377, 318, 274, 210, 186, 141, 130, 108, 91.

Anal. Calcd for $C_{22}H_{33}N_3O_7$: C, 58.52; H, 7.37; N, 9.31. Found: C, 58.64; H, 7.41; N, 9.02.

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Registry No. **2**, 56538-57-9; **3**, 103711-22-4; **4**, 103711-23-5; **5**, 103711-24-6; **6** (diastereomer 1), 103711-25-7; **6** (diastereomer 2), 103711-26-8; **7a**, 103711-28-0; **7b**, 103711-30-4; **8a**, 103711-31-5; **8b**, 103711-32-6; **9** (diastereomer 1), 103711-33-7; **9** (diastereomer 2), 103711-34-8; **10** (diastereomer 1), 103711-35-9; **10** (diastereomer 2), 103711-36-0; **11** (diastereomer 1), 103711-37-1; **11** (diastereomer 2), 103711-38-2; 2-propanethiol, 75-33-2; L-alanine methyl ester, 10065-72-2; Cbz-L-alanine, 1142-20-7; BOC-L-leucine, 13139-15-6; *tert*-butyl carbamate, 4248-19-5; methyl iodide, 74-88-4.

Theoretical Structures for the Phenyl and Benzyl Radicals

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Although the spectroscopy, chemistry, and quantum chemistry of phenyl[1-3] and benzyl[4-6] radicals have received much attention, the equilibrium geometry of the ground state of the benzyl radical has not been reported. Johnson[1] performed a series of interesting calculations on the ground and several excited states of the phenyl radical; an optimized structure was reported for the ground state but a C_{2v} symmetry constraint and an STO-3G basis set were used. Since radical structure calculations using a STO-3G basis sets are only relatively reliable (for example, the methyl radical[7] was found to be nonplanar when an STO-3G basis set was used) and Johnson[1] restricted the geometry optimization by starting with a C_{2v} symmetry, we decided to refine the phenyl ground-state geometry by using a better basis set and a lower initial symmetry. In addition, we computed second derivatives in order to confirm that the optimized structures correspond to minima on the energy surface. We also investigated the ground-state structure for benzene by using ab initio methods; a comparison of the theoretical benzene structure with the accepted experimental structure[8] provides a useful benchmark for the quality of the calculated equilibrium geometries for the ground states of the phenyl and benzyl radicals.

Computational Details

The geometries for benzene, the phenyl radical, and the benzyl radical were computed by using the restricted open-shell Hartree–Fock (ROHF) formalism with a 4-31G basis set.[9] The calculations were performed by using the computer code GAMESS[10] which utilizes the gradient method to optimize geometries. The geometry optimization for the benzyl radical was conducted without using any symmetry as input into the GAMESS code. Only a vertical plane of symmetry was used to initiate the geometry optimization for the phenyl radical.

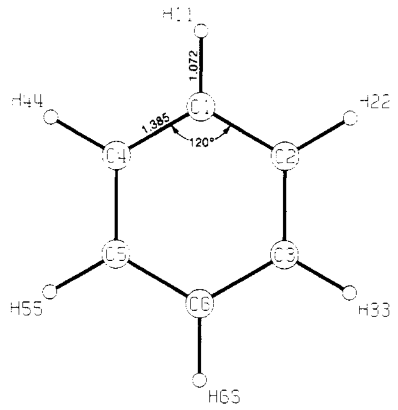

Figure 1. The ROHF-optimized geometry for the ground state of benzene; bond lengths in angstroms and bond angles in degrees; total energy = −230.37776 hartrees.

Second derivatives were calculated at the geometry of the optimized structure for both the phenyl and benzyl radicals. The vibrational frequencies, which will be reported separately, thus computed were all real, hence confirming that the optimized geometries indeed correspond to minima on the energy surfaces.

Two additional comments should be made: the first is that ROHF calculations at the 3-21G level for benzene and the phenyl radical gave the geometry obtained by using the 4-31G basis after rounding off bond lengths to the nearest thousandth of an angstrom and bond angles to the nearest tenth of a degree; the second is that unrestricted Hartree–Fock (UHF) calculations for the phenyl and benzyl radicals gave values for the spin eigenfunction S^2 much larger than 3/4, indicating considerable contamination from other electronic states. Consequently, UHF calculations do not appear to be appropriate for the phenyl and benzyl radicals.

Results and Discussion

A computer drawing for the optimized geometry of the ground electronic state for benzene is shown in Figure 1. The pertinent geometrical values are the CH and CC bond lengths which are slightly shorter than the accepted experimental[8] values, r_{CH} = 1.084 Å and r_{CC} = 1.397 Å, but equal to those obtained by Pulay, Fogarasi, and Boggs[11] using similar ab initio calculations. The computational results for the phenyl and benzyl radicals should follow the same trend.

