On the Aromatic Stabilization of Benzenoid Hydrocarbons

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A general scheme for estimation of aromatic stabilization energies of benzenoid hydrocarbons based on selected topological features has been presented. The reactions have been applied to benzene, naphthalene, anthracene, phenanthrene, pyrene, tetracene, benz[a]anthracene, chrysene, [4]-helicene, anthanthrene and coronene.

For years benzenoid hydrocarbons played the role of chemical bricks, easy-available objects able to imitate the smallest subunits of graphene.[[1]](#endnote-2) Many systems having various topology have been rationally devised and synthesised, among them Müllen’s beautiful macromolecular and supramolecular giants,[[2]](#endnote-3) prior to graphene's successfull discovery.[[3]](#endnote-4) Due to their high degree of structural homogeneity they have also been intensively exploited to study various hypotheses concerning π-electron delocalization and its impact on electronic[[4]](#endnote-5) and magnetic,[[5]](#endnote-6) structural features[[6]](#endnote-7) or chemical behaviour.[[7]](#endnote-8) Their stabilities were mostly analysed with theuse of graph-topological methods,[[8]](#endnote-9),[[9]](#endnote-10) enabling easy extention to large or even infinite nanosheets. More exact estimations of resonance energy (*RE*) or of the aromatic stabilization energy (*ASE*) using experimental thermodynamic or computational quantum mechanical data concerned mostly benzene or monocyclic systems, although there were also some attempts at larger systems.[[10]](#endnote-11) The most commonly-used approach for benzenoid hydrocarbons was proposed by George et al. in 1970s[[11]](#endnote-12) based on comparison of the energy of an aromatic system and with acyclic reference systems:

½ (2a-b) CH2=CH-CH=CH2 → CaHb + ½ (3a-2b) CH2=CH2

As pointed out earlier,[[12]](#endnote-13) despite its simple and general formulation it is a rather deficient approach for three main reasons: (i) the reactions fails to balance different types of bonds (the reference systems have no CC bonds without hydrogen atoms attached, although this can be solved in a simple way[[13]](#endnote-14)), (ii) it’s not easy to decide whether *syn-* or *anti-* butadiene should be used as reference (in polycyclic systems both formal topological units can be distinguished),10,[[14]](#endnote-15) (iii) the reaction does not balance strain, hyperconjugation and similar effects, which prevents its application e.g. to bent aromatics. Although butadiene may serve as a good reference for benzene, in polycyclics larger linear and branched polyenes should be considered.10 This can be viewed as another flaw of the approach based on butadiene. Instead, we propose to compare the energies of aromatics with appropriate reference systems having both as similar as possible sigma frameworks (the same topology) and effectively enforced localization of the π-electron structure.10,[[15]](#endnote-16) From a chemical perspective this can be most effectively achieved for methylene substituted derivatives, where all carbon atoms have the same hybridization, and similarly for polyenes where the localization of bonds leads to additive energy relationships.10,[[16]](#endnote-17) Our preliminary work based on different reaction schemes gave very consistent ASE values for corannulene and coronene.12 In this paper we investigate benzene and other benzenoid hydrocarbons: naphthalene, anthracene, tetracene, benz[a]anthracene, chrysene, [4]-helicene, pyrene, phenanthrene, anthanthrene. Coronene is reinvestigated as well.

Consider a chemical system as a molecular graph G, defined by a set of topological features χ(G). A topological feature is a stoichiometric or structural characteristic that can be distinguished in different chemical systems. It is reasonable to assume that two systems A and B characterized by exactly the same set of all *n* topological features {1,2,3,4, ……*n*} have the same energy. Therefore the difference in energy between two systems can be represented as a function of differences of their respective topological features i. This can be expressed in the following way:

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |

In practice we limit the number of topological features to *k* well- defined characteristics (*k* < *n*).

|  |  |
| --- | --- |
| Forwe obtain | (3) |

where *ε* is the estimated error in *E.*

If an aromatic molecule and reference model system (with localized π electron structure) are denoted as A and B respectively, then *ε* gives an estimate of the *ASE*. The exact value is not obtained because a finite set of topological features χ(G) is considered and consequently not all topological features contributing to the energy are taken into account.

