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Polyaromatic hydrocarbon oxyradical stability

Dmitry Yu. Zubarev[a], Neil Robertson[b], Dominik Domin[a,c],
Jarrod McClean[a], Jin-Hua Wang[a,d], William A. Lester, Jr.[a,c,*],
Russell Whitesides[b,e], Xiao-Qing You[b], Michael Frenklach[b,e]

[a] *Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California at Berkeley, Berkeley, California 94720-1460, USA*
[b] *Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California 94720-1740, USA*
[c] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[d] *State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China*
[e] *Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

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Abstract. A simple connection is established between aromaticity and overall stability of five-ring linear polyaromatic hydrocarbon oxyradicals. A chemically intuitive model is developed that exhibits a linear trend between an inexpensive geometric measure of aromaticity and the energetic stability of a model graphene edge with oxygen at different positions. It is believed to be an important step in establishing reaction pathways of soot and graphene oxidation.

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1 Introduction

While development of alternative sources of energy and reduction of carbon emissions remain crucial in the battle for environmental and public health, the fact remains that combustion reactions and carbon fuels will be prevalent for some time. As such, it is critical to investigate means of mitigating the dangers inherent to some of these methods.

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[*] Corresponding author. *Email address:* `walester@lbl.gov` (W. A. Lester, Jr.)

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One of the most harmful byproducts of these processes is soot, which is known to consist of polyaromatic hydrocarbon fragments. Additionally, one of the primary pathways by which soot production is alleviated is oxidation. Past theoretical studies of soot oxidation have focused on the model cases of oxidation reactions of one-ring aromatics [1–4] and oxygen chemisorption at selective sites of two- and three-ring aromatics [5–8].A crucial first step towards the understanding of these pathways is knowledge of the stability of oxyradical intermediates.

Many of the systems of interest are, unfortunately, too large to treat by highly accurate methods. It is the goal of this work to develop an efficient and accurate model based on intuitive notions of aromaticity for determining the stability of polycyclic aromatic hydrocarbon oxyradical fragments.

2 Computational details

The geometries of oxyradical derivatives of pentacene depicted in Fig. 1 were optimized at the UB3LYP/6-311G(d, p) level of theory [9–12] in the Gaussian 03 software package [13]. The results of these calculations were verified by ab initio perturbation theory (RO-RI-SOS-MP2/6-311G(d, p)) at the UB3LYP geometries in the Q-Chem [14] software package. The expectation value of the S^2 operator was found to be 0.75 for all oxyradicals as a consequence of the restricted open shell formalism. A normal mode calculation confirmed all structures represented an energy minimum. A factor [15] of 0.967 was used to scale vibrational frequencies and zero-point energies (ZPE).

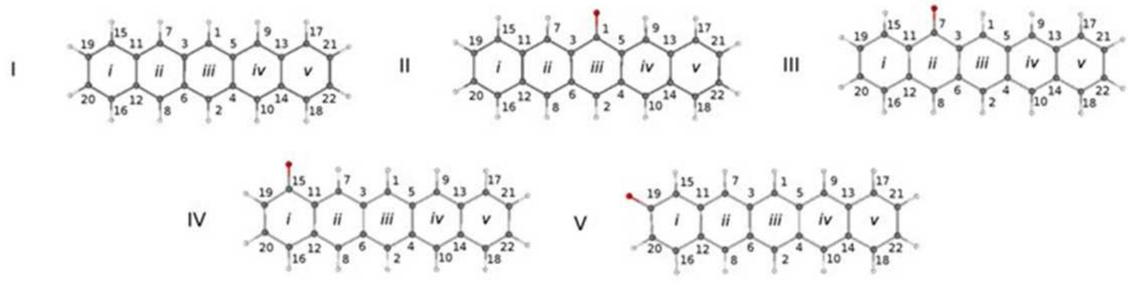

Figure 1: Structures of the pentacene molecule (I) and pentacene oxyradicals with the oxygen atom in different positions (II - V). Connections between atoms are drawn on the basis of interatomic distance. Upper case Roman numerals designate oxyradicals with different O atom positions; lower case italic Roman numerals designate six-atom rings; Arabic numerals enumerate C atoms.

A simple geometric measure of aromaticity known as the harmonic oscillator model of aromaticity (HOMA) [16], was used. HOMA offers an inexpensive evaluation of local aromatic character based on a simple comparison to an ideal aromatic benzene. HOMA