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Intramolecular Hydrogen Bonding and Conformations of α,α-Dialkyl- and α-Alkyl-*o*-methoxybenzyl Alcohols. II. Enthalpies of Hydrogen Bond Formation and Molecular Force Field Calculations on α-Alkyl-substituted Benzyl Alcohols

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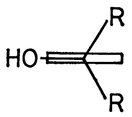
Enthalpies of intramolecular hydrogen bond formation (ΔH) were determined for a series of α-mono- and α,α-dialkyl-*o*-methoxybenzyl alcohols and related compounds. The $-\Delta H$ values of the unsubstituted and α,α-dialkyl-*o*-methoxybenzyl alcohols are more than 2.5 kJ mol^{-1}, while those for the corresponding α-monoalkyl derivatives are at most 1 kJ mol^{-1}. This tendency is in accordance with the results on their $\Delta\nu_{OH}$ and $\varepsilon_b/\varepsilon_f$ values, showing the hydrogen bonded conformations of the α-monoalkyl derivatives are less favorable than those of the other alcohols in discussion. Molecular force field calculations on α-alkyl- and α,α-dialkylbenzyl alcohols were also carried out. The results shows that the hydroxyl/aryl coplanar conformation ($\omega=0°$) is the most stable for the unsubstituted and α,α-dialkylbenzyl alcohols and the hydroxyl/aryl non-coplanar conformation ($\omega=30°$) for α-alkylbenzyl alcohols. Since the OH···O distance might be farther and, hence, the overlap between the unshared electron pairs on the methoxyl oxygen and the anti-bonding OH orbital might be less in the non-coplanar conformation, α-monoalkyl-*o*-methoxybenzyl alcohols are less favorable than the corresponding α,α-dialkyl derivatives in the intramolecular hydrogen bond formation.

The conformations of several benzyl alcohols have been discussed by the measurement of infrared and NMR spectra. Thus Ōki and Iwamura have concluded the existence of weak attractive interaction similar to hydrogen bonding between hydroxyl group and aromatic π-electron system.[1)] The OH···π interaction might be favored when the hydroxyl group approached from upright the plane of aromatic nucleus, taking conformation II. On the other hand, α,α-di-*t*-butylbenzyl alcohol is a highly crowded molecule, the rotation around the C(benzyl)–C(aromatic) bond being so slow as to make it possible to observe the signals of 2- and 6-protons separately by ^{1}H-NMR measurement.[2,3)] This fact strongly suggests that conformer I or a similar one predominates over conformer II. We have also measured the infrared OH stretching absorptions and ^{1}H-NMR of α-alkyl-*o*-methoxybenzyl alcohols and discussed on their conformations.[4)] A remarkable difference in the preference of hydrogen-bonded conformer has been observed between the α-monoalkyl and α,α-dialkyl-substituted derivatives.



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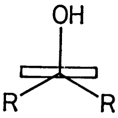


II

In order to study further on this point, the enthalpies of the intramolecular hydrogen bond formation are determined with these alcohols. The most favorable conformers are also estimated theoretically by the molecular force field approaches.

Experimental

Preparation of Materials. Unsubstituted and α,α-dialkylbenzyl alcohols were prepared by the known procedures.[5,6)] α-Monoalkylbenzyl alcohols were obtained by the Grignard reactions of *o*-methoxybenzaldehyde with the corresponding alkylmagnesium bromides. 2-Methoxy-α,α,3,5-tetramethylbenzyl alcohol was prepared similarly by the addition reaction to acetone of 2-methoxy-3,5-dimethylphenylmagnesium bromide, which was derived from 2,4-xylenol. Bp 89.0—90.0 °C/2 mmHg; MS (70 eV) *m*/*e*, 194.

Measurement of Infrared Spectra. Infrared OH stretching absorptions were recorded with a Hitachi Model 225 grating infrared spectrophotometer. The temperature dependence measurements were carried out on the dilute carbon tetrachloride solutions at the temperature ranging from 290 to 312 K. Throughout each measurement, temperature of the solution was kept sufficiently constant (The temperature variation was kept within 0.5 K). The results are given in Table 1. The enthalpies of the hydrogen bond formation was obtained as the gradients of the $\log_{10}(\varepsilon_b/\varepsilon_f)$ *vs.* $1/T$ plot by the least squares calculations.

