Polar curved polycyclic aromatic hydrocarbons in soot formation

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Abstract

In this paper we consider the impact of polar curved polycyclic aromatic hydrocarbons (cPAH) on the process of soot formation by employing electronic structure calculations to determine the earliest onset of curvature integration and the binding energy of curved homodimers. The earliest (smallest size) onset of curvature integration was found to be a six ring PAH with at least one pentagonal ring. The σ bonding in the presence of pentagons led to curvature, however, the π bonding strongly favoured a planar geometry delaying the onset of curvature and therefore the induction of a flexoelectric dipole moment. The binding energies of cPAH dimers were found to be of similar magnitude to flat PAH containing one or two pentagons, with an alignment of the dipole moments vectors. For the more curved structures, steric effects reduced the dispersion interactions to significantly reduce the interaction energy compared with flat PAH. Homogeneous nucleation of cPAH at flame temperatures then appears unlikely, however, significant interactions are expected between chemi-ions and polar cPAH molecules suggesting heterogeneous nucleation should be explored.

Highlights

- The earliest onset of curvature in pericondensed aromatic was determined to be six rings with at least one ring being pentagonal.
- Interactions between curved PAH dimers were found to be similar to planar PAH for one or two pentagonal rings. Three pentagonal rings or greater bound with less energy.
- Interactions between curved PAH and ions are considered to be substantial and should be explored further.



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1 Introduction

Carbon particulate emissions from incomplete combustion of hydrocarbons in engines and open fires contributes to climate change [1, 27] and impacts human health [23]. Considerable efforts to mitigate the formation of soot has led to an increased understanding of the gas phase chemistry and the dynamics of soot particles as they agglomerate. However, significant uncertainty remains around the transition from molecules into a solid particle [42]. Recent high resolution transmission electron microscopy (HRTEM) studies have shown that a significant fraction of curved polycyclic aromatic hydrocarbons (cPAH) is present in soot [3, 39] – the majority of fringes (corresponding to aromatic molecules imaged perpendicular to the electron beam) appear to contain a single peak in the curvature, indicating the presence of pentagonal rings. The conclusion was supported by curvature analysis of the fringes using geometrical [39] and statistical models of the curvature [46]: significant curvature has been found in 28–49% of the fringes, indicating the integration of 1–3 pentagons in their structure. Corannulene [22] and fullerenes [13] have also been synthesised in flames, so the presence of these curved fragments does not come as a surprise.

The integration of pentagons strains the carbon skeleton of the cPAH, "squeezing" electron density from the concave to the convex side of the curved molecule resulting in a large flexoelectric dipole in direction normal to the skeleton [26]. For the size of fragments found in primary soot particles determined from HRTEM and optical band gap methods (10-20 rings) [2] we predicted a dipole in the range of 4–6.5 debye [26] (which is two to three times that of water, 1.85 debye [37]). Figure 1 shows the electrostatic potential around coronene, corannulene and water to illustrate the effect. The quadrupolar potential of the flat coronene with the negative potential on the two sides of the molecule's plane is due to the π -bonds. These become significantly polarised for the curved corannulene, giving a dipole moment of 2.07 debye [24], similar in magnitude to water.

The idea that curved structures may have a role in the soot formation has been discussed by Homann [17]. For ion-induced nucleation of soot around chemi-ions [5], the rate of nascent soot formation will be significantly enhanced if cPAH are present, due to the



Figure 1: Cross section of the electric potential, (+) blue, (-) red, for coronene (left), corannulene (middle) and water (right).

long-ranged ion-dipole interactions. Here, we work on two aspects of the problem for the relation curvature-nucleation. We begin this paper with a discussion of the earliest onset of curvature integration as a given structure increases in size. Further, we calculate the binding energy of dimers of curved PAH to investigate the effect of curvature on homogeneous nucleation. The interaction between polar molecules, non-polar molecules and chemi-ions, presumably affecting soot formation, are then discussed.

