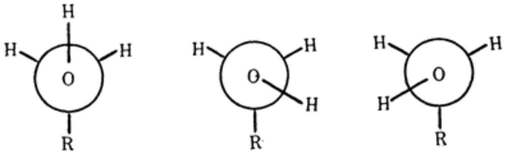
ν_{O-H} *Absorption and Rotational Isomerism of Fluoro-alcohols*[1]

By Michinori Ōki and Hiizu Iwamura

(Received June 15, 1962)

In a previous paper[2] it was presented that the ordinary saturated alcohols possess doublet character of O-H fundamental stretching vibration (ν_{O-H}). Considering the lack of this character in methanol and *tert*-butyl alcohol, and classifying the ν_{O-H} frequencies in reference to the types of the alcohols, the authors have succeeded in a tentative explanation that the occurrence of the doublet bands should be due to the rotational isomerism about the C-O bond as an axis.

In the meantime, Piccolini and Winstein[3] have been led to the same conclusion based on the measurement with some seventy saturated alcohols. Partly because of the fact that they took advantage of the spectra in the first overtone 1.4 μ region, their data are not always in quantitative agreement with the present authors'. In this respect, it seems desirable to add another example to confirm the existence of the rotational isomers about the C-O bond in alcohols.



I II II′

Of the three rotational isomers, I, II and II′, in primary alcohols, relative stabilities will be determined by the interaction between the hydroxyl group and group R. As far as R is an alkyl group, only the van der Waals repulsive force is to be considered, hence I is expected to be predominant over II and II′. In this connection it was shown[2] that the intensity of the band corresponding to I is about twice as stronger as that of (II+II′), in spite of just the reverse statistical factor, and that the ratio of the integrated intensities, A_I/A_{II}, amounts to 6.0 when R is *tert*-butyl. Since it is unlikely that the molar absorption intensity

---

[1] Part XVII of the "Intramolecular Interaction between Hydroxyl Group and π-Electrons", Part XVI: M. Ōki and H. Iwamura, This Bulletin, 35, 1552 (1962).

[2] M. Ōki and H. Iwamura, ibid., 32, 950 (1959).

[3] R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

TABLE I. ν_{O-H} ABSORPTIONS OF FLUORO-ALCOHOLS

	Band	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	A_I/A_{II}
FCH_2CH_2OH	I	3634.6	25.6	1.17	0.43
	II	3620.9	20.0	2.74	
CF_3CH_2OH	I	3636.2	12.4	0.30	0.042
	II	3619.8	22.2	6.87	
$CF_3CF_2CH_2OH$	I	3635.5	19.4	2.46	0.29
	II	3619.8	23.6	8.60	

of ν_{O-H} differs appreciably in I and II, A_I/A_{II} may be a good estimate of the population ratio between I and II. Then it comes out that I is about 400 cal./mol. more stable than II. The ratio, B_1/B_2, of ca. 8 by Piccolini and Winstein³⁾ will produce unreasonably great energy difference between the two rotational isomers.

When a hetero-atom is introduced in group R, another situation will arise in addition to the mere repulsive force. The apparent absorption curves and ν_{O-H} data of the fluorinated primary alcohols measured in dilute carbon tetrachloride solution (ca. 0.003 mol./l.) are shown in Fig. 1 and in Table I, respectively. They were determined with a Perkin-Elmer 112G grating IR spectrometer with the spectral slit width of 1 cm^{-1} ⁴,⁵⁾.

All three show doublet ν_{O-H} at 3635 and 3620 cm^{-1}, respectively. The former is as high as that of methanol and can validly be assigned to the conformation I of the ordinary primary alcohols. According to the generalization put forward in the previous paper²⁾, conformational isomer II should have its ν_{O-H} at 3626～3629 cm^{-1}. There is a slight shift to the lower frequency in the present examples. The intensities of the doublet bands have suffered from more conspicuous effect. Contrary to the corresponding ethanol and 1-propanol, the lower-lying bands have acquired superiority over the higher ones, as shown in the A_I/A_{II} column in Table I. These data are in accord with the idea of the rotational isomerism around the C–O bond and may be explained as follows.

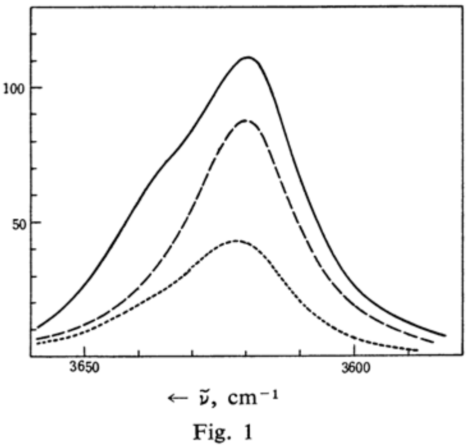


Fig. 1

······ FCH_2CH_2OH
--- $CF_3CH_{20}OH$
—— $CF_3CF_2CH_2OH$

In isomers II and II′, it is possible for the hydroxyl group to take part in some kinds of O–H···F interaction which stabilizes the molecule. In ethylene fluorohydrin there seems to be no apparent energy difference between I and II, because A_I/A_{II} is nearly equal to the frequency factor of 1/2. However, the statement is not strictly true, since (II+II′) contains further isomerism with respect to the $C_\alpha-C_\beta$ axis. Band II, therefore, consists of the sum of these isomers and it is the mean energy of them that is comparable with that of I. When the number of the fluorine atoms at β-carbon atom is raised to three, rotational degree of freedom about the $C_\alpha-C_\beta$ bond produces no isomerism and all conformations belonging to (II+II′) have O–H···F interaction with the consequence of almost exclusive population in these isomers. In pentafluoropropanol, the existence of one or two of the rotational isomers in respect of the $C_\alpha-C_\beta$ axis in type (II+II′) become impossible, because of overcrowding of the CF_3 and OH groups. This effect disfavors the residence of the molecule in conformation (II+II′) relative to I, and has already been observed in a pair of ethanol and 1-propanol which have their A_I/A_{II} of 1.8 and 2.6, respectively²⁾. The rates of the increase in the relative intensity are 1.44 in ethanol—1-propanol, and 6.9 in trifluoroethanol—pentafluoropropanol. Exaltation in the latter is the due consequence of the longer C–F bond length and the larger van der Waals radius of fluorine atom.

It may be concluded that, by introducing fluorine atom in R of primary alcohols,

---

4) M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

5) Samples of trifluoroethanol and pentafluoropropanol were given by Dr. Robert West of the University of Wisconsin, U. S. A., to whom the authors' thanks are due. Ethylene fluorohydrin was prepared according to the literature: B. C. Saunders, G. J. Stacey and I. G. E. Wilding, *J. Chem. Soc.*, **1949**, 773. Their physical constants agreed well with those in the literatures.

RCH_2OH, the relative population between the isomers around C–O axis has been reversed, and thus another example has been complied favorably for the existence of the rotational isomerides about the C–O bond as an axis.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo