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Prefered Orientation and π-Bonding of the Hydroxyl Group in 1,2-Benzocycloalken-3-ols

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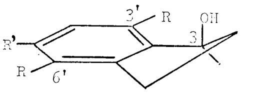
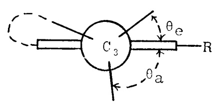
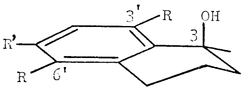
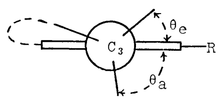
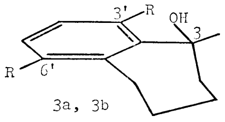
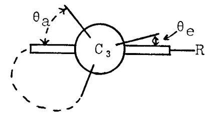
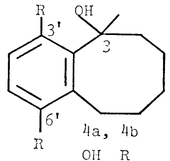
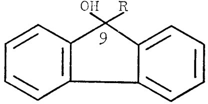
The various values of ν_{OH} of 1,2-benzocycloalken-3-ols observed in dilute CCl_4 solutions have been explained in terms of the inclination angle of the C–O bond to the plane of the benzene ring (θ) and the conformational isomerism of the OH group with respect to the C–O bond. The ν_{OH} shift caused by OH⋯π bonding is angle-dependent, *i.e.*, 9 cm^{-1} if θ=50—90°, or 17 cm^{-1} if θ=38—45°.

Intramolecular OH⋯π bondings have been extensively investigated by IR spectroscopy and have accepted successful application to the conformational and structural elucidation of various systems containing both hydroxyl group and π-source.[1] Oki, Iwamura, *et al.* found the geometry dependence of the π-bonded ν_{OH} or π-bond shift ($\Delta\nu_{OH}$) in biphenyl-2-ols,[2] alkenols,[3] and 2-phenylalkanols.[4] Such dependence has not however been reported in 1-phenylalkanols. The axial and equatorial OH groups of 1,2-benzocyclohexen-3-ols however show π-bonded ν_{OH}'s of 3618 and 3600 cm^{-1} respectively.[4,5]

In the present work, the angular dependence of $\Delta\nu_{OH}$ in a series of 1,2-benzocycloalken-3-ols having different inclination angles between the C–O bond and the plane of the benzene ring (θ's) have been studied. The range of θ has been from 10 to 82°. Table 1 gives the compounds examined and the relevant θ's for the axial and equatorial† C–O bonds (θ_a and θ_e), as measured using Dreiding models. In this work, the cyclopentene, cyclohexene, and cycloheptene rings have been assumed to take the envelope,[6–8] half-chair,[9] and chair conformations,[10–12] respectively. The cyclopentadiene rings of **5**'s have been assumed to be coplanar with the benzene rings.

TABLE 1. INCLINATION ANGLES OF THE C–O BOND, θ_a AND θ_e (°)

Compound		θ_a	θ_e
 1a, 1b, 1c		75	45
 2a, 2b, 2c		82	38
 3a, 3b		50	10
 4a, 4b		—	—
 5a, 5b		60	60

Compound number	R	R′
1a—**5a**	H	H
1b—**5b**	CH_3	H
1c and **2c**	H	NO_2

Results and Discussion

Table 2 gives the ν_{OH} data observed in CCl_4, in which each alcohol exhibits at least one maximum at 3600, 3607, 3616, 3620, or 3626 cm^{-1}. The last ν_{OH} is characteristic of monomeric secondary alcohols[13] and the remaining ν_{OH}'s will be assigned later.