2 Methodology

The electronic structure calculations and geometry optimisations were performed using the Gaussian 09 software [12]. For the curvature integration calculations, the hybrid density functional theory (DFT) method B3LYP with the 6-311G(d,p) basis set was used, which has been found to provide structures for small curved aromatics to the quality of those determined from x-ray crystallography [15, 32]. We found this level of theory to provide molecular dipole moments to within 6% error compared with the experimental value for corannulene [26].Care was taken to ensure that geometry optimisations provided a structure not at a saddle point geometry (e.g., small cPAH can invert through a planar transition state geometry [36]). C₁ symmetry was enforced for all structures, initial geometries were purposely curved away from planar and frequency calculations ensured no negative frequencies indicating convex minima in the potential energy were found. To compute dimerisation energies of flat PAH (fPAH), we have previously made use of symmetry-adapted perturbation theory DFT methods SAPT(DFT) which were found to reproduce the exfoliation energies of graphene [40]. In this case, the intermolecular potential energy was easily sampled by increasing the interplanar distance between the dimers and calculating the binding energy as a function of distance. However, for cPAH dimers, a more complex geometry can result from the symmetry breaking of the curvature and full geometry-optimised structures were sought. This required a sufficiently rapid and scalable method in order to optimise the geometry of the largest structures. We therefore made use of a hybrid DFT method with an empirical dispersion correction called B97D [16]. This method has been shown to produce binding energy to accuracies of CCSD(T) or SAPT(DFT) methods for two cPAH, corannulene and sumanene [4, 19]. (See Supplementary Information for further details.)

3 Results and discussion

3.1 Curvature integration

A direct relationship exists between the curvature of sp² hybridised carbon atoms (measured via pyramidalisation angle θ_p) and the local dipole moment in curved PAH (through the flexoelectric constant $f_{\theta p} = 2.24$ D/rad [25]). The definition of the pyramidalisation angle is illustrated in Fig. 2: there exists a vector that makes equal angles ($\theta_{\sigma\pi}$) with the three sigma bonds; the pyramidalisation angle is $\theta_p = \theta_{\sigma\pi} - 90^\circ$. It is proportional to the mean local curvature of the carbon skeleton[21] and is a natural characteristic of the

deformation of the carbon skeleton.



Figure 2: Geometrical definition of the pyramidalisation angle θ_p and the respective $\theta_{\sigma\pi}$ angle.

Small PAH have flat configurations even if pentagons are integrated. In order to predict at which stage of PAH formation in flames a significant flexoelectric dipole moment will occur, it is important to find the onset of curvature integration as a PAH grows. Various mechanisms for pentagon integration have been proposed, such as acetylene addition to fluoranthene [34], dehydrogenation of a five-member bay site [43, 44], oxidation of a zigzag edge [38], dehydrogenation of aromers [17] or a C_1/C_2 mechanism [45]. Our goal here is not to comment on which mechanisms are of most importance, but to determine the smallest PAH size that leads to curvature, and to expand the set of structures explored in Martin et al. [25]. Figure 3 shows the various strategies employed to increase the size.

The geometry of hexagonal and pentagonal nets should dictate that once two hexagonal rings border a pentagonal ring, curvature should be integrated. Considering the base structures, labelled **ac**, **fa**, **ph**, **be** and **1a** in Figure 3, no curvature is observed until the pentagon is entirely enclosed by five hexagonal rings. To understand the discrepancy between a geometrical net and that found in the calculated structures, the bonding must be considered. The σ -bonding of the sp² aromatic network containing pentagons favours curvature by limiting the bond lengths (1.3–1.6 Å) and providing an angle potential optimal at 120°, incompatible with pentagonal structure. The π -bonding network, however, resists bending (leading to a large elastic modulus of 21.5 eV/Å² [29]) and favours planarisation of the molecules. The π -bonding dominates for two to four bordering hexagons with the bond lengths and angles changing to accommodate the planar structure. The planarisation is only overcome for the structure with a pentagon completely enclosed by hexagons (**1a**).

