

POLANSKY'S BENZENOID CHARACTER AND THE ELECTRON CONTENT OF RINGS OF BENZENOID HYDROCARBONS

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Abstract

In 2004 Balaban and Randić put forward a method to assess the π -*electron content* EC of rings of benzenoid hydrocarbons. Much earlier, in the 1960s, Oskar Polansky conceived and elaborated the concept of *benzenoid character* ρ of the same rings. We show that EC and ρ are linearly correlated, implying that the π -electron content of a ring is just another way of expressing its benzenoid character (or vice versa). The fine details of the correlation between EC and ρ are established.

INTRODUCTION

In two recently published papers [1, 2] Balaban and Randić examined the distribution of π -electrons in benzenoid hydrocarbons, using Kekulé structures. They distributed the π -electrons among rings, associating $EC(R)$ electrons to a ring R . It could be demonstrated [3] that

$$EC(R) = 2 \sum_{\ast} P_{rs}^P + \sum_{\ast\ast} P_{rs}^P$$

where P_{rs}^P is the Pauling bond order of the bond rs , and where \sum_{\ast} and $\sum_{\ast\ast}$ indicate, respectively, summation over the bonds of the ring R which belong solely to R , and which are shared by R and another ring. The quantity $EC(R)$ was eventually named [3, 4] the π -electron content of the ring R .

In the 1960s Oskar Polansky (in cooperation with Gerhard Derflinger) invented the *pars orbital method* by which he could determine the degree of similarity between the wave function in a certain domain of a molecule, and the wave function of a smaller molecule whose structure matches that of the domain considered [5]. In particular, he compared the wave function in a hexagon of a benzenoid hydrocarbon with the wave function of benzene. The measure of their similarity was named *benzenoid character* (originally: *Benzolcharakter*). Also butadienoid, allyloid and other characters were defined, whereas the ethylenoid character was found to be simply equal to the Coulson bond order of the respective carbon-carbon bond [5]. Numerous applications of the *pars orbital method* were eventually reported [6-18].

The benzenoid character $\rho(R)$ of a six-membered ring R was shown to obey the relation [5]

$$\rho(R) = \frac{1}{9} \left[2 \left(P_{12}^C + P_{23}^C + P_{34}^C + P_{45}^C + P_{56}^C + P_{61}^C \right) - \left(P_{14}^C + P_{25}^C + P_{36}^C \right) \right]$$

where P_{rs}^C stands for the Coulson bond order of the bond rs , and where it is assumed that the carbon atoms of R are labelled consecutively by 1,2,3,4,5,6.

CORRELATING EC WITH ρ

In the paper [5] the benzenoid characters of the rings of a large number of benzenoid hydrocarbons were reported, a total of 152 ρ -values, not counting the symmetry-equivalent rings. For the same rings we calculated the EC -values using a pertinent computer program based on the Ham-Ruedenberg formula for Pauling bond orders [19]. The respective correlation is shown in Fig. 1. As seen, the correlation is linear, yet not particularly good; the respective correlation coefficient is equal to 0.9778.

