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PARTITIONING OF π-ELECTRONS IN RINGS OF AZA-DERIVATIVES OF TRIPHENYLENE

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In the rings of aza-derivatives of benzenoid hydrocarbons, the π-electrons are shifted relative to the parent hydrocarbon. This effect strongly depends on the position of the heteroatom(s), and follows a pattern that is not easy to predict by means of intuitive reasoning. We studied this effect in the case of the aza-derivatives of the simplest fully benzenoid hydrocarbon – triphenylene, and established the basic regularities on which it depends.

Key words: benzenoid hydrocarbons; triphenylene; aza-triphenylenes, π-electron content of ring

РАСПРЕДЕЛБА НА π-ЕЛЕКТРОНИТЕ ВО ПРСТЕНИТЕ НА АЗА-ДЕРИВАТИТЕ НА ТРИФЕНИЛЕНОТ

Во прстените на аза-дериватите на бензеноидните јаглеводороди π-електроните се поместени во однос на основниот јаглеводород. Овој ефект многу зависи од положбата на хетероатомите и не може лесно да се предвиди врз основа на интуитивно резонирање. Овој ефект е проучуван кај аза-деривати на наједноставниот целосно бензеноиден јаглеводород – трифениленот. Утврдени се основните правилности од кои тој зависи.

Клучни зборови: бензеноидни јаглеводороди; трифенилен; аза-трифенилени; π-електронска содржина на прстенот

INTRODUCTION

In a series of papers [1–4] Randić and Balaban put forward a method for assessing the π-electron content of rings in polycyclic molecules, by means of which the π-electron distribution in numerous classes of polycyclic aromatic hydrocarbons was studied [1–12]. Recently this method was extended and made applicable to heteroatom–containing conjugated molecules, in particular, to aza-derivatives of benzenoid systems [13]. Because of the enormously large number of possible aza-derivatives of benzenoid molecules [14], until now the partitioning of π-electrons into rings was examined only in the case of aza-derivatives of naphthalene [15] and monoaza-derivatives of linear polyacenes [16]. In the parent hydrocarbons of these heteroconjugated molecules (i. e., in polyacenes), the distribution of π-electrons into rings is (nearly) uniform [5, 11, 12]. Therefore, the changes of the electron contents of rings in these compounds, caused by the heteroatom(s), is easy to envisage [15, 16]. In this paper we examine a diametrically different type of polycyclic conjugated systems, where the parent hydrocarbon is fully benzenoid [17], thus possessing a highly non-uniform distribution of π-electrons into rings [10]. We consider here triphenylene, the smallest and

simplest fully benzenoid hydrocarbon [17], see Fig. 1.

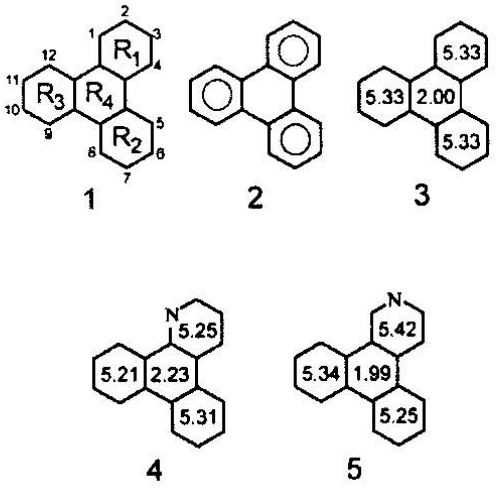

Fig. 1. Triphenylene $C_{18}H_{12}$: numbering of its carbon atoms and rings (1), Clar aromatic sextet formula (2), and distribution of π-electrons calculated according to the Randić–Balaban method (3). The positions 1, 4, 5, 8, 9, and 12 in triphenylene (see diagram 1) are refereed to as α, whereas the positions 2, 3, 6, 7, 10, and 11 are referred to as β. The partition of the π-electrons into rings of 1-aza- and 2-aza-triphenylene are shown in diagrams 4 and 5, respectively.

The distribution of π-electrons in the rings of triphenylene is highly non-uniform, as should be expected from its (unique) aromatic sextet formula (diagram 2 in Fig. 1). Indeed, the Randić–Balaban method gives that the π-electron content of each of the rings R_1, R_2, and R_3 is equal to 5.3333, whereas the central ring R_4 possesses only two π-electrons (diagram 3 in Fig. 1).

When a nitrogen atom is substituted in positions α or β of triphenylene, the π-electron contents of the rings significantly changes, as seen from diagrams 4 and 5 in Fig. 1.

