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Do large polycyclic aromatic hydrocarbons and graphene bend? How popular theoretical methods complicate finding the answer to this question

Peter B. Karadakov*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.

ABSTRACT

Theoretical studies of the vibrational frequencies of $C_{6n^2}H_{6n}$ ($n = 2-12$) coronenes, show that, despite full conjugation, delocalization and aromaticity, the stability of the planar geometry rapidly decreases with size. A switch to a nonplanar geometry can be expected at around $n = 9-12$; any larger gas-phase coronene, including graphene, should be nonplanar. When applied to coronenes, popular quantum chemical methods, including Hartree-Fock and density functional theory, are shown to produce anomalous imaginary frequencies suggesting unrealistic geometry distortions; this reveals a serious methodological problem in calculations on extended systems which needs to be resolved through further basis set development.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs, also known as polyarenes) involve two or more fused benzene rings. All carbon atoms in a PAH are sp^2 hybridized; this gives rise, in the absence of steric repulsions, to an especially stable fully conjugated delocalized aromatic π electron system which supports a planar structure. Theoretical studies of large PAHs from the coronene family, up to $C_{384}H_{48}$, using density functional theory (DFT), show no deviations from planarity [1]. However, the largest PAH, a single graphene sheet, is expected to bend: According to Novoselov *et al.* [2], “Planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes”. This paper addresses the question whether there is a limiting size after which PAHs no longer remain planar, but prefer a bent geometry instead, by theoretical studies of the vibrational frequencies of coronenes, PAHs with a general molecular formula $C_{6n^2}H_{6n}$, for $n = 2-12$ ($C_{24}H_{12}$ to $C_{864}H_{72}$), using *ab initio* and DFT quantum chemical methods. It turns out that

* E-mail address: peter.karadakov@york.ac.uk

finding the answer to this question requires more than just a “brute force” application of computing power. The choice of theoretical methods to use and the interpretation of the results are somewhat less than straightforward because of a well-known deficiency of a number of popular methods which have been shown to erroneously predict that benzene and certain arenes are nonplanar [3]. This deficiency has been attributed to an “insidious two-electron intramolecular basis set incompleteness error,” and it has been found to affect post-Hartree Fock (post-HF) methods, including Møller-Plesset perturbation theory (MP2 and MP3) and configuration interaction (CISD), when combined with a number of common basis sets. While it was initially claimed that the HF method and DFT, as one-electron approaches, do not suffer from this error [3], subsequent HF and DFT studies of planar coronene ($C_{24}H_{12}$) have reported imaginary vibrational frequencies, which might be indicative of a tendency to abandon planarity; these were observed in calculations using the MPWB1K exchange-correlation functional with the standard 6-31+G(d) basis [4], and in HF and B3LYP calculations with a non-standard TZP($\alpha_d = 0.6$) basis [5]. The results reported in this paper demonstrate that the deficiency identified in Ref. 3 is much more widespread than previously thought, affecting even a very popular DFT approach, B3LYP/6-31G(d), for coronenes with $n \geq 4$ ($C_{96}H_{24}$ and beyond); HF/6-31+G and B3LYP/6-31+G(d) are affected even earlier, for coronenes with $n \geq 3$ ($C_{54}H_{18}$ and beyond). It is shown that larger coronenes and, by extrapolation, graphene, exhibit an imaginary frequency, different from the anomalous imaginary frequencies caused by the deficiency, and indicative of a preference for a nonplanar umbrella-like geometry.

2. Results and discussion

The gas-phase D_{6h} molecular geometries of coronene ($C_{24}H_{12}$), circumcoronene ($C_{54}H_{18}$), circumcircumcoronene ($C_{96}H_{24}$), and higher members of the $C_{6n^2}H_{6n}$ coronene family, up to $n = 12$ ($C_{864}H_{72}$), see Figure 1, were optimized at the closed-shell (“restricted”) HF/6-31G and B3LYP/6-31G levels of theory, then harmonic vibrational frequencies were calculated at the optimized geometries. Additional calculations of this type were carried out for smaller coronenes, using a well-established post-HF *ab initio* approach (MP2) and other DFT methods (B3LYP-D3, M06, M06-2X, MPWB1K, MPW1B95, MPWB95 and PW6B95) with different (mainly popular standard) basis sets. Unless otherwise stated, the computational results were

obtained with GAUSSIAN09 [6]. All frequency data discussed in this paper are provided in the Appendix (see Table A1), together with further details about the calculations.

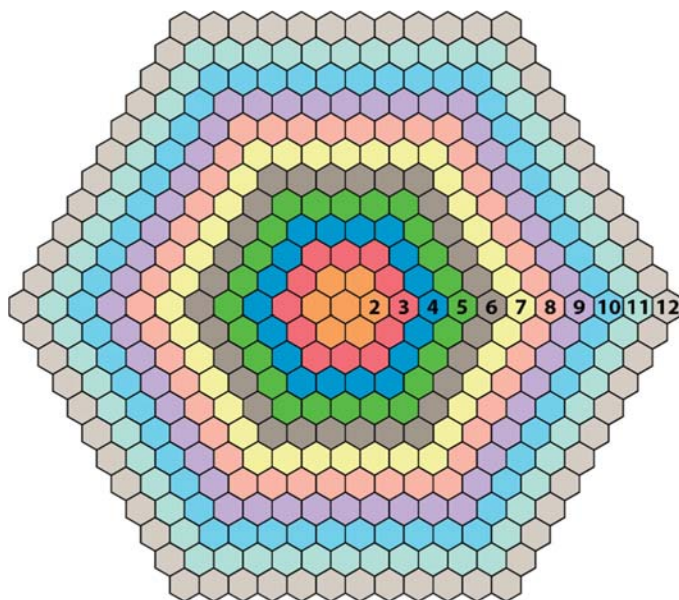


Figure 1. $C_{6n}^2H_{6n}$ coronenes for $n = 2-12$ ($C_{24}H_{12}$ to $C_{864}H_{72}$). The carbon frameworks for subsequent values of n are shown as stacked colored honeycomb shapes, numbered with n and aligned along the principal C_6 symmetry axis of the D_{6h} point group.

