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ORIGINAL PAPER

Local aromaticity in benzo- and benzocyclobutadieno-annelated anthracenes

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Abstract Considerations based on the energetics of cyclic conjugation in individual rings indicate that benzocyclobutadieno-annelation has the opposite effect on local aromaticity in benzenoid hydrocarbons to benzo-annelation. This finding is now tested and corroborated by density functional theory (DFT) calculations of the geometry of all benzo- and benzocyclobutadieno-annelated congeners of anthracene. The harmonic oscillator model of aromaticity (HOMA) and some similar (geometry-based) indices of local aromaticity are found to have the same dependence on the modes of annelation as the molecular-graph-based energy effects.

Keywords Aromaticity · Molecular geometry · DFT calculation · Anthracene · Benzocyclobutadieno-annelated anthracenes

Introduction

The effect of benzo-annelation on local aromaticity in benzenoid hydrocarbons was recently studied in detail (see [1, 2] and the references cited therein). The main quantity by which local aromaticity was assessed in these works was the effect of cyclic conjugation in the considered six-membered ring on total π-electron energy. This energy effect (*ef*) was calculated by a technique developed within chemical graph theory, whose details are reviewed elsewhere [3]. In spite of the fact that in all previously examined cases the *ef* approach gave consistent and chemically sound results, because of its theoretical simplicity it was purposeful to check its predictions by means of more advanced quantum chemical methods (see, e.g., [4]).

In the case of benzenoid hydrocarbons, we examined the effect of benzo-annelation on the six-membered ring, marked X in species **1**–**3** in Fig. 1.

The two main general rules discovered by means of the *ef* approach are the following [1, 2]:

Rule 1. Linear benzo-annelation (cf. **2** in Fig. 1) decreases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species **1**. In particular, $ef(\mathrm{X},\mathbf{2}) < ef(\mathrm{X},\mathbf{1})$.

Rule 2. Angular benzo-annelation (cf. **3** in Fig. 1) increases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species **1**. In particular, $ef(\mathrm{X},\mathbf{3}) > ef(\mathrm{X},\mathbf{1})$.

As before [1–3], the *ef* values are expressed in the units of the Hückel molecular orbital (HMO) carbon–carbon resonance integral β, whose value for thermochemical purposes is around -137 kJ mol^{-1} [5].

We have recently started the examination of the effect on cyclic conjugation of another type of annelation, which we refer to as benzocyclobutadieno- or BCBD-annelation [6], see **4** and **5** in Fig. 1, as well as the examples depicted in Fig. 3. Surprisingly, we found that the effect of BCBD-annelation is opposite to that of benzo-annelation. Thus, instead of rules 1 and 2, the following rules seem to hold generally:

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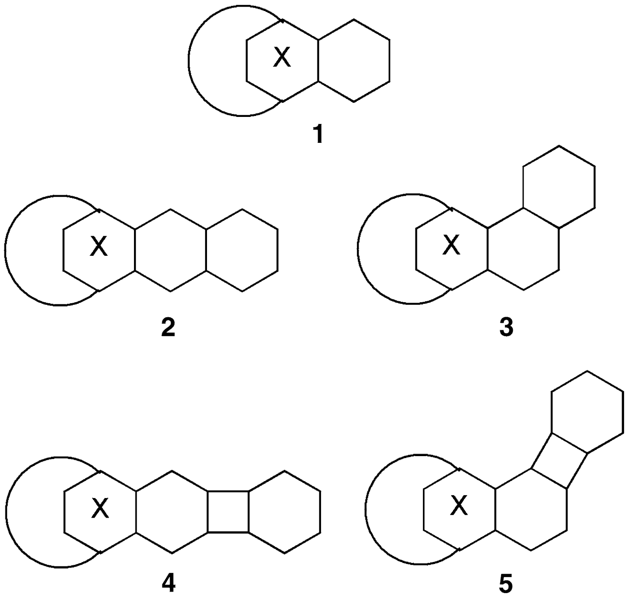


Fig. 1 A benzenoid molecule (**1**), its benzo-annelated derivatives (**2** and **3**), and its benzocyclobutadieno-annelated derivatives (**4** and **5**). The annelation modes **2** and **4** are referred to as linear, whereas those of **3** and **5** are angular. In this work we are concerned with the local aromaticity of the six-membered ring marked *X*

Rule 3. Linear BCBD-annelation (cf. **4** in Fig. 1) increases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species **1**. In particular, *ef*(X,**4**) $>$ *ef*(X,**1**).

