There are two classes of π systems with non-bonding molecular orbitals (NBMO) determined by the molecular topology: homo-nuclear alternant systems and quasi-alternant systems, respectively.

Homonuclear alternant radicals

The presence of NBMOs in alternant non-classical (non-Kekulé) radicals and polyradicals follows from the Coulson-Rushbrooke-Longuet-Higgins (CRLH) theorem [2, 3]. According to this theorem, a homonuclear alternant π-electron system (hydrocarbon) has at least

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

7* - 6 = 1 NBMO   2 x 7* - 13 = 1 NBMO   2 x 4* - 7 = 1 NBMO

Scheme 1.
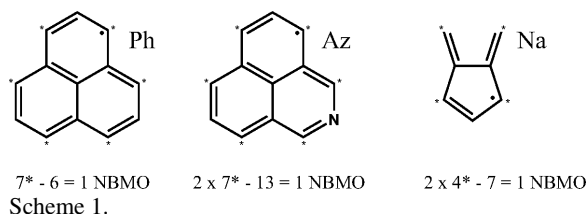
NBMOs, where $\{S^*\}$ and $\{U^\circ\}$ are the number of the starred and un-starred π centers, respectively. In such systems, for which the CRLH theorem is valid, every un-starred C° atom is connected with one or two starred C^* atoms and *vice versa*. An example is the phenalenyl radical (Ph) shown in Scheme 1 (here and below only one resonance formula is depicted).

Quasi-alternant radicals

The application of the CRLH theorem is limited to homonuclear alternant systems, *i. e.*, alternant hydrocarbons. The theorem has been extended (ECRLH) [4, 5]. Radicals for which the ECRLH theorem is valid are designated as quasi-alternant non-classical (non-Kekulé) (QANC) radicals [6].

Within the CRLH theorem one always considers two subsets of homonuclear non-bonded π centers: the subset of starred $\{S^*\}$ and the subset of un-starred $\{U^\circ\}$ ones. According to the ECRLH theorem [4, 5] only one subset of non-bonded (disjoint) π centers
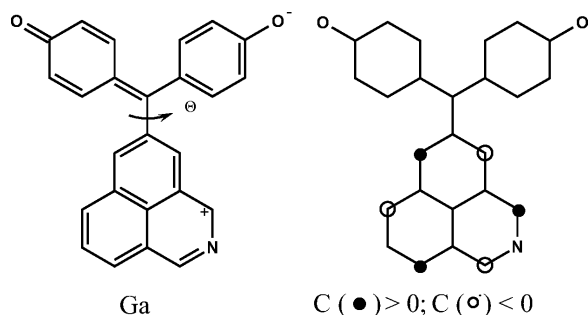
Ga $C(\bullet) > 0; C(\circ) < 0$

Fig. 1. Localization of the NBMO within the Az fragment of the Az$^\bullet$–Ga$^\bullet$ system.

Pm(n)   Wz-1

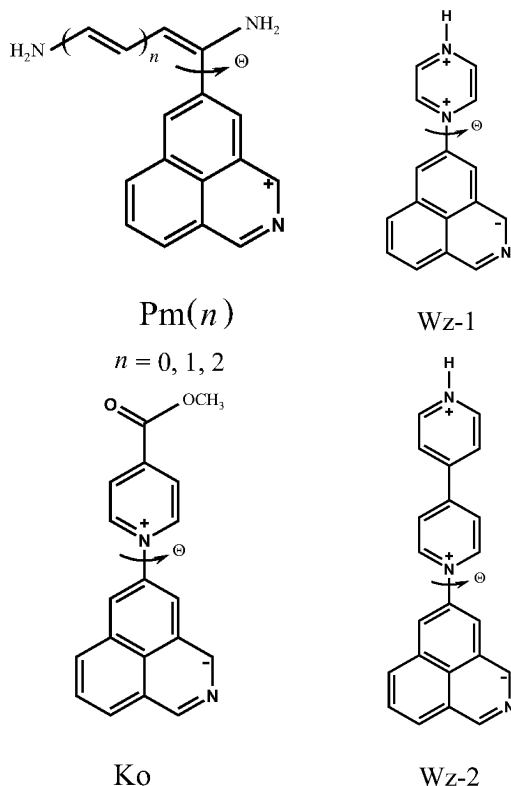$n = 0, 1, 2$

Ko   Wz-2

Fig. 2. Investigated molecules. The Az radical is linked with polymethine radicals with an even number of methine groups, Pm(n), a Kosower-type radical, Ko, and Weitz-type radicals, Wz-1(2). The molecule Ga with the galvinoxyl radical is shown in Fig. 1.

is responsible for the appearance of NBMOs. A system with M π centers and a maximum set of starred homonuclear non-bonded (disjoint) π centers $\{S^*\}$ must have at least

$$N = 2S^* - M \qquad (2)$$

NBMOs.

