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The Conformation of 1-Alkyl-2-phenylpropan-1-ols Studied by Ab Initio MO Calculations. Relevance of the CH/π and OH/π Hydrogen Bonds

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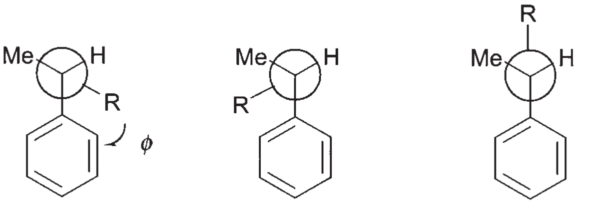
Ab initio MO calculations were carried out, at the MP2/6-311G(d,p)//MP2/6-31G(d) level, for the conformation of a series of diastereoisomers of 1-alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ and 2-phenylalkanes $CH_3CH(C_6H_5)CH_2R$ (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9). A rotamer where R is *gauche* to C_6H_5 and *anti* to the benzylic methyl group has been found to be the most populated. The distances between the CH and OH hydrogens and the phenyl group in the interacted rotamers have been found to be short. The distribution of the possible rotamers depends on the presence or absence of the OH group and the configuration of the alcohol diastereoisomers. The results are discussed in the context of weak attractive molecular forces; the CH/π, OH/π, and CH/O hydrogen bonds, as well as unfavorable steric effects occurring between R and Me and between vicinal CH groups.

In previous papers, we reported that alkyl 1-phenylethyl ketones and sulfoxide diastereoisomers $CH_3CH(C_6H_5)$–X–R (X = CO,[1] SO[2]) prefer a conformation where R is *gauche* to C_6H_5 (Ph) and *anti* to the benzylic Me group (rotamer **a** in Fig. 1),[3] irrespective of the nature of the alkyl group R. The second most favorable one has been found, generally, to bear R flanked by Ph and Me (rotamer **b**). To accommodate the above results, we suggested the importance of CH/π[4–7] and CH/O[8–10] hydrogen bonds for controlling the conformation of these molecules.

In order to explore the generality and to reveal the origin of the phenomenon, we studied the conformation of 1-alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ and 2-phenylalkanes $CH_3CH(C_6H_5)CH_2R$ (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9), by MP2/6-311G(d,p)//MP2/6-31G(d) level calculations. The alcohols differ from the previously reported molecules in that the OH group has freedom to rotate, and the number of possible conformations increases, accordingly. The OH/π hydrogen bond[11] may work in certain geometries in these alcohols. It is interesting to compare the effect of two types of π-interactions: the CH/π and OH/π hydrogen bonds.



a (ϕ ~ 60°) **b** (ϕ ~ -60°) **c** (ϕ ~ 180°)

Fig. 1. Three stable conformations of 1-alkyl-2-phenylpropyl compounds $CH_3CH(C_6H_5)XR$.

Method

The basis sets implemented in the Gaussian 98 program[12] were employed without any modification, as in the previous studies. Electron correlation energies were calculated by applying the second-order Møller–Plesset (MP2) perturbation theory. The geometry of the molecules was optimized at the MP2/6-31G(d) level of the approximation. Using these geometries, single-point calculations were performed at the MP2/6-311G(d,p) level to estimate the conformational energies. Vibrational frequencies were calculated using the analytical second derivatives at the same level of the geometry optimization for each conformer. Using these results, the thermal energy corrections were added to the total energy at 298.15 K and 1 atm (101.325 kPa), using the principal isotope for each element type.

Results and Discussions

Conformation of 2-Phenylalkanes. First, we discuss the conformation of 2-phenylalkanes $CH_3CH(C_6H_5)CH_2R$ **1**. Table 1 lists the relative Gibbs energy[13] and the abundance of three stable conformations (**a**, **b**, **c**) of 2-phenylbutane (R = CH_3), 2-phenylpentane (R = C_2H_5), 2-methyl-4-phenylpentane (R = *i*-C_3H_7), and 2,2-dimethyl-4-phenylpentane (R = *t*-