Coronene ($C_{24}H_{12}$, $n = 2$) shows only real vibrational frequencies in HF and B3LYP calculations making use of the 6-31G, 6-31G(d) and cc-pVDZ basis sets, in HF, B3LYP, B3LYP-D3, M06 and M06-2X calculations with the 6-31+G(d) basis, as well as in HF/6-311+G(d,p), HF/6-311++G(d,p), MPW1B95/6-311G(d) and MPW1B95/aug-cc-pVDZ calculations. In agreement with previous work [5,6], MPWB1K/6-31+G(d), HF/TZP($\alpha_d = 0.6$) and B3LYP/TZP($\alpha_d = 0.6$) are found to yield a single imaginary vibrational frequency each, associated with a b_{2g} normal mode which suggests a minor out-of-plane D_{6h} to D_{3d} distortion of the molecular geometry. This distortion was incorrectly identified as D_{6h} to C_{2h} in Ref. 5, where it was found to help with the assignment of phantom bands in the solid state infrared spectrum of coronene. However, a D_{6h} to D_{3d} distortion can still be used to interpret this spectrum, as an “infrared active quasidegenerate a_u, b_u doublet” in C_{2h} [5] corresponds to an infrared active degenerate e_u normal mode in D_{3d} . A single b_{2g} normal mode with an imaginary frequency is also

observed in calculations using the MPW1B95, MPWB95 and PW6B95 functionals with the 6-31+G(d) basis (the PW6B95 calculation was performed using NWCHEM [7]), as well as in MPW1B95/6-311+G(d). While this list of HF/DFT levels of theory is far from exhaustive, it is obvious that, when used with certain basis sets, HF and DFT predict that coronene has a nonplanar geometry. The outcome of the calculation is not determined by the choice of the basis set only, as indicated by the behaviour of different DFT functionals in combination with the 6-31+G(d) basis; however, when a method is used with different basis sets, basis sets that are closer to being near linearly dependent are more likely to yield imaginary frequencies. GAUSSIAN09 and other quantum-chemical packages deal with near linearly dependent basis sets by throwing away eigenvectors of the basis set overlap matrix corresponding to eigenvalues which are below a certain threshold. It is important to note that when using the default threshold of 10^{-6} , GAUSSIAN09 discards one out of the 528 basis functions in HF and B3LYP calculations on coronene with the TZP($\alpha_d = 0.6$) basis and all vibrational frequencies are obtained as real; decreasing the threshold to allow inclusion of all basis functions results in the appearance of a single imaginary frequency in each of the respective calculations, as reported above.

MP2 calculations on coronene utilizing the 3-21G, 6-31G(d), cc-pVDZ and def2-SVP basis sets yield three imaginary frequencies each, b_{2g} and e_{2u} ; MP2/6-31G and MP2/6-311G(d) yield six imaginary frequencies each, b_{2g} , e_{2u} , e_{1g} and b_{2g} (here and elsewhere in the text normal modes are listed in order of increasing square of the frequency). If MP2 is used with the 6-31G(d, $\alpha_d = 0.25$) basis recommended in Ref. 8, in which the exponent for d functions on carbons is set to 0.25, all frequencies become real, supporting a planar molecular geometry (standard 6-31G(d) uses $\alpha_d = 0.8$). An MP2/6-31G(d, $\alpha_d = 0.4$) calculation also produces only real frequencies, but MP2/6-31G(d, $\alpha_d = 0.5$) already shows one imaginary frequency. MP2 calculations utilizing the much larger def2-TZVP and cc-pVTZ basis sets, both of which include f functions on carbons, produce only real frequencies, but at a very high computational cost. MP2/def2-TZVP and MP2/cc-pVTZ are the highest levels of theory at which the vibrational frequencies in coronene have been studied so far and the fact that, at these levels of theory, the respective D_{6h} molecular geometries of coronene are stable with respect to any distortions, suggests that the imaginary frequencies observed when using other theoretical approaches should be viewed as computational anomalies. To study the effect of including f functions on the

carbons on the MP2 results, additional calculations were carried out in the 6-311G(f) (obtained from 6-311G(df) by deleting the d functions), 6-311G(df) and 6-311G(2df) basis sets. The MP2/6-311G(f) calculation produced 18 imaginary frequencies, b_{2g} , e_{2u} , e_{1g} , b_{2g} , a_{2u} , e_{2u} , a_{1u} , e_{1g} , e_{1g} , e_{2u} , b_{2g} and a_{2u} , which shows that replacing the d functions on the carbons by f functions makes the problem even worse. However, at the MP2/6-311G(df) and MP2/6-311G(2df) levels the number of anomalous imaginary frequencies decreases, to six (b_{2g} , e_{2u} , e_{1g} and b_{2g}) and just one (b_{2g}), respectively, an indication that this number is closely related to the balance between d and f functions on carbons.

As according to the MP2/def2-TZVP and MP2/cc-pVTZ results, coronene is unlikely to experience a D_{6h} to D_{3d} distortion in the gas phase, there should be another reason why the D_{3d} molecular geometry fits in well with its solid state infrared spectrum: A detailed analysis of the crystal structure of coronene [9] showed that the individual coronene molecules are non-planar and close to S_6 symmetry; e_u normal modes are infrared active in S_6 . It appears that the results of a more recent independent crystal structure determination [10] (used in Ref. 5), which suggested that individual coronene molecules attain a non-planar C_{2h} geometry in the solid state, are less accurate than those reported much earlier in Ref. 9.

