EFFECT OF BENZOCYCLOBUTADIENO–ANNELATION ON CYCLIC CONJUGATION IN CORONENE

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ABSTRACT. Earlier studies showed that the intensity of cyclic conjugation in the six-membered rings of benzenoid hydrocarbons can be significantly altered by means of benzo-annelation. In particular, linear (resp. angular) benzo-annelation was found to decrease (resp. increase) the intensity of cyclic conjugation. We now examine the analogous effect of benzocyclobutadieno-annelation, and study it on benzocyclobutadieno-annelated coronenes. We found that the effects caused by benzocyclobutadieno-annelation are opposite to those caused by benzo-annelation, and are stronger.

INTRODUCTION

Some time ago, one of the present authors elaborated a quantum-theory-based approach, enabling the calculation of the energy-contribution caused by the interaction of π-electrons within individual rings of polycyclic conjugated molecules; for details of this method see the reviews [1, 2] and the references cited therein. The energy-effect thus determined may serve as a reliable measure of the intensity of cyclic conjugation in the underlying ring.

In a series of earlier works [3–7] we have applied this theory to examine the effects of benzo-annelation on the intensity of cyclic conjugation in individual rings of benzenoid hydrocarbons (see Fig. 1).
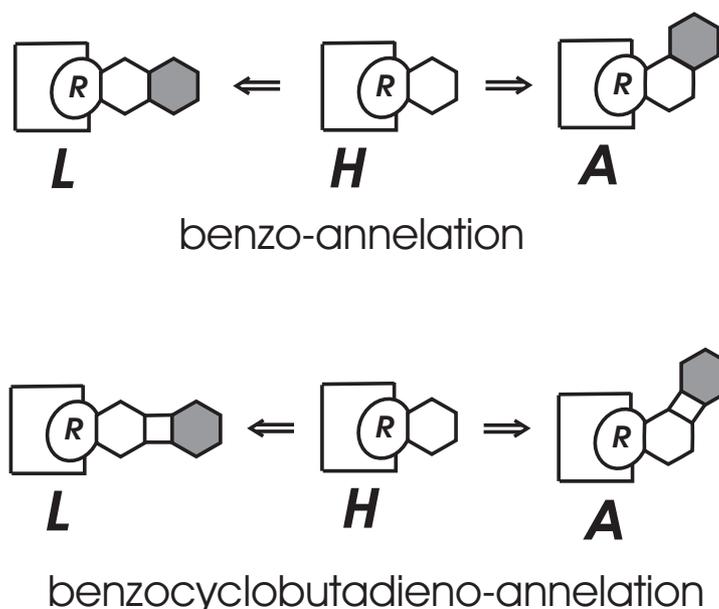
Fig. 1. Various modes of attaching a new six-membered ring to the parent benzenoid hydrocarbon H. With regard to the ring R, benzo– and benzocyclobutadieno-annelation can be either linear (L) or angular (A).

In all the studied cases, the following regularities were observed:

Rule 1. Benzo-annelation in angular position to a six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 2. Benzo-annelation in linear position to a six-membered ring decreases the intensity of cyclic conjugation in this ring.

Rule 3. The effects specified in Rules 1 and 2 are proportional to the number of benzo-annelated rings.

Because benzo-annelation is not the only way in which a new six-membered ring can be attached to the parent benzenoid hydrocarbon (see Fig. 1), we have recently undertaken also studies of cyclic conjugation in benzocyclobutadieno-annelated polycyclic conjugated hydrocarbons [8–11]. Throughout this paper (as well as in the papers [8–11]) "*benzocyclobutadieno*" will be abbreviated by BCBD.

Initially, it was expected that instead of Rules 1–3, the following "reverse" regularities would apply:

Rule 1*. Benzocyclobutadieno-annelation in angular position to a six-membered ring decreases the intensity of cyclic conjugation in this ring.

Rule 2*. Benzocyclobutadieno-annelation in linear position to a six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 3*. The effects specified in Rules 1* and 2* are proportional to the number of benzocyclobutadieno-annelated rings.

Although no definitive conclusions could be drawn so far, the results obtained until now (especially in the works [10, 11]) show that in the general case Rules 1*–3* do not hold, i. e., that there exist noteworthy violations of them. In view of this, in order to further increase our understanding of the regularities for cyclic conjugation in BCBD-annelated benzenoid hydrocarbons, we have studied the BCBD-derivatives of coronene. From the paper [5] we know that coronene has a single mono-BCBD-derivative, and additional three di–, three tri–, three tetra–, one penta–, and one hexa-BCBD–derivative, a total of 12 BCBD-congeners.

