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CYCLIC CONJUGATION IN BENZO-ANNELATED CORONENES

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The cyclic conjugation in benzo-annelated coronenes is studied by means of the energy effect (*ef*) and π-electron content (*EC*) of the six-membered rings. Some peculiarities of the π-electron structure of benzo-coronenes, inferred by the Clar aromatic sextet theory, could be tested and verified. A regularity that earlier was discovered in the case of perylene congeners is now shown to hold also for benzo-annelated coronenes: Benzenoid rings that are annelated linearly with regard to the central hexagon H_0 of coronene decrease the intensity of cyclic conjugation in H_0 and this effect is proportional to the number of linearly annelated rings. A very good linear correlation exists between the *ef*- and *EC*-values.

Key words: polycyclic aromatic hydrocarbons; cyclic conjugation; energy effect of cyclic conjugation; π-electron content; coronene; benzo-annelated coronene

ЦИКЛИЧНО КОНЈУГИРАЊЕ КАЈ БЕНЗО-АНЕЛИРАНИ КОРОНЕНИ

Проучувано е цикличното конјугирање кај бензо-анелирани коронени со користење на енергетскиот ефект (*ef*) и π-електронскиот состав (*EC*) во шесточлени прстени. Некои необичности во π-електронската структура на бензокоронените, изведена според Кларовата ароматична секстетна теорија, можат да се тестираат и утврдат. Покажано е дека регуларноста која порано е откриена кај конгенерите на перилен, важи и кај бензо-анелираните коронени: бензенските прстени кои линерано се анелирани во однос на централниот хексагон H_0 на коронените го намалуваат интензитетот на цикличното спрегање во H_0 и овој ефект е пропорционален со бројот на линеарно анелирани прстени. Многу добра линереана согласност е најдена помеѓу вредностите на *ef* и *EC*.

Клучни зборови: полициклични ароматични јаглеводороди; циклична конјугација; енергетски ефект на циклично конјугирање; π-електронски состав; коронени; бензо-анелирани коронени

1. INTRODUCTION

Benzenoid hydrocarbons have been in the focus of interest of the theoretical organic chemistry for almost a whole century [1–6]. Several methods were devised for assessing the intensity of cyclic conjugations in benzenoid rings. The oldest such approach seems to be what nowadays is referred to as the *Clar aromatic sextet theory* [1, 2, 6].

Eric Clar and other chemists [7] formulated several formal requirements for using the circle symbol in benzenoids and for constructing the *Clar aromatic sextet formulas* [1, 2, 6, 8]: (i) Circles are never drawn in adjacent hexagons. (ii) The remaining rings must have a Kekulé structure with 0, 1, or 2 double bonds. (iii) As many circles as possible must be drawn subject to the two previous constraints. If the Clar formula is unique, and if all benzenoid rings are either "full" (with a circle inscribed) or "empty" (with no double bonds), then the underlying molecule is said to be "fully benzenoid". The experimental support for the Clar theory was obtained from electronic absorption and NMR spectra [1], from the reactivity or lack of reactivity of polycyclic benzenoids in Diels-Alder reactions [9–11], and, recently, from scanning tunneling microscopy [12]. Among benzenoid hydrocarbons, the fully benzenoid species happen to be thermodynamically most stable and chemically least reactive [1, 2, 13–15].

In this work we are concerned with coronene and its benzo-annelated derivatives. The members of this class of benzenoid hydrocarbons are stable, easy-to-synthesize compounds, most of which are known for a long time [14, 16]. In Fig. 1 it is shown how their rings are labelled.

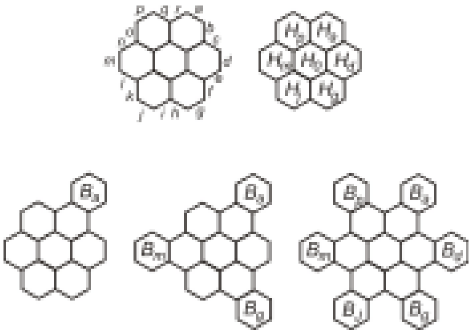

Fig. 1. The labelling of the peripheral carbon-carbons bonds of coronene (according to IUPAC rules [16]) and the labelling of its hexagons. On the below three formulae (of benzo[*a*]-coronene, tribenzo[*a*,*g*,*m*]coronene, and hexabenzo[*a*, *d*, *g*, *j*, *m*, *p*]coronene) the way of labelling of the annelated benzene rings is indicated

Within the Clar theory, the π-electron configuration of coronene is represented by means of two aromatic sextet formulae, cf. Fig. 2. The average of these formulae (which must not be viewed as a kind of "resonance"!) correctly reflects the fact that in all six peripheral hexagons (H_a , H_d , H_g , H_j , H_m , H_p) the intensity of cyclic conjugation is equal, whereas in the "empty" central ring (H_0) it is much weaker.

