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Partitioning of π-electrons in rings of diaza-derivatives of acenes

SONJA STANKOVIĆ[#], JELENA ĐURĐEVIĆ, IVAN GUTMAN[#*] and
RADMILA MILENTIJEVIĆ

Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia

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Abstract: A few years ago, a method was proposed for assessing the π-electron content (*EC*) of rings in heteroatom-containing benzenoid molecules. In this work, the effect of two nitrogen atoms at the opposite sides of a linear benzenoid molecule on the partitioning of its π-electrons was investigated. The results obtained can be explained by means of resonance-theoretical arguments.

Keywords: partitioning of π-electrons in rings; π-electron content of ring; aza-derivatives of acenes; resonance theory.

INTRODUCTION

Recent studies[1] have shown that acenes and their various derivatives can be used as organic semiconductors and are thus of great practical importance for electronics.[2] This, in particular, was found[3] to be the case with aza-derivatives of acenes. In a previous work,[4] the π-electron properties of monoaza acenes was considered. Here, the studies are extended to diaza species.

In 2004, Randić and Balaban[5,6] developed a method that makes it enabled the π-electron content of rings of polycyclic conjugated molecules to be assessed. This method was mainly applied to benzenoid and coronoid hydrocarbons.[5–23] Eventually, the method was extend to heteroatom-containing molecules.[24–26] The respective expression for the π-electron content of a ring R reads:[24]

$$EC(\mathrm{R}) = 2\sum_{*}\tilde{P}^{\mathrm{HR}}_{\mathrm{rs}} + \sum_{**}\tilde{P}^{\mathrm{HR}}_{\mathrm{rs}} \qquad (1)$$

where $\tilde{P}^{\mathrm{HR}}_{\mathrm{rs}}$ is the modified Ham–Ruedenberg bond order and where $\sum_{*}$ and $\sum_{**}$ indicate, respectively, summation over those bonds rs belonging solely to the ring R, and summation over the bonds rs that are shared by the ring R and another ring. The modified Ham–Ruedenberg bond order is given by:[24]

$$\tilde{P}^{\mathrm{HR}}_{\mathrm{rs}} = P^{\mathrm{HR}}_{\mathrm{rs}} + \frac{A_{\mathrm{rr}}}{\delta_{\mathrm{r}}}P^{\mathrm{HR}}_{\mathrm{rr}} + \frac{A_{\mathrm{ss}}}{\delta_{\mathrm{s}}}P^{\mathrm{HR}}_{\mathrm{ss}} \qquad (2)$$

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[*] Corresponding author. E-mail: gutman@kg.ac.yu

[#] Serbian Chemical Society member.

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where $P_{\mathrm{rs}}^{\mathrm{HR}}$ is the ordinary Ham–Ruedenberg bond order,[27] δ_{r} and δ_{s} are, respectively, the degrees[28] of the vertices r and s, whereas A_{rr} and A_{ss} are the corresponding diagonal elements of the adjacency matrix.[28] In the case of nitrogen-containing conjugated molecules, the following standard HMO parameterization is employed:[29]

$$A_{\mathrm{rr}} = \begin{cases} 0.5 & \text{if the atom in position r is nitrogen} \\ 0.0 & \text{if the atom in position r is carbon} \end{cases}$$

Recently, rules for the effect of a nitrogen atom on the partitioning of π-electrons in rings of monoaza acenes were established.[4] The most important of these are the following:

When the nitrogen atom is in position α (see Fig. 1), then the minimal value of the π-electron content is in the ring R_1 to which the nitrogen atom belongs. The π-electron contents of the other rings monotonically increase as their distance from R_1 increases. Therefore, the terminal ring R_h has the maximal *EC* value.

If the nitrogen atom is in position β (see Fig. 1), then the π-electron content of the ring R_1 is maximal and of its first neighbor minimal. The π-electron contents of the rings R_3, R_4,... monotonically increase with the distance from R_1, becoming maximal at the terminal ring R_h.

