

Partitioning of π -electrons in rings of aza-derivatives of naphthalene

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Abstract: A recently proposed method for calculating the π -electron contents (EC) of rings of heteroatom-containing polycyclic conjugated molecules was applied to the aza-derivatives of naphthalene. The main finding was that a nitrogen atom in position α (resp. β) diminishes (resp. increases) the EC -value of the respective ring. Such a regularity in the displacement of π -electrons can be (qualitatively) rationalized by means of resonance-theoretical reasoning.

Keywords: π -electron content of ring, heterocyclic conjugated molecules, quinoline, isoquinoline, resonance theory.

INTRODUCTION

In 2004, a method for the partitioning of π -electrons in the rings of polycyclic conjugated hydrocarbons was suggested by means of which the π -electron content of a ring can be assessed by examining the Kekulé structures.^{1,2} The method is based on an earlier observation^{3,4} that instead of the standard way of drawing a Kekulé structure (by specifying the position of the double bonds,^{5,6} it may be represented by indicating the count of π -electrons in each ring.

The construction of so-called “algebraic Kekulé structures” is achieved as follows.^{3,4} The number $EC(R,k)$ of π -electrons in ring R of the Kekulé structure k is defined as two times the number of double bonds that belong solely to R plus the number of double bonds that are shared by R and another ring; a simple example is found in Fig. 1.

The π -electron content $EC(R)$ of a ring R is defined as the arithmetic average of the $EC(R,k)$ -values,^{1,2} *i. e.*

$$EC(R) = \frac{1}{K} \sum_k EC(R, k) \quad (1)$$

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where the summation in (1) goes over all K Kekulé structures of the conjugated molecule considered.

It was immediately recognized⁷ that the right-hand side of (1) can be expressed in terms of the Pauling bond orders, $P_{rs}(\text{Pauling})$, so that:

$$EC(\text{R}) = 2 \sum_{*} P_{rs}(\text{Pauling}) + \sum_{**} P_{rs}(\text{Pauling}) \quad (2)$$

where \sum indicates summation over those bonds rs which belong solely to ring R, whereas \sum^{*} indicates summation over the bonds rs which are shared by ring R and another^{**} ring.

A large number of studies and applications of the EC -concept were reported. Most of these were concerned with the six-membered rings of benzenoid and coronoid systems.^{1,2,7-26} Only in a few papers^{27,28} were non-benzenoid hydrocarbons considered and none in which heteroatom-containing conjugated species were studied.

The reason for avoiding the study of the EC -values of heteroatom-containing conjugated molecules is simple: It is not legitimate to apply the model based on Eqs. (1) and (2) to heteroatom-containing conjugated systems. Namely, the employment of these two equations would give results identical to those for the parent hydrocarbon, which is an evident chemical nonsense.

A way out of this difficulty was recently proposed.²⁹

Calculating the π -electron contents of rings of heteroatom-containing conjugated molecules

The essence of the method, put forward by one of the present authors,²⁹ is that instead of Eq. (2), calculation of the π -electron content of a ring R is achieved by means of the expression:

$$EC'(\text{R}) = 2 \sum_{*} P_{rs}(\text{HR})' + \sum_{**} P_{rs}(\text{HR})' \quad (3)$$

where $P_{rs}(\text{HR})'$ is a modified version of the Ham–Ruedenberg bond order³⁰⁻³² (for details see below). As in the case of benzenoid hydrocarbons, the Ham–Ruedenberg and the Pauling bond orders coincide,^{33,34} the π -electron contents obtained *via* Eqs. (2) and (3) also coincide. On the other hand, the Ham–Ruedenberg bond order can be, without any difficulty, calculated for any heteroatom-containing conjugated system (except those possessing non-bonding molecular orbitals). Therefore, by means of Eq. (3), the π -electron contents can be calculated for rings of any heteroatom-containing conjugated molecule (except in the rare and chemically insignificant cases when the π -electron system considered has non-bonding molecular orbitals).