As a rule, the two lowest real vibrational frequencies obtained in the calculations on coronene carried out in this work correspond to e_{2u} and a_{2u} normal modes (the only exceptions are MP2/6-31G(d) and MP2/6-311G(f), see Table A1). The range of frequencies obtained for the lowest degenerate e_{2u} normal mode is relatively narrow, from 82.3 cm^{-1} (MP2/6-311G(d)) to 98.9 cm^{-1} (HF/6-31G), with MP2/cc-pVTZ at 90.6 cm^{-1} ; the range for the lowest a_{2u} normal mode is wider, from 114.4 cm^{-1} (MP2/3-21G) to 141.2 cm^{-1} (HF/6-31G), with MP2/cc-pVTZ at 139.2 cm^{-1} . If, excluding the unrealistic distortions associated with anomalous imaginary vibrational frequencies, a higher member of the $C_{6n^2}H_{6n}$ coronene family favours a geometry of symmetry lower than D_{6h} , one of the lower real vibrational frequencies (most likely, one of those corresponding to the lowest e_{2u} and a_{2u} normal modes) can be expected to decrease gradually with the increase of coronene size until it becomes imaginary.

Circumcoronene ($C_{54}H_{18}$, $n = 3$) is found to have, similarly to coronene, only real vibrational frequencies in HF and B3LYP calculations using the 6-31G, 6-31G(d), cc-pVDZ and aug-cc-pVDZ basis sets. However, in contrast to the coronene results, for circumcoronene HF and B3LYP with the 6-31+G(d) basis yield three imaginary frequencies each, e_{2u} and b_{2g} , under

the default GAUSSIAN09 threshold of 10^{-6} for discarding near linearly dependent eigenvectors of the basis set overlap matrix; in either case the number of retained basis functions is 1000 out of a total of 1062. If the threshold is decreased to the minimum allowed by GAUSSIAN09 which in this case turned out to be 8×10^{-8} , the number of retained basis functions increases to 1015, and the HF/6-31+G(d) calculation produces six imaginary frequencies, b_{2g} , e_{2u} , e_{1g} and b_{2g} . A GAMESS-US [11] HF/6-31+G(d) calculation on circumcoronene using the default treatment of near linearly dependent basis functions retains 1011 basis functions and also produces an analogous set of six imaginary frequencies. These results confirm the connection between the extent of linear dependence present in the basis set and the number of anomalous imaginary vibrational frequencies. An MP2/6-31G calculation on circumcoronene furnishes no fewer than nineteen imaginary frequencies, b_{2g} , e_{2u} , e_{1g} , b_{2g} , a_{1u} , a_{2u} , e_{2u} , e_{1g} , e_{1g} , b_{2g} , e_{2u} and e_{2u} ; for coronene, the same level of theory produces six imaginary frequencies. This is the first manifestation of another feature of the anomalous imaginary vibrational frequencies in coronenes: Once anomalous imaginary frequencies are found at a certain level of theory for a member of the coronene family, the number of these frequencies increases for subsequent members of the family.

Just as for coronene, the two lowest real vibrational frequencies obtained in all calculations on circumcoronene are associated with e_{2u} and a_{2u} normal modes. Each of these frequencies is about twice lower than the corresponding frequency in coronene: The range of frequencies obtained for the lowest degenerate e_{2u} normal mode is from 38.8 cm^{-1} (MP2/6-31G) to 45.0 cm^{-1} (HF/6-31G); the range for the lowest a_{2u} normal mode is from 51.7 cm^{-1} (MP2/6-31G) to 61.6 cm^{-1} (HF/6-31G). This is a clear indication that circumcoronene is more flexible than coronene.

Unexpectedly, at the B3LYP/6-31G(d) level of theory, circumcircumcoronene ($\text{C}_{96}\text{H}_{24}$, $n = 4$) shows a single imaginary vibrational frequency of $354.7i \text{ cm}^{-1}$, associated with a b_{2g} normal mode. The large magnitude of this imaginary frequency and the fact that the b_{2g} normal mode with a similar atomic displacement pattern in the preceding member of the coronene series, circumcoronene, at the same B3LYP/6-31G(d) level, corresponds to the 26th vibrational frequency, 377.2 cm^{-1} , indicate that we are dealing with a computational anomaly rather than with a genuine propensity towards distortion. This is confirmed by the results of the other calculations on circumcircumcoronene: HF/6-31G(d), as well as HF and B3LYP with the 6-31G

and cc-pVDZ basis sets furnish only real vibrational frequencies. Here again, the two lowest real vibrational frequencies correspond to e_{2u} and a_{2u} normal modes, ranging from 23.7 cm^{-1} (B3LYP/cc-pVDZ) to 26.4 cm^{-1} (HF/6-31G) for e_{2u} , and from 30.2 cm^{-1} (B3LYP/6-31G(d)) to 33.1 cm^{-1} (HF/6-31G) for a_{2u} . These numbers imply a further increase in flexibility in comparison to circumcoronene. The atomic displacements in the B3LYP/6-31G(d) b_{2g} ($354.7i\text{ cm}^{-1}$) and a_{2u} (30.2 cm^{-1}) normal modes of circumcircumcoronene are shown in Figure 2.

