Molecular Structure

DOI: 10.1002/anie.201409896

An Accurate Molecular Structure of Phenyl, the Simplest Aryl Radical**

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Abstract: *The phenyl radical ($C_6H_5^{\bullet}$) is the prototypical σ-type aryl radical and one of the most common aromatic building blocks for larger ring molecules. Using a combination of rotational spectroscopy of singly substituted isotopic species and vibrational corrections calculated theoretically, an extremely accurate molecular structure has been determined. Relative to benzene, the phenyl radical has a substantially larger C-C_{ipso}-C bond angle [125.8(3)° vs. 120°], and a shorter distance [2.713(3) Å vs. 2.783(2) Å] between the ipso and para carbon atoms.*

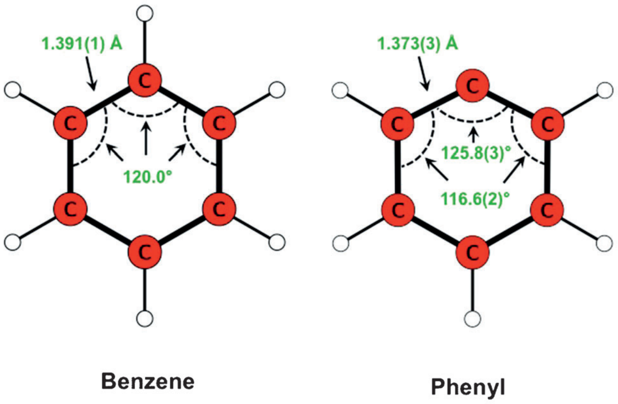

Figure 1. Side-by-side comparison of the structures of benzene[14] and the phenyl radical (r_e^{SE}, see Table 1). Bond lengths are in Å, and angles are in degrees. Parenthetical values are 1σ uncertainties in units of the last digit. The C–H bond lengths of phenyl [either 1.081(2) Å or 1.082(3) Å] and benzene [1.080(2) Å] are essentially identical.

The phenyl radical ($C_6H_5^{\bullet}$) is a highly reactive species formed by the homolytic cleavage of a C–H bond in benzene (Figure 1), the prototypical aromatic compound.[1] It is one of the most common aromatic radicals, and plays a central role in many reactions, ranging from astronomy[2] to combustion[3] and biochemistry.[4] As the simplest aryl radical, it also serves as the benchmark for computational investigations of larger, open-shell ring molecules.[5] The reactivity of aryl radicals is due to the localization of the unpaired electron in a σ-type orbital at the C–H cleavage site, as indicated by the very high C–H bond dissociation energy of benzene (465 ± 3 kJ mol^{-1}).[6] Despite the fundamental importance of $C_6H_5^{\bullet}$, its structure has never been experimentally determined.

Because phenyl and larger aryl radicals are crucial reactive intermediates in many different chemical processes, a detailed understanding of their properties is a key component in the development of predictive and meaningful chemical models. In combustion, for example, these models make predictions about fuel efficiency and can be used to minimize negative environmental and health impacts arising from polycyclic aromatic hydrocarbon and soot formation.[7] Because reactivity is closely linked to the various properties of the unpaired electron, it is important that theoretical methods describe the radical site accurately. Owing to effects such as electron correlation and spin contamination, σ-type aromatic radicals pose one of the more difficult challenges for quantum chemistry. In this context, the phenyl radical is an ideal benchmark for theory, allowing the accuracy of computed properties to be assessed, so that larger aryl radicals can then be predicted with confidence. Essentially the full gamut of theoretical approaches has been employed to predict the structure and properties of $C_6H_5^{\bullet}$, including Hartree–Fock, Møller–Plesset perturbation theory (MP2), CASSCF, coupled cluster, and density functional methods.[4,7,8]

The phenyl radical has a planar geometry, a $^2A_1$ ground electronic state, and C_{2v} symmetry. It has been extensively studied in the condensed phase;[9] in the gas phase, its

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[**] The experimental work in Cambridge was supported by the NSF, grant number CHE-1058063. The theoretical studies were supported by the Robert A. Welch Foundation (grant F-1283) of Houston, Texas, and the US Department of Energy, Office of Basic Energy Sciences (contract DE-FG02-07ER15884). K.N.C. was supported by a CfA Postdoctoral Fellowship from the Smithsonian Astrophysical Observatory. We thank E. S. Palmer for technical assistance, and G. B. Ellison, D. J. Nesbitt, and C. Puzzarini for helpful discussions.