In each compound, the prefered orientation of the C–O bond is determined by at least one of the following factors: (1) the interaction between the equatorial hydroxyl group and the *peri*-substituent (*peri*-interaction), (2) 1,3-diaxial and/or other steric interactions, and (3) OH⋯π bonding. A previous IR study of **2a** and **2b**[5] indicated that an axial orientation, free from factor (1), is prefered. In the IR and NMR studies of substituted 1-tetralols and analogs by Hanaya, *et al.*[14] factor (1) was found to predominate over (2) with a few exceptions. The same will not always apply to the **1**'s and **3**'s, however, since the substituent arrangements in space are different. In the **1**'s where the equatorial hydroxyl and the *peri*-substituent are less eclipsed than in the **2**'s, the *peri*-interaction will be less. In the **3**'s, with the substituents in a more eclipsed position, the *peri*- and also the 1,3-diaxial interactions will be greater. Nevertheless, the prefered orientation will be decided by examining the *peri*-substituent effects on the relative absorption intensities.

The strongest OH bands of **1a** and **1b** appear at 3601 and 3607 cm^{-1} respectively. The shift to higher frequency in **1b** is due to the steric effects of the *peri*-methyl substituent which are expected to cause changes in the population of the OH conformers around the C–O bond and/or conversion of the prefered orientation of the C–O bond. If the former is true and if the most favoured OH conformer of **1a** is that of Type II (see Table 4), this conformer would convert to Type

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† In the text, "axial" and "equatorial" mean "quasi-axial" and "quasi-equatorial," respectively.

Table 2. ν_{OH} data for the benzocycloalken-3-ols in dilute CCl_4 solutions (cm^{-1})

Compound	Substituent	Equatorial, bonded ν_{OH}, ε	Axial, bonded ν_{OH}, ε	Free ν_{OH}, ε
1a	—	3601,[b] 52	3616,[b] sh	3627, br[a]
1b	3′,6′-Dimethyl		3607, 60, 20[c] 3615, sh	
1c	5′-Nitro	3600, 50	3616, sh	3626, 52
2a[5]	—	3603,[d] 32	3618,[d] 50	
2b[5]	3′,6′-Dimethyl		3610, sh 3621, 65	
2c	5′-Nitro	3600, sh	3617, 55	3626, sh
3a	—		3619, 65, 20[c]	3630, br[a]
3b	3′,6′-Dimethyl		3621, 79, 17[c]	
4a	—		3615, 77, 20[c]	
4b	3′,6′-Dimethyl		3620, 80, 18[c]	
5a	—	3601, 110, 14,[c] and 3620, br[a]		
5b	9-Methyl	3599,[e] 140, 11[c]		

a) br: unusually broadened part (ν_{OH} is uncertain). b) Reported: 3594, 3610sh (W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, **1965**, 1170); 3605, 3620 (J. M. Brewster and J. G. Buta, *J. Am. Chem. Soc.*, **88**, 2233 (1966)). c) Apparent half band width. d) Reported:[4] 3601, 3618. e) Reported: 3602 (A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963)).

Table 3. Chemical shifts (δ) and coupling constants (J) for H(1) of the benzocycloalken-3-ols[a]

Compound	In CCl_4	In $CDCl_3$
1a	4.98, t(J: 5.8, 5.8 Hz)	4.3, t(J: 6, 6 Hz)[15]
2a	4.48, m[c]	3.9, m[15]
3a[b]	4.77, m[d]	4.9, m[15]
4a	4.88, dd(J: 4.5, 11.5 Hz)	—
1b	5.08, dd(J: 2.5, 5.6 Hz)	5.15, dd(J: 2.5, 6.2 Hz)
2b	4.63, t(J: 3.0, 3.0 Hz)	—
3b[b]	5.27, dd(J: 2.5, 6.0 Hz)	5.35, dd(J: 2.5, 6.5 Hz)
4b	5.25, dd(J: 4.5, 9.5 Hz)	—

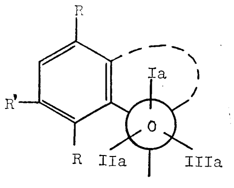
a) δ of H(1) is concentration-dependent. b) Saturated solution. c) The unresolved multiplet has a width of 12 Hz at the half height and a double intensity at the center relative to the side signals. d) The unresolved multiplet has a width of 12 Hz at the half height.