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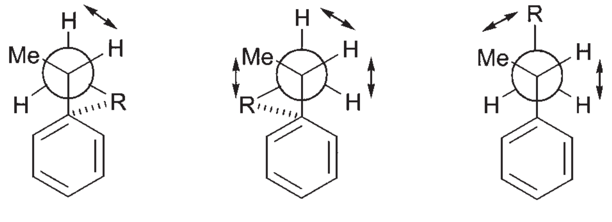
Table 1. (A) Relative Gibbs Free Energies (in kJ mol^{-1}) at 298 K and 1 atm (101.325 kPa) of Three Stable Conformations (**a**, **b**, **c**) of $CH_3CH(C_6H_5)CH_2$–R **1**: 2-Phenylbutane (R = CH_3), 2-Phenylpentane (R = C_2H_5), 2-Methyl-4-phenylpentane (R = *i*-C_3H_7), and 2,2-Dimethyl-4-phenylpentane (R = *t*-C_4H_9) Calculated by the MP2/6-311G(d,p)//MP2/6-31G(d) Level of Theory. (B) Relative Abundance (%) of the Three Stable Conformations of $CH_3CH(C_6H_5)CH_2R$

	Rotamer **a**	Rotamer **b**	Rotamer **c**
(A) Gibbs energy			
R = CH_3	0.00 (58)[a] [5][b]	6.96 (−62) [5]	4.57 (173)
R = C_2H_5	0.00 (59) [5]	6.96 (−62) [5]	4.90 (172)
	1.71 (54) [5]	14.9 (−55) [6]	7.14 (177)
	5.81 (64) [6]	18.8 (−64) [5]	16.3 ($\underline{142}$)[c]
R = *i*-C_3H_7	0.00 (53) [5]	13.4 (−63) [5]	5.97 (177)
	5.04 (68) [6]	13.8 (−56) [6]	15.1 ($\underline{139}$)
	9.68 (62) [6]	29.6 (−51) [6]	17.5 ($\underline{138}$)
R = *t*-C_4H_9	0.00 (63) [6]	22.5 (−72) [6]	7.44 ($\underline{136}$)
(B) Relative abundance			
R = CH_3	82.0	5.0	13.0
R = C_2H_5	86.0	3.4	10.6
R = *i*-C_3H_7	91.9	0.7	7.4
R = *t*-C_4H_9	95.3	0.0	4.7

a) Optimized torsion angles R–C–C–Ph, $\phi/^\circ$ are given in the parentheses. b) Number in the bracket for rotamer **a** and **b** indicates the number of atoms forming the intramolecular CH/π hydrogen bond. c) Torsion angles deviated from the standard value are underlined.



a (ϕ ~ 60°) **b** (ϕ ~ -60°) **c** (ϕ ~ 180°)

Fig. 2. Three stable conformations of alkylbenzenes $CH_3CH(C_6H_5)CH_2R$: 2-phenylbutane (R = CH_3), 2-phenylpentane (R = C_2H_5), 2-methyl-4-phenylpentane (R = *i*-C_3H_7), and 2,2-dimethyl-4-phenylpentane (R = *t*-C_4H_9). Dotted lines indicate CH/ interactions. Arrows show repulsive steric interactions.

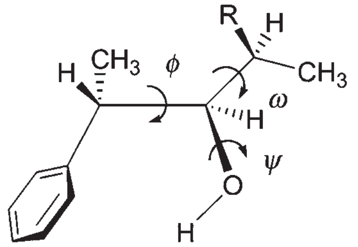


Fig. 3. Angles defined for the torsion about the C_{ipso}–$C_{benzylic}$–C–R (ϕ), $C_{benzylic}$–C–O–H (ψ), and $C_{benzylic}$–C–Cα–Cβ (ω) bonds.

C_4H_9). For 2-phenylpentane and 2-methyl-4-phenylpentane, three stable geometries are possible with respect to the rotation around the C–Cα(alkyl) bond; the number of stable rotamer increases to 9, accordingly.

It is noted that rotamer **a** is the most stable in every case. In this rotamer, R is *gauche* to Ph and *anti* to Me (torsion about the central C–C bond ϕ 53–68°). The result is compatible with previous data obtained for related aralkyl compounds. Thus, in alkyl 1-phenylethyl ketones (ϕ 71–93°) and sulfoxides (ϕ 45–67°), the geometry corresponding to rotamer **a** has been found to be the most stable. In the above ketones and sulfoxides, rotamer **b** (ϕ ca. −60°, whereby R is flanked by Me and Ph (allegedly the most crowded one), was often the next most stable. This suggests that the CH/π interaction is the dominant factor in controlling the conformation of these aralkyl molecules. In the present case of hydrocarbons, rotamer **c** (R/Ph *anti*: ϕ ca. 180°) has been found to be more stable than rotamer **b**.[14] In Table 1 we note that the value of ϕ in one of the geometries corresponding to **c** deviates (136–142°) from the standard angle. The departure from the standard value is understood in terms of a steric clash that may occur between one of the methyl groups in R and Me. Figure 2 shows the interactions involved in **1**.

