

Cyclic conjugation in mono- and dicyclopenta-derivatives of anthracene and phenanthrene

Ivan Gutman*, Jelena Đurđević, Boris Furtula & Bojana Milivojević

Faculty of Science, P.O. Box 60, 34000 Kragujevac, Serbia

Email: gutman@kg.ac.yu

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The energy effects of cycles and pairs of cycles in mono- and dicyclopenta-derivatives of anthracene and phenanthrene are computed by a graph-theoretical method. Our results show that there is no significant difference between the extent of cyclic conjugation in anthracene and its cyclopenta-derivative (aceanthrylene) and phenanthrene and its cyclopenta-derivative (acephenanthrylene). In contrast to this, the presence of two cyclopentane rings causes drastic changes in the modes of cyclic conjugation. Our results provide an explanation for the peculiar stability order: dicyclopenta[*de,mn*]anthracene (never isolated) < dicyclopenta[*de,kl*]anthracene (stable) < dicyclopenta[*jk,mn*]phenanthrene (stable even at >1000°C).

It is well known in (theoretical) organic chemistry that cyclic arrangement of π -electrons in unsaturated conjugated compounds may cause a significant increase or a significant decrease of thermodynamic stability, relative to analogous acyclic systems^{1,2}. This phenomenon is closely connected with the concepts of aromaticity and antiaromaticity³⁻⁷. Calculating the energy effects of individual cycles in polycyclic conjugated molecules became possible in the 1970s⁸⁻¹⁰, when pertinent graph-theoretical methods were elaborated¹¹. Analogous methods for the calculation of the energy effects of multiplets (pairs, triplets, quartets, etc.) of cycles became available only quite recently¹².

The theory of cyclic conjugation, based on the energy effects of cycles in polycyclic conjugated molecules found numerous chemical applications (see the review¹³ and elsewhere¹⁴⁻¹⁷; for some alternative approaches see refs. 18-20). However, practically all these applications are concerned with benzenoid hydrocarbons and phenylenes, i.e., with alternant hydrocarbons. The first analysis of cyclic conjugation in non-alternant species seems to be done only in recent times^{21,22}. We have examined the modes of cyclic conjugation of the two simplest mono- and dicyclopenta derivatives of a benzenoid hydrocarbon, namely of acenaphthylene (1) and pyracylene (2) (ref. 22). In the present work we extend these studies to their next homologues, namely, mono- and dicyclopenta-derivatives of anthracene and phenanthrene (Fig. 1).

Aceanthrylene (5) is a stable compound²³, forming scarlet crystals with melting point 103-104°C. It behaves as a reactive olefin, evidenced by its tendency to polymerize in the presence of acids. This behaviour is in good agreement with the view that the compound 5 consists of an aromatic anthracene unit to which a strained double bond is attached. The properties of acephenanthrylene (6) are similar²⁴, except that (as expected) 6 is somewhat more stable than 5. In particular, 6 forms yellow crystals with m. pt. 141-142°C.

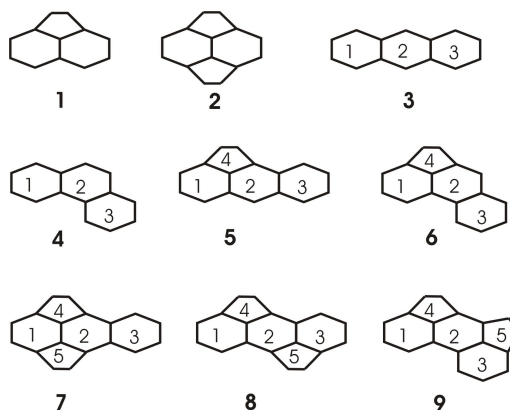


Fig. 1 – Cyclic conjugation in acenaphthylene (1) and pyracylene (2) was studied earlier.²² In this work we report the cyclopenta-derivatives of anthracene (3) and phenanthrene (4), aceanthrylene (5) and acephenanthrylene (6), as well as their dicyclopenta-derivatives, dicyclopenta[*de,mn*]anthracene (7), dicyclopenta[*de,kl*]anthracene (8), and dicyclopenta[*jk,mn*]phenanthrene (9). The numbering of the rings of these compounds is indicated. Note that 7 has two adjacent internal carbon atoms, whereas the two internal carbon atoms in 8 and 9 are not adjacent.

