

Rotational Isomerism around the C-O Bond in Alcohols. Assignments of the OH IR Bands

Jan M. Bakke

Laboratory of Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

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On the basis of an analysis involving IR and NMR spectroscopy, the OH stretch bands of ethanol, 2,2-dimethylpropanol and 2-propanol have been reassigned. The major bands were connected with the *gauche* rotamer in all 3 cases. These results were used to assign the OH bands of 2-phenylethanol, 2,2-diphenylethanol, 2-phenylpropanol and 1-phenyl-2-propanol. The *gauche* rotamers were also dominant for these compounds. Using the technique described, an estimate of the population of the rotamers was possible.

The infrared spectra of saturated alcohols in inert solvents at low concentrations show OH stretch bands in the 3650–3600 cm^{-1} region. For many alcohols, more than one band is observed. The accepted explanation for this is the existence of rotamers around the C-O bond, each with its own absorption band.¹⁻³ The assignments of the bands to the respective rotamers have been based on stereochemical considerations and on comparisons of the $\Delta\nu_{\text{max}}$ with those of alcohols without rotational isomerism (e.g., methanol and *t*-butyl alcohol). A number of interesting theoretical studies have also appeared.⁴

We have studied the conformations of a number of unsaturated alcohols by NMR and IR spectroscopy.^{5,6} One of the points investigated was the rotational composition around the C-O bond as expressed by the $^3J_{\text{CH-OH}}$. It is accepted that this follows a Karplus-type relationship and that the rotational composition can be derived from it.^{7,8} From this, a correlation of $^3J_{\text{CH-OH}}$ with the corresponding OH stretch frequencies was expected to give information on the question of intramolecular hydrogen bonds. We were able to show that in aryl alcohols, such bonds are of no conformational importance,^{6,9} but the correlation of the NMR data with earlier assignments from the IR spectra was often impossible. We have here attempted to correlate the IR and NMR data for some simple alcohols and then tried to

use the results for some more complicated ones. In Table 1, the OH stretch frequencies and $^3J_{\text{CH-OH}}$ are given for the investigated compounds.

We assumed that the hydroxyl hydrogen was staggered with the groups on the hydroxyl bearing carbon (Figs. 1, 2). Eclipsed conformations have been proposed for sterically very crowded alcohols hydrogen-bonded to crowded bases.⁷ However, for the compounds discussed here, we believe only staggered conformations need to be considered.¹⁰⁻¹³

Methanol has three energetically equivalent rotamers, and accordingly shows one symmetric OH band (3644 cm^{-1}). The $^3J_{\text{CH-OH}}$ coupling constant (5.46 Hz) is in accordance with this model and with one where the coupling constant is the approximate average between two *gauche* ($^3J = 2.2$ Hz) and one *anti* ($^3J = 12.5$ Hz).

Ethanol has one *anti* and two equivalent *gauche* rotamers around the C-O bond (Fig. 1) and in accordance with this shows two bands in the OH region (3637 and 3627 cm^{-1} , Table 1). The 3637 cm^{-1} band has a frequency close to that of methanol (3644 cm^{-1}) and has therefore been assigned to the *anti* rotamer.¹⁻³ Microwave spectroscopy studies indicated the *anti* form to dominate in the gas phase,^{14,15} and *ab initio* MO calculations suggested this form to have a relative stability of 0.63 kcal mol⁻¹.¹⁴ In dilute CCl₄ solution, an IR spectroscopy study of CH₃CH₂OH

Table 1. IR (OH stretching bands) and NMR ($^3J_{\text{CH-OH}}$) data of alcohols in $\text{CCl}_4/\text{CFCl}_3$ ^a at $c < 10^{-2}$ M

Compound	ν_1	ν_2	$100 A_1^b$	Ref.	$^3J_{\text{CH-OH}}$	Gauche^c
			$A_1 + A_2$			rotamer/%
Methanol	3643.8	—	100	1	5.46	—
Ethanol	3637.3	3627	64	1	5.13	65
2,2-Dimethyl-propanol	3642.0	3632	85	1	5.70	86
2-Propanol	3627.1	3617	63	1	4.50	75
2-Phenyl-ethanol	3630	3601	59	Present study	6.35	85
2,2-Diphenyl-ethanol	3623	3598	23	Present study	6.64	97
2-Phenyl-propanol	3637	3601	48	Present study	6.41	92
1-Phenyl-2-propanol	3620	3598	44	Present study	3.61	85

^a CCl_4 and CFCl_3 have equivalent solvent properties.⁶

^b A_1 and A_2 are the areas of bands 1 and 2.

