Popular Theoretical Methods Predict Benzene and Arenes To Be Nonplanar

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Remarkably, ab initio computations on benzene (**1**) at electron-correlated MP2, MP3, CISD, and CCSD levels using a number of popular basis sets[1] give anomalous, nonplanar equilibrium structures. For example, planar (D_{6h}) benzene has at least one sizable imaginary vibrational frequency at MP2/6-311G ($723i$ cm^{-1}, b_{2g}), MP2/6-311++G ($1844i$ cm^{-1}, b_{2g}; $462i$ cm^{-1}, e_{2u}), MP3/6-31++G-(d,p) ($862i$ cm^{-1}, b_{2g}), CISD/6-311G ($190i$ cm^{-1}, b_{2g}), and CISD/6-311++G(d,p) ($511i$ cm^{-1}, b_{2g}). Similar unexpected results at the same levels of theory are found for other planar aromatic molecules: naphthalene (**2**), the cyclopentadienyl (**3**) and indenyl anions (**4**), the tropylium cation (**5**), anthracene (**6**), and pyridine (**7**) (Figure 1). In contrast, RHF, BLYP, and B3LYP computations[1] with the same basis sets exclusively yield real frequencies for **1**−**7**. Extensive frequency tabulations at numerous levels of theory are provided as Supporting Information. These anomalous results serve as stark warnings for black-box ab initio studies of aromatic hydrocarbons, particularly large, polycyclic species for which only limited basis sets are feasible.

Much previous research has compared the established experimental planar structure (D_{6h}) and vibrational frequencies of benzene, the aromatic prototype, to computational results from Møller−Plesset (MPn),[2−7] configuration interaction (CI),[6] coupled-cluster (CC),[8−10] and complete-active-space self-consistent-field (CASSCF)[11] wave functions (inter alia), as well as density functional theory (DFT).[4,12] Surprisingly, the wide-scale nonplanarity failures reported here have not been documented previously. Some years ago, it was established that correlated wave functions with limited basis sets often yield erroneously small (but real) vibrational frequencies for the low-lying trans-bending modes of acetylene, ethylene, benzene, and related molecules.[13−15] Subsequently, Martin, Taylor, and Lee[10] studied benzene at the CCSD(T) level with large spdf basis sets and found that two out-of-plane (OOP) bending frequencies, $\omega_4(b_{2g})$ and $\omega_5(b_{2g})$, exhibited "pathological basis set dependences due to basis set superposition error". Torii and co-workers[7] reported that the accuracy of computed MP2 frequencies for benzene, furan, thiophene, p-benzoquinone, and p-benzoquinodimethane depended strongly on carbon d function (α_d) exponents, especially for the normal modes with alternate OOP carbon motions. Goodman et al.[2] showed that the disparity between the experimental and MP2/6-311G(d,p) benzene OOP $\omega_4(b_{2g})$ frequency exceeded 30%. Dkhissi and co-workers[16] found that the corresponding pyridine frequency (b_1) was 228 cm^{-1} lower than the experimental value (745 cm^{-1}) at MP2/6-31++G(d,p). Lampert et al.[17] observed similar errors for phenol, benzaldehyde, and salicylaldehyde OOP modes. Nonetheless, gross failures in predicting *imaginary* OOP or linear bending frequencies for *semirigid* molecules using popular theoretical methods have not been reported, to our knowledge.
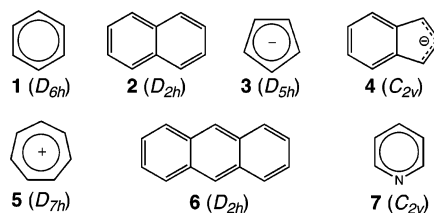

Figure 1. Arene nonplanarity failures of popular ab initio methods.

The spurious benzene imaginary vibrational frequencies principally correspond to out-of-plane D_{3d}-symmetric chair (b_{2g}) or C_{2v}-symmetric boat (e_{2u}) distortions. We have excluded several possible causes of these computational anomalies: (1) When stringent numerical precision requirements are imposed, the peculiar frequencies are reproducible, generally to ca. 1 cm^{-1}, with different computers, operating systems, and program packages.[18] (2) The anomalies are not due merely to deficiencies in MP2 theory but also can result with higher-order CC, CI, and MPn electron correlation methods. (3) Because the RHF reference wave functions for the correlated methods exhibit no *spatial* orbital instabilities in the immediate vicinity of the D_{6h} structure of benzene, the spurious vibrational frequencies are not attributable to nearby force constant singularities caused by electronic symmetry breaking.[19] (4) Since the imaginary-frequency modes can be followed smoothly to lower-energy minima, variational wave function collapse upon distortion from D_{6h} symmetry is not a problem. For example, the $1101i$ cm^{-1} b_{2g} mode at MP2/6-311+G leads smoothly to a D_{3d} minimum 0.56 kcal mol^{-1} lower in energy, with a 5.8° ring torsional angle and a 388 cm^{-1} (e_u) lowest frequency.

What is the origin of the benzene nonplanarity failures? Our analysis has focused on MP2 theory for convenience. Table 1 lists some basis sets (Group A) that yield imaginary OOP frequencies for planar benzene at the MP2 level, as well as similar basis sets (Group B) that give all real frequencies. Diffuse functions on hydrogen (++ augmentation) are problematic, but several variations of the 6-311G basis, including the often used 6-311+G(d,p), give imaginary frequencies without such spatially extended functions. In contrast, the traditional Dunning basis sets of DZ- or TZ-type,[20] and also those of correlation-consistent (cc) construction,[21] yield planar benzene in MP2 computations.

