HIGH PRESSURE HRNMR: THE p- AND T-DEPENDENCE OF THE HINDERED MOTIONS OF THE AMIDE GROUP IN A SERIES OF NAPHTHOIC ACID- AND BENZAMIDES.

J. Hauer, E. W. Lang, H.-D. Lüdemann

Institut für Biophysik und Physikalische Biochemie
Universität Regensburg, Postfach 397, D-8400 Regensburg

From the temperature and pressure dependence of the chemical exchange broadened proton NMR-spectra of N,N-dialkylamides the free activation energy $\Delta G^{\ddagger}$ and the activation volume $\Delta V^{\ddagger}$ are determined. The emphasis in the series of compounds presented here is to study systematically the influence of sterical hindrance upon $\Delta V^{\ddagger}$ in some 2,6 disubstituted N,N-dimethylbenzamides (diagram 1), and to investigate the contribution of the size of the N,-alkyl-substituents in some 1-Naphthoic acid N,N-dialkylamides upon $\Delta V^{\ddagger}$ (diagram 2). For the naphthoic acid amides with conformationally flexible N-alkylsubstituents (-ethyl, -n-propyl, -n-octyl, -benzyl) a second exchange process is observed. This process is ascribed to the rotation of the whole amide group around the carbonyl-aryl bond (II

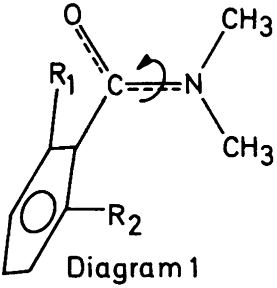

Diagram 1

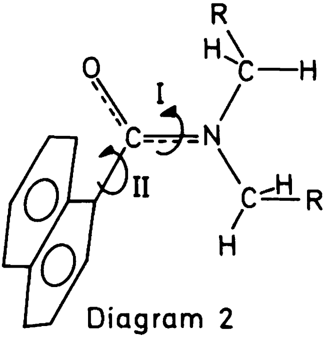

Diagram 2

in diagram 2).

Experimental: The data have been obtained at 100.1 MHz with a Varian XL-100-FT-Spectrometer, in a modified Yamada (1) strengthened glass cell (2). The spectra were simulated by application of the non-iterative part of the DNMR 5 program (3). Temperatures are accurate to ± 0.5 K.

RESULTS AND DISCUSSION

Table 1 compiles the $\Delta G^{\ddagger}$ and $\Delta V^{\ddagger}$ for the 2,6 disubstituted N,N-Dimethylbenzamides.

Table 1: Activation parameters for the benzamides

Substituent $R_1=R_2$	$\Delta G^{\ddagger}$ $(kJ \cdot mol^{-1})$	$\Delta V^{\ddagger}$ $(cm^3 mol^{-1})$
H	63	7.5±0.5
F	84	7.5±1
OCH_3	84	7.5±1
NO_2	98	5.5±1
NH_2	56	5.0±0.5
Cl_2	95	4 ±1
CH_3	97	3 ±1

The bulky 2,6 substituents do force the dimethylamide groups in a position perpendicular to the plane of the benzene ring. The increase in $\Delta G^{\ddagger}$ results from the loss of electronic interaction between the π-electrons of the benzene ring and the carbonyl group and from the sterical interaction between the N-methylgroups and the 2,6-substituents in the transition state. The series shows clearly, that $\Delta V^{\ddagger}$ and $\Delta G^{\ddagger}$ are not correlated.

The decrease in $\Delta V^{\ddagger}$ is only qualitatively parallel to the increase of overlap between the 2,6-substituents and the N-methylgroup but can still be understood in terms a simple sterical model (4).

Table 2 gives the data obtained for the two exchange processes in the 1-naphthamides.

Table 2: Activation parameters for the 1-naphthamides

R	$\Delta G^{\ddagger}_{I}$ (kJ·mol^{-1})	$\Delta V^{\ddagger}_{I}$ (cm^{3}mol^{-1})	$\Delta G^{\ddagger}_{II}$ (kJ·mol^{-1})	$\Delta V^{\ddagger}_{II}$ (cm^{3}mol^{-1})
-H	74	7.5±1	-	-
$-CH_3$	72	6.5±0.5	62	0±1
$-CH_2-CH_3$	74	6.5±1	63	0±1
$-(CH_2)_6-CH_3$	76	6.5±1	n.d.	-
$-C_6H_5$	73	8.5±1	63	0±1

For these compounds the activation parameters obtained for both processes are practically independent of the size of the substituents. Moreover the rotation of the whole amide group is essentially pressure independent. The best explanation that can be offered for these results at the moment is, that the high moments of inertia of the groups, that do have to be rotated, slow down the motions of these group, compared to the translatoric diffusion of the solvent molecules. The space required for the rotating groups is thus severely reduced.

ACKNOWLEDGEMENTS:

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