Attempts to synthesize dicyclopenta[*de,mn*]anthracene (**7**) failed and, to the authors' best knowledge, this compound has not been obtained so far^{25,26}. Instead of **7** always its isomer dicyclopenta[*de,kl*]anthracene (**8**) was obtained^{25,26}. The latter is a reasonably stable compound, which, however, upon heating to temperatures over 900°C (ref. 27) or to 1100°C (ref. 25) is transformed into dicyclopenta[*jk,mn*]phenanthrene (**9**). Thus **9** appears to be significantly more stable than **8**.

Dang *et al.*²⁶ maintain that the cause of the nonexistence (or, at least, very low stability) of **7** is the high strain energy of its pyracylene moiety. This, however, contradicts both the facts that pyracylene itself is a stable compound^{28,29} and that so also are **8** and **9**. Herein, we put forth arguments indicating that the low stability of **7**, the medium stability of **8**, and the high stability of **9** can be explained by the energy effects of their cycles and pairs of cycles.

Theoretical

Details of the theory by means of which it is possible to "extract" the contribution coming from an individual cycle to the total π -electron energy of a polycyclic conjugated molecule have been outlined in several earlier publications (see the review¹³ and the references cited therein). The energy effect of a cycle Z in a conjugated molecule whose molecular graph is G will be denoted by $ef(Z|G)$ or simply by $ef(Z)$ if the underlying molecule is evident from the context. All the hitherto reported ef -values were computed by using the integral expression

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

where $G-Z$ is the subgraph obtained from G by deleting the vertices of the cycle Z , where $\phi(H, x)$ is the characteristic polynomial of the graph H , and where $i = \sqrt{-1}$. In the present study, the energy effects are expressed in the units of the HMO carbon-carbon resonance integral β (refs 13-16). Therefore, $ef > 0$ and $ef < 0$ mean, respectively, thermodynamic stabilization and destabilization.

Equation (1) is perfectly well applicable in the case of alternant hydrocarbons. From the way in which it has been derived⁹ and from the theory of Coulson-type integrals^{11,30}, it is known that Eq. (1) can be applied in the case when all bonding π -electron MOs are doubly occupied and all antibonding MOs are

empty. This condition is automatically satisfied in non-charged alternant conjugated π -electron systems (such as benzenoids and phenylenes). In the case of non-alternant molecules this condition may be violated, implying that Eq. (1) is not applicable. For the mono- and dicyclopenta-derivatives studied in this work, such a violation occurs only with the compound **7**; it has 10 bonding and only 8 antibonding π -electron MOs, so that its 18 π -electrons occupy 9 bonding MOs, leaving one bonding MO empty.

Because of the above-specified problem, instead of Eq.(1) in the present study we had to apply the following (numerically much more difficult) direct approach.

We calculated the zeros $\lambda_i(G)$, $i = 1, 2, K, n$, of the polynomial $\phi(G, x)$ and labelled them in a non-increasing order, i. e.,

$$\lambda_1(G) \geq \lambda_2(G) \geq \Lambda \geq \lambda_n(G).$$

Next, we calculated the zeros $\lambda_i(G, Z)$, $i = 1, 2, K, n$, of the polynomial $\phi(G, x) + 2\phi(G-Z, x)$ (some of which may be complex numbers) and labelled them so that their real parts form a non-increasing sequence, i. e.,

$$\text{Re}[\lambda_1(G, Z)] \geq \text{Re}[\lambda_2(G, Z)] \geq \Lambda \geq \text{Re}[\lambda_n(G, Z)].$$

Then, assuming that n is even,

$$ef(Z|G) = 2 \sum_{k=1}^{n/2} \lambda_k(G) - 2 \sum_{k=1}^{n/2} \text{Re}[\lambda_k(G, Z)] \quad \dots (2)$$

In order to compute the energy effect $ef(Z_a, Z_b | G)$ of a pair of disjoint cycles Z_a, Z_b (for details see ref. 12), instead of $\phi(G, x) + 2\phi(G-Z, x)$ we have to find the zeros of the polynomial $\phi(G, x) - 4\phi(G-Z_a-Z_b, x)$, and then to proceed analogously to Eq. (2). In order to compute the energy effect $ef(Z_a, Z_b, Z_c | G)$ of a triplet of mutually disjoint cycles Z_a, Z_b, Z_c (for details see ref. 12), instead of $\phi(G, x) + 2\phi(G-Z, x)$ we have to find the zeros of the polynomial $\phi(G, x) + 8\phi(G-Z_a-Z_b-Z_c, x)$, and then to proceed analogously to Eq. (2). Among the conjugated molecules **3-9**, studied in this work, only **7** has a triplet of mutually disjoint cycles. None of these systems possess quartets, quintets, etc. of mutually disjoint cycles.