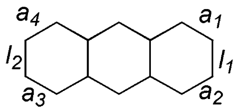
Rule 4. Angular BCBD-annelation (cf. **5** in Fig. 1) decreases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species **1**. In particular, *ef*(X,**5**) $<$ *ef*(X,**1**).

The considerations in this paper pertain to benzo- and BCBD-annelated anthracenes. In order to simplify our notation, the sites of annelation in anthracene are labeled as indicated in Fig. 2; the labeling of the BCBD-derivatives should be evident from the examples depicted in Fig. 3, and the labeling of the benzo-annelated derivatives is analogous.

A characteristic example illustrating rules 1–4 is given in Table 1. One should note that in all cases, the Δ*ef*(benzo) and Δ*ef*(BCBD) values have opposite signs.

In order to further test (and possibly corroborate) these somewhat unusual findings, we have approached the local aromaticity problem from another direction, based on the geometry of the benzo- and BCBD-annelated congeners, as determined by means of advanced density functional theory (DFT) calculations.

Fig. 2 Labeling of the sites of annelation of anthracene



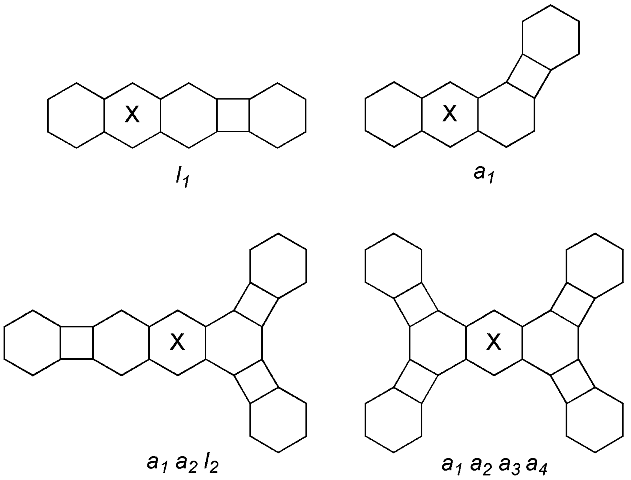


Fig. 3 Labeling of some BCBD-annelated congeners of anthracene. The labeling of benzo-annelated congeners is analogous. *X* indicates the ring whose local aromaticity is examined

Table 1 The change of the energy effect (*ef*) of the ring X caused by benzo- and BCBD-annelation

Compound	Δ*ef*(benzo)	Δ*ef*(BCBD)
a_1	+0.0143	−0.0074
l_1	−0.0118	+0.0105
a_1a_2	+0.0255	−0.0118
a_1a_3	+0.0348	−0.0125
a_1a_4	+0.0349	−0.0125
a_1l_2	−0.0020	+0.0001
l_1l_2	−0.0200	+0.0256
$a_1a_2a_3$	+0.0513	−0.0219
$a_1a_2l_2$	+0.0057	−0.0124
$a_1a_2a_3a_4$	+0.0727	−0.0246

Δ*ef*(benzo) is the difference between the *ef* value of the ring X of the benzo-annelated congener and the *ef* value of the same ring in anthracene; the meaning of Δ*ef*(bcbd) is analogous. For the labeling of the benzo- and BCBD-congeners of anthracene, see Figs. 2 and 3. The *ef* value of the ring X in anthracene is 0.0653 β

Numerical work

In this paper we consider only anthracene and its benzo- and BCBD-annelated congeners. This choice was made because anthracene is relatively small and symmetric, but nevertheless has a total of ten benzo-annelated and ten BCBD-annelated congeners. This choice makes the DFT calculations of all possible congeners feasible. Furthermore, anthracene and all its considered derivatives are perfectly planar with negligible steric strain.

