Resolution of 1[21] and **3b**,**c**[22] and assignment of absolute configuration will be reported separately.

General Procedure. A mixture of the racemic or partially resolved amine (25 mmol) and 25 mmol (+)-MTPA[23] was dissolved in 0.5 mL of benzene-d_6 (or $CDCl_3$) and the NMR spectrum recorded.

Acknowledgment. We are grateful to our colleagues at McNeil for contributing data for Table I and especially Dr. Bruce E. Maryanoff and David F. McComsey for constructive conversations. We also thank Professor Harry S. Mosher for helpful discussion of MTPA applications. The use of the facilities at the South Carolina Nuclear Magnetic Resonace Spectroscopy Center, funded by the National Science Foundation Grant CHE78-18723, is acknowledged.

Registry No. (±)-1, 103729-18-6; 1·(+)-MTPA, 103639-53-8; (±)-2, 86562-23-4; 2·(+)-MTPA, 103639-54-9; (±)-3a, 90390-52-6; (6*R*,10b*S*)-3a·(+)-MTPA, 103729-10-8; (6*S*,10b*R*)-3a·(+)-MTPA, 103729-15-3; (±)-3b, 90390-54-8; 3b·(+)-MTPA, 103729-12-0; (±)-3c, 90390-64-0; (6*S*,10b*R*)-3c·(+)-MTPA, 103729-17-5; (6*R*,10b*S*)-3c·(+)-MTPA, 103729-14-2; (±)-4, 7398-61-0; (+)-(*R*)-4, 19342-01-9; (*S*)-4·(+)-MTPA, 103639-55-0; (*R*)-4·(+)-MTPA, 103639-60-7; (±)-5, 42882-26-8; (+)-(*R*)-5, 5933-40-4; (*R*)-5·(+)-MTPA, 103639-56-1; (*S*)-5·(+)-MTPA, 103639-61-8; (±)-6, 103729-19-7; (*S*)-6·(+)-MTPA, 103639-58-3; (*R*)-6·(+)-MTPA, 103639-62-9; (±)-7, 618-36-0; (*R*)-(+)-7, 3886-69-9; 7·(+)-MTPA, 103639-59-4; (*S*)-(−)-MTPA, 17257-71-5; (*R*)-(+)-MTPA, 20445-31-2.

(21) Carson, J. R.; Carmosin, R. J.; Costanzo, M. J.; Villani, F. J., Jr., unpublished results.
(22) Maryanoff, B. E.; McComsey, D. F.; Costanzo, M. J., manuscript in preparation.
(23) Use of (*S*)-(−)-MTPA of course gives opposite sense of nonequivalence, which can be useful for examining partially obscured resonances.

Differentially Protected α-Aminoglycine

Mark G. Bock,* Robert M. DiPardo, and Roger M. Freidinger

Department of Medicinal Chemistry, Merck Sharp & Dohme Research Laboratories, West Point, Pennsylvania 19486

Received May 15, 1986

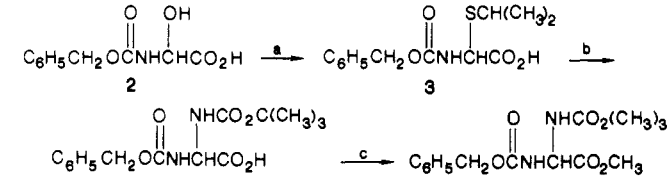
A number of methods have been devised to stabilize biologically active peptides against metabolic degradation and to study their structure–activity relationships.[1] Among these is the preparation of partially modified retro-inverso-peptide structures.[2] Implicit in this approach is the notion that the requisite α,α-diamino residues are readily accessible and that these species can be incorporated into the desired peptide sequence in standard fashion.[3] Recent additional interest in α,α-diamino compounds derives from their possible application in the study of peptide carrier systems designed with the intent of transporting therapeutically useful compounds into microbial cells.[4] There are thus several applications[5] for which one would like to have an α,α-diamino residue available for use in peptide synthesis. In this connection, we report the preparation of α-aminoglycine (**1**), in protected form, which complements existing methodology,[3a-c,4] and demonstrate its manipulation in the synthesis of simple dipeptides.

