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Precise Equilibrium Structure of Benzene

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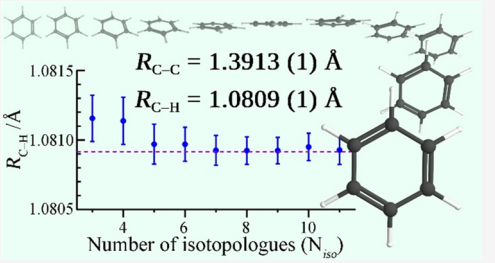
ABSTRACT: Recent advances in gas-phase structure determination afford outstanding agreement between the CCSD(T)/cc-pCVTZ-corrected semi-experimental (r_e^{SE}) equilibrium structures and their corresponding best theoretical estimates (BTEs) of the equilibrium structures (r_e) based upon corrections to the CCSD(T)/cc-pCV5Z geometries for the aromatic heterocycles pyrimidine and pyridazine. Herein, that same analysis is extended to the fundamental aromatic molecule benzene, using published experimental spectroscopic data for a total of 11 available isotopologues. The incorporation of rotational constants from all of these isotopologues and CCSD(T) corrections to address the impacts of both the vibration-rotation interaction and electron-mass distribution results in a highly precise and accurate r_e^{SE} structure. The CCSD(T)/cc-pCV5Z optimized geometry has been further corrected to address a finite basis set, untreated electron correlation, relativistic effects, and a breakdown of the Born−Oppenheimer approximation. This analysis achieves outstanding agreement between the r_e (BTE) and r_e^{SE} structural parameters of benzene to a highly satisfying level (0.0001 Å), an agreement that surpasses our recently published structures of the aforementioned nitrogen-substituted benzene analogues. The D_{6h} geometry of benzene is now known to an unprecedented precision: R_{C-C} = 1.3913 (1) Å and R_{C-H} = 1.0809 (1) Å. The mutual agreement between theory and experiment presented in this work validates both, substantially resolving all discrepancies between the r_e^{SE} and theoretical r_e structures available in the literature.



INTRODUCTION

The structure of benzene represents a foundational component of chemistry.[1] The deduction of the structure of benzene as a cyclic compound,[2] the establishment of equal carbon-carbon bond lengths, the understanding of reactivity (substitution *vs* addition), and the rationalization of the symmetrical D_{6h} structure in terms of quantum mechanics inexorably link the structure of benzene to aromaticity,[3] conjugation, resonance, and theories of structure and bonding, some of the most profound topics in the field of chemistry. Studies of benzene date from the earliest days of what is considered modern chemistry to the current day. Our own studies of the benzene molecule, described herein, which afford molecular structure parameters of exquisite precision, are prompted by the fundamental nature of the problem, a desire to investigate recent conclusions concerning various aspects of the structure of benzene,[4−6] and an analysis of factors that are relevant to the characterization of the molecule in space.

BACKGROUND

The determination of molecular structure by use of diffraction techniques on single-crystal substances is a powerful method that is widely utilized across a range of scientific disciplines. Less widely appreciated is the determination of molecular structure by measurement of high-resolution rotational spectroscopy. The rotational constants (reciprocal of the moments of inertia) are very sensitive to isotopic substitution, enabling the determination of the molecular structure for molecules in which a suitable number of isotopologues can be measured in the gas phase. The techniques are different and complementary. Structures determined using diffraction techniques (typically X-ray or neutron) may reflect the influence of crystal-packing forces. The effect of temperature, as evident in the thermal ellipsoids, may reduce the intrinsic precision of the structure determination. Structure determination by rotational spectroscopy requires that the molecule can be measured in the gas phase (which may require laser ablation or other methods for nonvolatile samples[7]) and that a sufficient number of isotopologues can be observed in natural abundance or prepared by synthetic methods. When applicable, rotational spectroscopy affords the true, gas-phase structure of the ground vibrational state of the molecule, and the precision of the determination can be exceptionally high.

Combining experimentally determined rotational constants and computationally derived corrections to the rotational constants has been shown to produce highly precise and accurate "semi-experimental" equilibrium structures (r_e^{SE}).[8−13]

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The experimentally observable rotational constants (B_0) differ from the equilibrium rotational constants (B_e) due primarily to the vibration-rotation interaction. Thus, the effective (r_0) or substitution (r_s) structures derived from the experimentally observable rotational constants are not directly comparable to computationally derived equilibrium structures (r_e) that represent the energy minimum on the potential energy surface.[14,15] The aforementioned semi-experimental equilibrium structures (r_e^{SE}), which are directly comparable, are obtainable from experimental rotational constants if corrections are applied for both the vibration-rotation interaction[8−10,16] and the electron-mass distribution[10,16,17] (eq 1).

$$B_e^{\beta} = B^{''\beta} + \frac{1}{2}\sum_i \alpha_i^{\beta} - \frac{m_e}{M_p} g^{\beta\beta} B^{\beta} \tag{1}$$

The r_e^{SE} structure of methane by Boggs and co-workers[18] is noteworthy in that it unambiguously determined the equilibrium geometry of a fundamental organic molecule and the quintessential $\sigma_{C(sp^3)}$−H bond distance. In the process of determining the methane r_e^{SE} structure, they established a method of correcting the effective or observable rotational constants with computed vibration-rotation interaction constants to obtain a mixed or semi-experimental structure. The motivation behind combining experimental and computed values is that the experimental B_0 constants can be determined with remarkable accuracy and precision and that the computational equilibrium geometry (r_e) and potential energy function are close enough to their real counterparts (particularly at presently practical levels of theory) that the small errors in the computed sums of the vibration-rotation interaction constants can be neglected. This assumption has proven useful to the structure determination of a variety of molecules, including the r_e^{SE} geometries of several prototypical organic molecules, *e.g.*, ethylene,[19] propene,[20] acetylene,[21,22] butadiene,[19] formaldehyde,[8] ketene,[23,24] phenyl radical,[16,25] and benzene.[26] These precise structures provide important benchmarks for the fundamental C−H bond distances and angles for sp-, sp^2-, and sp^3-hybridized carbon atoms.

Semi-experimental equilibrium structures using *ab initio* or density functional theory (DFT) methods have been determined for several aromatic species with five-membered (furan,[16,27,28] pyrrole,[16,27,28] imidazole,[27,28] pyrazole,[16,27,28] 1,3,4-oxadiazole,[29] thiophene,[16,27,28,30] thiazole,[31,32] 1*H*-1,2,4-triazole,[33] 1*H*- and 2*H*-1,2,3-triazoles,[34] isomeric thiadiazoles[31]) and six-membered (benzene,[16,26−28,35−37] phenyl radical,[16,25] pyridine,[16,27,28] pyridazine,[16,27,28,38,39] pyrimidine,[11,16,28,40] and *s*-triazine[41]) rings. The accuracy and precision of these r_e^{SE} structures are highly dependent on the quality of the experimental rotational constants, availability of rotational constants for isotopologues that substitute all atoms, the number of isotopologues relative to the number of structural parameters, the sophistication of the computational methods employed, and the application of corrections for both the vibration-rotation interaction and electron-mass distribution.