For the sake of completeness we briefly repeat the definition of the Ham–Ruedenberg bond orders.³⁰

Let $C_i = (C_{i1}, C_{i2}, \dots, C_{in})$ be a normalized eigenvector of the adjacency matrix $A = \|A_{ij}\|$ of the molecular (Hückel) graph representing the conjugated system under consideration,^{35,36} here n stands for the number of vertices of the molecular graph. There exist n linearly independent eigenvectors and, therefore, $i = 1, 2, \dots, n$. Let λ_i be the eigenvalue of A , corresponding to the eigenvector C_i , $i = 1, 2, \dots, n$.

Within the Hückel molecular orbital (HMO) theory, C_i and λ_i are in a simple manner related to, respectively, the i -th molecular orbital and the i -th molecular orbital energy level. Let g_i be the occupation number of the i -th MO. Then the Ham–Ruedenberg bond order is defined as:

$$P_{rs}(\text{HR}) = \sum_{i=1}^n g_i \frac{C_{ir} C_{is}}{\lambda_i}$$

where it is assumed that no eigenvalue is equal to zero (*i.e.*, that there are no non-bonding MOs). The modified Ham–Ruedenberg bond order, used in Eq. (3), is defined as:

$$P_{rs}(\text{HR})' = P_{rs}(\text{HR}) + \frac{A_{rr}}{\delta_r} P_{rr}(\text{HR}) + \frac{A_{ss}}{\delta_s} P_{ss}(\text{HR})$$

where δ_r and δ_s are, respectively, the degrees (number of first neighbors)³⁵ of the vertices r and s .

In the case of conjugated hydrocarbons, all diagonal elements of the adjacency matrix A are equal to zero and then there is no difference between the Ham–Ruedenberg bond order $P_{rs}(\text{HR})$ and its modified version $P_{rs}(\text{HR})'$. If heteroatoms are present, then some diagonal elements of the adjacency matrix are different from zero, implying that $P_{rs}(\text{HR}) \neq P_{rs}(\text{HR})'$.

More details on $P_{rs}(\text{HR})$ and $P_{rs}(\text{HR})'$ can be found in the literature.²⁹

TWO SIMPLEST EXAMPLES: QUINOLINE AND ISOQUINOLINE

In order to obtain some experience with the application of formula (3) to the partitioning of π -electrons in polycyclic, heteroatom-containing, conjugated molecules, two monoaza-derivatives of naphthalene, namely quinoline (1-azanaphthalene) and isoquinoline (2-azanaphthalene), were examined.

The numbering of the sites of naphthalene (according to the IUPAC rules) and the labeling of its two rings are shown in Fig. 1.

The EC -values of naphthalene are determined by symmetry: since the total number of π -electrons is ten, the π -electron content of each ring must be 5.00. This result is, of course, obtained also by using Eqs. (1) or (2) or (3).

In order to compute the analogous π -electron contents of the aza-derivatives of naphthalene (which can be done only by means of Eq. (3)), an appropriate parametrization for the diagonal elements of the adjacency matrix had to be used. We employed the standard HMO parameters,³⁷ namely:

$$A_{rr} = \begin{cases} 0.5 & \text{if the atom in position } r \text{ is nitrogen} \\ 0.0 & \text{if the atom in position } r \text{ is carbon} \end{cases} \quad (4)$$

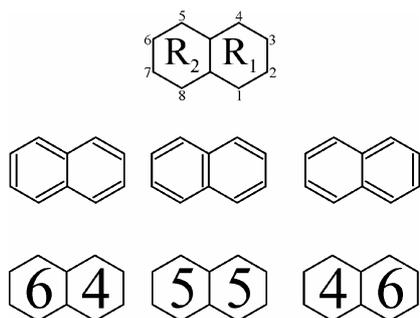


Fig. 1. The numbering of the sites of naphthalene (according to the IUPAC rules) and the labeling of its two rings. In this paper, the sites 1, 4, 5, and 8 are referred to as α and the sites 2, 3, 6, and 7 as β . Also shown are the three Kekulé structures of naphthalene and the corresponding "algebraic Kekulé structures"^{3,4} According to the Randić-Balaban method,^{1,2} Eq. (1), the π -electron content of each ring is equal to the arithmetic average of the respective numerals inscribed in the "algebraic Kekulé structures". For instance, $EC(R_1) = (4+5+6)/3 = 5.00$.

