Intramolecular Hydrogen Bonds. IV.[1] Phenylalkane-diols

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The present investigation is concerned with intramolecular hydrogen bonding in the systems of poly-functional compounds in which one or more proton-donating groups can form a hydrogen bond with a few proton-accepting groups. Such systems are complicated because various types of intramolecular hydrogen bonding may simultaneously appear, depending on the thermodynamical stability of the geometries to be formed through the intramolecular hydrogen bonding between the groups. Of such compounds, some phenylalkane-diols, such as diaryl pinacols[2] and phenylcycloalkane-diols,[3] have recently been investigated by means of infrared spectroscopy in the OH-stretching region.

This paper will deal with intramolecular hydrogen bonding in phenyl-α,ω-alkane-diols and with its limitation through the length of an alkylene chain intervening between the hydroxyl groups.

Intramolecular hydrogen bonding occurs in α,ω-alkane-diols $HO-(CH_2)_n-OH$ and in ω-phenylalkanols $Ph-(CH_2)_n-OH$ when n is an integer of from 2 to 4* in the former[5,6] and from 1 to 2 in the latter.[7,8] As n increases, the separation between the free and the bonded OH band ($\Delta\nu$) increases from 32 through 78 to 156 cm^{-1} in the former[5] and from 17 to 30 cm^{-1} in the latter.[8] Moreover, the intensity ratio of the free OH band to the bonded OH generally grows with the increasing n.

In consideration of these facts, it is to be expected, in the present series of $Ph-CHOH-(CH_2)_n-OH$, that the primary alcoholic hydroxyl group will predominantly form a hydrogen bond with both the secondary hydroxyl group and the π-electrons of the phenyl group when n is equal to 1, and with only the former when n is 2 or 3. However, it forms a hydrogen bond with neither of them when n is 4. At the same time, the secondary hydroxyl group may be expected to form a hydrogen bond with both the proton-accepting groups when n is an interger of from 1 to 3, but with the π-electrons only when n is 4.

In this paper, the free OH group is that OH which contains an unbonded H atom, i.e., which includes an OH group not participating in any hydrogen bond and an OH group whose oxygen atom hydrogen-bonds to the hydrogen of another OH. The bonding of the oxygen atom of a free OH group to the hydrogen of another OH group has, in general, little effect upon the frequency of the free OH group.[5,10] Accordingly, the following discussion and assignments will be made mainly on the basis of the frequencies and the intensities of the bonded OH bands, with some

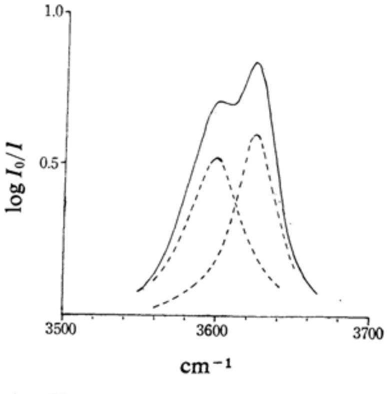

Fig. 1. IR spectrum of phenylethane-1,2-diol (I).

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1) Part III: N. Mori, S. Ōmura, H. Yamakawa and Y. Tsuzuki, This Bulletin, **38**, 1627 (1965).

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2) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957); E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6472 (1962); P. Tomboulian, *J. Org. Chem.*, **26**, 2652 (1951); W. A. Mosher and N. D. Heindel, ibid., **28**, 2154 (1963).

3) a) D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961); M. T. Davies, D. F. Dobson, D. F. Hayman, G. B. Jackman, M. G. Lester, V. Petrow, O. Stephenson and A. A. Webb, *Tetrahedron*, **18**, 751 (1956); E. Galantay, ibid., **19**, 319 (1963). b) E. M. Philbin, T. S. Wheeler, F. V. Brutcher and W. Bauer, *J. Org. Chem.*, **27**, 4114 (1962); D. C. Staiff and A. C. Huitric, ibid., **28**, 3531 (1963); H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **85**, 784 (1963).

* Kuhn and Wires[4] have recently reported that a slight intramolecular hydrogen bonding appears also when n is 5, although other investigators[6,9] previously reported its absence in this case.

4) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

5) L. P. Kuhn, ibid., **74**, 2492 (1952).

6) A. B. Foster, A. H. Haines and M. Stacey, *Tetrahedron*, **16**, 177 (1961).

7) P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

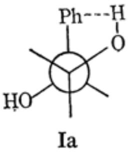
8) M. Ōki and H. Iwamura, This Bulletin, **32**, 1135 (1959).

9) D. W. Davidson, *Can. J. Chem.*, **39**, 2139 (1961).