Recently, a new standard of agreement has been achieved between semi-experimental (r_e^{SE}) and computational (r_e) structures for several aromatic heterocycles.[30,32−34,39,40] In each of these works, experimental rotational constants have been obtained for isotopic substitutions of all atoms, with most atoms substituted multiple times across the set of isotopologues employed. The isotopologue data sets provide many more independent rotational constants than there are structural parameters, providing highly redundant structural information. The experimental rotational constants in all of these works were corrected (CCSD(T)/cc-pCVTZ) for both the vibration-rotation interaction and electron-mass distribution. In these aromatic heterocycles, the structural parameters are very precisely determined, with bond distances often established to a few ten-thousandths of an Angstrom and bond angles to a few hundredths of a degree. Compared to CCSD(T)/cc-pCV5Z structural parameters corrected for residual basis set and correlation effects, relativistic effects, and the breakdown of the Born−Oppenheimer approximation, most parameters (referred to as the "best theoretical estimate", BTE) are in quite satisfactory agreement with their corresponding r_e^{SE} values.

A few trends have begun to emerge from these collective works. First, for species containing hydrogen, carbon, and nitrogen,[33,34,39,40] the computed BTE parameters have usually been within the 2σ uncertainties of their semi-experimental values. This level of agreement cannot be achieved with CCSD(T)/cc-pCVQZ geometries and required the CCSD(T)/cc-pCV5Z optimized structures, along with the aforementioned corrections. Additionally, for some molecules, a set of isotopologues involving a single isotopic substitution of each atom is sufficient to achieve this level of agreement, but in other cases, larger sets of isotopologues are required. There is currently no clear method of determining *a priori* how many isotopologues are necessary for a particular structure determination. Furthermore, the incorporation of many isotopologues serves to confirm the accuracy of the structure and tends to reduce the experimental uncertainty of the parameters. Finally, as seen for thiophene[30] and thiazole,[32] when a heavy atom prevents the principal axes from rotating substantially upon isotopic substitution, the agreement between theory and experiment is reduced, in spite of the availability of a large set of isotopologues. For these sulfur-containing rings, only about half of the values for the computed parameters fall within the 2σ uncertainties of their semi-experimental values. The discrepancy between the theoretical and experimental geometries for these species has been attributed to the very close proximity of one or more atoms to a principal inertial axis. A related issue is that the large mass of sulfur prevents substantial rotation of the axes upon isotopic substitution, which might otherwise mitigate that proximity. Efforts are underway to determine comparable r_e^{SE} structures for several additional heteroaromatic and substituted aromatic compounds.

As the most important aromatic molecule, it would be difficult to overstate the significance of benzene to the entire chemistry community. Its structure has been established by multiple methods, including X-ray crystallography,[42−48] electron diffraction,[49−52] neutron diffraction,[45,53] Raman spectroscopy,[5,6,54] infrared,[16,26−28,35,36] and rotational spectroscopy.[37,55,56] X-ray crystallography determines a temperature-dependent molecular structure of benzene (r_α) where all of the molecules are in close contact and the structure is influenced by the intermolecular forces inherent in the solid phase. Electron and neutron diffraction determine a temperature-dependent molecular structure (r_g), where the parameters are based upon the mean relative nuclear positions. Rotational spectroscopy or methods that yield information about the rotational constants, such as rotationally resolved UV/vis, IR, and Raman spectroscopy, can be used to

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Table 1. Benzene Isotopologues: Molecular Symmetry, Experimental Rotational Constants, and Method of Observation

	symmetry	experimental method	A_0 (MHz)[a]	B_0 (MHz)	C_0 (MHz)
C_6H_6	D_{6h}	IR,[35,57] UV/vis[61−63]	5689.212 (9)[62,63]		
C_6H_5D	C_{2v}	microwave[55]	5689.144 (6)	5323.934 (6)	2749.674 (6)
o-$C_6H_4D_2$	C_{2v}	microwave[37,56]	5498.062 (4)[56]	5164.242 (4)	2662.496 (4)
m-$C_6H_4D_2$	C_{2v}	microwave[56]	5502.669 (7)	5152.057 (6)	2660.358 (6)
1,2,3-$C_6H_3D_3$	C_{2v}	microwave[37]	5168.017 (15)	5151.933 (6)	2579.579 (6)
o-$C_6H_2D_4$	C_{2v}	microwave[37]	5163.715 (6)	4846.814 (6)	2499.792 (3)
m-$C_6H_2D_4$	C_{2v}	microwave[37]	5151.99 (12)	4850.31 (12)	2497.90 (3)
C_6HD_5	C_{2v}	microwave[37]	4998.17 (15)	4707.22 (15)	2423.97 (6)
C_6D_6	D_{6h}	IR,[35] UV/vis[62]	4707.125 (6)[62]		
$^{13}C_6H_6$	D_{6h}	IR[35,58]	5337.92 (6)[58]		
$^{13}C_6D_6$	D_{6h}	IR[60]	4464.37 (24)		
$^{13}C^{12}C_5H_6$[b]	C_{2v}	IR[59]	5689.31	5568.17	2814.03
$^{13}C^{12}C_5H_6$[c]	C_{2v}	Raman[6]	5689.474 (18)	5568.473 (23)	2868.6 (73)
$^{13}C^{12}C_5D_6$[c]	C_{2v}	Raman[6]	4707.541 (36)	4624.188 (31)	2332.0 (16)

[a]Values and statistical uncertainties from the most recent reference. [b]The rotational constants from ref 59 were not determined directly and are thus not suitable for inclusion in a structure determination. [c]The statistical uncertainties of the rotational constants from ref 6 are relatively large, and the inertial defects deviate substantially from the other isotopologues. As a result, these isotopologues are not suitable for inclusion in a structure determination.

Table 2. Semi-experimental Equilibrium (r_e^{SE}), Diffraction (r_g), and Mass-Dependent (r_m) Structures of Benzene

	corrections to B_0	N_{iso}[a]	R_{C-C} (Å)[b]	R_{C-H} (Å)[b]
r_e^{SE} Plíva et al.[35]	vibration-rotation, molar mass	3	1.3893	1.0857
r_e^{SE} Gauss and Stanton;[26] see also Demaison et al.[36]	vibration-rotation, SDQ-MBPT(4)/cc-pVTZ	4	1.3914 (10)	1.0802 (20)
r_e^{SE} Piccardo et al.[27,28]	vibration-rotation and electron mass, B3LYP/SNSD	4	1.3919 (1)	1.0795 (1)
r_e^{SE} Penocchio et al.[16]	vibration-rotation and electron mass, B2PLYP/cc-pVTZ	4	1.3916 (1)	1.0799 (1)
r_e^{SE} Kunishige et al.[4,37]	vibration-rotation, molar mass	9	1.3892	1.0864
r_g (neutron, solid, −135 °C) Bacon et al.[53]			1.398	1.090
r_g (electron, gas) Kimura et al.[51]			1.3969 (30)	1.0845 (20)
$r_m^{(2L)}$ Heo et al.[5,6]		13	1.3921 (15)	1.0769 (76)
r_e^{SE} this work	vibration-rotation and electron mass, CCSD(T)/cc-pCVTZ	**11**[c]	**1.39134 (2)**	**1.08093 (10)**
r_e^{SE} this work (recommended)	vibration-rotation and electron mass, CCSD(T)/cc-pCVTZ	**11**[c]	**1.3913 (1)**	**1.0809 (1)**

[a]Number of isotopologues. [b]Statistical uncertainties for previous works are reported as available. The statistical uncertainty for the current work is reported at the 2σ level. [c]All previously available microwave transitions for asymmetric-top isotopologues[37,55,56] were refit (*vide infra*) to obtain more accurate rotational constants. Rotational constants from the more recent rotationally resolved UV/vis works were used for symmetric-top isotopologues when available.[62,63] Rotational constants from other symmetric-top isotopologues come from high-resolution infrared spectroscopy.[35,60]

determine the ground-state (r_0), substitution (r_s), mass-dependent (r_m), or semi-experimental equilibrium (r_e^{SE}) structures.