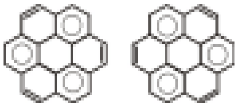

Fig. 2. The two Clar aromatic sextet formulae of coronene

The π-electron configuration of benzo[*a*]coronene is different, see Fig. 3. This molecule has a unique Clar formula, in which the rings H_d , H_j , and H_p , as well as B_a are "full", thus possessing a significantly stronger cyclic conjugation than the rings H_g and H_m . (The ring H_a in benzo[*a*]coronene has a branching pattern different from the rings H_d , H_g , H_j , H_m , and H_p and therefore, as far as cyclic conjugation is concerned, it is not comparable with the latter rings.) The Clar-theory-based π-electron configuration of dibenzo[*a*,*g*]-coronene is analogous: here the extent of cyclic conjugation in H_d , H_j , and H_p is predicted to be higher than in H_m .

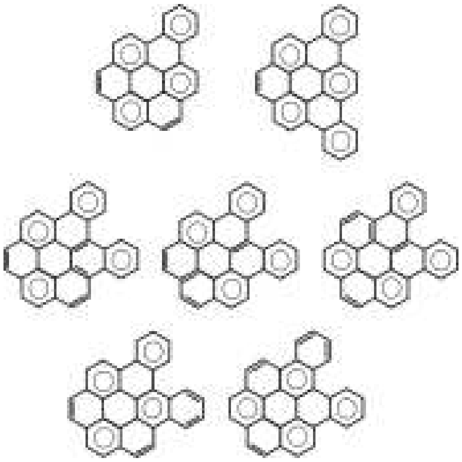

Fig. 3. The unique Clar aromatic sextet formulae of benzo[*a*]coronene and dibenzo[*a*,*g*]coronene, and the five such formulae of dibenzo[*a*,*d*]coronene. Clar-theory-based considerations point towards a marked difference between the patterns of cyclic conjugation of dibenzo[*a*,*d*]coronene and dibenzo[*a*,*g*]coronene

The situation is completely different in the case of dibenzo[*a*,*d*]coronene. It has five distinct Clar formulae (depicted in Fig. 3), which imply a roughly uniform cyclic conjugation in the rings H_g, H_j , H_m and H_p (but, of course, not in the rings H_a and H_d).

The present work is an attempt to test the above described peculiarities of the π-electron configuration of benzo-annelated coronenes, by using methods different from and independent of the Clar theory.

2. METHODS

In this work we assess the intensity of cyclic conjugation in a ring of a benzenoid hydrocarbon by means of two indicators: π-electron content *EC* [17–21] and π-electron energy effect *ef* [22–27].

The *EC* concept relies on π-electron partitions based on how these electrons are assigned from all resonance (Kekulé) structures to each ring's share. Randić formulated three assumptions [5], namely (i) a shared C=C bond contributes with one π-electron to each ring; (ii) an unshared C=C bond in a ring contributes to this ring with both π-electrons; and (iii) all resonance structures have equal weights, so that the final partition is the arithmetical average of all C=C bond contributions. Thus, *EC* is the average content of π-electrons in the underlying ring, calculated from equally weighted Kekulé structures. Randić and Balaban applied this approach to benzenoid and other conjugated hydrocarbons [17–19]; more details on *EC* can be found in the papers [20, 21].

One of the present authors put forward a method by means of which it was possible to asses the contribution of any individual cycle (present in a polycyclic conjugated molecule) on the total π-electron energy [22]. Details on this "energy effect" (*ef*) can be found in the reviews [23, 24] and elsewhere [25–27].