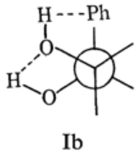
10) L. P. Kuhn, *J. Am. Chem. Soc.*, **80**, 5950 (1958).

consideration also of those of the free OH bands.

The spectrum of phenylethane-1, 2-diol (I) contains a partially resolved doublet with maxma at 3624 and 3600 cm^{-1}; this doublet can graphically be separated into two symmetric components, as is shown in Fig. 1, which can reproduce almost the same doublet as the original one by overlapping with each other. The former frequency accords with the free ν_{OH} of 3627 cm^{-1} of α-phenylethanol,[8)] and the latter, with the bonded ν_{OH} of ca. 3605 cm^{-1} of β-phenylethanol.[7,8,11)] Consequently, diol I may predominantly take form Ia rather than form Ib:



Ia



Ib

The secondary OH group in Ia is completely free, but in Ib it is hydrogen-bonded with the primary one. Form Ib may be absent because this diol shows no OH band near 3550 cm^{-1}, at which point *cis*-1-phenylcyclohexane-1, 2-diol containing a hydrogen-bonded conformation similar to form Ib shows a strong band due to the tertiary OH group bonded to the secondary OH.[3a)] Also, the diol may be free from hydrogen bonding between the secondary OH group and the π-electrons because there is no absorption band near 3616 cm^{-1}, at which point α-phenylethanol shows a bonded OH band.[8)]

1-Phenylpropane-1, 3-diol (II) shows two unsymmetric bands at 3615 and 3547 cm^{-1}, the former having a shoulder on the higher frequency side and the latter, a shoulder on the lower frequency side. Therefore, the bands can be resolved into four substantially symmetric components by graphical separation, as is shown in Fig. 2. The bands at 3638 and 3531 cm^{-1} may be assigned to the free and the bonded OH group, as in IIa, and similarly, the other pair of 3615 and 3547 cm^{-1}, to the bonded OH groups, as in IIb.

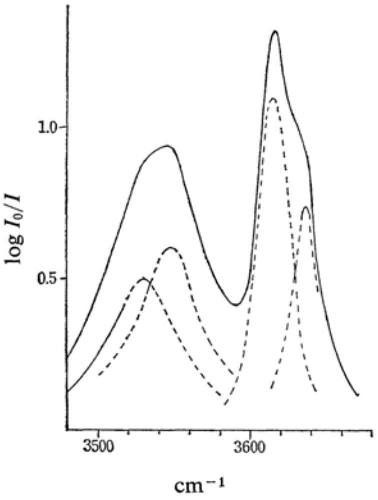
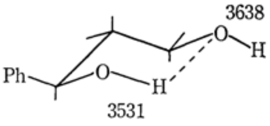
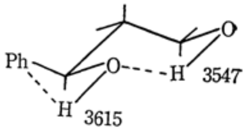


Fig. 2. IR spectrum of 1-phenylpropane-1, 3-diol (II).



IIa



IIb

The separation between the primary OH bands is 91 cm^{-1}, but for the secondary OH bands it is 84 cm^{-1}. In the latter case, however, it is increased to a reasonable value of 93 cm^{-1} by replacing the bonded secondary OH frequency in IIb by the free one of 3624 cm^{-1} of compound I.

1-Phenylbutane-1, 4-diol (III) similarly shows two unsymmetric bands, with peaks at 3614 and 3452 cm^{-1}, which have shoulders at about 3636 and 3473 cm^{-1} respectively, as Fig. 3 shows. The former band could graphically be separated into two components, whose maxima are at 3636 and 3614 cm^{-1}, but the latter band was difficult to divide into components and the apparent shoulder was taken to be the peak of the additional unresolved components. As is shown in forms IIIa and IIIb, these bands may, respectively, be assigned to the free

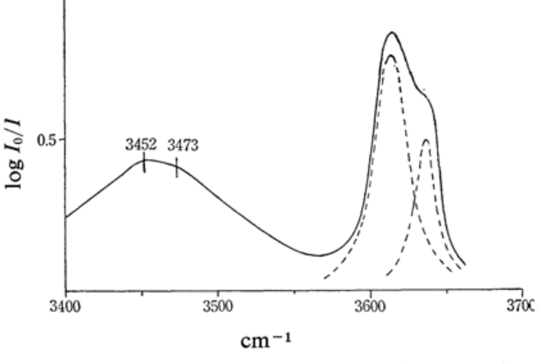


Fig. 3. IR spectrum of 1-phenylbutane-1, 4-diol (III).

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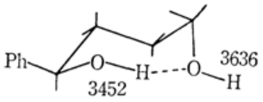
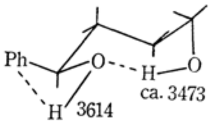
11) F. Dalton, *J. Chem. Soc.*, **1962**, 1566.

primary OH group, the secondary OH bonded to the π-electrons, the primary OH bonded to the secondary OH, and the secondary OH bonded to the primary OH.



