

# CYCLIC CONJUGATION IN PYRACYLENE

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*Cyclic conjugation of the  $\pi$ -electrons in pyracylene is studied by means of the energy-effects ( $ef$ ) of its various cycles. The calculated  $ef$ -values imply that cyclic conjugation significantly destabilizes the pyracylene molecule. This seems to contradict the experimental findings that pyracylene is a reasonably stable conjugated species. We show how this apparent failure of the theory can be avoided, and how the main features of pyracylene's molecular geometry can be rationalized.*

**Keywords** Pyracylene, cyclic conjugation, energy effect of cyclic conjugation, molecular geometry

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## INTRODUCTION

In polycyclic conjugated molecules the cyclic interaction of the  $\pi$ -electrons may cause significant thermodynamic stabilization or destabilization (sometimes referred to as “aromaticity” and “antiaromaticity”) (1–5). The overall energy effect of cyclic conjugation is usually expressed in terms of resonance energy (of which several variants have been proposed (3–5)). It is also possible to express the energy effect of each individual cycle (6–9), as well as of pairs, triplets, etc. of cycles (10).

In catacondensed benzenoid hydrocarbons the energy effects of cyclic conjugation follow a relatively simple pattern, obeying the Hückel  $(4n + 2)$ -rule (9,11). In non-benzenoid species the situation is much more complicated (12–14), and violations from the  $(4n + 2)$ -rule are sometimes encountered (7,12).

In the present work the energy effects ( $ef$ ) of cycles are computed by our standard procedure (7,9,10). The energy effect ( $ef$ ) of an individual cycle  $Z$  is given by

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

whereas  $ef$  of a pair of disjoint cycles  $Z_a, Z_b$  is given by

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

In the above formulas,  $G$  denotes the molecular graph,  $\phi(G, x)$  its characteristic polynomial, and  $i = \sqrt{-1}$ . Further details can be found in the review (9) and in the references cited therein. Note that the above formulas apply to non-charged conjugated hydrocarbons in their ground state. For charged systems appropriate modifications are needed (14).

The  $ef$ -values, calculated according to Eqs. (1) and (2), are expressed in units of the HMO carbon–carbon resonance integral  $\beta$ . Therefore, positive (resp. negative)  $ef$ -values imply thermodynamic stabilization (resp. destabilization).

## PYRACYLENE

Because of its peculiar conjugation mode, pyracylene (compound **1** in Figure 1) was for a long time in the focus of interest of theoretical chemists. Various theoretical approaches (see, for example, (15–18)) implied that it would be a rather unstable

compound. This conclusion was in excellent agreement with the then known experimental results (19,20), according to which pyracylene could only exist in dilute solution, whereas its solid form decomposed within a few minutes. Later experimental work (21,22) showed that pyracylene is much more stable, so that the purified solid compound could be stored for several days at room temperature (or for many months at  $-20^{\circ}\text{C}$ ) without any sign of decomposition.

Figure 1 comes about here

The geometry of pyracylene was determined by X-ray diffraction (22), see Figure 2.

Figure 2 comes about here

The  $ef$ -values of the various cycles present in pyracylene have not been reported so far, and are now given in the subsequent section. From these data one could arrive at a similar conclusion as the earlier studies (15–18), namely that pyracylene is a highly reactive, unstable, antiaromatic species. We, however, show how these data should be interpreted, *cum grano salis*, so as to avoid the disagreement with the experimental findings (22). Furthermore, by using the  $ef$ -values, the main features of pyracylene's molecular geometry can be rationalized.

## THE ENERGY EFFECTS OF THE CYCLES OF PYRACYLENE

The pyracylene molecule has four rings, but a total of 14 cycles. In addition, it possesses a pair of disjoint (five membered) cycles. The cycles of pyracylene and their labelling are shown in Figure 3. The energy effects of all these cycles, computed according to Eqs. (1) and (2), are given in Table 1. In this table are given also the corresponding  $ef$ -values of acenaphthylene (**2**) and naphthalene (**3**), as well as of their vinyl-derivatives **4** and **5**, cf. Figure 1.