Accurate and precise semi-experimental equilibrium structure (r_e^{SE}) determination does, of course, require high-quality experimental rotational constants. Fortunately, in the case of benzene, such constants can be derived from three types of already published studies: rotationally resolved IR and UV/vis spectra of the four possible symmetric-top species (D_{6h}) or Fourier-transform microwave (FTMW) spectra of the partially deuteriated isotopologues (C_{2v}). These latter works overcame an important challenge for the spectroscopy of benzene. By virtue of their broken symmetry upon deuteriation, these isotopologues possess weak permanent dipole moments, making pure rotational spectroscopy possible, albeit very challenging.

As shown in Table 1, published rotational constants are available for 12 isotopologues of benzene, having been measured *via* IR[35,57−60] or UV/vis[61,62] spectroscopy for the symmetric tops (D_{6h}) and microwave spectroscopy for the asymmetric tops (C_{2v}).[37,55,56] The symmetric-top species have only a single independent rotational constant ($A_0 = B_0 \approx 2C_0$) that can be determined experimentally, thus only a single constant (A_0) is displayed for these species. The rotational constant of the normal isotopologue has been investigated thoroughly, first using IR by Plíva et al.[57] and then by several others using IR[59] or UV/vis.[61−63] The heavy-atom, D_{6h} isotopologues ($^{13}C_6H_6$,[35,58] C_6D_6,[35,62] and $^{13}C_6D_6$[60]) have been similarly investigated. By FTMW spectroscopy, Bauder and co-workers analyzed the pure rotational spectra of C_6H_5D and *ortho*- and *meta*-$C_6H_4D_2$ from purchased or synthesized samples.[55,56] By high-temperature H/D exchange of a mixture of C_6H_6 and C_6D_6, Kunishige et al.[37] were able to obtain rotational constants using FTMW for all seven C_{2v} symmetric species that possess a small permanent dipole moment. Earlier values of the rotational constants for $^{13}C^{12}C_5H_6$ were assumed based upon an r_0 structure and not determined directly,[59] thus they are not known to the same level of precision and accuracy as the other isotopologues. Recently, spectroscopic constants for five isotopologues were reported by Heo et al.,[5,6] including direct measurements of $^{13}C^{12}C_5H_6$ and $^{13}C^{12}C_5D_6$ for the first

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time,[64] using mass-selected, rotationally resolved Raman spectroscopy.

The modern history of the equilibrium structure of benzene began in 1990, when Plíva et al.[35] determined rotational constants by observing ν_{13} of C_6D_6 and ν_{12} of $^{13}C_6H_6$ *via* high-resolution infrared spectroscopy. Combining these rotational constants with the previously reported B_0 value for C_6H_6,[57] Plíva et al. determined (Table 2) the first r_e^{SE} with a quasi-empirical molar-mass correction for the vibration-rotation interaction based upon eq 2.

$$B_e^{\beta} = B''^{\beta} + 1.787 \times 10^{-3}\left(\frac{B_1''^{\beta}}{B_2''^{\beta}}\right)\sqrt{\left(\frac{M_1}{M_2}\right)} \quad (2)$$

This structure used a small set of isotopologues—those required for a single substitution of each unique atom. All three of these isotopologues have D_{6h} symmetry, and thus the three independent rotational constants are sufficient to determine the two structural parameters (R_{C-C} and R_{C-H}), statistically with one degree of freedom.

Gauss and Stanton[26] produced the first r_e^{SE} structure of benzene that incorporated computed vibration-rotation interaction corrections ($B_0 - B_e$) and rotational constants from an additional D_{6h} symmetric isotopologue, $^{13}C_6D_6$. The CCSD(T)/cc-pVQZ r_e structural parameters were within the statistical uncertainties of their r_e^{SE} values. The additional isotopologue increased the number of independent rotational constants used to determine the two structural parameters from three to four (two degrees of freedom). As shown in Table 2, the earlier structure[35] slightly underestimated the R_{C-C} distance and overestimated the R_{C-H} distance. The discrepancy between these first two r_e^{SE} structures arose, in part, because of the inadequate assumption used in the original r_e^{SE} that the vibration-rotation interaction scales with molar mass. The work of Stanton and Gauss was extended by Demaison et al.,[36] in conjunction with a study of how fluorination deforms the aromatic ring, leading to a new r_e^{SE} structure for benzene that included corrections to the rotational constants for the electron-mass distribution. This additional correction, obtained using a DFT method, did not have an impact on the structural parameters at their reported level of precision. In the intervening years, two additional r_e^{SE} structures[16,27,28] were determined using DFT methods to calculate not only the electron-mass corrections, but also the vibration-rotation interaction corrections. As has been demonstrated for other aromatic compounds, r_e^{SE} structures determined using the more expedient DFT methods display reasonable agreement with r_e^{SE} structures determined using higher-level CCSD(T) methods.[30,32,39,40]

The aforementioned r_e^{SE} structures only take advantage of the four symmetric-top benzene isotopologues. Kunishige et al.[37] determined a new r_e^{SE} structure using a combined data set of rotational constants from nine isotopologues by including data from previous works.[55,56,62,63] That work did not include the available rotational constants for $^{13}C_6H_6$ or $^{13}C_6D_6$.[35,58,60] By excluding the two [^{13}C]-isotopologues, no direct isotopic substitution of a carbon atom was included in this isotopologue data set. The rotational constant corrections employed used the same quasi-empirical molar-mass correction as Plíva et al., eq 2,[35] and thus it is unsurprising that the most recent structural determination is in close agreement with the geometry determined in that early work. The close agreement of the r_e^{SE} structures of Plíva et al. and Kunishige et al. does demonstrate though, that it is possible to obtain an adequate equilibrium structure without isotopic substitution of all atoms, if the available number of independent rotational constants substantially exceeds the number of parameters to be determined. The close clustering of the two types of semi-experimental equilibrium structures (those using quasi-empirical molar mass for $B_0 - B_e$ versus those using computed $B_0 - B_e$) highlights the importance of exactly how the vibration-rotation interaction correction is obtained.