The measurements were carried out within a relatively narrow range of temperature. Since the influence of temperature dependent broadening were shown to be negligible with some typicals of the absorption bands in this range of temperature, the peak heights (absorbance) of the bands were used to evaluate the relative equilibrium constants instead of integrated intensities. Fortunately the free and the hydrogen-bonded bands were rather well resolved, which made possible to use the peak intensities without any correction for the effect of the overlapping bands in most instances.

Molecular Force Field Calculations. We have employed the empirical force field proposed by Allinger and coworkers[7)] to calculate steric energies and geometries of the benzyl alcohols. The geometries corresponding to the potential minima were obtained by the full optimization calculations, while the other labile conformations were calculated by restricting the torsional angle around C(aryl)–C(benzyl) bond.

Results and Discussion

The infrared OH absorptions of some newly prepared α,α-dialkylbenzyl alcohols, 1-(*o*-methoxyphenyl)cycloalkanols and 2-(8-chromanyl)-2-propanol are given in Table 2. The strength of hydrogen bond can be evaluated by the hydrogen bond shift ($\Delta\nu_{OH}$) of the

TABLE 1. THE TEMPERATURE DEPENDENCE DATA

T/K	ε_f/l mol^{-1} cm^{-1}	ε_b/l mol^{-1} cm^{-1}
a) *o*-Methoxybenzyl alcohol (**3**), $c=4.95\times10^{-3}$ mol/l.		
295.7	27.6	54.3
303.1	29.0	54.2
309.2	28.4	52.1
315.3	29.1	50.5
321.2	29.4	50.0
b) α-Methyl-*o*-methoxybenzyl alcohol (**4**), $c=4.84\times10^{-3}$ mol/l.		
292.8	51.4	27.2
297.8	51.7	27.0
302.8	51.8	26.9
309.8	50.7	25.8
317.8	49.0	24.8
c) α-Ethyl-*o*-methoxybenzyl alcohol (**5**), $c=3.94\times10^{-3}$ mol/l.		
293.0	51.9	28.6
300.4	51.1	28.0
307.2	50.5	27.4
314.2	50.5	28.1
321.3	50.2	26.9
d) α-Isopropyl-*o*-methoxybenzyl alcohol (**6**), $c=5.00\times10^{-3}$ mol/l.		
292.6	59.5	30.1
299.3	58.8	29.3
307.2	57.2	28.6
313.8	55.6	27.0
320.1	56.5	27.6
e) α-*t*-Butyl-*o*-methoxybenzyl alcohol (**7**), $c=4.28\times10^{-3}$ mol/l.		
293.5	49.1	24.3
299.6	47.8	23.8
307.3	46.1	22.7
313.6	45.9	22.6
319.7	45.7	22.4
f) α,α-Dimethyl-*o*-methoxybenzyl alcohol (**8**), $c=4.98\times10^{-3}$ mol/l.		
293.2	22.8	97.9
300.0	22.9	92.7
308.1	22.9	87.3
314.8	23.7	86.0
321.3	24.9	85.1
g) α,α-Diethyl-*o*-methoxybenzyl alcohol (**9**), $c=5.07\times10^{-3}$ mol/l.		
293.3	40.6	68.1
299.9	40.7	65.8
308.8	39.6	62.6
316.2	38.5	60.6
322.8	38.2	58.2
h) α,α-Dipropyl-*o*-methoxybenzyl alcohol (**10**), $c=4.70\times10^{-3}$ mol/l.		
292.4	38.4	60.7
297.9	37.1	58.0
305.8	37.5	56.6
312.9	38.0	55.5
318.6	38.1	54.9
i) α,α-Diisopropyl-*o*-methoxybenzyl alcohol (**11**), $c=3.10\times10^{-3}$ mol/l.		
292.6	24.2	132.9
297.3	24.4	130.6
302.2	24.5	128.4
310.2	25.0	124.5
318.6	25.5	120.1
j) α,α-Dibutyl-*o*-methoxybenzyl alcohol (**12**), $c=4.54\times10^{-3}$ mol/l.		
292.6	40.7	67.1
297.2	40.7	65.6
304.3	40.1	63.0
310.0	39.4	62.3
315.6	38.4	60.0
k) α,α-Di-*t*-butyl-*o*-methoxybenzyl alcohol (**13**), $c=3.22\times10^{-3}$ mol/l.		
295.6	20.0	118.0
301.6	20.1	114.5
307.7	20.3	110.2
314.7	21.0	108.5
319.2	21.3	108.2
l) α,α-Dipentyl-*o*-methoxybenzyl alcohol (**14**), $c=4.45\times10^{-3}$ mol/l.		
293.1	40.8	66.5
299.1	41.6	64.8
307.4	41.2	63.0
314.2	41.2	60.9
319.3	40.5	60.1
m) 1-(*o*-Methoxyphenyl)cyclopentanol (**15**), $c=4.06\times10^{-3}$ mol/l.		
294.2	22.0	62.6
301.2	22.1	60.8
309.5	22.1	59.5
316.9	22.2	58.5
322.0	22.2	57.1
n) 1-(*o*-Methoxyphenyl)cyclohexanol (**16**), $c=3.89\times10^{-3}$ mol/l.		
293.2	15.3	90.7
299.9	16.3	88.7
307.4	17.6	88.2
313.3	18.0	86.6
319.2	18.7	84.3
o) 1-(*o*-Methoxyphenyl)cycloheptanol (**17**), $c=4.37\times10^{-3}$ mol/l.		
291.4	14.2	82.5
298.0	14.0	79.5
303.8	14.2	77.8
308.5	15.0	76.8
315.0	14.5	73.9