In Fig. 2 are depicted coronene and its five BCBD-derivatives.
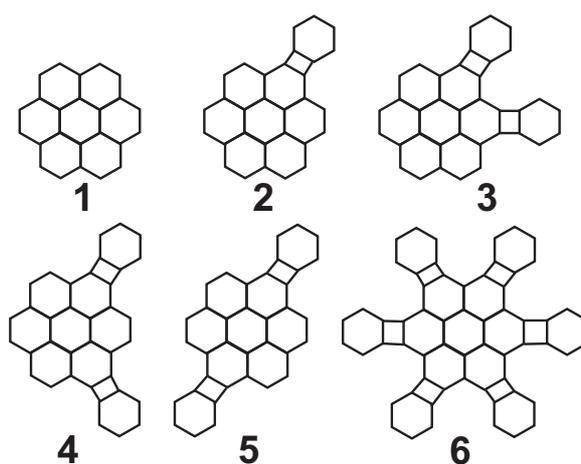
Fig. 2. Coronene (**1**), BCBD-coronene (**2**), the three isomeric di-BCBD-coronenes (**3, 4, 5**) and hexa-BCBD-coronene (**6**).

2. THE METHOD AND NUMERICAL WORK

As already mentioned, we use a molecular-orbital-based method, by means of which we asses the energy contribution, denoted by ef, of an individual ring to the total π-electron energy. Details of this approach can be found in the reviews [1,2]. For the present considerations it is sufficient to recall that the ef-values are expressed in units of the HMO carbon–carbon resonance integral β. Therefore, positive ef-values indicate thermodynamic stabilization caused by cyclic conjugation, and the greater is ef, the stronger is the cyclic conjugation in the underlying ring.

Calculations were done by means of a in-house software, which evaluates the integral

$$ef(R,G) = \frac{2}{\pi} \int\limits_0^{+\infty} \ln \frac{\phi(G,ix)}{\phi(G,ix) + 2\,\phi(G-R,ix)} \, dx$$

where G is the molecular graph of the polycyclic conjugated system [12,13], $\phi(G,x)$ is its characteristic polynomial, $G-R$ is the subgraph obtained by deleting from G the vertices belonging to the cycle R, and $i = \sqrt{-1}$.

The ef-values of all six-membered rings in coronene and its all BCBD-derivatives were calculated. Their numerical values are available from the authors (M. J.) upon request. In the subsequent section we present just a few characteristic examples.

RESULTS AND DISCUSSION

Observation 1. In all BCBD-annelated coronenes, Rule 1* holds. Characteristic examples are shown in Fig. 3.
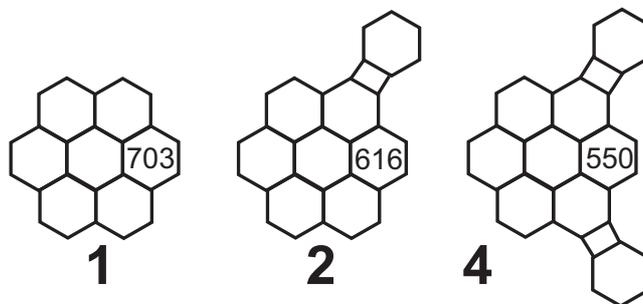
Fig. 3. The ef-values, multiplied by $10\,000$, of a ring without angular BCBD-annelation (**1**), with one and with two angular BCBD-annelations (**2**) and (**4**), respectively.

Observation 2. In all BCBD-annelated coronenes, Rule 2* holds. Characteristic examples are shown in Fig. 4.
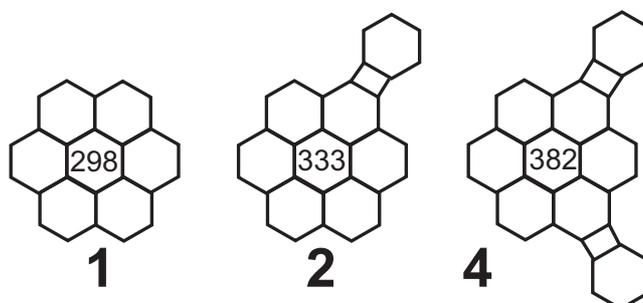
Fig. 4. The ef-values, multiplied by $10\,000$, of a ring without linear BCBD-annelation (**1**), with one and with two linear BCBD-annelations (**2**) and (**4**), respectively.