In order to better envision the effect of heteroatoms on the electron content of a ring R_i, in what follows we report the values of

$$\Delta EC(R_i) = EC(R_i)_{\text{h.c.m.}} - EC(R_i)_{\text{p.h.}} \qquad (1)$$

namely, the difference between the π-electron content $EC(R_i)$ of the ring R_i in the heteroatom-containing molecule (h.c.m.), and the respective $EC(R_i)$-value of the parent hydrocarbon (p.h.). In the cases studied in this paper, the parent hydrocarbon and its heteroatom-containing derivatives possess equal number of π-electrons. Therefore,

$$\sum_i \Delta EC(R_i) = 0 ,$$

and, in particular, for triphenylene (cf. Fig. 1):

$$\sum_{i=1}^{4} \Delta EC(R_i) = 0 .$$

NUMERICAL WORK

Details of the computation of the π-electron content of rings of benzenoid hydrocarbons and their aza-derivatives can be found elsewhere [1, 8, 13, 16]. The calculations reported here (as well as in [15, 16]) were executed with an in-house computer program CELERN. The ΔEC-values of various mono-, di-, and tri-aza-triphenylene derivatives are given in Table 1.

Table 1

ΔEC-values, Eq. (1), of the rings R_i, i = 1, 2, 3, 4, (Fig. 1) of all aza-derivatives of triphenylene in which every ring contains at most one N-atom

Position of N atoms	Type of isomer	$\Delta EC(R_1)$	$\Delta EC(R_2)$	$\Delta EC(R_3)$	$\Delta EC(R_4)$
1	α	–0.0826	–0.0237	–0.1219	+0.2283
2	β	+0.0870	–0.0812	+0.0055	–0.0112
1, 6	α β	–0.0735	+0.0678	–0.1846	+0.1904
1, 7	α β	–0.1609	+0.0629	–0.1174	+0.2155
1, 8	α α	–0.1055	–0.1055	–0.2264	0.4374
1, 9	α α	–0.1068	–0.1461	–0.2037	+0.4566
1, 10	α β	–0.1592	–0.0289	–0.0152	+0.2034
1, 11	α β	–0.0755	–0.1018	–0.0353	+0.2127
1, 12	α α	–0.2009	–0.0630	–0.2009	+0.4649
2, 7	β β	+0.0237	+0.0237	+0.0023	–0.0495
2, 10	β β	+0.0061	–0.0752	+0.0917	–0.0225
2, 11	β β	+0.0976	–0.1443	+0.0976	–0.0507
1, 5, 9	α α α	–0.2283	–0.2283	–0.2283	0.6850
1, 5, 10	α α β	–0.2560	–0.1104	–0.0373	+0.4039
1, 5, 11	α α β	–0.1976	–0.1820	–0.0598	+0.4395
1, 6, 11	α β β	–0.1502	+0.0624	–0.0783	+0.1662
1, 6, 12	α β α	–0.1944	+0.0286	–0.2534	+0.4193
1, 7, 10	α β β	–0.2118	+0.0633	–0.0066	+0.1552
1, 7, 11	α β β	–0.1532	–0.0149	–0.0217	+0.1899
1, 8, 12	α α α	–0.2274	–0.1475	–0.2992	0.6742
2, 6, 10	β β β	+0.0113	+0.0113	+0.0113	–0.0338
2, 7, 11	β β β	+0.0342	–0.0399	+0.0942	–0.0884

The starting point for our studies was naphthalene and its two monoaza derivatives (quinoline and isoquinoline) [15]. Their ΔEC-values are shown in Fig. 2.

6 7

Fig. 2. The ΔEC-values (Eq. 1) of the rings of quinoline (6) and isoquinoline (7)

As seen from Fig. 2, a nitrogen atom in position α (as in quinoline) diminishes the π-electron content of the ring to which it belongs and, consequently, increases the π-electron content of the other ring. The effect of a nitrogen atom in position β (as in isoquinoline) is opposite. Such a seemingly unusual displacement of π-electrons in aza-substituted naphthalenes could be explained by resonance-theoretical arguments [15, 16].

In 1-aza-triphenylene there is a nitrogen atom in position α, and therefore it is expected that it also will shift the π-electrons away from ring R_1, i.e. that $\Delta EC(R_1)$ will be negative. This indeed is found to be the case (see Fig. 1 and Table 1). Similarly, in 2-aza-triphenylene, in which the nitrogen atom is in position β, the π-electron content of ring R_1 is greater than in the parent hydrocarbon, i.e. $\Delta(R_1) > 0$.

In the case of 1-aza-triphenylene, the unexpected finding is that not only ring R_1 (in which the N-atom is located), but also ring R_3 looses π-electrons, whereas the π-electron content of ring R_2 remains practically unchanged.

In the case of 2-aza-triphenylene, the π-electron density that is attracted into ring R_1 (in which the N-atom is located) comes almost completely from ring R_2, whereas the π-electron content of rings R_3 and R_4 remain practically same as in the parent hydrocarbon.