$H_2NCH(NH_2)CO_2H$
1

The synthetic process is summarized in Scheme I. 2-Propanethiol is amidoalkylated with α-hydroxy-*N*-(benzyloxycarbonyl)glycine (**2**) according to the method of Ben-Ishai to give the crystalline α-isopropylthio derivative **3**.[6] The second amino group is then introduced via a mercuric ion mediated displacement of the isopropylthio moiety with *tert*-butyl carbamate. In this way, protected α-aminoglycine **4** is accessible in 70% overall yield from **2** as a stable solid which can be stored in the refrigerator indefinitely. The acyl imine which is presumably the intermediate in the alkylthio displacement can be intercepted with other primary carbamates as well, for example, ethyl carbamate. However, treatment of **3** with ammonia and mercury salts to give monoprotected α-aminoglycine (cf. **8a**) was found not be an efficient process.

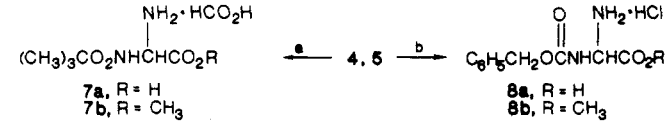
The differentially protected **4** is poised for further elaboration at both the amino and carboxy termini, in either order. Accordingly, the coupling of **4** with L-alanine methyl ester in the presence of common carbodiimide reagents afforded the corresponding dipeptide **6**, as a mixture of diastereomers, 86% yield. Alternatively, esterification of **4** leads to **5**, which is stable indefinitely at room temperature and which can be further modified as outlined in Scheme II. No difficulty is encountered in selectively removing the amino protecting groups of **4** or **5** as either the benzyloxycarbonyl (Cbz) or *tert*-butyloxycarbonyl (Boc) groups are readily cleaved to give **7** and **8**, respectively. These compounds are also stable materials (0 °C, dry) although we have found it advisable to use **7a** and **7b** as soon as they are generated. As a further illustration of their application in peptide synthesis, **7b** was coupled with

Scheme I[a]



[a] (a) $(CH_3)_2CHSH$, H_2SO_4 (catalyst), HOAc; (b) $(CH_3)_3CCO_2N-H_2$, Hg^{2+}, THF; (c) CH_3I, K_2CO_3, DMF.

Scheme II



[a] (a) Pd/C, HCO_2H–H_2O, CH_3OH. (b) HCl(g), EtOAc.

(1) Veber, D. F.; Freidinger, R. M. *Trends NeuroSci. (Pers. Ed.)* **1985**, *8*, 392 and references cited therein.
(2) (a) Goodman, M.; Chorev, M. *Acc. Chem. Res.* **1979**, *12*, 1. (b) Goodman, M.; Chorev, M. *Perspectives in Peptide Chemistry*; Eberle, A., Geiger, R., Wieland, T., Eds.; Karger: Basel, 1981; p 283.
(3) (a) Chorev, M.; Willson, C. G.; Goodman, M. *J. Am. Chem. Soc.* **1977**, *99*, 8075. (b) Chorev, M.; Goodman, M. *Int. J. Pept. Protein Res.* **1983**, *21*, 258. (c) Pallai, P.; Goodman, M. *J. Chem. Soc., Chem. Commun.* **1982**, 280. (d) Chorev, M.; Shavitz, R.; Goodman, M.; Minick, S.; Guillemin, R. *Science (Washington, D.C.)* **1979**, *204*, 1210. (e) Pallai, P. V.; Richman, S.; Struthers, R. S.; Goodman, M. *Int. J. Pept. Protein Res.* **1983**, *21*, 84. (f) Fuller, W. D.; Goodman, M.; Verlander, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 5821. (g) Loudon, G. M.; DeBons, F. E. *J. Org. Chem.* **1980**, *45*, 1703.
(4) Kingsbury, W. D.; Boehm, C. J.; Mehta, R. J.; Grappel, S. F.; Gilvarg, C. *J. Med. Chem.* **1984**, *27*, 1447.
(5) For a recent application in heterocyclic synthesis, see: Bock, M. G.; DiPardo, R. M.; Evans, B. E.; Rittle, K. E.; Veber, D. F.; Freidinger, R. M., submitted for publication in *Tetrahedron Lett.*
(6) Zoller, U.; Ben-Ishai, D. *Tetrahedron* **1975**, *31*, 863.