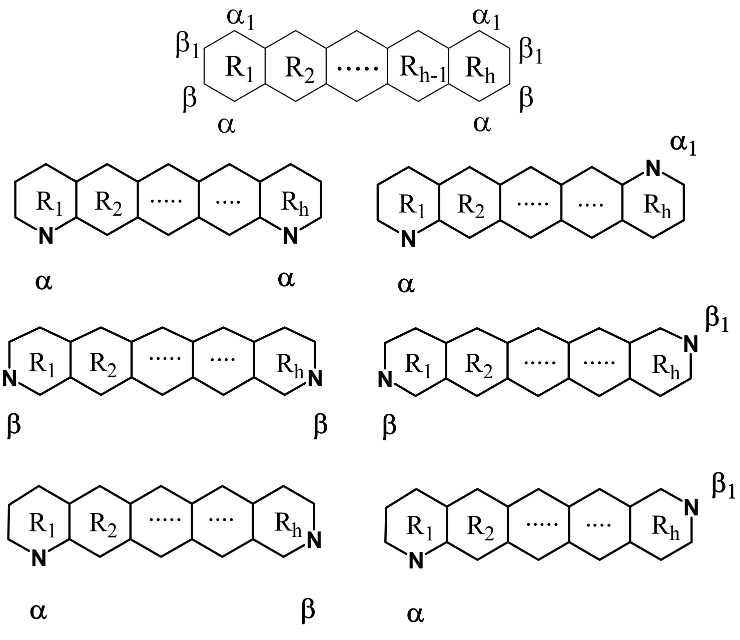

Fig. 1. The diaza-derivatives of acenes and the labeling of the positions of the nitrogen atoms. There are two different positions of the nitrogen atoms (α or α_1 and β or β_1), but there are six diaza-derivatives (αα, $\alpha\alpha_1$, ββ, $\beta\beta_1$, αβ and $\alpha\beta_1$).

As seen from the above rules, the effect of a heteroatom located in a terminal ring of an acene extends to the other terminal ring. Bearing this in mind, it seems to be purposeful to investigate the effect of two nitrogen atoms, located at the opposite sides of the acene molecule.

π-ELECTRON CONTENT OF RINGS OF DIAZA-ACENES

In order to best express the effects of heteroatoms on the partitioning of π-electrons in polycyclic aromatic compounds, the difference between the *EC* value of the heteroatom-containing molecule (h.c.m.) and the *EC* value of the parent hydrocarbon (p.h.) is used:[4]

$$\Delta EC(\mathrm{R}) = EC(\mathrm{R})_{\mathrm{h.c.m.}} - EC(\mathrm{R})_{\mathrm{p.h.}} \tag{3}$$

The general forms of diaza-acenes with nitrogen atoms in the terminal rings, as well as the labeling of their hexagons are shown in Fig. 1. As can be seen, the nitrogen atoms can be in two different positions (α or α_1 and β or β_1). Consequently, there are six different arrangements of two nitrogen atoms ($\alpha\alpha$, $\alpha\alpha_1$, $\beta\beta$, $\beta\beta_1$, $\alpha\beta$ and $\alpha\beta_1$).

The ΔEC values of all rings of the six possible diaza-acenes with h hexagons, $2 \le h \le 10$, were calculated. Some of these results (for $h \le 6$) are collected in Tables I, II, and III.

TABLE I. The ΔEC values of the rings of $\alpha\alpha$ and $\alpha\alpha_1$ diaza-acenes with h hexagons; notation the same as in Fig. 1. Positive (resp. negative) ΔEC(R) means that the π-electron content of the ring R has increased (resp. decreased) relative to the π-electron content of the same ring in the parent hydrocarbon

h	Position	$\Delta EC(R_1)$	$\Delta EC(R_2)$	$\Delta EC(R_3)$	$\Delta EC(R_4)$	$\Delta EC(R_5)$	$\Delta EC(R_6)$
2	$\alpha\alpha$	0.0	0.0	–	–	–	–
	$\alpha\alpha_1$	0.0	0.0	–	–	–	–
3	$\alpha\alpha$	–0.0146	0.0293	–0.0146	–	–	–
	$\alpha\alpha_1$	–0.0182	0.0363	–0.0182	–	–	–
4	$\alpha\alpha$	–0.0181	0.0181	0.0181	–0.0181	–	–
	$\alpha\alpha_1$	–0.0216	0.0216	0.0216	–0.0216	–	–
5	$\alpha\alpha$	–0.0181	0.0105	0.0152	0.0105	–0.0181	–
	$\alpha\alpha_1$	–0.0211	0.0124	0.0174	0.0124	–0.0211	–
6	$\alpha\alpha$	–0.0166	0.0047	0.0119	0.0119	0.0047	–0.0166
	$\alpha\alpha_1$	–0.0191	0.0059	0.0133	0.0133	0.0059	–0.0191