Conformational Energy of 1-Alkyl-2-phenylpropan-1-ols. Unlike the compounds previously studied, **2** and **3** bear a hydroxy group, which has freedom to rotate around the C–C–O–H bond. Therefore, we define angles ϕ, ψ, and ω, respectively, for torsion about the C_{ipso}–$C_{benzylic}$–C–R, $C_{benzylic}$–C–O–H, and $C_{benzylic}$–C–Cα–Cβ bonds (Fig. 3). Rotation around one of these bonds will give rise to three energy minima. Thus, nine stable rotamers may be obtained when R = methyl or *t*-butyl. For R = ethyl and isopropyl, we must consider the rotation around the C–C–Cα–Cβ bond (ω); 27 geometries are possible in these cases.

Table 2 lists the relative steric energy of the stable conformations of alcohol diastereoisomers $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**: 3-phenylbutan-2-ol (R = CH_3), 2-phenylpentan-3-ol (R = C_2H_5),[15] 2-methyl-4-phenylpentan-3-ol (R = *i*-C_3H_7),[16] and 2,2-dimethyl-4-phenylpentan-3-ol (R = *t*-C_4H_9).[17]

Perusal of Table 2 demonstrates that rotamer **a** is favorable in many cases. Thus, in **2**, this type of geometry is the most stable, irrespective of the nature of R, a result consistent with the notion that the CH/π interaction is an important factor in controlling the conformation of aralkyl compounds. In **3**, rotamer **a** is one of the most stable, and is almost the only rotamer when R = *t*-butyl. The result suggests that an unfavorable steric clash occurs in rotamers **b** and **c**, between Me and *t*-Bu; this certainly overrides the influence from other effects.

One of the geometries corresponding to rotamer **c** is also favorable; this is the most stable one in the methyl, ethyl, and isopropyl homologues of **3**. The stability of rotamer **c** may be ascribed to the OH/π interaction (Fig. 4). Besides the stabilizing effect of the CH/π and CH/O hydrogen bonds, the OH/π interaction seems to play an appreciable role in stabilizing the respective rotamers. Thus, rotamer **b** in **2**, whereby the attractive OH/π bond may operate, is more stable than that in **3**; the OH/π interaction cannot occur in rotamer **b** of **3**. It is noteworthy in

Table 2. Relative Gibbs Energies (in kJ mol^{-1}) at 298 K and 1 atm (101.325 kPa) of the Three Stable Conformations (**a**, **b**, **c**) of Diastereomeric 1-Alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**. 3-Phenylbutan-2-ol (R = CH_3), 2-Phenylpentan-3-ol (R = C_2H_5), 2-Methyl-4-phenylpentan-3-ol (R = i-C_3H_7), and 2,2-Dimethyl-4-phenylpentan-3-ol (R = t-C_4H_9). Data for the Primary Alcohol (R = H) are Listed for Comparison

	Rotamer **a**	Rotamer **b**	Rotamer **c**
(A) $CH_3CH(C_6H_5)CH(R)OH$ **2**			
R = CH_3	0.18 (57)[a)]	2.35 (−64)	4.85 (161)
	1.85 (61)	7.66 (−52)	1.29 (178)
	0.00 (56)	6.86 (−53)	7.36 (157)
R = C_2H_5	1.25 (56)	8.17 (−53)	6.12 (160)
	1.36 (61)	7.74 (−51)	0.74 (178)
	0.00 (57)	2.51 (−64)	7.95 (156)
	2.15 (53)	17.8 (−40)	16.6 (145)
	4.00 (57)	20.1 (−40)	14.4 (176)
	3.91 (52)	13.7 (−58)	19.2 (145)
	7.42 (58)	16.5 (−52)	6.58 (168)
	8.77 (60)	17.8 (−52)	3.36 (179)
	7.18 (58)	15.2 (−59)	9.74 (157)
R = i-C_3H_7	0.00 (52)	14.9 (−53)	4.90 (170)
	0.17 (56)	14.6 (−53)	0.36 (178)
	0.06 (51)	11.2 (−60)	7.51 (160)
	9.79 (56)	23.9 (−39)	15.2 (143)
	12.2 (76)	19.0 (−40)	11.8 (175)
	10.8 (71)	14.9 (−57)	16.4 (142)
	7.50 (60)	26.1 (−47)	14.7 (144)
	10.3 (62)	28.5 (−48)	14.1 (173)
	10.0 (58)	27.8 (−56)	17.6 (143)
R = t-C_4H_9	0.00 (60)	16.1 (−48)	6.28 (142)
	0.31 (64)	16.1 (−49)	1.17 (172)
	1.13 (59)	15.7 (−57)	5.64 (141)