IIIa



IIIb

1-Phenylpentane-1, 5-diol (IV) shows a strong band at 3615 cm^{-1} and a very weak, broad band at about 3491 cm^{-1}. The former has a shoulder on the higher frequency side and can be separated into two symmetric bands, at 3636 and 3615 cm^{-1}, which may be due to the free primary OH group and the secondary OH bonded to the π-electrons respectively. Since the absorbance of the free primary OH band is lower than that of the secondary OH band, the weak band is probably due to the primary OH group whose H atom hydrogen-bonds with the oxygen of the bonded secondary OH group, in spite of the fact that the phenyl group makes the secondary OH group more acidic than the primary OH.[3a] 5-Methoxypentanol shows a weak, broad band due to the internally bonded OH group at 3501 cm^{-1}.[6]

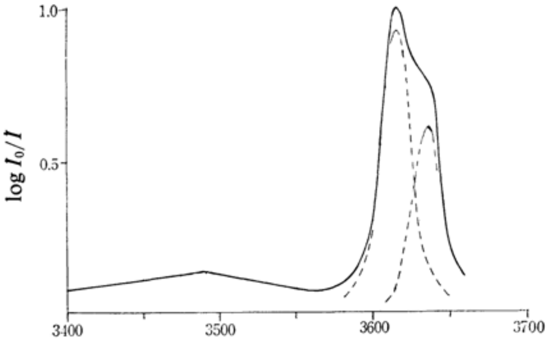
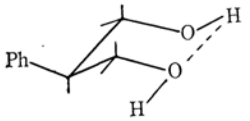


Fig. 4. IR spectrum of 1-phenylpentane-1, 5-diol (IV).

2-Phenylpropane-1, 3-diol (V) shows two almost symmetric bands at 3634 and 3553 cm^{-1}, which accord with those of 2-alkylpropane-1, 3-diols.[12] The following internally-bonded form Va may be the most favorable for this compound:



Va

The phenylalkane-diols will also contain a certain proportion of molecules in which both the OH groups are free and/or one of them is free and the other forms a hydrogen bond with the phenyl group; this proportion may not be significantly high in the case of diols other than I and IV.

TABLE I. SUMMARY OF INFRARED DATA FOR Ph-CHOH-$(CH_2)_n$-OH

Compound	n	ν_{OH}, cm^{-1}	log I_0/I	$\Delta\nu_{1/2}$
I	1	3624	0.60	35
		3600	0.52	46
II	2	3638	0.74	25
		3615	1.10	30
		3547	0.60	52
		3531	0.50	60
III	3	3636	0.49	16
		3614	0.76	25
		3473 3452	0.43	136
IV	4	3636	0.61	22
		3615	0.94	23
		3491	0.13	
V		3634	0.19	27
		3553	0.12	24

Experimental

Compound I was prepared from styrene by the method described in the literature.[13] Compounds II and V were synthesized in the usual way by the hydrogenolysis of ethyl β-phenyl-β-hydroxypropionate[14] and diethyl phenylmalonate[15] with lithium aluminum hydride, while compounds III and IV were similarly prepared from the ethyl esters of ω-benzoyl-propionic and -butyric acid[16] and recrystallized from ether. Their properties and data of analysis are shown in Table II.

TABLE II

Compound	M. p., °C (B. p., °C/mmHg)	Calcd.		Found	
		C	H	C	H
I	65—66[13]				
II	(152/5[17]) $n_D^{25}=1.4528$				
III	75 (155/2)	For $C_{10}H_{14}O_2$ 72.26	8.49	72.53	8.78
IV	53.5 (165—166/4)	For $C_{11}H_{16}O_2$ 73.30	8.95	73.25	9.35
V	48.5—49.5[18] (167/9)				

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[12] P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961).

[13] N. A. Milas and S. Sussmann, ibid., **59**, 2345 (1937).

[14] E. C. Horning (Editor-in-chief), "Organic Syntheses", Coll. Vol. III, 408 (1955).

[15] A. H. Blatt (Editor-in-chief), ibid., Coll, Vol. II, 288 (1948).

[16] A. H. Blatt, ibid., Coll. Vol. II, 81 (1948).

[17] A. St. Pfau and P. Plattner, *Helv. Chim. Acta*, **15**, 1250 (1632).

[18] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 3121 (1948).

The infrared measurements were carried out by a method previously reported,[1] at a concentration of 0.004 mol./l. in carbon tetrachloride, except that saturated solutions of compounds I and V were used because of their low solubility. The infrared data are summarized in Table I.

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