

THE O-H... π BONDING AND CONFORMATION OF β -PHENYLETHANOLS

Hiizu Iwamura

Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

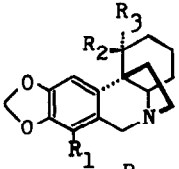
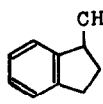
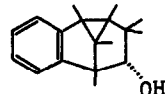
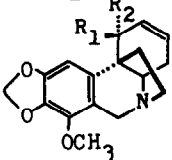
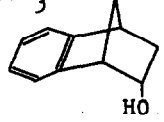
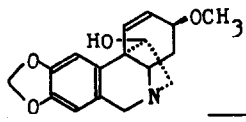
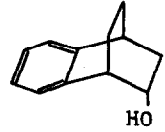
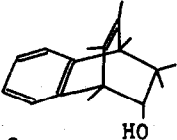
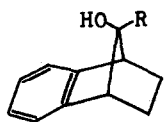
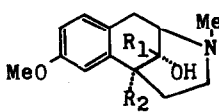
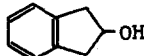
(Received in Japan 21 April 1970; received in UK for publication 5 May 1970)

IR spectroscopic observation of the intramolecular O-H... π hydrogen bonding in olefinic and aromatic alcohols has recently been widely applied to determination of the configuration of the hydroxyl group with respect to the olefinic and aromatic centers.^{1,2} In contrast with the O-H...O hydrogen bonding,³ however, less effort seems to have been made to correlate quantitatively the spectroscopic parameters⁴ with the molecular geometry. The situation may be due to difficulty in locating the site of the proton accepting center which is distributed over more than one carbon atoms carrying the π -electrons; in the case of O-H...O bonding it is easier to define the site of the lone pair of electrons of the proton acceptor. We now wish to report a useful empirical correlation which allows one to estimate the conformation of β -phenylethanols from their O-H stretching frequencies($\nu_{\text{O-H}}$).

In Chart I are summarized the $\nu_{\text{O-H}}$ absorption frequencies of a wide variety of conformationally-fixed β -phenylethanols. The spectral measurement was carried out on a Perkin-Elmer 112G grating infrared spectrometer as described before.² All the data quoted from the literature are explicitly mentioned to have been obtained on a dilute solution in carbon tetrachloride with a spectrometer equipped with a grating or a fluoride prism.

It is not always proper to regard the apparent difference in frequencies of the doublet absorption peaks of a given alcohol as the $\nu_{\text{O-H}}$ shift representing the strength of the hydrogen bonding, because the conformational environment of the hydroxyl group which is well-documented with its influence on the $\nu_{\text{O-H}}$

Chart I

	R ₁	R ₂	R ₃	$\nu_{\text{O-H}}$ bonded ⁵	
	H	OH	H	— 3616 cm ⁻¹ (15°)	
<u>1b</u>	OMe	OH	H	— 3616 (15°)	<u>4</u> 3638, 3605 ⁶ (65°)
<u>2a</u>	H	H	OH	3620, 3602 (165°)	
<u>2b</u>	OMe	H	OH	3620, 3599 (165°)	<u>5</u> — 3580 ⁷ (110°)
	R ₁	R ₂			
<u>3a</u>	OH	H	—	3614 ⁵ (20°)	
<u>3b</u>	H	OH		3613, 3584 (160°)	
					<u>6</u> 3624, 3576 (115°)
				— 3560 (115°)	<u>7</u>
					<u>8</u> 3618, 3586 (120°)
					<u>9</u> 3635, 3580 ⁹ (120°)
					<u>10a</u> R H 3619, 3575 ¹⁰ (145°)
					<u>10b</u> Me 3625, 3576 (145°)
	R ₁	R ₂			
<u>11a</u>	H	Me		3634, 3591 ¹¹ (155°)	
<u>11b</u>	Me	Me		3622, 3586 (155°)	<u>12</u> 3620, 3592 ¹² (165°)
<u>11c</u>	H	Et		3625, 3595 (155°)	
<u>11d</u>	Me	Et		3610, 3591 (155°)	

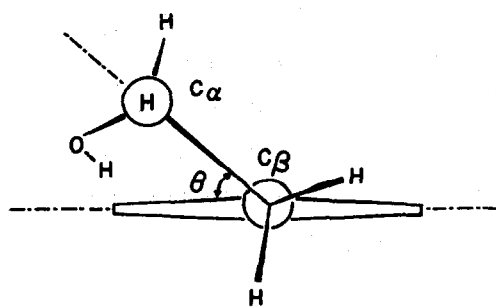


Figure 1 Definition of θ in β -phenylethanol.

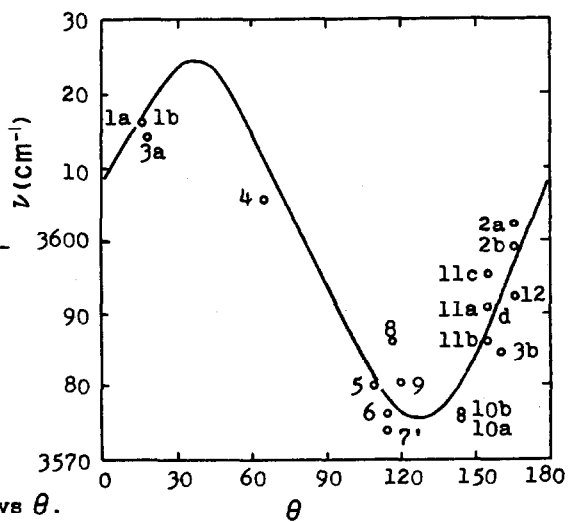


Figure 2 π -bonded $\nu_{\text{O-H}}$ vs. θ .

frequency¹³ is not necessarily equal in the free and the bonded forms. To avoid this ambiguity and for simplicity's sake, the bonded frequency itself is to be compared in this paper without reference to the free $\nu_{\text{O-H}}$. It is apparent that the lower the bonded O-H frequency the stronger is the O-H... π bonding.

