

Relation between electron and energy contents of hexagons in catacondensed benzenoid hydrocarbons

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The concept of electron content (*EC*) of hexagons in benzenoid hydrocarbons has been recently introduced in a series of scientific papers. In full analogy to it one may conceive also the energy content (*ec*) of hexagons. These contents are mutually related, but not in a manner that could be anticipated. On the basis of the *EC*- and *ec*-values calculated for a large number of catacondensed benzenoid hydrocarbons we establish the actual relation between these quantities. Within hexagons of the same type (terminal, linearly annelated, angularly annelated, and branched) the relation between *ec* and *EC* is nearly linear and the respective regression lines are nearly parallel and equidistant.

The Pauling bond order¹ was introduced in the 1930s and was used for the prediction the lengths of chemical bonds in organic molecules²⁻⁷. We denote it by p_{rs}^p , where *r* and *s* indicate adjacent atoms in the respective molecule. It is equal to the ratio of the number of Kekulé structures in which the bond *rs* is double, and the number of all Kekulé structures.

The sum of Pauling bond orders over all bonds, times two, is equal to the total number of π -electrons in the conjugated system considered^{8,9}. Based on this observation, one may use the Pauling bond orders to (formally) distribute the π -electrons of a polycyclic conjugated hydrocarbon into its rings.

The concept of electron content (*EC*) was recently introduced by Balaban and Randić^{10,11} and further examined and elaborated by several authors^{9,12-14}. It is equal to the sum of Pauling bond orders of bonds belonging to the considered ring (*R*). A bond *rs* that solely belongs to the ring *R* contributes to its electron contents by $2p_{rs}^p$. If the bond *rs* is shared by two rings (say, *R* and *R_i*), then it contributes to the electron contents of both *R* and *R_i* by p_{rs}^p . More formally⁹,

$$EC(R) = 2 \sum_{*} p_{rs}^p + \sum_{**} p_{rs}^p \quad \dots(1)$$

with \sum_{*} and \sum_{**} indicating summations over bonds belonging solely to *R*, and over bonds shared by *R*

and another ring, respectively. The sum of *EC*-values over all rings is equal to the total number of π -electrons. In particular, in the case of catacondensed benzenoid systems, the sum of electron contents of all hexagons obeys the relation:

$$\sum_{i=1}^h EC_i(G) = 4h + 2 \quad \dots(2)$$

where *h* stands for the number of hexagons.

In Table 1 are given the electron contents of the rings (hexagons) of naphtho[1,2-*b*]triphenylene, the structure of which is depicted in Fig. 1.

The most frequently employed bond order for prediction of bond lengths is the molecular-orbital-based Coulson bond order¹⁵⁻¹⁷, which we denote

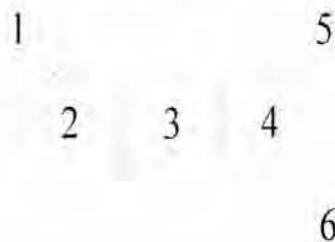


Fig. 1 — Naphtho[1,2-*b*]triphenylene, a catacondensed benzenoid system with six hexagons. It has 26 π -electrons and its total π -electron energy is $E_{\pi} = 36.7149\beta$. In Table 1 are given the electron and energy contents of all its hexagons

Table 1 — Electron and energy contents of rings of naphtho[1,2-*b*]triphenylene, cf. Fig. 1

hexagon	EC	ec
1	5.2273	6.9389
2	3.5000	5.5385
3	4.7273	6.0188
4	1.8182	4.1952
5	5.3636	7.0107
6	5.3636	7.0128
sum	26.0000	36.7149

by p_{rs}^C . It is known that the sum of Coulson bond orders over all bonds of a conjugated π -electron system, times two, is equal to the total π -electron energy of that system (expressed in units of the carbon-carbon resonance integral β). This property of the Coulson bond order makes it possible to employ a procedure analogous to the one described above, and partition the total π -electron energy into rings. The energy content of a ring R , denoted by $ec(R)$, is thus defined by means of the expression

$$ec(R) = 2 \sum_{rs} p_{rs}^C + \sum_{rs} p_{rs}^C \quad \dots(3)$$

in which the notation is analogous to that in Eq. (1).

The sum of energy contents of all rings is equal to the total π -electron energy E_π . In the case of benzenoid systems, in full analogy to Eq. (2) we have

$$\sum_{i=1}^h ec_i(R) = E_\pi \quad \dots(4)$$

More details on the properties and chemical applications of E_π can be found in the recent papers^{18,20} and the references cited therein.

In Table 1 are also given the energy contents of the rings of naphtho[1,2-*b*]triphenylene.

At this point what first needs to be clarified is whether there exists any correlation between $ec(R)$ and $EC(R)$, and if yes, what its main characteristics are.

Technical details

In order to investigate the possible relation between $ec(R)$ and $EC(R)$ it was necessary to compute

the electron and energy contents of hexagons for a reasonably large set of polycyclic benzenoid molecules. This task required the usage of a specially designed computer program, which we named *CELER* (= Content of **E**lectrons and **E**nergy in **R**ing); details on *CELER* are available from the authors, upon request.

By means of *CELER* we calculated the electron and energy contents of the hexagons of all catacondensed benzenoid systems with up to five rings, and of all catacondensed systems with six rings, containing a branched hexagon. One example is given in Table 1.

