

Local aromaticity in benzo- and benzocyclobutadieno-annelated perylenes

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Abstract

The effects of benzo- and benzocyclobutadieno- (BCBD-) annelation on the local aromaticity of the central ring *X* of perylene were examined. The local aromaticity of the ring *X* was estimated using a graph-theory based index, *ef*, and two geometry-based indices, *HOMA* and Σ . The findings resulting from the application of the *ef* index are to some extent contradictory to those obtained on the basis of *HOMA* and Σ . Namely, the geometry-based indices indicate that the effect of benzo-annelation is opposite to that of BCBD-annelation, whereas *ef* predicts that angular BCBD-annelation has very little influence to the local aromaticity of the central ring of perylene. Since the geometry-based indices are more sophisticated than the graph-theory-based index, one should conclude that the predictions emanating from the application of *HOMA* and Σ are more reliable.

Keywords: Aromaticity, molecular geometry, benzo-annelated perylenes, benzocyclobutadieno-annelated perylenes, DFT calculations

1. Introduction

Aromaticity is an important concept in modern organic chemistry. This term is related either to some typical properties or to a specific structure. It has been almost generally accepted that aromaticity is associated with the ground-state properties of polycyclic π -electron compounds which are more stable than their chain analogues, have bond lengths between those typical for single and double ones, and have a π -electron ring current that is induced when the system is exposed to external magnetic fields, leading to increased values of the magnetic susceptibility and specific values of ¹H NMR chemical shifts. These properties are easily measurable and concern molecules in their ground electronic state. Thus, they can be readily transformed into the numerical parameters describing the aromatic character (aromaticity indices) of molecules or their fragments.

A more subtle problem is that what one calls “aromaticity”, needs not be (as is usually not) uniformly distributed over the entire conjugated π -electron system. To overcome this difficulty, so-called local aromaticity indices have been introduced, capable of measuring the extent of aromaticity in some pertinently selected domains of the underlying π -electron system.

The local aromaticity indices: *ef* (energy effect) (Gutman 2005a), *HOMA* (Harmonic Oscillator Model of Aromaticity) (Kruszewski and Krygowski 1972; Krygowski 1993;

