Effect of Hydrogen Bonding on the Rotational Barriers of Partial Double Bonds. III. 2,6-Dihydroxyaryl Carbonyl Compounds

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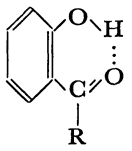
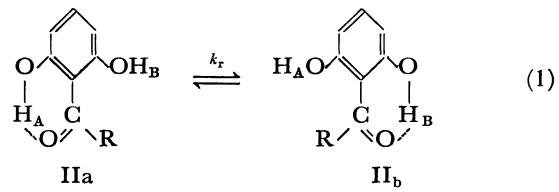
Activation parameters of internal rotation around C_{ar}–$C_{carbonyl}$ bonds are determined by means of DNMR spectroscopy for 2,6-dihydroxybezaldehyde and some 2,6-dihydroxybenzoates. The ΔG^* and ΔH^* of these compounds are *ca.* 10 kJ mol^{-1} higher than those for the reference compounds void of *ortho*-hydroxyl groups, and the excess stabilization is attributed to the contribution of the intramolecular hydrogen bonding. The intramolecular hydrogen bonding in these compounds were discussed on the basis of their infrared spectra in the ν_{OH} region.

The intramolecular hydrogen bond is formed when the hydrogen donating and the hydrogen accepting groups are located close enough to interact each other, and the whole molecule is stabilized at the sacrifice of the freedom of the intramolecular motion. Thus, the intramolecular hydrogen bonding in salicylaldehyde and salicylate esters fixes their molecules to the conformation I, and the rotational barrier around the C_{ar}–$C_{carbonyl}$ single bonds becomes considerably higher.



I : R=H or OCH_3

In other words, the coplanar conformation I of ortho-hydroxy derivatives are stabilized by the intramolecular hydrogen bonding in addition to the π-stabilization energy of conjugation common with the aryl carbonyl compounds void of the hydrogen bond, and the difference in the barrier heights between the aryl carbonyl compounds with and without *o*-hydroxyl group will reflect the energy of the intramolecular hydrogen bonding. In the previous report of the present authors, the hydrogen bond energy of *o*-hydroxybenzaldehyde was estimated in this way from the rotational barriers of 2,6-diformylphenols.[1,2] Rotational barriers of partial double bonds (C_{sp^2}–C_{sp^2} single bonds) can be best estimated by the techniques of dynamic nuclear magnetic resonance (DNMR) from the separations or from the widths of the NMR signals at various temperatures.[3–6]



IIa $\qquad$ II_b $\qquad$ (1)

For this purpose, such protons should be chosen as the probe of the intramolecular rotation that they are equivalent in the condition of fast exchange but nonequivalent when the exchange is slow. Since two hydroxyl protons (H_A and H_B in II) of 2,6-dihydroxyaryl carbonyl compound are suitable for this purpose, the DNMR measurements were carried out on these compounds and their intramolecular hydrogen bonding was discussed in this paper.

Experimental

Preparation of Materials. 2,6-Dihydroxybenzaldehyde and 2,6-dihydroxyacetophenone were prepared from resorcinol by the methods in literatures.[7,8] 2,6-Dihydroxybenzoate esters were obtained by reacting the corresponding alkyl halides with silver 2,6-dihydroxybenzoates.[9] All materials and solvents employed in this investigation were purified either by distillation or by recrystalization.

Measurement of the Spectra. Infrared spectra were recorded on a Hitachi Model 225 infrared spectrometer. Nuclear magnetic resonance spectra were obtained on a JEOL JNM C-60H spectrometer. Chemical shifts are given as parts per million (ppm) downfield from TMS.

Evaluation of the Rotational Barriers from the Line Shapes Above Coalescence. Because of the relatively low coalescence temperature (T_c), the exchange rate of the two equivalent protons without the splitting caused by spin-spin coupling (H_A and H_B in II) was obtained from the half-widths W^* (in Hz) of the signal above T_c by the following equation.[3]

$$(\pi\delta\nu\tau)^{-1} = [(\delta\nu/W^*)^2 - (W^*/\delta\nu)^2 + 2]^{1/2}$$

where $\delta\nu$ refers to the chemical shift difference (in Hz) of the two protons H_A and H_B. As the measurements were carried out within the temperature range where the signals were considerably broader than usual, it is assumed that the exchange contribution W^* to the observed line width W is by far greater than that from the natural width (hence, $W=W^*$).

