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The Hall rule in fluoranthene-type benzenoid hydrocarbons

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Abstract: The applicability of the Hall rule (linear relation between the total π-electron energy and the number of Kekulé structures) was investigated in the case of fluoranthene-type benzenoid hydrocarbons. It was found that the original Hall rule is not obeyed, but holds for sets of isomers with a fixed number of bay regions. For such groups of isomers, two apparently contradictory Hall-type rules were conceived, and it was found that both give almost identical numerical results.

Keywords: Hall rule; total π-electron energy; Kekulé structures; fluoranthene; benzenoid hydrocarbons; fluoranthene-type hydrocarbons.

INTRODUCTION

The Hall rule, discovered by George Hall in the 1970s[1] and formulated in a quantitative manner in the 1980s,[2,3] claims that within a set of isomeric benzenoid hydrocarbons, the total π-electron energy, E, increases in a linear manner with the number of Kekulé structures, K. Later studies[4–9] showed that the Hall rule holds only for benzenoid molecules of small and moderate size (with up to 9 hexagons) and is violated in the case of larger systems. Recently a modified version of the Hall rule was proposed,[10] in which the dependence of E on K is not strictly linear.

Details of the theory of benzenoid hydrocarbons, including the Hall rule, can be found in a book,[11] review,[12] and the references cited therein.

Whereas benzenoid hydrocarbons have been in the focus of interest of theoretical chemists for more than a century (see the recent papers[13–18] and the references quoted therein), a very similar class of conjugated molecules has almost completely evaded their attention. These are the fluoranthene-type benzenoids, obtained by condensing two benzenoid fragments *via* a five-membered (cyclopentadiene) ring. Four representatives of the fluoranthene-type benzenoid family are depicted in Fig. 1, together with a diagram indicating their general structure.

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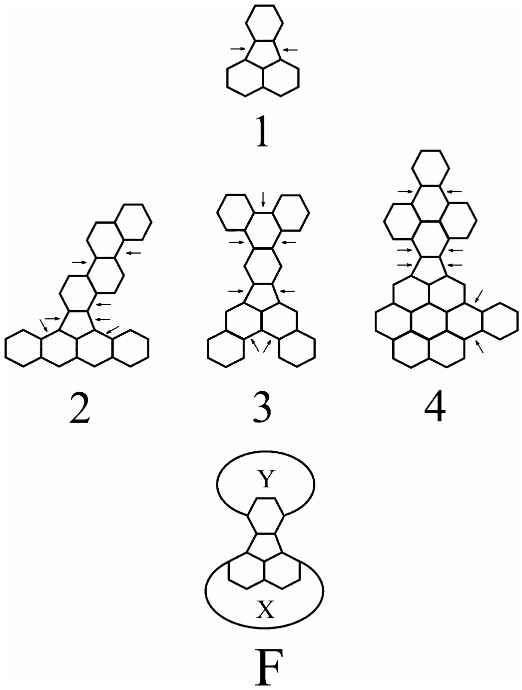

Fig. 1. Fluoranthene (**1**) and three other members of the family of fluoranthene-type benzenoid molecules (**2**, **3**, **4**). Diagram F shows the general structure of a fluoranthene-type system: two benzenoid fragments (X and Y) are joined *via* a five-membered ring. The arrows point to edges, the count of which is the number of bay regions, B; thus $B(\mathbf{1}) = 2$, $B(\mathbf{2}) = 7$, $B(\mathbf{3}) = 7$ and $B(\mathbf{4}) = 8$.

Whereas scores of papers and books are devoted to the theoretical chemistry of benzenoid hydrocarbons, the first article in which fluoranthene-type benzenoids were systematically investigated was published only quite recently.[19] Almost nothing is known on the topological and structure–property relations of fluoranthene-type benzenoid molecules. The aim of the present work (as well as of studies that we intend to accomplish in the future) is to contribute towards filling this hitherto overseen gap in the theory of polycyclic conjugated molecules.