Recent works by Heo et al.[5,6] demonstrated that a direct fit of the available rotational data to a set of isotope-dependent r_0 structures is not feasible due to an insufficient number of independent moments of inertia to determine the structural parameters. In the process, they cast doubt on the previous report of a lack of isotope effect on the C−H and C−D bond distances[4] and attribute the observation to an artifact of an undetermined fit. The $r_m^{(2L)}$ structure presented in that work is determined using mass-dependent corrections to the moments of inertia (I_0 constants) to approximate an equilibrium (r_e) structure. Due to the selection rules in the rotational Raman spectroscopic data from Heo et al., neither the value of C_0 nor the inertial defect are meaningfully determined. Thus, the structure they obtained is negatively impacted by the inclusion of two isotopologues with poor rotational constant determination ($^{13}C^{12}C_5H_6$ and $^{13}C^{12}C_5D_6$).[6] The inertial defects of the benzene isotopologues will be discussed later in this work.

COMPUTATIONAL METHODS

The methods employed in this work are the same as those used in recent r_e^{SE} structure determinations of several aromatic heterocycles (pyrimidine,[40] pyridazine,[39] thiophene,[30] thiazole,[32] 1*H*-1,2,4-triazole,[33] 1*H*- and 2*H*-1,2,3-triazoles[34]), to allow for the most meaningful comparisons between molecules with the aim of achieving satisfactory agreement between r_e^{SE} and BTE structures. All CCSD(T) calculations[65,66] in this work were performed using CFOUR.[67] Geometry optimizations were performed at the CCSD(T) level with the cc-pCV*X*Z basis set where *X* = *T*, *Q*, and 5.[68,69] The structure computed at CCSD(T)/cc-pCVTZ was subsequently used for a second-order vibrational perturbation (VPT2) anharmonic frequency calculation by evaluating the cubic force constants using analytical second derivatives at displaced points.[70−72] The VPT2 calculation was used to obtain anharmonic frequencies for each isotopologue and provide vibration-rotation interaction corrections ($B_0 - B_e$), along with quartic centrifugal distortion terms, (in both the A and S reductions, III^r representation). Although sextic centrifugal distortion constants were computed, they were not included in the newly obtained least-squares fits of the C_{2v} isotopologues. The impact of the sextic centrifugal distortion constants is expected to be negligible at the *J* and K_a ranges observed. Electron-mass contributions to the observable rotational constants were determined at CCSD(T)/cc-pCVTZ via a rotational *g*-tensor calculation for each isotopologue (eq 1).[10,16,17] Four additional computational corrections to the CCSD(T)/cc-pCV5Z structure are used to determine the best theoretical structure:

1. Residual basis set effects beyond cc-pCV5Z.[73,74]
2. Residual electron correlation effects beyond the CCSD(T) treatment.[75−78]
3. Effects of scalar (mass-velocity and Darwin) relativistic effects.[79−81]
4. The diagonal Born−Oppenheimer correction (DBOC), calculated for the normal isotopic species, C_6H_6 (*vide infra*).[82,83]

Details regarding the calculation of these corrections are provided in the Supporting Information.

These corrections were performed using the method described in detail in previous works.[30,32−34,39,40] The effects of electron

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Table 3. Spectroscopic Constants for Benzene Asymmetric-Top Isotopologues Determined in the Current Analysis and Used in the r_e^{SE} Structure Determination of Benzene (S-Reduced Hamiltonian, III^r Representation)[a]

	C_6H_5D	o-$C_6H_4D_2$	m-$C_6H_4D_2$	1,2,3-$C_6H_3D_3$
A_0 (MHz)	5689.1388 (78)	5498.0596 (36)	5502.6763 (68)	5168.014 (14)
B_0 (MHz)	5323.9345 (75)	5164.2423 (32)	5152.0624 (67)	5151.939 (44)
C_0 (MHz)	2749.7028 (71)	2662.4989 (27)	2660.3604 (66)	2579.5784 (56)
D_J (kHz)	[1.116]	[1.0189]	[1.0176]	[0.930]
D_{JK} (kHz)	−1.850 (58)	−1.723 (30)	−1.694 (10)	[−1.549]
D_K (kHz)	[0.837]	[0.762]	[0.760]	[0.697]
d_1 (kHz)	−0.0430 (21)	−0.0366 (10)	−0.03590 (98)	[−0.00130]
d_2 (kHz)	[−0.0109]	[0.00772]	[0.00744]	[−0.000131]
N_{lines}[b]	20	21	20	6
σ_{fit} (MHz)	0.042	0.026	0.029	0.034
	o-$C_6H_2D_4$	m-$C_6H_2D_4$	C_6HD_5	
A_0 (MHz)	5163.7209 (41)	5151.8302 (70)	4998.2780 (54)	
B_0 (MHz)	4846.829 (12)	4850.2708 (66)	4707.3430 (49)	
C_0 (MHz)	2499.7901 (16)	2497.91678 (65)	2423.93450 (87)	
D_J (kHz)	[0.853]	[0.852]	[0.782]	
D_{JK} (kHz)	[−1.414]	[−1.413]	[−1.295]	
D_K (kHz)	[0.633]	[0.633]	[0.579]	
d_1 (kHz)	[−0.0314]	[−0.0301]	[−0.0265]	
d_2 (kHz)	[−0.00773]	[−0.00773]	[0.00553]	
N_{lines}[b]	6	4	4	
σ_{fit} (MHz)	0.010	0.001	0.003	

[a]Values in square brackets held fixed at the CCSD(T)/cc-pCVTZ predicted value in the least-squares fit. [b]Number of independent transitions.

correlation were also explored in somewhat greater detail.[76] The *xrefit* module of CFOUR was utilized to obtain the semi-experimental r_e^{SE} structure by least-squares fitting all of the isotopologue equilibrium moments of inertia determined from the input rotational constants and the vibration-rotation interaction and electron-mass corrections. A recently described script, *xrefiteration*,[39] was used to investigate the impact of incorporating each isotopologue beyond those in the original isotopologue set used by Plíva et al.[35] The script selects the next isotopologue to incorporate into the data set based upon its ability to most lower the statistical uncertainties of the parameters. *Xrefiteration* continues adding isotopologues with the greatest lowering of the uncertainties until all isotopologues are incorporated into the r_e^{SE} structure.

RESULTS AND DISCUSSION

Structure Determination. To determine the most precise and accurate semi-experimental structure possible and to achieve the desired consistency with our previous works, the microwave frequency data of the asymmetric-top isotopologues were reanalyzed to produce slightly improved rotational constants. Where sufficient numbers of transitions were not available to satisfactorily determine quartic centrifugal distortion constants, their values were held constant at their CCSD(T)/cc-pCVTZ values. Holding these constants at their computed values, as opposed to omitting them, provides more physically meaningful values of the rotational constants, which is critical for structure determination. Each set of transitions was least-squares fit using Kisiel's ASFIT program,[84−87] using both an A- and S-reduced Hamiltonians in the III^r representation. Output files for all least-squares fits are available in the Supporting Information. The rotational constants from each least-squares fit were converted to the determinable constants (B'') using eqs S1−S6,[88] removing the impact of centrifugal distortion from the rotational constant. For all species, all of the determinable constants from the A and S reductions agreed to within 0.008 MHz, with most agreeing to 0.001 MHz, indicating that both reduced Hamiltonians were adequately modeling the data set. In a fashion consistent with previous works,[30,32,39,40] B'' constants were converted to their corresponding moments of inertia and used in the structure determination. The newly determined S reduction, III^r representation spectroscopic constants are presented in Table 3 for each asymmetric-top isotopologue.[64] The A reduction, III^r representation spectroscopic constants, all computed quartic centrifugal distortion constants, and all determinable constants are provided in the Supporting Information.