The optimized geometry for the phenyl radical is shown in Figure 2. Note that the radical structure is significantly different from the benzene geometry. The salient features are that the α-CC bonds are ≃0.03Å shorter than those in benzene while the C2C1C4 bond angle increases by ≃5°; only small changes are found for the other geometric parameters. The change in these parameters from the corresponding benzene values reflect the distortion of the ring

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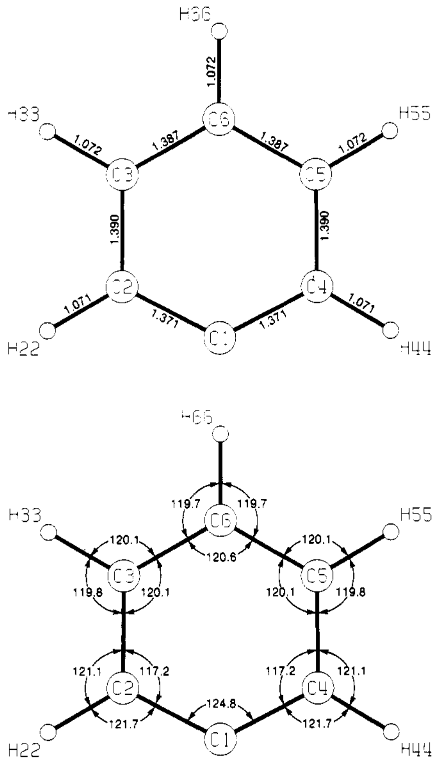

Figure 2. The ROHF-optimized geometry for the $^2A_1$ ground state of the phenyl radical; bond lengths in angstroms and bond angles in degrees; total energy = −229.725501 hartrees.

from a regular hexagon. In spite of this, however, the phenyl ring remains planar.

The phenyl radical geometry reported herein differs somewhat from the results reported by Johnson.[1] Although the bond angles are comparable the CH bond lengths given here are ≃0.03Å shorter, this is attributed to basis set differences.

The optimized geometry for the benzyl radical is illustrated by the computer drawing in Figure 3. Figure 3 shows that the phenyl ring is distorted in the molecular plane reflecting the presence of the unpaired electron on C1. The α-CH bond lengths, C1H11 and C1H22, are shorter than the other CH bond lengths in the system. The α-CC bond, C1C2, is the longest CC bond in the system but nevertheless it is very short for a CC single bond length.

The extent to which the phenyl ring interacts with the CH_2 group is revealed by comparing the geometry in the vicinity of the radical centers in the benzyl and ethyl systems.[12] The α-CH and α-CC bond lengths for the ethyl radical are 1.079 and 1.498 Å; these are considerably longer than those computed for the benzyl system listed in Figure 3. We attribute this to the interaction of the radical center with the phenyl ring.

Another feature is that the geometry tends to distort to a quinoidal type structure. Thus, the C1C2 bond length, as noted above, is much shorter than a CC single bond length (1.528 Å in ethane[12]) and, along with the shorter C4C6 and C3C5 bond lengths, it is tempting to represent the benzyl radical structure as one with alternating double and single CC bonds.

Summary

The computed equilibrium geometries are reported for the phenyl and benzyl radicals. The structures are calculated by using restricted open-shell Hartree–Fock calculations in conjunction with gradient optimization routines. The symmetry of each radical is C_{2v}. The phenyl radical structure distorts from the D_{6h} symmetry of benzene with the shortening of the CC bonds α to the carbon atom containing the unpaired electron. The benzyl radical contains α-CH and α-CC bonds shorter than those found in the ethyl radical. We attribute this to the interaction of the singly occupied orbital on the radical center with the phenyl ring, a phenomenon certainly consistent with the planar character of the system.

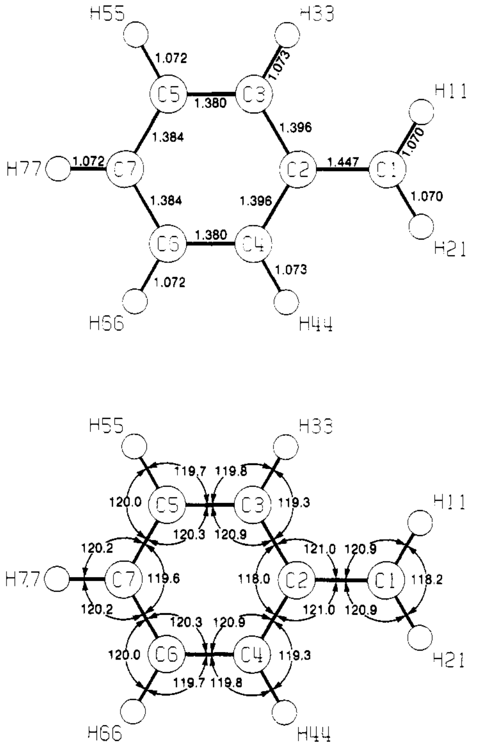

Figure 3. The ROHF-optimized geometry for the $^2B_2$ ground state of the benzyl radical; bond lengths in angstroms and bond angles in degrees; total energy = −265.837128 hartrees.

Registry No. Phenyl radical, 2396-01-2; benzyl radical, 2154-56-5.

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Nucleophilic Trapping of Intermediates in the Singlet Oxygenations of Isomeric 1,4-Di-*tert*-butoxy-1,3-butadienes

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We have previously reported the reactions of (*E,E*)-**1**, (*E,Z*)-**2**, and (*Z,Z*)-1,4-di-*tert*-butoxy-1,3-butadiene (**3**) with singlet oxygen[1] (Scheme I). Especially noteworthy in this previous study was the dramatic effect of solvent on the product composition in the reaction of diene **3** and the insensitivity of the product ratio over the same solvent range in the reaction of diene **1**.[2] A a result of this observation, it was suggested that a perepoxide intermediate

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