Results and Discussion

Kinetic studies of some alkyl 2,6-dihydroxybenzoates in chloroform-*d* and of 2,6-dihydroxybenzaldehyde in diethyl ether were carried out employing the techniques of DNMR spectroscpy. From Eq. 1, the rate constants (k_r in s^{-1}) of the intramolecular exchange process between H_A and H_B due to the rotational interconversion between II_a and II_b were calculated from the half widths (in Hz) observed at various temperatures, and given, together with the half widths, in Table 1.

In 2,6-dihydroxy-benzaldehyde and -acetophenone, H_A and H_B are the free and the intramolecularly hydrogen bonded hydroxyl protons, while, in alkyl 2,6-dihydroxybenzoates, they are the hydroxyl protons intramolecularly hydrogen bonded to the alkoxyl and to the carbonyl groups of the ester.

The Arrhenius plot (k_r *vs.* $1/T$ plot in Fig. 1) gives the enthalpy and the entropy of activation of the interconversion between the degenerate geometrical isomers II_a and II_b, and thus obtained activation parameters

Table 1. Kinetic data for the internal rotation around the C_{ar}-$C_{carbonyl}$ bonds of some 2,6-dihydroxyaryl carbonyl compounds[a)]

	T/K	W/Hz	k_r/s^{-1}
2,6-Dihydroxybenzaldehyde **1** (Solvent: $C_2H_5OC_2H_5$)	251.5	5.55	7567
	248.3	6.45	6247
	243.6	10.05	3687
	238.1	18.40	1907
	233.6	24.30	1434
	231.3	29.50	1184
	229.0	33.45	1049
	223.4	55.50	669
	222.7	58.50	640
	221.2	74.30	531
	219.6	99.90	428
Methyl 2,6-dihydroxybenzoate **3** (Solvent: $CDCl_3$)	224.2	17.50	1983
	218.4	38.40	979
	215.1	64.80	625
	212.1	87.60	498
	211.8	105.00	437
Ethyl 2,6-dihydroxybenzoate **4** (Solvent: $CDCl_3$)	251.7	8.80	5212
	246.1	10.50	4175
	240.4	21.00	1893
	228.4	60.00	691
	227.9	67.00	631
	225.7	80.00	550
Propyl 2,6-dihydroxybenzoate **5** (Solvent: $CDCl_3$)	254.2	10.00	3625
	245.2	23.50	1579
	239.2	36.50	1029
	233.9	46.00	834
	230.5	94.00	474

a) The $\Delta\nu$ values given in Table 2 were used for the calculations of k_r values, and $W=W^*$ is assumed. (See text.)

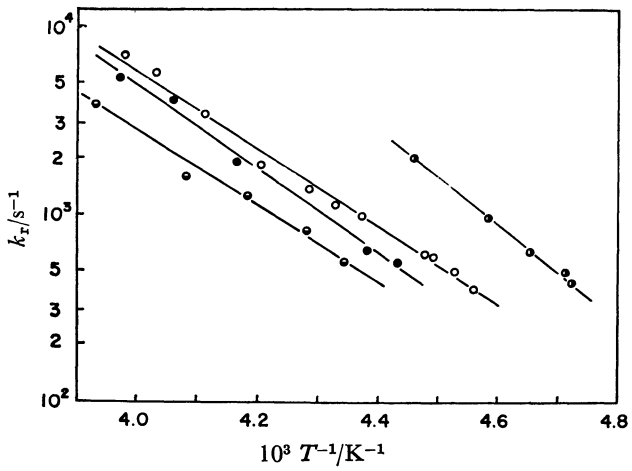
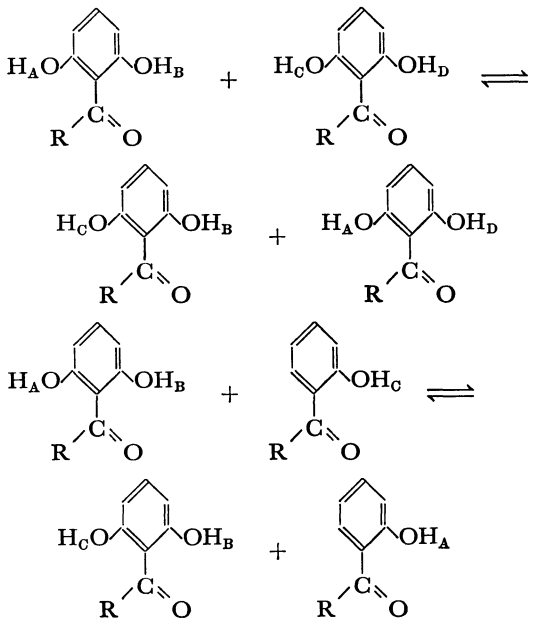


Fig. 1. Arrhenius plots for 2,6-dihydroxybenzaldehyde (—○—), methyl 2,6-dihydroxybenzoate (—◑—), ethyl 2,6-dihydroxybenzoate (—●—), and propyl 2,6-dihydroxybenzoate (—◒—).



are shown in Table 2. The activation parameters of 2,6-dihydroxyacetophenone could not be determined owing to its very low coalescence temperature (≈195 K) which made difficult the determination of the exact resonance frequencies of the free and the hydrogen bonded hydroxyl protons.