After determining the geometry of the underlying molecules, we can assess the local aromaticity of the ring X by using the harmonic oscillator model of aromaticity (HOMA) index [7–9]:

$$\mathrm{HOMA} = \mathrm{HOMA}(\mathrm{X}) = 1 - \frac{\alpha}{n}\sum_{i,j}\left(R_{\mathrm{opt}} - R_{ij}\right)^2$$

where $\alpha = 25.77 \times 10^{-3}$, $n = 6$, $R_{\mathrm{opt}} = 138.8$ pm, R_{ij} are the lengths (in pm) of the respective bonds of the ring X, and where the summation embraces the six carbon–carbon bonds of X. As is well known [7–9], HOMA measures the deviation of the lengths of the carbon–carbon bonds (in the respective ring) from a value pertaining to a perfectly aromatic compound (namely, benzene).

In addition to HOMA, we have also considered a "naive" index $\Sigma = \Sigma(\mathrm{X})$, equal to the sum of the lengths of the six carbon–carbon bonds of the ring X. The idea behind Σ is that if cyclic conjugation in a ring increases (decreases), then the double-bond character of the involved carbon–carbon bonds increases (decreases), causing on average a shortening (extension) of the carbon–carbon bonds of X.

The geometries of all investigated molecules were optimized with the Gaussian 09 program package [10], using the B3LYP hybrid functional [11, 12] and 6–311+G(d,p) basis set. This triple split basis set adds *p* functions to hydrogen atoms in addition to the *d* functions and diffuse functions on carbon atoms. As previously documented (see, e.g., [13]), this model yields reliable molecular geometries, especially for such stable, singlet ground state species as those studied in the present work. Details of the calculated geometry of anthracene and its 10 + 10 annelated congeners can be found in the "Electronic supplementary material."

The numerical results relevant for our studies are presented in Table 2.

Results and discussion

Before discussing the results shown in Tables 1 and 2, we first point out that a reasonably good linear correlation exists between HOMA and Σ, see Fig. 4. This means that, at least in the case of the central ring X of annelated anthracenes, both HOMA and Σ reflect the same π-electron characteristic of X, which we may view as its local aromaticity.

The correlation between HOMA and *ef* is much weaker, as seen from Fig. 5. The correlation between Σ and *ef* is of similar quality (data not shown).

By comparing the data in Table 2 with those in Table 1, we see that there is a great deal of agreement between the graph-theory-based *ef* results and the DFT-geometry-based results. From a qualitative point of view, agreement exists if the sign of the *ef* value is the same as the sign of the respective HOMA value and opposite to the sign of the Σ value. Thus, generally speaking, the DFT results are in a reasonably good agreement with the rules found by means of the *ef* approach.

In the following discussion we pay attention to the cases of disagreement. In Table 2 these "anomalies" are indicated by superscript letters. What first needs to be observed is that the anomalies always involve linear annelation.

The most evident of these is the linearly BCBD-annelated species l_1 (cf. Fig. 3). Its positive ΔHOMA value (0.0904) is in good agreement with rule 3. On the other hand, its positive $\Delta\Sigma$ value (0.266 pm) indicates that, on average, the carbon–carbon bonds of the ring X became longer, which—from this geometric point of view—would imply that BCBD-annelation has lowered the intensity of cyclic conjugation. This lowering, however, is more than seven times smaller than the analogous effect in the angularly annelated isomer a_1 (for which $\Delta\Sigma = 1.970$ pm).

Table 2 The change of HOMA and Σ indices of the ring X caused by benzo- and BCBD-annelation

Compound	ΔHOMA(benzo)	ΔHOMA(BCBD)	ΔΣ(benzo) (pm)	ΔΣ(BCBD) (pm)
a_1	+0.0391	−0.1013	−1.209	+1.970
l_1	−0.0904	+0.0904	+1.817	+0.266[a]
a_1a_2	+0.0733	−0.2539	−2.225	+4.356
a_1a_3	+0.0955	−0.2014	−2.581	+3.839
a_1a_4	+0.0973	−0.2007	−2.638	+3.858
a_1l_2	−0.0818	−0.1590[a]	+0.970	+2.502[a]
l_1l_2	−0.1326	−0.0080[a]	+3.151	−0.025
$a_1a_2a_3$	+0.1341	−0.3535	−3.738	+6.135
$a_1a_2l_2$	−0.0465[a]	−0.3536	+0.004	+5.297
$a_1a_2a_3a_4$	+0.1693	−0.4860	−4.889	+8.164