Figure 3 and Table 1 come about here

The  $ef$ -values of the five-, six-, nine-, and ten-membered cycles of pyracylene may be compared with the energy effects of the corresponding cycles of acenaphthylene

and naphthalene. However, because the  $ef$ -value of a cycle depends also on its extent of branching (for details see (9)), it is more legitimate to compare the energy effects of the cycles of pyracylene with the equally branched cycles of the vinyl-derivatives of acenaphthylene (4) and naphthalene (5). Needless to say that the vinyl-groups in 4 and 5 should have negligible influence on the intensity of cyclic conjugation.

The data given in Table 1 clearly show that cyclic conjugation in pyracylene is energetically significantly less favorable than in the compounds 4 and 5. The fact that this destabilization is caused by the presence of two disjoint five-membered cycles is best seen from the large negative  $ef$ -value of the pair of cycles  $Z_3, Z_4$ .

A somewhat surprising finding is that in pyracylene also the ten-membered cycle  $Z_{12}$  has a destabilizing effect, contrary to the analogous effects in 2, 3, 4, and 5, violating thus the Hückel  $(4n + 2)$ -rule. On the other hand, the perimeter of pyracylene, the twelve-membered cycle  $Z_{1234}$ , has also a destabilizing effect, this time in agreement with the Hückel  $(4n + 2)$ -rule. In fact, of the 15 distinct  $ef$ -values only those corresponding to the two 6-membered and four 9-membered cycles are positive.

## INTERPRETING THE CALCULATED $ef$ -VALUES OF PYRACYLENE

Based on the  $ef$ -values of its cycles (see Table 1), pyracylene could be “predicted” to be a highly unstable, antiaromatic species. However, the considerations leading to such a conclusion are based on the assumption that the molecule is planar and that all its carbon-carbon bonds have (nearly) equal lengths. In other words, the assumption is that all the calculated cyclic conjugation effects are actually acting.

The real molecule has no obligation to obey the above assumptions. If the cyclic conjugation in a “planar  $\pi$ -electron system in which all carbon-carbon bonds have equal lengths” is energetically unfavorable, then one should expect that the real molecule will change its geometry so as to avoid the destabilizing energy effects. This appears to happen in the case of pyracylene.

From the experimentally determined (22) geometry of pyracylene (see Figure 2) one can easily recognize the modes by which the “planar  $\pi$ -electron system in which all carbon-carbon bonds have equal lengths” has been distorted. The bonds  $b$  have significantly extended, whereas the bonds  $a$  have significantly shortened. According

to their lengths, the bonds  $a$  can be considered as almost purely double, whereas the bonds  $b$  as almost purely single. The remaining bonds ( $c$ ,  $d$ ,  $e$ , and  $f$ ) have lengths similar to those in naphthalene.

By such a change in geometry, all the (destabilizing) cyclic conjugation effects arising from the five-membered rings  $Z_1$  and  $Z_4$  have been eliminated or, at least, significantly attenuated. On the other hand, the cyclic conjugation effects of  $Z_2$ ,  $Z_3$ , and  $Z_{34}$  are turned similar to those in naphthalene, thus causing stabilization.

We thus see that the actual geometry of pyracylene can be understood as a result of a distortion from the idealized “equal-bond-length-state”, such as to minimize the destabilizing, and maximize the stabilizing cyclic conjugation effects. The direction of this distortion could be “predicted” (or, at this moment only rationalized) by knowing the respective  $ef$ -values (given in Table 1).