Table 1. (Continued)

T/K	ε_f/l mol^{-1} cm^{-1}	ε_b/l mol^{-1} cm^{-1}	T/K	ε_f/l mol^{-1} cm^{-1}	ε_b/l mol^{-1} cm^{-1}
p) 2-(8-Chromanyl)-2-propanol (**18**), c=4.05×10^{-3} mol/l.			q) 2-Methoxy-α,α,3,5-tetramethylbenzyl alcohol (**19**), c=3.98×10^{-3} mol/l.		
293.6	9.1	62.3	294.0	19.7	51.9
301.4	9.1	59.3	301.5	19.8	49.6
308.7	9.1	56.3	309.4	20.2	48.6
315.0	9.8	56.6	315.8	20.2	47.2
321.9	10.0	55.2	322.2	20.3	46.1

Table 2. OH stretching absorptions of some *o*-methoxybenzyl alcohols and related compounds

Compd No.	Substituent R$_1$	R$_2$	ν_f (ε_f)[a]	ν_b (ε_b)[a]
3	H	H	3637 (27.6)	3607[c] (54.3)
10	n-C$_3$H$_7$	n-C$_3$H$_7$	3619 (38.4)	3557 (60.7)
11	i-C$_3$H$_7$	i-C$_3$H$_7$[b]	3616 (24.3)	3542 (132.9)
12	n-C$_4$H$_9$	n-C$_4$H$_9$	3619 (40.7)	3557 (67.1)
13	t-C$_4$H$_9$	t-C$_4$H$_9$[b]	3616 (20.1)	3508 (114.5)
14	n-C$_5$H$_{11}$	n-C$_5$H$_{11}$	3618 (40.1)	3556 (66.5)
15	-(CH$_2$)$_4$-		3603 (21.1)	3576 (63.4)
16	-(CH$_2$)$_5$-		3604 (18.8)	3567 (112.9)
17	-(CH$_2$)$_6$-		3600 (12.9)	3580 (78.1)
18	2-(8-Chromanyl)-2-propanol		3609 (9.1)	3560 (62.3)
19	2-Methoxy-α,α,3,5-tetramethylbenzyl alcohol		3607 (19.7)	3525 (51.9)