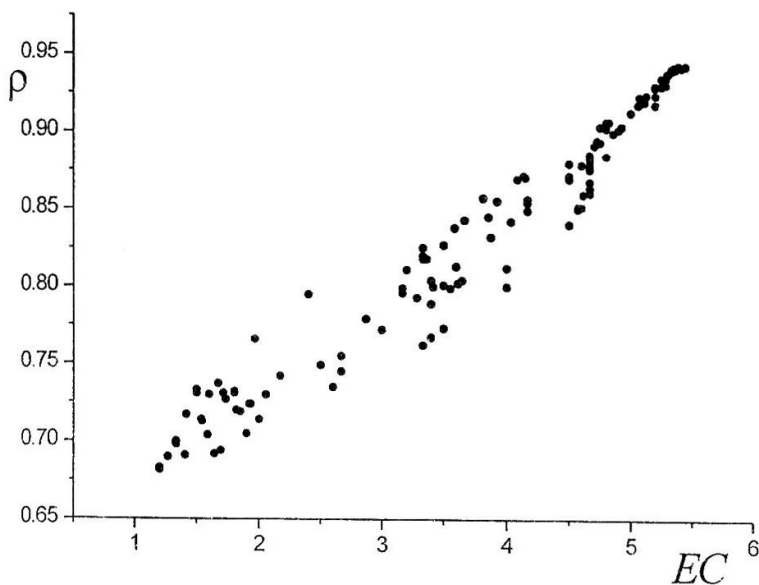


Fig. 1. Plot of the Polansky-Derfingler benzenoid character ρ vs. the Balaban-Randić π -electron content EC of the 152 symmetry-nonequivalent rings in the 39 benzenoid hydrocarbons examined in the work [5].

The fine details of the correlation between ρ and EC are seen when the consideration is restricted to data points pertaining to equally annelated rings. In benzenoid systems 12 different annelation modes are possible [20], depicted in Fig. 2. The respective 12 groups of data points are shown in Figs. 3a-3 ℓ .

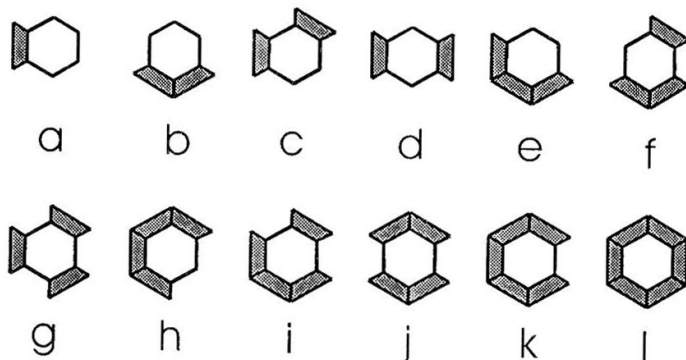


Fig. 2. The twelve different annelation modes of hexagons in benzenoid molecules.

From Figs. 3a-3 ℓ we see that in the majority of cases (namely for the annelation modes *a*, *b*, *c*, *d*, *e*, *g*, *i*, ℓ), there is a reasonably good linear correlation between ρ and EC . In the cases *h* and *k* the data points are so close to each other that no correlation is visible. In the case *f* and especially *j* the data points form two well separated clusters. By direct checking we found that the left-hand side clusters pertain to rings that in Clar aromatic sextet theory [20] are “empty”, whereas the right-hand side clusters to rings that in Clar theory are “full”.

It is worth noting that there are remarkably many equally annelated rings with the same EC -value, but with different ρ -values. This particularly applies to the mode *b*, where of the 33 distinct data points 17 have $EC = 4.6667$. Such a high degeneracy of the π -electrons content, which is not encountered in the case the benzenoid characters, shows that Polansky's almost 40 years old indicator of the electron properties of individual rings in benzenoid hydrocarbons is much more structure-sensitive than its newly invented counterpart.