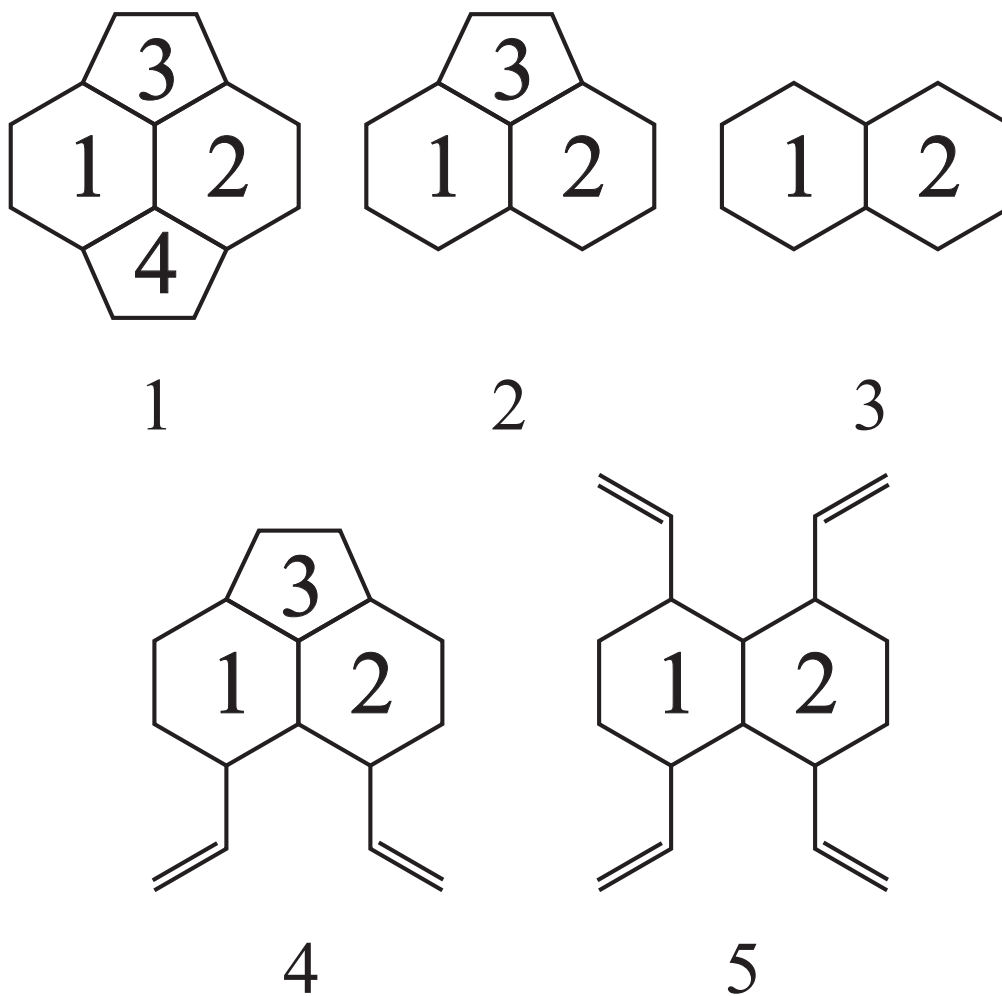
In our opinion the case of pyracylene, discussed here in detail, should serve as a guideline for interpreting the  $ef$ -values (calculated according to Eqs. (1) and (2)) also in other non-benzenoid polycyclic conjugated  $\pi$ -electron systems.

## References

- [1] A. T. Balaban, Is Aromaticity Outmoded?, *Pure Appl. Chem.* 52 (1980): 1409–1429.
- [2] J. A. N. F. Gomes and R. B. Mallion, Aromaticity and Ring Currents, *Chem. Rev.* 101 (2001): 1349–1383.
- [3] L. J. Schaad and B. A. Hess, Dewar Resonance Energy, *Chem. Rev.* 101 (2001): 1465–1476.
- [4] M. Randić, Aromaticity of Polycyclic Conjugated Hydrocarbons, *Chem. Rev.* 103 (2003): 3449–3606.
- [5] M. K. Cyrański, Energetic Aspects of Cyclic  $\pi$ -Electron Delocalization: Evaluation of the Methods of Estimating Aromatic Stabilization Energies, *Chem. Rev.* 105 (2005): 3773–3811.