If more than one nitrogen atom is present, then the displacement of π-electrons can be viewed as a result of the interference of several, above described, α- and β-effects. For instance, if two α-nitrogen atoms are present (as in 1,8-, 1,9-, and 1,12-diaza-triphenylenes), then in all three rings R_1, R_2, and R_3 the π-electron content is diminished more than in 1-aza-triphenylene. Consequently, the π-electron content of ring R_4 is increased relative to 1-aza-triphenylene. In some (αβ)-diaza-derivatives (namely, in 1,6- and 1,7-diaza-triphenylenes), the two N-atoms shift the π-electrons in the same direction, resulting in a decreased EC-value of rings R_1 (in which the α nitrogen atom is located) and R_3, and an increased EC-value of ring R_2 (in which the β nitrogen atom is located). In the other two (αβ)-diaza-derivatives (1,10- and 1,11-diaza-triphenylenes), the two N-atoms act in opposite directions, causing a negative ΔEC-value for ring R_3 (in which the β nitrogen atom is located). From these latter examples we see that the effect of the α nitrogen atom appears to be stronger than the effect of the β nitrogen atom. More details on the (sometimes quite perplexed) interference-effects in di- and tri-aza triphenylene derivatives can be seen in the data given in Table 1.

In what follows we show that these unusual and contra–intuitive displacements of electrons in aza-derivatives of triphenylene can be, but only *a posteriori*, rationalized by resonance-theoretical considerations. We demonstrate this only for the simplest cases – the 1- and 2-aza-triphenylenes.

RESONANCE-THEORETICAL ANALYSIS OF MONOAZA-TRIPHENYLENES

We first examine the monoaza-triphenylene with the heteroatom in position α, i.e. 1-aza-triphenylene, because its resonance-theoretical analysis is simpler.

In Fig. 3 depicted are two Kekulé structures of 1-aza-triphenylene (k_{11}, k_{12}), out of nine total. Inscribed in the rings are the respective π-electron contents. (A double bond that belongs solely to a ring R contributes to the electron content by two electrons; 22 double bond shared by R and another ring, contributes by one electron [1, 2]; an electron pair in ionic resonance forms contributes by two electrons [16].) If the π-electron contents are averaged over all nine Kekulé structures, we arrive at a partitioning that coincides with the partitioning of π-electrons in the parent hydrocarbons, shown in diagram 3 in Fig. 1. Therefore, in order to obtain displacements of π-electrons caused by the heteroatom, we have to take into account ionic resonance structures.

Because nitrogen is more electronegative than carbon, we consider only those charge-separated resonance forms in which the negative charge is located at the nitrogen.

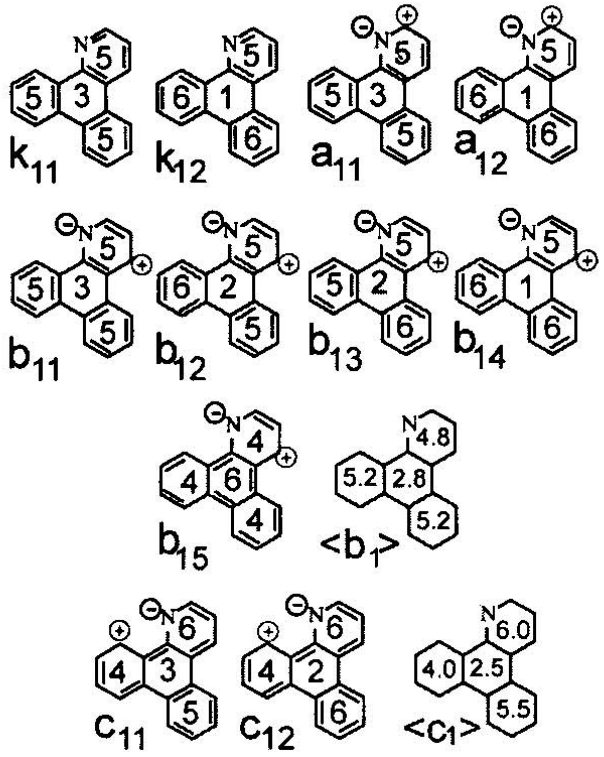

Fig. 3. Kekulé structures (k_{11}, k_{12} and ionic resonance structures (a_{1i}, i = 1, 2, b_{1i}, i 1, ... , 5, c_{1i}, i = 1, 2) of 1-aza-triphenylene, with π-electron contents of rings indicated. Diagrams $\langle b_1 \rangle$ and $\langle c_1 \rangle$ show the average π-electron content of the rings of the resonance forms b_{1i} and c_{1i}, respectively. For details see the text

