Preferred Conformation of 1-Phenyl-2-propanol. *Ab initio* and Molecular Mechanics Calculations with Geometry Optimization

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Synopsis. The most stable conformation of 1-phenyl-2-propanol, optimized by *ab initio* and molecular mechanics (MM2) calculations, is a phenyl-methyl anti and phenyl-OH gauche conformation with an intramolecular OH-π hydrogen bond.

Weak interactions such as OH-π hydrogen bond,[1] CH-π interaction,[2] and van der Waals interaction[3] often play an important role in determining conformations of various organic molecules. We have reported recently the stereochemistry of $C_6H_5CH_2XR$-type compounds (X=CHOH, C=O, S=O; R=CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9) by use of molecular mechanics (MMI) and pointed out the importance of the nonbonded weak interaction.[4] In order to understand the nature of these weak interactions in detail, we studied in this letter conformations of 1-phenyl-2-propanol with *ab initio* molecular orbital as well as molecular mechanics calculations.

Methods

We used the programs Gaussian 80[5] for *ab initio* calculation and MM2[6] for molecular mechanics calculation. The geometries of conformers were optimized with the Hartree-Fock method with the STO-3G basis set. It took about 5 h in CPU time to reach one of the local energy minima of 1-phenyl-2-propanol. At the STO-3G geometries, the energies and electron distributions were recalculated with the 4-31G basis set. Comparing with STO-3G calculations, 4-31G calculations give more reliable results about energy difference of isomers. In the case of geometry optimization by MM2, the required CPU time for this molecule was about 10—20 s.

Results and Discussion

The *ab initio* calculation showed that the most stable conformer was a phenyl–methyl anti and phenyl–OH gauche type with an intramolecular OH-π hydrogen bond (Table 1). The OH-π hydrogen bond energy was estimated to be 2.20 kcal† mol^{-1} from the energy difference between conformers **B** and **C**. From the temperature dependent IR measurement on 1-phenyl-2-propanol($\bar{\nu}_{OH}$(free)=3626 cm^{-1}, $\bar{\nu}_{OH\text{-}\pi}$= 3604 cm^{-1}), we determined experimentally this energy to be 1.0 kcal mol^{-1}. The *ab initio* calculation overestimates the hydrogen-bond interaction in this case. From the dihedral angle H(6)–C(1)–C(4)–C(9), we found that the benzene ring was twisted around the C(4)–C(1) bond in **A** and **D** conformers so as to avert the steric congestion between methyl and

Table 1. Relative energies, optimized geometries, vibrational frequency and electron distribution of 1-phenyl-2-propanol

Conformation	**A**	**B**	**C**	**D**
E/kcal mol^{-1}	−0.64	0.0[a]	−2.20	+0.38
R_{OH}/Å	0.991	0.990	0.990	0.993
C-O-H/deg	104.01	104.07	104.07	104.09
W[b](4-1-2-15)/deg	−60.92	−177.50	−178.09	60.0
W(6-1-4-9)	41.10	32.66	33.25	24.26
Population				
C=(Ph)[c]	6.167	6.159	6.171	6.161
H(OH)	0.608	0.605	0.596	0.605
O	8.730	8.724	8.736	8.725
O-H	0.253	0.254	0.249	0.254
OH-Ph(×10^2)[d]	−0.029	−0.016	1.62	−0.021
CH_3-Ph(×10^3)[e]	4.79	−0.33	−0.29	7.44
$\bar{\nu}_{OH}$/cm^{-1}	4240	4240	4240	4240
Scaled	3600	3600	3600	3600

a) The total energy is −422.05271 hartree with the 4-31G basis set at a STO-3G optimized geometry. b) Dihedral angle. c) Averaged value of the population on the carbon atoms in the benzene ring. d) Sum of the OH proton-carbon overlap population over 6 carbon atoms of the benzene ring. e) Sum of the CH_3 proton-carbon overlap population over 3 CH_3 protons and 6 benzene-ring carbon atoms.

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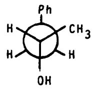
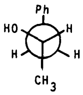
† 1 cal_{th}=4.184 J.

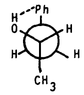
phenyl groups. In conformers **A** and **D**, these dihedral angles change from the normal angle(30°) to 41° and 24°, respectively.



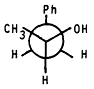
A



B



C



D

The population analysis reveals the evidence for the intramolecular OH-π hydrogen bond as follows:

1) In conformer **C** (dihedral angle C(1)–C(2)–O(3)–H(8): −59.73°) there is a small positive sum of populations (1.62×10^{-2}) between the OH proton and the carbon atoms of the benzene ring, indicating a bonding interaction. In the other conformers, in which these dihedral angles are nearly 180° and OH proton cannot interact with benzene ring, the sums are all negative.