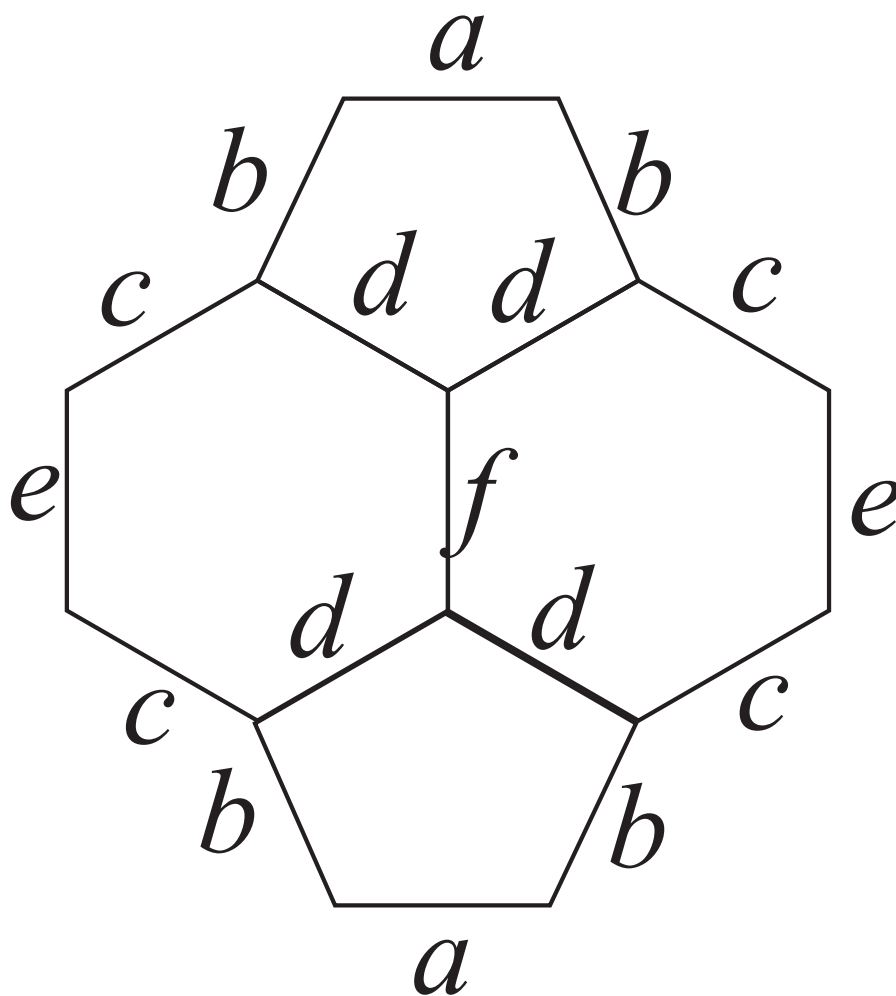
- [6] A. T. Balaban and M. Randić, Partitioning of  $\pi$ -Electrons in Rings of Polycyclic Conjugated Hydrocarbons. 6. Comparisons with other Methods for Estimating the Local Aromaticity of Rings in Polycyclic Benzenoids, *J. Math. Chem.* **37** (2005): 443–453.
- [7] I. Gutman and S. Bosanac, Quantitative Approach to Hückel Rule. The Relations Between the Cycles of a Molecular Graph and the Thermodynamic Stability of a Conjugated Molecule, *Tetrahedron* **33** (1977): 1809–1812.
- [8] J. Aihara, Resonance Energies of Benzenoid Hydrocarbons, *J. Am. Chem. Soc.* **99** (1977): 2048–2053.
- [9] I. Gutman, Cyclic Conjugation Energy Effects in Polycyclic  $\pi$ -Electron Systems, *Monatsh. Chem.* **136** (2005): 1055–1069.
- [10] I. Gutman, S. Stanković, J. Đurđević, and B. Furtula, On the Cycle–Dependence of Topological Resonance Energy, *J. Chem. Inf. Model.* **47** (2007): 776–781.
- [11] I. Gutman, Hückel Rule in Catacondensed Benzenoid Hydrocarbons, *MATCH Commun. Math. Comput. Chem.* **29** (1993): 51–60.
- [12] I. Gutman and M. Stanković, On the Hückel ( $4m+2$ ) Rule in Polycyclic Alternant Hydrocarbons, *J. Mol. Struct. (Theochem)* **309** (1994): 301–304.
- [13] I. Gutman, V. Ivanov–Petrović, and J. R. Dias, Cyclic Conjugation in Total Resonant Sextet Benzenoid Hydrocarbons, *Polycyclic Aromatic Compounds* **18** (2000): 221–229.
- [14] I. Gutman, Z. Marković, and I. Juranić, A Clar–Type Regularity for Dianions of Benzenoid Hydrocarbons, *Polycyclic Aromatic Compounds* **13** (1999): 33–40.
- [15] W. C. Herndon, Perturbational MO Theory and Reactivity of Non-alternant Hydrocarbons, *Tetrahedron* **28** (1972): 3675–3685.
- [16] W. C. Herndon, Resonance Theory. VI. Bond Orders, *J. Am. Chem. Soc.* **96** (1974): 7605–7614.
- [17] D. Cvetković, I. Gutman, and N. Trinajstić, Graphical Studies on the Relations Between the Structure and Reactivity of Conjugated Systems: The Role of Non-bonding Molecular Orbitals, *J. Mol. Struct.* **28** (1975): 289–303.
- [18] J. Aihara, Thermodynamic Stability of Polycyclic Aromatic Hydrocarbons Detected in Our Environment, *Bull. Chem. Soc. Japan* **61** (1988): 1451–1451.

