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

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Relations are established between the π-electron content (*EC*) and the π-electron energy content (*ec*) of hexagons in pericondensed benzenoid hydrocarbons. Whereas in catacondensed benzenoids only four types of differently annelated hexagons need to be distinguished [Furtula, Gutman & Turković, *Indian J Chem* 43A (2004)], in pericondensed systems there are 12 different annelation types. We show that within each of the 12 classes of equally annelated hexagons there exists a linear correlation between *EC* and *ec*. These correlations can be explained by means of the Cruickshank-Sparks equations, which relate the Pauling and Coulson bond orders. In addition, within each annelation class there is a correlation between the *ec*-value of a hexagon and the effect *ef* of the same hexagon on the total π-electron energy of the corresponding benzenoid molecule. Most of these latter correlations are curvilinear. Our main conclusions are that (a) *ec* is proportional to *EC* and (b) *ec* is proportional to *ef*, but (c) the mode of the annelation of the respective hexagon strongly influences the actual form of these interdependencies.

Introduction

The distribution of π-electrons in the rings of benzenoid hydrocarbons was considered in a recent paper,[1] where references to earlier work on this matter can be found. When the π-electron content $EC(R)$ of a ring R is defined according to Balaban and Randić,[2,3] then $ER(R)$ can be computed from the Pauling bond orders p_{rs}^{P} as:

$$EC(R) = 2\sum_{*} p_{rs}^{P} + \sum_{**} p_{rs}^{P} \qquad \ldots(1)$$

where $\sum_{*}$ and $\sum_{**}$ denote summations, respectively, over bonds that belong only to R and bonds that are shared by R and another ring. Formula (1) was first reported by Gutman *et al.*[4] and its usage was eventually explained in due detail[1,5]:

In analogy to (1) one can conceive the π-electron energy content of a ring R, denoted by $ec = ec(R)$, which conforms to the relation[5]

$$ec(R) = 2\sum_{*} p_{rs}^{C} + \sum_{**} p_{rs}^{C} \qquad \ldots(2)$$

where p_{rs}^{C} stands for the Coulson bond order.

In the earlier paper[5] we analyzed the relations between the *EC*- and *ec*-values of hexagons of benzenoid hydrocarbons, restricting the considerations to catacondensed species. The reason for this limitation was that the *EC*- and *ec*-values depend very much on the mode of annelation of the respective hexagon. In catacondensed benzenoids only four annelation types are encountered, whereas the hexagons of pericondensed benzenoids may be annelated in 12 different ways[6]. The annelation modes occurring in benzenoid hydrocarbons are shown in Fig. 1

It may be recalled that a benzenoid hydrocarbon is said to be pericondensed if it has a carbon atom simultaneously belonging to three hexagons; if there are no such carbon atoms, then one speaks of catacondensed systems[6]. From Fig. 1 it is easily seen that the annelation modes **B**, **E**, **F**, **H**, **I**, **J**, **K** and **L** require that there are three hexagons sharing the same carbon atom. Therefore, these annelation modes may occur only in pericondensed benzenoid hydrocarbons.

This work is in cotinuation of our earlier work[5], extending it to pericondensed benzenoids. Because a rather complicated *EC/ec*-correlation pattern is expected, we first construct an approximate mathematical model for the *EC-ec* dependence. For this we use a modified version of the Cruickshank-Sparks equations, which relates the Coulson and Pauling bond orders in benzenoid hydrocarbons.
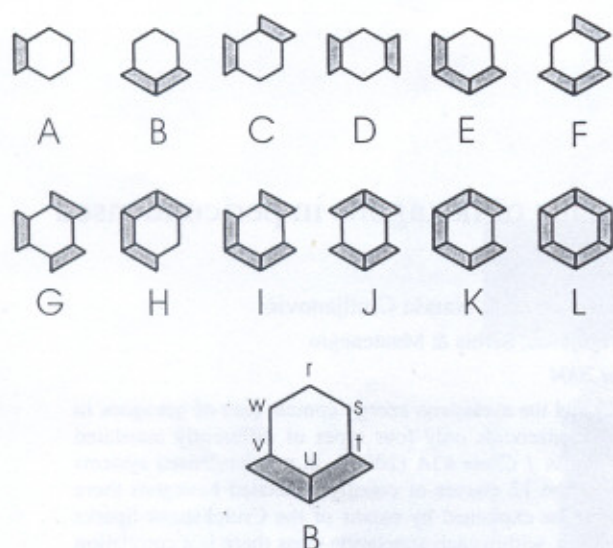
Fig. 1 — The twelve different annelation modes of hexagons in benzenoid systems. In catacondesned benzenoids only modes **A**, **C**, **D** and **G** can occur, whereas in pericondensed systems all the twelve modes are encountered.