Supporting information for this article (including additional details of experimental and theoretical methods, tables of measured lines, derived spectroscopic constants, and vibrational corrections) is available on the WWW under http://dx.doi.org/10.1002/anie.201409896.

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infrared, visible, and ultraviolet spectra have been measured.[10] Because phenyl is an asymmetric rotor possessing a nonzero dipole moment (0.87 D)[5] along its intermediate principal (b) inertial axis, and its A and B rotational constants are similar in magnitude, its rotational spectrum is very close to that of an oblate symmetric top. At high spectral resolution its lowest-J transitions consist of many closely spaced features, owing to the interaction of the unpaired electron with both molecular rotation and the magnetic moments of the five protons. Much of this structure collapses with increasing frequency, however, and the millimeter-wave band becomes an ideal spectral window to observe this radical in which R-branch transitions, appearing every $2C$ (~5.9 GHz), are well-described by a small number of spectroscopic constants. Using this approach the rotational spectra of normal and perdeutero-phenyl radical have been previously reported.[11]

Since rotational lines of both C_6H_5 and C_6D_5 are observed with high signal-to-noise ratio in a low-pressure electrical discharge using benzene (or perdeutero-benzene) as a precursor, and isotopic samples enriched in single ^{13}C (i.e., $^{13}CC_5H_6$) and ^2H (i.e., C_6H_5D) are commercially available, searches for its rare isotopologues have now been undertaken. Millimeter-wave spectra of the seven unique, singly substituted isotopic species have been measured to high accuracy: the *ortho*-, *meta*-, and *para*-isotopic species of C_6H_4D and $^{13}CC_5H_5$, in addition to *ipso*-$^{13}CC_5H_5$. In total, at least three R-branch series, consisting of 28 to 91 K-components, were observed between 157 and 272 GHz for each isotopic species.

A typical experimental spectrum along with simulated and best-fit stick spectra is shown in Figure 2 for *ortho*-C_6H_4D. To deconvolve the closely spaced line pattern from the instrument response function, a second derivative of a Lorentzian line shape (required to remove $1/f$ noise) was used to fit individual K-components. Measured frequencies determined in this way are very accurate (to better than 1 ppm), and are given in Tables S1–S9 (Supporting Information, SI) for normal and isotopic phenyl. Spectroscopic constants, derived using a standard asymmetric-top Hamiltonian, are summarized in Tables S10 and S11. With the exception of the *ipso*-^{13}C isotopic species, the structure of each R-branch series is dominated by four constants: the three rotational constants (A, B, and C) and one spin-rotation tensor (ε_{cc}) element. For *ipso*-$^{13}CC_5H_5$, an additional constant, the Fermi contact hyperfine $b_F(^{13}C)$ term, was also required to reproduce the spectra. In this fit $b_F(^{13}C)$ was constrained to the value derived from the ESR spectra ($A_{iso} = 129$ G),[9] because the root-mean-square (rms) of the fit is largely insensitive to the value of this constant at the high rotational quantum numbers J measured here. The experimentally derived (vibrationally averaged) inertial defects ($\Delta_0 = I_C - I_B - I_A$) for the seven new isotopic species are close in magnitude to one another and to that found for normal phenyl, a qualitative indication that the spectral assignments are correct; all are slightly positive (ranging from 0.0352 to 0.0474 $u\text{Å}^2$) owing to zero-point vibrational effects.

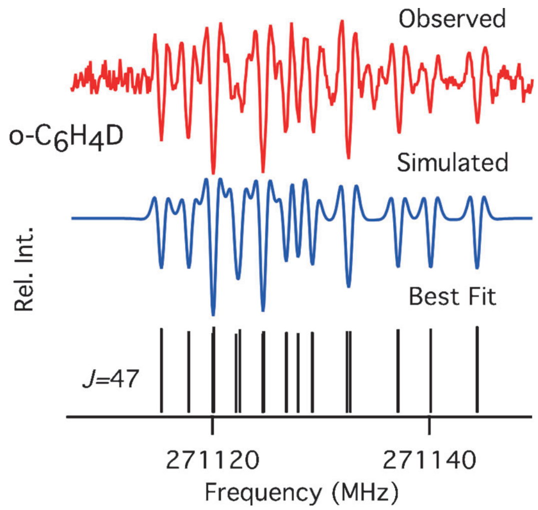

Figure 2. Observed and calculated millimeter-wave spectrum of *ortho*-C_6H_4D near 270 GHz. The stick spectrum is derived from the best-fit constants in Table S10; convoluting this spectrum with the instrument response function yields the simulated spectrum. The observed spectrum is the result of 20 min of integration.

To determine a semi-experimental molecular structure (r_e^{SE}), the measured rotational constants of normal phenyl, C_6D_5, and the seven singly substituted isotopic species were corrected for the effects of zero-point vibrational motion and electronic contributions using second-order perturbation theory.[12] These corrections have been calculated at the CCSD(T) level of theory with an atomic natural orbital basis set in the frozen core approximation; they have been applied (Table S12) to the experimental constants using the expression $B_e^{SE} = B_0 + \Delta B_0$ to yield semi-experimental equilibrium rotational constants (Table S12); similar equations apply for A_e^{SE} and C_e^{SE}. Inertial defects derived from these vibrationally and electronically corrected constants are also quite uniform and smaller by more than an order of magnitude (the largest nonzero value is now only 0.0035 $u\text{Å}^2$, but most are closer to 0.001 $u\text{Å}^2$), confirming that the level of the electronic structure method used and second-order vibrational perturbation theory adequately treats the vibrational and electronic structure of this radical, and that the radical has a planar equilibrium geometry.

Using a standard nonlinear least squares fitting procedure,[13] the ten unique structural parameters (four bond angles and six bond lengths) were then optimized to simultaneously reproduce the C_e^{SE} rotational constants of all nine isotopic species, as well as the A_e^{SE} rotational constants of the three C_6H_4D isotopic species, C_6D_5 and C_6H_5. This combination of constants was chosen because the C rotational constant can be determined extremely precisely for a nearly oblate top, whereas the A constants are most accurately known for the deuterated and normal species, owing to their higher signal-to-noise ratio spectra. The structure derived in this manner is summarized in Table 1 (and Table S13), and is very accurate; the bond lengths are determined to ±3 mÅ or better, and the bond angles are known to better than ±0.4° degrees. The r_e^{SE} structure reproduces the nine C_e^{SE} constants of isotopic phenyl to better than ±0.02 MHz, and the five A_e^{SE} constants to better than ±0.55 MHz.

In Figure 1 the r_e^{SE} structure of phenyl compared to that of benzene is shown.[14] Although the r(CH) bond lengths in

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Table 1: Structural parameters of phenyl derived from the semi-experimental approach described here and two ab initio methods. Bond lengths are given in Å and angles are in degrees. Parenthetical values are 1σ uncertainties in units of the last digit.

Parameter	r_e^{SE}	CCSD(T)/ cc-CVQZ	CCSD(T)/ CBS + CV + aug[5]
$r(C_iC_o)$	1.373(3)	1.3741	1.3693
$r(C_oC_m)$	1.398(3)	1.3993	1.3947
$r(C_mC_p)$	1.393(3)	1.3926	1.3882
$r(C_oH)$	1.081(2)	1.0806	1.0811
$r(C_mH)$	1.081(2)	1.0817	1.0822
$r(C_pH)$	1.082(3)	1.0808	1.0812
$\theta(C_oC_iC_o)$	125.8(3)	125.74	125.78
$\theta(C_iC_oC_m)$	116.6(2)	116.61	116.56
$\theta(HC_oC_i)$	122.4(3)	122.35	122.44
$\theta(HC_mC_o)$	119.8(3)	119.66	119.56

