

Diels–Alder Cycloadditions of 1,3-Butadiene to Polycyclic Aromatic Hydrocarbons (PAH). Quantifying the Reactivity Likeness of Bowl-Shaped PAHs to C₆₀

Jordi Mestres*[†] and Miquel Solà[‡]

Department of Molecular Design & Informatics, N.V. Organon, 5340 BH Oss, The Netherlands, and the Institut de Química Computacional, Universitat de Girona, 17071, Girona, Catalonia, Spain

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Bowl-shaped polycyclic aromatic hydrocarbons (PAH) are compounds constituted by five- and six-member carbon rings arranged as in fullerene structures.¹ These so-called “buckybowls” have attracted recently considerable attention in the field of fullerene chemistry due to the possibility that their curved surfaces could exhibit reactivity characteristics similar to those found in fullerenes.^{1a,b} However, synthesis of these compounds represents nowadays a great challenge to organic chemists, and, consequently, experimental studies aiming at exploring the chemistry of these curved PAH are still largely limited. Only C₂₀H₁₀ (corannulene, the polar cap of C₆₀),² C₂₂H₁₀ (cyclopentacorannulene),³ C₂₆H₁₂,^{1b} C₃₀H₁₀,^{1b} two C₃₀H₁₂ isomers,⁴ and C₃₆H₁₂⁵ have been recently obtained through flash vacuum pyrolysis. Within this landscape, the aim of this report is to apply computational methods to assess quantitatively the reactivity likeness of a series of bowl-shaped PAHs to C₆₀.

As an example of a typical fullerene reaction, the Diels–Alder (DA) reaction has been selected to perform this comparative reactivity study. In a DA reaction, fullerenes act as electron-deficient dienophiles, and thus they are especially well suited for these thermally allowed [4 + 2] cycloadditions. For this reason, the DA reaction in fullerenes has been widely investigated both experimentally⁶ and theoretically.^{7,8} In all studies, one of the

Table 1. Bond Lengths (R_{6-6} , in Å) and Pyramidalization Angles (P_{6-6} , in deg) for the Central 6–6 Carbons. Also Given Are the Average Pyramidalization Angles for All Carbons (P_{av} , in deg) and the HOMO and LUMO Orbital Energies (ϵ_{HOMO} and ϵ_{LUMO} , respectively, in eV)

dienophile	R_{6-6}	P_{6-6}	P_{av}	ϵ_{HOMO}	ϵ_{LUMO}
C ₁₀ H ₈	1.419	0.0	0.0	−8.71	−0.27
C ₂₆ H ₁₂	1.346	10.4	3.3	−8.65	−1.36
C ₃₀ H ₁₂ ¹	1.357	12.1	5.0	−8.67	−1.31
C ₃₀ H ₁₂ ²	1.376	12.2	6.7 ^a	−8.61	−1.47
C ₃₄ H ₁₂	1.381	12.7	7.4 ^a	−8.76	−1.41
C ₃₈ H ₁₂	1.386	12.0	6.9	−8.70	−1.76
C ₄₂ H ₁₂	1.389	12.5	6.9	−8.79	−1.80
C ₅₀ H ₈	1.386	11.7	9.5	−8.78	−2.48
C ₅₈ H ₄	1.385	11.6	10.7	−9.16	−2.77
C ₆₀ ^b	1.385	11.6	11.6	−9.64	−2.95

^a Carbons of the added methylene groups are not considered.

^b From ref 7b.

characteristics observed is that dienes prefer to attack the shorter carbon–carbon bond linking two six-membered rings (6–6 carbons) rather than the carbon–carbon bond in the junction between six- and five-membered rings (6–5 carbons).^{6–9} Accordingly, only 6–6 attacks of 1,3-butadiene to PAH will be discussed in this study.

The series of bowl-shaped PAH considered in the present work (Figure 1) was systematically constructed following three criteria: (i) they are structural fragments of C₆₀; (ii) they possess a central 6–6 bond; (iii) they show structural symmetry with respect to the 6–6 bond to be attacked. When necessary, methylene groups were added to external five-membered rings in order to mimic the situation in C₆₀ of having alternate 6–6 and 6–5 bonds of double- and single-like character, respectively. Overall, eight bowl-shaped PAH were analyzed: C₂₆H₁₂, two C₃₀H₁₂ isomers, C₃₄H₁₂, C₃₈H₁₂, C₄₂H₁₂, C₅₀H₈, and C₅₈H₄. In addition, naphthalene (C₁₀H₈) and C₆₀ were taken as planar and curved limit references, respectively, for discussion. Full geometry optimizations of all reactant, transition states, and adduct structures were carried out at the AM1 semiempirical level¹⁰ as implemented in the Gaussian 94 program.¹¹

Some of the structural and electronic parameters mainly responsible for the reactivity characteristics of the dienophiles are collected in Table 1. These include the bond distance (R_{6-6}) and pyramidalization angle (P_{6-6})

* To whom correspondence should be addressed.