^cAs defined in Fig. 1 and 2, from NMR (present study).

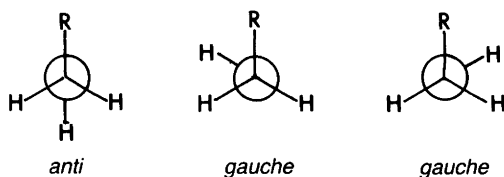


Fig. 1. Rotamers around the C-O bond for primary alcohols.

	R
Methanol	H
Ethanol	CH_3
2,2-Dimethylpropanol	$\text{C}(\text{CH}_3)_3$
2-Phenylethanol	CH_2Ph
2,2-Diphenylethanol	$\text{CH}(\text{Ph})_2$
2-Phenylpropanol	$\text{CHPh} \cdot \text{CH}_3$

concluded that the *anti* rotamer was the dominant one;¹⁶ another, of ethanol itself, that the *gauche* form was the most stable.¹⁷ The results from the MO calculations (assuming “free” molecules) could not be applied to molecules in solution, especially for systems with such small energy differences as those found for ethanol.⁴ The rotamer distribution in solution can not therefore be found unambiguously by calculations or IR spectroscopy alone.

However, the results from the NMR study (Table 1) can be interpreted in only one way. If the Karplus relationship is assumed to hold, eth-

anol consists of approx. 65 % *gauche* and 35 % *anti* rotamers, that is, the statistical distribution. If we further assume that the integrated molecular absorption coefficients are of the same magnitude for the two bands, the assignment of the IR stretch region must be reversed, i.e., the major band (3637 cm^{-1}) is connected with the *gauche* rotamer, the minor one with the *anti*.

The assumption of the magnitudes of the two integrated absorption coefficients is supported by the fact that the two coefficients are similar for methanol and *t*-butyl alcohol (4700 and $3300 \text{ M}^{-1} \text{ cm}^{-2}$) even if ν_{max} has changed by 27 cm^{-1} (from 3644 to 3617 cm^{-1}).²¹ Furthermore, the areas of the two bands of ethanol are difficult to determine because of overlap; the estimate of A_1/A_2

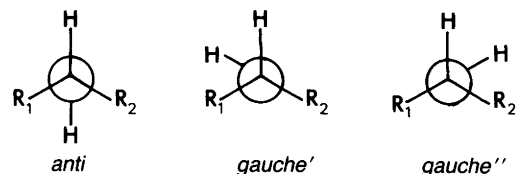


Fig. 2. Rotamers around the C-O bond for secondary alcohols.

	R_1	R_2
2-Propanol	CH_3	CH_3
1-Phenyl-2-propanol	CH_3	CH_2Ph

has varied from 1.7 to 11.0.³ The uncertainty in the estimate of the integrated molecular absorption coefficients is therefore far less than the determination of the areas themselves, and the estimates from the NMR spectra are more accurate than what have been available from the IR spectra. If a band is caused by a hydrogen-bonded species, an increase in the integrated absorption coefficient is observed.¹⁸ However, none of the alcohols above have any possibility for intramolecular hydrogen bonding.

2,2-Dimethylpropanol shows IR and NMR spectra of the same type as those of ethanol, except that the ratio $100 A_1/(A_1+A_2)$ has increased from 65 % for ethanol to 86 % for 2,2-dimethylpropanol (Table 1). The $^3J_{\text{CH}\cdot\text{OH}}$ has also increased from 5.13 Hz to 5.70 Hz (76 % *gauche*). The increase in the *gauche* structure is somewhat surprising as the *gauche* rotamer must be more crowded than the corresponding one of ethanol. An alternative explanation might be that the dominant rotamer of 2,2-dimethylpropanol was the one with the hydroxyl hydrogen eclipsed with one of the carbon hydrogens. However, we find this highly unlikely, as the *anti* rotamer would be sterically more favourable than an eclipsed one. As the *anti* rotamer is *not* the dominant one, we can only conclude that for 2,2-dimethylpropanol, the *gauche* rotamer is also the major one and that the band at 3642 cm^{-1} must be assigned to this.

