*Journal of Fluorine Chemistry*, 13 (1979) 77 – 79

Received: September 29, 1978

SHORT COMMUNICATION

# Vibrational Spectra of o-Fluorobenzyl Alcohol

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Intramolecular hydrogen bonds are formed only if certain spatial conditions exist. The number of compounds in which these conditions exist are fairly limited, and most hydrogen bonds involve intermolecular bonding. The fluorine and hydroxyl hydrogen in o-fluorobenzyl alcohol can approach each other close enough to form an intramolecular H-bond, and vibrational spectra have been obtained for this compound to check for the presence of such bonding.

Infrared spectra obtained with a Beckman IR12 spectrophotometer for the neat liquid and for solutions in $CS_2$ and $CCl_4$ in the O-H stretch region are shown in Fig. 1. The Raman spectrum of the neat liquid, obtained with a Beckman Model 700 spectrometer, is shown in Fig. 2.

The most notable observation in the spectra is that the associated O-H stretch band is a broad band centered at ca. 3350 $cm^{-1}$. In solution, the 'free' O-H stretch band appears at 3624 $cm^{-1}$. These observations show the presence of intermolecular H-bonding rather than intramolecular bonding. Intramolecular H-bonding results in a more narrow band than intermolecular bonding, observed at ca. 3550 $cm^{-1}$ (1). Also, the solvent effects on the two types of bonding are different.

If the C-O-H group were coplanar with the benzene ring with the O-H and F on the same side of the methylene carbon, the hydroxyl hydrogen and fluorine would be only about 1.4A apart, which is less than the sum of the van der Waals radii. Intramolecular H-bonding occurs in o-chlorophenol (1), with the Cl-H

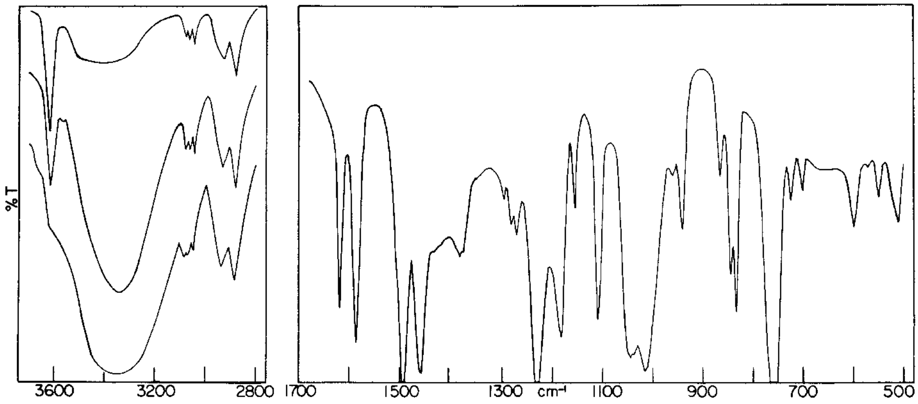

Fig. 1. Infrared spectra (redrawn) of o-fluorobenzyl alcohol. 500-1700 cm$^{-1}$, neat. 2800-3600 cm$^{-1}$: bottom curve, neat; middle curve, 10% in $CCl_4$; top curve, 2% in $CCl_4$.

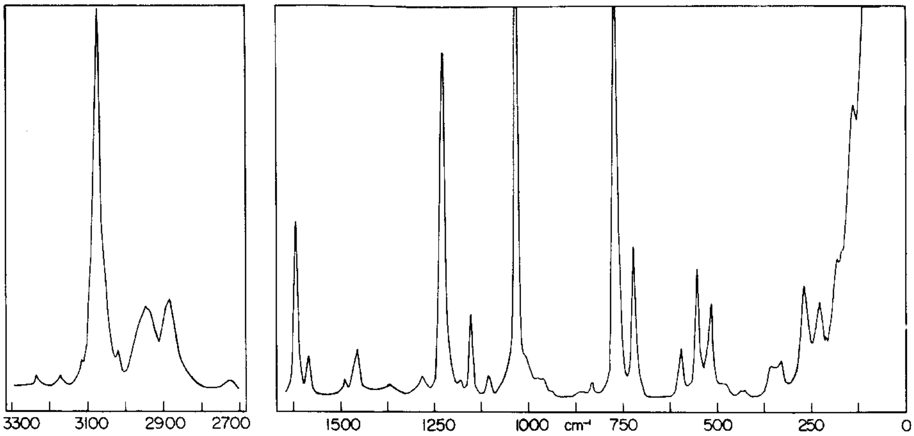

Fig. 2. Raman spectrum (redrawn) of o-fluorobenzyl alcohol (neat)

distance being about 2.4A. If the F and H were bonded, the H should be rotated out of the C-C-O plane to an optimum distance from the fluorine, so that intramolecular H-bonding might be expected to be present in this compound. However, in this conformation, the oxygen-fluorine distance would be only 2.4-

2.6A, apparently resulting in significant electrostatic repulsion. Since the intramolecular H-bonded species doesn't exist, the stability of the intramolecular H-bonded species must be more than offset by the O--F repulsion. The stability gained by intermolecular H-bonding apparently plays no role in the absence of intramolecular H-bonding, i.e., the O--F repulsion alone is sufficient to prevent such bonding. Otherwise, the intramolecular H-bonded species should appear in dilute solution as the concentration of the associated species decreases. However, the infrared spectrum shows only an increase in intensity of the "free" O-H band and a decrease in intensity of the "associated" O-H band.

The Author is grateful to The Robert A. Welch Foundation, Houston, Texas, for financial support of this work.

1 H. E. Hallam,'Infrared Spectroscopy and Molecular Structure,' M. Davies, Ed., Elsevier Publishing Co., New York, 1963, p 415.