[†] N. V. Organon.

[‡] Universitat de Girona.

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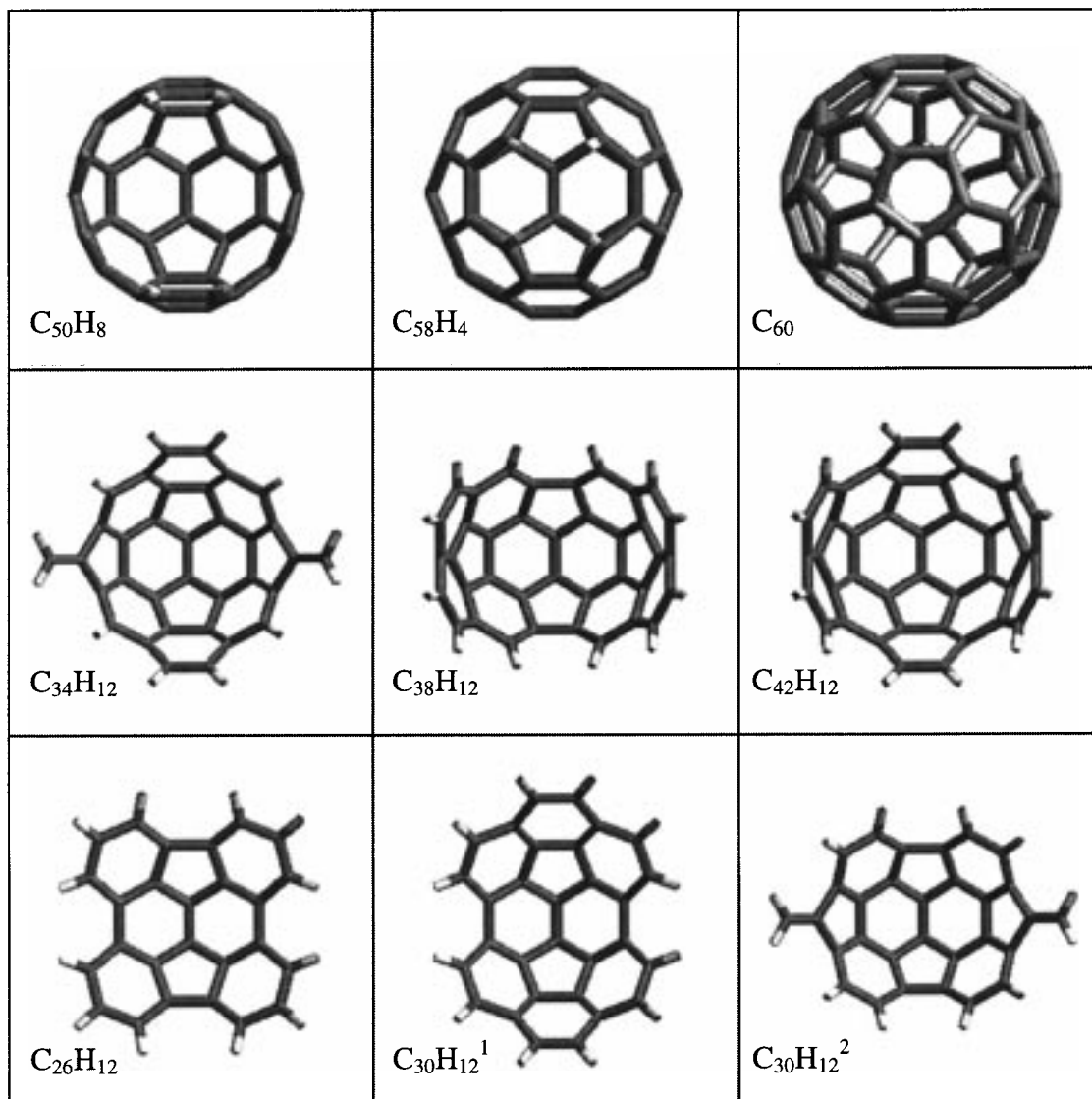


Figure 1. The eight bowl-shaped PAHs considered in this study.

