

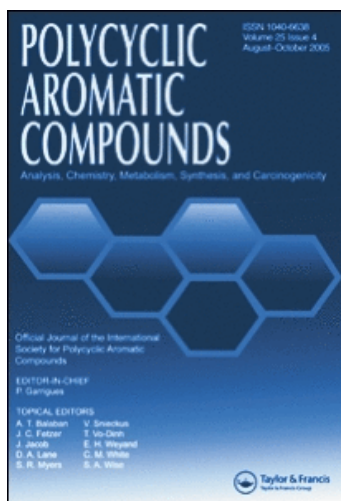
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### A Case of Breakdown of the Kekulé-Structure Model

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# A Case of Breakdown of the Kekulé–Structure Model

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For a long time, Kekulé structures have been used to predict and rationalize the stability, geometry, and  $\pi$ -electron properties of polycyclic conjugated molecules, especially hydrocarbons. We now point out an example, demonstrating that the Kekulé–structure model is not generally applicable. Namely, the molecule of dibenzo[*cd,mn*]indeno[123, *gf*]pyrene is perfectly planar and strain-free. Yet, its geometry (determined by means of an unrestricted symmetry–broken UB3LYP/6-311G(d,p) DFT method) is in complete disagreement with what one would expect on the basis of its Kekulé structures.

**Key Words:** fluoranthenes, Kekulé structure, localized double bond, molecular geometry

## INTRODUCTION

From the times of Pauling (1), Clar (2), and Herndon (3), Kekulé structures have been used for predicting and rationalizing the properties of polycyclic conjugated molecules. Extensive literature exists on this matter, see (4, 5) and the references cited therein. From Kekulé structures one could gain quantitative estimates of carbon–carbon bond lengths (1, 4, 6, 7), reactivity (8, 9), ionization potentials (10), thermochemical parameters (11), total  $\pi$ -electron energy (12–14), distribution of  $\pi$ -electrons (15–19), as well as various resonance energies (3–5, 20) and measures of aromaticity (5, 21–23). All these approaches were based on the assumption that the Kekulé structures provide a realistic picture of the true  $\pi$ -electron configuration of the underlying conjugated molecule. The evidence that has accumulated in favor of this assumption and its *quantitative* agreement with experimental findings is vast and compelling, cf. (1–23). Without intending to deny its validity for the majority of polycyclic  $\pi$ -electron systems, we wish to point out that there exist cases in which it fails, and where its application would lead to conclusions that are in striking disagreement with reality.

One such case is dibenzo[*cd,mn*]indeno[123, *gf*]pyrene (**1**), a fluoranthene–type conjugated system whose structure is depicted in Figure 1.

The system **1** was noticed within our studies of the  $\pi$ -electron properties of fluoranthene and its congeners (see [24–28] and the references cited therein). In Ref. (28) we analyzed the Kekulé structures of fluoranthene congeners and noticed that some

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