

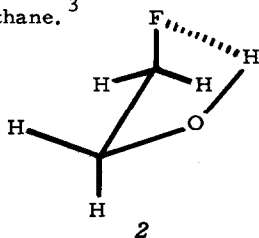
THE QUESTION OF INTRAMOLECULAR HYDROGEN BONDING IN 2-FLUOROETHANOL<sup>1a</sup>

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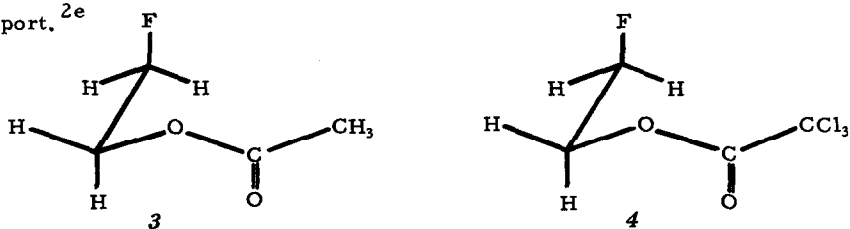
Several investigations<sup>2a-f</sup> have shown, by a variety of spectral techniques, that 2-fluoroethanol (*1*) exists both in the liquid and vapor state, predominantly (>95%) in the conformation with hydroxyl and fluorine *gauche* to one another. Notable is the recent electron-diffraction study in which *1* was shown to be greater than 90% *gauche* in the vapor phase at 156°. <sup>3</sup> In every instance, this marked conformational preference for the *gauche* form has been attributed to the formation of a strong intramolecular hydrogen bond between the electronegative fluorine atom and the hydroxyl proton which are in close proximity in this configuration. That this is the case is presumably also supported by the observation that the CCF bond angle of 107.7° is compressed relative to fluoroethane. <sup>3</sup>



Strong evidence against the previous interpretations is provided by the recent results of Abraham and coworkers<sup>4</sup> on the rotational isomerism of 2-fluoroethyl acetate (*3*) and 2-fluoroethyl trichloroacetate (*4*), in which there is no possibility for an intramolecular hydrogen bond, and yet, populations of the *gauche* conformation are here also greater than 95%. This demonstrates convincingly that the postulated intramolecular hydrogen bond is not needed for the predominance of the *gauche* forms.

Abraham's results suggest possible interest in our nmr investigation of the importance of intramolecular hydrogen bonding in *1*. Being intrigued by the presumed strength of the intra-

molecular hydrogen bond, we have reexamined the conformational equilibria with the aid of a LACON 3 analysis of the 60-MHz pmr spectra and found that for both 50% and 5% *v/v*  $\text{CDCl}_3$  solutions at  $38^\circ$ , the *gauche* isomer of **1** predominates (>95%) in complete agreement with the previous report.<sup>2e</sup>



In addition, we have studied the concentration dependence of the hydrogen bonding in **1** by following the OH chemical shift in carbon tetrachloride in a manner analogous to studies made previously for ethanol itself.<sup>5</sup> The chemical shifts of pure, neat **1** are:  $\text{CH}_2\text{F}$ ,  $\delta$  4.50;  $\text{CH}_2\text{O}$ ,  $\delta$  3.80 and  $\text{OH}$ ,  $\delta$  4.75. This can be compared to the chemical shift of the hydroxylic proton of neat ethanol,  $\delta$  5.13.<sup>6,7</sup> Data over the whole concentration range in  $\text{CCl}_4$  could not be measured because **1** is only about 4% soluble in  $\text{CCl}_4$ . However, the important low-concentration range (mole fraction 0.019 to 0.0020, *i.e.*, 4% to 0.5% *v/v*) is readily accessible. The samples were prepared volumetrically and each point is the average of three determinations obtained immediately after dissolution, using a Varian A56/60 spectrometer at a probe temperature of  $38^\circ$ . A plot of the OH chemical shift *vs.* concentration is shown in Figure 1.