Cycles in the mono- and dicyclopenta-derivatives of anthracene and phenanthrene

While anthracene and phenanthrene possess only 6 cycles and a single pair of disjoint cycles, each of the cyclopenta-derivatives **5** and **6** possess 12 cycles and 3 pairs of disjoint cycles. The cyclic structure of the dicyclopenta-derivatives is far more complex; **7** has 23 cycles, 7 pairs of disjoint cycles and one triplet of mutually disjoint cycles, whereas **8** and **9** have 22 cycles and 9 pairs of disjoint cycles. The way in which the cycles of these compounds are labeled should be evident from the examples given in Fig. 2.

Results and Discussion

The calculated *ef*-values of all cycles and multiplets of independent cycles of the compounds **3-9** are given in Tables 1-4. In Tables 1 and 2 are

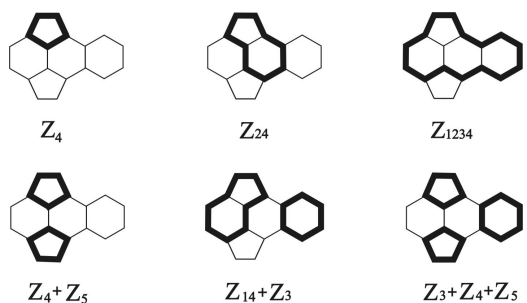


Fig. 2 – Thick lines indicate some cycles and pairs of cycles of dicyclopenta[*de,mm*]anthracene (**7**). These are denoted in accordance with the labeling of the rings shown in Fig. 1. In addition, the unique triplet of mutually independent cycles of **7** (denoted by $Z_3+Z_4+Z_5$) is also shown.

Table 1 – Energy effects (in β -units) of the cycles of anthracene (**3**) and its cyclopenta-derivatives **5**, **7** and **8**, resulting from the six-membered rings

Cycle	Size	3	5	7	8
Z_1	6	0.0951	0.0809	0.0673	0.0881
Z_2	6	0.0653	0.0527	0.0460	0.0173
Z_3	6	0.0951	0.1128	0.0985	0.0881
Z_{12}	10	0.0369	0.0271	0.0469	-0.0011
Z_{23}	10	0.0369	0.0300	0.0458	-0.0011
Z_{123}	14	0.0279	0.0214	0.0468	-0.0053
Z_1+Z_3	6+6	0.0051	0.0057	0.0011	0.0049

Table 2 – Energy effects (in β -units) of the cycles of phenanthrene (**4**) and its cyclopenta-derivatives **6** and **9**, resulting from the six-membered rings

Cycle	Size	4	6	9
Z_1	6	0.1586	0.1373	0.1615
Z_2	6	0.0534	0.0466	0.0406
Z_3	6	0.1586	0.1541	0.1615
Z_{12}	10	0.0275	0.0218	0.0214
Z_{23}	10	0.0275	0.0245	0.0214
Z_{123}	14	0.0198	0.0167	0.0168
Z_1+Z_3	6+6	0.0453	0.0395	0.0403

Table 3 – Energy effects (in β -units) of the cycles of the compounds **5**, **6**, **7**, **8** and **9** involving their five-membered rings, up to size 12. If there are several symmetry-equivalent cycles, then only one is specified

Cycle	Size	5	6	7	8	9
Z_4	5	0.0206	0.0099	-0.1221	-0.0141	-0.0320
Z_{14}	9	0.0092	0.0053	0.1110	0.0233	-0.0330
Z_{24}	9	0.0034	0.0021	0.0229	0.0076	0.0058
Z_{124}	11	-0.0016	-0.0010	-0.0069	0.0053	-0.0027
Z_{145}	12	-	-	-0.1171	-	-
Z_{245}	12	-	-	-0.0371	-0.0025	-0.0028

Table 4 – Energy effects (in β -units) of pairs of disjoint cycles of the compounds **5**, **6**, **7**, **8** and **9** involving their five-membered rings, up to size 9. If there are several symmetry-equivalent cycles, then only one is specified

Cycles	Size	5	6	7	8	9
Z_4+Z_5	5+5	-	-	-0.2011	-0.0440	-0.0444
Z_4+Z_3	5+6	0.0074	0.0019	-0.0717	-0.0351	0.0089
Z_5+Z_{14}	5+9	-	-	-	-0.0373	-0.0317
Z_3+Z_{14}	6+9	0.0022	0.0012	0.0285	0.0100	0.0068
$Z_{14}+Z_{35}$	9+9	-	-	-	-0.0341	-0.0283
$Z_4+Z_5+Z_3$	5+5+6	-	-	-0.1142	-	-

given the energy effects resulting from the six-membered rings and their combinations. In Table 3 are given the energy effects of cycles involving one or more five-membered rings. In Table 4 are given the energy effects of pairs of disjoint cycles involving one or more five-membered rings, as well as of the triplet $Z_4+Z_5+Z_3$ in the compound **7**. The energy effects of larger cycles are insignificantly small and have not been included into Tables 3 and 4.