	Rotamer **a**	Rotamer **b**	Rotamer **c**
(B) $CH_3CH(C_6H_5)CH(R)OH$ **3**			
R = CH_3	2.85 (51)	8.32 (−68)	9.38 (179)
	0.48 (64)	9.87 (−64)	8.95 (175)
	4.86 (49)	8.23 (−69)	0.00 (175)
R = C_2H_5	3.96 (48)	8.79 (−66)	10.1 (178)
	2.26 (63)	9.45 (−66)	8.62 (173)
	6.42 (47)	7.49 (−69)	0.00 (175)
	3.37 (52)	20.1 (−54)	21.1 (178)
	0.06 (64)	24.0 (−50)	20.4 (178)
	3.63 (49)	19.0 (−59)	10.6 (176)
	11.0 (58)	18.5 (−78)	10.5 (179)
	10.9 (63)	19.7 (−75)	10.7 (178)
	12.9 (56)	18.5 (−77)	1.85 (177)
R = i-C_3H_7	3.93 (49)	20.3 (−80)	28.6 (143)
	2.03 (65)	21.0 (−79)	shoulder
	4.27 (48)	19.0 (−79)	15.8 (150)
	7.87 (64)	21.1 (−67)	shoulder
	10.0 (57)	18.4 (−67)	12.7 (175)
	8.87 (60)	20.3 (−51)	21.8 (179)
	12.6 (67)	28.1 (−56)	10.1 (180)
	13.6 (56)	31.9 (−54)	0.00 (178)
	10.5 (57)	29.5 (−57)	9.05 (177)
R = t-C_4H_9	0.58 (68)	23.3 (−75)	shoulder
	1.20 (57)	20.0 (−75)	6.07 (176)
	0.00 (59)	21.6 (−56)	15.57 (179)
(C) $C_6H_5CHCH_3CH_2OH$			
	6.90 (50)	5.90 (−65)	8.65 (178)
	2.75 (62)	6.85 (−61)	8.28 (178)
	8.28 (45)	5.33 (−66)	0.00 (176)

a) Optimized torsion angles R–C–C–Ph, ϕ/° are given in the parentheses. Data corresponding to the OH/π-interacted ones are underlined.

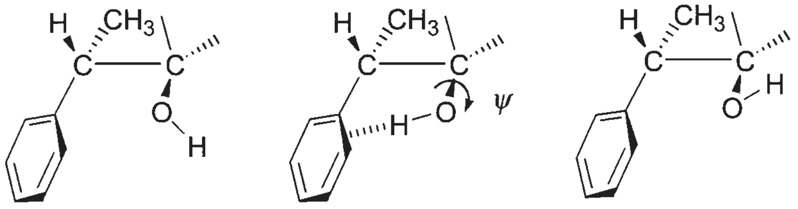


Fig. 4. Three possible conformations of alcohols **2** and **3** (R = CH_3) around the torsion $C_{benzylic}$–C–O–H (ψ).

this regard that one of the three rotamers (Table 2, underlined) is more favorable than the other two. The most stable one among the three rotamers involves the OH/π hydrogen bond. Such an effect is only noted in rotamers **b** and **c** of **2**, and in rotamers **a** and **c** of **3**; in these geometries the OH/π bond is expected to occur. In support of this suggestion, ϕ is normal in the OH/π-interacted (more stable) rotamers, while in the non-interacted ones they are often recorded as irregular ϕ values. Figure 5 gives stereo views of the three conformations of rotamer **a** of methyl homologues around the torsion $C_{benzylic}$–C–O–H (ψ).

CH/π and OH/π Distances of 1-Alkyl-2-phenylpropan-1-ols. Table 3 compiles the interatomic distances of the CH/π and OH/π-interacted geometries; only rotamers with a relative conformational energy <4.18 kJ mol^{-1} are listed. It is remarkable that the distance CH/C_{ipso} is shorter, in most cases, than the CH/C_{ortho} distance. This shows that 5- or 6-member intramolecular CH/π bonds occur at C_{ipso}, and contribute to stabilizing rotamer **a**.

The OH/C_{ortho} distance is shorter than the OH/C_{ipso} distance in almost every case, suggesting that the OH group prefers the *ortho* carbon. In rotamer **c** of **3**, however, the OH/C_{ipso} distance is found to be the shortest in every case (<2.4 Å, underlined). The OH/π interaction at C_{ipso} seems to be preferred, if CH/π or other interactions do not occur concurrently.