We extended our previous set of structures [25] to include more molecules containing pentagons incompletely enclosed by hexagons (containing sp^3 carbons). We analysed curved geometries obtained via two pathways: by increasing the hexagonal aromatic network around the structure or by acetylene addition to zig-zag edge site, as suggested by Pope and Howard [34]. For structures **fa** and **ph**, with a single pentagon and three bordering hexagons, additional hexagonal network growth did not give rise to curvature. However, for the structure **be** with four hexagonal rings enclosing the pentagonal ring, we found that hexagonal growth did lead to curvature and a flexoelectric dipole. However, substantial growth was required – the initial addition of hexagonal aromatic rings to the left and right of the pentagonal ring lead to planar structures. Significantly more hexagonal rings were required to curve the arenes containing a single non-enclosed pentagon rings. We also found that substantial curvature could be induced by the geometry with two unenclosed pentagons joined by two hexagons (Figure 3 **cp**). An effective curvature integration mechanism was also found for the addition of acetylene to benzo(ghi)fluoranthene, **be**. This



Figure 3: Optimised geometries are shown from above and side. The curved structures are framed. The most pyramidalised carbon atom of each structure is denoted by a red circle and its θ_p value is quoted underneath, along with the dipole moment calculated at the B3LYP/6-311G(d,p) level of theory. Base structures with single pentagons with two acenaphthylene **ac**, three fluoranthene **fa**, phenanthrindene **ph**, four benzo(ghi)fluoranthene **be** or five corannulene **1a** bordering hexagons are shown along the diagonal with hexagonal extension top right, and acetylene addition bottom left.

rapidly increased the maximal pyramidalisation angle ($\theta_{p,max} = 6.8, 9.3, 10.5^{\circ}$ for one, two and three acetylene additions, respectively) and dipole moment of these structures ($\mu = 1.51, 2.45, 3.03$ debye). This mechanism was also explored for corannulene and a substantial dipole moment was found with these non-integrated pentagonal rings giving dipole moments of 2.93, 3.49, 3.96, 4.36 to 4.73 debye. The additional pentagonal rings around the edges produced curvature more effectively due to pentagonal rings' decreased internal angles compared with the hexagons, which provides more σ strain on the carbon network. This is further highlighted by comparing the curvature of pentacetylcorannulene (**pa**) and pentabenzocorannulene (**pb**). The former was found to be more pyramidalised, $\theta_{p,max} = 12.3^{\circ}$, compared with the latter, $\theta_{p,max} = 9.2^{\circ}$. Acetylene additions to zig-zag sites (producing edge-based peripheral pentagonal rings) are not persistent at high temperature and are prone to acetylene desorption, migration or rearrangement into hexagonal rings [43]. However, if further acetylene addition proceeds to enclose the pentagonal ring by hexagons, it would represent the most effective manner to integrate curvature, with the second most effective being acetylene addition to zig-zag edge site.

Returning to the question of the critical size for the onset of curvature, Figure 4 shows the dipole moment as a function of ring number. It is seen that the onset of curvature occurs at 6 rings for the pentagon enclosure and acetylene curvature integration strategies. For the hexagonal extension strategy, the onset of curvature was found to be at 10 rings.



Figure 4: Dipole moment as a function of the number of rings for different curvature integration strategies. These strategies are also shown in Figure 3 with 5-enclosure being represented by 1a as well as the structures previously calculated[25], hex. extension in the upper right half and 5-rim in the bottom left of Figure 3. Curved structures are indicated by a plus symbol. The triangles correspond to ac, fa, ph and be.

3.2 Interactions between cPAH

We will now consider the impact of the curvature on the dimerisation of arenes in the size range found in soot (4–20 rings), with the pericondensed species having pentagonal rings entirely enclosed by hexagons. The binding dimerisation energy (defined as the minimum energy of all possible dimer conformations) has been used as a measure of the stability of clusters of flat PAH molecules previously [6, 28, 41, 42]. Figure 5 shows the binding energies of cPAH compared with fPAH dimers of pyrene, coronene, ovalene, hexabenzocoronene and circumcoronene taken from [41]. For structures containing one to two pentagonal rings, we found similar binding energies for curved and planar PAH of similar masses. However, further increases in the number of pentagons destabilized the cPAH dimers significantly compared with flat PAH dimers.