As a convenient measure expressing the geometrical relationship between the hydroxyl group and the aromatic π -orbitals in β -phenylethanols, let us define θ as the dihedral angle between the plane of the benzene ring and that made by the carbon atoms C_α and C_β of the side chain, and C_1 of the benzene ring. Note that as shown in Figure 1 the OH should be contained by definition in the quadrant defined by θ , and not by the supplementary angle of θ . For each alcohol in Chart I, the angle θ was measured on a Dreiding model and/or estimated on the basis of the geometry of the partial structure when this is known. The θ values are also included in Chart I.

Graphic presentation gives the reasonably smooth bonded $\nu_{\text{O-H}}$ versus θ curve as shown in Figure 2, which could be approximated by Equation 1.

$$\nu_{\text{O-H}}^{\text{bonded}}(\text{cm}^{-1}) = 3625 - 50 \cos 2(\theta - 30^\circ) \quad (1)$$

The relationship may well be rationalized by inspection of molecular models (see Figure 1) in such a way that, when $\theta = 120^\circ$, the OH hydrogen atom is situated right above the π -cloud of the C_1 atom of the benzene ring and the overlap between the hydroxyl group and the π -electrons is expected to be maximum. Compounds 6 to 10 are the typical examples. At $\theta = 30^\circ$, the hydroxyl hydrogen lies on the plane of the benzene ring, pointing the node of the π -electrons with the result of no effective bonding at all. Correspondingly, $\nu_{\text{O-H}}$'s appear at the normal free $\nu_{\text{O-H}}$ region of $3620 \sim 3627 \text{ cm}^{-1}$ in 1a, 1b and 3a. The argument is based on the reasonable assumption that, in most of the bonded conformation of β -phenylethanols, the C_α -O bond may be staggered with the C_β - C_1 bond; in other words the dihedral angle between the planes of $\text{O}-C_\alpha-C_\beta$ and $C_\alpha-C_\beta-C_1$ will be approximately 60° .

Application of the relationship found in this paper to the conformational analysis of chroman-4-ols will be reported in due course.

Acknowledgment. The author expresses his appreciation to Professor M. Ōki for his interest and encouragement throughout this work.

REFERENCES

- (1) M. Tichý, "Advances in Organic Chemistry; Methods and Results", Vol. 5, R. A. Raphael, E. C. Taylor and H. Wynberg, Ed., p. 115, John Wiley & Sons, Inc., New York, N. Y. 1965, and papers cited therein.
- (2) M. Ōki, H. Iwamura, T. Onoda and M. Iwamura, Tetrahedron, 24, 1905 (1968); Y. Matsui, M. Takasuka and T. Kubota, Shionogi Kenkyusho Nempo (Ann. Rept. Shionogi Res. Lab.), 15, 125 (1965); T. Kubota, M. Takasuka and Y. Matsui, ibid., 16, 63 (1966).
- (3) G. C. Pimentel and A. L. McClellan, "Hydrogen Bond", p. 82, W. H. Freeman & Co., San Francisco, 1960; L. P. Kuhn, J. Am. Chem. Soc., 74, 2492 (1952); 76, 4323 (1954).
- (4) Recently M. Takasuka, Y. Matsui, S. Kubota and H. Tanida (Proceedings of the 2nd Symposium on Structural Organic Chemistry, Osaka, Nov. 1969, p. 68) suggested a possible correlation between the integrated intensity of the π -bonded ν_{O-H} and the structure of olefinic alcohols, prompting the present author to communicate his result.
- (5) H. M. Fales and W. C. Wildman, J. Am. Chem. Soc., 85, 784 (1963).
- (6) J. H. Brewster and J. G. Buta, ibid., 88, 2233 (1966).
- (7) H. Hart and R. K. Murray, Jr., ibid., 91, 2183 (1969).
- (8) H. M. Fales and W. C. Wildman, ibid., 82, 197 (1960).
- (9) A. C. G. Gray and H. Hart, ibid., 90, 2569 (1968).
- (10) H. Tanida, T. Tsuji and H. Ishitobi, ibid., 86, 4904 (1964).
- (11) H. Kugita and E. L. May, J. Org. Chem., 26, 1954 (1961); E. L. May and H. Kugita, ibid., 26, 188 (1961); S. Saito and E. L. May, ibid., 26, 4536 (1961).
- (12) W. R. Jackson and C. H. McMullen, J. Chem. Soc., 1170 (1965).
- (13) M. Ōki and H. Iwamura, Bull. Chem. Soc. Japan, 32, 950 (1959); R. Piccolini and S. Winstein, Tetrahedron Letters, 4 (1959); L. Joris, P. von R. Schleyer and E. Osawa, Tetrahedron, 24, 4759 (1968).