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The Effect of Intramolecular Hydrogen Bonding on the Rotational Barriers about the C-N Bonds of *o*-Hydroxyarenecarboxamides

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Rotational barriers about the C-N bonds of several *o*-hydroxyarenecarboxamides were determined in four solvents (namely, chloroform, pyridine, methanol, and dimethyl sulfoxide) by DNMR spectroscopy and compared with those of arenecarboxamides void of ortho-hydroxyl group. The height of the rotational barrier is correlated with the strength of the intramolecular O-H···O=C hydrogen bond. The unusual solvent effect on the rotational barriers of these hydroxy-amides are ascribed to the cleavage of the intramolecularly hydrogen bonded chelate ring which occurs in both hydrogen-donating and -accepting solvents.

Rather extensive studies have been reported on the dynamic NMR spectroscopic behaviors of amides,[1-7] and rotational barriers about the C-N bonds of unsaturated and aromatic amides have been shown to be strongly affected by the conjugative properties of their hydrocarbon moiety with the carbonyl group, as revealed by the rotational barriers of *N,N*-dimethylacrylamide[1] and *N,N*-dimethylbenzamide[2] (69.8 and 64.9 kJ mol^{-1}, respectively) which are considerably lower than that of *N,N*-dimethylformamide (87.4 kJ mol^{-1}).[3] Several *o*-substituted benzamides have higher rotational barriers than those of the unsubstituted and the high barrier has been ascribed to the steric inhibition, at least partly, of the conjugation between the aryl and the carboxamide groups.[2,7] Several years ago, we reported on the effect of intramolecular hydrogen bonding on the rotational barrier of *N,N*-dimethylsalicylamide.[8] The report showed that the rotational barrier of the *o*-hydroxy amide is significantly lower than those of usual *N,N*-dimethylbenzamides. Similar lowering in the rotational barrier due to the effect of hydrogen bonding was also illustrated with *o*-aminobenzamide by Jackman in his book.[9]

In this research, the rotational barriers of several other *N,N*-dimethyl-*o*-hydroxyarenecarboxamides were determined in order to further clarify the effect of intramolecular hydrogen bonding. Solvent effect on the rotational barriers of several benzamides were also studied systematically and the peculiar solvent effect on the rotational barriers of *o*-hydroxyarenecarboxamides was disclosed and interpreted.

Experimental

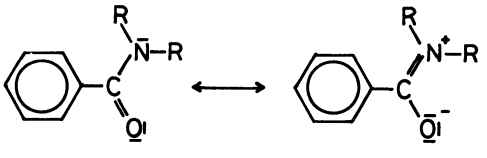
N,N-Dimethyl- and *N,N*-dibenzylarenecarboxamides were prepared as usual by the reaction of the corresponding aroyl chlorides with dimethyl- and dibenzylamines, respectively.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer using 10-mm probe. The samples for the measurements were prepared by dissolving ca. 100 mg of the amide in ca. 1.5 ml of the solvent, the concentrations of the solutions being adjusted to be ca. 0.5 mol dm^{-3}. Chloroform-*d*, methanol-d_4, pyridine-d_5, and dimethyl-d_6 sulfoxide (DMSO-d_6) were used as solvents throughout this work. The ^{1}H and ^{13}C spectra were obtained at 89.56 and 22.50 MHz, respectively. Temperature-dependent NMR in order to obtain ΔG^* were measured with an aid of JES-VT-3 variable temperature apparatus. The ΔG^* values were determined at the coalescence temperatures. In order to evaluate the ΔG^* values very accurately, the rates of exchange between the two sites were computed by the simulation of line shapes near the coalescence temperature and used supplementally.

Results and Discussion

Variable temperature measurements on the methyl ^{1}H signals of various *N,N*-dimethyl- and *N,N*-dibenzyl-*o*-hydroxyarenecarboxamides were carried out in four perdeuterated solvents, namely, chloroform, methanol, pyridine, and dimethyl sulfoxide (DMSO) and the free energies for of activation of the internal rotation about the C-N partial double bonds (hereafter named "rotational barrier(s)" and noted as ΔG^*) were determined.[10] The rotational barriers of the amides hereby measured in these solvents are given in Table 1a together with some from the similar measurements on methyl ^{13}C signals. The rotational barriers from the both nuclei agree with each other excellently, showing the reliability of the ΔG^* values.