Since the activation parameters are obtained only for the fastest process, any other process faster than the internal rotation will prevent the determination of the rotational barrier height. Thus, the effect of intermolecular exchange processes (rate constant k_e), such as Eq. 2, is checked by the measurement of the spectra on salicylaldehyde–methyl salicylate–chloroform-*d* and methyl 2,6-dihydroxybenzoate–salicylaldehyde–chloroform-*d* ternary systems.

The OH proton signals of the two species appear separately and quite sharply in the spectra of the above ternary systems even at room temperature and when their chemical shift difference is only 5 Hz or so.[10)]

Table 2. Activation parameters for the internal rotation in some 2,6-dihydroxyaryl carbonyl compounds and related substances

Compound	T_c/K	$\Delta\nu$/Hz	ΔG^*/kJ mol^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
1	215.6	143.0	41.8	37.4	−21
2	≈195		≈33		
Benzaldehyde	150		33.1		
3	207.5	147.6	40.2	41.8	+8
4	222.1	150.0	43.1	41.1	−9
5	227.1	148.0	44.1	38.4	−25
6[a)]	<163		<34.7[b)]		

a) 3,4,5-Trimethoxybenzoic acid as the reference substance without intramolecular hydrogen bond. b) To calculate the upper limit of the ΔG^* value, $\Delta\nu$ is assmed to be 10 Hz, which corresponds to the chemical shift difference between H_3 and H_5 of 2,6-diformylphenol in the frozen state.

Thus, the intermolecular exchange processes are proven to be slower than the intramolecular process, *i.e.* $k_r \gg k_e$.

The ΔG^* and ΔH^* for 2,6-dihydroxybenzaldehyde (**1**) are 41.8 and 37.4 kJ mol^{-1}, respectively, and a little smaller than those of 2,6-diformylphenols (46.4 and 43.9 kJ mol^{-1}, respectively, for the *p*-methyl derivative in chloroform-*d*).[1] The measurement on **1** was carried out in diethyl ether instead of chloroform-*d*, and the lower energy barrier in **1** is at least partly due to the effect of the more polar solvent. While, the steric interaction between formyl hydrogen atom and the free hydroxyl group should be slightly repulsive, which may contribute additionally to the instabilization of the planar hydrogen bonded conformation. However, the stabilization due to the intramolecular hydrogen bond is remarkably more predominant, and the planar conformations of **1** are about 9 kJ mol^{-1} more stable than those of benzaldehyde. The activation parameters for 2,6-dihydroxyacetophenone (**2**) could not be determined exactly because of its lower T_c and of its poor solubilities in available solvents (chloroform, diethyl ether, vinyl chloride, *etc.*) under the experimental conditions. The remarkably lower rotational barrier of **2** must be caused by the increase in steric hindrance, since the C–H···OH interaction in **1** is replaced by much serious repulsive interaction between the methyl and the hydroxyl groups in this molecule. Judging from the Stuart molecular models, the most stable conformation of **2** is expected to become nonplanar, and its rotational barrier might be illustrated schematically by the broken line in Fig. 2. The nonplanar conformation is supported by the fact that the ν_{OH} absorption due to the chelated hydroxyl group is very weak in the infrared spectrum of **2** in dilute carbon tetrachloride solution.

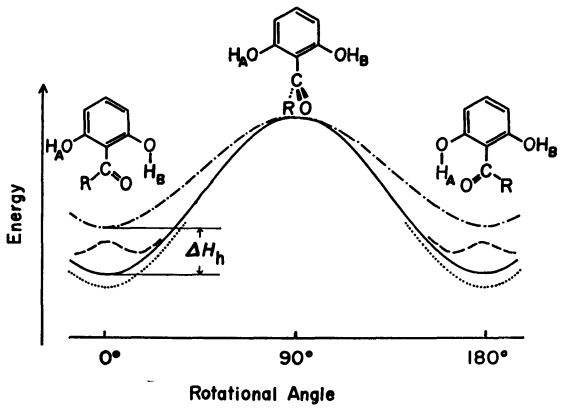
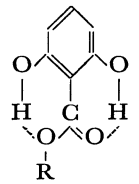


Fig. 2. Schematic diagrams for the potential energy barriers of 2,6-dihydroxybenzaldehyde (——), 2,6-dihydroxyacetophenone (----), and 2,6-dihydroxybenzoate esters (·····).
The potential barriers of benzaldehyde (—·—·) is also illustrated as reference.