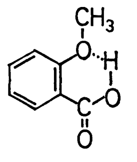
a) Frequencies in cm^{-1} and molar absorptivity in l·mol^{-1}cm^{-1}. Sufixes f and b refer to the free and the intramolecularly hydrogen-bonded species, respectively. b) Diisopropyl and di-*t*-butyl derivatives were re-examined and their spectral data were corrected. c) The ν_{OH} band of the OH···π interacted form of variously substituted benzyl alcohols (XC$_6$H$_4$CH$_2$OH) were shown to appear within a narrow frequency range between 3617.4 and 3616.0 cm^{-1}. (See Ref. 1) Since the frequency of this band is considerably lower, it was assigned to the OH···O interacted form of **3**.

OH stretching band, which is defined as the difference in the OH frequencies of the free and the hydrogen bonded species. The $\Delta\nu_{OH}$ is often related with the OH···O distance of hydrogen bond system.[8] Thus it can be a measure for the strength of the hydrogen bond. The enthalpy of hydrogen bond formation serves as another scale for the strength of the hydrogen bond, being determined from the temperature dependence measurement of the OH absorption intensities of free and hydrogen bonded species.[9] Results are given in Table 3 together with the $\Delta\nu_{OH}$ and $\varepsilon_b/\varepsilon_f$ values.

Enthalpies of Hydrogen Bond Formation and the Hydrogen Bond Shifts of OH Stretching Bands. Enthalpies of intramolecular hydrogen bond formation is generally smaller than those of intermolecular hydrogen bond formation when hydrogen donating and accepting groups are similar. The hydrogen bond enthalpies for the benzyl alcohols are rather small even when compared with those of similar six-membered hydrogen-bonded chelates. The enthalpies of intramolecular hydrogen bond formation (ΔH) for *o*-methoxybenzoic acid (**1**)[10] and 3-methoxy-1-propanol (**2**)[11] have been determined to be −13.8 and −8.8 kJ/mol, respectively.

Table 3. Enthalpies of hydrogen bond formation and ν_{OH} hydrogen bond shifts of *o*-methoxybenzyl alcohols and related compounds

Compd No.	Substituent R$_1$	R$_2$	ΔH/kJ mol^{-1}	$\Delta\nu$/cm^{-1}	$\varepsilon_b/\varepsilon_f$
3	H	H	4.72	30	1.97
4	H	CH$_3$	1.25	36	0.72
5	H	C$_2$H$_5$	0.79	48	0.57
6	H	i-C$_3$H$_7$	1.00	42	0.54
7	H	t-C$_4$H$_9$	0.42	60	0.42
8	CH$_3$	CH$_3$	6.40	58	3.70
9	C$_2$H$_5$	C$_2$H$_5$	2.59	64	1.64
10	n-C$_3$H$_7$	n-C$_3$H$_7$	2.88	62	1.58
11	i-C$_3$H$_7$	i-C$_3$H$_7$	5.48	74	5.47
12	n-C$_4$H$_9$	n-C$_4$H$_9$	2.51	62	1.65
13	t-C$_4$H$_9$	t-C$_4$H$_9$	5.85	108	5.70
14	n-C$_5$H$_{11}$	n-C$_5$H$_{11}$	2.80	62	1.63
15	-(CH$_2$)$_4$-		2.80	27	3.00
16	-(CH$_2$)$_5$-		7.94	37	6.01
17	-(CH$_2$)$_6$-		4.81	20	6.05
18	2-(8-Chromanyl)-2-propanol		6.06	49	6.85
19	2-Methoxy-α,α,3,5-tetramethylbenzyl alcohol		4.18	82	2.64



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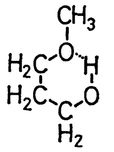

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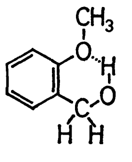
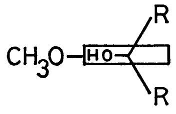