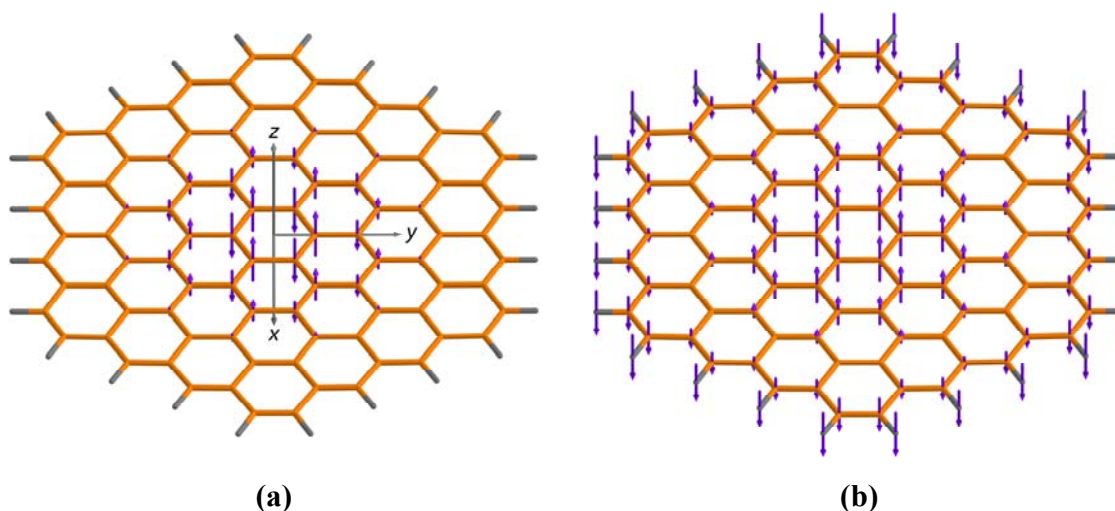


Figure 2. Atomic displacements in two low normal modes of circumcircumcoronene ($C_{96}H_{24}$) at the B3LYP/6-31G(d) level of theory: (a) b_{2g} ($354.7i\text{ cm}^{-1}$) normal mode; (b) a_{2u} (30.2 cm^{-1}) normal mode. If a coronene has one or more anomalous normal modes with imaginary frequencies, these start with a b_{2g} normal mode with atomic displacements very similar to the pattern shown in (a). One of the two lowest real vibrational frequencies in smaller coronenes corresponds to an a_{2u} normal mode with atomic displacements following the pattern shown in (b), which is sometimes referred to as a “(0,1) drumhead” mode [1]. In larger coronenes the frequency of this mode decreases until it becomes imaginary; when this happens, the planar geometry becomes unstable with respect to a distortion to an umbrella-like geometry. The orientation of the coordinate system used in all calculations reported in this work is shown in (a).

Despite the fact that the results reported in this paper indicate that the number of anomalous imaginary vibrational frequencies depends on the extent of linear dependence present in the basis set, the single anomalous imaginary frequency found for circumcircumcoronene at the B3LYP/6-31G(d) level of theory occurs within a basis set which is considered to be free from

linear dependence: The lowest eigenvalue of the basis set overlap matrix is reported as 1.15×10^{-5} which is well above the default GAUSSIAN09 threshold of 10^{-6} , and the calculation makes use of all 1488 basis functions. In fact, out of all GAUSSIAN09 calculations discussed in this paper, including those on the largest coronene that was studied, $C_{864}H_{72}$ (*vide infra*), eigenvalues of the basis set overlap matrix under 10^{-6} triggering discarding of the associated eigenvectors were found only in calculations carried out in basis sets containing diffuse functions, 6-31+G(d), 6-311+G(d), 6-311++G(d,p) and aug-cc-pVDZ, and in the TZP($\alpha_d = 0.6$) basis; all other basis sets were observed to be free from linear dependence (according to the GAUSSIAN09 default treatment), and yet calculations within some of these basis sets showed anomalous vibrational frequencies.

In circumcircumcircumcoronene ($C_{150}H_{30}$, $n = 5$) the number of imaginary vibrational frequencies at the B3LYP/6-31G(d) level of theory increases to three, b_{2g} and e_{2u} . HF/6-31G(d), as well as HF and B3LYP with the 6-31G and cc-pVDZ basis sets return only real vibrational frequencies. As for the preceding members of the coronene series, the two lowest real vibrational frequencies correspond to e_{2u} and a_{2u} normal modes. For $C_{150}H_{30}$ these range from 16.0 cm^{-1} (B3LYP/cc-pVDZ) to 17.8 cm^{-1} (HF/6-31G) for e_{2u} , and from 18.1 cm^{-1} (B3LYP/6-31G(d)) to 19.7 cm^{-1} (HF/6-31G) for a_{2u} . While flexibility continues to increase with coronene size, the gap between the two lowest normal mode frequencies becomes very small, and a_{2u} can be expected to become lower than e_{2u} in higher members of the coronene series.

The $n = 6$ coronene ($C_{216}H_{36}$) was studied at the same levels of theory as its two predecessors, $C_{150}H_{30}$ and $C_{96}H_{24}$: HF and B3LYP with the 6-31G, 6-31G(d) and cc-pVDZ basis sets. Similarly to $C_{96}H_{24}$ and $C_{150}H_{30}$, imaginary frequencies are obtained only in the B3LYP/6-31G(d) calculation; the number of these frequencies goes up to seven, b_{2g} , e_{2u} , e_{1g} , b_{2g} and a_{1u} . All HF calculations and B3LYP/6-31G(d) show the normal modes with the lowest real frequencies as a_{2u} followed by e_{2u} ; the corresponding ranges are 10.7 cm^{-1} (HF/6-31G(d)) to 12.2 cm^{-1} (HF/6-31G) for a_{2u} , and 11.8 cm^{-1} (B3LYP/6-31G(d)) to 13.3 cm^{-1} (HF/6-31G(d)) for e_{2u} . The frequency of the e_{2u} normal mode is still lower than that of a_{2u} for B3LYP with the 6-31G and cc-pVDZ basis sets, but the differences between the e_{2u} and a_{2u} frequencies are under 0.1 cm^{-1} .

The HF and B3LYP calculations for the $n = 7$ coronene ($C_{294}H_{42}$) were carried out with the 6-31G and 6-31G(d) basis sets. The number of imaginary frequencies in the B3LYP/6-

31G(d) calculation rises to twelve, b_{2g} , e_{2u} , e_{1g} , b_{2g} , a_{1u} , a_{2u} , e_{2u} and e_{1g} ; all vibrational frequencies obtained in the other three calculations are real. The lowest real vibrational frequency is associated with an a_{2u} normal mode, in the range 5.7 cm^{-1} (HF/6-31G(d)) to 7.6 cm^{-1} (B3LYP/6-31G(d)); the frequencies of the next e_{2u} normal mode are in the range 9.1 cm^{-1} (B3LYP/6-31G(d)) to 10.5 cm^{-1} (HF/6-31G(d)). Clearly, at this coronene size, corresponding to a central benzene ring surrounded by six concentric layers of fused benzene rings, the stabilization of the planar geometry coming from aromaticity and conjugation is all but gone, and the energy required to distort the molecule to an umbrella-like C_{6v} geometry is very low.