It is plausible to assume that the most significant ionic resonance forms are those in which the charge separation is minimal. In our case these are the nine resonance structures of which in Fig. 3 are depicted only two: a_{11} and a_{12}. Because these imply the precisely same partitioning of π-electrons into rings as the Kekulé structures (compare a_{11} with k_{11} and a_{12} with k_{12}), we must include into the consideration resonance forms with greater charge separation. The next such resonance forms are b_{11}, b_{12}, ... , b_{15}. The average of their π-electron contents is shown in diagram $\langle b_1 \rangle$. From $\langle b_1 \rangle$ it can be seen that a shift of the electron contents from rings R_1, R_2, and R_3 into ring R_4 takes place. However, according to $\langle b_1 \rangle$ the rings R_2 and R_3 would have equal π-electron contents, which disagrees with the results of our calculations (diagram 4 in Fig. 1). To avoid this, we need to consider resonance forms with still greater charge separation. These are c_{11} and c_{12}, whose average π-electron contents is shown in diagram $\langle c_1 \rangle$. We see that the π-electron content of ring R_3 is diminished relative to R_2. With this the results of our calculations for 1-aza-triphenylene (diagram 4) are shown to be in qualitative agreement with the predictions of resonance theory.

The analysis of 2-aza-triphenylene is analogous, yet somewhat more complicated. The respective resonance forms are shown in Fig. 4.

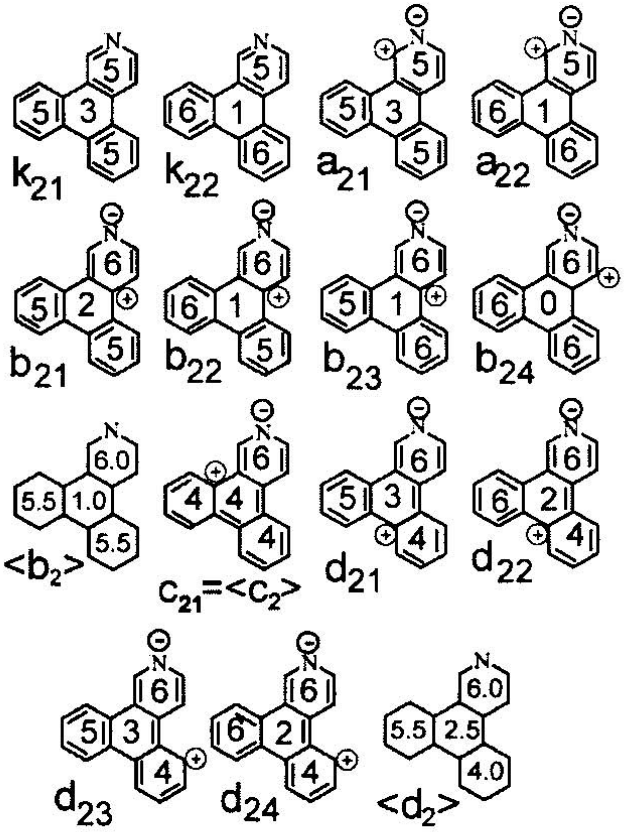

Fig. 4. Kekulé structures (k_{21}, k_{22}) and ionic resonance structures (a_{2i}, i = 1, 2, b_{2i}, i = 1, ... , 4, c_{21}, d_{2i}, i = 1, ... , 4) of 2-aza-triphenylene, with π-electron contents of rings indicated. Diagrams $\langle b_2 \rangle$, $\langle c_2 \rangle$, and $\langle d_2 \rangle$ show the average π-electron contents of the rings of the resonance forms b_{2i}, c_{2i}, and d_{2i}, respectively. For details see the text

For the same reasons outlined before, taking into account only the Kekulé structures (k_{21}, k_{22}, ...) and the ionic forms with minimal charge separation (a_{21}, a_{22}, ...) would not result in any heteroatom-caused shift. Therefore we consider the ionic structures b_{21}, b_{22}, b_{23}, b_{24} that result in an average π-electron content shown in diagram $\langle b_2 \rangle$. From $\langle b_2 \rangle$ it can be seen that the π-electron density is shifted in direction of rings R_1, R_2, and R_3. This agrees with the calculated *EC*-value for ring R_1, but not for rings R_2 and R_3 (see diagram 5 in Fig. 1). In order to explain this discrepancy we need to include into the consideration ionic resonance forms with grater charge separation. The single structure c_{21} implies the diminishing of the *EC*-

values of R_2 and R_3, but no difference between $EC(R_2)$ and $EC(R_3)$. Only by considering the ionic forms d_{21}, d_{22}, d_{23}, d_{24} and their average $<d_2>$, we see why $EC(R_2)$ is less than $EC(R_3)$.

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