Corrections to each rotational constant were applied as described by eq 1. Computed $B_0 - B_e$ and $B'' - B_e$ vibration-rotation interaction corrections were applied to the symmetric-top and asymmetric-top species, respectively. Each of the rotational constants was also corrected for the electron-mass distribution at the same level of theory. The quality of the rotational constants and their corrections can be seen in the inertial defects (Δ_i) for the C_{2v} isotopologues used in the current r_e^{SE} determination, provided in Table 4. For a planar, asymmetric-top molecule, the vibration-rotation interaction and electron-mass corrections result in an inertial defect closer to the ideal value of zero for the equilibrium inertial defect (Δ_{ie}).[30,32,39,40] The four symmetric-top benzene isotopologues used in these studies, which possess only one independent rotational constant, do not allow for an experimental evaluation of the quality of the corrections, since determination of the other rotational constants presupposes an inertial defect of zero. These inertial defects for the asymmetric-top isotopologues display the same trends as observed for pyridazine[39] and pyrimidine,[40] where the uncorrected inertial defects ($\Delta_{i\,0}$) are *ca.* 0.030 uÅ^2 for each isotopologue. After accounting for the vibration-rotation interaction, the inertial defects ($\Delta_{i\,e}$) are overcorrected and reduced to an average value of −0.011 uÅ^2. Further correction for the electron-mass distribution reduces the inertial defects ($\Delta_{i\,e}$) to an average value of 0.0018 uÅ^2,

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Table 4. Inertial Defects (Δ_i) of Benzene Isotopologues Used in the Current r_e^{SE} Structure Determination

isotopologue	$\Delta_{i\,0}$ (uÅ^2)[b]	$\Delta_{i\,e}$ (uÅ^2)[b,c]	$\Delta_{i\,e}$ (uÅ^2)[b,d]
C_6H_6[a]			
C_6H_5D	0.036 0	−0.009 56	0.002 95
o-$C_6H_4D_2$	0.033 0	−0.010 27	0.002 24
m-$C_6H_4D_2$	0.031 4	−0.011 97	0.000 55
1,2,3-$C_6H_3D_3$	0.030 7	−0.010 35	0.002 17
o-$C_6H_2D_4$	0.027 5	−0.011 05	0.002 10
m-$C_6H_2D_4$	0.027 2	−0.011 45	0.001 06
C_6HD_5	0.025 0	−0.011 13	0.001 39
C_6D_6[a]			
$^{13}C_6H_6$[a]			
$^{13}C_6D_6$[a]			
average ($\bar{x}$)	0.0301	−0.0108	0.0018
std. dev. (s)	0.0038	0.0008	0.0008

[a]For a symmetric top, $A'' = B'' \approx 2C''$. The IR analyses assume that $\Delta_{i0} = 0$, when reporting B and C, *i.e.*, $B'' = 2C''$. Thus, no inertial defect values are provided for these species. [b]Inertial defect ($\Delta_i = I_c - I_a - I_b$). [c]Inertial defect using B_e with vibration-rotation interaction corrections only. [d]Inertial defect using B_e with vibration-rotation interaction and electron-mass corrections.

which is a factor of 17 smaller than the uncorrected ($\Delta_{i\,0}$) values. The magnitudes of the fully corrected inertial defects ($\Delta_{i\,e}$) are similar in absolute value to those of other aromatic species treated in a similar fashion,[30,32,39,40] giving further confidence in the experimentally determined rotational constants and theoretical corrections. The rotational constants for all isotopologues appear to be quite adequately determined, despite the very limited transition data sets available for some isotopologues.

With the corrected rotational constants, a highly precise and accurate semi-experimental equilibrium structure is determined by least-squares fitting all available rotational constants.[89,90] For benzene, this allows for a highly redundant determination of two structural parameters from a total of 18 independent moments of inertia (16 degrees of freedom), 4 from the symmetric-top isotopologues, and 14 from the seven asymmetric-top isotopologues. Both structural parameters (R_{C-C} and R_{C-H}, Figure 1, Table 2) are thus highly overdetermined, and their values have very small statistical uncertainties—more than an order of magnitude smaller than those of pyridazine[39] and pyrimidine.[40] The value of R_{C-C} determined in this work is 1.391 34 (2) Å and that of R_{C-H} is 1.080 93 (10) Å.

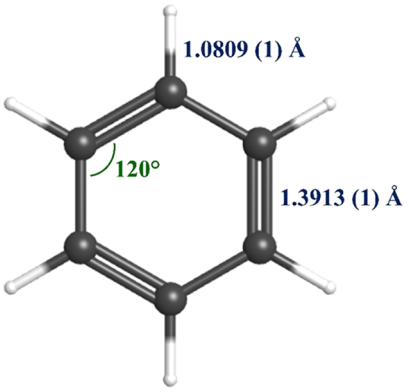

Figure 1. Benzene (D_{6h}) semi-experimental (r_e^{SE}) structure from 11 isotopologues. Bond angles of 120° are a consequence of D_{6h} symmetry and are consistent with the observed spectroscopic characteristics of a symmetric top molecule.

While the statistical error obtained in the fitting process might suggest that the semi-experimental equilibrium structure for benzene obtained here is accurate to a few hundred thousandths of an Angstrom (10^{-5} Å), there is a systematic error inherent in our method that shows that such a conclusion may be illusory. This argument centers on an issue that is almost universally, and safely, ignored in structure determination, but which must eventually be considered as one tries for higher and higher precision. Specifically, while the equilibrium structure defined by the minimum of the potential energy surface is the same for all isotopologues within the clamped-nucleus Born−Oppenheimer approximation, the first-order correction obtained by averaging the nuclear kinetic energy operator over the electronic wavefunction (the DBOC, often called the adiabatic correction) leads to a mass-dependent potential energy surface. Fortunately, the magnitude of this effect is so small (of order $10^{-4} - 10^{-5}$ Å) as to be entirely negligible with respect to the vibrationally induced mass-dependent effects that impact all determinations based on ground-state rotational constants. Even for most equilibrium structure determinations, these changes can be ignored, as bond lengths are typically determined to *ca.* 0.001 Å in such studies. In light of recent works that have produced r_e^{SE} structures that have extended this accuracy by almost an additional order of magnitude, however, it is worthwhile to consider the mass-dependence of the equilibrium structure that arises from the DBOC and its consequences in such highly precise structure determinations.[91] The present example provides an excellent case about which to frame such a discussion.

