Intramolecular Interaction between the Hydroxyl Group and the Oxirane Ring

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We wish to report evidence for the presence of intramolecular interaction between the OH group and the oxirane ring and apparently the first experimental support for an electron density map[1] of the oxirane ring.

Glycidol (I) shows three absorption maxima in the 3μ region (Table 1). The band at the highest frequency can be assigned to the free OH group on the basis of analogous situations found in the other primary alcohols,[2] and the other bands can be assigned from the following considerations.

2, 3-Epoxy-3-methyl-1-butanol (II) has no absorption below 3600 cm^{-1}, giving only two bands attributable to the free and the interacting OH group. The results can best be interpreted, as the molecular models suggest, by assuming that the CH_3 group prevents the OH group from approaching the top of the 3-membered ring surface, *i. e.*, the lone-pair electrons of the oxygen atom closely, although that conformation is indispensable for the formation of the intramolecular O-H$\cdots$O bond. Thus the absorption at the lowest frequency (below 3600 cm^{-1}) of glycidol is assigned to the OH group bonded to the epoxide O.

The band at *ca.* 3610 cm^{-1} does not shift much when CH_3 groups are introduced into the 3 position, but it shifts to a lower frequency when a methyl group is attached to the 2 position:[3] (compare the bands of I, II, and III in Table 1). The results may be attributed to the fact that, the inductive effect of the CH_3 group is conveyed to the C_2-O bond *via* the C_3-O and C_2-C_3 bond, thus reducing the effect in the case of II, whereas in the case of 2, 3-epoxy-2-methyl-1-propanol (III) the ν_{OH} frequency is lowered because the electron density is increased by the inductive effect. Thus the oxirane ring can interact with the OH group as does the cyclopropane ring.[4] Therefore, the band at *ca.* 3610 cm^{-1} is assigned to the OH group interacting with the ring. These results, together with the fact that II has a band corresponding to the interaction, suggest that the interaction is favored when the hydroxyl group approaches the oxirane from the plane of the ring.

TABLE 1. THE ν_{OH} DATA OF SOME EPOXY-ALCOHOLS*

Compound	Absorption maxima (cm^{-1})**
I	3638 (0.2), 3611.8 (2.9), 3590 (3.1)
II	3638 (1.6), 3612.4 (4.0)
III	3639 (0.3), 3608.9 (2.1), 3578 (4.2)
IV	3628 (0.3), 3607.4 (5.0)
V	3623.6 (4.8), 3612 (0.2), 3567 (1.8)

* Slit width: 0.8 cm^{-1}.
Concentration *ca.* 3×10^{-3} mol/*l* in CCl_4.

** Numericals in parentheses represent A ($\times10^{-3}$ mol$^{-1}\cdot l\cdot$cm^{-2}).

The results also indicate that the interaction is taking place with the electrons of the C-O bond and not with those of the C-C bond; if the latter were the case, II would be expected to show the frequency shift. This consideration is now supported by the following data. The ν_{OH} data of threo and erythro isomers of 3, 4-epoxy-4-methyl-2-pentanol (IV and V respectively) are given in Table 1. The Dreiding model indicates that the stable conformations of the erythro and threo isomer will be those in which the dihedral angles made by the two C-$H_{methine}$ bonds are close to 180°. NMR spectra are in conformity with this expectation, J_{vic} being 8.0 and 8.5 Hz for threo and erythro isomers respectively. It then follows that IV will show a strong interaction between the OH group and the epoxide ring, and that V will have a high proportion of the free OH group. The results are in accord with these expectations. If the C_2-C_3 bond were interacting, the erythro isomer would also give a strong band corresponding to the interacting OH group.

Thus, the oxirane ring interacts with the OH group, using the electrons of the C-O bond, and that the interaction is favored when the OH group approaches not from the top but from the plane of the ring. The conclusion agrees with the electron density map of oxirane proposed by Walsh[1].

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[1] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[2] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

[3] Carbon 2 is the one which bears 1-hydroxyalkyl group.

[4] P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958). Various data of this sort have been accumulated in this laboratory; some of them were presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.