Monocyclopenta derivatives

From the *ef*-values shown in Tables 1 and 2 it can be seen that the intensity of cyclic conjugation in the benzenoid part of aceanthrylene (**5**) and acephenanthrylene (**6**) is essentially the same as in the parent benzenoid systems, anthracene (**3**) and phenanthrene (**4**), respectively. Some *ef*-values have increased slightly and some decreased slightly, but the changes are far from significant.

In **5** and **6** we have, in addition, energy effects from the cycles that involve the five-membered ring. These are found in Table 3 and are, without exception, very small.

Thus we arrive at the conclusion that a single five-membered ring attached to anthracene and phenanthrene does not cause any major change in the modes of cyclic conjugation, compared to the parent benzenoid. This agrees well with the experimentally established facts that aceanthrylene and acephenanthrylene behave as aromatic systems with an additional double bond (in the five-membered ring).

Dicyclopenta derivatives

The situation with the dicyclopenta-derivatives of anthracene and phenanthrene (**7**, **8**, **9**) is drastically different. Here some very strong (mainly destabilizing) energy effects are encountered. We first focus our attention on the two anthracene derivatives.

Dicyclopenta[*de,mn*]anthracene (**7**) versus dicyclopenta[*de,kl*]anthracene (**8**)

The data collected in Table 1 show, somewhat surprisingly, that cyclic conjugation within the anthracene core stabilizes **7** much more than **8**. This is especially the case with the ten-membered cycles (Z_{12} and Z_{22}) and the 14-membered cycle Z_{123} . A completely different outcome is observed in the case of the effects of the five-membered rings. This time, the two five membered rings (Z_4 , Z_5 & Z_4+Z_5) have a drastic destabilizing energy effect in **7**, whereas the analogous energy effects in **8** are much weaker, some-

times negligibly small. There are also other major differences between **7** and **8**, as far as their modes of cyclic conjugation are concerned. The 9-membered cycles Z_{14} and Z_{15} in **7** have significantly greater stabilizing effects than the cycles Z_{14} and Z_{35} in **8**. Contrary to this, Z_{145} , Z_3+Z_4 , Z_3+Z_5 , and especially $Z_3+Z_4+Z_5$, have strong destabilizing energy effects in **7**, with nothing similar found in **8**. In our opinion, these latter cyclic conjugation modes are responsible for the very low stability of **7** as compared with **8**, in fair agreement with the experimental findings.

An interesting option for further research would be the examination of the possibility for **7** to undergo a Stone-Wales rearrangement, affording an isomeric system (which would also be interesting to analyze, and compare energetically with **8** for rationalizing why **7** would prefer to isomerize thermally into **8** rather than undergoing a Stone-Wales rearrangement).

Dicyclopenta[*de,kl*]anthracene (**8**) versus dicyclopenta[*jk,mn*]phenanthrene (**9**)

The comparative study of cyclic conjugation of **8** and **9** reveals another surprising detail. This time there is practically no difference in the sign and intensity of cyclic conjugation in the cycles that embrace one or both five-membered rings (*cf.* Tables 3 and 4). Great differences are, however, observed between the energy effects resulting from the six-membered rings (the last columns in Tables 1 and 2). This means that the stability difference between **8** and **9** is a direct consequence of the stability difference between the parent benzenoid systems **3** and **4**. In other words, the structural/electronic factors making **9** more stable than **8** are basically the same as the factors that make phenanthrene more stable than anthracene.

The present analysis, based on our previously developed theory of cyclic conjugation, reveals how perplexing the structure/property dependence is in the case of the thermodynamic stability of polycyclic conjugated molecules (as measured by their total π -electron energy). We were able to identify those few modes of cyclic conjugation that are (mainly) responsible for the stability order of the underlying compounds. Although an analysis of this kind cannot be considered as an explanation of the stability order, it certainly contributes towards a better understanding of it, and teaches us how complicated, unexpected, and often counterintuitive the structural factors are that determine the chemical behaviour of a polycyclic conjugated molecule.

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