0022-3263/86/1951-3718$01.50/0

Cbz-L-alanine to give **9** in 81% yield; **8b** was coupled with Boc-L-methionine and Boc-L-leucine, by using standard methodology, to afford **10** and **11** in 71% and 50% yield, respectively.

In summary, α-aminoglycine was prepared by using an efficient process. Its ready availability should facilitate its application in peptide structure–functioin studies as well as in organic synthesis.

Experimental Section

Commercial chemicals were used as obtained without further purification, except for solvents, which were purified and dried, where appropriate, before use by standard methods. Melting points were determined in open capillaries on a Thomas-Hoover Unimelt apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Nicolet NT-360 spectrometer with an internal lock on the deuterium resonance of the solvent. Fast atom bombardment (FAB) mass spectra were run on a Finnigan-Mat 731 instrument and electron impact (EI) and field desorption (FD) spectra were determined on a VG 7035 spectrometer. All chromatography was carried out on silica gel 60F-254 (E. Merck).

α-(Isopropylthio)-*N*-(benzyloxycarbonyl)glycine (3): prepared according to Zoller and Ben-Ishai[6] in 77% yield; mp 82–84 °C; NMr ($CDCl_3$) δ 1.35 (t, 6 H, J = 7 Hz), 3.27 (hep, 1 H, J = 7 Hz), 5.15 (m, 2 H), 5.40 (d, 1 H, J = 9 Hz, α-proton), 5.64 (d, 1 H, J = 9 Hz, NH), 6.0–6.4 (br s, 1 H, CO_2H), 7.35 (m, 5H); MS m/e 238 (M – CO_2H), 209, 162, 148, 108, 107, 92, 91, 77.

Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94. Found: C, 55.09; H, 6.13; N, 5.22.

α-(*tert*-Butyloxycarbonylamino)-*N*$^\alpha$-(benzyloxycarbonyl)glycine (4). To a solution of 75 mL of tetrahydrofuran containing 4.1 g (14.5 mmol) of **3** and 7.3 g (62.3 mmol) of *tert*-butyl carbamate was added 5.9 g (21.7 mmol) mercuric chloride. The resulting solution was heated at 65 °C for 20 h. The reaction mixture was diluted with ether (150 mL) and filtered. The filtrate was washed with ether (200 mL) and the filtrate extracted with 10% sodium hydroxide solution (2 × 75 mL). The aqueous extracts were washed with ether and acidified to pH 4 with concentrated HCl. The resulting milkly white suspension was extracted with ether (3 × 150 mL), and the combined organic extracts were dried ($MgSO_4$) and rotoevaporated to give a white, free-flowing powder. Recrystallization from ether afforded 4.3 g (91%) of the analytical product: mp 158–159 °C dec; NMR (Me_2SO-d_6) δ 1.38 (s, 9 H), 5.05 (s, 2 H), 5.28 (t, 1 H, J = 8 Hz, C*H*CO_2H), 7.35 (m, 6 H), 7.85 (d, 1 H, J = 8 Hz); MS, m/e 279 (M – CO_2H), 268 (M – C_4H_8) 223, 179, 151, 108, 107, 91, 79.

Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.55; H, 6.22; N, 8.64. Found: C, 55.51; H, 6.32; N, 8.57.

