WHY IS PHENANTHRENE MORE STABLE THAN ANTHRACENE?

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By means of a recently developed molecular-orbital-based method it is possible to estimate the energy effects of individual cycles, as well as pairs, triplets, etc. of cycles in polycyclic conjugated molecules. From these energy-effects one can better understand which structural details are responsible for the thermodynamic stability of the underlying molecule. In particular, it is possible to rationalize (in a quantitative manner) the causes of differences in the thermodynamic stability of isomers. Such an analysis is here performed on the two isomeric benzenoid hydrocarbons with three hexagons – anthracene and phenanthrene.

Key words: benzenoid hydrocarbons; anthracene; phenanthrene; energy-effect of cyclic conjugation

ЗОШТО ФЕНАНТРЕНОТ Е ПОСТАБИЛЕН ОД АНТРАЦЕНОТ?

Со помош на еден неодамна развиен молекулско орбитален метод можат да се проценат енергетските ефекти на индивидуалните циклуси, како и парови, тројки итн. циклусите во полициклично конјугирани молекули. Со помош на овие енергетски ефекти може подобро да се види кои структурни детали се одговорни за термодинамичката стабилност на посматраните молекули. Конкретно, може да се разбере (на квантитативен начин) што е причина за разликата во термодинамичката стабилност на изомерите. Овде една ваква анализа е извршна на два изомерни бензеноидни јаглеводороди со три хексагони – антрацен и фенантрен.

Клучни зборови: бензеноидни јаглеводороди; антрацен; фенантрен; енергетски ефект на циклична конјугација

INTRODUCTION

Chemical graph theory is a part of theoretical chemistry that employs a sophisticated mathematical apparatus, and is therefore not much attractive to chemists. However, in many cases it is found useful, or even necessary, for explaining experimental results. Within this theory, it is sometimes possible to explain and rationalize the dependence of chemical and physical properties of substances on molecular structure. This, in particular, applies to benzenoid hydrocarbons [1]. Although in what follows we focus our attention to a pair of very small and long time known benzenoid hydrocarbons, one should bear in mind that the chemistry of these compounds is nowadays in great expansion, and that gigantic benzenoids (referred to as "graphenes") have recently been synthesized [2–4].

It is a well-known fact that among isomers, the stability of benzenoid compounds increases with the number of Kekulé structures [1, 5]. A textbook example of this regularity is provided by the pair phenanthrene (possessing 5 Kekulé structures) and anthracene (possessing 4 Kekulé structures). The claim that the former is more stable is in agreement with all available experimental results.

However, a critical-minded chemist may argue that this is no explanation whatsoever why phenanthrene is more stable than anthracene. Namely, one concluded that the stability of benze-

noid compounds increases with the number of Kekulé structures *because* this regularity holds for the pair phenanthrene/anthracene as well as for many other pairs of benzenoid isomers.

In this paper we show how the stability order of phenanthrene and anthracene could be explained by using a completely different way of reasoning, namely by comparing the energy-effects of their various cycles.

METHOD

There are several possible ways for quantifying cyclic conjugation of polycyclic conjugated molecules, for instance methods based on the analysis of Kekulé structures and Clar aromatic sextet formulas. Details of these approaches can be found in the books [1, 6, 7] and reviews [8, 9]. Another, conceptually different approach is the (molecular-orbital-based) calculation of the energy-effect that results from conjugation in a particular cycle, or pairs of cycles, or triplets of cycles, etc. A pioneering work along these lines was published already in the 1960s [10], but the complete theory could be formulated only after appropriate graph-theoretical methods were developed. The energy-effects of individual cycles in polycyclic conjugated molecules were first calculated by one of the present authors [11], and independently (in a somewhat different manner) by Aihara [12]. Details of this theory of cyclic conjugation are found in the review [13].

Let G be molecular graph, representing a polycyclic conjugated molecule, and Z a cycle contained in it. Then the energy-effect resulting from the cyclic interaction of π-electron interactions within Z is expressed as

$$ef(G;Z) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G,ix)}{\phi(G,ix) + 2\phi(G-Z,ix)} \right| dx , \quad (1)$$

where $\phi(G,x)$ is the characteristic polynomial of G, and $\phi(G-Z)$ is the characteristic polynomial of the subgraph G-Z, obtained by deleting the cycle Z from G. As usual, $i = \sqrt{-1}$. For more details on the quantity ef see the review [13] and elsewhere [14–16].

Recently [16] formula (1) was modified so as to express the energy-effect of cyclic conjugation caused by pairs, triplets, etc. of cycles. It was shown [16] that non-zero energy-effects have only

mutually disjoint cycles. In particular, if Z_a and Z_b are two of disjoint cycles of the molecular graph G, then:

$$ef(G;Z_a,Z_b) =$$

$$= \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G,ix)}{\phi(G,ix) - 4\phi(G-Z_a-Z_b,ix)} \right| dx . \quad (2)$$

In case of a triplet Z_a , Z_b , Z_c of mutually disjoint cycles:

$$ef(G;Z_a,Z_b,Z_c) =$$

$$= \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G,ix)}{\phi(G,ix) + 8\phi(G-Z_a-Z_b-Z_c,ix)} \right| dx .$$

The energy-effects of quartets, quintets, etc. of mutually disjoint cycles are calculated analogously [16].

The above-specified energy-effects are in the units of the HMO resonance integral β, whose value is negative. Therefore, if $ef > 0$, then the respective interaction of π-electrons causes thermodynamic stabilization. Otherwise, $ef < 0$ implies thermodynamic destabilization.

CYCLES IN PHENANTHRENE AND ANTHRACENE

The method described in the preceding section was applied to the pair of isomeric benzenoid hydrocarbons with three hexagons, namely anthracene and phenanthrene. In Fig. 1 are depicted the formulas of anthracene and phenanthrene, and indicated the labeling of their hexagons.
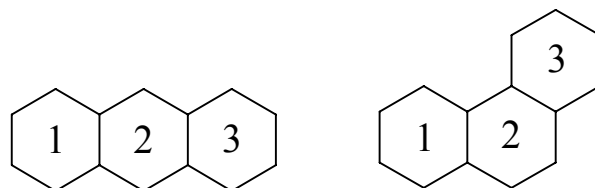

Fig. 1. Anthracene and phenanthrene, and the labeling of their hexagons

It is known that in unbranched catacondensed benzenoid systems (such as anthracene and phenanthrene) there are 2^h-1 cycles, pairs, triplets, etc. of mutually disjoint cycles, where h is the number of hexagons. Thus, in case of anthracene and phenanthrene there are 7 (= 2^3-1) cycles plus one pair of disjoint cycles; these are shown in Figs. 2 and 3.
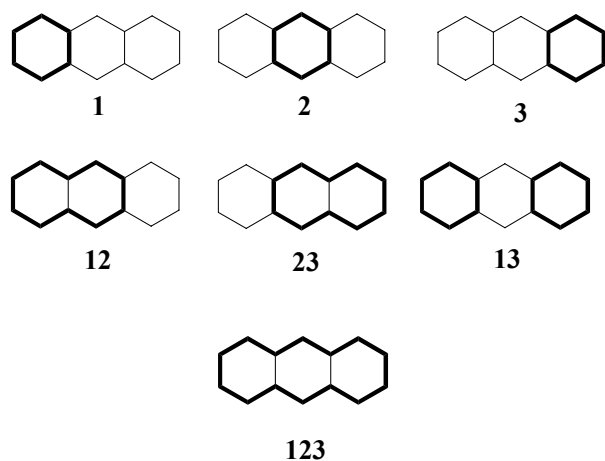
Fig. 2. All possible cycles and pairs of disjoint cycles
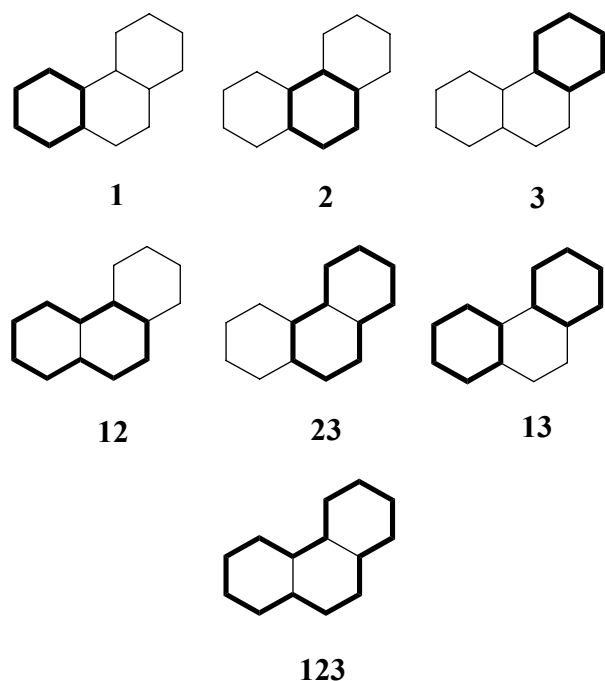in anthracene, and their labeling (cf. Fig. 1)

Fig. 3. All possible cycles and pairs of disjoint cycles
in phenanthrene, and their labeling (cf. Fig. 1).

The examination of cyclic conjugation of a large number of benzenoid hydrocarbons [13] showed that in the majority of cases, the energy-effect decreases when the size of cycle increases. This means that the greatest energy effects have the six-membered cycles, the energy effects of 10-membered cycles are smaller, etc. This regularity is seen in Table 1, which contains the *ef*-values of anthracene and phenanthrene. Recall that the cycles **1**, **2**, and **3** are 6-membered, the cycles **12** and **23** are 10-membered, the cycle **123** is 14-membered. In addition, **13** is a pair of 6-membered cycles.

At this point we mention that all cycles in catacondensed benzenoid systems are of size ($4k + 2$), $k = 1, 2,...$ [17], and that all cycles have a stabilizing energy-effect (positive *ef*-values) [18].

COMPARING CYCLIC CONJUGATION ENERGY-EFFECTS OF ANTHRACENE AND PHENANTHRENE

Using Eqs. (1) and (2) we have computed the energy-effects of all cycles and of the single pair of disjoint cycles of anthracene and phenanthrene. The respective results are given in Table 1.

T a b l e   1

The energy-effects (in β-units) of the cycles
of anthracene and phenanthrene. The labeling
of the cycles is indicated in Figs. 2 and 3.
All ef-values are positive, but for some cycles
the differences are significant.

Cycle(s)	Anthracene	Phenanthrene
1	0.0951	0.1586
2	0.0653	0.0534
3	0.0951	0.1586
12	0.0369	0.0275
13	0.0051	0.0453
23	0.0369	0.0275
123	0.0279	0.0198

In Table 1 we see some "expected" and some "unexpected" results. First of all, not all cycles favor phenanthrene relative to anthracene, implying that the fact that phenanthrene is thermodynamically more stable than anthracene is a result of a complex interference of several (oppositely directed) cyclic conjugation energy-effects. The energy-effects that favor phenanthrene relative to anthracene are only those pertaining to the (symmetry-equivalent) cycles **1** and **3**, as well as to their pair **13**. All other cyclic-conjugation energy-effects, namely those originating from the cycles **2**, **12**, **23**, and **123**, stabilize anthracene more than phenanthrene. A closer inspection of the data in Table 1 reveals that the "reason" why phenanthrene is thermodynamically more stable than anthracene is that in phenanthrene, the (symmetry-equivalent) six-membered cycles **1** and **3** have a much greater stabilization effect than in anthracene. The energy-effects of **1** and **3** overshadow all other energy-effects.

It is worth noting that the energy-effect of the pair of cycles **13** is almost ten times greater in phenanthrene than in anthracene. This detail is easily rationalized in terms of Clar theory [1, 6].

Another interesting observation is that the 14-membered cycle **123** has an almost 50% greater stabilization effect in anthracene than in phenanthrene. Bearing in mind that **123** is the perimeter of the considered molecules, we see that cyclic conjugation along the perimeter favors anthracene relative to phenanthrene. However, this energy-effect is small compared to the effects of other (smaller) cycles, and cannot revert the actual stability order. This example shows that the "perimeter rule", found in some older textbooks of theoretical organic chemistry (e. g. in [19,20]), is a blunder and should no more be seriously taken into account.