A PROBLEM RELATED WITH THE HALL RULE

According to the Hall rule, if X is a benzenoid molecule with h hexagons, $h \leq 9$, then its total π-electron energy $E(X)$ and Kekulé structure count $K(X)$ are (as a good approximation) related as:[2,3]

$$E(X) = aK(X) + b$$

where a and b are constants that depend on h.

Now, a fluoranthene F is composed of two benzenoid fragments X and Y (*cf.* Fig. 1) and its total π-electron energy is up to an additive constant equal to $E(X) + E(Y)$. On the other hand, the Kekulé structure count of F is equal to $K(X)K(Y)$. Therefore, one arrives at the following seemingly contradictory Expressions (1) and (2):

1. If the Hall rule is applicable to the entire fluoranthene, then:

$$E(F) = a_1[K(X)K(Y)] + b_1 \tag{1}$$

2. Since the Hall rule is applicable to the benzenoid fragments X and Y, it has to be:

$$E(\mathrm{F}) = a_2[K(\mathrm{X}) + K(\mathrm{Y})] + b_2 \tag{2}$$

In the above (approximate) formulas, a_1, b_1, a_2 and b_2 are pertinently chosen constants (see below). In Eq. (2), for the sake of simplicity, it is assumed that the fragments X and Y have an equal number of hexagons.

In order to decide which of the two Hall-type relations hold, Eq. (1) or Eq. (2), a detailed numerical study was undertaken.

NUMERICAL WORK

In order to test the validity of Eqs. (1) and (2), a data set was constructed consisting of all possible fluoranthene isomers in which both fragments X and Y are tetracyclic catacondensed benzenoids, a total of 290 isomers (two of these are compounds **2** and **3** in Fig. 1). Five tetracyclic catacondensed benzenoids exist, *i.e.*, naphthacene (K = 5), benzo[a]anthracene (K = 7), chrysene (K = 8), benzo[c]phenanthrene (K = 8), and triphenylene (K = 9). Therefore, the Kekulé structure counts of the considered fluoranthene isomers assume one of the following nine values: 25, 35, 40, 45, 49, 56, 63, 64, and 72. (There are no isomers with $K = 9^2 = 81$ because triphenlyene cannot be the X-fragment of a fluoranthene-type benzenoid molecule).

The correlation between the total π-electron energy (E) and the Kekulé structure count (K) of the considered fluoranthene isomers is shown in Fig. 2. At the first glance, the correlation is prohibitively bad.

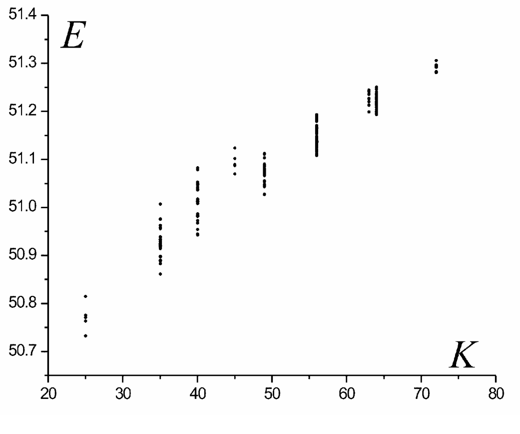

Fig. 2. The total π-electron energies (E) of isomeric fluoranthenes *vs*. their Kekulé structure counts (K). It is easily seen that in addition to K, there is at least one more structural feature that influences E. This structural feature was recognized as the number of bay regions, B (see Fig. 1).