ΔHOMA(benzo) is the difference between the HOMA value of the ring X of the benzo-annelated congener and the HOMA value of the same ring in anthracene; the meaning of ΔHOMA(BCBD), ΔΣ(benz), and ΔΣ(BCBD) is analogous. The labeling of the compounds is the same as in Table 1. The HOMA and Σ values of the ring X in anthracene are 0.7205 and 848.1 pm, respectively

[a] Anomalous values; these are discussed in the "Results and discussion"

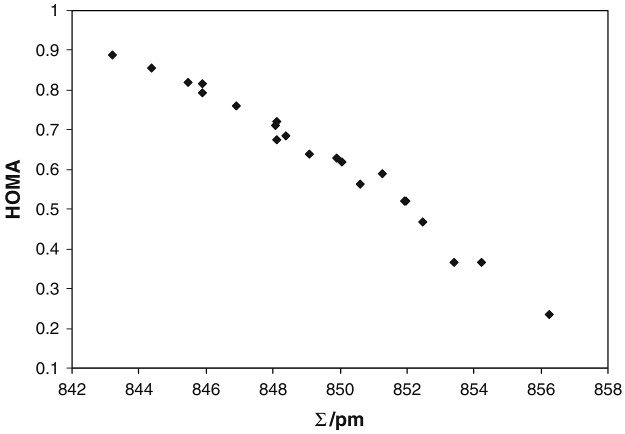


Fig. 4 Correlation between HOMA and Σ values of the ring X of anthracene and its benzo- and BCBD-annelated congeners. All data points lie on the same regression line; the correlation coefficient is −0.987

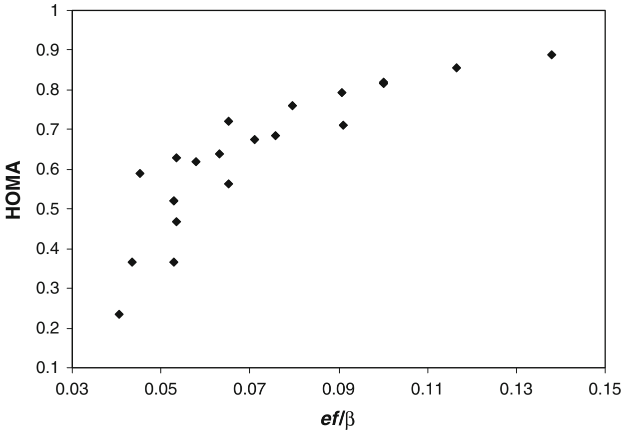


Fig. 5 The weak, non-linear, but increasing correlation between HOMA and *ef* for the same rings as in Fig. 4. The correlation between Σ and *ef* is of similar quality (except that it is decreasing) and is not shown

In the twofold linearly annelated species l_1l_2 ("Electronic supplementary material") we found a small decrease of aromatic character of the ring X (ΔHOMA = −0.0080), which directly contradicts rule 3. (For the same compound, the ΔΣ value, −0.025 pm, is consistent with rule 3.) In any case we must note that both the ΔHOMA and ΔΣ values are quite close to zero, which could be interpreted as if the twofold linear BCBD-annelation leaves the local aromaticity of the ring X practically unchanged. This latter conclusion also contradicts rule 3.

The other anomalies indicated in Table 2 could be understood as a consequence of the competition between the stabilizing linear and destabilizing angular BCBD-annelation. Evidently, in some cases the linear effect dominates over the angular effect, whereas in some other cases the opposite occurs. Which of these effects would be found to prevail, depends on the method employed (*ef*, HOMA, or Σ), and thus cannot be formulated in some generally valid rule.

In summary, our assessment of local aromaticity, based on DFT molecular geometry, confirmed the validity of rules 1, 2, and 4, and thus confirmed the predictions made by means of the simple graph-theory-based energy effects *ef*. On the other hand, the finding of several violations of rule 3 can be understood as just a new manifestation of the previously established fact (see, e.g., [14–16]) that energetic and geometric criteria or aromaticity may lead to contradictory conclusions. However, because the presently used DFT method provides a far more accurate description of the electronic structure of a polycyclic conjugated molecule than a graph-theory-based approach, we are inclined to conclude that the predictions made by means of the *ef* method should be taken and interpreted with due caution and cum grano salis.

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