The Effect of the Two Types of Dibenzoannulation of Pentalene on Molecular Energies and Magnetically Induced Currents

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Table S1. Experimentally observed and calculated bond lengths of dibenzo[α,f]pentalene.

![Dibenzo[α,f]pentalene](image)

<table>
<thead>
<tr>
<th>molecule A</th>
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<th>R = R₁ = H&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup> Experimentally obtained by X-ray analysis. Data are for the two crystallographically independent molecules (A and B), taken from ref. 16 in the manuscript. <sup>b</sup> Calculated at the (U)B3LYP/6-311+G(d,p) level of theory (this work).
Table S2. Experimentally observed and calculated $^1$H NMR chemical shifts of dibenzo[a,f]pentalene (ppm) relative to TMS.

![Diagram of dibenzo[a,f]pentalene]

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<th>$R = \text{Mes}$, $R_1 = \text{H}$&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>$C_a$</td>
<td>$C_a$</td>
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<sup>a</sup>Experimental data taken from ref. 16 in the manuscript. <sup>b</sup>Calculated at the (U)B3LYP/6-311+G(d,p) level of theory (this work). <sup>c</sup>Average values.
Table S3. Spin densities in dibenzopentalenes obtained by Hirshfeld\textsuperscript{1} population analysis.

![Diagram of dibenzopentalenes]

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S1: Additional examination of factors responsible for energy lowering upon closed-shell to open-shell singlet transition of dibenzo[\textit{a,f}]pentalene

The closed-shell/open-shell singlet transition mainly involves changes of the \textit{ortho}-quinodimethane subunit (Figure S1A). In the performed energy decomposition scheme closed-shell and open-shell dibenzo[\textit{a,f}]pentalene species were formed from fragments C and D, which should form two \(\sigma\) and two \(\pi\) bonds in the closed-shell species and are, thus, taken in their quintet electronic state (Figure S1B). If open-shell species is to be formed, the two fragments should change their electronic state, which is also accompanied by geometry changes. For the [\textit{a,f}]-DBP\textsubscript{os} to be formed, the two fragments can have open-shell singlet states or triplet states (Figure S1C). The results of the analyses are shown in Table S4.

![Figure S1. Transition from closed-shell to open-shell dibenzo[\textit{a,f}]-pentalene (A), formation of the closed-shell [\textit{a,f}]-DBP (B) and open-shell [\textit{a,f}]-DBP (C) from fragments C and D.](image)

The two analyses are consistent with one another and also with the results described in the manuscript. As the data in Table S4 show, the slight energy lowering comes exclusively from deformation energy component, which should be related to benzene subunit formation that drives the molecule toward singlet diradical. The large and negative \(\Delta E_{\text{def}} = -56.35\text{ kcal/mol}\) and \(\Delta E_{\text{def}} = -57.44\text{ kcal/mol}\) for [\textit{a,f}]-DBP\textsubscript{os} are also reflections of benzene formation within fragment D.
Table S4. Contribution of various energy components to the total binding interactions between fragments C and D in dibenzo[\(a,f\)]pentalene in its closed-shell and open-shell singlet states and energy changes (values in bold) upon closed-shell $\rightarrow$ open-shell transition.\(^a\) Values are in kcal/mol, calculated at the UB3LYP/6-311+G(d,p) level.

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<th>Molecule</th>
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<th>(\Delta \Delta E_{\text{def}})</th>
<th>(\Delta E_{\text{int}})</th>
<th>(\Delta \Delta E_{\text{elstat}})</th>
<th>(\Delta E_{\text{Pauli}})</th>
<th>(\Delta E_{\text{oi}})</th>
<th>(\Delta E_{\text{disp}})</th>
<th>Interacting fragments$^b$</th>
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<td>([a,f]-\text{DBP}_\text{cs})</td>
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\(^a\) \(\Delta E_{\text{tot}}\) = total binding energy between two fragments, \(\Delta E_{\text{def}}\) = deformation energy, \(\Delta E_{\text{int}}\) = interaction energy, \(\Delta E_{\text{elstat}}\) = electrostatic energy, \(\Delta E_{\text{Pauli}}\) = Pauli repulsion, \(\Delta E_{\text{oi}}\) = orbital interaction energy, \(\Delta E_{\text{disp}}\) = dispersion energy, \(\Delta E_{\text{iso}}\) = isomerization energy. $^b$ quin = quintet, s os = open-shell singlet, t = triplet.
Absolute energies and x, y, z coordinates of optimized structures

[a,e]-DBP singlet
E = $-615.8507052$ a.u.

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[\(a,e\)]-DBP triplet

\[ E = -615.7992303 \text{ a.u.} \]

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