Due to the rapid increase in computational cost, it was decided to use just two levels of theory, HF/6-31G and B3LYP/6-31G, for the $n = 8$ –11 members of the coronene family ($C_{384}H_{48}$, $C_{486}H_{54}$, $C_{600}H_{60}$ and $C_{726}H_{66}$). Both levels yield only real vibrational frequencies for $C_{384}H_{48}$ ($n = 8$), the lowest of these corresponds to an a_{2u} normal mode, 4.0 cm^{-1} (HF/6-31G) and 5.5 cm^{-1} (B3LYP/6-31G).

Following the gradual decrease of the frequency associated with the lowest real a_{2u} normal mode observed in $n = 1$ –8 coronenes, for the $n = 9$ coronene ($C_{486}H_{54}$), at the HF/6-31G level of theory, this frequency becomes imaginary, $0.7i\text{ cm}^{-1}$. Thus, the HF/6-31G level of theory predicts that the $n = 9$ coronene ($C_{486}H_{54}$) is not planar, but prefers a very slightly bent umbrella-like C_{6v} geometry. At the B3LYP/6-31G level all $C_{486}H_{54}$ frequencies are obtained as real, and the lowest one, 3.8 cm^{-1} , corresponds to an a_{2u} normal mode.

In the $n = 10$ and $n = 11$ coronenes ($C_{600}H_{60}$ and $C_{726}H_{66}$) the tendency towards bending associated with the HF/6-31G a_{2u} normal mode becomes more pronounced, as its frequency changes to $2.8i$ and $3.2i\text{ cm}^{-1}$, respectively. The lowest normal modes at the B3LYP/6-31G level remain real, a_{2u} , with frequencies of 2.6 and 1.7 cm^{-1} , respectively. In contrast to the observed appearance of further anomalous imaginary frequencies with the increase of the coronene size, for example, for the $n = 4$ –7 coronenes at the B3LYP/6-31G(d) level of theory, the $n = 9$ –11 coronenes have just one HF/6-31G imaginary frequency each.

The levels of theory applied to the largest coronene studied in this paper, $C_{864}H_{72}$ ($n = 12$), were HF and B3LYP with the 6-31G and 4-31G basis sets. The reason for carrying out additional calculations with the smaller 4-31G basis set is that B3LYP/4-31G harmonic frequencies scaled by a single scale factor have been found [1,12] to be in excellent agreement

with experimental results about the mid-infrared fundamental frequencies of PAH molecules. At the HF/4-31G level, C₈₆₄H₅₄ shows a single imaginary frequency, $3.3i \text{ cm}^{-1}$ (a_{2u}), which is also present at the HF/6-31G level, at $3.2i \text{ cm}^{-1}$ (just slightly larger in magnitude than the corresponding frequency in the $n = 11$ coronene). However, at the HF/6-31G level, C₈₆₄H₅₄ has also a second imaginary frequency, $45.1i \text{ cm}^{-1}$ (a_{2g}). The a_{2g} imaginary normal mode suggests a tendency towards distortion in which planarity is preserved, but the point group of the molecule changes from D_{6h} to C_{6h} . The relatively large magnitude of the a_{2g} imaginary frequency and the fact that the a_{2g} normal mode with similar atomic displacements in the preceding $n = 11$ coronene (C₇₂₆H₆₆), at the same HF/6-31G level, corresponds to the 122nd vibrational frequency, 205.6 cm^{-1} , indicate that we are dealing with a hitherto unseen type of an anomalous imaginary normal mode. The lowest normal mode at the B3LYP/6-31G level, a_{2u} , experiences a further decrease to just 1.0 cm^{-1} , but remains real. At the B3LYP/4-31G level, C₈₆₄H₅₄ has a single imaginary frequency of a very low magnitude, $0.2i \text{ cm}^{-1}$ (a_{2u}), which marks the onset of a preference for a bent umbrella-like C_{6v} geometry.

In order to find out whether the imaginary frequencies reported in this paper (see Table A1 in the Appendix) could have been influenced by wavefunction instabilities leading to broken-symmetry wavefunctions, the closed-shell HF and B3LYP wavefunctions for selected coronenes exhibiting at least one imaginary frequency at the respective level of theory were subjected to stability analyses (see Table A2 in the Appendix). All of the investigated HF wavefunctions turned out to be singlet stable and triplet (non-singlet) unstable; all of the investigated B3LYP wavefunctions turned out to be both singlet and triplet stable. In agreement with the findings of Ref. 13, the closed-shell B3LYP wavefunctions were found to be more stable than their HF counterparts, both in the singlet and triplet stability problems. These results indicate that it is highly unlikely that the imaginary frequencies observed at various levels of theory for a number of $n = 2$ – 12 coronenes are related to wavefunction instabilities. The non-singlet instabilities of the investigated closed-shell HF wavefunctions imply the existence of unrestricted HF (UHF) solutions with lower energies; none of these UHF solutions are likely to be associated with possible distortions of the nuclear framework.

3. Conclusions

The *ab initio* and DFT theoretical studies of the vibrational frequencies of $n = 2-12$ coronenes ($C_{6n^2}H_{6n}$) presented in this paper show that, contrary to chemical intuition, which takes into account features such as full conjugation, delocalization and aromaticity, the extent of stabilization of the planar geometry rapidly decreases with the increase of the size of the molecule. At the HF/6-31G level of theory coronenes with $n \geq 9$ favour umbrella-like geometries and, most likely, this also happens around $n = 9$ at the HF/4-31G level. At the B3LYP/4-31G level, the switch to umbrella-like geometries occurs at $n = 12$. B3LYP/6-31G still supports a planar geometry even at $n = 12$, but the rate of decrease of the frequency of the lowest a_{2u} normal mode with n suggests that this frequency is very likely to become imaginary for one of the next few members of the coronene series. According to the theoretical results obtained in this paper, any sufficiently large single gas-phase coronene molecule should be nonplanar; the same applies to graphene, in which the preference for a nonplanar geometry should be even more pronounced.