On Cruickshank-Sparks Equations

Although both the Pauling[7] and the Coulson[8] bond orders are classical notions of theoretical (quantum) chemistry, their relation has not been much studied. No generally valid connection between p_{rs}^P and p_{rs}^C could be established so far. Cruickshank and Sparks[9] discovered that in the case of benzenoid hydrocarbons there exists a not very accurate relation between the two bond orders, but only within carbon-carbon bonds of the same type.

One has to distinguish between three types of carbon-carbon bonds: with two, with one, and without any hydrogen atoms attached. We refer to these bond types as α, β and γ, respectively.

The original Cruickshank-Sparks formulae (obtained by a standard least-squares optimization) read[9]:

$$p_{rs}^C = 0.30 p_{rs}^P + 0.52 \qquad \text{for } \alpha\text{-type bonds}$$

$$p_{rs}^C = 0.25 p_{rs}^P + 0.48 \qquad \text{for } \beta\text{-type bonds}$$

$$p_{rs}^C = 0.33 p_{rs}^P + 0.41 \qquad \text{for } \gamma\text{-type bonds}$$

As seen, the above three regression lines are not parallel.

We have repeated the required calculation, employing a data set consisting exclusively of bond orders of pericondensed benzenoids. Further, for reasons explained elsewhere,[5] we adjusted the least-squares optimization so that the regression lines be parallel. The following formulae were obtained:

$$\left. \begin{array}{l} p_{rs}^C = 0.275 p_{rs}^P + 0.532 \ \text{ for } \alpha\text{-type bonds} \\ p_{rs}^C = 0.275 p_{rs}^P + 0.465 \ \text{ for } \beta\text{-type bonds} \\ p_{rs}^C = 0.275 p_{rs}^P + 0.428 \ \text{ for } \gamma\text{-type bonds} \end{array} \right\} \quad \text{...(3)}$$

These modified Cruickshank-Sparks formulae were used to model the relations between the π-electron content and π-electron energy content of hexagons of pericondensed benzenoids. More on the Cruickshank-Sparks formulae and their applications was reported elsewhere.[10]

A Mathematical Model for the *EC-ec* Dependence

Combining formulae (3) with (1) and (2) we can obtain an approximate relation between *ec* and *EC* for hexagons of a given type.

Consider, for instance, a hexagon *R* of type **B** and label its carbon atoms by *r*, *s*, *t*, *u*, *v*, *w* as indicated in Fig. 1. Then the hexagon *R* has two α-type bonds (*rs* and *rw*) and two β-type bonds (*st* and *vw*) that belong only to *R*, as well as two bonds of type γ (*tu* and *uv*), that are shared between *R* and another hexagon. Therefore:

$$ec(R) = 2\left[p_{rs}^C + p_{rw}^C + p_{st}^C + p_{vw}^C \right] + \left[p_{tu}^C + p_{uv}^C \right]$$

$$= 2\left[\left(0.275 p_{rs}^P + 0.532\right) + \left(0.275 p_{rw}^P + 0.532\right) \right.$$

$$\left. + \left(0.275 p_{st}^P + 0.465\right) + \left(0.275 p_{vw}^P + 0.465\right) \right]$$

$$+ \left[\left(0.275 p_{tu}^P + 0.428\right) + \left(0.275 p_{uv}^P + 0.428\right) \right]$$

$$= 0.275\left[2\left(p_{rs}^P + p_{rw}^P + p_{st}^P + p_{vw}^P \right) + \left(p_{tu}^P + p_{uv}^P \right) \right] + 4.843$$

$$= 0.275 \, EC(R) + 4.843$$

In an analogous manner we calculate the relations between *ec* and *EC* for all twelve types of annelation modes:

$ec = 0.2746\ EC + 5.4795$ for hexagons of type **A**

$ec = 0.2746\ EC + 4.8430$ for hexagons of type **B**

$ec = 0.2746\ EC + 4.6342$ for hexagons of type **C**

$ec = 0.2746\ EC + 4.5738$ for hexagons of type **D**

$ec = 0.2746\ EC + 4.2065$ for hexagons of type **E**

$ec = 0.2746\ EC + 3.9977$ for hexagons of type **F**

$ec = 0.2746\ EC + 3.8493$ for hexagons of type **G**

$ec = 0.2746\ EC + 3.5700$ for hexagons of type **H**

$ec = 0.2746\ EC + 3.4216$ for hexagons of type **I**

$ec = 0.2746\ EC + 3.4216$ for hexagons of type **J**

$ec = 0.2746\ EC + 2.9939$ for hexagons of type **K**

$ec = 0.2746\ EC + 2.5662$ for hexagons of type **L**

Note that the relations for hexagons of type **I** and **J** coincide.

Numerical Work

Using the computer program[5] CELER the EC- and ec-values of the hexagons of 63 pericondensed benzenoid molecules were calculated. The molecules were taken from tables found in the book by Trinajstić et al.[11] and a review[12]. Plots of the data thus obtained are displayed in Figs 2a and 2b. Because the ec/EC-dependence of hexagons of type **A**, **C**, **D** and **G** was discussed elsewhere,[5] the results obtained for them are not shown.

As seen from Figs 2a and 2b, our theoretical model for the relation between ec and EC is in fairly good agreement with the calculated data points. Thus, our calculations confirm the following: (a) It is necessary to separately consider hexagons with different types of annelation; (b) within each group of equally annelated hexagons a reasonably good linear correlation exists between the π-electron content and the π-electron energy content which means that the domains of a benzenoid hydrocarbon that are electron-rich are also energy-rich; and (c) the Cruickshank-Sparks formulae provide a clue for the understanding why and how the mode of annelation of a hexagon influences the mutual dependence of its electron and energy contents.
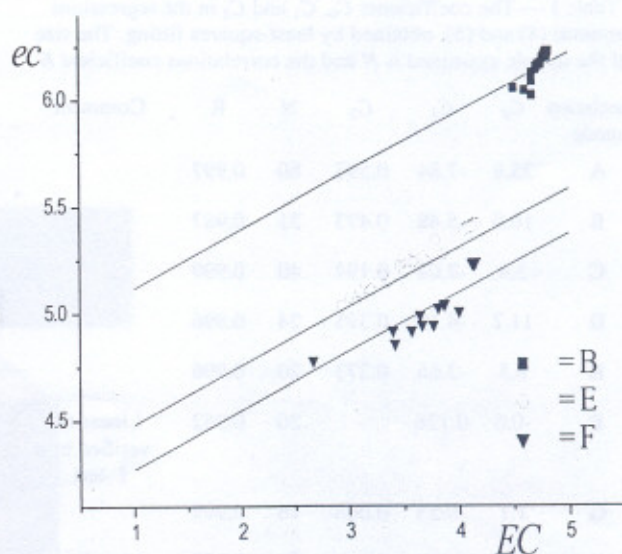