For benzenoid hydrocarbons we distinguish the following easy defined topological features χ(G): the number of carbon atoms (χC(G)), the number of hydrogen atoms (χH(G)), the number of double bonds in the *syn* () or *anti* conformation () (denoted as χ*syn*(G)or χ*anti*(G), respectively) and the number of unfavourable interactions between CH2 groups situated in *ortho* position relative to each other in the ring () (χ*ortho*(G)) or situated parallel () (χ*p*(G)).

Most comprehensively the procedure can be presented for benzene. In this case we have only four methylene substituted reference systems, that lead to π-electron structure localization. Their structures and topological features are given below.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |
| C = H | 8 | 8 | 10 | 12 | 6 |
| *syn* | 0 | 2 | 3 | 6 | 3 |
| *anti* | 4 | 2 | 2 | 0 | 0 |
| *orhto* | 0 | 1 | 3 | 6 | 0 |

To estimate the energy of localized (reference structure), EB, the following homodesmotic reaction can be formulated:

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *c*1 |  | + *c*2 |  | + *c*3 |  | + *c*4 |  | → |  |
|  | (R1) |  | (R2) |  | (R3) |  | (R4) |  | (B) |

Since the number of topological features on both sides of reaction must match, the *c*i coefficients can be found by solving the following set of linear equations:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *c*1CH (R1) + | *c*2CH (R2) + | *c*3CH (R3) + | *c*4CH (R4) = | CH (B) | (4) |
| *c*1*syn* (R1) + | *c*2*syn* (R2) + | *c*3*syn* (R3) + | *c*4*syn* (R4) = | *syn* (B) |  |
| *c*1*anti* (R1) + | *c*2*anti* (R2) + | *c*3*anti* (R3) + | *c*4*anti* (R4) = | *anti* (B) |  |
| *c*1*ortho* (R1) + | *c*2*ortho* (R2) + | *c*3*ortho* (R3) + | *c*4*ortho* (R4) = | *ortho* (B) |  |

Since two CXHY isomers having the same number of  bonds have (*syn* + *anti*) constant, a set of linearly dependent equations is obtained. The reaction coefficients are *c*1=(*t*-1), *c*2=3, *c*3=(-2*t*-1) and *c*4=*t*. The energy of the localized system (B) can be obtained from the following equation:

|  |  |
| --- | --- |
|  | (5) |
| Hence: |  |
|  | (6) |

Where EA is the energy of (delocalized) benzene. The EB (and therefore ASE) has the estimated error (*ε*B), which is smaller if a larger number of topological features is taken into account. It is clear that *ε*B depends also on the reaction coefficients *c*i(*t*). If they are bigger, the error is also bigger. The minimization of the function

|  |  |
| --- | --- |
|  | **(7)** |

within the least square procedure leads to *t* = ‑ 1/6 (see the ESI and Figure 1). Thus the estimated *ASE* value for benzene is 29.1 kcal/mol, perfectly in line with other reliable estimations.10

|  |  |
| --- | --- |
|  | 3da |

Figure 1. The *F*(*t*) and *F*(*t,u*) functions for benzene and pyrene

The procedure for polycyclic systems is slightly more complicated because more reference compounds may be considered and hence more reactions can be constructed. An example for pyrene is shown below:

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *c*1 |  | + *c*2 |  | + *c*3 |  | + *c*4 |  | + *c*5 |  | → |  |

In this case a solution based on set of linear equations, constructed in a similar way as for benzene, leads to the stoichiometric coefficients *ci*(*t,u*),

** ** and ****, which depend on two parameters *t* and *u.* Finding the minimum of the corresponding two-dimentional function (*F*(*t,u*)=1/9(54*t*2‑216*t*+20*u*2+62*u*‑18*tu*+269)) by a least-squaresprocedure leads to values of *tmin*= ****and *umin* =**** (see Figure 1 and the ESI for details),which results in a value of 48.6 kcal/mol for the *ASE* of pyrene. The other values based on different reactions are very consistent with each other.[[17]](#endnote-18) They are given in Table 1, together with the reaction coefficients. The resulting *ASE* is 49 kcal/mol with the standard deviation based on 15 reactions of only 1.6 kcal/mol!

