

REAFFIRMATION OF INTRAMOLECULAR INTERACTION  
IN CYCLOPROPYLMETHANOL

Michinori ÔKI and Hiizu IWAMURA

Department of Chemistry, Faculty of Science,  
The University of Tokyo, Tokyo 113, Japan.

(Received in Japan 4 August 1973; received in UK for publication 31 August 1973)

Numerous examples of the reaction of cyclopropane with proton are known and the study on the interaction between the cyclopropane ring and the hydroxyl group is interesting as one of the model cases of the reaction process. Since the first indication of the existence of such an interaction taking place intramolecularly,<sup>1)</sup> Schleyer et al. elaborated the work<sup>2)</sup> to indicate that the interaction is common to many compounds. We have independently studied such an interaction and, in accordance with the work of Schleyer et al., established the presence of the interaction and indicated that the interaction is preferred when the OH group approaches the cyclopropane within the ring plane,<sup>3)</sup> as predicted by Hoffmann.<sup>4)</sup> The intermolecular interaction was extensively studied by Yoshida et al. also.<sup>5)</sup>

Recently Pierre and Perraud published a paper,<sup>6)</sup> throwing a serious doubt on the presence of intramolecular interaction between the cyclopropane ring and the hydroxyl group in cyclopropylmethanol, mainly from the results of nuclear magnetic resonance study. We now wish to elaborate our previous work and to present some hitherto unpublished data to answer the critical comment by Pierre and Perraud. We still believe that the intramolecular OH...cyclopropane interaction really exists in cyclopropylmethanol for the reasons which follow.

Infrared Spectra. The O-H stretching absorptions of cyclopropylmethanol occur at 3633.7 and 3619  $\text{cm}^{-1}$  with the integrated intensities of 2.3 and  $2.6 \times 10^3$   $\text{mole}^{-1} \cdot \text{l} \cdot \text{cm}^{-2}$ , respectively, when the spectrum was recorded on a Perkin Elmer 112-G grating spectrophotometer. The difference in wave numbers of the bands is

close to normal primary alcohols but the ratio of the intensities is quite different. The ratio of integrated intensities for cyclopropylmethanol is 1.1, whereas those for ethanol, 1-propanol, and isobutyl alcohol are 0.56, 0.38, and 0.50, respectively. The situation of cyclopropylmethanol is reminiscent of the cases of allyl alcohol and benzyl alcohol in which the intramolecular OH- $\pi$  interaction is present.<sup>7)</sup> It may also be added that the shift in wave numbers for the two bands in allyl and benzyl alcohols is not large. The abnormal intensity ratio, which is not mentioned in the paper by Pierre and Perraud, is thus suggestive of the presence of intramolecular OH-cyclopropane interaction. It would be almost impossible to explain why 1-cyclopropylethanol has still stronger band at the lower frequency and 1-(2,2-dimethylcyclopropyl)ethanol show only one band at  $3616.9\text{ cm}^{-1}$ , if the intramolecular interaction were denied in cyclopropylmethanol derivatives.<sup>3)</sup>

The Chemical Shift of the OH Protons at Infinite Dilution. The dependence of chemical shifts of OH protons on concentration, as measured in carbon tetrachloride, is shown in Fig. 1. Ethanol was chosen as a standard rather than 2-propanol<sup>6)</sup> because cyclopropylmethanol is a primary alcohol and the chemical shifts at the infinite dilution must be different from the secondary alcohol. Fig. 1 indicates that, at infinite dilution, the OH proton signal of cyclopropylmethanol appears at a lower magnetic field by 0.23 ppm than the OH proton of ethanol.

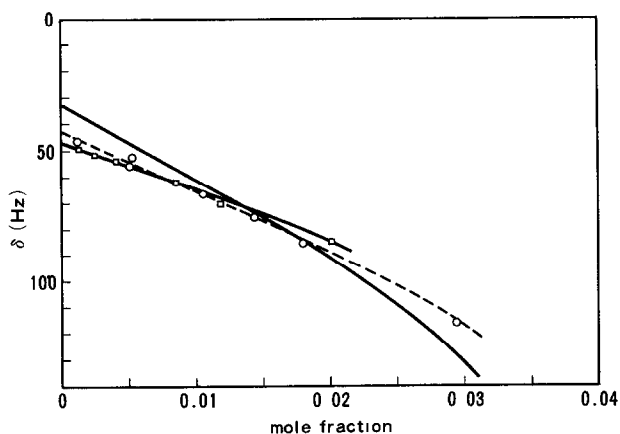


Fig. 1  
Dependence of the Chemical  
Shifts on Concentration at  
60 MHz.