When applied to coronenes, a number of *ab initio* and DFT levels of theory give anomalous imaginary frequencies, associated with normal modes leading to structures of lower symmetry. Surprisingly, this behaviour is observed even for B3LYP/6-31G(d), one of the most popular quantum chemical approaches, for coronenes with $n \geq 4$. As the current results show that the likelihood of getting these anomalous imaginary frequencies and their number increase with the size of the molecule, it is hardly an exaggeration to state that no *ab initio* or DFT quantum chemical approach can be considered “immune” when applied to a sufficiently large delocalized system. HF and DFT are certainly not “immune”, as considered previously [3], and it is doubtful that the “insidious two-electron intramolecular basis set incompleteness error” [3] is the only or even the main factor behind this pathological behaviour. In fact, there is close resemblance between the normal modes associated with anomalous imaginary frequencies obtained at different levels of theory, even for different coronenes: For example, the symmetries of the first twelve of the nineteen normal modes with imaginary frequencies obtained in the MP2/6-31G calculation on circumcoronene, b_{2g} , e_{2u} , e_{1g} , b_{2g} , a_{1u} , a_{2u} , e_{2u} , and e_{1g} , are exactly the same as those of the twelve normal modes with imaginary frequencies from the B3LYP/6-31G(d) calculation on the $n = 7$ coronene ($C_{294}H_{42}$); the patterns of the corresponding atomic displacements are also very similar.

While the problem of having anomalous imaginary frequencies in the MP2 calculations on coronene ($C_{24}H_{12}$) can be resolved by using the def2-TZVP or cc-pVTZ basis sets (as shown,

vide supra, the smaller def2-SVP and cc-pVDZ are not enough), this is not an option for larger molecules because of the huge computational cost. Local MP2 (LMP2) approaches [14] are often used to introduce correlation effects in calculations on extended systems; if these approaches are employed for the calculation of harmonic vibrational frequencies [15], in the presence of delocalization and with relatively small basis sets, they would suffer from the same pathological behaviour as canonical MP2. As all three imaginary frequencies obtained in an MP2/6-31G(d) calculation on coronene can be eliminated by a simple reduction of the exponent for d functions on carbons from 0.8 to 0.25, it is clear that there is a need to develop new, relatively small basis sets which would work reliably for delocalized extended systems in combination with the existing well-established *ab initio* and DFT approaches.

Appendix: Further computational details, frequency and wavefunction stability data

Further computational details. GAUSSIAN09 calculations: All geometry optimizations were carried out under the “VeryTight” convergence criteria. All DFT calculations made use of the “SuperFine” integration grid. All two-electron integrals larger than 10^{-12} were included in the calculations by setting “Acc2E=12”. All MP2 calculations were of the “MP2(Full)” type (including all electrons in the correlation treatment). Unless stated otherwise, the calculations made use of the default treatment of linear dependence in basis sets, in which the threshold for discarding eigenvectors of the basis set overlap matrix corresponding to small eigenvalues is set to 10^{-6} . If a different threshold was chosen, this threshold was used both in the geometry optimization and in the frequency calculation. NWCHEM and GAMESS-US calculations: These calculations were carried out without modifying any of the respective program defaults except for the choice of method and basis set.

Table A1. Lowest harmonic vibrational frequencies of the $C_{6n^2}H_{6n}$ ($n = 2-12$) coronenes. All imaginary (if any, in bold) and the two lowest real harmonic vibrational frequencies of the coronenes studied in this work, calculated at different levels of theory (cm^{-1}). The corresponding normal modes are labelled by the irreducible representations of the D_{6h} point group.

C ₂₄ H ₁₂ ($n = 2$)	Lowest harmonic vibrational frequencies
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HF/6-31G	98.9 e_{2u} , 141.3 a_{2u}
HF/6-31G(d)	96.5 e_{2u} , 137.5 a_{2u}
HF/cc-pVDZ	95.5 e_{2u} , 136.8 a_{2u}
HF/6-31+G(d)	95.3 e_{2u} , 135.5 a_{2u}
HF/6-311+G(d,p)	95.1 e_{2u} , 137.3 a_{2u}
HF/6-311++G(d,p)	95.0 e_{2u} , 136.5 a_{2u}
HF/TZP($\alpha_d = 0.6$) ¹	95.2 e_{2u} , 135.4 a_{2u}
HF/TZP($\alpha_d = 0.6$) ²	126.7i b_{2g} , 95.3 e_{2u} , 135.5 a_{2u}
B3LYP/6-31G	91.6 e_{2u} , 130.1 a_{2u}
B3LYP/6-31G(d)	89.8 e_{2u} , 129.8 a_{2u}
B3LYP/cc-pVDZ	89.0 e_{2u} , 129.5 a_{2u}
B3LYP/6-31+G(d)	88.4 e_{2u} , 127.4 a_{2u}
B3LYP/TZP($\alpha_d = 0.6$) ¹	87.3 e_{2u} , 124.7 a_{2u}
B3LYP/TZP($\alpha_d = 0.6$) ²	685.6i b_{2g} , 87.2 e_{2u} , 124.6 a_{2u}
B3LYP-D3/6-31+G(d)	85.9 e_{2u} , 123.0 a_{2u}
M06/6-31+G(d)	88.3 e_{2u} , 122.9 a_{2u}
M06-2X/6-31+G(d)	88.4 e_{2u} , 123.3 a_{2u}
MPW1B95/6-31+G(d)	429.0i b_{2g} , 87.6 e_{2u} , 126.1 a_{2u}
MPW1B95/6-311G(d)	87.5 e_{2u} , 126.9 a_{2u}
MPW1B95/6-311+G(d)	734.2i b_{2g} , 86.9 e_{2u} , 126.3 a_{2u}
MPW1B95/aug-cc-pVDZ	88.0 e_{2u} , 129.3 a_{2u}
MPWB1K/6-31+G(d)	442.0i b_{2g} , 89.2 e_{2u} , 127.7 a_{2u}
MPWB95/6-31+G(d)	354.7i b_{2g} , 83.3 e_{2u} , 122.4 a_{2u}
PW91B95/6-31+G(d)	360.3i b_{2g} , 83.6 e_{2u} , 122.1 a_{2u}
PW6B95/6-31+G(d) ³	364.8i b_{2g} , 93.7 e_{2u} , 135.7 a_{2u}
MP2/3-21G	1070.3i b_{2g} , 414.0i e_{2u} , 85.0 e_{2u} , 114.4 a_{2u}
MP2/6-31G	1894.3i b_{2g} , 1038.8i e_{2u} , 372.2i e_{1g} , 297.1i b_{2g} , 83.1 e_{2u} , 114.9 a_{2u}
MP2/6-31G(d)	1785.0i b_{2g} , 897.2i e_{2u} , 61.9 e_{1g} , 85.3 e_{2u} , 124.9 a_{2u}
MP2/6-31G(d, $\alpha_d = 0.25$)	90.9 e_{2u} , 137.5 a_{2u}
MP2/6-31G(d, $\alpha_d = 0.4$)	88.1 e_{2u} , 126.3 a_{2u}
MP2/6-31G(d, $\alpha_d = 0.5$)	756.7i b_{2g} , 86.9 e_{2u} , 126.9 a_{2u}