of the 6–6 carbons attacked,¹² the average pyramidalization angle (P_{av}) for all carbons, and the HOMO and LUMO orbital energies (ϵ_{HOMO} and ϵ_{LUMO}). As can be observed, the R_{6-6} value in $C_{10}H_8$ is the largest along the series. The presence of pentagonal rings in buckybowl reduces the π delocalization and enhances the double-bond character of the central 6–6 bond. This effect is especially remarkable in $C_{26}H_{12}$, the smallest bowl-shaped PAH, which has a R_{6-6} value 0.073 Å shorter than $C_{10}H_8$. As molecular size and pyramidalization increase, R_{6-6} values become larger and slowly converge to the value in C_{60} . As regards to the orbital energies, it is found that while ϵ_{HOMO} barely changes among the dienophiles, ϵ_{LUMO} increases almost monotonically from naphthalene to C_{60} . For instance, from $C_{10}H_8$ to $C_{50}H_8$ ϵ_{HOMO} values are found within a range of 0.18 eV, whereas ϵ_{LUMO} values increase by 2.21 eV.¹³ As a result of ϵ_{LUMO} being stabilized more than ϵ_{HOMO} with the increase in molecular size and pyramidalization,^{14,15} one can anticipate a corresponding increase in the DA reactivity of the PAHs and

an eventual convergence to the reactivity of C_{60} (vide infra).

Table 2 contains the calculated AM1 reactivity parameters for the DA cycloaddition of 1,3-butadiene to each one of the dienophiles considered in this study.¹⁶ Besides the reaction enthalpy and enthalpy barriers for the DA and retro-DA reactions, another parameter referred as “induced pyramidalization”¹⁷ has been included to account for the increase in curvature the 6–6 carbons being

(13) The experimental electron affinities obtained for $C_{26}H_{12}$ and C_{60} are 1.16 and 2.65 eV (Chen, G. D.; Ma, S. G.; Cooks, R. G.; Bronstein, H. E.; Best, M. D.; Scott, L. T. *J. Mass Spectrom.* **1997**, *32*, 1305). The respective calculated electron affinities from the LUMO orbital energies at the AM1 semiempirical level are 1.36 and 2.95 eV, in qualitative good agreement with both the values and trend found experimentally.

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(12) Pyramidalization angles have been calculated using the π -orbital axis vector approach (POAV1) as implemented in the POAV3 program (Haddon, R. C. *POAV3 Program*, QCPE 508/QCMP 044, *QCPE Bull.* **1988**, 8).

Table 2. Induced Pyramidalization for the Central 6–6 Carbons of the Dienophile at the Transition State (iP_{6-6}^{\ddagger} , in deg), and Reaction Enthalpy (ΔH_r) and Enthalpy Barriers for the Diels–Alder (ΔH_{DA}^{\ddagger}) and retro-Diels–Alder ($\Delta H_{RDA}^{\ddagger}$) Reactions in kcal/mol

dienophile	iP_{6-6}^{\ddagger}	ΔH_{DA}^{\ddagger}	$\Delta H_{RDA}^{\ddagger}$	ΔH_r
C ₁₀ H ₈	10.0	55.3	43.8	11.5
C ₂₆ H ₁₂	3.9	21.9	63.2	−41.3
C ₃₀ H ₁₂ ¹	3.1	19.3	67.5	−48.2
C ₃₀ H ₁₂ ²	2.7	16.1	70.1	−54.0
C ₃₄ H ₁₂	2.6	16.1	71.2	−55.1
C ₃₈ H ₁₂	2.8	16.3	69.3	−53.0
C ₄₂ H ₁₂	2.6	15.9	70.5	−54.6
C ₅₀ H ₈	3.0	17.7	67.1	−49.4
C ₅₈ H ₄	2.9	16.7	67.0	−50.3
C ₆₀ ^a	2.9	16.3	67.1	−50.8

^a From ref 7b.

attacked experience as the diene approaches the dienophile. This “induced pyramidalization” (iP_{6-6}^{\ddagger}) should reflect the relief of strain associated with the “local term” in Haddon’s strain energy analysis.^{14,18} As extracted from results in Table 2, the originally planar 6–6 carbons in naphthalene (C₁₀H₈) suffer a pyramidalization of 10.0° ($iP_{6-6}^{\ddagger} = 10.0^\circ$) upon 1,3-butadiene attack. This large iP_{6-6}^{\ddagger} is translated into a very high enthalpy barrier (55.3 kcal/mol) and an endothermic reaction enthalpy (11.5 kcal/mol). In contrast, the pyramidalization angle of the 6–6 carbons in C₆₀ at the transition state increases from 11.6° to 14.5° ($iP_{6-6}^{\ddagger} = 2.9^\circ$). Compared to naphthalene, this small iP_{6-6}^{\ddagger} value is translated in a much lower enthalpy barrier (16.3 kcal/mol) and a strongly exothermic reaction enthalpy (−50.8 kcal/mol). Further comparison of the iP_{6-6}^{\ddagger} and ΔH_{DA}^{\ddagger} values along the series of PAH in Table 2 evidences a good relationship between these two values. A rationale for this trend can be derived in terms of the Hammond’s postulate. As the structures of the reactant PAH and the transition state with 1,3-butadiene become more similar at the site where the reaction occurs (mainly reflected by the value of iP_{6-6}^{\ddagger}), the enthalpy barrier is reduced, and, consequently, the reaction enthalpy is increased.

