STUDY OF HINDERED ROTATION ABOUT C—N BOND IN CARBAMATES

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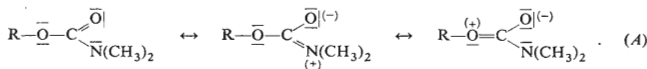
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NMR spectra of methyl groups of phenyl and α-naphthyl N,N-dimethylcarbamates have been measured at various temperatures and concentrations in tetrachloromethane, chlorobenzene, pyridine and formamide. Activation parameters of rotation about C—N bond have been calculated. The $\Delta G^{\neq}$ values $14\cdot4 \pm 0\cdot3$ and $14\cdot5 \pm 0\cdot3$ kcal/mol have been found for the phenyl and α-naphthyl derivatives respectively. These values are independent of concentration and solvent type.

The rotation about C—N bond of amides was studied in detail by means of high resolution NMR spectroscopy with respect to both the amide structure and solvent type[1]. The compounds of ROCONR$_2$ type have been given much less attention. Rogers and Woodbrey[2] studied NMR spectra of $(CH_3)_2NCOOC_2H_5$ and $(CF_3)_2NCOOC_2H_5$. They found that these compounds showed no spectral change up to their solidification point which would indicate a hindrance to rotation about C—N bond. In contrast to this, Lustig[3] and Valega[4] found a doubling or at least broadening of absorption of N-methyl groups (indicating hindered rotation) in all the cases of aliphatic and aromatic N,N-dimethylcarbamates which they studied in various solvents. Sandström[5] proved hindered rotation in $CH_3OC(S)N(CH_3)_2$ and $CH_3SC(S)N(CH_3)_2$, too, and he determined the respective $\Delta G^{\neq}$ values.

The magnitude of rotation barrier about C—N bond in carbamates can be affected by cross conjugation[1] (*A*).

$$R-\overline{O}-C\overset{\overline{O}|}{\underset{\overline{N}(CH_3)_2}{}} \quad \leftrightarrow \quad R-\overline{O}-C\overset{\overline{O}|^{(-)}}{\underset{\underset{(+)}{N(CH_3)_2}}{}} \quad \leftrightarrow \quad R-\overset{(+)}{\underline{O}}=C\overset{\overline{O}|^{(-)}}{\underset{\overline{N}(CH_3)_2}{}} \quad . \quad (A)$$

As there are no studies on such influence of cross conjugation, we have decided to study two simple aryl N,N-dimethylcarbamates, *viz.* phenyl and α-naphthyl derivatives *I* and *II*. Compounds of very different nature were chosen as solvents to enable the estimation of their influence on $\Delta G^{\neq}$. We are interested in the influence of structure on the activation barrier of rotation from the point of view of biological activity, too.

EXPERIMENTAL

Phenyl N,N-dimethylcarbamate (*I*) m.p. 44—46°C, ref.[4] 44—46°C and α-naphthyl N,N-di-methylcarbamate (*II*) m.p. 54—56°C, ref.[6] 52—55°C, were prepared by reaction of dimethylcarba-moyl chloride with phenol resp. α-naphthol and were purified by crystallization from cyclohexane. The solvents used were of p.a. purity grade and were distilled and stored over molecular sieves before measurements. The samples for measurements of NMR spectra were prepared by dis-solving the weighed amount of the substance in 1 ml of the solvent containing 5% hexamethyl-disiloxane and 1% acetone (internal standard of homogeneity). In the case of formamide only 5% acetone was used. NMR spectra were measured by means of a BS 487 A Tesla apparatus equip-ped with a temperature control probe at 80 MHz. The temperature was adjusted by means of a device calibrated by means of a thermocouple with a precision of ± 0.5°C. The speed of the recording of spectra was 0.05 Hz/s. The resolution power of the spectrometer was kept in the range $3 - 5 \cdot 10^{-9}$ at all the temperatures. The parameters for calculation of rate constants were read from the charts by means of a calibrated universal frequency counter with a precission of ± 0.1 Hz.