Figure 5: Binding energy of flat and curved PAH molecules as a function of molecular mass.

To analyse the reasons for this behaviour, let us consider corannulene and coronene – small PAH whose similar binding energies allow the role of dispersion and dipoledipole interactions to be analysed. SAPT(DFT) calculations show a reduced dispersion interaction in corannulene dimers of -136 kJ/mol [4] compared with -145 kJ/mol [33] for coronene. This is also seen in the greater intermolecular distance between the two molecules centre of masses, in the dimer of corannulene, 3.62 Å compared with 3.58 Å for coronene. The role of the dipole can be evaluated via the electrostatic contribution, which for corannulene is 22% of the attractive potential compared with 13% for coronene dimer. We also observed a dipole of the dimers increased in comparison with the sum of the two static dipole moments, indicating a small contribution from induced dipoles (Debye interaction). SAPT(DFT) found induced polarisation to make up 4% of the attractive force in the case of corannulene [4]. (See the Supplementary Material for full details with comparisons to B97D simulations.)

Thus, while the dipole moment contributes to the binding energy, the molecule's curvature causes a decrease in the dispersion interactions due to steric effects. The intermolecular distance increases to 4.4–5 Å for one to three pentagons and to ~6-7 Å for four or more pentagons integrated (see Supplementary Material). Due to the short range of the dispersion interactions (scaling as $\propto 1/r^6$) this significantly reduces the binding energy, most evidently for the structures with three or more pentagonal rings. For the highly strained structures a tilt towards a herringbone configuration was also found for the geometries.

This is due to the positively charged hydrogen atoms interacting with the negative charge of the π -electron cloud around the carbon at the rim of the bowl; a similar effect has been observed in crystal structures [11].

The similar binding energy of cPAH with one to two pentagonal rings to planar fPAH indicates that homogeneous nucleation of either species is unlikely to occur at flame temperatures [41]. Some preliminary molecular dynamics simulations have been performed on dimers 3c by Chung and Violi [9] and a similar clustering behaviour was seen compared with planar fPAH. This is consistent with corannulene's sublimation temperature at standard conditions of 640 K [8]), which is similar to perylene 660 K at [30], a planar PAH with the same number of carbon atoms. The similar sublimation temperature indicates similar binding energies.

3.3 Interactions between cPAH and other species

Permanent dipole-dipole interactions between cPAH and polar molecules contribute to the binding energies. Calculations have found significant interactions between water and corannulene, with similar binding strengths to water dimers, -12.0 kJ/mol [31] compared with -13.2 kJ/mol [35] respectively. In comparison, the water-graphite interaction energy is -9 kJ/mol [20]. These energies are of the order of *RT* at flame temperatures (12 kJ/mol 1500 K). A stronger interactions could be expected for heterodimers of cPAH, especially if the smaller molecule fits well in the concave side of the larger molecule. The order of magnitude of these interaction energies shows that, although they could contribute to nucleation, it is unlikely they to make a qualitative difference at flame temperature.

A much more significant interaction of cPAH with another species will be with ions, as numerous examples from the literature show. Synthesised cPAHs such as corannulene, (1a), are known to bind small ions strongly (93-289 kJ/mol [10]). Anion binding is enhanced on the concave side by increased interaction with the positive hydrogen atoms and the increased dispersion interactions [7]. Cations can also bind to the concave face by interacting with the small excess negative charge present (Figure 1), but most significantly they bind via dispersion interactions in this configuration [10]. Binding on the convex face is favoured above the pentagonal ring but can also around the rim carbon atoms where charge is concentrated due to the C-H bond, see Figure 1. Similar binding energies are found between ions and the cPAH corannulene / ions and the fPAH coronene [6, 10]. Yet, corannulene has increased capacity for lithium in battery applications (capacities of 372 and 602 mAh/g found for graphite and corannulene respectively [47]). Chen and Wang recently considered the stabilisation of clusters of fPAH bound to a chemi-ion. A sandwich complex was found to have significant binding energies; however, the third fPAH added was weakly bound [6]. Curved aromatic molecules differ from planar fPAH most of all in their capacity for long-ranged interactions with ions (potential $\propto -1/r^2$); this means that larger clusters could be stabilised by ion-cPAH interaction. More work is required to further explore this possibility.