From the values of the enthalpy barriers in Table 2, a characteristic “reactivity vector” for a given PAH *i* can be defined as $\mathbf{r}_i = (\Delta H_{DA}^{\ddagger}, \Delta H_{RDA}^{\ddagger})$. Then, the reactivity likeness of each PAH to C₆₀ can be quantitatively assessed by evaluating the euclidean distance between the “reactivity vectors” of each PAH and C₆₀ as $d = (\mathbf{r}_i \cdot \mathbf{r}_{C60} + \mathbf{r}_{C60} \cdot \mathbf{r}_{C60} - 2 \cdot \mathbf{r}_i \cdot \mathbf{r}_{C60})^{1/2}$. Figure 2 depicts the values of *d* for the series of PAH. As can be observed, despite being the smallest bowl-shaped PAH, C₂₆H₁₂ retains most of the reactivity characteristics of C₆₀ (see Table 2). However, the two C₃₀H₁₂ isomers represent a significant improvement with respect to C₂₆H₁₂. In contrast, reac-

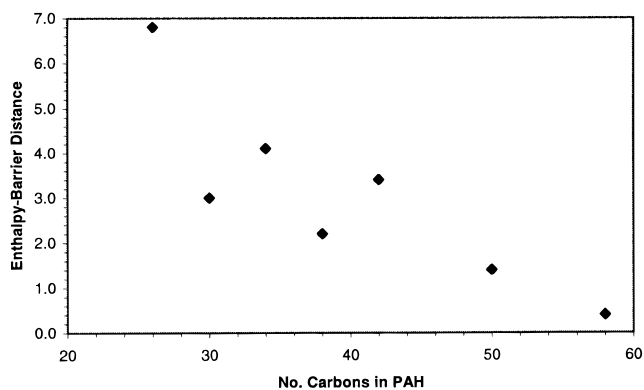


Figure 2. A representation of the enthalpy-barrier euclidean distance (in kcal/mol) to C₆₀ for the eight bowl-shaped PAHs analyzed.

tivity likeness to C₆₀ is not improved in C₃₄H₁₂. Interestingly, C₃₈H₁₂ is the next PAH improving the reactivity patterns of C₃₀H₁₂, with a value of ΔH_{DA}^{\ddagger} remarkably similar to that in C₆₀ (see Table 2), while C₄₂H₁₂ has reactivity parameters less similar to C₆₀ than those found in C₃₀H₁₂. Finally, fast convergence to the reactivity of C₆₀ is achieved for C₅₀H₈ and C₅₈H₄.

The structures of C₂₆H₁₂ and C₃₀H₁₂¹ have been already synthesized, and it has been proposed that they might display fullerene-like chemistry.¹⁹ It has been shown here that, for the case of the DA reaction, they have indeed reactivity patterns similar to those of C₆₀, with C₃₀H₁₂ being closer to C₆₀ than C₂₆H₁₂. In addition, in the absence of experimental data, computational methods can provide a valuable means for guiding synthetic efforts and targeting chemical experiments to those buckybowl structures potentially exhibiting the most interesting reactivity patterns with respect to C₆₀. In this respect, to achieve a closer reactivity likeness to C₆₀, the present results encourage direct experimental efforts toward the synthesis of C₃₈H₁₂. The question of which is the smallest bowl-shaped PAH exhibiting C₆₀-like reactivity can now be addressed quantitatively by compromising molecular size, synthetic feasibility, and the present values for reactivity likeness.

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Supporting Information Available: Coordinates of all the structures discussed in the manuscript (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) The induced pyramidalization in the attacked 6–6 carbons of the dienophile at the transition state, iP_{6-6}^{\ddagger} , is defined as the difference between the pyramidalization of the 6–6 carbons at the transition state and the original pyramidalization of the 6–6 carbons in the dienophile.

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