A detailed inspection of the data shown in Fig. 2 indicates that some structural parameter other than the Kekulé structure count influences the value of E, and that its effect is of a similar magnitude as that of the Kekulè structures. It was not to difficult to identify this structural feature, since an analogous problem was a considered long time ago and solved within the theory of benzenoid hydrocarbons.[11,20]

On the perimeter of a benzenoid of a fluoranthene-type system, there are bonds between carbon atoms to which no hydrogen atoms are attached. In the terminology of molecular graphs, on the perimeter there are edges connecting two vertices of degree 3. The number of such carbon–carbon bonds (*i.e.*, edges) is called "the number of bay regions" and is denoted by B. Examples illustrating the bay-region concept are to be found in Fig. 1.

It was established[20] that within isomeric benzenoid hydrocarbons with a fixed number of Kekulé structures, the total π-electron energy depends in a nearly linear (increasing) manner on the parameter B. Theoretical considerations[19] (based on the structure-dependence of the spectral moments) suggest that an analogous regularity should be expected also in the case of fluoranthenes. That this indeed is the case is seen from Fig. 3 and the data collected in Table I.

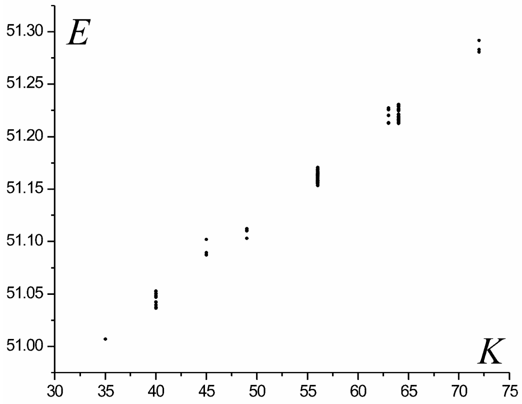

Fig. 3. The total π-electron energies (E) of isomeric fluoranthenes possessing $B = 7$ bay regions *vs.* their Kekulé structure counts (K). The relatively good quality of this correlation confirms Eq. (1); the statistical data for this correlation and those for other values of B are given in Table I.

TABLE I. Data showing the quality of the correlation between the total π-electron energy and the two different counts of Kekulé structures, Eqs. (1) and (2), for isomeric fluoranthene-type benzenoid hydrocarbons with a fixed number of bay regions (B); *N.I.*: number of isomers, R: correlation coefficient. The correlations for $B = 7$ are shown in Figs. 3 and 4.

B	*N.I.*	R (Eq. (1))	R (Eq. (2))
2	1	–	–
3	2	–	–
4	20	0.9802	0.9861
5	59	0.9938	0.9955
6	93	0.9939	0.9941
7	79	0.9953	0.9947
8	36	0.9948	0.9955

However, when an analogous analysis is performed by plotting E not *versus* $K = K(X)K(Y)$ but *versus* $K(X) + K(Y)$, almost identical results are obtained, see Fig. 4 and Table I.

The way in which the coefficients a_1 and b_1 in Eq. (1) depend on the number of bay regions is shown in Fig. 5. The dependence of a_2 and b_2 in Eq. (2) is analogous. Other statistical data on the Correlations (1) and (2) can be obtained from the authors, upon request.

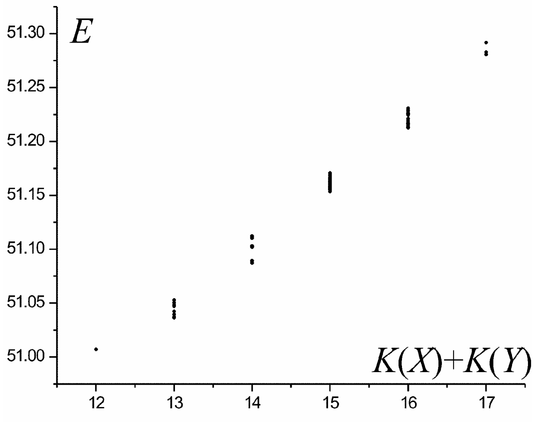

Fig. 4. The total π-electron energies (E) of isomeric fluoranthenes possessing $B = 7$ bay regions *vs.* $K(X) + K(Y)$. The relatively good quality of this correlation confirms Eq. (2); the statistical data for this correlation and those for other values of B are given in Table I.