In Table 3 are also given distances from OH to the midpoint of the two carbon atoms (OH/$C_{midpoint}$). It is noted that, in **2**, the distance OH/$C_{midpoint}$ is shortest among the three OH/C distances.[18] The OH group may form a bifurcated hydrogen bond with C_{ipso} and C_{ortho}. Oki and Iwamura pointed out this

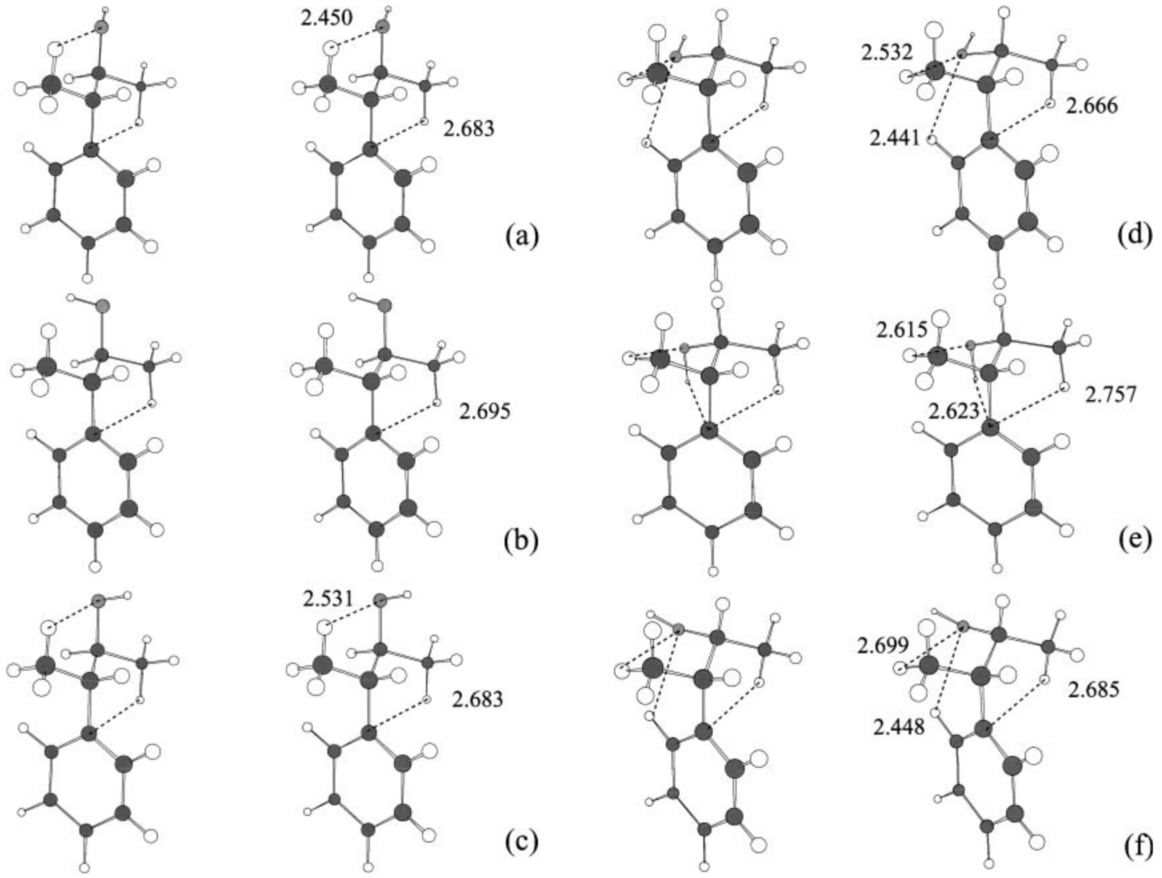


Fig. 5. Stereo views of the three conformations of rotamer **a** of methyl homologues around the torsion $C_{benzylic}$–C–O–H. (a) **2** ($\phi = 57°$, $\psi = 180°$), (b) **2** ($\phi = 61°$, $\psi = 69°$), (c) **2** ($\phi = 56°$, $\psi = 291°$), (d) **3** ($\phi = 51°$, $\psi = 176°$), (e) **3** ($\phi = 64°$, $\psi = 68°$), (f) **3** ($\phi = 49°$, $\psi = 291°$). Dotted lines show putative CH/π, OH/π, and CH/O hydrogen bonds; the interatomic distances are given in Å.

possibility for ω-arylalkanols[19] and 2-hydroxybiphenyls[20] by analyzing the electronic substituent effect in the infrared spectra.