Table 1. Coefficients *c*i and the *ASE* values [kcal/mol] for pyrene.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |  | *ASE* |
| -0.550 | 0.667 | 1.883 | 0 | 0 | 0 | -0.297 | 0 | -0.703 | 1 | **48.6** |
| -2.300 | 4.300 | 0 | -1.100 | 1.100 | 0 | -1.000 | 0 | 0 | 1 | **50.0** |
| -2.000 | 4.000 | 0 | -1.000 | 1.000 | 0 | 0 | 0 | -1.000 | 1 | **48.8** |
| -0.833 | 2.833 | 0 | -1.833 | 0 | 1.833 | -1.000 | 0 | 0 | 1 | **50.3** |
| -0.667 | 2.667 | 0 | -1.667 | 0 | 1.667 | 0 | 0 | -1.000 | 1 | **49.1** |
| -0.320 | 2.320 | 0 | -1.760 | 0 | 0 | -1.000 | 1.760 | 0 | 1 | **52.5** |
| -2.150 | 4.150 | 0 | 0 | 0 | 0 | 0.550 | 0 | -1.550 | 1 | **46.5** |
| -0.200 | 2.200 | 0 | -1.600 | 0 | 0 | 0 | 1.600 | -1.000 | 1 | **51.1** |
| -1.538 | 3.538 | 0 | 0 | -1.692 | 1.692 | -1.000 | 0 | 0 | 1 | **47.1** |
| -1.308 | 3.308 | 0 | 0 | -1.538 | 1.538 | 0 | 0 | -1.000 | 1 | **46.2** |
| -0.833 | 2.833 | 0 | 0 | -1.833 | 0 | -1.000 | 1.833 | 0 | 1 | **49.4** |
| -0.667 | 2.667 | 0 | 0 | -1.667 | 0 | 0 | 1.667 | -1.000 | 1 | **48.3** |
| -2.300 | 4.300 | 0 | 0 | 0 | -1.100 | -1.000 | 1.100 | 0 | 1 | **49.5** |
| -2.000 | 4.000 | 0 | 0 | 0 | -1.000 | 0 | 1.000 | -1.000 | 1 | **48.4** |
| -0.667 | 0.667 | 2.000 | 0 | 0 | 0 | -1.000 | 0 | 0 | 1 | **49.3** |

In the case of polycyclic systems, another complication comes from the fact that they are represented by different canonical structures. In principle they are characterized by different sets of topological features *syn* and *anti*, which although unlikely for benzene, result in sets of different aromatic stabilization energies. In fact, slightly modified reactions are obtained for other canonical representations, but all of them are again very consistent (see ESI and Table 3). In this context it is reasonable to assume that the *ASE* is the largest possible stabilization of an aromatic molecule compared to a model system with localized π-electron structure.

Table 2. The minimal, maximal values of *ASE* [kcal/mol] and their standard deviations based on 15 reactions[[18]](#endnote-19) (see the ESI).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | *ASEmin* | s.d. *ASEmin* | *ASEmax* | s.d. *ASEmax* |
| Benzene\* | 29.1 | ‑ | 29.1 | ‑ |
| Naphthalene | 33.4 | 0.7 | 39.4 | 0.8 |
| Anthracene | 36.2 | 1.0 | 42.0 | 1.9 |
| Phenanthrene | 41.7 | 2.9 | 51.4 | 2.7 |
| Pyrene | 40.8 | 1.1 | 49.0 | 1.7 |
| Tetracene | 34.8 | 2.1 | 39.2 | 2.2 |
| Benz[a]anthracene | 44.0 | 3.2 | 54.5 | 0.9 |
| Chrysene | 48.3 | 2.1 | 56.4 | 2.7 |
| [4]-helicene | 44.8 | 1.6 | 51.9 | 1.9 |
| Antanthrene | 39.4 | 2.4 | 46.2 | 2.3 |
| Coronene | 45.8 | 2.3 | 58.1 | 1.9 |
| \* based on one reaction | | | | |

Table 2 presents minimal and maximal values of *ASE* calculated for the benzenoid hydrocarbons: benzene, naphthalene, anthracene, phenanthrene, pyrene, tetracene, benz[a]anthracene, chrysene, [4]-helicene, anthanthrene and coronene. They are mean values based on 15 reaction schemes (except for benzene). Their standard deviations clearly indicate that the procedure described in this paper is very consistent. What’s important is that the stabilization refers to model systems that represent a limiting case of chemically achievable localization of π-bonds. It should also be pointed out that the procedure enables exact reproduction of their energies (within c.a. 1-2 kcal/mol error), proving that the topological features are perfectly additive for the reference compounds (see Table 4S ESI).