3

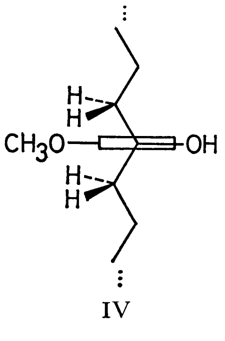
On the other hands, the $-\Delta H$ values for the *o*-methoxybenzyl alcohols in Table 3 are at most 8 kJ/mol, most of them being less than 6 kJ/mol. This is due to the fact that the alcoholic hydroxyl group is a weak hydrogen donor and the oxygen atom of aromatic ether is a weak hydrogen acceptor in forming hydrogen bonds. In compound **1**, the carboxylic OH group is a very strong donor, while the aliphatic ether group in **2** is a stronger hydrogen acceptor than the aromatic ether group in **3**.

When compared among the benzyl alcohols, α-monoalkyl alcohols **4**—**7** have shown to have smaller $\Delta\nu_{OH}$ and $\varepsilon_b/\varepsilon_f$ values than the alcohols in other series, having been supposed to be less favorable in forming hydrogen bonds.[4] This tendency is again obvious with the $-\Delta H$ values in Table 3. The intramolecularly hydrogen bonded conformers of the α-monoalkyl alcohols are at most only 1 kJ/mol more stable than the free conformers, in contrast to the unsubstituted and α,α-dialkyl benzyl alcohols of which hydrogen-bonded conformers are more than 2.5 kJ/mol more stable than the free conformers.

In the series of α,α-dialkylbenzyl alcohols, α,α-diethyl and higher homologous α,α-di(*n*-alkyl) derivatives have considerably low $-\Delta H$ values around 2.5 kJ/mol. The anomalous behavior was first suspected when the $\varepsilon_b/\varepsilon_f$ and $-\Delta H$ values were compared among a series of dialkyl derivatives carrying $CH_{3-n}(CH_3)_n$ groups, where n is 0, 1, 2, and 3. To investigate further on this point, infrared OH stretching absorptions of homologous di(*n*-alkyl) derivatives with propyl, butyl, and pentyl groups were measured, giving very similar ν_f, ν_b, $\Delta\nu_{OH}$, $\varepsilon_b/\varepsilon_f$, and $-\Delta H$ values as shown in Tables 2 and 3. The Hydrogen bond shifts ($\Delta\nu_{OH}$) of dialkyl derivatives increase in the order of the bulkiness of alkyl substituent $[CH_3<C_2H_5<CH(CH_3)_2<C(CH_3)_3]$, revealing no indication of anomaly. The $\Delta\nu_{OH}$ value has been correlated to be nearly inversely proportional to the OH···O distance, giving a measure to the strength of intramolecular hydrogen bond. Thus, the order is rationalized by taking the buttressing effect of the alkyl groups in the intramolecularly hydrogen-bonded conformation (III) into consideration. A strong hydrogen bond is not necessary to be favorable in the equilibrium of its formation reaction, however. The hydrogen bonded conformation can be unfavorable when the steric hindrance and other unfavorable entropy effects in other parts of molecule is serious. Thus the lower $-\Delta H$, as well as the lower $\varepsilon_b/\varepsilon_f$, for **9** and its homologs should be related either to the unfavorable steric effect in other part of the intramolecularly hydrogen bonded conformation or to the favorable steric circumstances in the free conformation. The possible free conformation with extended chain (IV) of α,α-di-*n*-alkylbenzyl alcohols are presumably more stable than those for α,α-diisopropyl- and α,α-di-*t*-butylbenzyl alcohols, because the alkyl-methoxyl repulsion is less in the former. An evidence in support of this explanation was obtained from the measurements on 1-(2-methoxyphenyl)cycloalkanols. Anomalously low ΔH and $\varepsilon_b/\varepsilon_f$ values were not observed with these cyclic alcohols the end of whose alkyl chain are connected to each other. These compounds cannot take the extended chain conformation IV. 1-(2-Methoxyphenyl)cycloalkanols **15**—**17** have the ν_f bands considerably lower than those of other open chain alcohols investigated. They are located between 3604 and 3600 cm^{-1}, assignable to OH···π interacted hydroxyl groups according to the extensive works by Ōki and Iwamura[1b] who attributed the bands at 3620.5 and 3605.2 cm^{-1} of 1-phenylcyclohexanol to the free and the OH···π interacted forms, respectively. The higher ν_{OH} bands of the open chain alcohols **3**—**14**, on the contrary, lies in the frequency region higher than 3616 cm^{-1}. They were assigned to the free OH absorptions according to the fact that the free ν_{OH} bands of 2-phenyl-2-propanol and 3-phenyl-3-pentanol were shown to appear at 3620.6 and 3618.2 cm^{-1}, respectively.[1a]