The NBMOs are present even if the π system is non-alternant and if the π centers belonging to the non-starred subset $\{U^\circ\}$ are heteroatomic or non-alternant systems. Typical examples are the stable 2-azaphenalenyl radical (Az), which has been synthesized and characterized by Rubin *et al.* [7], and the non-alternant radical (Na) (see Scheme 1).

The following corollary rooted in the ECRLH theorem (for a proof, see [5] and [1]) determines the structural principle of the investigated non-Kekulé molecules.

Let us consider a π system consisting of a radical subunit R$^\bullet$, for which the CRLH or ECRLH theorem is valid, *i. e.*, R$^\bullet$ has one NBMO, linked with a mono-radical M (the radical M$^\bullet$ has no NBMO):

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

If the π center r of R$^\bullet$ which is connected with a starred π center s of M$^\bullet$ belongs to the set of the non-starred atoms $\{U^\circ\}$ the MO coefficient $C^\circ_r = 0$, then all the NBMO coefficients in the fragment (radical) M$^\bullet$ are zero, *i. e.*, the NBMO coefficients are non-zero only for the starred π centers in R$^\bullet$, and the NBMO is strictly localized within the subunit (radical) R$^\bullet$. The localization of the NBMO within the Az fragment of a R$^\bullet$–M$^\bullet$ system which consists of Coppinger's radical (galvinoxyl) [8] and the Az radical is illustrated in Fig. 1.

Objects of Investigations

The investigated systems are shown in Fig. 2. In all systems the radical subunit R$^\bullet$ is the Az radical connected with a Kosower radical [9] Ko, a Weitz-type radical [10 – 12] Wz-1(2), or polymethine radicals [13 – 15] (with an even number of methine groups between the terminal groups) Pm(n).

Computational Methods

Numerical results were obtained with the semiempirical AM1 method [16] using the MOPAC 97 program package. Numerical results were obtained also with AM1/CIS (m,n), AM1/CISD (m,n) and AM1/CAS (m,n) methods using an upgraded version of the MOPAC program [17]. m and n are the numbers of the MOs determining the active CI space. For more detailed studies of the ground state multiplicity of the Wz-2 system, *ab initio* and DFT methods were also performed (GAUSSIAN 03 [18]).

Table 1. Calculated values [AM1/CAS(16,16)] of the longest-wavelength singlet-singlet, $\Delta E_S(1,2)$, and singlet-triplet transitions, $\Delta E_T(1,2)$, for the investigated molecules (Figs. 1 and 2). $f_{1(2)}$ are the corresponding oscillator strengths. All entries are in eV. Θ represents the AM1 optimized dihedral angles in degrees.

Molecule	Θ	$\Delta E_S(1)$	$f_1 \times 10^3$	$\Delta E_S(2)$	$f_2 \times 10^3$	$\Delta E_T(1)$	$\Delta E_T(2)$
Pm(0)	45.0	1.28	8	2.98	25	1.16	2.40
Pm(1)	44.7	0.75	2	2.68	100	0.69	2.14
Pm(2)	44.7	0.69	2	2.54	7	0.65	2.06
Wz-1	53.8	0.92	6	2.77	26	0.74	2.28
Wz-2	26.7	0.27	2	2.10	1	−0.14	1.85
Ko	41.3	0.12	1	–	–	−0.12	1.03
Ga	45.4	1.29	186	1.59	5	0.03	1.42
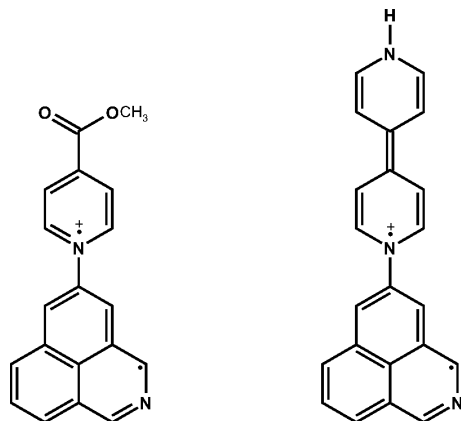
Scheme 2.