Rotameric Abundance of 1-Alkyl-2-phenylpropan-1-ols. The number of possible rotamers is numerous, and it is difficult to take an overview of the whole aspect. In the following discussion, we consider the conformational equilibria rather than the stability of each rotamer. Table 4 summarizes the abundance of the three stable rotamers estimated according to the Boltzmann distribution. In general, we see rotamer **a** to be the most populated, and rotamer **c** to be the second one. Rotamer **b** is the least populated.

The above result can be understood in terms of the interplay of various molecular forces (Fig. 6). The attractive forces are the CH/π, OH/π, and CH/O hydrogen bonds. The stability of rotamer **a** is ascribed to the CH/π interaction. The stability of rotamer **c** is attributed to the OH/π hydrogen bond. In rotamer **c**, the OH/π interaction may work in both diastereomeric alcohols. Table 4 also gives the rotameric abundance of the unsubstituted alcohol, 2-phenyl-1-propanol. In this molecule, the CH/π interaction does not occur due to the absence of an alkyl group. Rotamer **c** is the most abundant; this again illustrates the stabilizing effect of the OH/π hydrogen bond. The CH_3/O hydrogen bond may operate in rotamers **a** and **c** of **2** and in **a** and **b** of **3**.

The destabilizing interactions are of steric (repulsive van der Waals) origin: Me vs R and H vs H. According to Allinger, the steric congestion between *gauche* vicinal CH groups is very severe.[21] The C–H bond length is ca. 1.08 Å, while that of C–C is ca. 1.54 Å. The vicinal *gauche* CHs are close to each other in this molecular circumstance. An unfavorable steric effect might thus become greater relative to that from the *gauche* H/R relationship.[22] The attractive CH/π interaction and destabilizing Me/R interaction bring rotamer **a** to preponderate in most cases. The Me/R repulsion will make rotamer **b** unfavorable, especially when R is isopropyl or *t*-butyl. In **2**, rotamer **c** is destabilized by two kinds of unfavorable steric effects (R/Me, H/H), while in **3** the vicinal H/H interaction does not occur. The abrupt drop in the population of rotamer **c** in *t*-butyl **3** is noteworthy. This might occur by the unfavorable Me/*t*-Bu interaction. Such an effect does not occur in **2**, however. At present we have no explanation for this.

Comparison of the Computational Results with Experimental Data. Kodama et al. studied the conformation of a diastereomeric pair of 2,2-dimethyl-4-phenylpentan-3-ol (**2** and **3**, R = t-C_4H_9).[23] Based on a simulation of the lanthanoide shift reagent-induced chemical shifts (LIS), they concluded rotamer **a** to prevail in the conformational equilibrium of both the diastereoisomers. This conclusion was supported by ^{13}C NMR data; the carbon signal attributed to the benzylic methyl group

Table 3. Interatomic CH/C and OH/C Distances (Å) of the Stable Conformations of Diastereoisomeric Alcohols, $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**, Calculated by the Ab Initio Method: MP2/6-311G(d,p)//MP2/6-31G(d). In the Parentheses are Relative Gibbs Energies

			CH/π distance		OH/π distance		
		ϕ/°	C_{ipso}	C_{ortho}	C_{ipso}	C_{ortho}	$C_{midpoint}$
2	R = CH_3	57 (0.18)	2.684	3.106			
		61 (1.85)	2.695	3.057			
		56 (0.00)	2.684	3.125			
		−64 (2.35)	2.794	2.764	2.555	2.514	2.436
		178 (1.29)			2.514	2.475	2.394
	R = C_2H_5	56 (1.25)	2.620	3.074			
		61 (1.36)	2.622	2.971			
		57 (0.00)	2.604	3.035			
		53 (2.15)	2.691	2.998			
		57 (4.00)	2.684	3.094			
		52 (3.91)	2.675	2.970			
		−64 (2.51)	2.783	2.761	2.541	2.505	2.424
		178 (0.74)			2.523	2.480	2.401
		179 (3.36)			2.489	2.466	2.376
	R = i-C_3H_7	52 (0.00)	2.628	2.915			
		56 (0.17)	2.605	3.096			
		51 (0.06)	2.592	2.922			
		178 (0.36)			2.470	2.456	2.360
	R = t-C_4H_9	60 (0.00)	2.486	2.725			
		64 (0.31)	2.496	2.674			
		59 (1.13)	2.490	2.709			
		172 (1.17)			2.484	2.440	2.360
3	R = CH_3	51 (2.85)	2.667	3.063			
		64 (0.48)	2.757	2.853	2.623	2.495	2.461
		175 (0.00)			2.383	2.629	2.409
	R = C_2H_5	48 (3.96)	2.669	2.903			
		63 (2.26)	2.737	2.848	2.617	2.480	2.451
		52 (3.37)	2.629	3.049			
		64 (0.06)	2.747	2.843	2.597	2.474	2.437
		49 (3.63)	2.669	2.907			
		175 (0.00)			2.374	2.624	2.402
		177 (1.85)			2.380	2.593	2.388
	R = i-C_3H_7	49 (3.93)	2.645	2.858			
		65 (2.03)	2.748	2.853	2.576	2.443	2.410
		178 (0.00)			2.377	2.579	2.379
	R = t-C_4H_9	68 (0.58)	2.607	2.631	2.686	2.460	2.477
		57 (1.20)	2.541	2.791			
		59 (0.00)	2.538	2.791			