— ethanol  
 -□-□-□- cyclopropylmethanol  
 -○-○-○- 2-cyclopropylethanol

The chemical shift of the OH proton is generally affected by the degree of stretching of the O-H bond due to formation of the hydrogen bond, the electronegativity of the R part of the alcohol ROH, and the magnetic environment caused by the acceptor. (2-Methyl-2-oxiranyl)methanol is not a suitable standard in discussing the presence or absence of the hydrogen bond, because this compound is known to possess strong intramolecular OH-O bond from the infrared study.<sup>8)</sup>

Comparison of the situation with that of OH- $\pi$  interaction is preferable since both OH- $\pi$  and OH-cyclopropane interactions are weak and of the like nature. Previously, we were able to correlate the OH proton shifts of allylmethanol and phenethyl alcohols with the O-H stretching intensities.<sup>9)</sup> The paper revealed that, in like alcohols, the proton chemical shifts of the OH group at infinite dilution were almost the same when the intramolecular interaction was absent. When the OH- $\pi$  interaction did exist, the OH proton showed the paramagnetic shift to a certain extent. In this sense, the important point in the data given in Fig. 1 is that the OH proton of cyclopropylmethanol appears at the lower magnetic field than that of ethanol at infinite dilution: this can be taken as an indication of the presence of OH-cyclopropane interaction. Undoubtedly (2-methyl-2-oxiranyl)-methanol should give OH proton signal at further lower magnetic field at infinite dilution because there exists a strong OH-O bond and an OH-oxirane interaction.

The chemical shift of the OH proton in intramolecularly interacting species of cyclopropylmethanol may be calculated by applying the method successfully used for the OH- $\pi$  case. Assuming the integrated intensities of 2.3 and 2.6 be proportional to the concentration, the mole fraction of the interacting species is 0.57. Dividing the observed chemical shift difference, 0.23 ppm, by the mole fraction gives the value of 0.40 ppm. Thus it is concluded that the interacting form of cyclopropylmethanol should give OH proton signal at 0.95 ppm from TMS.

From Fig. 1, the presence of OH-cyclopropane interaction in 2-cyclopropylethanol can also be deduced, although it was rather ambiguous from the infrared study. The presence of the interaction became clear only when the OH stretching absorptions of 2,2-dicyclopropylethanol were studied,<sup>3)</sup> whereas the paramagnetic shift of the OH proton of 2-cyclopropylethanol is the evidence for the presence of that interaction. The shift to a lesser extent than that of cyclopropylmethano

must be the indication of less mole fraction of the interacting species, in agreement with the infrared study.

The Coupling Constants of the Protons. Great care must be exercised when the results are transformed to the other part where the conditions are different. Therefore, we do not wish to discuss the fine part of the spin-spin coupling constants. We agree with Pierre and Perraud in that the gauche forms predominate and the fact is reflected in the vicinal coupling constants. The populations of rotational isomers about the  $C_{OH}-C_{cyclopropyl}$  bond may not be different in carbon tetrachloride and in dimethyl sulfoxide at moderate concentrations. In both cases, intermolecular association due to hydrogen bond formation occurs to a fair extent. The glycidol derivative, however, is again not a suitable criterion to diagnose the presence or absence of the  $OH \cdots 3$ -membered ring interaction because of the presence of intramolecular OH-O bond. The conformation of the OH-O bonded form must be greatly deformed, when the molecules are dispersed in dimethyl sulfoxide and, as a consequence, the intermolecular hydrogen bond is formed. Therefore it seems that the coupling constant data must be reexamined very carefully, if they are to be used for discussing the absence of the interaction.

#### References

- 1) P. von R. Schleyer, D. S. Trifan, and R. Backskai, *J. Amer. Chem. Soc.*, 80, 6691 (1958).
- 2) L. Joris, P. von R. Schleyer, and R. Gleiter, *ibid.*, 90, 327 (1968).
- 3) M. Ōki, H. Iwamura, T. Murayama, and I. Oka, *Bull. Chem. Soc. Jap.*, 42, 1986 (1969).
- 4) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).
- 5) Z. Yoshida, N. Ishiba, and H. Kusumoto, *J. Amer. Chem. Soc.*, 91, 2279 (1969).
- 6) J. L. Pierre and R. Perraud, *Tetrahedron Lett.*, 1935 (1973).
- 7) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jap.*, 32, 950, 955 (1959).
- 8) M. Ōki and T. Murayama, *ibid.*, 40, 1997 (1967); 46, 259 (1973).
- 9) M. Ōki and H. Iwamura, *Tetrahedron*, 16, 139 (1961).