The quantity *ef* is the difference between the total π-electron energy (tentatively, but not necessarily) calculated within the Hückel molecular orbital (HMO) approximation and a quasi-energy, in which the contributions coming from the considered cycle are neglected, whereas contributions coming from any other structural feature are regularly taken into account. In the present work (as well as elsewhere [22–27] the *ef*-values are expressed in HMO β-units, where β stands for the HMO carbon-carbon resonance integral. Because β is a negative-valued quantity, positive *ef*-values imply thermodynamic stabilization; the greater is the (positive) value of *ef*, the stronger is the (stabilizing) cyclic conjugation in the underlying ring.

3. NUMERICAL WORK

Counting only the species in which the benzene rings are annelated via a single carbon-carbon bond, coronene has one benzo-, three dibenzo-, three tribenzo-, three tetrabenzo-, one pentabenzo- and one hexabenzo-derivative, thus a total of 12 benzo-annelated derivatives.

Calculations of both *EC* and *ef* of the ring *Z* were done by our in-house computer programs, using the formulae

$$EC = 2\sum_{rs}^{*} P_{rs} + \sum_{rs}^{**} P_{rs} \tag{1}$$

and

$$ef = \frac{2}{\pi}\int_{0}^{\infty} \ln \frac{\phi(G,ix)}{\phi(G,ix)+2\phi(G-Z,ix)}\,dx\,. \tag{2}$$

In Eq. (1), P_{rs} is the Pauling bond order of the bond between the carbon atoms r and s . The summation $\sum_{rs}^{*}$ goes over the bonds *rs* of the ring *Z* which belong solely to this ring, whereas the summation $\sum_{rs}^{**}$ embraces the bonds *rs* which lie between the ring *Z* and another ring. For more details see [28].

In Eq. (2), the molecular graph [6] is denoted by *G* and by *G-Z* the subgraph obtained by deleting the ring *Z* from *G*. The characteristic polynomial of the graph *G* is $\phi(G,x)$ and $i=\sqrt{-1}$. For more details see [23, 24].

The *EC*-values of all rings of coronene and its benzo-annelated congeners are given in Tables 1a and 1b. The analogous *ef*-values are found in Tables 2a and 2b.

Table 1a

π-electron contents (EC) of the core rings of coronene and its benzo-annelated congeners; for notation see Fig. 1

Molecule	$EC(H_a)$	$EC(H_d)$	$EC(H_g)$	$EC(H_j)$	$EC(H_m)$	$EC(H_p)$	$EC(H_0)$
Coronene	3.7000	3.7000	3.7000	3.7000	3.7000	3.7000	1.8000
[*a*]	2.2647	3.8824	3.6176	3.7647	3.6176	3.8824	1.7353
[*a*,*d*]	2.5000	2.5000	3.8214	3.6786	3.6786	3.8214	1.6429
[*a*,*g*]	2.1525	4.0508	2.1525	3.9322	3.5424	3.9322	1.6949
[*a*,*j*]	2.3509	3.8070	3.8070	2.3509	3.8070	3.8070	1.6491
[*a*,*d*,*g*]	2.4043	2.7340	2.4043	3.8723	3.5957	3.8723	1.5745
[*a*,*d*,*j*]	2.5729	2.3854	4.0000	2.2292	3.8542	3.7500	1.5833
[*a*,*g*,*m*]	2.0577	4.0865	2.0577	4.0865	2.0577	4.0865	1.6731
[*a*,*d*,*g*,*j*]	2.4744	2.6410	2.6410	2.4744	3.7949	3.7949	1.4872
[*a*,*d*,*g*,*m*]	2.3049	2.7927	2.3049	4.0366	2.1220	4.0366	1.5366
[*a*,*d*,*j*,*m*]	2.4500	2.4500	3.9500	2.4500	2.4500	3.9500	1.5000
[*a*,*d*,*g*,*j*,*m*]	2.3636	2.6970	2.5606	2.6970	2. 3636	3.9848	1.4242
[*a*,*d*,*g*,*j*,*m*,*p*]	2.6111	2.6111	2.6111	2.6111	2.6111	2.6111	1.3333

Table 1b

π-electron contents (EC) of the annelated rings of benzo-annelated coronenes; for notation see Fig. 1