α-(*tert*-Butyloxycarbonylamino)-*N*$^\alpha$-(benzyloxycarbonyl)glycine Methyl Ester (5). Acid **4** (800 mg, 2.46 mmol) was dissolved in 4 mL of DMF and treated with potassium carbonate (518 mg, 3.75 mmol) and methyl iodide (162 μL, 2.60 mmol). After 3 h, extractive workup afforded a white solid, which was recrystallized from ether to give 800 mg (96%) of the product: mp 115–116 °C; NMR ($CDCl_3$) δ 1.45 (s, 9 H), 3.8 (s, 3 H), 5.13 (s, 2 H), 5.34 (t, 1 H, J = 7 Hz), 5.93 (br s, 1 H), 6.16 (br s, 1 H), 7.35 (m, 5 H); MS m/e 282 (M – C_4H_8), 279 (M – CO_2CH_3), 223, 179, 135, 133, 115, 108, 107, 91, 79.

Anal. Calcd for $C_{16}H_{22}N_2O_6$: C, 56.80; H, 6.55; N, 8.28. Found: C, 57.01; H, 6.54; N, 8.35.

α-Amino-*N*$^\alpha$-(*tert*-butyloxycarbonyl)glycine (7a). A magnetically stirred solution of 40 mL of methanol and 4.5 mL of 90% formic acid at 0 °C was treated with 200 mg of 10% palladium/carbon catalyst under nitrogen. To the resulting suspension was added **4** (200 mg, 0.62 mmol), and stirring was continued for 2 h. The reaction mixture was filtered through Celite, and the filtrate was rotoevaporated. The resulting oil was dissolved in a minimum amount of ethyl acetate and stored at −20 °C. **7a** precipitated from solution as a whilte solid (120 mg, 83%): mp 105–106 °C; NMR (Me_2SO-d_6) δ 1.40 (s, 9 H, *t*-Bu), 4.52 (d, 1 H, J = 7 Hz, α-proton), 6.15 (br s, exchangeable), 7.05 (d, 1 H, J = 7 Hz, NH), 8.32 (s, 1 H, *H*CO_2H); MS FAB m/e 212 (sodium salt). NMR analysis showed decomposition to *tert*-butyl carbamate and other products on prolonged standing at room temperature.

α-Amino-*N*$^\alpha$-(*tert*-butyloxycarbonyl)glycine Methyl Ester (7b): prepared according to the method for **7a** in 90% yield and isolated as a gummy oil; NMR (D_2O) δ 1.47 (s, 9 H, *t*-Bu), 3.85 (s, 3 H, CO_2CH_3), 3.95 (s, 1 H, α-proton), 5.13 (br s, 1 H, NHCO), 8.46 (s, 1 H, *H*CO_2H).

α-Amino-*N*$^\alpha$-(benzyloxycarbonyl)glycine (8a). Compound **4** (500 mg, 1.54 mmol) was dissolved in 70 mL of ethyl acetate and stirred at 0 °C. A continuous stream of hydrogen chloride gas was passed into the solution for 30 min. The reaction mixture was then warmed to room temperature and stirred 30 min more. Concentration under reduced pressure and trituration with ether afforded 410 mg (98%) of **8a** as a white, amorphous solid: mp 135 °C dec; NMR (Me_2SO-d_6) δ 5.13 (s, 2 H, $CH_2C_6H_5$), 5.24 (d, 1 H, J = 7 Hz, C*H*CO_2H), 7.36 (m, 5 H), 8.63 (br s, 2 H), 8.85 (d, 1 H, J = 7 Hz, CON*H*); MS FAB, m/e 246 (sodium salt). This material which was stable in the solid state could be stored unchanged at −20 °C and was of sufficient quality for all subsequent reactions. Recrystallization from ethanol–ether gave while needles, mp 126–128 °C. HPLC and NMR analysis showed extensive decomposition to benzyl carbamate and other products on prolonged standing at room temperature.