Observation 3. In all BCBD-annelated coronenes, Rule 3* holds. Characteristic examples are shown in Figs. 3 and 4. In Fig. 5 we present the plot of the ef-values of the central ring in n-fold BCBD-annelated coronenes as a function of n. One should recall that the central ring is always linearly annelated.
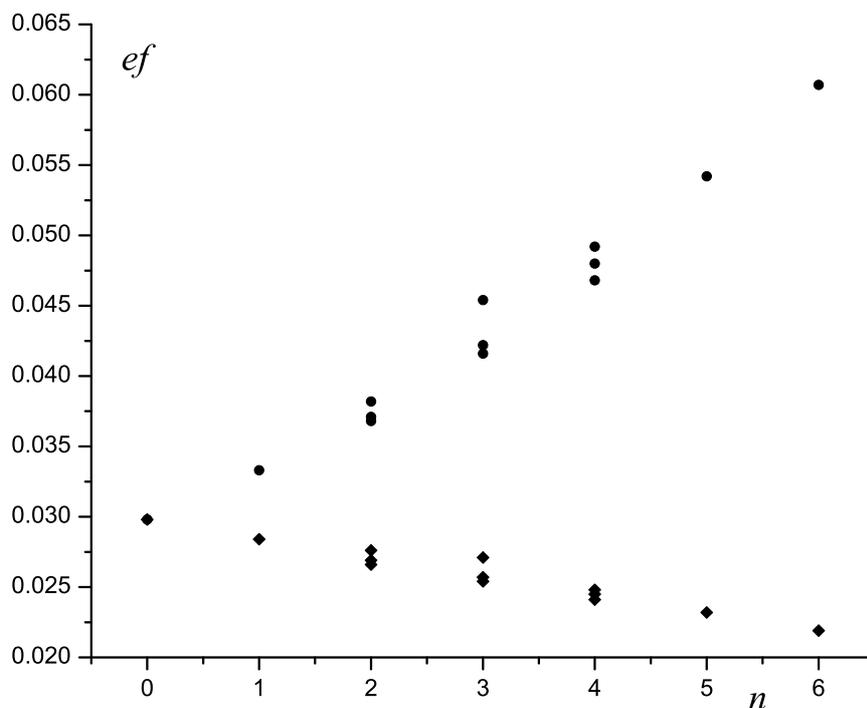
Fig. 5. The ef-values of the central ring of n-fold BCBD-annelated coronenes (circles) and benzo-annelated coronenes (diamonds).

For comparative purposes, in Fig. 5 are presented also the ef-values of benzo-annelated coronenes [5]. According to Rule 3*, the ef-values increase with increasing number n of BCBD-annelations. According to Rule 3, the ef-values decrease with increasing number n of benzo-annelations. From the data shown in Fig. 5 it can be seen that the effect of linear BCBD-annelation is significantly stronger than the analogous effect of benzo-annelation; see Observation 5.

Observation 4. If the number of BCBD-annelations is the same, their effect on the ef-value is almost independent of the actual position of the annelated fragments. A characteristic example is shown in Fig. 6.
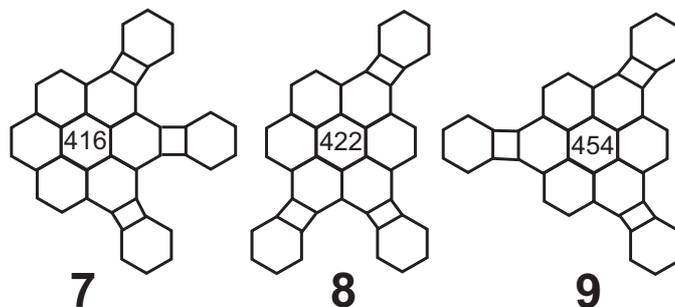
Fig. 6. The ef-values, multiplied by $10\,000$, of the central ring of three isomeric threefold-BCBD-annelated coronenes. These values are not equal, but their differences are insignificant, cf. Fig. 5.