Molecule	$EC(B_a)$	$EC(B_d)$	$EC(B_g)$	$EC(B_j)$	$EC(B_m)$	$EC(B_p)$
[*a*]	5.2353	–	–	–	–	–
[*a,d*]	5.1786	5.1786	–	–	–	–
[*a,g*]	5.2712	–	5.2712	–	–	–
[*a,j*]	5.2105	–	–	5.2105	–	–
[*a,d,g*]	5.2128	5.1170	5.2128	–	–	–
[*a,d,j*]	5.1562	5.2188	–	5.2500	–	–
[*a,g,m*]	5.2981	–	5.2981	–	5.2981	–
[*a,d,g,j*]	5.1923	5.1538	5.1538	5.1923	–	–
[*a,d,g,m*]	5.2439	5.0976	5.2439	–	5.2805	–
[*a,d,j,m*]	5.2000	5.2000	–	5.2000	5.2000	–
[*a,d,g,j,m*]	5.2273	5.1364	5.1818	5.1364	5.2273	–
[*a,d,g,j,m,p*]	5.1667	5.1667	5.1667	5.1667	5.1667	5.1667

Table 2a

Same data as in Table 1a, for π-electron energy effects (ef)

Molecule	$ef(H_a)$	$ef(H_d)$	$ef(H_g)$	$ef(H_j)$	$ef(H_m)$	$ef(H_p)$	$ef(H_0)$
Coronene	0.0703	0.0703	0.0703	0.0703	0.0703	0.0703	0.0298
[*a*]	0.0314	0.0863	0.0667	0.0737	0.0667	0.0863	0.0284
[*a,d*]	0.0384	0.0384	0.0839	0.0699	0.0699	0.0839	0.0266
[*a,g*]	0.0299	0.1058	0.0299	0.0895	0.0632	0.0895	0.0276
[*a,j*]	0.0329	0.0822	0.0822	0.0329	0.0822	0.0822	0.0269
[*a,d,g*]	0.0371	0.0470	0.0371	0.0872	0.0660	0.0872	0.0254
[*a,d,j*]	0.0398	0.0364	0.1035	0.0311	0.0852	0.0796	0.0257
[*a,g,m*]	0.0284	0.1085	0.0284	0.1085	0.0284	0.1085	0.0271
[*a,d,g,j*]	0.0385	0.0456	0.0456	0.0385	0.0825	0.0825	0.0241
[*a,d,g,m*]	0.0352	0.0483	0.0352	0.1064	0.0295	0.1064	0.0248
[*a,d,j,m*]	0.0376	0.0376	0.1006	0.0376	0.0376	0.1006	0.0245
[*a,d,g,j,m*]	0.0363	0.0469	0.0441	0.0469	0.0363	0.1035	0.0232
[*a,d,g,j,m,p*]	0.0453	0.0453	0.0453	0.0453	0.0453	0.0453	0.0219

Table 2b

Same data as in Table 1b, for π-electron energy effects (ef)

Molecule	$ef(B_a)$	$ef(B_d)$	$ef(B_g)$	$ef(B_j)$	$ef(B_m)$	$ef(B_p)$
[*a*]	0.1714	–	–	–	–	–
[*a,d*]	0.1599	0.1599	–	–	–	–
[*a,g*]	0.1770	–	0.1770	–	–	–
[*a,j*]	0.1681	–	–	0.1681	–	–
[*a,d,g*]	0.1646	0.1487	0.1646	–	–	–
[*a,d,j*]	0.1573	0.1656	–	0.1741	–	–
[*a,g,m*]	0.1816	–	0.1816	–	0.1816	–
[*a,d,g,j*]	0.1620	0.1532	0.1532	0.1620	–	–
[*a,d,g,m*]	0.1693	0.1465	0.1693	–	0.1791	–
[*a,d,j,m*]	0.1633	0.1633	–	0.1633	0.1633	–
[*a,d,g,j,m*]	0.1672	0.1513	0.1569	0.1513	0.1672	–
[*a,d,g,j,m,p*]	0.1552	0.1552	0.1552	0.1552	0.1552	0.1552

What first needs to be checked is if the *ef*- and *EC*-values yield consistent results. That this indeed is the case is seen from Figs. 4 and 5: the correlation between *ef* and *EC* is linear and remarkably good. This means that the (stabilizing) energy effect of the cyclic conjugation is proportional to the amount of π-electrons in the underlying ring. In other words, both *ef* and *EC* point towards the same regularities for the structure-dependency of cyclic conjugation in the rings of coronene congeners; these regularities are discussed in due detail in the subsequent section.