4 Conclusion

The earliest onset of the bending of the carbon skeleton in PAH containing integrated pentagons was investigated for different sequences of structural changes. Curvature integration is driven by the strain imposed on the carbon skeleton by the bond length and angle restrictions due to the σ -bonding, but it is resisted by the π -bonding which favours planar geometry. It turns out that the latter effect is dominant for small species, resulting in a relatively well defined critical size of the pentagon-containing structures that has to be overcome for curvature to occur. The onset size has been found to be six rings for growth by pentagon enclosure and rim based pentagonal rings, and 10 ring for hexagonal extension for a pentagonal rings was found to increase the curvature to a greater degree than the addition of hexagonal rings.

The binding energy in homodimers of curved PAH with one or two pentagonal rings was found to be comparable with that of planar PAH molecules, due to a cancellation of the reduced dispersion contribution from steric effects with the dipole-dipole interactions. In structures with greater than three pentagons, the steric effect dominates over the electrostatic, leading to binding energy of cPAH significantly lower than fPAH.

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A Appendix

A.1 Dispersion corrected hybrid density functional theory

The dispersion corrected hybrid density functional theory method B97D applies an empirical correction to the B97 DFT method to describe the dispersion interactions $E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}$.[16] The form of this correction is a damped attractive potential of the form.

$$E_{\rm disp} = -s_6 \sum_{i=1}^{N_{\rm at}-1} \sum_{j=i+1}^{N_{\rm at}} \frac{C_6^{ij}}{R_{ij}^6} f_{\rm dmp}\left(R_{ij}\right)$$
(A.1)

where N_{at} is the number of atoms in the system and energy is computed as the sum of the binary interaction energies of all atomic pairs; s_6 is a scaling factor that depends on the DFT used (we used B97 with a s_6 value of 1.25; it is also mentioned that the spin dependent components of the exact exchange integrated into B97 hybrid were also modified as they were linear dependent on this scaling coefficient, C_6^{ij} are the dispersion coefficients for the atomic pair ij and R_{ij} is the respective intermolecular distance. A damping constant is used to ensure stability in the calculations for overlapping geometries:

$$f_{\rm dmp}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_{\rm r}-1)}}$$
(A.2)

where R_r are the vdW radii and d = 20. The dispersion coefficients and vdW radii for carbon and hydrogen used are $C_6^{\rm C} = 1.75$, $R_r^{\rm C} = 1.452$ Å and $C_6^{\rm H} = 0.14$, $R_r^{\rm H} = 1.001$ Å respectively with the coefficient between two different atoms being determined using the geometric mean $C_6^{ij} = \sqrt{C_6^i C_6^j}$.

Table 1 shows the absolute error of dipole moment calculated using B97D, B3LYP and MP2 compared with the experimentally determined value for corannulene 2.071 D.[24] Both B3LYP and B97D accurately determined the dipole moment as the basis set size increased (which is not the case for MP2) as we have found previously.[26]

Table 1: Table of the difference of the dipole moments from the experimentally determined value 2.07 D[24] for corannulene at various levels of theory in debye with percentage errors in brackets

Basis set	Func. no.	B3LYP		B97D		MP2	
6-31G(d)	320	0.35	(16.9%)	0.16	(7.8%)	0.10	(4.9%)
6-311+G(d,p)	500	0.12	(5.6%)	0.19	(9.1%)	0.60	(28.8%)
cc-pVTZ	740	0.08	(3.7%)	0.01	(0.6%)	0.35	(16.8%)
cc-pVQZ	1400	0.03	(1.3%)	0.05	(2.2%)	_	_

A.2 Dimerisation interaction energy

Full geometry optimisations of the dimers were performed at this level of theory with basis set superposition error (BSSE) corrected for in the final electronic structure calculation (we did not think BSSE error would impact the geometry optimisation substantially as it was found to be <2% in all cases). The results are shown in Table 2 as well as plotted as a function of molecular mass in Figure 5 in the main text.