2-Propanol also shows two bands in the OH region (3627 and 3617 cm^{-1}). The first of these (the major one) has been assigned to the *gauche* rotamer out of analogy with the bands and assignments of ethanol. We have reversed the assignments of ethanol, but from the $^3J_{\text{CH}\cdot\text{OH}}$ observed for 2-propanol (4.5 Hz) the *gauche* rotamer must be the dominant one (75 %), again close to the statistical distribution. The band at 3627 cm^{-1} is accordingly assigned to the *gauche* rotamer.

From these examples, it is clear that the assignments of the IR bands cannot be made from an analogy with other alcohols or by stereochemical considerations alone. If, however, one accepts the validity of the Karplus relationship for vicinal coupling constants over a C-O bond, and also assumes the integrated molecular absorption coefficients to be of comparable magnitude for bands in this region, more information can be extracted from the IR and NMR spectra than has been possible until now. We have used some phenyl-substituted ethanols to show this (Table

1). We do not discuss the total conformation of these compounds, only the populations of the rotamers around the C-O bond, and we are not concerned here with the existence of intramolecular hydrogen bonds. A report on these questions will be communicated shortly.

For the compound 2-phenylethanol, two bands in IR were observed, at 3630 and 3601 cm^{-1} . From IR alone, it is not possible to assign these bands with any certainty. The one at 3630 cm^{-1} might, from analogy with ethanol, be connected to the *anti* rotamer (Fig. 1), the other to the *gauche* (with an intramolecular hydrogen bond).^{19,20} The NMR spectrum, however, shows that the *gauche* rotamers are the dominant ones (85 %). Both bands in the IR are therefore connected to *gauche* rotamers; the 15 % *anti* would only show as a shoulder on one of the two bands. The two *gauche* rotamers (Fig. 1) are mirror images. The reason for the existence of two *gauche* bands in the IR must therefore be found in the rest of the molecule; the reciprocal conformation of the hydroxyl and the phenyl groups must obviously be of importance. The assignment of the IR bands therefore makes a more reliable estimate of the $\Delta\nu_{\text{max}}$ of the two bands possible and thereby a more reliable estimate of the strength of the interactions in the molecule.

As to the integrated molecular absorption coefficients of these compounds, a note of caution must be added. An intramolecular hydrogen bond might increase the coefficient,¹⁸ resulting in a too large estimate of the population of such species (band at approx. 3600 cm^{-1}). However, such a bond, if present at all, must be weak and the increase therefore a small one. The error introduced, if any, must therefore be small.

In the compound 2,2-diphenylethanol, the *gauche* rotamer has increased to 97 % of the C-O rotamers (NMR), and the area of the high frequency IR bands has decreased from 59 % for 2-phenylethanol to 23 % for this compound (Table 1). The frequencies are almost the same for the two compounds (Table 1). This then strengthens the idea put forward for 2-phenylethanol, that the low-frequency band was connected to a rotamer with an interaction between the OH and phenyl group and that this conformer has an IR band at about 3600 cm^{-1} .

Again, in 2-phenylpropanol the dominant rotamer is the *gauche* one (NMR) and the low frequency band is most probably connected to a

conformer with an interaction between the OH and phenyl groups. The high frequency band must also be caused by a *gauche* rotamer, but this one without that interaction (see above).

From NMR, the dominant rotamer in 1-phenyl-2-propanol is again the *gauche* one. In this molecule, in contrast to the primary alcohols discussed above, there are two unequivalent rotamers around the OH bond (Fig. 2). From the discussions above, it appears reasonable to assign the band at 3598 cm^{-1} to a rotamer with an interaction between the OH and phenyl groups, corresponding to approx. 50% of the rotamers. The band at 3620 cm^{-1} may then be assigned to either the same rotamer but without that interaction, or to the other *gauche* rotamer, or to a mixture of these two. The spectra presented do not permit any safe conclusion on this point.

Conclusion

By a combination of IR and NMR spectroscopy, it has been possible to assign the OH stretch IR bands to specific rotamers around the C-O bond. From the integrated areas of the bands, it has further been possible to assess the population of these rotamers. The assignments have also made it possible to make more reliable estimates of the Δv_{max} for the two IR bands of the same compound; specifically, that comparisons can be made between the bands of species with similar conformations. Further use of this technique on the questions of intramolecular hydrogen bonding will be reported in a future paper.

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