α-Amino-*N*$^\alpha$-(benzyloxycarbonyl)glycine Methyl Ester (8b): prepared according to the method for **8a** in 93% yield: mp 136–137 °C; NMR (Me_2SO-d_6) δ 3.75 (s, 3 H), 5.13 (s, 2 H), 5.37 (m, 1 H), 7.37 (m, 5 H); MS (free base) FI/FD, m/e 239 (M + H); MS (free base) EI, m/e 179 (M – CO_2CH_3), 151, 135, 115 108, 91.

Anal. Calcd for $C_{11}H_{15}ClN_2O_4$: C, 48.10; H, 5.50; N, 10.20. Found: C, 48.17; H, 5.50; N, 10.45.

General Procedure for Dipeptide Synthesis. The α-aminoglycine residue (0.6 mmol) was combined at room temperature with the appropriate amino acid derivative (0.9 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.9 mmol), and 1-hydroxybenzotriazole (0.9 mmol) in 2 mL of dimethyl formamide with exclusion of moisture. The pH of the reaction mixture was adjusted to approximately 8.5 (moist pH paper) with triethylamine. The reaction mixture was stirred at room temperature (1–14 h), and the solvent was removed under reduced pressure. The residue was partitioned between ethyl acetate and citric acid solution (10%). The organic phase was washed with citric acid solution (10%), sodium bicarbonate solution (50%), and brine. The dried (Na_2SO_4) organic extracts were rotoevaporated to yield the crude product, which was purified chromatographically and/or by crystallization.

***N*$^\alpha$-Cbz-*N*$^\alpha$-Boc-Gly-L-Ala-OCH$_3$ (6)**: white solid, mixture of diastereomers; R_f 0.38 (1:1 hexane–ethyl acetate); mp 180–182 °C; NMR ($CDCl_3$) δ 1.41 (d, 3 H, J = 7 Hz), 1.45 (s, 9 H), 3.75 (s, 3 H), 4.57 (br q, 1 H, J = 7 Hz), 5.15 (br s, 2 H), 5.46 (t, 1 H, J = 6 Hz, α-proton Gly), 5.7 (br s, 1 H, NH), 5.95 (br s, 1 H, NH), 7.15 (br s, 1 H, NH), 7.35 (m, 5 H); MS FAB, m/e 410 (M + H).

Anal. Calcd for $C_{19}H_{27}N_3O_7 \cdot 0.4H_2O$: C, 54.77; H, 6.73; N, 10.08. Found: C, 55.01; H, 6.81; N, 9.83.

***N*$^\alpha$-Boc-*N*$^\alpha$-(*N*$^\alpha$-Cbz-L-Ala)-Gly-OCH$_3$ (9)**: white solid, mixture of diastereomers; R_f 0.29 (1:1 hexane–ethyl acetate); mp 150–152 °C; NMR ($CDCl_3$) δ 1.40 (d, 3 H, J = 7 Hz), 1.44 (s, 9 H), 3.79 and 3.80 (s, 3 H), 4.29 (br q, 1 H, J = 7 Hz), 5.13 (m, 2 H), 5.29 (br d, 1 H, J = 7 Hz), 5.41 (br t, 1 H, $J \sim$ 7 Hz), 5.94 (br s, 1 H), 7.36 (m, 5 H); MS FAB, m/e 410 (M + H).

Anal. Calcd for $C_{19}H_{27}N_3O_7 \cdot 0.5H_2O$: C, 54.53; H, 6.75; N, 10.04. Found: C, 54.69; H, 6.84; N, 9.71.