The rotational barriers about the C-N partial double bonds of amides were shown to become higher as the solvents become more polar. This trend was ascribed to the effect of polar solvents which favor the polar mesomeric structure **II** and stabilize the ground state rather than the transition state of the internal rotation.[7] In this investigation, the solvent effect was reexamined with the aim of elucidating the effect of hydrogen-donating and hydrogen-accepting abilities of solvents on the rotational barriers of the amides.



(I) (II)

Table 1a. Rotational Barriers about the C-N Bonds (ΔG^*) and Coalescence Temperatures (T_c) of *N,N*-Dialkylarenecarboxamides from ^{1}H DNMR in Several Solvents

No.	X	ΔG^*/kJ mol^{-1} (T_c/K)[a]				$\Delta\Delta G^*_{solv}$/kJ mol^{-1} [b]		
		Chloroform	Methanol	Pyridine	DMSO	CD_3OD	C_5D_5N	DMSO
(a)	*N,N*-Dimethylbenzamides $XC_6H_4CON(CH_3)_2$							
1	H	65.5 (302.0)	67.8 (308.6)	63.2 (299.7)	—	+2.3	−2.3	—
2	*p*-Cl	64.6 (296.2)	67.2 (304.5)	63.3 (297.8)	65.1 (295.3)	+2.6	−1.3	+0.5
3	*p*-CH_3O	61.4 (274.7)	63.3 (278.0)	58.8 (274.7)	—	+1.9	−2.6	—
4	*p*-CH_3	64.0 (292.2)	66.5 (300.3)	62.0 (291.0)	—	+2.5	−2.0	—
5	*p*-OH	63.2 (283.5)	61.4 (263.6)	57.6 (265.8)	—	−1.8	−3.6	—
6	*o*-Cl	—	—	78.5 (373.0)	80.4 (375.5)			
7	*o*-CH_3O	—	—	75.7 (358.0)	77.5 (361.2)			
8	*o*-CH_3	74.1 (349.2)	—	72.6 (347.0)	74.6 (350.2)	—	−1.5	+0.5
9	*o*-OH	51.1 (236.8)	59.6 (275.7)	57.1 (265.3)	—	+8.5	+6.0	—
10	2-OH 5-Cl	51.3 (239.0)	61.1 (282.5)	59.2 (274.6)	63.1 (291.3)	+9.8	+7.9	+11.8
11	2-OH 5-NO_2	51.6 (241.0)	61.6 (286.6)	61.0 (284.8)	64.1 (298.3)	+10.0	+9.4	+12.5
12	2-OH 5-CH_3O	51.3 (231.8)	59.7 (275.0)	56.8 (259.8)	—	+8.4	+5.5	—
13	2-OH 3,5-Me_2	50.9 (234.0)	55.4 (255.0)	53.6 (239.6)	—	+4.5	+2.7	—
14	2-CH_3O 3,5-Me_2	—	—	77.6 (357.4)	79.2 (359.4)			
(b)	*N,N*-Dibenzylbenzamides $XC_6H_4CON(CH_2C_6H_5)_2$							
15	H	64.3 (304.3)	65.0 (305.0)	62.6 (302.0)	63.5 (297.0)	+0.7	−1.7	−0.8
16	*p*-Cl	63.1 (300.8)	63.3 (299.5)	62.8 (301.0)	63.6 (297.0)	+0.2	−0.3	+0.5
17	*p*-CH_3O	60.3 (284.8)	59.9 (279.0)	59.0 (281.0)	—	−0.4	−0.7	—
18	*p*-CH_3	63.3 (299.4)	63.8 (299.8)	62.0 (296.3)	—	+0.5	−1.3	—
19	*o*-OH	54.1 (240.5)	62.1 (294.7)	61.8 (295.5)	65.9 (311.2)	+8.0	+7.7	+11.8
20	*o*-Cl	68.3 (306.3)	—	67.0 (295.0)	—	—	−1.3	—
21	*o*-CH_3O	67.0 (299.0)	68.2 (306.2)	67.7 (304.5)	68.4 (305.2)	+1.2	+0.7	+1.4
(c)	*N,N*-Dimethylnaphthamides $XC_{10}H_6CON(CH_3)_2$							
22	1-$CONMe_2$	—	—	74.6 (351.6)	76.4 (355.8)			
				*74.4 (367.2)	*75.4 (372.0)			
23	2-$CONMe_2$	65.9 (298.1)	68.6 (307.2)	64.2 (296.8)	63.9 (290.0)	+2.7	−1.7	−2.0
				*64.8 (321.8)	*64.6 (321.2)			
24	1-$CONMe_2$ 2-OH	55.9 (258.4)	66.9 (317.6)	65.4 (302.8)	69.0 (319.3)	+11.0	+9.5	+13.1
25	2-$CONMe_2$ 1-OH	49.0 (220.8)	52.0 (233.7)	—	—	+3.0	—	—
26	2-$CONMe_2$ 3-OH	55.6 (246.9)	66.3 (301.8)	63.6 (291.0)	67.4 (307.6)	+10.7	+8.0	+11.8
27	1-$CONMe_2$ 2-CH_3O	—	—	90.5 (419.5)	91.9 (424.0)			
28	2-$CONMe_2$ 1-CH_3O	—	—	78.2 (360.5)	79.8 (362.7)			
				*77.6 (380.9)	*79.5 (390.7)			
29	2-$CONMe_2$ 3-CH_3O	—	—	78.9 (365.3)	81.7 (372.0)			
				*78.8 (385.4)	*79.9 (388.2)			