RESULTS AND DISCUSSION

Dependences of differences in chemical shifts of methyl groups of carbamates *I* and *II* on temperature were studied for various concentrations of the substances in tetra-chloromethane, chlorobenzene, pyridine and formamide from the temperatures close above the melting point of the solution to about 15°C (non-exchanging chemi-cal shift δv_∞). All the dependences were linear in the temperature range mentioned. The slopes of the dependences found $(\Delta \delta v_\infty / \Delta T)$ are given in Table I together with the values δv_∞ for 0°C. The values δv_∞ are temperature independent for solutions of car-bamate *II* in tetrachloromethane and for those of *I* and *II* in formamide at all the concentrations used. The slopes $\Delta \delta v_\infty / \Delta T$ for carbamate *I* in tetrachloromethane are
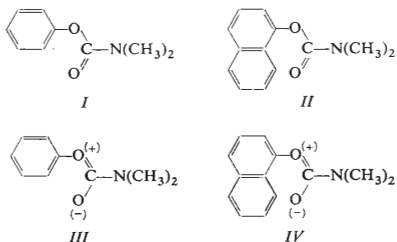
negative and only slightly greater than the slopes of analogous dependences for N,N-dimethylformamide and N,N-dimethylacetamide in various solvents[7,8]. In chlo-robenzene and pyridine the slopes have rather unusual positive values for the both compounds. The value $\Delta \delta v_\infty / \Delta T$ is twice as large for carbamate *I* in pyridine as

TABLE I

Dependence of Non-Exchanging Chemical Shift of Compounds I and II on Concentrations and Temperature

Solvent	I			II		
	conc.[a]	$\delta\nu_\infty$[b]	$\Delta\delta\nu_\infty/\Delta T$[c]	conc.[a]	$\delta\nu_\infty$[b]	$\Delta\delta\nu_\infty/\Delta T$[c]
CCl_4	0·15	10·00	— 0·028	0·13	18·2	0·000
	0·31	9·85	— 0·013	0·26	16·6	0·000
	0·45	9·57	— 0·016			
	0·68	9·21	— 0·010			
C_6H_5Cl	0·15	1·75	0·021	0·11	10·02	0·038
	0·60	1·51	0·025	0·23	10·12	0·030
C_5H_5N	0·15	0·60	0·074	0·23	11·71	0·039
	0·30	0·80	0·073	0·46	10·84	0·033
	0·60	0·80	0·071			
$HCONH_2$	0·15	9·70	0·000	0·23	18·0	0·000
	0·60	9·30	0·000	0·46	17·0	0·000

[a] mol/l, [b] Hz at 0°C, [c] Hz/deg.

TABLE II

Activation Parameters of Rotation about C—N Bond in Compounds I and II at 298 K

Solvent	I				II			
	conc.[a]	$\Delta H^{\neq}$[b]	$\Delta S^{\neq}$[c]	$\Delta G^{\neq}$[d]	conc.[a]	$\Delta H^{\neq}$[b]	$\Delta S^{\neq}$[c]	$\Delta G^{\neq}$[d]
CCl_4	0·15	$15\cdot5 \pm 0\cdot3$	3·8	14·3	0·13	$15\cdot4 \pm 0\cdot3$	3·9	14·2
	0·31	$15\cdot4 \pm 0\cdot3$	3·8	14·2	0·26	$15\cdot7 \pm 0\cdot3$	4·9	14·2
	0·45	$14\cdot9 \pm 0\cdot3$	5·1	14·3				
	0·68	$16\cdot3 \pm 0\cdot3$	6·5	14·4				
C_6H_5Cl	0·15	$15\cdot4 \pm 0\cdot4$	2·8	14·5	0·11	$16\cdot1 \pm 0\cdot3$	4·9	14·6
	0·60	$15\cdot7 \pm 0\cdot4$	4·3	14·4	0·23	$16\cdot4 \pm 0\cdot3$	6·4	14·5
C_5H_5N	0·15	$15\cdot5 \pm 0\cdot7$	4·7	14·0	0·23	$15\cdot4 \pm 0\cdot3$	3·7	14·3
	0·30	$15\cdot5 \pm 0\cdot7$	5·1	14·0	0·46	$16\cdot1 \pm 0\cdot3$	5·3	14·5
$HCONH_2$	0·15	$16\cdot5 \pm 0\cdot3$	5·7	14·8	0·23	$16\cdot5 \pm 0\cdot3$	5·5	14·8
	0·60	$16\cdot8 \pm 0\cdot3$	7·1	14·7	0·46	$16\cdot8 \pm 0\cdot3$	6·6	14·8

