

# Testing the PCP-rule

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**Abstract** According to the recently discovered phenylcyclopentadienyl (PCP) rule, the intensity of cyclic conjugation in the five-membered ring of acenaphthylene and fluoranthene-type polycyclic conjugated hydrocarbons increases with the number of PCP fragments present in the molecule. We now tested this rule by DFT calculations at the B3LYP/6-31G(d) level of theory and confirmed its validity.

**Keywords** Acenaphthylene-type hydrocarbons · Fluoranthene-type hydrocarbons · PCP-rule · DFT theory

## Introduction

The theory of benzenoid hydrocarbons [1] is nowadays one of the best developed areas of theoretical organic chemistry. Motivated by recent progress in this field (see Refs. [2–8] and the references quoted therein) we have undertaken a systematic study [9, 10] of a class of polycyclic conjugated systems closely related to benzenoid hydrocarbons—the acenaphthylenes and fluoranthenes. These differ from “true” benzenoids by possessing a five-membered ring (for examples see Fig. 1). A more formal definition of acenaphthylenes and fluoranthenes can be found elsewhere [9].

In Fig. 2 are shown the general formulas of acenaphthylenes (**A**) and fluoranthenes (**F**); the carbon–carbon bonds (belonging to the five-membered ring) that will play

a key role in the considerations below are indicated  $x$ ,  $y$ , and  $z$ .

According to classical theories of benzenoid and similar polycyclic conjugated molecules [1, 3], in the five-membered ring of acenaphthylenes and fluoranthenes there would be no cyclic conjugation. This assertion is based on the fact that in all Kekulé structures of acenaphthylenes and fluoranthenes the carbon–carbon bonds  $x$  and  $y$  are single, and that in all Kekulé structures of acenaphthylenes, the carbon–carbon bond  $z$  is double; for examples see Fig. 3.

Investigating the energy effect of cyclic conjugation by using the method described in detail in Gutman’s review [11], we found that in the five-membered ring of acenaphthylenes and fluoranthenes there nevertheless exists weak cyclic conjugation. In addition, we established [10] that this (weak) cyclic conjugation effect is amplified by the presence of six-membered rings connected to the five-membered ring by a single carbon–carbon bond. We named this effect the PCP-rule, where PCP is the abbreviation for “phenylcyclopentadienyl”. According to the PCP-rule, the intensity of cyclic conjugation in the five-membered ring increases with the number of PCP fragments present in the respective acenaphthylene and fluoranthene. In Fig. 4 these PCP fragments are indicated for two selected examples.

Two simple examples illustrating the PCP-rule are provided by the isomeric acenaphthylenes **3** and **4** and the isomeric fluoranthenes **8** and **9** (Fig. 1). Whereas **3** has one PCP fragment, its isomer **4** has two PCP fragments. The energy effects of their five-membered rings are 0.0255 and 0.0390  $\beta$ -units. Whereas **8** has one PCP fragment, its isomer **9** has two PCP fragments. The energy effects of their five-membered rings are 0.0066 and 0.0105  $\beta$ -units. The fluoranthenes **5**, **6**, **9**, **13**, and **15** have 0, 1, 2, 3, and 4 PCP fragments. The energy effects of their five-membered rings

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