Observation 5. The stabilizing effect of linear BCBD-annelation is greater than the destabilizing effect of linear benzo-annelation. Characteristic examples are shown in Fig. 7.
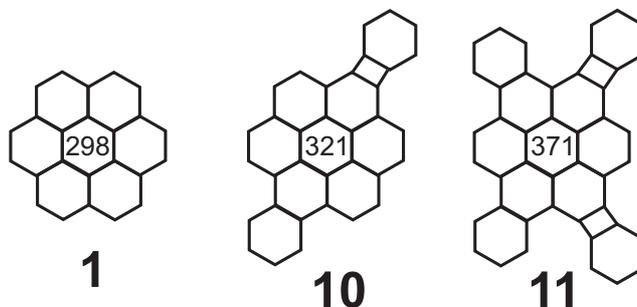
Fig. 7. Coronene congeners with one and two pairs of symmetrically arranged BCBD- and benzo-annelations, compounds **10** and **11**, respectively. The ef-values of their central rings exceed the ef-value in the non-annelated coronene (**1**).

In an earlier work [5] the ef-values of rings in benzo-annelated coronenes were examined. Therefore, it would be of some interest to see if these ef-values are anyhow correlated with the analogous ef-values in BCBD-annelated coronenes. That such a correlation does exist is seen from Fig. 8.
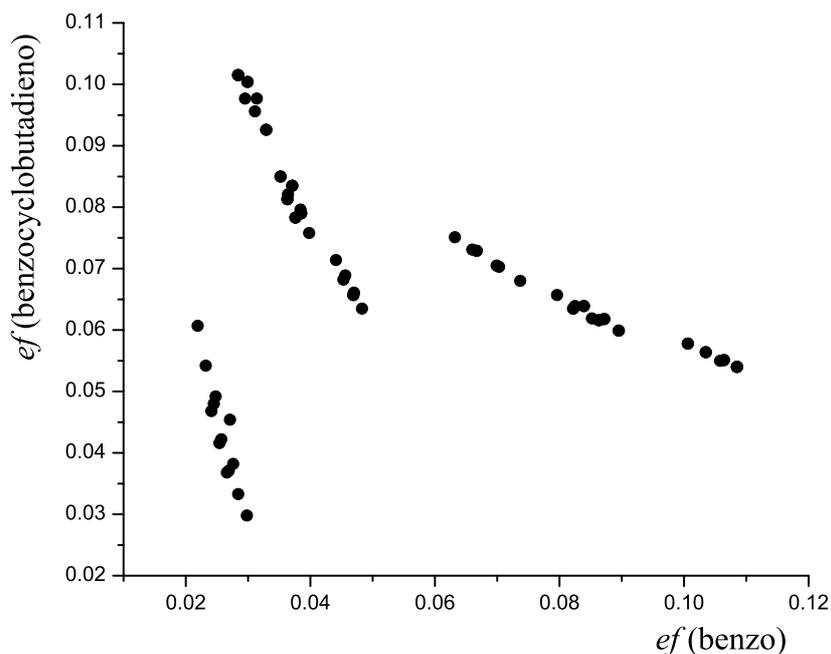
Fig. 8. The ef-values of the seven rings of the coronene fragment in BCBD-annelated coronenes plotted versus the analogous ef-values of benzo-annelated coronenes. For details see text.

From Fig. 8 we see that the data points belong to three well separated clusters, and that within each cluster there is a reasonably good decreasing linear correlation. By a detailed examination we established that the bottom, left–hand side group of data points corresponds to the central ring of the coronene congeners, the right–hand side cluster to the non-annelated peripheral six-membered rings (to which two hydrogen atoms are attached), whereas the middle, upper data points to the annelated six-membered rings. The negative linear correlation within each of these groups is in harmony with the above stated Rules 1–3 and 1*–3*, and may be viewed as a direct consequence thereof.

In Fig. 9 is shown the correlation between the ef-values of the benzene ring, attached by the two considered modes of annelation. The correlation is linear, but not particularly good. It may be that there is some kind of clustering of the data

