

# Local aromaticity in benzo- and benzocyclobutadieno-annelated anthracenes

Alexandru T. Balaban · Ivan Gutman ·  
Svetlana Marković · Dušica Simijonović

Received: 14 January 2011 / Accepted: 17 May 2011 / Published online: 10 June 2011  
© Springer-Verlag 2011

**Abstract** Considerations based on the energetics of cyclic conjugation in individual rings indicate that benzocyclobutadieno-annulation has the opposite effect on local aromaticity in benzenoid hydrocarbons to benzo-annulation. This finding is now tested and corroborated by density functional theory (DFT) calculations of the geometry of all benzo- and benzocyclobutadieno-annelated congeners of anthracene. The harmonic oscillator model of aromaticity (HOMA) and some similar (geometry-based) indices of local aromaticity are found to have the same dependence on the modes of annulation as the molecular-graph-based energy effects.

**Keywords** Aromaticity · Molecular geometry · DFT calculation · Anthracene · Benzocyclobutadieno-annelated anthracenes

## Introduction

The effect of benzo-annulation on local aromaticity in benzenoid hydrocarbons was recently studied in detail (see [1, 2] and the references cited therein). The main quantity by

which local aromaticity was assessed in these works was the effect of cyclic conjugation in the considered six-membered ring on total  $\pi$ -electron energy. This energy effect ( $ef$ ) was calculated by a technique developed within chemical graph theory, whose details are reviewed elsewhere [3]. In spite of the fact that in all previously examined cases the  $ef$  approach gave consistent and chemically sound results, because of its theoretical simplicity it was purposeful to check its predictions by means of more advanced quantum chemical methods (see, e.g., [4]).

In the case of benzenoid hydrocarbons, we examined the effect of benzo-annulation on the six-membered ring, marked X in species 1–3 in Fig. 1.

The two main general rules discovered by means of the  $ef$  approach are the following [1, 2]:

**Rule 1.** Linear benzo-annulation (cf. 2 in Fig. 1) decreases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species 1. In particular,  $ef(X, 2) < ef(X, 1)$ .

**Rule 2.** Angular benzo-annulation (cf. 3 in Fig. 1) increases the intensity of cyclic conjugation in the ring X, relative to its value in the non-annelated parent species 1. In particular,  $ef(X, 3) > ef(X, 1)$ .

As before [1–3], the  $ef$  values are expressed in the units of the Hückel molecular orbital (HMO) carbon–carbon resonance integral  $\beta$ , whose value for thermochemical purposes is around  $-137 \text{ kJ mol}^{-1}$  [5].

We have recently started the examination of the effect on cyclic conjugation of another type of annulation, which we refer to as benzocyclobutadieno- or BCBD-annulation [6], see 4 and 5 in Fig. 1, as well as the examples depicted in Fig. 3. Surprisingly, we found that the effect of BCBD-annulation is opposite to that of benzo-annulation. Thus, instead of rules 1 and 2, the following rules seem to hold generally:

**Electronic supplementary material** The online version of this article (doi:10.1007/s00706-011-0531-5) contains supplementary material, which is available to authorized users.

A. T. Balaban  
Texas A & M University at Galveston, Galveston,  
TX 77551, USA  
e-mail: balabana@tamug.tamu.edu

I. Gutman (✉) · S. Marković · D. Simijonović  
Faculty of Science, Institute of Chemistry,  
University of Kragujevac, Kragujevac, Serbia  
e-mail: gutman@kg.ac.rs