- [19] B. M. Trost and G. M. Bright, Pyracylene. Pentalenoid System, *J. Am. Chem. Soc.* 89 (1967): 4244–4245.
- [20] B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, Perturbed [12]Annulenes. Synthesis of Pyracylenes, *J. Am. Chem. Soc.* 93 (1971): 737–745.
- [21] G. Schaden, Short Time Pyrolysis and Spectroscopy of Unstable Compounds. Part 10. A Simple Synthesis of Pyracylene, *J. Org. Chem.* 48 (1983): 5385–5386.
- [22] B. Freimuth, S. Gerber, A. Riesen, J. Wirz, and M. Zehnder, Molecular and Electronic Structure of Pyracylene, *J. Am. Chem. Soc.* 112 (1990): 738–744.

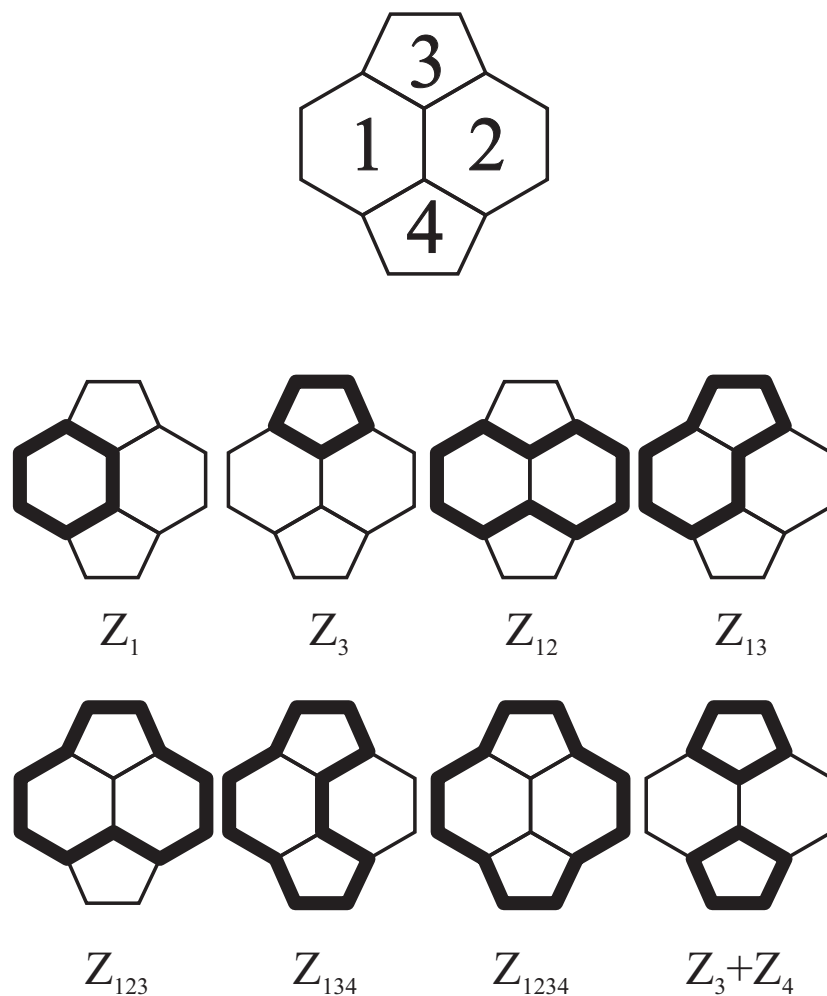


**FIGURE 1.** Pyracylene (1), the conjugated  $\pi$ -electron systems whose  $ef$ -values are used for comparative purposes (2–5), and the labelling of their rings.





**FIGURE 2.** The symmetry-equivalent carbon-carbon bonds of pyracylene are marked by same letters. The experimentally determined (22) bond lengths are:  $r_a = 134.6 \text{ pm}$ ,  $r_b = 149.2 \text{ pm}$ ,  $r_c = 137.29 \text{ pm}$ ,  $r_d = 139.7 \text{ pm}$ ,  $r_e = 144.3 \text{ pm}$ , and  $r_f = 136.0 \text{ pm}$ .



**FIGURE 3.