[a] mol/l, [b] kcal/mol, the error in $\Delta H^{\neq}$ determination is expressed by standard deviation, [c] e.u., [d] kcal/mol.

compared with that for carbamate *II*, and it is considerably higher than in the other solvents used. Carbamate *I* shows a high $\Delta\delta v_\infty/\Delta T$ value together with a small δv_∞ value, and therefore, the plot of δv_∞ against temperature crosses zero. This means that the both methyl groups of carbamate *I* have the same chemical shift at a temperature about 263 K (according to concentration). As far as we know, this is the first case where such a phenomenon was observed. Neumann and coworkers[9] approached to a similar state when studying the rotation about C—N bond in N,N-dimethyl-carbamoyl chloride in tetrachloromethane. From Table I it is obvious that the values δv_∞ are at least twice as high for carbamate *II* as those for *I* at 0°C. The concentration dependences of δv_∞ (at 0°C) and $\Delta\delta v_\infty/\Delta T$ are not very clean-cut, as they could not be measured in a wider concentration range.

The rate constants of rotation about C—N bond and the respective activation parameters* were calculated by means of approximative equations for chemical exchange between two non-equivalent equally frequent position without mutual interaction. The equations used for calculation go out from the ratio of intensities, distance and broadening of signals of N-methyl groups below the coalescence temperature and narrowing of the signal above this temperature (equations see ref.[7]). The dependences of δv_∞ and $1/T_2^0$ on temperature were taken into account during calculation.

The values of activation parameters of rotation about C—N bonds of carbamates *I* and *II* are summarized in Table II, wherefrom it is obvious that ΔS^+ has a relatively small positive value (lower than 10 e.u.) similar to rotation of N,N-dimethylamides[1]. ΔG^+ is the most often discussed value in connection with hindered rotation, because it is subject to a smaller error than ΔH^+ value. The values ΔG^+ given for the both compounds in Table II are, within experimental error, constant irrespective of solvent and concentration.** The mean values of ΔG^+ are 14·4 and 14·5 kcal/mol for rotation about C—N bond of carbamates *I* and *II* respectively.

The ΔG^+ values of carbamates *I* and *II* are almost equal and considerably low. Lower values as compared with other N,N-dimethylamides (21, 18·1 and 17·8 kcal/mol for N,N,-dimethylformamide, N,N-dimethylacetamide and N,N-dimethylpropion-amide respectively)[1] were found also for N,N-dimethylcarbamoyl chloride ($\Delta G^+ = 17$ kcal/mol)[1] and N,N-dimethylbenzamide ($\Delta G^+ = 15\cdot8$ kcal/mol)[10], i.e. for such compounds which could exhibit cross conjugation. In the case of the compounds studied by us the resonance formulas of the type *III* and *IV* are more significant than with N,N-dimethylcarbamoyl chloride or N,N-dimethylbenzamide, and, accordingly, the ΔG^+ values of rotation about C—N bond are the lowest, too.

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* The activation parameters were calculated with the presumption of transmission coefficient being unity as it is usual[1].
** Independence of ΔG^+ on concentration and type of solvent was observed previously in a study of some amides[1].

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