Most important in the above context are geometrical parameters involving light atoms, and a simple calculation (SCF with the cc-pCVTZ basis set) reveals that the C−H bonds in C_6H_6 are about 0.000 07 Å longer than the C−D bonds in C_6D_6. While one can certainly carry out higher-level calculations to estimate the magnitude of this difference, the present value provides an adequate basis for establishing an order-of-magnitude estimate for the magnitude of this effect. A crude method of estimating its impact on structure determination (which has not previously been done, to the best of our knowledge) is to do the following:

1. Assume that all C−D bonds found in isotopically substituted benzenes are 0.000 07 Å shorter than the corresponding C−H bonds, and further assume that the rest of the structural parameters remain the same. That is, the local symmetry of the carbon framework in all isotopologues is taken as D_{6h} with equal C−C distances, and all C−H (C−D) bonds point radially away from the center of the C_6 framework.
2. Carry out a least-squares adjustment of the corresponding geometrical parameters to best fit the semi-experimental equilibrium rotational constants.

When this procedure is followed, the C−H distance obtained from the refinement is 0.000 16 Å longer than in the standard r_e^{SE} determination that assumes an isotopically independent structure. Meanwhile, the refined C−C distance also changes, but by just −0.000 02 Å; the opposing signs of the bond length changes are such that the effects on the

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moments of inertia largely cancel, as is required to again obtain the optimal least-squares structural solution. While further analysis and discussion of this result is certainly possible, we will restrict attention here to its most important consequence. Using the result above, the resulting equilibrium C−C and C−H bond lengths of benzene go from the standard r_e^{SE} values of 1.391 34 and 1.080 93 Å, respectively, to 1.391 32 and 1.081 09 Å. Thus, the latter results are likely "better", but apply to C_6H_6 only, and indeed challenge the entire meaning of "the equilibrium structure of benzene" that is featured in the title of this paper. When one goes beyond the standard isotopically invariant notion of equilibrium structure, it is no longer possible to talk about the equilibrium structure of a particular molecule, but only that of a specific isotopic species. It is unclear to us that there is much to be gained from engaging in such a pursuit. More important is that the present analysis reveals that the magnitude of the systematic error owing to neglect of this effect is probably no more than about 0.000 2 Å for any C−H distance, and considerably less for all bond distances involving nonhydrogen atoms. The effect of another systematic deficiency of the approach—the assumption that the vibrational corrections to rotational constants are adequately treated by second-order vibrational perturbation theory—remains, but its magnitude is unknown. The outstanding agreement between the r_e^{SE} structure and the high-level theoretical structure (the BTE), however, is such that the magnitude of this effect is likely to be similar to or smaller than that of the mass-dependence discussed here. Taken as a whole, the discussion above suggests that extreme care must be exercised in analyzing derived r_e^{SE} structures beyond the fourth decimal place (in Å), no matter the quality of the data and vibrational and electronic corrections used to obtain them, as the residual systematic errors arising from the effects described above are also of this magnitude.

In conclusion, the recommended "equilibrium structure for benzene" is a flat, planar molecule, with R_{C-C} = 1.391 3 (1) Å and R_{C-H} = 1.080 9 (1) Å, with both (quite conservative) error bars attributed in large part to systematic deficiencies of the r_e^{SE} arising from neglect of the mass-dependent adiabatic correction. It is rather unlikely that this result can be bettered, so the present determination of the structure of benzene should be regarded as definitive.

Analysis of Structural Data. The agreement between the semi-experimental structure (r_e^{SE}) and the computed/theoretical structures changes only slightly upon comparison with the CCSD(T)/cc-pCV5Z structure *vs* the best theoretical estimate (BTE) (Table 5). In other words, the sum of the four corrections used to determine the BTE [ΔR(best)] is small. The individual corrections, however, would have a much larger effect. In this case, there is a significant cancellation of the basis set [ΔR(basis)] and relativistic [ΔR(rel)] corrections by the correlation [ΔR(corr)] and diagonal Born−Oppenheimer [ΔR(DBOC)] corrections, resulting in the small overall [ΔR(best)] corrections. Unlike the previous works on aromatic heterocycles,[30,32−34,39,40] the BTE structure is not in better (or worse) agreement than the CCSD(T)/cc-pCV5Z r_e structure with the r_e^{SE} structure. A graphical summary of the final BTE and r_e^{SE} structures as compared to the previously published benzene r_e^{SE} structures is provided in Figure 2. It is apparent that the r_e^{SE} structures[35,37] determined by quasi-empirical molar-mass adjustments to B_0 are not in good agreement with the r_e^{SE} structures determined using computed vibration-rotation interaction corrections (with or without electron-mass corrections). The molar-mass adjusted r_e^{SE} structure parameters[35,37] underestimate the R_{C-C} distance and overestimate the R_{C-H} distance. While the vibration-rotation interaction is indeed a mass-dependent correction, isotopologues of the same mass do not have the same corrections to each rotational constant. For example, the corrections to A_0, B_0, and C_0 at the CCSD(T) level are 40.48, 36.94, and 19.93 MHz for *o*-$C_6H_4D_2$, while the same corrections are 40.58, 36.77, and 19.91 MHz for *m*-$C_6H_4D_2$. As shown by the differences in the r_e^{SE} structures, these small differences in the adjustments to the rotational constants have a substantial impact on the resulting $\Delta_{i\,e}$ and r_e^{SE} structural parameters.

Table 5. Comparison of Experimental and Computed Structural Parameters, alongside Corrections (ΔR) Used to Obtain the Best Theoretical Estimate

	R_{C-C} (Å)	R_{C-H} (Å)
CCSD(T)/cc-pCVTZ	1.394 43	1.082 07
CCSD(T)/cc-pCVQZ	1.391 82	1.081 13
CCSD(T)/cc-pCV5Z	**1.391 22**	**1.080 89**
ΔR(basis)	−0.000 18	−0.000 08
ΔR(corr)	0.000 61	0.000 09
ΔR(rel)	−0.000 24	−0.000 11
ΔR(DBOC)[a]	0.000 02	0.000 13
ΔR(best)	0.000 21	0.000 02
r_e BTE	**1.391 43**	**1.080 91**
r_e^{SE}	**1.391 34 (2)**	**1.080 93 (10)**
r_e^{SE} (recommended)	**1.391 3 (1)**	**1.080 9 (1)**

[a]The DBOC refers to the normal isotopologue of benzene (C_6H_6).

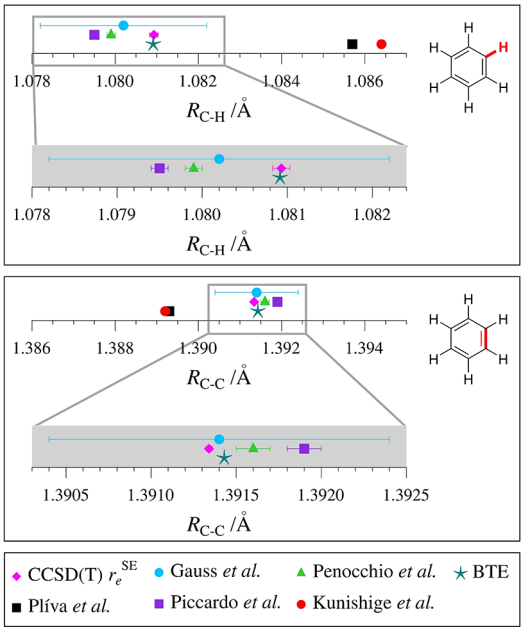

Figure 2. Graphical comparison of the benzene structural parameters with bond distances in Ångstrom (Å). Uncertainties shown for current, CCSD(T) r_e^{SE} are 2σ, while those for structures from Plíva et al.,[35] Gauss and Stanton,[26] Piccardo et al.,[27,28] Penocchio et al.,[16] and Kunishige et al.[37] are as reported in the respective works. Plots immediately left of molecular structure images share the same *x*-axis scale and, in many cases, the uncertainty bars cannot be discerned because they fall beneath the symbol. Even in the expanded sections (gray bands), the uncertainty bars for the CCSD(T) r_e^{SE} value for R_{C-C} cannot be discerned because they fall beneath the symbol.