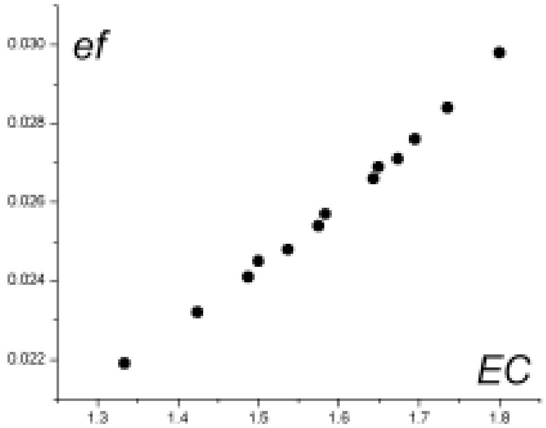

Fig. 4. The π-electron energy effect (*ef*) of the central ring H_0 of coronene congeners vs. its π-electron content (*EC*), cf. Fig. 1 and Tables 1a and 2a.

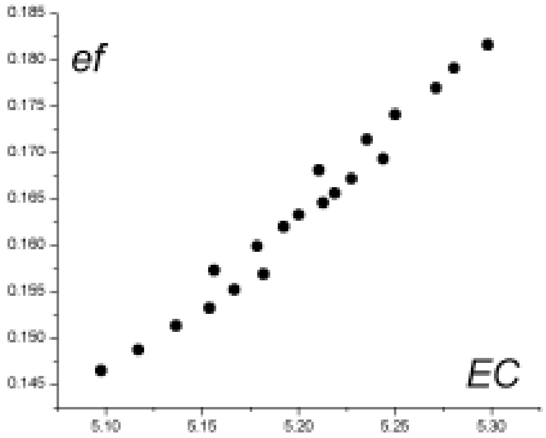

Fig. 5. The π-electron energy effects (*ef*) of the annelated benzene rings of coronene congeners vs. their π-electron content (*EC*), cf. Fig. 1 and Tables 1b and 2b. The data points lie on three parallel lines, depending on whether the annelated benzene ring is of the type **A** (upper line), **B**, (middle line) or **C** (lower line), cf. Fig. 6.

The correlation shown in Fig. 5 is peculiar: the data points form three nearly parallel lines. Their detailed analysis revealed that these lines are determined by the type of the neighborhood of the considered annelated benzene ring, as shown in Fig. 6.

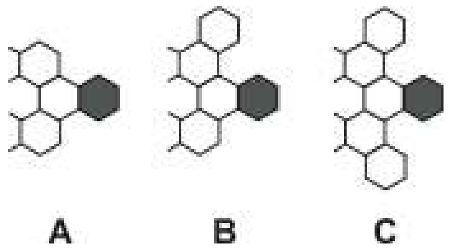

Fig. 6. Three types of the neighborhood of an annelated benzene ring (shaded). Rings of the type **A**, **B**, and **C** pertain, respectively, to the upper, middle, and lower line in Fig 5

4. RESULTS AND DISCUSSION

The data collected in Tables 1 and 2 clearly, and without a single exception, confirm the validity of the predictions deduced from the Clar theory. However, whereas the inferences of the Clar theory are only qualitative, by means of *EC* or *ef* we gain (at least a limited) quantitative insight into the phenomena studied.

Thus, if the intensity of cyclic conjugation in a ring is assessed by either the π-electron content (*EC*) or by the π-electron energy effect (*ef*), we observe the following regularities.

(i) In coronene congeners having a unique Clar formula (namely, in benzo[*a*]coronene, dibenzo[*a*,*g*]coronene, and tribenzo[*a*,*d*,*m*]coronene, cf. Fig. 3), the rings in which circles are inscribed (the "full" rings) have greater *EC*- and *ef*-values than the other comparable rings.

(ii) In coronene congeners having a unique Clar formula, the intensity of cyclic conjugation in "full" rings is increased relative to that in coronene. In other rings cyclic conjugation is weaker.

For instance, in benzo[a]coronene for the "full" rings we have $EC(H_j) = 3.76$, $EC(H_p) = 3.88$, $ef(H_j) = 0.074$, $ef(H_p) = 0.086$, whereas for the structurally similar ring H_m (in which there is one localized double bond), $EC = 3.62$ and $ef = 0.067$. Since, for coronene $EC(H_j) = EC(H_m) = EC(H_p) = 3.70$ and $ef(H_j) = ef(H_m) = ef(H_p) = 0.070$, we see that cyclic conjugation in the "full" rings H_j and H_p has increased whereas in the "half-empty" ring H_m has decreased.