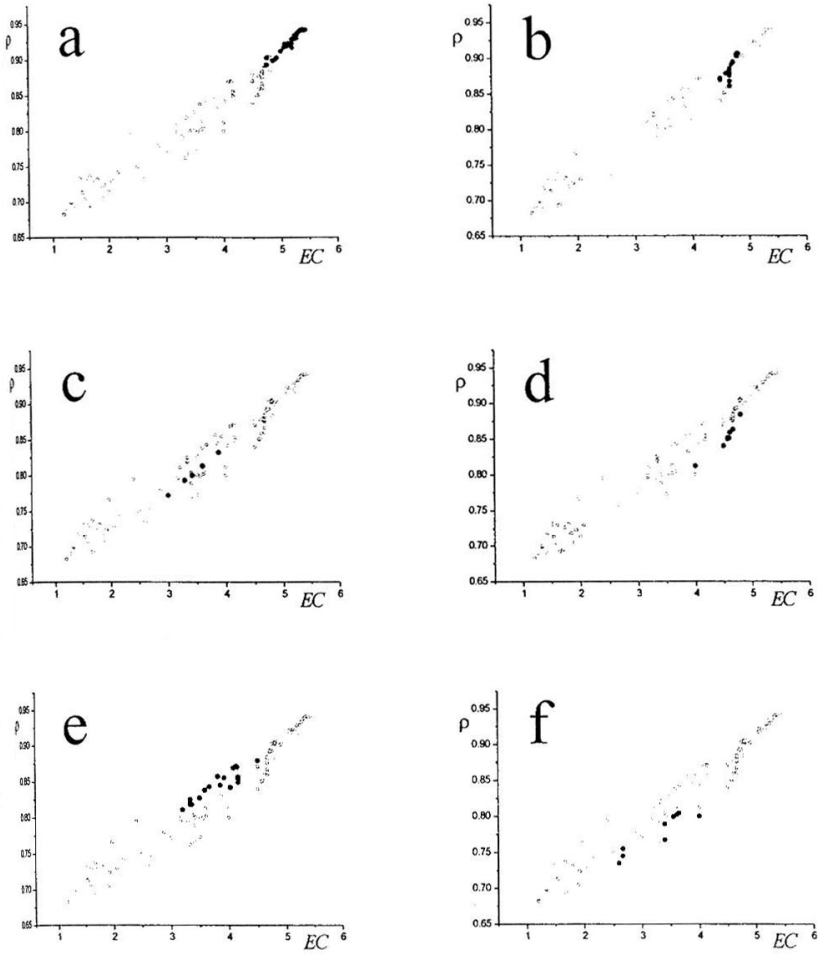


Fig. 3. Same data as in Fig. 1, with black dots emphasizing a group of equally annelated rings. The label in the upper left corner indicates the annulation mode (cf. Fig. 2).

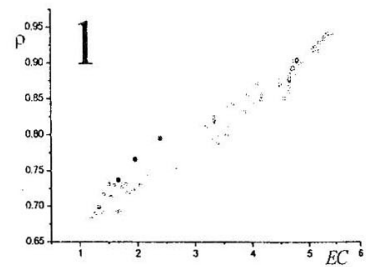
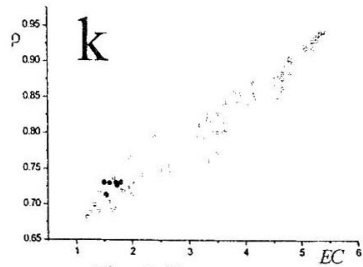
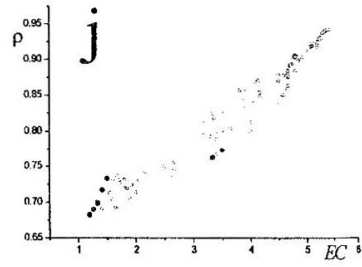
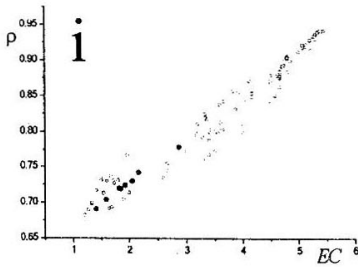
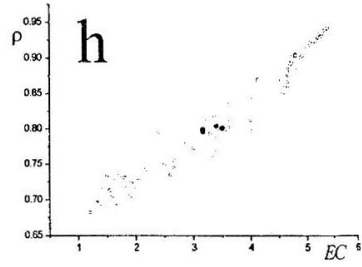
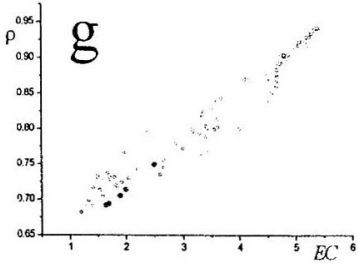


Fig. 3./Cont.

Anyway, our analysis reveals that the π -electron content of a ring is just another way of expressing its benzenoid character (or vice versa). In other words, both ρ and EC seem to measure one and the same local property of benzenoid hydrocarbons, with ρ providing a somewhat sharper image.

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