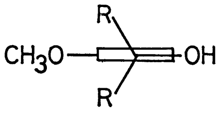


III

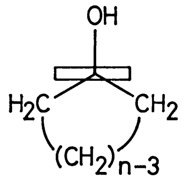


IV

From the results in molecular force field calculations, the free conformers of the dialkyl alcohols without ring structures are estimated to take the OH periplanar conformation V which is unfavorable to have the OH···π interaction. The methoxycycloalkanols **15**—**17**, on the contrary, takes preferably the free conformation (VI) in which the hydroxyl group is clinal to the plane of aromatic ring because of steric hindrance between the alicyclic ring and the *ortho*-methoxyl group expected in conformation V. The conformer VI is supposed to be sterically more crowded than the conformer V of the open chain series. This should be a reason for the larger $-\Delta H$ of the alcohols **15**—**17**. The clinal conformation VI is very favorable to have the OH···π interaction to which the low frequency shifts of the ν_f bands of **15**—**17** is due.



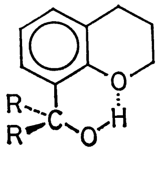
V



n=5, 6, and 7

VI

In order to investigate the effect of the conformation of hydrogen-accepting alkoxyl group upon the hydrogen bonding, 2-(8-chromanyl)-2-propanol (**18**) and 2-methoxy-α,α,3,5-tetramethylbenzyl alcohol (**19**) were prepared and their behavior in intramolecular hydrogen bond formation was examined. The intramolecularly hydrogen bonded conformer of **18** is supposed to take conformation VII, which is very similar to



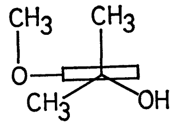
VII

Table 4. Steric energies(E)[a)] and some geometrical parameters[b)] of the benzyl alcohols $C_6H_5CR^1R^2OH$ calculated by use of MMI program

R^1	R^2	E/kJ mol^{-1}				$\angle OC_\alpha C_{ipso}$	$\angle C_\alpha C_{ipso}C_2$	$l(C_{ipso}\text{-}C_\alpha)$
		$\omega=0°$	$\omega=30°$	$\omega=60°$	$\omega=90°$			
H	H	47.40 (0.00)	47.90 (0.50)	48.66 (1.26)	50.70 (3.30)	112.34°	120.85°	1.510 Å
H	CH_3	48.23 (2.25)	45.98 (0.00)	49.78 (3.80)	—	109.53	120.45	1.515 Å
H	C_2H_5	54.59 (2.67)	51.92 (0.00)	54.67 (2.75)	—	109.18	120.36	1.515 Å
H	i-C_3H_7	59.36 (3.60)	55.76 (0.00)	58.31 (2.55)	—	108.90	120.51	1.515 Å
H	t-C_4H_9	76.20 (17.60)	58.60 (0.00)	71.85 (13.25)	—	108.22	120.37	1.524 Å
CH_3	CH_3	44.68 (0.00)	47.44 (2.76)	—	62.24 (17.56)	108.93	120.71	1.525 Å
C_2H_5	C_2H_5	57.89 (0.00)	64.08 (6.19)	—	87.15 (29.26)	109.00	120.64	1.523 Å
i-C_3H_7	i-C_3H_7	84.02 (0.00)	84.77 (0.75)	—	147.89 (63.87)	107.00	120.23	1.531 Å
t-C_4H_9	t-C_4H_9	141.45 (0.00)	146.30 (4.85)	—	251.47 (110.02)	103.75	119.73	1.541 Å

