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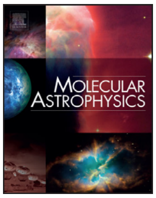

Research paper

Kekulene: Structure, stability and nature of H•••H interactions in large PAHs

J. Poater[a,b,*], J. Paauwe[c], S. Pan[d], G. Merino[d], C. Fonseca Guerra[c,e], F.M. Bickelhaupt[c,f,*]

[a] Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Catalonia, Spain
[b] ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
[c] Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands
[d] Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados Unidad Mérida, Km. 6 Antigua carretera a Progreso, Apdo. Postal 73, Cordemex, 97310, Mérida, Yuc., México
[e] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[f] Institute of Molecules and Materials (IMM), Radboud University, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands

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ABSTRACT

We have quantum chemically analyzed how the stability of small and larger polycyclic aromatic hydrocarbons (PAHs) is determined by characteristic patterns in their structure using density functional theory at the BLYP/TZ2P level. In particular, we focus on the effect of the nonbonded H•••H interactions that occur in the bay region of kinked (or armchair) PAHs, but not in straight (or zigzag) PAHs. Model systems comprise anthracene, phenanthrene, and kekulene as well as derivatives thereof. Our main goals are: (1) to explore how nonbonded H•••H interactions in armchair configurations of kinked PAHs affect the geometry and stability of PAHs and how their effect changes as the number of such interactions in a PAH increases; (2) to understand the extent of stabilization upon the substitution of a bay C–H fragment by either $C^{\bullet}$ or N; and (3) to examine the origin of such stabilizing/destabilizing interactions.

1. Introduction

Kekulene is a large polycyclic aromatic hydrocarbon (PAH) with formula $C_{48}H_{24}$, firstly synthesized by Diederich and Staab (1978). It is constituted by 12 annelated C_6 cores that are arranged in the shape of a closed six-membered super-ring (see Fig. 1). Kekulene is expected to act like a “superbenzene” and, hence, a “superaromatic” system due to its planar cyclic conjugation and its D_{6h} structure. However, despite its 48 π-electrons neither bond length equalization nor any appreciable extra stabilization energy is perceived that would justify to consider it as a superaromatic molecule (Diederich and Staab, 1978; Krieger et al., 1979; Jiao and Schleyer 1996; Steiner et al., 2001).

As any PAH, kekulene is also relevant in an either direct or indirect way in astrochemical and prebiotic biochemistry contexts. PAHs are the major repository of gaseous carbon in the galaxy (Ehrenfreund and Charnley, 2000) and their presence in the interstellar medium has been proven through the observation of the so-called aromatic infrared bands in infrared emission spectra (Candian et al., 2014; Zhen et al., 2016; Tielens, 2008; Blasberger et al., 2017). Nevertheless, an unambiguous radio-frequency identification is difficult due to a small (or, in symmetrical PAHs, even nil) permanent dipole moment (Charnley et al., 2005). On the other hand, heteroaromatic PAHs involving CH/N substitution (NPAHs) are crucial in astrochemistry because, given their strong dipole moment, they can be spectroscopically detected via their rotational transitions. Furthermore, NPAHs were proposed to be involved in the astrochemical evolution of the interstellar medium (Parker et al., 2015; Koziol and Goldman, 2015). For instance, NPAHs have been detected in the atmosphere of Titan (Imanaka et al., 2004; Landera and Mebel, 2010; Ricca et al., 2001). In addition, the simplest nitrogen heterocycles, like pyridine or pyridine, may have been detected on Comet Halley (Ehrenfreund and Charnley, 2000). Even though pyridine itself has not been confirmed to be detected, it is relevant in its role of the archetypal building block of biomolecules that have been observed, such as, nucleobases or NPAHs (Parker et al., 2015). A variety of such (hetero) aromatic compounds are confirmed to play a key role in terrestrial

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[*] Corresponding authors.
E-mail addresses: jordi.poater@ub.edu (J. Poater), f.m.bickelhaupt@vu.nl (F.M. Bickelhaupt).

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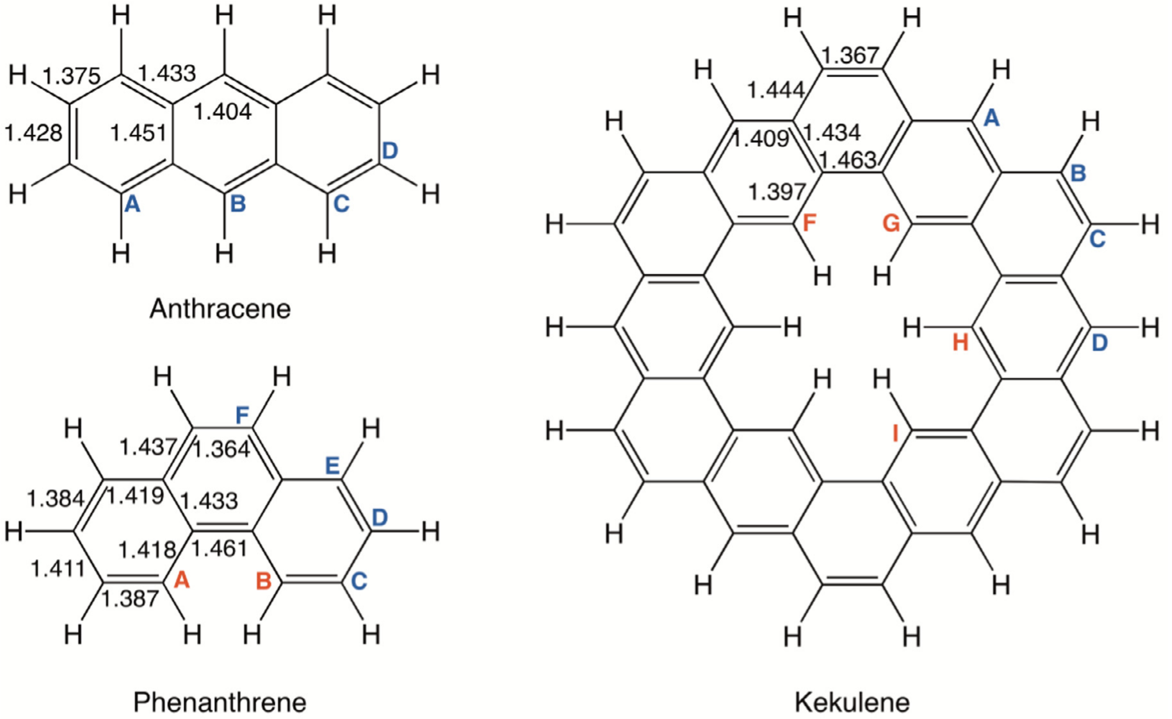