a) The asterisks in the table denote the rotational barriers (and T_c) from ^{13}C DNMR. b) $\Delta\Delta G^*_{solv} = \Delta G^*$(solvent) $- \Delta G^*(CDCl_3)$.

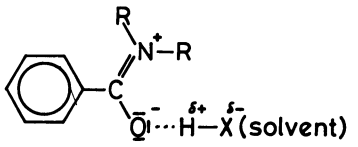
Strong intramolecular C=O···H-O hydrogen bond in *o*-hydroxyarenecarboxamides is expected to be kept intact in chloroform which is known as a less polar solvent. The persistence of the intramolecular hydrogen bond was proved by the appearance of the chelated O-H absorption in their infrared spectra (Table 3).[11] Methanol is a protic solvent and may interact with the amides as a hydrogen donor. Thus, its hydroxyl group can form a hydrogen bond very probably with the carbonyl oxygen atom of the amide.

Table 1b. Chemical Shifts for of *N*-Methyl (CH_3) and *N*-Methylene (CH_2) Protons of the *N,N*-Dialkyl Amides in Table 1a

No. of Compd.	Chemical shift δ/ppm			
	$CDCl_3$	CD_3OD	C_5D_5N	$(CD_3)_2SO$
(a) CH_3 proton chemical shifts				
1	3.05	3.03	2.99	2.93
2	3.07	3.03	2.89	2.96
3	3.06	3.04	2.96	2.96
4	3.05	3.03	2.92	2.93
5	3.06	3.04	2.97	2.96
6	2.99	—	2.88	2.88
7	2.98	2.97	2.89	2.85
8	2.98	—	2.89	2.87
9	3.17	3.01	3.02	2.88
10	3.17	3.01	3.00	2.88
11	3.24	3.02	3.03	2.91
12	3.16	3.01	3.02	2.88
13	3.15	3.02	2.92	2.91
14	2.99	—	2.92	2.87
22	2.98	2.99	2.89	2.92
23	3.04	3.07	2.97	3.02
24	3.04	3.04	3.02	2.90
25	3.19	3.08	2.91	3.00
26	3.23	3.03	3.03	2.90
27	3.03	3.00	2.95	2.90
28	3.06	3.05	2.94	2.97
29	3.01	3.00	2.92	2.90
(b) CH_2 proton chemical shifts				
15	4.55	4.54	4.67	4.49
16	4.53	4.55	4.68	4.51
17	4.58	4.56	4.73	4.51
18	4.56	4.54	4.67	4.49
19	4.69	4.48	4.45	4.45
20	4.22	4.15	4.34	4.27
21	4.24	4.23	4.36	4.22