The results thus obtained are shown in Fig. 2.

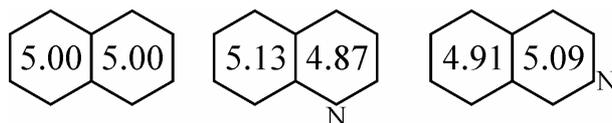


Fig. 2. The partitioning of the ten π -electrons of naphthalene, quinoline, and isoquinoline in their rings. Note that the value 5.00 for the rings of naphthalene is a consequence of molecular symmetry.

As seen from Fig. 2, the nitrogen atom in quinoline (belonging to ring R_1) causes a decrease of the π -electron content of R_1 and therefore an increase of the π -electron content of R_2 . The analogous effects in isoquinoline are opposite. As explained below (see the data in Table I), the partitioning of the π -electrons in the rings of quinoline and isoquinoline reflect a more general regularity: a nitrogen atom in position α decreases and in position β increases the π -electron content of the ring to which it belongs.

At this point it is legitimate to ask if the partitioning of π -electrons as shown in Fig. 2 is chemically sound and in agreement with existing chemical theories. In the subsequent section it is demonstrated that the present results agree with the (qualitative) predictions of the resonance theory.³⁸

A RESONANCE-THEORETICAL ANALYSIS

Isoquinoline is examined first, because its resonance-theoretical analysis is somewhat simpler.

The nine relevant resonance structures of isoquinoline are depicted in Fig. 3. (Because nitrogen is more electronegative than carbon, only those charge-separated resonance forms in which the negative charge is located at the nitrogen are considered.)

It is plausible to assume³⁸ that the most significant resonance forms of isoquinoline are those in which there is no (formal) charge separation, namely the

structures **1**, **2** and **3**. If only these were taken into account, then the π -electron contents of the rings R_1 and R_2 would be predicted to be equal to those in naphthalene. Therefore, it is necessary to include into the consideration also the charge-separated species. As already explained, it is assumed that the negative charge is located at the nitrogen atom.

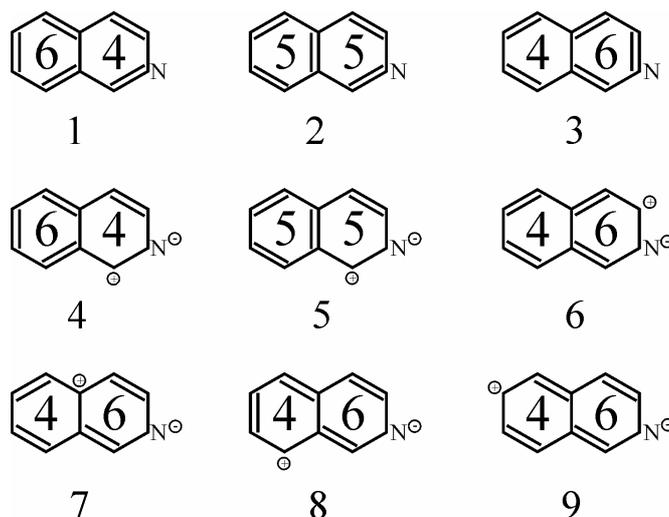


Fig. 3. The significant resonance forms of isoquinoline. The numerals in the rings indicate the count of π -electrons that belong to the particular ring. These are fully analogous to the $EC(R,k)$ -values described in the text and illustrated in Fig. 1.

Of the six possible resonance structures of this kind, those in which the charge separation is minimal (namely **4**, **5** and **6**) are the most significant. These, however, also imply equal π -electron contents of the rings R_1 and R_2 . Therefore attention needs to be focused on the energetically less favorable resonance structures **7**, **8** and **9**, in which the charges are at greater distance. In the latter three resonance structures there are more π -electrons in ring R_1 than in R_2 (*cf.* Fig. 3).

In summary, by taking into account all the nine resonance structures **1–9** of isoquinoline, it can be concluded that some displacement of the π -electrons occurs from ring R_2 into the ring R_1 . This (qualitatively) agrees with what was found by the calculations.

The case of quinoline is somewhat more perplexing. Its relevant resonance forms are depicted in Fig. 4.