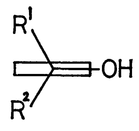
a) The relative values with reference to the most stable conformers are given in parentheses. b) The bond angles and the bond lengths for the most stable conformers are given.

that of **8**. In line with this consequence, the $\Delta\nu_{OH}$ and the $-\Delta H$ values of **18** are very close to those of **8**. The $\varepsilon_b/\varepsilon_f$ value of **18** is significantly larger than the corresponding ratio of **8**, however. The alkoxyl group in **18** is fixed antiperiplanar to the 2-hydroxy-2-propyl moiety by the condensed dihydropyran ring and is favorable entropically to the intramolecular hydrogen bond formation, causing the larger $\varepsilon_b/\varepsilon_f$. Introduction of the 3-methyl group onto the hydrogen bonded molecule as in **19** prevents the antiperiplanar conformation favorable for the hydrogen bonding. Thus, the $-\Delta H$ and $\varepsilon_b/\varepsilon_f$ values of **19** are considerably lower than the corresponding quantities of **8** due to the increase in steric energy and the restriction of the conformation in the hydrogen bonded conformer. In contrast, the $\Delta\nu_{OH}$ increases remarkably because the OH···O distance becomes closer due to the buttresing effect caused by the 3-methyl group. Thus, it is probable that the intramolecular hydrogen bonds can be persistent even in cases when the alkoxyl group is not coplanar to the chelate ring formed by the hydrogen bonding. Similar tendency has been observed with the hydrogen bond chelates containing carboxyl groups as hydrogen donors.[12)] The ethereal oxygen atom can interact with hydroxyl and other hydrogen donating groups in various conformations because it has two pairs of unshared electrons. The alcohol **19** has a low frequency ν_f band locating at 3607 cm^{-1}. Since the 3-methyl group in **19** enforces the methoxyl group to take nonplanar conformation and to approach nearer to the 2-hydroxy-2-propyl moiety, the most favorable conformation of the free species tends to have a nonplanar hydroxyl group favorable to interact with the aromatic π-electrons (just illustrated schematically by VIII).



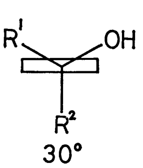
VIII

Estimation of the Most Stable Conformations by Molecular Force Field Approach. The probable conformations of these alcohols were then discussed on the basis of the molecular force field calculations carried out by use of the MMI version of the computer program developed by Allinger and co-workers.[7)] As the force field involving hydrogen bond system has not yet been available, the calculations were carried out on benzyl alcohol and its α-substituted derivatives void of methoxyl group. The results are given in Table 4. Here, in this Table, the torsional angle ω refers to the dihedral angle between the aromatic ring and the hydroxyl group (as illustrated in IX—XII). The results show that the most stable conformation of α-monoalkylbenzyl alcohols are X in which ω is around 30° and that those of α,α-dialkylbenzyl alcohols are IX with $\omega=0°$.[13)] The optimized torsional angles were calculated to be 31.3°, 32.2°, 33.1°, and 34.4° for the most stable conformers of α-methyl, α-ethyl, α-isopropyl, and α-t-butylbenzyl alcohols, respectively.



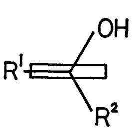
$\omega = 0°$

IX



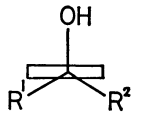
30°

X



60°

XI



90°

XII

As expected from the repulsive force operating between the alkyl and the hydroxyl groups, the torsional angles increase in the same order. Since the methoxyl group on the aromatic ring is ignored in calculations, the results should be applied on the methoxy alcohols **3**—**14** with care. Nevertheless the hydrogen bonded conformations might be rather properly estimated since the methoxyl group lies far from the alkyl group(s).