Fig. 1. Definition of C–H groups in anthracene, phenanthrene and kekulene together with bond distances (in Å), computed at the BLYP/TZ2P level.

biochemistry and were almost certainly crucial ingredients in prebiotic chemistry of the Earth (Ehrenfreund et al., 2006).

So, clearly the structural and bonding properties of PAHs are of importance for many areas of chemistry. Particularly, the nature of the interactions between adjacent hydrogen atoms in PAHs is an essential issue. PAHs may have, among others, zigzag edges, such as in the linear anthracene molecule, and armchair edges, such as in the bent or kinked phenanthrene molecule (see Fig. 1). The former has *solo* hydrogen atoms, that is, non-adjacent hydrogens or hydrogens pointing away from each other. On the other hand, kinked PAHs with armchair edges have pairs of hydrogens, in the so-called bay regions, that are oriented towards each other (A and B in phenanthrene, Fig. 1).

Introducing a kink in a PAH stabilizes the system with respect to its linear isomer, despite the occurrence of sterically crowded bay hydrogens in the kinked PAH. This is illustrated by the archetypal linear and kinked PAHs, anthracene and phenanthrene, respectively. The higher stability of the kinked phenanthrene compared to the linear anthracene was previously examined by means of molecular orbital (MO) and quantitative bond energy decomposition analyses (EDA) (Poater et al., 2007a). The nonbonded H•••H interaction in the bay region of phenanthrene is not responsible of such stability because it is Pauli repulsive and hence destabilizing (Poater et al., 2007a). This outcome was supported by numerical experiments removing bay hydrogens of phenanthrene, which enhances the stability of kinked system relative to a corresponding linear form. Spectroscopic evidence for the repulsive nature of the H•••H interaction in phenanthrene was provided by Grimme and Erker (Grimme et al., 2009). These findings falsify earlier atoms-in-molecules (AIM) investigations, which claimed that the H•••H interactions are stabilizing and that they are responsible for the higher stability of phenanthrene relative to anthracene (Matta et al., 2003).

Kekulene is an interesting case for exploring the nature of larger PAHs and how they are affected by nonbonded H•••H interactions. It contains six such H•••H interactions in its internal bay or cavity, in contrast to only one such H•••H interaction in phenanthrene. Herein, we quantum chemically analyze how the stability of small and larger PAHs is determined by patterns in their structure using density functional theory at the BLYP/TZ2P level. In particular, we focus on the effect of the nonbonded H•••H interactions that occur in the bay region of kinked (or armchair) PAHs, but not in straight (or zigzag) PAHs. Our model systems comprise anthracene, phenanthrene, and kekulene and derivatives thereof. We aim at three main objectives: (1) to explore how nonbonded H•••H interactions in armchair configurations of kinked PAHs play on the geometry and stability as the number of such interactions in a PAH increases; (2) to understand the extent of stabilization upon the substitution of a bay C–H fragment by either C$^\bullet$ or N; and (3) to examine the origin of such stabilizing/destabilizing interactions.

To this end, we first formulate the hypothesis that if close H•••H contacts are destabilizing, then removing one of the involved H atoms would relieve it. Later on, the analysis is complemented by substituting the C–H groups from which H atoms were stripped by N atoms. What makes the resulting hetero PAHs interesting is that they are significantly more viable than their equivalent PAH radicals and biradicals. Thus, they also offer a way to probe the effect of switching off destabilizing H•••H interactions experimentally! Besides, hetero PAHs are also relevant for astrochemistry, as pointed out above. Finally, in order to clarify the nature of the bonding in the various situations, we extend our detailed bonding analyses to simple bimolecular model systems, [X•••Y], with all possible combinations of X, Y=nonaromatic CH_4, $CH_3^\bullet$ and NH_3; or aromatic C_6H_6, $C_6H_5^\bullet$ and C_5H_5N, arranged in such a way that the mutual distance of the [C] –H, [C]$^\bullet$ and [N] moieties correspond to those in our aromatic and heteroaromatic PAH models.

2. Methods

2.1. General procedure

All computations were done with the ADF program (te Velde et al., 2001; http://www.scm.com) using the BLYP functional in