MP2/6-311G(d)	2727.8i b_{2g} , 1337.1i e_{2u} , 501.1i e_{1g} , 449.7i b_{2g} , 82.3 e_{2u} , 123.7 a_{2u}
MP2/6-311G(f)	6129.9i b_{2g} , 3386.2i e_{2u} , 1832.6i e_{1g} , 1675.6i b_{2g} , 1141.7i a_{2u} , 1134.2i e_{2u} , 951.6i a_{1u} , 693.1i e_{1g} , 346.6i e_{1g} , 256.2i e_{2u} , 159.6i b_{2g} , 37.3i a_{2u} , 59.3 e_{2u} , 99.1 b_{1g}
MP2/6-311G(df)	2983.4i b_{2g} , 1541.1i e_{2u} , 661.0i e_{1g} , 571.7i b_{2g} , 76.3 e_{2u} , 113.6 a_{2u}
MP2/6-311G(2df)	-27.4i b_{2g} , 86.8 e_{2u} , 125.6 a_{2u}
MP2/def2-SVP	1545.8i b_{2g} , 640.3i e_{2u} , 82.5 e_{2u} , 124.2 a_{2u}
MP2/cc-pVDZ	1547.5i b_{2g} , 631.1i e_{2u} , 85.5 e_{2u} , 124.3 a_{2u}
MP2/def2-TZVP ⁴	88.1 e_{2u} , 130.0 a_{2u}
MP2/cc-pVTZ	90.6 e_{2u} , 139.2 a_{2u}
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$C_{54}H_{18}$ ($n = 3$)	Lowest harmonic vibrational frequencies
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HF/6-31G	45.0 e_{2u} , 61.6 a_{2u}
HF/6-31G(d)	44.1 e_{2u} , 59.4 a_{2u}
HF/cc-pVDZ	43.5 e_{2u} , 59.3 a_{2u}
HF/6-31+G(d) ⁵	429.5i e_{2u} , 196.5i b_{2g} , 43.3 e_{2u} , 58.4 a_{2u}
HF/6-31+G(d) ⁶	3493.7i b_{2g} , 1716.5i e_{2u} , 552.0i e_{1g} , 452.1 b_{2g} , 43.1 e_{2u} , 58.0 a_{2u}
HF/6-31+G(d) ⁷	3494.0i b_{2g} , 1716.4i e_{2u} , 547.7i e_{1g} , 450.2i b_{2g} , 43.1 e_{2u} , 58.0 a_{2u}
HF/aug-cc-pVDZ	43.8 e_{2u} , 60.7 a_{2u}
B3LYP/6-31G	41.7 e_{2u} , 56.4 a_{2u}
B3LYP/6-31G(d)	40.8 e_{2u} , 56.3 a_{2u}
B3LYP/cc-pVDZ	40.4 e_{2u} , 56.3 a_{2u}
B3LYP/6-31+G(d)	689.8i e_{2u} , 514.8i b_{2g} , 39.9 e_{2u} , 55.0 a_{2u}
HF/aug-cc-pVDZ	40.0 e_{2u} , 54.5 a_{2u}
MP2/6-31G	3316.2i b_{2g} , 2367.5i e_{2u} , 1641.6i e_{1g} , 1568.5i b_{2g} , 1135.8i a_{1u} , 1045.9i a_{2u} , 1006.0i e_{2u} , 692.7i e_{1g} , 478.9i e_{1g} , 463.3i b_{2g} , 275.4i e_{2u} , 164.7i e_{2u} , 160.1i a_{2u} , 38.8 e_{2u} , 51.7 a_{2u}
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$C_{96}H_{24}$ ($n = 4$)	Lowest harmonic vibrational frequencies
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HF/6-31G	26.4 e_{2u} , 33.2 a_{2u}
HF/6-31G(d)	26.1 e_{2u} , 31.4 a_{2u}
HF/cc-pVDZ	25.7 e_{2u} , 31.5 a_{2u}