Again, if only the resonance structures **1**, **2** and **3** (with no charge separation) and **4**, **5** and **6** (with charge separation at minimum distance) are considered, no π -electron displacement would be predicted.

The next two (equally) significant resonance forms of quinoline are **7** and **8**. These imply a shift of the π -electrons from ring R_1 to ring R_2 . Thus, structures **7**

and **8** (together with **1–6**) imply that the π -electron content of ring R_1 of quinoline is less than that of ring R_2 .

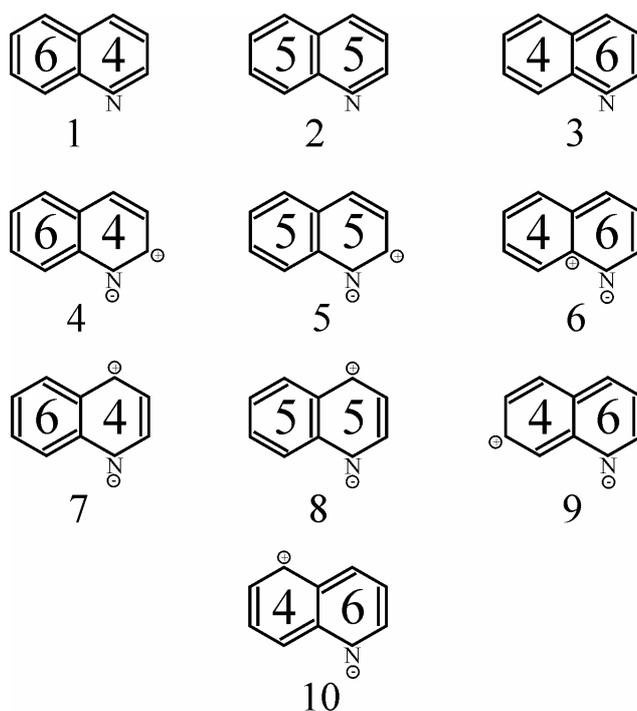


Fig. 4. Same as in Fig. 3, for quinoline.

However, quinoline has two more resonance structures, **9** and **10**, in which ring R_1 has a greater π -electron content than ring R_2 . The charge separation in **9** and **10** is greater than in **7** and **8**. Consequently, **9** and **10** are energetically less favorable than **7** and **8** and, therefore, their influence on the partition of the π -electrons should be less pronounced. Thus, if it is accepted that the effect of the resonance structures **9** and **10** can be neglected, relative to the effect of **7** and **8**, then the present findings agree with resonance theory.

NUMERICAL WORK AND DISCUSSION

Using Eq. (3) and the parametrization specified by Eq. (4), the electron contents of the rings of all aza-derivatives of naphthalene were computed. The results for monoaza-, diaza-, triaza- and tetraaza-naphthalenes are given in Table I, whereas the results for (chemically less realistic) pentaaza-, hexaaza- and heptaaza-naphthalenes can be obtained from the authors (R. K.) upon request.

The data in Table I enable several regularities in the partition of the π -electrons in the rings to be envisaged. Of these, the most remarkable are the following:

TABLE I. π -Electron contents, calculated by means of Eq. (3), of the rings R_1 and R_2 of monoaza-, diaza-, triaza-, and tetraaza-derivatives of naphthalene. P. N. A. = position of the nitrogen atom(s), according to the numbering shown in Fig. 1, in which the labeling of the rings (R_1, R_2) is also indicated.