Since the oxygen atom can behave as a biligated ligand, the intermolecular hydrogen bond itself may not induce directly the destruction of the intramolecular hydrogen bond but should, at least, weaken the bond considerably. Both pyridine and DMSO are known as strong hydrogen acceptors and expected to cleave the intramolecular hydrogen bond. Of these two, the hydrogen accepting power of DMSO is particularly strong and the intramolecular hydrogen bond in the *o*-hydroxy amides should be destroyed almost completely in this solvent.

Though it is not the main purpose of this paper, it may be useful to survey briefly the general tendency of the perturbation caused by the solvent on the rotational barriers of the amides void of *o*-hydroxyl group. As easily deduced from the $\Delta\Delta G^*$ solv values defined as the difference in ΔG^* between the respective solvent and chloroform ($\Delta\Delta G^*_{solv}=\Delta G^*(solvent)-\Delta G^*(CDCl_3)$) and given in Table 1, the rotational barrier icreases in the following order of the solvent: pyridine chloroform DMSO methanol. This sequence does not agree with the increasing order of dielectric constants[10] but coincides with the order of increasing acidity of C–H or O–H group in the solvent molecule, suggesting the participation of the hydrogen-bond-like interaction **III** of the solvent X–H group with the carbonyl oxygen of the amide, which stabilizes the mesomeric structure II. However, the effect is not very significant and perturbs the rotational barrier at most by 3 or 4 kJ mol^{-1}.



(III)

In contrasts, the rotational barriers of *o*-hydroxy amides **9—13**, **19**, and **24—26** suffer a very large solvent effect. The increases in the rotational barriers by about 10 kJ mol^{-1} were observed both in hydrogen-donating and in hydrogen-accepting solvents. In order to rationalize the large increase in ΔG^* by the influence of the solvent, the effect of *o*-hydroxyl group on the rotational barrier was reinvestigated. Ortho-substituent effect can be evaluated separately by the increment $\Delta\Delta G^*_{ortho}$ which is defined as the difference in ΔG^* between the ortho-substituted and the unsubstituted (para-substituted) amides.

The $\Delta\Delta G^*_{ortho}$ values for several ortho-substituted arene-carboxamides are given in Table 2. Considerably large positive $\Delta\Delta G^*_{ortho}$ values (more than 10 kJ mol^{-1} in many cases) for *o*-substituted *N,N*-dimethylarenecarboxamides **6—8**, **14**, **27—29** can be attributed to the steric inhibition of resonance pointed out by Jackman et al.[2] In *N,N*-dibenzyl amides **20** and **21**, the ortho effect is apparently diminished, probably due to the destabilization of planar (or nearly planar) ground state caused by the bulkier benzyl group.

On the contrary, *o*-hydroxyarenecarboxamides **9—13**, **19**, and **24—26** have negative $\Delta\Delta G^*_{ortho}$ values. The decrease in the rotational barrier comes to as large as ca. 17 kJ mol^{-1} in chloroform in which the dissolved amide is supposed to maintain the chelation by intramolecular hydrogen bonding. When the solvent is capable of forming hydrogen bond with the *o*-hydroxy amide either as a hydrogen acceptor or a hydrogen donor, the difference ($\Delta\Delta G^*_{ortho}$) tends to be less negative. The $\Delta\Delta G^*_{ortho}$ becomes even positive in DMSO which is known to act as a very strong hydrogen acceptor in forming hydrogen bond. Negative $\Delta\Delta G^*_{ortho}$ value corresponds to the fact that the rotational barrier is lower than that of the unsubstituted or para-substituted amide used as the reference. On the basis of MO calculations, the lowering of the rotational barrier is attributed to the

decreased C-N bond order in chelated *o*-hydroxyarenecarboxamide in our previous report.[8]

