CHEMISTRY LETTERS, pp. 777-780, 1974. Published by the Chemical Society of Japan

EFFECT OF THE INTRAMOLECULAR HYDROGEN BONDING ON THE ROTATIONAL BARRIERS OF THE C-N BOND IN N,N-DIMETHYLBENZAMIDES

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The free energies of activation for the restricted rotation around the amide C-N bond has been determined for a series of o-substituted benzamides, and the extraordinarily low barrier in o-hydroxybenzamide is attributed to the effect of the intramolecular hydrogen bond.

The rotational barriers around the amide C-N bonds have been investigated rather extensively by means of DNMR measurement.[1-4] However, relatively few results have been reported on ortho-substituted benzamides. As a part of the investigations on the effect of the hydrogen bonding on the rotational barriers,[5] the temperature dependent NMR spectrum of o-hydroxy-N,N-dimethylbenzamide was obtained, and compared with other, mostly ortho-substituted, benzamides. The free energies of activation($\Delta G^{\neq}$) were obtained from the coalescence temperatures of the two methyl signals in the proton NMR spectra. The results are shown in the Table, in which the $\Delta G^{\neq}$ values are calibrated to give the free energies at 25°C. The theoretical rotational barrier heights (in β unit) and the C-N bond orders for some of these benzamides are given in the last two columns of the Table.

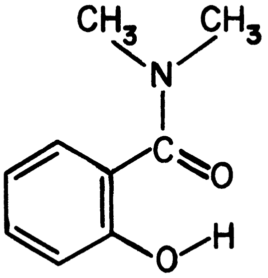
The rotational barrier of the o-hydroxy derivative is remarkably lower than those of usual N,N-dimethylbenzamides. o-Hydroxy-aromatic carbonyl compounds usually form strong intramolecular O-H---O hydrogen bonds between the hydroxyl and the carbonyl groups, and the chelate ring is supposed to be quasi-aromatic.

Table Free Energies of Activation for the Restricted Rotation Around the C-N Bonds of Some N,N-Dimethylbenzamides $XC_6H_4CON(CH_3)_2$

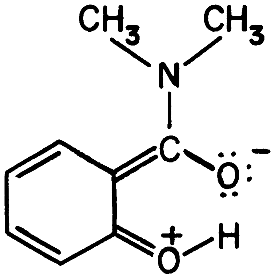
X	Solvent	Coalescence Temp Tc/K	$\Delta\nu$/Hz	$\Delta G^{\ddagger}$/KJmol^{-1} (at 298.2K)	π-Bond Order of Amide C-N Bond	Theoretical Activation Energy/β
o-OH	CH_2Cl_2	232.9	6.50	53.1	0.508**	0.217**
H	$CDCl_3$	290.7	10.5	64.0	0.546	0.239
p-OH	$CDCl_3$	279.2	4.20	65.3	0.532	0.231
o-OCH_3	$CHCl_2CHCl_2$	356.8	16.0	75.7*	0.521	0.230
o-CH_3	$CHCl_2CHCl_2$	343.8	19.32	72.4	-	-
o-Cl	$CHCl_2CHCl_2$	375.2	16.2	76.6	-	-

*) The value at Tc.

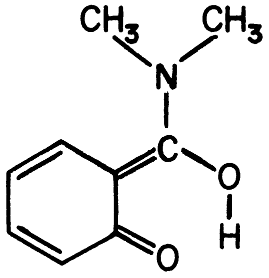
**) The effect of the intramolecular hydrogen bond is taken into accounts by assuming the non-zero resonance integral ($\beta_{O \cdot O} = 0.2\beta_0$) between the non-bonded oxygen atoms.6)



(1)

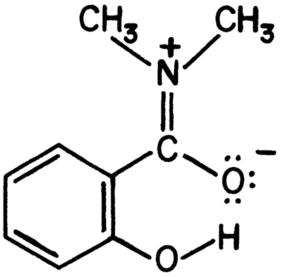


(2)



(3)

In other words, the resonance forms (2) and/or (3) may contribute to stabilize the chelate ring. The results of the simple LCAO-MO calculation also support this conclusion, in which higher C-OH and C_1-$C_{carbonyl}$ bond orders are obtained. The quasi-aromatic character of the chelate ring should decrease the C-N bond order by suppressing the resonance contribution of (4), and this interpretation is in accordance with the experiment which gives the lower $\Delta G^{\ddagger}$ for the o-hydroxy-derivative.



(4)

The other o-substituted N,N-dimethylbenzamides, on the whole, have higher C-N rotational barriers than that of the unsubstituted benzamide. o-Methoxy substituent is assumed to cause nearly a same electronic effect as the o-hydroxy substituent on the benzamide system, but is incapable of participating in the formation of the intramolecular hydrogen bond. Thus, the $\Delta G^{\ddagger}$ value of o-methoxy-N,N-dimethylbenzamide is specially useful to discriminate the electronic and the hydrogen bonding effects, and the higher $\Delta G^{\ddagger}$ value for this compound provides another evidence for the fact that the intramolecular hydrogen bond is responsible for the lower rotational barrier in the o-hydroxy-derivative. The barrier height of the p-hydroxy derivative is also normal.

Somewhat higher rotational barriers of o-substituted benzamides must be the consequence of the steric hindrance to the conjugation between the aromatic nucleus and the carbonyl group, which, in turn, strengthens the conjugation between the carbonyl group and the lone pair electrons on the nitrogen atom.

References

1) L. K. Jackman, T. E. Kavanagh, and R. C. Hadden, Org. Magn. Resonance, 1, 109(1916).

2) P. K. Korver, K. Spaargaren, P. J. van der Haak, and Th. J. de Boer, Org. Magn. Resonance, 2, 295 (1970); 3, 605 and 615 (1971).

3) G. P. Schiemenz and G. Stein, Tetrahedron, 26, 2007 (1970).

4) K. Spaargaren, C. Kruk, T. A. Molenaar-langeveld, P. K. Korver, P. J. van der Haak, and Th. J. de Boer, Spectrochim. Acta, 28A, 965 (1972).

5) M. Tabei, T. Tezuka, and M. Hirota, Tetrahedron, 27, 301 (1971).

6) M. Hirota and F. Shinozaki, Bull. Chem. Soc. Jap., 42, 2614 (1969).

(Received May 18, 1974)