Numerical Results and Discussion

Transition energies

In Table 1 are given the calculated values of the longest-wavelength singlet-singlet and singlet-triplet transitions for the investigated molecules. The results were obtained by means of the AM1/CAS(16,16) method using geometries optimized with the AM1 method.

In all cases the energies of the first singlet-singlet transitions are $\Delta E_S(1) < 1$ eV (with the exception of the systems Pm(0) and Ga). Also the energies of the first singlet-triplet transitions are $\Delta E_T(1) < 1$ eV.

The negative values of the first singlet-triplet transition of the Wz-2 and Ko systems indicate triplet states, *i.e.* the ground state corresponds to a triplet diradical. In Scheme 2 only one resonance formula is depicted for these systems.

The calculated values of the transition energies $\Delta E_S(1)$ and $\Delta E_T(1)$ of the Pm(0) molecule with different methods and with different widths of the configuration interaction (CI) are shown in Table 2. The

Table 2. Calculated values of the longest-wavelength singlet-singlet and singlet-triplet transition energies (eV) of the Pm(0) molecule with different methods and with different widths of the configuration interaction (see Section 4).

Method	$\Delta E_S(1)$ (eV)	$f \times 10^3$	$\Delta E_T(1)$ (eV)
CIS(8,8)	1.57	23	1.28
CIS(14,14)	1.54	17	1.23
CIS(20,20)	1.53	17	1.18
CISD(8,8)	1.41	13	1.57
CISD(14,14)	1.55	10	1.54
CISD(20,20)	1.51	10	1.39
CAS(8,8)	1.20	11	1.04
CAS(14,14)	1.28	8	1.17
CAS(20,20)	1.33	9	1.21

Table 3. Calculated energy differences, $\Delta E_S(1)$ and $\Delta E_T(1)$ (in eV), obtained with semi-empirical post-HF and *ab initio* methods, for molecule Wz-2.

Method	$\Delta E_S(1)$ (eV)	$\Delta E_T(1)$ (eV)
AM1/CAS(10,10)	0.29	−0.14
AM1/CAS(16,16)	0.27	−0.14
AM1/CAS(20,20)	0.36	−0.11
CASSCF(4,3)/3-21G*	0.38	−0.06
B3LYP/3-21G*	0.61	−0.02
B3LYP/6-31G**	0.60	−0.02

results were obtained using the geometries optimized also with the AM1 method. The results in Table 2 show that the extension of the configuration interaction does not change the numerical results substantially. This result is valid also for the other investigated systems.

Table 3 presents the calculated energy differences $\Delta E_S(1)$ and $\Delta E_T(1)$ (in eV) for molecule Wz-2 using *ab initio* and DFT methods. The numerical results are a quantitative illustration of the important qualitative result, the triplet ground state of the Wz-2 system. The results of the Ko system are similar.

Conclusions and Outlook

A class of non-Kekulé molecular systems with a new structural principle and low exitation energies was investigated theoretically. The systems consist of a non-Kekulé monoradical, $R^\bullet$, possessing a non-bonding molecular orbital (NBMO), and are connected with another monoradical, $M^\bullet$, without NBMO(s). Here, only systems (molecules) $Az^\bullet – M^\bullet$ with one example of a radical subunit $R^\bullet$, namely the 2-azaphenalenyl radical, Az, have been studied. The multiformity of the stable radicals of types $R^\bullet$ and $M^\bullet$ determines the expediency of the theoretical and experimental investigations of this group of molecular systems.

The investigated model compounds are characterized by very low excitation energies with longest-wavelength absorptions in the near infrared region [11, 19]. The molecular species are candidates of building blocks of one-dimensional (1-D) stacks with intermolecular π-electron systems of conjugation with non-conventional physical properties. 1-D stacks with ferromagnetically coupled electrons within the half-filled band or with a metallic ground state can result depending on the multiplicity of the molecular building blocks [20 – 22].

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