I by *peri*-methyl substitution, relieving the resulting interaction between the OH hydrogen and *peri*-methyl. This conversion, however, can not explain the observed ν_{OH} shift to higher frequency, since the ν_{OH} of Type I should be lower than that of Type II.[13] Conversion of Type I to II is unlikely. It appears reasonable to assume that **1a** prefers the equatorial C–O orientation (ν_{OH}: 3601 cm^{-1}), not taking into account the question of the prefered OH conformer. The orientation is converted to the axial form (ν_{OH}: 3607 cm^{-1}) by the introduction of the *peri*-methyl group, which relieves the resulting interaction between the equatorial hydroxyl and *peri*-methyl. Both **2a** and **2b** prefer an axial orientation.[4,5] In the case of **3a** and **3b**, the single 3620 cm^{-1} band is practically unchanged by the introduction of the *peri*-methyl group and thus the axial orientation seems to be exclusively prefered.

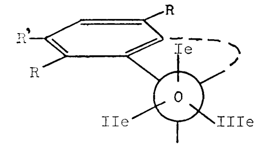
A comparison of the relative intensities of the axial and equatorial OH bands indicates that the axial orientation is increasingly prefered in the sequence from **1a** to **3a** or with a decrease in θ_e and exclusively prefered in **1b** to **3b**. This result is consistent with the ^1H NMR results (Table 3). Indeed, the J-coupling data for the H(1) of **1a** to **3a** in $CDCl_3$, which are similar to those in CCl_4, suggest the preference for axial orientation in **2a** and **3a** but not in **1a**.[15] The $J_{1,2}$ values for **1b** to **3b** are of a magnitude expected from the Karplus relationship and are very similar to those observed for analogs with equatorial H(1).[8,11,12,16] It appears that the prefered axial orientation is caused predominantly by the *peri*-interaction which becomes greater with decreasing θ_e and increasing size of the *peri*-substituent ($H < CH_3$).

The π-bondings of the axial and the equatorial OH species assigned above may be expected from the considerably low values of ν_{OH}. In fact, the nitro substituent in **1c** and **2c** increases the relative intensity of the free OH band, indicating at least one of the OH species to be π-bonded. Iwamura and Hanaya[4] assigned the 3618 and 3600 cm^{-1} bands of 1,2-benzocyclohexen-3-ols to the axial and equatorial π-bonded OH species, respectively, by taking account of the usual conformational and π-bonding effects on ν_{OH} and expected the π-bond shifts to be 9 and 18 cm^{-1}. On a similar base, the ν_{OH} values in Table 2 may be assigned to Types I, II, and III of the OH conformers,

Table 4. Types of OH conformers and assignments of the maximum ν_{OH} bands



Axial C–O orientation



Equatorial C–O orientation

Type of OH conformer	Free ν_{OH} assumed[18]	Compounds 1a—1c			Compounds 2a—2c			Compounds 3a, 3b		
		ν_{OH} observed	$\Delta\nu_{OH}$	$\theta°$	ν_{OH} observed	$\Delta\nu_{OH}$	$\theta°$	ν_{OH} observed	$\Delta\nu_{OH}$	$\theta°$
Ia	3618	3607	11	75	—		82	—		50
IIa	3627	3616sh	11		3618	9		3620	7	
IIIa	3627	3626	1		3626sh	1		—		
Ie	3618	3600	18	45	3602	16	38	—		10
IIe	3627	—			—			—		
IIIe	3627	3626			3626sh	1		—		