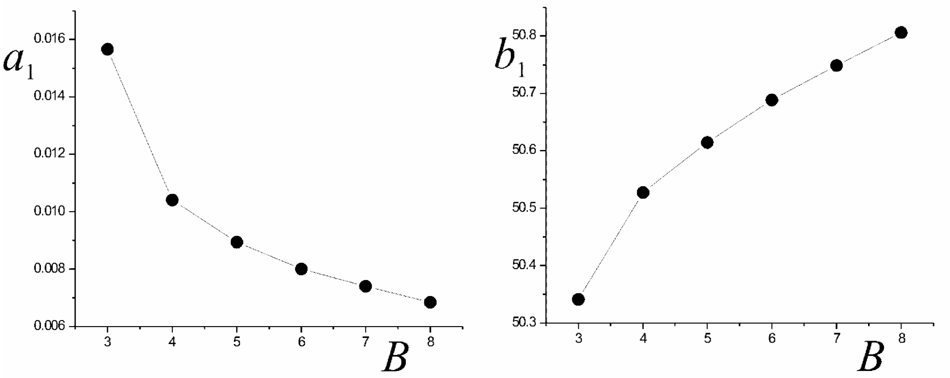

Fig. 5. Dependence of the coefficients a_1 and b_1 in Eq. (1) on the parameter B. The B-dependence of the coefficients a_2 and b_2 in Eq. (2) is almost identical and is therefore not shown.

DISCUSSION AND CONCLUDING REMARKS

The main difference between benzenoid- and fluoranthene-type systems is in the role of the bay regions. The effect of bay regions in fluoranthene-type hydrocarbons is much more pronounced and, therefore, only isomers with equal B-values may be compared. Thus, whereas in the case of benzenoid hydrocarbons, the Hall rule applies to all isomers irrespective of their B-values, in fluoranthenes the Hall-type regularities (either Eq. (1) or Eq. (2)) are valid only within groups of isomers with a fixed number of bay regions. If fluoranthene isomers with non-equal B-values are considered, then the correlation between E and K is very weak (yet linear), as seen in Fig. 2.

From the data presented in the preceding section, one arrives at a somewhat unexpected conclusion: Both forms of the Hall rule, the approximate Formulas (1) and (2), have equal precision and their accuracy is practically identical. This, in turn, means that the original Hall rule can be applied with similar success to both the entire fluoranthene molecules and the two benzenoid fragments that form these molecules. Although the mathematical form of the two Hall rules appears to be significantly different and not mutually consistent, the quality of their numerical performance is indistinguishable.

In summary, it was shown in this paper that in the case of fluoranthene-type benzenoid hydrocarbons, the original Hall rule is not applicable. However, under certain restricted conditions (*e.g.*, fixed *B*-values) regularities similar to the Hall rule could be established. These results indicate that the single five-membered ring in the fluoranthene molecule drastically perturbs the regular π-electron configuration found in ordinary benzenoid hydrocarbons.

ИЗВОД

HALL-ОВО ПРАВИЛО У БЕНЗЕНОИДНИМ УГЉОВОДОНИЦИМА ФЛУОРАНТЕНСКОГ ТИПА

ЈЕЛЕНА ЂУРЂЕВИЋ, СЛАВКО РАДЕНКОВИЋ и ИВАН ГУТМАН

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Испитивана је примењивост Hall-овог правила (линеарне релације између укупне π-електронске енергије и броја Kekulé-ових структура) у случају бензеноидних угљоводоника флуорантенског типа. Нађено је да оригинално Hall-ово правило није задовољено, али да важи за групе изомера са фиксираним бројем залива. За такве групе изомера, дошло се до два наизглед контрадикторна правила Hall-овог типа, и нађено је да оба дају готово идентичне нумеричке резултате.

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