The results show similar displacements of the π-electrons in the cases $\alpha\alpha$, $\alpha\alpha_1$, as well as in the cases $\beta\beta$, $\beta\beta_1$, and $\alpha\beta$, $\alpha\beta_1$. Therefore, attention was focued on the cases $\alpha\alpha$, $\beta\beta$ and $\alpha\beta$. From the ΔEC values given in Tables I, II, and III, the following conclusions can be reached:

If the nitrogen atoms are in positions α (or α_1), then they cause a decrease of the π-electron content of the rings R_1 and R_h (see Table I).

TABLE II. Same data as in Table I but for $\beta\beta$ and $\beta\beta_1$ diaza-acenes

h	Position	$\Delta EC(R_1)$	$\Delta EC(R_2)$	$\Delta EC(R_3)$	$\Delta EC(R_4)$	$\Delta EC(R_5)$	$\Delta EC(R_6)$
2	$\beta\beta$	0.0	0.0	–	–	–	–
	$\beta\beta_1$	0.0	0.0	–	–	–	–
3	$\beta\beta$	0.0546	–0.1093	0.0546	–	–	–
	$\beta\beta_1$	0.0515	–0.1029	0.0515	–	–	–
4	$\beta\beta$	0.0707	–0.0707	–0.0707	0.0707	–	–
	$\beta\beta_1$	0.0673	–0.0673	–0.0673	0.0673	–	–
5	$\beta\beta$	0.0770	–0.0652	–0.0234	–0.0652	0.0770	–
	$\beta\beta_1$	0.0740	–0.0.633	–0.0214	–0.0633	0.0740	–
6	$\beta\beta$	0.0805	–0.0670	–0.0135	–0.0135	–0.0670	0.0805
	$\beta\beta_1$	0.0780	–0.0658	–0.0122	–0.0122	–0.0658	0.0780

TABLE III. Same data as in Table I but for $\alpha\beta$ and $\alpha\beta_1$ diaza-acenes

h	Position	$\Delta EC(R_1)$	$\Delta EC(R_2)$	$\Delta EC(R_3)$	$\Delta EC(R_4)$	$\Delta EC(R_5)$	$\Delta EC(R_6)$
2	$\alpha\beta$	–0.0873	0.0873	–	–	–	–
	$\alpha\beta_1$	–0.0851	0.0851	–	–	–	–
3	$\alpha\beta$	–0.0431	–0.0332	0.0763	–	–	–
	$\alpha\beta_1$	–0.0390	–0.0398	0.0789	–	–	–
4	$\alpha\beta$	–0.0296	0.0024	–0.0480	0.0753	–	–
	$\alpha\beta_1$	–0.0258	–0.0011	–0.0514	0.0783	–	–
5	$\alpha\beta$	–0.0237	0.0064	–0.0020	–0.0573	0.0767	–
	$\alpha\beta_1$	–0.0206	0.0045	–0.0041	–0.0592	0.0795	–
6	$\alpha\beta$	–0.0200	0.0039	0.0072	–0.0062	–0.0639	0.0790
	$\alpha\beta_1$	–0.0174	0.0027	0.0059	–0.0075	–0.0650	0.0814

If the nitrogen atoms are in position α (or α_1), the π-electron content of the other rings monotonically increase towards the center of the molecule. In particular, if h is odd, then the maximal EC value is at the ring $R_{(h+1)/2}$; if h is even, then the two rings $R_{h/2}$ and $R_{h/2+1}$ have greatest π-electron content.

If the nitrogen atoms are in position β (or β_1), then (contrary to the case of α-substitution) the greatest value of the π-electron content is in rings R_1 and R_h.

If the nitrogen atoms are in position β (or β_1), then the minimal ΔEC values are in the neighboring rings (R_2 and R_{h-1}). The π-electron contents of the other rings monotonically increase with distance from the terminal rings (see Table II).

If one nitrogen atom is in position α, and the other in position β (or β_1), then the π-electron contents of all rings are the result of two simultaneously, but in opposite sense acting, effects. Thus, the ring R_1, containing nitrogen in position α, has the minimal ΔEC value, whereas the ring R_h, containing nitrogen in position β (or β_1), shows the maximal ΔEC value (see Table III).