If the chelation is responsible for the low rotational barrier, the barrier is expected to gain the normal height when the intramolecular hydrogen bond is cleaved. As observed with **19** and **26**, this was realized by dissolving the *o*-hydroxy amides in DMSO. Small positive $\Delta\Delta G^{*}_{ortho}$ might arise from the normal ortho effect due to steric hindrance caused by the solvated hydroxyl group at the ortho-position. In sharp contrast to the *o*-hydroxy amides, the corresponding *o*-methoxyarenecarboxamides **7**, **14**, **21**, and **27—29** showed normal ortho effect due to steric hindrance to the aryl-carbonyl conjugation. Therefore, the lowering of the rotational barrier observed with the *o*-hydroxyamides is ascribable to the effect of intramolecular hydrogen bonding.

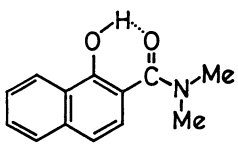
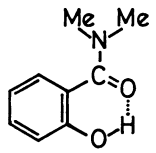
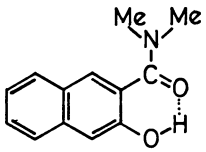
The strength of the intramolecular hydrogen bond in the six-membered chelate ring of this type has been correlated with the bond order (or bond length) of the bond joining the ring carbon atoms holding the hydroxyl and carbonyl substituents.[12,13] The chelate rings of *o*-hydroxyarenecarbaldehydes and *o*-hydroxyaryl ketones have been shown to be more stable when the double bond character of the respective C-C bond is higher and, hence, its bond length is shorter. From this point of view, the rotational barriers of three *o*-hydroxyamides **9**, **25**, and **26** were compared

Table 2. The Increase of Rotational Barrier Due to the Ortho Effect[a]
$\Delta\Delta G^{*}_{ortho} = \Delta G^{*}_{ortho} - \Delta G^{*}_{unsubst.}$

No. of compd.	$\Delta\Delta G^{*}_{ortho}$//kJ mol^{-1}			
	Chloroform	Methanol	Pyridine	DMSO
6	+15.3(+15.2)	—	—	—(+15.3)
7	—	—	+12.5(+16.9)	—
8	+8.6(+10.1)	—	+9.4(+10.6)	—
9	−14.4(−12.1)	−8.2(−2.3)	−6.1(−2.5)	—
10	−14.2	−6.7	−4.0	—
11	−13.9	−6.2	−2.2	—
12	−14.2	−8.1	−6.4	—
13	−14.6	−12.4	−9.6	—
16	+4.0(+5.2)	—	+4.4(+4.2)	—
17	+2.7(+6.7)	+3.2(+8.3)	+5.1(+8.7)	+4.9
19	−10.2	−3.0	−0.8	+2.4
24	—	—	−9.2	−7.4
25	−16.9	−16.6	—	—
26	−10.3	−2.3	−0.6	+3.5
27	—	—	+15.9	+14.5
28	—	—	+14.0	+15.9
29	—	—	+14.7	+17.8

a) $\Delta\Delta G^{*}_{ortho}{}'(=\Delta G^{*}_{ortho} - \Delta G^{*}_{para})$ are given in parentheses.

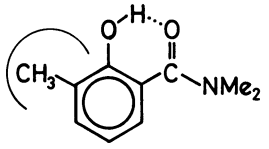
Table 3. Effect of the Strength of Intramolecular Hydrogen Bonding in the Chelate Ring upon the Rotational Barriers of *o*-Hydroxyarenecarboxamides

Chelated structure	 (**25**)	 (**9**)	 (**26**)
$\Delta G^{*}(CDCl_3)$/kJ mol^{-1}	49.0	51.1	55.6
d_{C-C}/Å[14]	1.371	1.397	1.412
$\delta_{OH}(CDCl_3)$/ppm[a]	11.55	9.99	9.37
$\nu_{C=O}$/cm^{-1} [b]	1634	1638	1648
ν_{O-H}/cm^{-1} [b]	3158(shoulder)[c]	3228	3245

a) Chemical shifts at infinite dilution in chloroform-*d*. b) Infrared absorption spectra both in the hydroxyl and carbonyl stretching regions were measured with the dilute carbon tetrachloride solutions using a 1 cm cell. c) Overlapped with C-H absorption bands.