To summarize, we find the chemical shift of the methylene protons to be essentially invariant with dilution, and no broadening of the  $\text{CH}_2\text{O}$  protons, as would be associated with slow exchange, is observed at the 0.5% concentration. Likewise, the OH resonance remained a sharp singlet. The chemical shift relative to TMS for the monomeric species obtained by extrapolation to infinite dilution is *ca.* 80 Hz ( $\delta$  1.33 ppm). This is not much different from that for ethanol itself, which is  $\delta$  1.04 ppm at infinite dilution.<sup>6,7</sup>

The concentration dependence of the OH chemical shift of primary alcohols such as ethanol is attributed to the disruption of hydrogen-bonded dimers, trimers, tetramers and higher solution polymers.<sup>5,7</sup> A strong intramolecular hydrogen bond would be expected to lead to only a small change in the chemical shift of the hydroxylic proton with concentration. Furthermore, the chemical shift of a proton engaged in a strong intramolecular hydrogen bond should be markedly deshielded and come at a substantially lower field than the OH proton of ethanol. Such behavior is exemplified by acetylacetone (**4**) ( $\delta_{\text{OH}}$  15.18 ppm<sup>8</sup>) and salicylaldehyde (**5**)

( $\delta_{\text{OH}}$  18.1 ppm).<sup>9</sup>

We believe the data with *I* to be indicative of, at most, only weak intramolecular association, and thus 2-fluoroethanol probably exists in the *gauche* form for the same reason(s) as the compounds studied by Abraham.<sup>4, 10</sup>

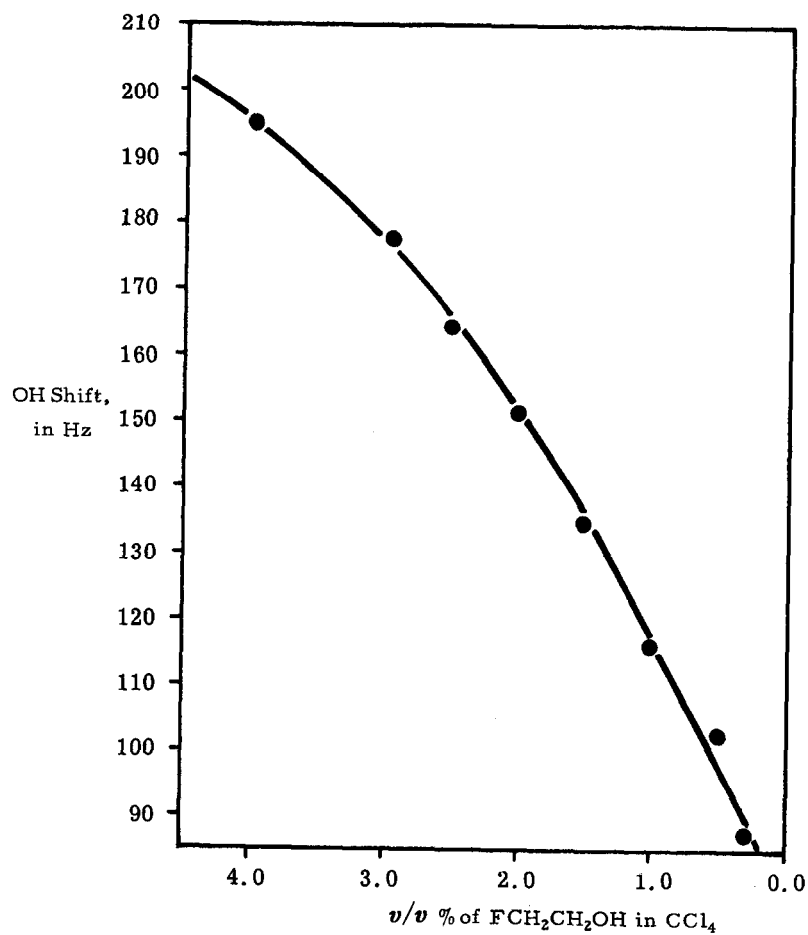


Figure 1. Variation of the chemical shift of the OH proton of 2-fluoroethanol as a function of concentration in CCl<sub>4</sub>.

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(b) Contribution No. 4893
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10. An obvious possibility for the lack of a strong intramolecular hydrogen bond in **I** is that, unlike acetylacetone, salicylaldehyde, etc., such a bond involves formation of a five-membered ring.