CONCLUDING REMARKS

The analysis of the isomeric pair anthracene – phenanthrene reveals a number of hitherto unobserved details in connection with their thermodynamic stability. The main factors influencing the difference between their thermodynamic stability are the differences in the cyclic conjugation of their π-electrons. According to a recently elaborated theory [16] the cyclic conjugation energy-effects in the considered benzenoid molecules can be separated into 7 contributions. Surprisingly, of these seven energy-effects, four are in favor of anthracene, and only three in favor of phenanthrene. However, two (symmetry-equivalent) energy-effects in phenanthrene are so much greater than those in anthracene that they determine the overall stability order.

We maintain that such a complicated situation is encountered also in the case of other isomeric benzenoid or non-benzenoid molecules. In fact, in larger polycyclic species the number of cyclic-conjugation energy-effects that needs to be taken into account will be much greater than those in the pair anthracene-phenanthrene, making the situation still more complex and complicated. Some of the energy-effect will favor one isomer, some the other isomer, and the final stability order will be the result of a complicated balance between these numerous, oppositely directed, energy-effects.

The general conclusion of this research would be that even in such a simple case as is the pair anthracene – phenanthrene, there are many cyclic-conjugation effects that influence thermo-

dynamic stability. Not all of these effects favor the same isomer, and it is neither trivial not obvious which of them will prevail.

REFERENCES

[1] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin,1989.

[2] M. D. Watson, A. Fechtenkötter, K. Müllen, Big is beautiful – "Aromaticity" revisited from the viewpoint of macromolecular and supramolecular benzene chemistry, *Chem. Rev.,* **101**, 1267–1300 (2001).

[3] J. Wu, W. Pisula, K. Müllen, Graphenes as potential material for electronics, *Chem. Rev.*, **107**, 718–747 (2007).

[4] I. Gutman, How many benzenoid hydrocarbons?, *Bull. Chem. Technol. Maced.*, **21**, 53–56 (2002).

[5] I. Gutman, S. Radenković, A simple formula for calculating resonance energy of benzenoid hydrocarbons, *Bull. Chem. Technol. Maced.*, **25**, 17–21 (2006).

[6] E. Clar, *The Aromatic Sextet*, Wiley, London,1972.

[7] N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, 1983; second revise ed. 1992.

[8] J. A. N. F. Gomes, R. B. Mallion, Aromaticity and ring currents, *Chem. Rev.*, **101**, 1349–1383 (2001).

[9] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.*, **103**, 3449–3606 (2003).

[10] R. Breslow, E. Mohácsi, Studies on d-orbital conjugation. III. Non-aromaticity of a derivative of the 1,3-dithiepinyl anion, a ten π-electron conjugated system, *J. Am. Chem. Soc.*, **85**, 431–434 (1963).

[11] I. Gutman, S. Bosanac, Quantitative approach to Hückel rule. The relations between the cycles of a molecular graph and the thermodynamic stability of a conjugated molecule, *Tetrahedron*, **33**, 1809–1812 (1977).

[12] J. Aihara, Resonance energies of benzenoid hydrocarbons, *J. Am. Chem. Soc.*, **99**, 2048–2053 (1977).

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

[14] I. Gutman, V. Ivanov-Petrović, Unusual modes of cyclic conjugation in phenylenes, *Bull. Chem. Technol. Maced.*, **16**, 91–96 (1997).

[15] I. Gutman, Ž. Tomović, On cyclic conjugation of the members of the pyrene/peropyrene series and their formally π-localized derivatives, *Bull. Chem. Technol. Maced.*, 20, 33–37 (2001).

[16] I. Gutman, S. Stanković, J. Đurđević, B. Furtula, On the cycle-dependence of topological resonance energy, *J. Chem. Inf. Model.,* **47**, 776–781 (2007).

[17] I. Gutman, S. J. Cyvin, Conjugated circuits in benzenoid hydrocarbons, *J. Mol. Struct. (Theochem)*, **184,** 159–163 (1989).

[18] I. Gutman, Hückel rule in catacondensed benzenoid hydrocarbons, *MATCH Commun. Math. Comput. Chem.*, **29**, 51–60 (1993).

[19] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961, pp. 288–289.

[20] J. N. Murrell, S. F. A. Kettle, J. M. Tedder, *Valence Theory*, Wiley, London, 1965, chapter 15.5.