Fig. 2a — Energy contents of hexagons of type **B**, **E** and **F** of pericondensed benzenoid hydrocarbons, versus their electron contents. Note that these hexagons are adjacent to 2 and 3 other hexagons. The lines correspond to the theoretical models obtained by means of the Cruickshank-Sparks equations; for details see text.
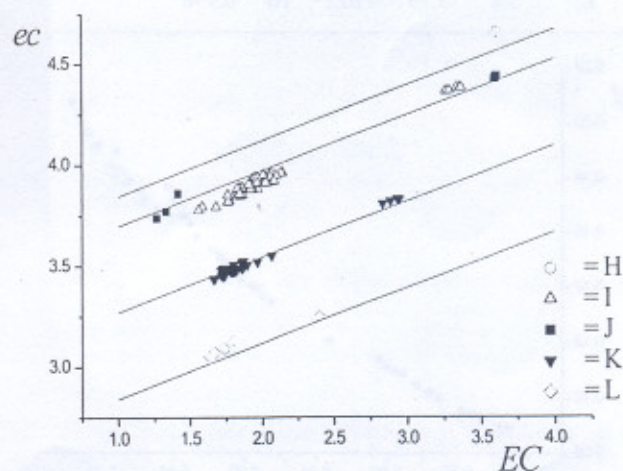

Fig. 2b — Same data as in Fig. 2a, for the hexagons of the type **H**, **I**, **J**, **K** and **L**. These hexagons are adjacent to 4, 5 and 6 other hexagons. Note that the ec/EC-dependence of the hexagons of type **I** and **J** is modelled by one and the same line, which agrees well with the calculated data points.

Relation between energy contents and energy effects of hexagons

Whereas the energy content of a hexagon is a completely new concept in the theory of benzenoid (or more generally: of polycyclic conjugated)

Table 1 — The coefficients C_0, C_1 and C_2 in the regressions formulae (4) and (5), obtained by least-squares fitting. The size of the sample examined is N and the correlations coefficient R

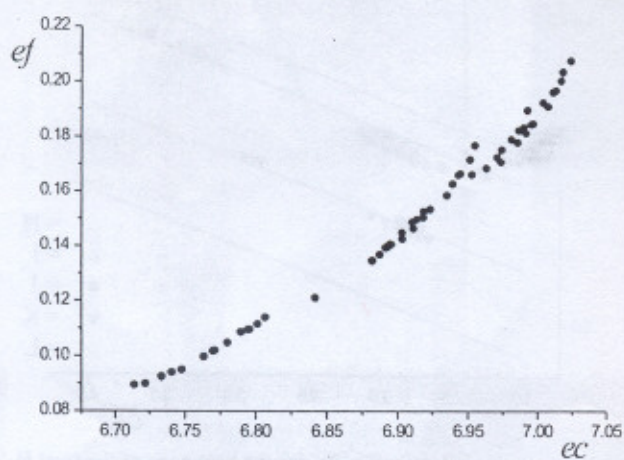| Annelation mode	C_0	C_1	C_2	N	R	Comment
A	25.8	-7.84	0.597	80	0.997	
B	16.0	-5.48	0.473	21	0.987	
C	5.4	-2.04	0.194	40	0.999	
D	11.7	-4.19	0.375	24	0.996	
E	6.5	-2.66	0.273	20	0.996	
F	-0.6	0.126	-	20	0.982	Linearity verified by F-test
G	1.1	-0.53	0.068	16	0.999	
H	-0.6	0.137	-	21	0.858	Very bad correlation
I	1.0	-0.56	0.079	20	0.997	
J	-0.2	0.050	-	20	0.996	See text
K	1.3	-0.76	0.117	20	0.997	
L	5.8	-3.79	0.622	10	0.996	

Fig. 3a — The energy-effect (ef) of hexagons of type A versus their energy content (ec).

molecules[5], a seemingly similar quantity, namely, the energy-effect of a cycle has been conceived and elaborated many years ago[13]. If C is a cycle (not necessarily a ring) of a polycyclic conjugated system whose molecular graph is G, then it is possible to compute its effect $ef = ef(G,C)$ on total π-electron energy. The theory behind the ef-concept is relatively
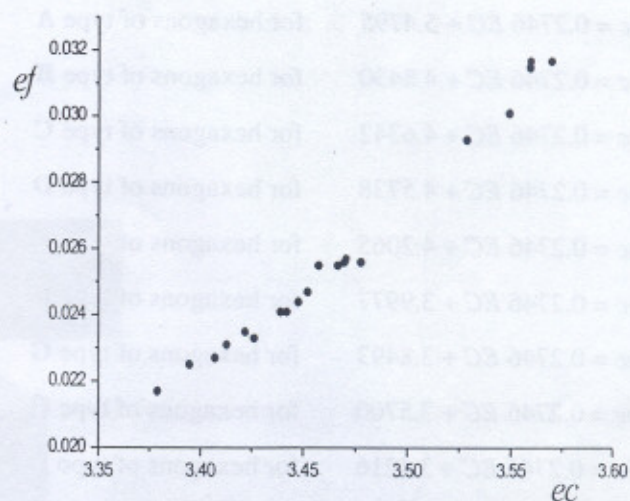