The results which conclude the conformation X of **4**—**7** with non-coplanar hydroxyl group to be the most stable coincide with the fact that the hydrogen bonded conformers of these alcohols are less favorable than those of the α,α-dialkylbenzyl alcohols as revealed by both the $\varepsilon_b/\varepsilon_f$ and the ΔH values in Table 3. The OH···O distance might become farther and, moreover, the overlap between the unshared electron pairs and the anti-bonding OH orbital might be less in conformation X than in conformation IX. The OH proton signals of **4**—**7** have shown to appear at higher fields than those of the corresponding dialkylbenzyl alcohols. This can be ascribed to the magnetic anisotropy effect on the hydroxyl protons lying above the aromatic rings to induce the high field shifts.

The introduction of α-alkyl groups causes considerable C_α–C_{ipso} bond stretching and O–C_α–C_{ipso} bond angle decrease but little C_α–C_{ipso}–C_2 bond angle alteration. As a result, the estimated distance between the hydroxyl and the methoxyl oxygen atoms decreases from 2.34 to 2.14 Å when the two benzylic hydrogen atoms are replaced with *t*-butyl groups.[14] This explains the $\Delta\nu_{OH}$ increase caused by the introduction of α,α-dialkyl groups. The consequences from the calculations on α,α-di-*t*-butylbenzyl alcohol (**20**) agrees with the fact that the protons at 2- and 6-positions of **20** are not isochronous because of the very high rotational barrier around C_{ipso}–C_{benzyl} bond.[2,3] The conformation IX which is estimated to be the most stable explains the unisochronous ^{1}H-NMR spectrum of **20** together with the rotational barrier supposed to be a little higher than 110 kJ/mol. The extended conformation IV of **9** was also confirmed by the calculation giving the torsional angle near 180° (177.1 and 177.9° exactly) for both of the C_α–$CH_2(CH_3)$ bonds.

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References

1) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **32**, 950 (1959); **35**, 1552 (1962); **36**, 1 (1963).

2) G. P. Newsereff and S. Sternhell, *Tetrahedron Lett.*, **1967**, 2539.

3) P. D. Bartlett, T. R. Steadman, T. T. Tidwell, and P. Weber, *Tetrahedron Lett.*, **1970**, 2915.

4) A. Yamashita, K. Hara, S. Aizawa, and M. Hirota, *Bull. Chem. Soc. Jpn.*, **47**, 2508 (1974).

5) M. Ōki, M. Hirota, H. Satonaka, and T. Hagiwara, *Tetrahedron Lett.*, **1967**, 1785.

6) S. Natelson and S. P. Gottfried, *J. Am. Chem. Soc.*, **61**, 1001 (1939); P. D. Bartlett and A. Schneider, *ibid.*, **67**, 140 (1945).

7) N. L. Allinger and Y. H. Yuh, MMI/MMPI program (1973), QCPE, #318.

8) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

9) Details of our experiments were reported previously. See, for example: M. Hirota, K. Shinozuka, and Y. Hamada, *Bull. Chem. Soc. Jpn.*, **47**, 2696 (1974).

10) M. Davies and D. M. F. Griffiths, *J. Chem. Soc.*, **1955**, 132. See also M. Ōki, M. Hirota, and S. Hirofuji, *Spectrochim. Acta*, **22**, 1537 (1966).

11) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

12) M. Ōki and M. Hirota, *Bull. Chem. Soc. Jpn.*, **36**, 290 (1963).

13) It cannot be deduced straightforwardly from this conclusion that the OH···π interacted conformer is unfavorable in α,α-dialkylbenzyl alcohols. The OH..π interacted conformation is known to be rather flexible, the torsional angle varying in a considerably wide range. As the torsional barriers of benzyl alcohol and its α-methyl-substituted derivatives are rather low, the interacted conformer may become the most stable owing to the additional stabilization due to attractive OH···π interaction.

14) The OH···O(CH_3) distance was calculated by assuming that the coordinates of *ortho*-methoxyl group is exactly the same as those of anisole. Similar calculations on α,α-dimethyl, α,α-diethyl, and α,α-diisopropyl derivatives gave 2.28, 2.28, and 2.23 Å (=10^{-1} nm), respectively, as O···O distances.