These regularities are in agreement with the displacements of π-electrons caused by a single heteroatom (nitrogen).[4,25,26] The main differences are the consequence of the simultaneous effect of two nitrogen atoms. In the subsequent section, it will be shown that these results are in agreement with the (qualitative) predictions of the resonance theory.

RESONANCE-THEORETICAL ANALYSIS

In this section, a resonance-theoretical analysis of the partitioning of π-electrons in the rings of acenes is described. Without loss of generality, only the case $h = 5$ (pentacene) will be considered. We first outline First, the resonance-theoretical approach to the ββ-forms is outlined.

It was shown elsewhere[4] that only ionic resonance structures need to be taken into account. The most important of these are the ionic structures with minimal charge separation. However, these structures result in the same distribution of π-electrons as in Kekulé structures, *i.e.*, as in the parent hydrocarbon.[4] Therefore, only the ionic structures with greater charge separation are considered. The relevant ionic structures of ββ diaza-pentacene are depicted in Fig. 2.

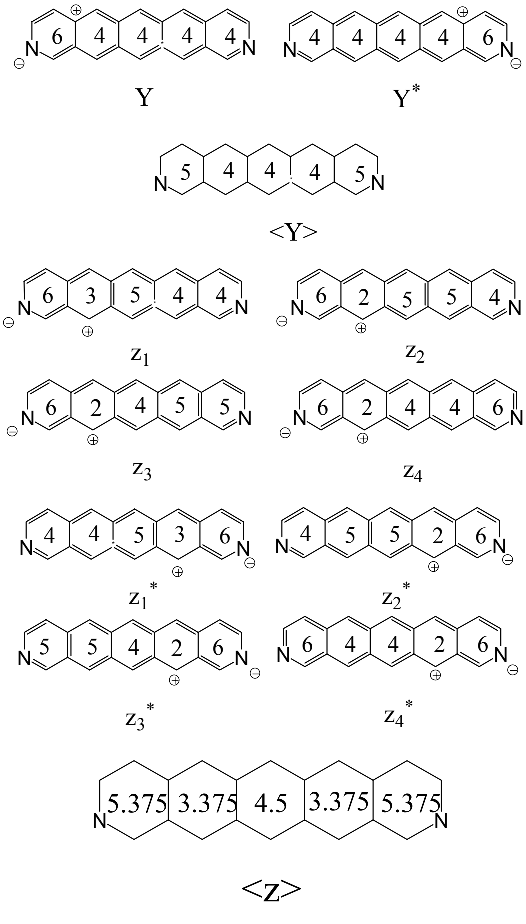

Fig. 2. The considered ionic resonance forms of ββ diaza-pentacene. The numerals inscribed in the rings indicate the number of π-electrons belonging to that ring; for details see text.

The structures Y, Y^* have positive charges in the *para* position to the negatively charged nitrogen atom. The next-significant structures are those with a positive charge at the neighboring ring ($z_1,\ldots, z_4, z_1^*,\ldots, z_4^*$). These forms are responsible for the differences between the *EC* values. Thus, by averaging the π-electron contents of rings Y and Y^* (denoted by <*Y*>), it can be seen that the terminal rings have the greatest π-electron contents. For the displacement of π-electrons among the internal rings, one has to use resonance forms with still greater charge separation ($z_1,\ldots, z_4, z_1^*,\ldots, z_4^*$) have to be employed. The average of the π-electron contents of these species (denoted by <*Z*>) yields: $EC(R_3) > EC(R_2)$, $EC(R_3) > EC(R_4)$, *i.e.*, $EC(R_2) < EC(R_3) < EC(R_1)$.

As can be seen, the diagrams depicted in Fig. 2 explain in a qualitative manner the results given in Table II.

The analogous resonance forms of αα diaza-pentacene are depicted in Figs. 3 and 4. Their resonance-theoretical analysis proceeds in a similar manner.