B3LYP/6-31G	24.4 e_{2u} , 30.5 a_{2u}
B3LYP/6-31G(d)	354.7i b_{2g} , 24.0 e_{2u} , 30.2 a_{2u}
B3LYP/cc-pVDZ	23.7 e_{2u} , 30.4 a_{2u}
C₁₅₀H₃₀ ($n = 5$)	Lowest harmonic vibrational frequencies
HF/6-31G	17.9 e_{2u} , 19.7 a_{2u}
HF/6-31G(d)	17.8 e_{2u} , 18.2 a_{2u}
HF/cc-pVDZ	17.5 e_{2u} , 18.3 a_{2u}
B3LYP/6-31G	16.3 e_{2u} , 18.4 a_{2u}
B3LYP/6-31G(d)	478.3i b_{2g} , 359.3i e_{2u} , 16.2 e_{2u} , 18.1 a_{2u}
B3LYP/cc-pVDZ	16.0 e_{2u} , 18.3 a_{2u}
C₂₁₆H₃₆ ($n = 6$)	Lowest harmonic vibrational frequencies
HF/6-31G	12.2 a_{2u} , 13.2 e_{2u}
HF/6-31G(d)	10.7 a_{2u} , 13.3 e_{2u}
HF/cc-pVDZ	10.9 a_{2u} , 13.0 e_{2u}
B3LYP/6-31G	11.9 e_{2u} , 11.9 a_{2u}
B3LYP/6-31G(d)	506.1i b_{2g} , 470.0i e_{2u} , 361.0i e_{1g} , 306.7i b_{2g} , 157.6i a_{1u} , 11.6 a_{2u} , 11.8 e_{2u}
B3LYP/cc-pVDZ	11.7 e_{2u} , 11.8 a_{2u}
C₂₉₄H₄₂ ($n = 7$)	Lowest harmonic vibrational frequencies
HF/6-31G	7.5 a_{2u} , 10.3 e_{2u}
HF/6-31G(d)	5.7 a_{2u} , 10.5 e_{2u}
B3LYP/6-31G	8.0 a_{2u} , 9.1 e_{2u}
B3LYP/6-31G(d)	509.3i b_{2g} , 505.2i e_{2u} , 459.5i e_{1g} , 420.7i b_{2g} , 380.4i a_{1u} , 346.8i a_{2u} , 296.5i e_{2u} , 195.8i e_{1g} , 7.6 a_{2u} , 9.1 e_{2u}
C₃₈₄H₄₈ ($n = 8$)	Lowest harmonic vibrational frequencies
HF/6-31G	4.1 a_{2u} , 8.4 e_{2u}
B3LYP/6-31G	5.5 a_{2u} , 7.3 e_{2u}
C₄₈₆H₅₄ ($n = 9$)	Lowest harmonic vibrational frequencies
HF/6-31G	0.7i a_{2u} , 7.0 e_{2u}
B3LYP/6-31G	3.8 a_{2u} , 6.0 e_{2u}
C₆₀₀H₆₀ ($n = 10$)	Lowest harmonic vibrational frequencies
HF/6-31G	2.8i a_{2u} , 6.0 e_{2u}
B3LYP/6-31G	2.6 a_{2u} , 5.0 e_{2u}

$C_{726}H_{66}$ ($n = 11$)	Lowest harmonic vibrational frequencies
HF/6-31G	3.2i a_{2u} , 5.2 e_{2u}
B3LYP/6-31G	1.7 a_{2u} , 4.3 e_{2u}
$C_{824}H_{72}$ ($n = 12$)	Lowest harmonic vibrational frequencies
HF/4-31G	3.3i a_{2u} , 4.6 e_{2u}
HF/6-31G	45.1i a_{2g} , 3.2i a_{2u} , 4.6 e_{2u}
B3LYP/4-31G	0.2i a_{2u} , 3.7 e_{2u}
B3LYP/6-31G	1.0 a_{2u} , 3.7 e_{2u}

¹ Default GAUSSIAN09 threshold for discarding near linearly dependent eigenvectors of the basis set overlap matrix, 10^{-6} ; 527 out of the 528 $C_{24}H_{12}$ TZP($\alpha_d = 0.6$) basis functions retained.

² Calculation utilizing all 528 TZP($\alpha_d = 0.6$) basis functions.

³ This calculation was carried out using NWCHEM [7].

⁴ Calculation utilizing all 816 def2-TZVP basis functions (the default GAUSSIAN09 threshold for discarding near linearly dependent eigenvectors of the basis set overlap matrix of 10^{-6} would eliminate one of these basis functions).

⁵ Default GAUSSIAN09 threshold for discarding near linearly dependent eigenvectors of the basis set overlap matrix, 10^{-6} ; 1000 out of the 1062 $C_{54}H_{18}$ 6-31+G(d) basis functions retained.

⁶ GAUSSIAN09 threshold for discarding near linearly dependent eigenvectors of the basis set overlap matrix decreased to the minimum allowed, 8×10^{-8} ; 1015 out of the 1062 $C_{54}H_{18}$ 6-31+G(d) basis functions retained.

⁷ GAMESS-US [11] calculation using the default treatment of near linearly dependent basis functions, 1011 out of the 1062 $C_{54}H_{18}$ 6-31+G(d) basis functions retained.

Table A2. Lowest eigenvalues of the singlet and triplet (non-singlet) wavefunction stability problems for selected coronenes at the respective optimized geometries.

Coronene	Level of theory	Singlet problem	Triplet problem
C ₂₄ H ₁₂ (<i>n</i> = 2)	HF/TZP($\alpha_d = 0.6$) ¹	0.1066	-0.0552
	B3LYP/TZP($\alpha_d = 0.6$) ¹	0.1111	0.0555
C ₅₄ H ₁₈ (<i>n</i> = 3)	HF/6-31+G(d) ²	0.0759	-0.0718
	B3LYP/6-31+G(d)	0.0763	0.0350
C ₉₆ H ₂₄ (<i>n</i> = 4)	B3LYP/6-31G(d)	0.0569	0.0212
C ₄₈₆ H ₅₄ (<i>n</i> = 9)	HF/6-31G	0.0256	-0.1156
C ₆₀₀ H ₆₀ (<i>n</i> = 10)	HF/6-31G	0.0196	-0.1223
C ₇₂₆ H ₆₆ (<i>n</i> = 11)	HF/6-31G	0.0123 ³	-0.1302
C ₈₂₄ H ₇₂ (<i>n</i> = 12)	HF/6-31G	0.0012 ³	-0.1395

¹ Calculation utilizing all 528 TZP($\alpha_d = 0.6$) basis functions.

² GAUSSIAN09 threshold for discarding near linearly dependent eigenvectors of the basis set overlap matrix decreased to the minimum allowed, 8×10^{-8} ; 1015 out of the 1062 C₅₄H₁₈ 6-31+G(d) basis functions retained.

³ These singlet stability analyses were carried out using GAUSSIAN09 Revision B.01. The corresponding calculations with GAUSSIAN09 Revision D.01 produced incorrect lowest eigenvalues of the singlet stability problems for C₇₂₆H₆₆ and C₈₂₄H₇₂, -5.5×10^3 and -7.4×10^3 , respectively, which are most likely due to numerical issues within the Davidson diagonalization.

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