both molecules are not significantly different, it is clear that C−H bond cleavage of benzene to form the radical results in a substantial increase of the heavy atom bond angle (~6°) at the radical site. This change in the bond angle leads to a commensurate decrease of ~0.02 Å in the two C_i-C_o bond lengths. These structural changes are consistent with a partial rehybridization of the *ipso* carbon atom from a pure sp^2 character in benzene to one now containing some degree of sp character in the radical. A similar behavior is observed in monosubstituted benzene molecules.[15] Although the deformation of the benzene ring is somewhat less than that derived here, these studies find that the *ipso* angle [that is, $\theta(C_oC_iC_o)$] is sensitive to the σ-inductive effect of the substituent. For fluorobenzene,[15] the net increase in the *ipso* angle (+2.6°) occurs because fluorine withdraws charge from the 2p electron of the *ipso* carbon, resulting in some sp hybridization at this atom.

Simple concepts from physical organic chemistry can be used to rationalize the structure of the phenyl radical. Although perhaps an oversimplified model, prior to bond scission, the bonding at each carbon atom of benzene is very similar to that of the CH_3 radical in its ground state, in which the bond angles are 120°.[16] C−H cleavage of CH_3 results in either a ground-state biradical, whose two unpaired electrons remain in separate orbitals (H-C-H angle $133.93\pm0.06°$),[17] or an excited state in which the electrons are singlet-coupled in one orbital ($102.4\pm0.4°$).[18] Because the out-of-plane electron in benzene is part of the aromatic sextet, however, it remains delocalized upon bond scission to form phenyl, and, like the $:CH_2$ biradical, the in-plane electron occupies a σ-type orbital. The heavy atom angle at the radical carbon of phenyl therefore increases relative to benzene, but due to the geometric constraint of the ring, it attains a value (125.8°) somewhat less than the analogous H-C-H angle in the $:CH_2$ biradical. Owing to effects of hyperconjugation, the same bond angle is even larger (~150°) in the phenyl cation.[19]

In conjunction with the new experimental studies, high-level coupled cluster calculations of the equilibrium structure of the phenyl radical were also performed. These calculations employ large one-particle basis sets, and include corrections for relatively high levels of electron correlation. The ab initio structure calculated at our highest level of theory, CCSD(T)/cc-pCVQZ, is given in Table 1, and agrees well with the r_e^{SE} structure; differences between the two are within 1σ of the experimental uncertainties for all but one parameter. Of course, for a molecule such as phenyl, a very high-level ab initio calculation such as this is expensive and becomes increasingly more so (at an alarming rate) as the size of the molecule grows. However, to get an equilibrium structure "right" with theory is not an easy task: one generally has to treat core correlation explicitly (as is done here), include triple excitations and use very large one-particle basis sets.

For example, the all-electron CCSD(T)/cc-pCVQZ optimization done here required a few weeks of computer time, whereas the evaluation of the vibrational corrections at a much lower level of theory was accomplished in a day. Hence, it is clear that the mixed procedure done here, in which experimental results are actually the central and most important quantities, and a lower level of theory suffices to determine the rather small but vital vibrational contribution to the rotational constants, is certainly the approach of choice for all but rather small molecules. As truly meaningful detailed structural comparisons should always be based on equilibrium structures, such an approach is immensely valuable.

There are a number of molecules of paramount importance to organic chemistry, and whose fundamental properties are therefore significant and enduring issues. Among these, of course, are benzene and the phenyl radical, and the accurate equilibrium structures of both have now been obtained by combining powerful techniques of modern spectroscopy and theory. Having both structures at hand allows them to be meaningfully compared and analyzed, and used as a benchmark for other structural analyses and comparisons of vital hydrocarbon species.

Received: October 9, 2014
Published online: December 17, 2014

Keywords: ab initio calculations · molecular structure · rotational spectroscopy

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