Benzene OOP distortions along the b_{2g} chair coordinate (τ) *increase* the Hartree−Fock (RHF) energy but make the MP2 electron correlation energy *more negative*. A D_{6h} imaginary frequency results when the MP2 contribution (which favors nonplanarity) is spuriously large and overcomes the RHF term (which favors planarity and usually dominates).

The MP2 correlation energy can be decomposed exactly into a sum over all pair energies (ϵ_{ij}) for correlating electrons in occupied orbitals i and j in the RHF reference wave function. The individual ϵ_{ij} quantities reveal that the predominant driving force for distortion

Table 1. Basis Set[a] Classification According to MP2 Out-of-Plane Vibrational Frequencies for D_{6h} Benzene

Group A: At Least One Imaginary Frequency			
3-21++G	6-31++G(d,p)	6-311+G(d,p)	[C(8s7p)/H(7s)]
3-21++G(d,p)	6-311G	6-311++G	
6-31++G	6-311+G	6-311++G(d)	[C(8s7p6d)/ H(7s6p)]
6-31++G(d)	6-311+G(d)	6-311++G(d,p)	
Group B: All Real Frequencies			
3-21G	6-31G	6-311G	DZVP(dft)
3-21G(d)	6-31G(d)	6-311G(d,p)	TZVP(dft)
3-21G(d,p)	6-31G(d,p)	DZ	cc-pVDZ
3-21+G	6-31+G	DZP	aug-cc-pVDZ
3-21+G(d)	6-31+G(d)	DZP+	cc-pVTZ
3-21+G(d,p)	6-31+G(d,p)	TZ	aug-cc-pVTZ

[a] Basis sets are specified in Supporting Information.

of benzene into D_{3d} symmetry with Group A basis sets is an artificially large, collective enhancement of the correlation energy between σ and π electrons. For example, among the 11 largest differences between MP2/6-311+G (Group A) and MP2/DZ (Group B) force constant components, $\epsilon_{ij}''(\tau)$, 10 involve $\sigma-\pi$ correlation, and in all these cases the push toward nonplanarity is strongest with 6-311+G, by a factor of 8 on average. Distorting from planarity improves the ability of the basis sets to recover $\sigma-\pi$ electron correlation, an artificial effect severe enough in Group A cases to overcome the usual π-MO preference for planarity due to electron delocalization.

We have employed a two-electron basis set incompleteness diagnostic,[22] evaluated using our integral codes for performing explicitly correlated R12 computations,[23] to document the nonplanarity phenomenon mathematically. As detailed in the Supporting Information, this diagnostic confirms that the anomalous benzene frequencies arise from an insidious intramolecular basis set incompleteness error (BSIE) that varies strongly with OOP geometric distortions, consistent with earlier observations.[10,15] Only correlated wave functions are susceptible to this two-electron BSIE. Both HF and DFT are immune because they are fundamentally one-electron theories.

The geometric sensitivity of the two-electron BSIE in benzene cannot be removed by saturating the basis set with sp valence orbitals and d polarization functions. We constructed expansive [C(8s7p)/H(7s)] and [C(8s7p6d)/H(7s6p)] basis sets comprising 216 and 504 atomic orbitals, respectively, by removing the higher angular momentum functions from the aug-cc-pV6Z set.[24] MP2 frequency computations on D_{6h} benzene were then executed with these basis sets to determine the sp and spd atomic-orbital limits. Amazingly, MP2/[C(8s7p)/H(7s)] gave five imaginary frequencies [$3632i$ (b_{2g}), $1706i$ (e_{2u}), $504i$ (e_{1g}) cm^{-1}], and MP2/[C(8s7p6d)/ H(7s6p)] retained one of these ($404i$ cm^{-1} for the b_{2g} chair mode). Hence, "MP2 benzene" is nonplanar in the sp and spd limits! No sp or spd basis can be claimed to yield a planar D_{6h} minimum at the MP2 level due to superior saturation and less absolute BSIE. Planar benzene is recovered in the complete basis set limit of MP2 theory, but successive sp, spd, spdf, ... atomic-orbital saturation is clearly a highly inefficient route to converge to this result.

Practical correlated computations for benzene (and arenes in general) must rely on minimizing the *differential* planar vs nonplanar two-electron BSIE. To balance such BSIEs, the basis set should not be rich in s, p, or even d functions if no higher angular momentum functions (particularly carbon f shells)[13] are present.

Otherwise, the nuclear framework may distort from planarity to mimic the effect of the missing higher polarization functions. This problem is not limited to arenes and may arise whenever there are multiply bonded moieties in carbon compounds.[13-15] The correlation-consistent (aug)-cc-pVnZ basis sets,[21] containing functions with all angular momentum values allowed for principal quantum number n, are fundamentally constructed to provide the necessary BSIE balance. Atomic natural orbital (ANO) basis sets, which minimize basis set superposition errors, are an even better choice in this regard.[10,15]

Supporting Information Available: Tables of vibrational frequencies, graphs of basis set incompleteness diagnostics, and complete citations for ref 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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