***N*$^\alpha$-Cbz-*N*$^\alpha$-(*N*$^\alpha$-Boc-L-Met)-Gly-OCH$_3$ (10)**: white solid, mixture of diastereomers; R_f 0.31 (1:1 hexane–ethyl acetate); mp 141–143 °C; NMR ($CDCl_3$) δ 1.45 (s, 9 H), 1.92 (m, 1 H), 2.06 (m, 1 H), 2.19 and 2.20 (s, 3 H, SCH_3), 2.54 (m, 2 H), 3.79 (s, 3 H), 4.33 (br s, 1 H), 5.11 (s, 2 H), 5.21 (br d, 1 H, $J \sim$ 7 Hz), 5.51 (t, 1 H, $J \sim$ 7 Hz), 6.26 (br s, 1 H), 7.35 (m, 5 H), 7.64 (br s, 1 H); MS, m/e 469 (M^+), 413 (M – C_4H_8), 395, 339, 321, 262, 244, 231, 218, 159, 144, 108, 91.

Anal. Calcd for $C_{21}H_{31}N_3O_7S$: C, 53.71; H, 6.65; N, 8.95. Found: C, 53.31; H, 6.70; N, 8.85.

***N*$^\alpha$-Cbz-*N*$^\alpha$-(*N*$^\alpha$-Boc-L-Leu)-Gly-OCH$_3$ (11)**: white solid, mixture of diastereomers; R_f 0.45 (1:1 hexane–ethyl acetate); mp 87–89 °C; NMR ($CDCl_3$) δ 0.93 (m, 6 H), 1.44 (s, 9 H), 1.45 (m, 1 H), 1.65 (m, 2 H), 3.79 (s, 3 H), 4.14 (br s, 1 H), 4.84 (br s, 1 H), 5.10 (m, 2 H), 5.48 (br t, 1 H, $J \sim$ 6 Hz), 6.23 (br s, 1 H), 7.35 (m, 5 H), 7.56 (br d, 1 H, $J \sim$ 6 Hz), MS, m/e 451 (M^+), 395, 392,

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.

Acknowledgment. It is a pleasure to acknowledge the assistance of J.-P. Moreau, J. S. Murphy, J. Smith, and Dr. S. Varga for analytical support. We thank Drs. D. F. Veber and P. S. Anderson for support and encouragement and M. Z. Banker for preparing the manuscript.

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

J. Pacansky,* B. Liu, and D. DeFrees†

IBM Almaden Research Center, San Jose, California 95120-6099

Received April 7, 1986

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.

† Present address: Molecular Research Institute, Palo Alto, CA 94304.

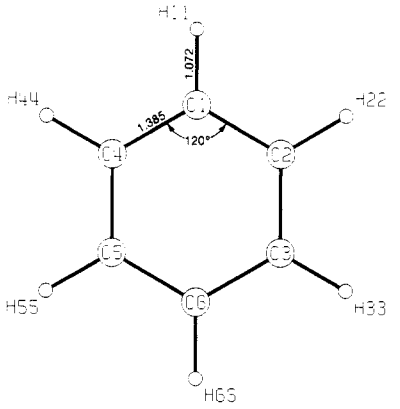


Figure 1. The ROHF-optimized geometry for the ground state of benzene; bond lengths in angstroms and bond angles in degrees; total energy = −230.37776 hartrees.

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 $\simeq$0.03Å shorter than those in benzene while the C2C1C4 bond angle increases by $\simeq$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

(1) Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 4857.
(2) Porter, G.; Ward, D. *Proc. R. Soc. London A* **1965**, *287*, 457.
(3) Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553.
(4) Martin, A.; Nicholas, DeP.; Boyd, R. J.; Arnold, D. R. **1982**, *60*, 3011.
(5) Rüchardt, C.; Beckhouse, H. D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 529.
(6) Hirst, D. M.; Linington, M. E. *Theor. Chim. Acta* **1972**, *26*, 179.
(7) Pacansky, J. *J. Phys. Chem.* **1982**, *86*, 485.
(8) Langseth, A.; Stoicheff, P. B. *Can. J. Phys.* **1956**, *34*, 350.
(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(10) Dupuis, M.; Wendoloski, J. J.; Spangler, D. *Nat. Res. Comput. Chem. Software Cat.* **1980**, *1*, QGO1.
(11) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999.

0022-3263/86/1951-3720$01.50/0