Table 4. Relative Abundance (%) of the Three Stable Rotamers of Diastereomeric 1-Alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**. Data for 2-Phenyl-1-propan-1-ol (R = H) are Given for Comparison

	Rotamer **a**	Rotamer **b**	Rotamer **c**
$CH_3CH(C_6H_5)CH(R)OH$ **2**			
R = CH_3	65.2	13.5	21.3
R = C_2H_5	65.2	9.4	25.4
R = i-C_3H_7	73.6	0.5	22.6
R = t-C_4H_9	75.6	0.2	24.2
$CH_3CH(C_6H_5)CH(R)OH$ **3**			
R = CH_3	52.9	3.7	43.4
R = C_2H_5	56.6	2.7	40.8
R = i-C_3H_7	47.1	0.1	52.8
R = t-C_4H_9	96.5	0.0	3.5
$C_6H_5CH(CH_3)CH_2OH$			
	24.2	15.4	60.4

was shifted upfield in **2** (δ 16.5) compared to that of **3** (δ 22.4). A greater γ-effect is anticipated for rotamer **a** of **2**, where OH is closer to Me in **2** than in **3** (Fig. 6). The above conclusion is consistent with the present computational result.

They also studied the conformation of diastereomeric pairs of alkyl 1-alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**, whereby a lower alkyl group replaced the t-butyl group:[24] 3-phenylbutan-2-ol (R = CH_3), 2-phenylpentan-3-ol (R = C_2H_5), and 2-methyl-4-phenylpentan-3-ol (R = i-C_3H_7).[25] On the same experimental ground, they concluded that rotamer **a** was generally the most populated. This agrees with the present results. However, in the above paper they reported that rotamer **b** was more preponderate than rotamer **c**, though the difference is small. This does not agree with the present results. At present, the reason remains unclear. A possibility is that complexation of the lanthanoide shift-reagent to the hydroxy group perturbed the formation of the