Results and Discussion

Energy contents versus electron contents are plotted in Fig. 2. From Fig. 2 it is obvious that the data points are separated into three groups. By direct checking we established that the data points are clustered with regard to the number of neighbouring

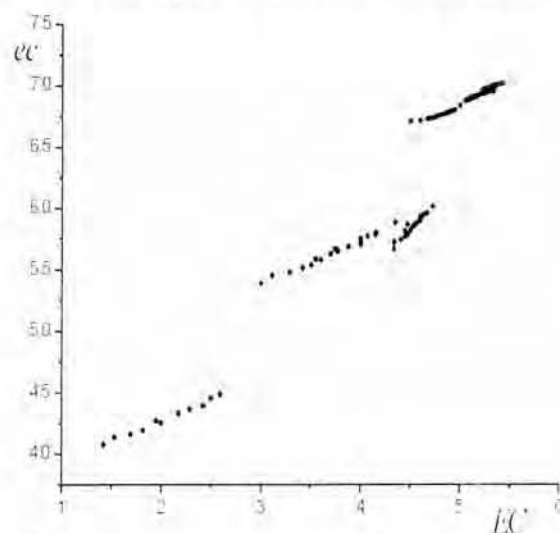


Fig. 2 — The energy contents (ec) of the hexagons of all catacondensed benzenoid systems with 5 and fewer hexagons and all branched catacondensed systems with 6 hexagons, versus the respective electron contents (EC). The data points on the upper right-hand side pertain to terminal hexagons (i. e., 1-hexagon neighbours, e. g., hexagons 1, 5 & 6 in Fig. 1). The data points on the lower left-hand side pertain to branched hexagons (i. e., 3-hexagon neighbours, e. g., hexagon 4 in Fig. 1). The data points in the middle correspond to 2-neighbour hexagons. There are two kinds of 2-neighbour hexagons — linear (e. g., hexagon 3 in Fig. 1) and bent (e. g., hexagon 2 in Fig. 1). The greater distortion in the data points for the 2-hexagon neighbours is the result of these two different arrangements: Bent hexagons have smaller EC -values than the linear ones, and therefore the data points pertaining to bent (resp. linear) hexagons are clustered on the left (resp. right) side of the central group of data points. For more details see text.

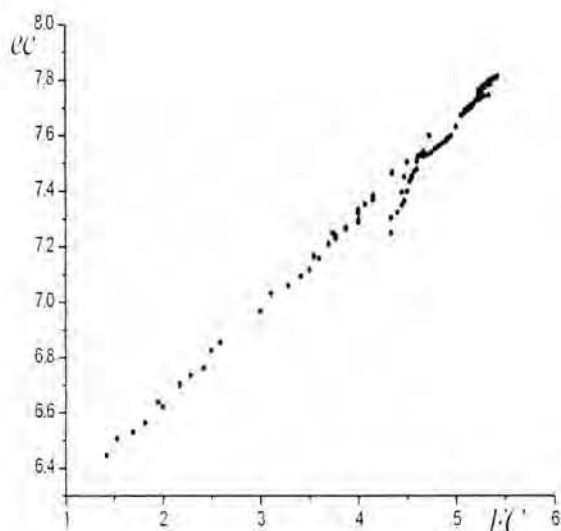


Fig. 3 — The same data as in Figure 2, except that $0.7897v$ was added to each ec -value; v is the number of neighbouring rings

hexagons. The points with $ec < 5$ (clustered on the lower left-hand side of Fig. 2) correspond to branched hexagons (hexagons having three neighbours). The points with $ec > 6.5$ (clustered on the upper right-hand side of Fig. 2) pertain to terminal hexagons (hexagons having a single neighbour). In the middle are lying the points that correspond to hexagons possessing two neighbours. This central cluster is further separated into two groups. The left-hand side points of the central cluster pertain to bent (i.e., angularly annelated), and the right-hand side points to linear (i.e., linearly annelated) hexagons.

These observations infer that the structural feature having the strongest influence on the relation between $ec(R)$ and $EC(R)$ is the number of neighbours. The simplest way to take into account such a neighbour-effect is to add to ec an increment, proportional to the number v of neighbouring rings ($v = 1$ for terminal, $v = 2$ for linearly or angularly annelated rings, $v = 3$ for branched rings). This leads to the regression model:

$$ec + v\gamma = aEC + b \quad \dots(5)$$

By least-squares fitting it was found that the optimal value of the parameter γ is 0.7897. For this value of γ , we obtain that $a = 0.339 \pm 0.003$, $b = 5.95 \pm 0.01$, with correlation coefficient equal to 0.9945. This reasonably good correlation between the electron and energy contents is shown in Fig. 3.

Conclusions

In this work we limited ourselves to catacondensed benzenoid hydrocarbons. Studies of pericondensed systems, which for sure will result in a much more complex correlation pattern, are in progress²¹. (Recall that whereas only four modes of hexagons exist in the case of catacondensed benzenoid systems, there are twelve such modes in pericondensed benzenoids, for details see the book⁷, p. 21.) Our main conclusion is that the correlation between EC and ec is linear, but different regression lines apply to hexagons with different numbers of neighbours. Each new neighbouring hexagon diminishes the ec -value by about 0.79 β -units.

Any dependence between EC and ec must be the consequence of some relation between the Pauling and Coulson bond orders. Although some research along these lines has been done long time ago^{2,22,23}, the details of the relation between the two bond orders were better understood only recently²⁴. In a subsequent paper²¹, we show that by means of these relations, the (empirically established) regularities for the electron and energy contents of rings of catacondensed benzenoids, reported in this paper, as well as for those of pericondensed benzenoids, can be rationalized.

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