** The symmetry-nonequivalent cycles of pyracylene. Their labelling follows the labelling of the rings, shown in Figure 1. Pyracylene possesses a total of 14 cycles (two cycles of type  $Z_1$ , two cycles of type  $Z_3$ , a single cycle of type  $Z_{12}$ , four cycles of type  $Z_{13}$ , etc). In addition, it possesses a unique pair of disjoint cycles ( $Z_3 + Z_4$ ).

cycle	size	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
$Z_1$	6	0.0275	0.1050	0.1211	0.0949	0.1056
$Z_2$	6	0.0275	0.1050	0.1211	0.0949	0.1056
$Z_3$	5	-0.0670	0.0114	–	0.0154	–
$Z_4$	5	-0.0670	–	–	–	–
$Z_{12}$	10	-0.0118	0.0567	0.0709	0.0469	0.0522
$Z_{13}$	9	0.0285	0.0049	–	0.0066	–
$Z_{14}$	9	0.0285	–	–	–	–
$Z_{23}$	9	0.0285	0.0049	–	0.0066	–
$Z_{24}$	9	0.0285	–	–	–	–
$Z_{123}$	11	-0.0089	-0.0026	–	-0.0024	–
$Z_{124}$	11	-0.0089	–	–	–	–
$Z_{134}$	12	-0.0601	–	–	–	–
$Z_{234}$	12	-0.0601	–	–	–	–
$Z_{1234}$	12	-0.0601	–	–	–	–
$Z_3 + Z_4$	5+5	-0.1155	–	–	–	–

**TABLE 1.** The energy effects of the cycles of pyracylene (**1**) and, for comparative purposes, of acenaphthylene (**2**), naphthalene (**3**), and their vinyl-derivatives **4** and **5**, cf. Figure 1. The labelling of the cycles is explained in Figure 3.

## Figure and Table Captions

**FIGURE 1.** Pyracylene (**1**), the conjugated  $\pi$ -electron systems whose  $ef$ -values are used for comparative purposes (**2–5**), and the labelling of their rings.

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