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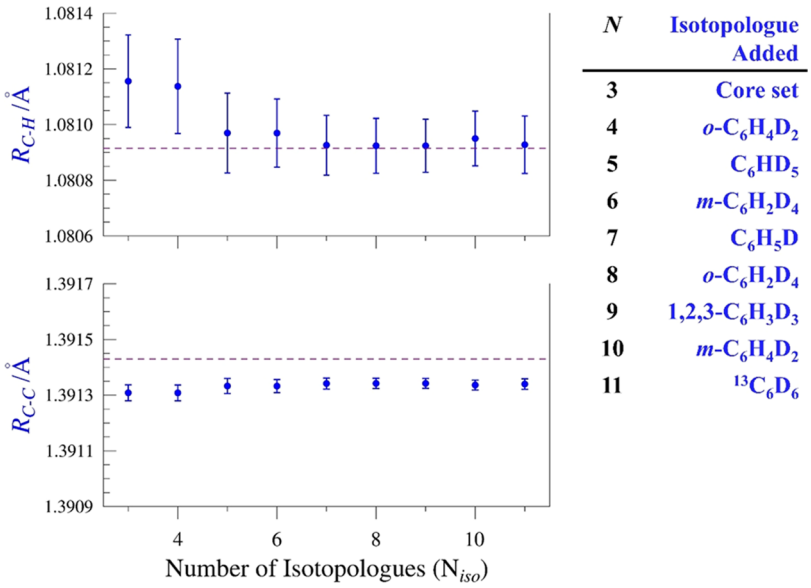

Figure 3. Plots of the benzene structural parameters as a function of the number of isotopologues (N_{iso}) and their 2σ uncertainties with consistent scales for both bond distances.

The substantially larger statistical uncertainty from the CCSD(T) r_e^{SE} of Gauss and Stanton compared to this work is due to the lack of inclusion of the electron-mass correction.[26] While the electron-mass correction has a small impact on the structural parameters, it has a major impact on their statistical uncertainties because an exactly planar model cannot exactly fit rotational constants with a nonzero inertial defect. It is also clear from Figure 2 that the DFT r_e^{SE} structures are quite good,[16,27,28] but systematically overestimate the R_{C-C} and underestimate the R_{C-H} distances. While the discrepancies are opposite those from the quexeasi-empirical, molar-mass corrected r_e^{SE} structures, an important principle is highlighted: these structural parameters are not entirely independent in benzene, due to its D_{6h} symmetry. Each of the R_{C-C} distances is one side of an equilateral triangle with the opposite vertex at the center of symmetry. Indeed, the way the *z*-matrix was written for the computational and structure determination input files in this work, the distance from the center to each C-atom was the optimized parameter rather than R_{C-C} directly. An error in the determination of the carbon-atom location impacts both the center-to-carbon distance and the R_{C-H} distance. Therefore, an alternate *z*-matrix was written to determine the distance of each H atom from the center of the molecule to determine the molecular radius, which was found to be 2.472 27 (8) Å. The molecular radius of the fully theoretical BTE geometry falls narrowly within the 2σ value of r_e^{SE} with an overestimation of 0.000 08 Å. Each of the r_e^{SE} structures using quasi-empirical molar-mass corrections to the rotational constants[35,37] overestimate the total size of the molecule, in addition to underestimating the R_{C-C} parameter. In contrast, the DFT r_e^{SE} structures estimate the total size of the molecule very well; the overestimation of the R_{C-C} and underestimation of the R_{C-H} distances cancel out. Thus, the source of the error in the DFT r_e^{SE} parameters is mostly due to location of the carbon atoms in the ring. Despite this, the overall success of the DFT r_e^{SE} structures[16,27,28] showcases the importance of actually computationally correcting the B_0 values, even at lower levels of theory. This is highly relevant to larger molecules or molecules containing larger atoms, where a CCSD(T)/cc-pCV5Z optimization and a CCSD(T)/cc-pCVTZ anharmonic frequency calculation may not be feasible.

As recently described,[39] the *xrefiteration* program provides insight into how each isotopologue impacts the overall structural fit and each structural parameter. The *xrefiteration* analysis was performed for the benzene structure determination, choosing the original set of three isotopologues (C_6H_6, C_6D_6, and $^{13}C_6H_6$) used by Plíva et al.[35] as the core set of isotopologues. Then, each isotopologue was sequentially added to the structural determination to assess the changes on the statistical uncertainties and parameter values. At each step of the routine, the isotopologue that provided the largest reduction to the statistical uncertainty of the structural parameters was chosen as the next isotopologue to be included. While three isotopologues are more than sufficient to determine the two structural parameters of benzene, it is clear that additional isotopologues provide important structural information to refine the parameters. Possibly the most important observation in Figure 3 is the near-convergence of the structure that occurs when two additional isotopologues (*o*-$C_6H_4D_2$ and C_6HD_5) are added to the structure determination. As the remaining six isotopologues (*m*-$C_6H_2D_4$, C_6H_5D, *o*-$C_6H_2D_4$, 1,2,3-$C_6H_3D_3$, *m*-$C_6H_4D_2$, and $^{13}C_6D_6$) are incorporated into the fit, it appears that the structure is well-converged and that these isotopologues only offer minor refinements to the structure and statistical uncertainties of the parameters.

Although all BTE parameters for pyridazine[39] and pyrimidine[40] fall within the 2σ statistical uncertainties of their corresponding r_e^{SE} parameters, this is not the case for the R_{C-C} distance in benzene. We believe this is due to its extremely small statistical uncertainty (0.000 02 Å). In contrast, the smallest statistical uncertainties of the best-determined R_{C-C} distances for pyridazine and pyrimidine are 0.000 75 and 0.000 45 Å, respectively. We believe that it is unreasonable to expect that any presently available theoretical method could achieve accuracy within 0.000 02 Å. (The discrepancy for benzene between the computed and r_e^{SE} R_{C-C}

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is only 0.000 10 Å, which is well within the analogous statistical uncertainty of 0.000 45 Å for pyridazine.) We also cannot exclude the possibility that there are small systematic errors in the r_e^{SE} structure, outside the estimation of the statistical error limits (2σ). For benzene, the ratio of determined r_e^{SE} parameters to independent moments of inertia is 2:14, compared to the 11:36 for pyridazine and 9:32 for pyrimidine. As there is no reason to assume that the theoretical treatments or experimental methods work better for benzene than pyridazine or pyrimidine, the very small statistical uncertainty and discrepancy (r_e^{SE} − BTE) observed for benzene are likely due to its D_{6h} symmetry, resulting in the existence of only two structural parameters.