Table 3. Infrared spectra of 2,6-dihydroxyaryl carbonyl compounds in the ν_{OH} region (3600—3000 cm^{-1})

Compound	c/mol l^{-1}	ν_{OH}/cm^{-1}	ε_{max}/l mol^{-1} cm^{-1}	Assignment[a]
1	0.013	3596.9	137	f.
		3140	27	h. c.
2	0.020	3593.2[b]	190	f.
3	0.010	3473.2	149	h. a.
		3202	70	h. c.
4	0.010	3461.0	129	h. a.
		3202	40	h. c.

a) f=free, h. c.=hydrogen-bonded to carbonyl oxygen atom, h. a.=hydrogen-bonded to alkoxyl oxygen atom. b) A broad absorption band centered at about 3150 cm^{-1} is observed, but its intensity is by far lower than that of **1**.



(III)

The infrared spectra of 2,6-dihydroxybenzoate esters (**3**,**4**) in Table 3 show the presence of two kinds of hydrogen bonded species. However, the absorption of the free species is not detected in any of their spectra. The fact is reasonably explained by assuming a planar conformation in which one hydroxyl group is chelated to the carbonyl oxygen atom and the other to the alkoxyl oxygen atom by forming intramolecular hydrogen bonds, as illustrated by III. Since the OH···O=C hydrogen bond is stronger than the OH···OR hydrogen bond,[11] the OH stretching absorption at the lower frequency is assigned to the hydroxyl group hydrogen bonded to the carbonyl, and the absorption at the higher ferquency to the hydroxyl group hydrogen bonded to the alkoxyl oxygen atom (as shown in Table 3).

The ΔG^* and ΔH^* values of the 2,6-hydroxybenzoates **3**, **4**, **5** are similar to those of **1** and a considerable stabilization due to the intramolecular hydrogen bond formation is suggested. In order to estimate the contribution of the hydrogen bonding to the stability of the planar conformation, DNMR measurement of methyl 3,4,5-trimethoxybenzoate **6**, as a reference, was also carried out. However, the aromatic proton signal of **6** was rather a sharp singlet even at 173 K, and no indication of splitting into an AB quartet was observed. The π-bond order of the C_{ar}–$C_{carbonyl}$ bond from MO calculation serves as a criterion for the potential barrier height.[12] The π-bond orders for benzoate ester and benzaldehyde are calculated to be 0.247 and 0.271, respectively, by PPP approximation, and the rotational barrier of **6** is expected to be lower than that of benzaldehyde. Anyhow, the rotational barrier is at least 10 kJ mol^{-1} higher than that of the reference compound, and the excess stabilization energy is again attributed to the contribution of the intramolecular hydrogen bonding. The OH···OR hydrogen bonding in the esters **3**—**5** must increase the stability of the planar conformation III, but its contribution cannot be determined quantitatively because of the uncertain activation parameters of the reference substance **6**.

The rotational barriers of the aryl carbonyl compunds are illustrated schematically in Fig. 2. In the transition state of the internal rotation het

aromatic nucleus is perpendicular to the plane of the carbonyl group, and both the hydrogen bonding and the steric hindrance do not affect its potential energy remarkably. Thence, the hydrogen bond energy can be estimated as the difference in ΔH^* (ΔH_h in Fig. 2) of the chelated and the reference substances. Hydrogen bond energies thus obtained are *ca.* 9 kJ mol^{-1} for 2,6-dihydroxybenzaldehyde and 8 kJ mol^{-1} for 2,6-dihydroxybenzoates. These values are considerably smaller than the hydrogen bond energies of the similar substances obtained by other methods.[13] The lower ΔH_h may be justified by the polar nature of the solvents used and the negative contribution of the steric hindrance in the planar conformation.

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11) D. N. Shigorin, "Hydrogen Bonding," ed by D. Hadzi, Pergamon Press, London (1959), p. 191.
12) The linear relation between the barrier height and the bond order has been reported by several authors. For example, see: K. Spaargaren, P. K. Korver, P. J. van der Haak, and Th. J. de Boer, *Org. Magn. Reson.*, **3**, 615 (1971).
13) Hydrogen bond energies are listed in the following: G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco (1960), pp. 356—360. See also, E. Funk and R. Mecke, "Hydrogen Bonding," ed by D. Hadzi, Pergamon, London (1959), p. 433 and M. Davies, *ibid.*, p. 393.