points, but if such does exist it is not easily recognizable and we did not succeed in its characterization.
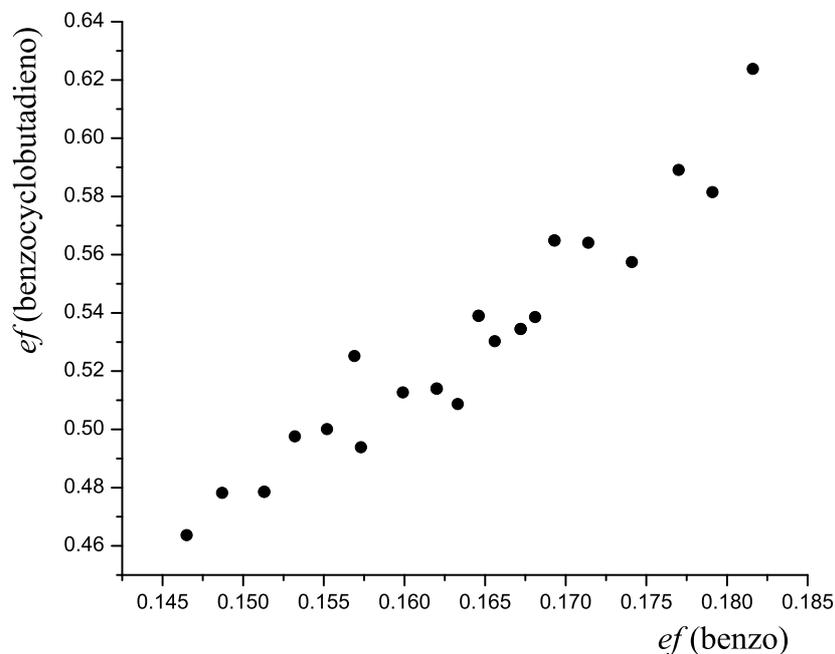
Fig. 8. The ef-values of the benzene rings annelated in BCBD-mode plotted versus the ef-values of the corresponding benzo-annelated benzene rings.

CONCLUDING REMARKS

The effect of benzocyclobutadieno-annelation on cyclic conjugation in the six-membered rings of coronene congeners was examined. In order to assess the magnitude of cyclic conjugation in an individual ring, its energy effect ef was computed. By using this standard procedure for quantifying cyclic conjugation, we found that in the case of BCBD-annelated coronenes, the earlier anticipated Rules 1*–3* are fully obeyed, without any exception.

We also found that the ef-values of BCBD– and benzo-annelated coronenes are strongly correlated, and established the fine details of this correlation.

REFERENCES

[1] I. Gutman, Cyclic conjugation energy effects in polycyclic π-electron systems, *Monatsh. Chem.* **136** (2005) 1055–1069.

[2] I. Gutman, Mathematical modeling of chemical phenomena, in: A. Graovac, I. Gutman, D. Vukičević (Eds.), *Mathematical Methods and Modelling for Students of Chemistry and Biology*, Hum, Zagreb, 2009, pp. 13–27.

[3] I. Gutman, N. Turković, J. Jovičić, Cyclic conjugation in benzo-annelated perylenes: How empty is the "empty" ring ?, *Monatsh. Chem.* **135** (2004) 1389–1394.

[4] S. Jeremić, S. Radenković, I. Gutman, Cyclic conjugation in benzo-annelated triphenylenes, *J. Serb. Chem. Soc.* **75** (2010) 943–950.

[5] S. Jeremić, S. Radenković, I. Gutman, Cyclic conjugation in benzo-annelated coronenes, *Maced. J. Chem. Chem. Engin.* **29** (2010) 63–69.

[6] A. T. Balaban, J. Đurđević, I. Gutman, S. Jeremić, S. Radenković, Correlations between local aromaticity indices of bipartite conjugated hydrocarbons, *J. Phys. Chem.* **A 114** (2010) 5870–5877.

[7] A. T. Balaban, I. Gutman, S. Jeremić, J. Đurđević, Effect of benzo–annelation on cyclic conjugation, *Monatsh. Chem.* **142** (2011) 53–57.

[8] I. Gutman, B. Furtula, A. T. Balaban, Effect of benzocyclobutadieno–annelation on cyclic conjugation in fluoranthene congeners, *J. Serb. Chem. Soc.* **76** (2011) 733–741.

[9] A. T. Balaban, I. Gutman, S. Marković, D. Simijonović, Local aromaticity in benzo– and benzocyclobutadieno–annelated anthracenes, *Monash. Chem.*, in press.

[10] I. Gutman, Effect of benzocyclobutadieno–annelation on cyclic conjugation, *Indian J. Chem.* **50A** (2011) 670–673.

[11] I. Gutman, B. Stojanovska, Effect of benzocyclobutadieno–annelation on cyclic conjugation in perylene, *Maced. J. Chem. Chem. Engin.* **30** (2011), in press.

[12] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemnistry*, Springer–Verlag, Berlin, 1986.

[13] I. Gutman, *Introduction to Chemical Graph Theory*, Fac. Sci. Kragujevac, Kragujevac, 2003 (in Serbian).