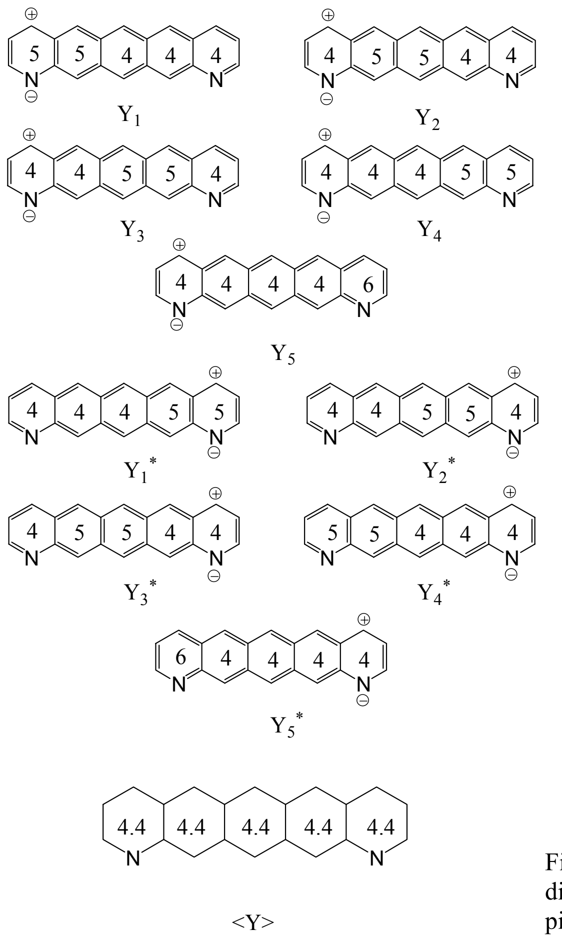

Fig. 3. The Y-type ionic structures of αα diaza-pentacene, analogous to those depicted in Fig. 2.

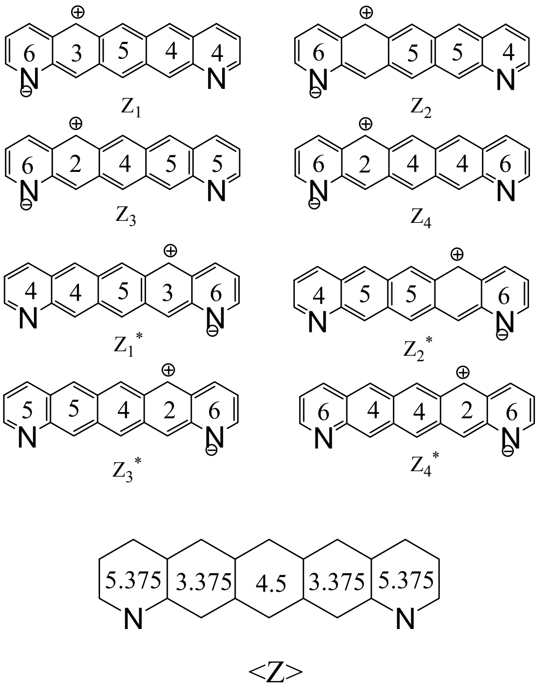

Fig. 4. The Z-type ionic structures of αα diaza-pentacene, analogous to those depicted in Fig. 2.

Equal *EC* values are arrived at from $Y_1,\ldots, Y_5^*$. However, this implies that the *EC* values increase relative to the parent hydrocarbon in rings R_1 and R_5, whereas they decrease in rings R_2, R_3 and R_4. By taking into account the Z-type structures, one obtains $EC(R_3) > EC(R_2)$, *i.e.*, $EC(R_3) > EC(R_4)$. In summary, one obtains: $EC(R_1) < EC(R_2) < EC(R_3)$, which is in agreement with the calculated results (*cf.* Table I).

The same reasoning can be applied also to αβ-type diaza-acenes, the details of which are omitted.

ИЗВОД

РАСПОДЕЛА π-ЕЛЕКТРОНА ПО ПРСТЕНОВИМА У ДИАЗА-ДЕРИВАТИМА АЦЕНА

СОЊА СТАНКОВИЋ, ЈЕЛЕНА ЂУРЂЕВИЋ, ИВАН ГУТМАН и РАДМИЛА МИЛЕНТИЈЕВИЋ

Природно–математички факултет у Крагујевцу

Недавно је предложена метода за рачунање π-електронског садржаја прстенова бензеноидних молекула који садрже хетероатом. У овом раду проучавана је расподела π-електрона у аценима који садрже два атома азота на супротним крајевима линеарног ланца. Добијени резултати објашњени су помоћу резонанционе теорије.

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