Interestingly, in all benzenoid systems the highest value of stabilization is always observed for the so-called Fries canonical structure,[[19]](#endnote-20) and the lowest value for the anti-Fries structure. The former is the structure having the maximal number of π-electron sextets (also maximal number of *syn* topological units), whereas the latter is characterized by the maximal number of *anti* topological units. A plot of the calculated *ASEmax* per π-electron versus the number of π-electrons (Figure 2) reveals clear lowering of stabilization energy in the series of acenes (correlation coefficient for the linear regression is *R*=0.999), which is in line with chemical stability of these systems[[20]](#endnote-21) and explains well why breaking the electron delocalization in central rings *e.g.* by addition reaction is easy affordable. In line with chemical expectations the angular system (phenanthrene) is more stable than the linear one (anthracene),[[21]](#endnote-22) while the relative aromatic stabilization of coronene is lower than the value for pyrene. In the family of chrysene is stabilized most (ASE=56.4 kcal/mol), whereas tetracene is stabilized least (ASE=39.2 kcal/mol). The sequence of compounds reflects the order of relative stabilities in this series perfectly. The sequence of compounds in four fused six-membered rings group match perfectly the order of their overall stabilities,[[22]](#endnote-23) with chrysene and tetracene stabilized most (ASE=56.4 kcal/mol) and least (ASE=39.2 kcal/mol), respectively. This is very important finding, as suggests that the differences in total energies between the isomers are (almost) solely due to different aromatic stabilization while other effects (like e.g. strain) have a minor differentiation role and influence all systems to similar extent.

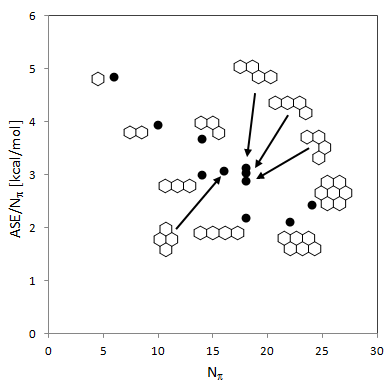


Figure 2. Dependence of *ASE*/*N*π versus the number of π‑electrons *N*π.

Summing up: a general scheme for estimation of aromatic stabilization energies of benzenoid hydrocarbons has been presented. This approach can easily be extended to non-benzenoid systems (in fact this kind of approach has already been applied for deriving the ASE for corannulene)12 or for heterocyclic molecules. The reference compounds have similar sigma framework as the aromatics and represent model systems, with most efficient (from achemical perspective) localized π-electron structures. The estimated aromatic stabilization energies based on different reaction schemes lead to very consistent values provided that the reaction coefficients are optimally derived. The maximal *ASE* values were always obtained for the Fries-type structure. The lowering of stability depends on topology and is accompanied by an increase of the size of a molecule.

The systems used for ASE estimations were fully optimized at B3LYP/6-311G\*\* level of theory (see the notes for details).

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Notes and references

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† Electronic Supplementary Information (ESI) available: Point groups, absolute electronic energies and Cartesian coordinates calculated at B3LYP/6-311G\*\* for benzene and naphthalene, anthracene, tetracene, phenanthrene, benz[a]anthracene, chrysene, [4]-helicene, pyrene, anthanthrene, coronene and its derivatives. The coefficients of the reactions used for *ASE* calculations. The sets of homodesmotic reaction coefficients *c*i showing additivity in theenergy of reference compounds. Full citation of Ref. [23]. See DOI: 10.1039/b000000x/

‡ All systems were optimized at the B3LYP/6-311G\*\* DFT level of theory using the Gaussian 03 program.[[23]](#endnote-24) The calculated geometries of benzene and naphthalene, anthracene, tetracene, phenanthrene, pyrene, benz[a]anthracene, chrysene, [4]-helicene, anthanthrene, coronene and their derivatives were true minima on potential energy surface with no imaginary vibrational frequencies. In the above mentioned cases zero point energy (ZPE) corrections were included.

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    [↑](#endnote-ref-24)