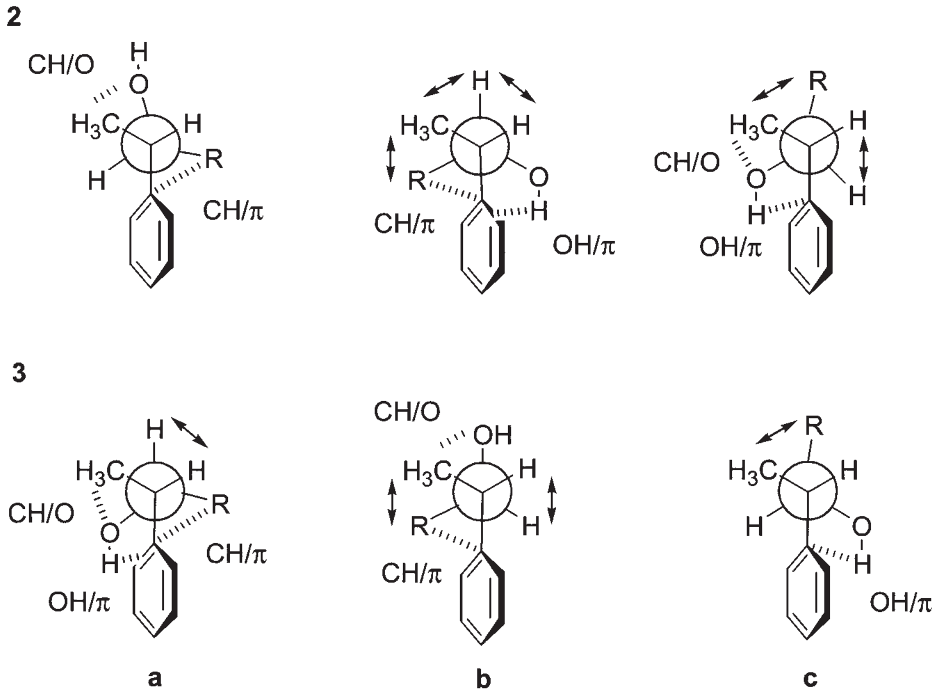


Fig. 6. Stable conformations of 1-alkyl-2-phenylpropan-1-ols $CH_3CH(C_6H_5)CH(R)OH$ **2** and **3**: 3-phenylbutan-2-ol ($R = CH_3$), 2-phenylpentan-3-ol ($R = C_2H_5$), 2-methyl-4-phenylpentan-3-ol ($R = i\text{-}C_3H_7$), and 2,2-dimethyl-4-phenylpentan-3-ol ($R = t\text{-}C_4H_9$). Dotted lines indicate CH/π, OH/π, and CH/O interactions. Arrows show repulsive steric interactions.

Table 5. Relative Abundance of the Stable Rotamers of Alkyl 1-Phenylethyl Sulfoxides $C_6H_5CHCH_3SO\text{–}R$

	Rotamer **a**	Rotamer **b**	Rotamer **c**
Sulfoxides **4**			
$R = CH_3$	77.1	14.2	8.7
$R = C_2H_5$	88.8	6.5	4.7
$R = i\text{-}C_3H_7$	90.1	4.1	5.8
$R = t\text{-}C_4H_9$	87.5	0.1	12.4
Sulfoxides **5**			
$R = CH_3$	84.7	15.1	0.2
$R = C_2H_5$	88.4	11.1	0.5
$R = i\text{-}C_3H_7$	94.3	5.4	0.3
$R = t\text{-}C_4H_9$	99.7	0.2	0.1

OH/π bonding to skew the estimation of the conformational equilibria by the experiments. Another possibility is that the experiments gave an incorrect conclusion due to an inappropriate model in the simulation procedure (e.g., wrong assumption for the LSR···O–S distance or the lanthanoide distribution). In any event, the present computational results correspond to the vapor phase (or in vacuo) conformation, whereas the experiments were carried out in solution.

Comparison of the Conformation of Alcohols with Sulfoxides. Table 5 gives the rotameric abundance of sulfoxide diastereoisomers **4** and **5**, computed by the conformational energies reported in our previous paper.[2] The configuration of **4** and **5** relates to **2** and **3**, respectively. An interesting point is the greater abundance of rotamer **b** noted for the sulfoxides, as compared to the alcohols. The stability of rotamer **b** (vs **c**) in sulfoxides may reflect the differences between the distance and angle parameters C–C vs C–S bonds. The difference in the structure between the alcohols and the sulfoxides also resides in the presence of a CHOH group in the former in place of S–O in the latter. The formation of an OH/π hydrogen bond is possible in **2** and **3**, while this cannot occur in the sulfoxides. A repulsive electrostatic interaction between the S–O dipole and the quadrupole of Ph in **4** and **5** may also be responsible for the low abundance of rotamer **c** in the sulfoxides.

Conclusion

Ab initio MO calculations of the steric energy of 1-alkyl-2-phenylpropan-1-ols and related hydrocarbons have revealed that the conformer whereby the alkyl group is *gauche* to phenyl and *anti* to the benzylic methyl group preponderates in every case. The result is consistent with the notion that the CH/π interaction is a dominant factor in determining the conformational equilibrium of aralkyl compounds. The next most populated one has been found to be a rotamer bearing the OH group close to the phenyl group. This indicates a significance of the OH/π hydrogen bond. We conclude that understanding weak nonconventional hydrogen bonds including the CH/π, OH/π, and CH/O[1,2,26] interactions is vital for elucidating stereochemical issues in organic chemistry. A potential role of the unfavorable *gauche* H/H interaction has been suggested. Stereochemical problems, remaining unsettled to these days, will become clearer in the context of the new paradigm. The necessary parameters for these molecular forces should be implemented in future versions of the force-field program.

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16 **2**: $(3R,4R/3S,4S)$; **3**: $(3R,4S/3S,4R)$ for R = isopropyl.

17 **2**: $(3R,4S/3S,4R)$; **3**: $(3R,4R/3S,4S)$ for R = *t*-butyl.

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