Intramolecular Interaction between Hydroxyl Group and π-Electrons. IX[1]. *The Energy of the Interaction in Benzyldimethylcarbinol*

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(Received February 8, 1960)

The determination of the energy of the intramolecular interaction between hydroxyl group and π-electrons in this laboratory has so far been confined to the phenolic series[1,2]. In a preceding paper[1], it was referred that alcohols having internal interaction show rather complicated O-H stretching absorption bands (ν_{O-H}) consisting of two free ν_{O-H} corresponding to rotational isomers about the C_α-O bond and an interacting ν_{O-H}, and that the present technique[3] of separating the apparent curve into three Lorentz function type curves leaves some ambiguity and makes the evaluation of the energy inaccurate. However, current studies[4] on the effect of molecular conformations on the intramolecular interaction between the alcoholic hydroxyl group and π-electrons have shown that, in order to make more detailed discussions, the strength of the interaction should be expressed quantitatively. To overcome the aforementioned difficulty the authors took advantage of the observation that the rotational isomers of tertiary alcohols can not be distinguished by the present dispersion of the spectrometer[5], and expected that, unlike 2-phenylethanol, the free ν_{O-H} of benzyldimethylcarbinol would be single[5] and that the apparent ν_{O-H} curve could be exactly separated into a free and an interacting ν_{O-H} by the usual method of Ramsay[6]. This expectation proved to be the case and the energy of the interaction was determined by measuring the temperature variation of the absorption as described previously[1]. The least square method was adopted to determine the six parameters; a_1, b_1, ν_1, a_2, b_2 and ν_2, in the Lorentz function;

$$D(\nu)=\frac{a_1}{(\nu-\nu_1)^2+b_1^2}+\frac{a_2}{(\nu-\nu_2)^2+b_2^2}$$

The data are summarized in Table I.

TABLE I. THE EFFECT OF TEMPERATURE ON THE ν_{O-H} ABSORPTION OF BENZYLDIMETHYLCARBINOL

$1/T\times10^3$	ν_{O-H}	ν	a	b	$\ln(A_1/A_2)$
3.37	1	3593.5	16.13	8.14	−0.292
	2	3614.9	25.11	9.46	
3.25	1	3594.3	18.46	8.97	−0.268
	2	3615.9	26.24	9.76	
3.16	1	3594.9	17.23	9.11	−0.340
	2	3616.0	25.93	9.76	
3.04	1	3595.4	17.22	9.28	−0.349
	2	3615.7	25.67	9.76	
2.94	1	3596.3	15.86	9.14	−0.397
	2	3617.4	24.95	9.67	

The energy difference ($-\Delta H$) was found to be 0.54±0.13 kcal./mol. This is far less than that of ordinary hydrogen bondings which range from 2.3 to 7 kcal./mol.[7] The energy value is not consistent with those estimated by Goldman and Crisler[8] and by Schleyer and coworkers[9], but is in good agreement with some conformational observations accumulated in this laboratory[10] for β-tetralol, cyclohexen-3-ol and ergosterol. Namely, these compounds only exhibit the free hydroxyl band and

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[1] Part VIII: M. Ōki and H. Iwamura, This Bulletin, in press.

[2] M. Ōki, H. Iwamura and Y. Urushibara, ibid., **31**, 769 (1958).

[3] M. Ōki and H. Iwamura, ibid., **32**, 1135 (1959).

[4] M. Ōki and H. Iwamura, ibid., **32**, 307 (1959); P. von Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

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

[6] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[7] C. A. Coulson, *Research*, **10**, 149 (1957).

[8] I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).

[9] While the present work was in progress, P. von Schleyer and his coworkers [*Tetrahedron Letters*, No. 14, (1959), p. 1] alluded that the energy of the intramolecular interaction in 2-phenylethanol was estimated to be about 1.4 kcal./mol. through temperature variation.

[10] M. Ōki, H. Iwamura and T. Onoda, unpublished work.

lack the interacting ν_{O-H}. These molecules could have been able to possess an internal interaction if the hydroxyl groups were oriented axially, while the axial conformation is known to be less stable than the equatorial conformation by about one kcal./mol.[11] Thus, if the energy of interaction were more than or at least nearly equal to one kcal./mol., the interaction should have been certainly permitted to exist to some extent. Therefore, the energy of the interaction in these cases must be fairly smaller than one kcal./mol. A full discussion will be given in the near future.

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