Fig 3b — Same data as in Fig. 3a, for hexagons of type K. Curvilinearity is confirmed by F-test at 99% confidence level.
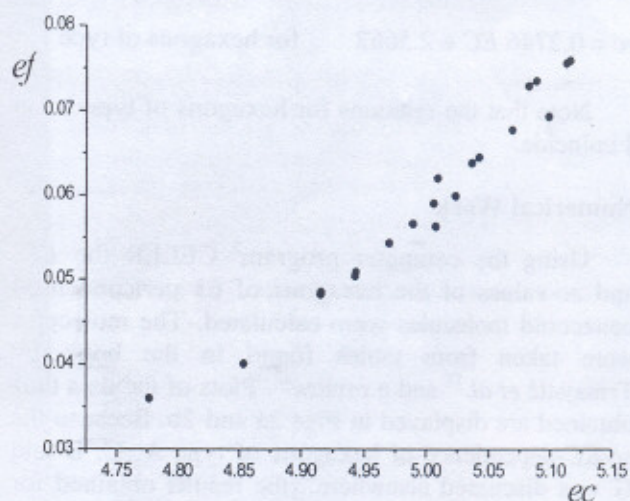

Fig 3c — Same data as in Fig. 3a & 3b, for hexagons of type F. These are the only hexagons for which the ef/ec-correlation is truly linear; for details see text.

complicated[14] and will not be repeated here. The mathematical expression according to which the ef-values are actually computed was given in many earlier publications; see, for instance, the review[15], the papers[16-18] and the references cited therein.

We found that also in this case it is necessary to separately consider differently annelated hexagons. Within each group of such hexagons a reasonably good correlation between the ef- and the ec-values could be established. In the majority of cases these correlations are curvilinear. Three characteristic examples are shown in Figs 3a, 3b and 3c.

In the case of curvilinear correlation between ef and ec, we determined the coefficients of the regression equation:

$$ef \approx C_0 + C_1\, ec + C_2\, ec^2 \qquad \qquad ...(4)$$

In the three cases when the correlation was found to be linear, the regression formula chosen was:

$$ef \approx C_0 + C_1\, ec . \qquad \qquad ...(5)$$

The respective statistical data are given in Table 1.

From Table 1 and Figs 3a-3c we recognise a generally valid property of all the twelve examined ec/ef-correlations: The energy contents of the hexagons monotonically increase with their energy-effects, or *vice versa*. This means that the electron-rich hexagons of a benzenoid hydrocarbon are those in which a strong cyclic conjugation takes place.

The fine details of the twelve examined correlations are remarkably dissimilar. These correlations are good, except in the case of **H**-type hexagons. These correlations are curvilinear (well reproduced by parabolic regression), except in the cases of **F**- and **J**-type hexagons. Whereas in the case of the **F**-type hexagons this correlation is simply linear (as could be verified by F-test, at 99% confidence level), a detailed examination of the **J**-type hexagons revealed the following. There is a single data point (pertaining to the central hexagon of peropyrene) that lies significantly far from the other data points. If this single "outlier" is removed, then a very good curvilinear correlation is obtained, with $C_0 = 0.9$, $C_1 = -0.52$, $C_2 = 0.074$, $R = 0.9993$.

Finding an explanation for such a non-uniform behaviour of differently annelated hexagons with regard to the ec/ef-correlation, and providing a mathematical model for it remains a task for the future.

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