It is also worth comparing the *EC*- and *ef*-values of the rings H_j , H_m , H_p in the two isomeric dibenzocoronenes (cf. Fig. 3):

dibenzo[*a*,*d*]coronene: *EC* = 3.68, 3.68, 3.82; *ef* = 0.070, 0.070, 0.083;

dibenzo[*a*,*g*]coronene: *EC* = 3.93, 3.54, 3.93; *ef* = 0.090, 0.063, 0.090.

Both *EC* and *ef* vary much more in the case of the [*a*,*g*]-isomer than in the case of the [*a*,*d*]-isomer.

(iii) Cyclic conjugation in the annelated benzene rings (the *B*-type rings, cf. Fig. 1), is remarkably high, far exceeding the conjugation in the central rings (the *H*-type rings, cf. Fig. 1). The greatest *EC*- and *ef*-values of the annelated benzene rings are found in the congeners having a unique Clar formula. The maximal *EC*- and *ef*-values are maximal at tribenzo[*a*,*d*,*m*]coronene (equal to 5.30 and 0.16, respectively), which is the only fully benzenoid system among the coronene congeners considered.

(iv) In coronene and all its benzo-annelated congeners the central ring H_0 is "empty" (with neither circles nor double bonds inscribed in it in any of the Clar formulae). Cyclic conjugation in H_0 is significantly weaker than in any other six-membered ring.

In an earlier work [29] (see also [30]), the *ef*-values of the "empty" ring of benzo-annelated perylenes were shown to depend on the mode of annelation: benzene rings annelated in an angular mode significantly increase *ef*, whereas linear annelation has a decreasing effect. An analogous regularity is now observed in the case of benzo-annelated coronenes. In coronene congeners all annelated benzene rings are in linear position with respect to the central ring H_0. Therefore, one would expect that $EC(H_0)$ and $ef(H_0)$ decrease proportionally to the number of annelated benzene rings. This indeed is found to be the case:

(v) The intensity of cyclic correlation in the central "empty" ring of coronene congeners is a decreasing linear function of the number of annelated benzene rings; details are given in Fig. 7.

(vi) In agreement with the correlations specified in the caption of Fig. 7, both $ef(H_0)$ and $EC(H_0)$ assume maximal values (equal to 0.070 and 1.80, respectively) in the case of coronene, and assume minimal values (equal to 0.021 and 1.33, respectively) in the case of hexabenzo[*a*,*d*,*g*,*j*,*m*,*p*]coronene.

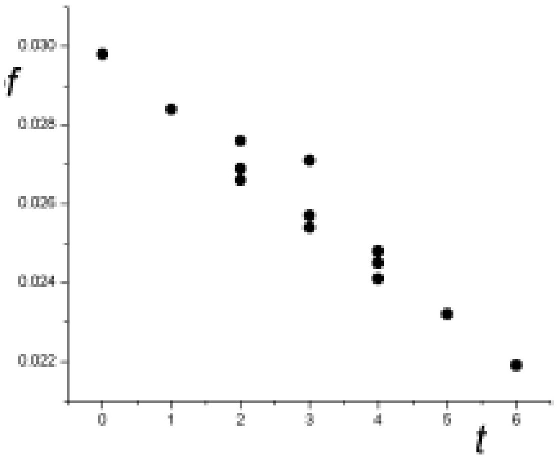

Fig. 7. Dependence of the π-electron energy effect (*ef*) of the central ring H_0 of coronene congeners on the number *t* of annelated benzene rings, cf. Table 2a. The least-squares regression line is $ef = 0.0030 - 0.0013\ t$, and the correlation coefficient is $R = -0.977$. An analogous good (decreasing) linear correlation is also found for the π-electron energy content: $EC = 1.820 - 0.078\ t$; $R = -0.972$, cf. Table 1a

* * * * *

Summarizing the results outlined in this paper we can say that by two independent approaches we have corroborated and quantitatively supported the somewhat counter-intuitive conclusions that the Clar aromatic sextet theory yields for the fine details of the π-electron configuration of some benzenoid hydrocarbons (in particular, of dibenzo-[*a*,*d*]- and dibenzo[*a*,*g*]coronene). We demonstrated this in the case of benzo-annelated coronenes, but we anticipate that this kind of vindication of the Clar theory can be extended to a much wider class of benzenoids.

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