(Table 3). As discussed previously, the partial double bond character of the amide C–N bond is expected to be reduced as the endocyclic C–C bond order increases and, hence, the chelation becomes favorable. Thus the higher bond order of the C–C bond holding the hydroxyl and carboxamide groups should result in the lower rotational barrier. Strengths of the intramolecular hydrogen bond of this type can be evaluated by the chemical shift of hydroxyl proton at infinite dilution, since the chemical shift in a very dilute solution of an inert solvent is affected predominantly by the intramolecular circumstances and tends to shift towards lower field as the hydrogen bond becomes stronger.[12,13] The infrared carbonyl spectra also help us to estimate the strength of the chelation by the low frequency shift which reflects the lowering of the carbonyl bond order. As shown in Table 3, the lowest OH chemical shift and the lowest carbonyl frequency of **25** provide experimental supports to the theoretical consequence that its chelation should be the strongest of the three hydroxyamides in Table 3. As a whole, the evidence from the spectra supports the conclusion from the bond order, and the chelation becomes gradually strong in the order of **26**, **9**, and **25**. In accord with this conclusion and the above deduction, the rotational barrier in chloroform is the lowest with **25** and the highest with **26**.

The rotational barrier of *N,N*-dimethylsalicylamide **9** seems insensitive to the electronic effect by the substituent para to the hydroxyl group. The ΔG^* values for a series of 5-substituted salicylamides **9**—**13** are identical with each other within the limit of experimental error (Table 1). *N,N*,3-Trimethylsalicylamide **13** is less susceptible to the solvent effect than other salicylamides **9**—**12** investigated. 3-Methyl group might prevent the hydroxyl group from taking the conformation anti to the carbonyl group in one hand and hinder the access of the solvent molecule to the hydroxyl group on the other hand. In this way, the intramolecular hydrogen bond of salicyl moiety is protected towards the attack of the solvent by the neighboring methyl group. Peri-hydrogen atom in 1-hydroxy-2-naphthamide **25** may also play a similar role in protecting its intramolecular hydrogen bond. Therefore, these amides are less sensitive to the effect of solvents capable of forming hydrogen bonds.



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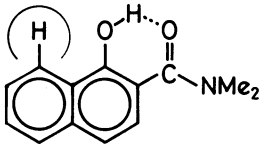

(V)

Chemical shifts of the CH_3 signals of *N,N*-dimethyl amides and the CH_2 signals of *N,N*-dibenzyl amides at temperatures higher than their coalescence temperatures (T_c) are given in Table 1b. Methyl and benzyl CH_2 signals should move towards down-field in the increasing order of ΔG^* due to increasing positive charge by the mesomeric contribution of **II**. As the solvent induced shift of the ^1H chemical shift is quite small, it seemed rather difficult to derive a definite conclusion from the solvent shift of the signal of individual amide. However, a general survey on the data in Table 1 allowed the conclusion that the expected trend is partly observed with the CH_3 signals of substituted benzamides **1**—**8** and naphthamides **23**, **24**, **27**—**29** void of an *o*-hydroxyl group, which showed up-field shifts of CH_3 signals and the lowering of ΔG^* in pyridine compared to those in chloroform. Apparently inverse solvent shift was observed with *o*-hydroxy amides **9**—**14**, **24**—**26**. This might be caused by the magnetic anisotropy effect by the hydrogen-bonded chelate ring. However, further study on the solvent effect is needed before we conclude the nature of the effect undoubtedly.

In conclusion, significantly low rotational barriers about the C–N partial double bonds of *N,N*-dialkylsalicylamides were shown very confidently to be originated from the chelation by intramolecular hydrogen bonding by examining the effects of solvents and structural changes on the barrier.

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