	Dipole ^a	$\sum \theta_P \mathbf{v}_{\pi}$	BE^b	\mathbf{D}^d	Tilt
	(debye)	(rad)	$(kJ mol^{-1})$	(Å)	(degrees)
1a	2.06	1.269	-66	3.62	0.0
2a	2.79	1.697	-72	3.88	0.0
2b	4.10	2.309	-94	4.08	13.1
2c	4.92	2.723	-107	4.30	10.5
2d	7.42	3.778	-228	4.63	0.0
2f	4.83	2.598	-124	4.23	0.0
3a	2.51	1.524	-80	3.63	0.0
3c	4.62	2.579	-97	4.50	5.6
3d	5.44	2.953	-90	4.70	22.9
4a	6.36	3.257	-78	6.05	5.5
5a	6.49	3.274	-68	7.00	6.2
6a	6.46	3.205	-69	7.70	40.1
pyr	0.0	0.000	-42^{c}	3.59	_
cor	0.0	0.000	-69 ^c	3.58	_
ova	0.0	0.000	-98 ^c	3.56	_
hbc	0.0	0.000	-140 ^c	3.52	_
cir	0.0	0.000	-182^{c}	3.46	_

 Table 2: Table of dipole moments, dimer binding energies, dimer equilibrium distances and molecular quadrupoles for PAH

^{*a*} Taken from [26]. ^{*b*} Binding energy. ^{*c*} Taken from [41] ^{*d*} Equilibrium distance.

The B97D method has been found previously to accurately compute the intermolecular energy between dimers of corannulene **1a** and sumanene **3a** determining the interaction to within 2% of that calculated by CCSD(T) benchmark and symmetry adapted perturbation theory SAPT(DFT) methods. [4, 19] Planar PAH such as pyrene and coronene have been found to be overbound by B97D methods[40] and B3LYP-D3 method found to better describe these molecules.[18] Recently SAPT(DFT) simulations on curved arene dimers have been performed which allow the contributions of the intermolecular interaction to be decoupled. These are shown in Table 3 where we compare them with the dispersion energy calculated using the empirical correction in the B97D functional for coronene and corannulene.

The dispersion interactions are found to be overpredicted by B97D in the case of the flat PAH coronene and underpredicted for curved PAH corannulene, in comparison with

	Coroner	ie	Corannulene		
	SAPT(DFT) ^a	B97D	SAPT(DFT) ^b	B97D	
total	-65.7	-85.9	-65.9	-66.4	
electrostatic	-27.5	_	-40.4	_	
repulsion	145.5	_	118.6	_	
induction	-38.9	_	-8.0	_	
dispersion	-144.9	-154.9	-136.0	-121.1	
R(Å)	3.58	3.51	3.62	3.62	

Table 3: *Table of intermolecular energies (kJ mol⁻¹)determined using SAPT(DFT) and B97D methods. Equilibrium distances are also shown.*

^a Taken from [33]. ^b Taken from [4].

SAPT(DFT) benchmark. Since we have shown the dipole moment to be well described by B97D, see above, the electrostatic interactions are not expected to differ with that of SAPT(DFT) and, therefore, the underbinding of the dispersion interactions are compensated by an underprediction of the exchange repulsion providing a binding energy close to that of the benchmark calculations for corannulene. For coronene this compensation does not hold with an overprediction of the dispersion interaction leading to an overpredicted binding energy. It is well known for dispersion corrected hybrid density functional theory methods with the B3LYP-D3 method providing a better binding energy for coronene with a lower C_6^C dispersion coefficient.[18] This indicates corannulene has a larger dispersion interaction compared with coronene which would follow from the electrons being more easily polarised on pyramidalised carbon atoms. This has recently been shown to be the case for different carbon nanoforms.[14]

The corannulene dimer was found to have a greater fraction of the attractive interaction coming from the electrostatic contribution, 22% compared with 13% for coronene, which, along with the increased intermolecular distance and reduced repulsion energy, stems from the contribution of the dipole moment to the binding energy.

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