Isotopologues and Radioastronomy. Using the r_e^{SE} determined in the current work, the rotational constants can be predicted very well for the $^{13}C^{12}C_5H_6$ isotopologue that were not able to be determined directly or not well determined in previous works.[6,59] As such, those values were not suitable for use in the r_e^{SE} determination in this work and are likely not useful for astronomical searches. With an accurate and precise r_e^{SE} structure determined from the 11 well-measured isotopologues now available, the rotational constants can be predicted with higher confidence. Using the B_e values for each isotopologue, the r_e^{SE}-predicted B_0 values can be obtained by applying reverse vibration-rotation interaction and electron-mass corrections. The resulting r_e^{SE}-predicted A_0, B_0, and C_0 values for all 13 isotopologues are available in the Supporting Information. The discrepancy between the experimentally determined and r_e^{SE}-predicted B_0 values is between 2−130 kHz for all of the species involved in the structure determination. We suggest that the best approach to estimating the frequencies of the microwave spectrum with currently available information is to use the rotational constants derived from the rotationally resolved Raman spectroscopy values for A_0 and B_0 with a C_0 value obtained from the computed inertial defect, which are quite consistent across the isotopologues for which they have been measured. Combined with the computed centrifugal distortion constants in this work, our conservative estimate suggests that the microwave transitions for $^{13}C^{12}C_5H_6$ can be predicted to within 1 MHz using the described rotational constants (A_0 = 5689.49 MHz, B_0 = 5568.44 MHz, and C_0 = 2813.58 MHz). This estimate is quite consistent with the corresponding one directly obtained from our r_e^{SE} structure as described earlier (A_0 = 5689.49 MHz, B_0 = 5568.40 MHz, and C_0 = 2813.58 MHz). These predictions of the $^{13}C^{12}C_5H_6$ rotational spectra can support future laboratory spectroscopy or radioastronomical search for this species.

In considering the potential of seeking benzene isotopologues with a permanent dipole moment in the ISM, it is necessary to examine the size of the permanent dipole moments and estimated abundances of species of interest. The column density of benzene in CRL 618 was estimated to be 5×10^{15} cm^{-2},[92] and the ratio of ^{12}C to ^{13}C in this region has been estimated as 11.6[93] or ≥32.[94] Using these two estimates and the 6-fold increase in abundance due to symmetry, $^{13}C^{12}C_5H_6$ may have a column density of up to 2.6×10^{15} cm^{-2}, or 9.4×10^{14} cm^{-2} by a more conservative estimate. Either of these column densities is quite respectable and higher than those estimated of other, similar molecules that have been detected in the ISM: benzonitrile (4.0×10^{11} cm^{-2}),[95] cyclopropenylidene (up to 5.0×10^{12} cm^{-2}),[96] cyclopentadiene (1.2×10^{13} cm^{-2}),[97] indene (1.6×10^{13} cm^{-2}),[97] and *o*-benzyne (5.0×10^{11} cm^{-2}).[98] To the detriment of the benzene isotopologue, its predicted dipole moment (CCSD(T)/cc-pCVTZ) is a mere 0.001 D. By contrast, those of benzonitrile (4.52 D),[99] cyclopropenylidene (3.43 D),[100] cyclopentadiene (0.416 D),[101] indene (0.62 D),[102] and *o*-benzyne (computed 1.38 D)[103] are all much larger. All else being equal, transitions of even cyclopentadiene would be 1.7×10^5 times more intense when accounting for the dipole moment-squared proportionality of transition intensity. Unfortunately, even the higher estimate of ^{13}C abundance in CRL 618 would predict the proportion of $^{13}C^{12}C_5H_6$ to cyclopentadiene (detected in TMC-1) to be only 2.2×10^2, 3 orders of magnitude lower than the proportion of cyclopentadiene:$^{13}C^{12}C_5H_6$ transition intensities. Even the most favorable predicted relative abundance ($^{13}C^{12}C_5H_6$ in CRL 618 to benzonitrile in TMC-1) is 6.5×10^3 and even smaller relative to the benzonitrile:$^{13}C^{12}C_5H_6$ transition intensity ratio (2.0×10^7). Since the signal-to-noise ratios of transitions currently used for detection of the aforementioned molecules are not several orders of magnitude, the mono-^{13}C-substituted isotopologue of benzene may be beyond the sensitivity of current radiotelescopes. Nevertheless, as technology improves, accurate spectroscopic constants will always be necessary for molecular detection.

CONCLUSIONS

Recent advances in methodology for gas-phase molecular structure determination establish that semi-experimental structures from a well-analyzed, broad set of isotopologues and using CCSD(T) corrections to the observable rotational constants is the preferred methodology of structure determination. For benzene, a minimum of five isotopologues, with a total of seven independent rotational constants, was required to determine a well-converged r_e^{SE}. Without knowing *a priori* which isotopologues will be most important or how many will be needed to converge an r_e^{SE} structure, the best practice clearly remains that high-quality rotational data for all available isotopologues should be incorporated into the structure determination. The structural parameters from the complete r_e^{SE} were determined to extraordinary precision with the bond lengths determined to 0.000 02 and 0.000 10 Å for R_{C-C} and R_{C-H}, respectively. The parameters of the BTE r_e are not in complete agreement with the r_e^{SE} structure, but this is not a cause for concern due to the very small deviation (0.000 1 Å). This deviation may represent the limit of the agreement that is possible between r_e^{SE} and computed r_e structures or an underestimation of the statistical uncertainty of this r_e^{SE} parameter. The r_e^{SE} structure determined in this study is sufficiently accurate that the rotational constants from previously unobserved isotopologues can be predicted with confidence for use in laboratory spectroscopy and radioastronomy.

Discussions of the structures of aromatic compounds tend to use benzene as a point of comparison for the R_{C-C} and R_{C-H} distances. The corresponding differences in bond distances are viewed as a reflection of the effect of various substituents on the ring or heteroatoms in the ring. The unambiguous quality of this r_e^{SE} structure allows these comparisons to be made such that virtually all of the uncertainty comes from the other aromatic species. Additionally, as the r_e^{SE} structure measures an unperturbed free molecule in the gas phase, this structure serves to gauge the magnitude of the lattice effects observed in solid-state structure determinations. For example, neutron diffraction r_g parameters of Bacon et al.[53] at −135 °C were

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1.398 and 1.090 Å for R_{C-C} and R_{C-H} distances, respectively. These thermally corrected and averaged values are quite different than the precise gas phase values, providing insight into their experimental precision, the differences between r_g and r_e^{SE} structures, and effects these molecules experience in the solid phase. Similarly, the difference between the gas-phase electron diffraction r_g parameters of Kimura et al.[51] and the r_e^{SE} values of this work can be used to assess the experimental precision of that work, as well as the differences between an r_g structure, based upon the average nuclear position, and an r_e^{SE} structure, based upon the equilibrium location of the atoms.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c03109.

Equations for calculating determinable constants and BTE corrections, spectroscopic constants (A reduction), determinable constants, computed quartic distortion constants, and the r_e^{SE}-predicted B_0 values (PDF)

Computational output files, output files from *xrefit* and *xrefiteration* routines (ZIP)

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Notes

The authors declare no competing financial interest.

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