as given in Table 4. In each type of conformer, the O–H is assumed to be staggered between the opposing bonds. OH···π bonding occurs in Types I and II in which the OH hydrogen is directed towards the π-cloud. In **1a** to **3a**, Type Ia, in which the O–H is pointing inside the cycloalkene ring, may be sterically unfavorable, since repulsion operates between the OH hydrogen and one or two axial hydrogens on the cycloalkene ring which are in close proximity.[17] In Type IIe also, the OH hydrogen is close to the *peri*-hydrogen. Thus, Types IIa and Ie, in which no overcrowding of the OH hydrogen may be expected, are probably prefered and may largely contribute to the axial and equatorial OH absorptions at 3618 and 3600 cm,$^{-1}$ respectively. The shifts from the free ν_{OH} values ($\Delta\nu_{OH}$)[18] are 7—11 and 16—18 cm^{-1}, respectively, which are ascribable to OH···π bonding.

In **1b** to **3b**, Type IIa may contain an additional interaction between the OH hydrogen and *peri*-methyl. With a decrease of θ_a or in moving from **3b** to **1b**, this interaction will increase and Type IIa becomes less possible, whereas the crowding in Type Ia will be relieved. Thus, the prefered conformer will be IIa in **3b** and **2b** (ν_{OH}: 3620 cm^{-1}; $\Delta\nu_{OH}$: 7 cm^{-1}), but it will be Ia in **1b** (ν_{OH}: 3607 cm^{-1}; $\Delta\nu_{OH}$: 11 cm^{-1}). The weak absorptions at 3610 and 3615 cm^{-1} which **2b** and **1b** exhibit may be assigned to Ia and IIa, respectively, as the less prefered conformers. Benzyl alcohols with $\theta=90°$[19] show π-bonded ν_{OH} (3617 cm^{-1})[13,20] which may be assigned to Type II, so that $\Delta\nu_{OH}$ is 10 cm^{-1}. These results indicate the angular dependence of the π-bond shift: $\Delta\nu_{OH}$ is *ca.* 9 cm^{-1} if $\theta=50$—90°, or *ca.* 17 cm^{-1} if $\theta=38$—45°. **5a** and **5b** ($\theta=60°$) exhibit intense bands at 3600 cm^{-1} which may be assigned to Type I, so that $\Delta\nu_{OH}$ is 18 cm^{-1}. This shift is larger than expected from the above relationship, probably because the OH may be π-bonded with the two benzene rings. The weak 3620 cm^{-1} band of **5a** is probably due to an OH species π-bonded with one benzene ring, so that $\Delta\nu_{OH}$ is 8 cm^{-1}, as expected. The IR and NMR data of **4a** and **4b** are similar to those of **3a** and **3b**. It thus appears that the cyclooctene ring[21] is not as flexible as expected from molecular models.[22] The above relationship between θ and $\Delta\nu_{OH}$ predicts that the C–O bond is axial ($\Delta\nu_{OH}$: 7 or 12 cm^{-1}).

Experimental

Samples. Most of the compounds examined are known substances. 5-Nitroindan-1-ol (**1c**) was prepared from the corresponding ketone by $NaBH_4$ reduction and purified by recrystallization; mp 82.1—82.9 °C; Found: C, 60.43; H, 5.07; N, 7.75%. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82%.

Measurements. IR spectra were recorded on a JASCO DS-403G grating spectrometer. The solvent was CCl_4 distilled over P_2O_5 before use and the concentration selected was *ca.* 0.003 mol/l or less, so as to avoid intermolecular association (cell length: 50 mm). The spectral slit width was 1.5 cm^{-1} at 3600 cm^{-1}.

^1H NMR spectra were measured using a JEOL JNM4H-100 spectrometer operating at 100 MHz for *ca.* 10 w/v% solutions in CCl_4 or $CDCl_3$ with TMS as an internal reference. All measurements were carried out at ambient temperature (20—25 °C).

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18) In the text, $\Delta\nu_{OH}$ is defined as the difference in ν_{OH} between π-bonded and free OH species both situated in similar steric environments.[3,4] The free ν_{OH}'s for Types I and II are assumed to be 3618 and 3627 cm^{-1}, respectively.

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