2) The overlap population of the OH bond in **C** (0.249) is the smallest among the conformers, indicating that the OH bond of **C** is the weakest. But the OH stretching frequencies estimated from the calculated diagonal force constant at the STO-3G level are essentially identical among these conformers (4220 $\mathrm{cm^{-1}}$, which gives 3600 $\mathrm{cm^{-1}}$ when scaled with a factor 1.17).[7] This may be due to the neglect of off-diagonal elements.

3) Conformer **C** has the smallest atomic population on the OH proton (0.596) and the largest average atomic population on the carbon atoms of the benzene ring (6.171). These values also support the presence of OH-π interaction.

From the optimized geometry of OH-π intramolecularly hydrogen bonded form (Fig. 1) we find the fact that the OH proton(8) is interacting equally with two carbon atoms (C(4), C(9)) of the benzene nucleus and is located above the surface with an OH(8)···C(4) or C(9) distance of 2.60 Å. Ōki and Iwamura[8] reported that the OH proton and the benzene nucleus were interacting in the same form as found above based on the IR experiments on similar 2-phenylethanol.

The geometry optimized MM2 calculation revealed the same preferred conformation. The optimized geometries of conformers are quite similar to those from *ab initio* calculations. The energy difference between **B** and **C** (−0.228 $\mathrm{kcal\,mol^{-1}}$) is thought to correspond to intramolecular OH-π hydrogen bond energy. Careful examination of the steric energy components of **B** and **C** conformers clearly indicates that the dipole energy term mainly contributes to the stabilization of OH-π hydrogen bonded form. But the hydrogen-bond energy is rather small in comparison with the experimental value (1.0 $\mathrm{kcal\,mol^{-1}}$). Therefore the present MM2 calculation is not adequate for studying the hydrogen bond system. It is necessary to add an extra energy term corresponding to the delocalization contribution of hydrogen bond to steric energy from MM2 in order to evaluate the hydrogen bond and steric energy correctly.

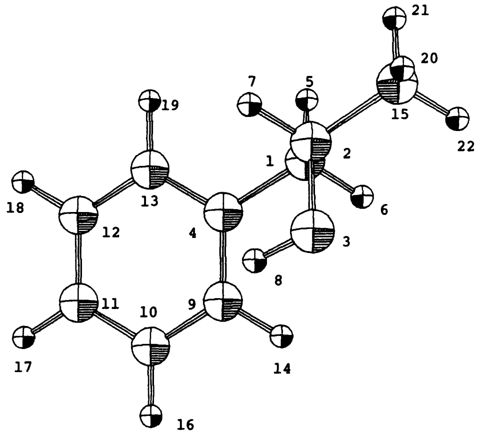


Fig. 1. Optimized Geometry of Conformer **C**.

As to the CH-π interaction, we cannot show a definitive evidence at this calculation level that CH_3 protons and the benzene nucleus are interacting. Some results may be taken to give the qualitative evidences of the CH-π interaction. In the conformer **A** and **D**, in which CH-π interaction is possible, a small positive overlap population is found (4.79×10^{-3} and 7.44×10^{-3}, respectively). This small positive bond population suggests a very small attractive interaction between CH_3 and π-electrons of the benzene ring. This suggests the presence of a delocalizative interaction between CH_3 and benzene ring. In addition, MM2 calculation estimates a considerably large attractive van der Waals interaction(−0.45 $\mathrm{kcal\,mol^{-1}}$) between CH_3 and the benzene nucleus in conformer **A**. In other conformers, this interaction energy (CH_3–Ph) is about 0.1 kcal $\mathrm{mol^{-1}}$ smaller than that of **A**.

References

1) K. Morokuma and G. Wipff, *Chem. Phys. Lett.*, **74**, 400 (1980); J. Sicher, M. Cherest, Y. Gault, and H. Felkin, *Collect. Czech. Chem. Commun.* **27**, 2907 (1962).

2) Y. Kodama, K. Nishihata, M. Nishio, and Y. Iitaka, *J. Chem. Soc. Perkin Trans. 2*, **1976**, 1490.

3) R. E. Carter and P. Stilbs, *J. Am. Chem. Soc.*, **98**, 7515 (1976); B. Aurivillius and R. E. Carter, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 1033.

4) M. Hirota, T. Sekiya, K. Abe, H. Tashiro, M. Karatsu, M. Nishio, and E. Osawa, *Tetrahedron*, **39**, 3091 (1983).

5) The *ab initio* calculations were performed by use of the Gaussian 80 (QCPE 13) program at the Institute for Molecular Science. With this program we can make an *ab initio* calculation of some molecules with the number of Contracted Gaussian Type Orbitals (CGTO) below 127. In the case of 4-31G calculations of 1-phenyl-2-propanol, the number of CGTO is 114.

6) QCPE 395, N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).

7) P. Pulay, "Modern Theoretical Chemistry," ed by H. F. Schaefer, Plenum Press, New York, (1978) Vol. 4, P. 153.

8) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **32**, 1135 (1959).