P. N. A.	$EC'(R_1)$	$EC'(R_2)$	P. N. A.	$EC'(R_1)$	$EC'(R_2)$
1	4.8742	5.1258	2	5.0907	4.9093
1,2	5.1823	4.8177	1,3	4.9706	5.0294
1,4	4.9040	4.0960	1,5	5.0000	5.0000
1,6	4.7995	5.2005	1,7	4.7614	5.2386
1,8	5.0000	5.0000	2,3	5.1565	4.8435
2,6	5.0000	5.0000	2,7	5.0000	5.0000
1,2,3	5.2472	4.7528	1,2,4	5.3243	4.6757
1,2,5	5.3385	4.6615	1,2,6	5.0832	4.9168
1,2,7	5.0970	4.9030	1,2,8	5.3133	4.6867
1,3,5	5.1049	4.8951	1,3,6	4.8954	5.1056
1,3,7	4.8455	5.1545	1,3,8	5.0804	4.9196
1,4,5	5.0300	4.9700	1,4,6	4.7824	5.2176
1,6,7	4.7938	5.2062	2,3,6	5.0370	4.9630
1,2,3,4	5.4945	4.5055	1,2,3,5	5.3205	4.6795
1,2,3,6	5.0877	4.9123	1,2,3,7	5.1430	4.8570
1,2,3,8	5.2993	4.7007	1,2,4,5	5.4494	4.5506
1,2,4,6	5.2118	4.7882	1,2,4,7	5.2448	4.7552
1,2,4,8	5.4826	4.5174	1,2,5,6	5.0000	5.0000
1,2,5,7	5.2573	4.7427	1,2,5,8	5.3638	4.6362
1,2,6,7	5.0796	4.9204	1,2,6,8	5.2183	4.7817
1,2,7,8	5.0000	5.0000	1,3,5,7	5.0000	5.0000
1,3,5,8	5.0839	4.9161	1,3,6,7	4.8940	5.1060
1,3,6,8	5.0000	5.0000	1,4,5,8	5.0000	5.0000
1,4,6,7	4.7927	5.2073	2,3,6,7	5.0000	5.0000

Rule 1. Nitrogen atoms in positions α decrease and in position β increase the π -electron content of the ring to which they belong.

Not a single violation of Rule 1 was found. Quinoline and isoquinoline are the simplest examples illustrating Rule 1. Another convincing example is $EC'(R_1) = 4.80$ and $EC'(R_1) = 4.76$ in 1,6-diaza- and 1,7-diaza-naphthalene, respectively, which should be compared with $EC'(R_1) = 4.87$ in the case of 1-aza-naphthalene. It can be seen that a nitrogen atom in a position in ring R_2 additionally decreases the π -electron content of ring R_1 .

Rule 2. Two α nitrogen atoms in the same ring have almost identical effects as a single α nitrogen atom. The same holds for nitrogen atoms in the β position.

Illustrations of Rule 2 are $EC'(R_1) = 4.90$ for 1,4-diazanaphthalene, compared with $EC'(R_1) = 4.87$ for 1-azanaphthalene (two and one α nitrogen atoms), and $EC'(R_1) = 4.78$ for 1,4,6-triazanaphthalene, to be compared with $EC'(R_1) = 4.79$ for 1,4,6,7-tetraazanaphthalene (one and two β nitrogen atoms).

There seems to be no generally valid answer to the obvious question: which effect, α or β is stronger. For instance, the ring R_1 in both 1,2-diaza- and 1,3-diaza-naphthalene possess an α and a β nitrogen atom. Yet, the π -electron contents of R_1 is greater than 5 in 1,2-diaza- and smaller than 5 in 1,3-diaza-naphthalene.

CONCLUDING REMARKS

In this paper, the results of the first study of the partitioning of π -electrons in rings of polycyclic conjugated molecules with heteroatoms are reported. For obvious reasons, the simplest possible such species, aza derivatives of naphthalene, were chosen to be examined. Already for these conjugated system, possessing only two rings, the number of isomers is enormous (*cf.* Table I). Extending such studies to systems with more than two rings promises to be rather difficult. Nevertheless, it is our plan to continue along these lines.

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ИЗВОД

ПОДЕЛА π -ЕЛЕКТРОНА У ПРСТЕНОВИМА АЗА-ДЕРИВАТА НАФТАЛЕНА

ИВАН ГУТМАН, БОРИС ФУРТУЛА и РАДМИЛА КОВАЧЕВИЋ

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Недавно предложена метода за рачунање π -електронског садржаја (EC) прстенова у полицикличним коњугованим молекулима који садрже хетероатоме примењена је на аза-дериwате нафталена. Најважнија уочена правилност је да азотов атом у положају α умањује EC -вредност одговарајућег прстена, док азотов атом у положају β ову вредност повећава. Овакво померање π -електрона може се (квалитативно) објаснити помоћу теорије резонанције.

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