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ROTATIONAL BARRIERS IN THE ESTER FUNCTION OF SOME CARBAMATES. THE USE OF AN ITERATIVE COMPUTER PROGRAM IN A NMR STUDY.

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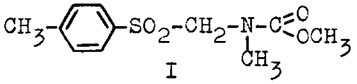
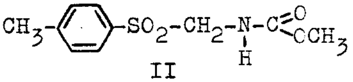
Under certain conditions[1] NMR spectroscopy is an excellent method for the study of rotatonial barriers in organic molecules. The classical example is N,N-dimethylformamide[2] which shows two distinct methyl absorptions due to hindered rotation around the partial double bond between the nitrogen atom and the carbonyl carbon atom. N,N-Disubstituted carbamates have been subject of several investigations[3,4,5]. In some cases (presumably dependent on the importance of cross-conjugation[4]) splitting of the signals of the N-alkyl groups has been found, again due to hindered rotation around the carbon-nitrogen bond.

To our surprise we found that in the NMR spectrum of methyl N-methyl-N-(p-methylphenylsulfonylmethyl) carbamate (I) the N-$\underline{CH_3}$ and the N-$\underline{CH_2}$ signals were sharp singlets but the ester methyl absorption was strongly broadened at the temperature of the probe (37°).

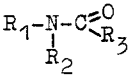

I


II

Only the line width of the last mentioned signal is temperature dependent. Lowering the temperature resulted in two sharp signals of unequal intensity for the methyl group in the carbomethoxy moiety (at δ 3.11 ppm and δ 3.48 ppm at 0° with hexadeuteroacetone as the solvent) Above the coalescence temperature (about 50°, solvent dependent) a single line was observed at δ 3.35 ppm.

Definite broadening of the ester methyl signal was also observed for compound II. Replacement of the hydrogen at the nitrogen atom by deuterium did not influence the linewidth of this signal.

The NMR spectra of the closely related compounds III-IX were also examined.



$R_1{-}N(R_2){-}C(=O)R_3$

III-IX

III R_1 = $p\text{-}CH_3C_6H_4SO_2CH_2$, R_2 = H R_3 = OCH_2CH_3;

IV R_1 = $p\text{-}CH_3C_6H_4SO_2CH_2$, R_2 = CH_3, R_3 = OCH_2CH_3;

V R_1 = $p\text{-}O_2NC_6H_4SO_2CH_2$, R_2 = CH_3, R_3 = OCH_2CH_3;

VI R_1 = $CH_3SO_2CH_2$, R_2 = CH_3, R_3 = OCH_2CH_3;

VII[6] R_1 = $p\text{-}CH_3C_6H_4SO_2CH_2CH_2$, R_2 = H, R_3 = OCH_2CH_3;

VIII R_1 = $p\text{-}CH_3C_6H_4SO_2CH_2$, R_2 = H, R_3 = CH_3;

IX R_1 = $p\text{-}CH_3C_6H_4SO_2CH_2$, R_2 = H, R_3 = CH_2CH_3.

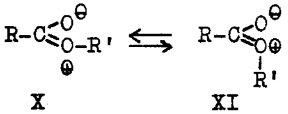
The compounds I-VI and VIII-IX were prepared by condensing the appropriate sulfinic acid with formaldehyde and the corresponding carbamate or carboxamide according to the method of Engberts and Strating[7,8].

In the carbamates III-V the only broadening observed was that of the ester ethyl absorption (at 37° in hexadeuteroacetone). For example, compound V showed two broadened signals at approximately δ 1.0 ppm and δ 3.8 ppm for the ester CH_3 and CH_2 absorptions respectively, but at 8° the spectrum exhibited two triplets at δ 0.87 ppm and δ 1.07 ppm (intensity ratio 1:1) and two quartets at δ 3.63 ppm and δ 3.90 ppm (intensity ratio 1:1). Broadening of the ester signals was also observed with benzene as the solvent.

In the compounds VI-IX no broadening was shown by any signal (at 37°).

In all cases the compounds were isolated unchanged from the solutions after completion of the experiments.

The spectra of the compounds I-V can be interpreted by assuming a barrier to internal rotation, but this barrier cannot be due to the well-known amide resonance because the N-alkyl signals remain unaltered in the temperature range used. Therefore the barrier to rotation must be within the ester group itself. It may be noted that simple esters occur almost exclusively in the cis-conformation X.[9]



$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\mathrm{O}^{\ominus}}{\underset{\oplus}{\mathrm{O}}\mathrm{{-}R'}} \leftrightarrows \mathrm{R{-}C}\genfrac{}{}{0pt}{}{\mathrm{O}^{\ominus}}{\underset{\mathrm{R'}}{\mathrm{O}^{\oplus}}}$$

X XI

The barrier described above for the carbamates I-V might be associated with the conversion X $\leftrightarrows$ XI.

The importance of steric interactions in determining the preferred rotational conformations in organic molecules has been pointed out by Mizushima[10]. However, in our case inspection of models gives little insight into this question. Possibly a combination of electronic and steric effects is responsible for the observed barrier, but clearly the presence of an arylsulfonyl group in the β-position to the nitrogen atom is essential. Further studies are currently in progress in our laboratory in order to establish the exact origin of this case of hindered internal rotation.

The conventional methods for the evaluation of the energy barrier to internal rotation by NMR spectroscopy have been reviewed recently[11,1 These methods often give inaccurate results and moreover they cannot be applied in our case because the populations of both conformations A and B of compound I are unequal. In order to overcome these difficulties we used the Bloch equations modified by Gutowsky and Saika[13] without additional approximations. By means of an iterative computer program (written in Algol) we were able to evaluate the lifetimes of both conformers of compound I at different temperatures. This was accomplished by fitting a theoretical curve to an experimental curve by adjusting five parameters (i.e. the chemical shifts ω_A and ω_B, the lifetimes τ_A and τ_B and the intensity parameter) according to the method of least squares. The broadening function was derived from the signal of the tetramethylsilane standard in the sample. From an Arrhenius plot of τ_A and τ_B (see table) the activation energies E_A (16.0 kcal/mole) and E_B (16.3 kcal/mole) were calculated. The respective frequency factors amounted to log ν_A = 12.3 and log ν_B = 12.4.

TABLE

Life Times of the Conformations A and B of Compound I

(30% w/v in Hexadeuteroacetone)

Temperature (°C)	τ_A (sec.)	τ_B (sec.)
14.5 ± 0.1	0.38 ± 0.02	0.54 ± 0.03
24.0 ± 0.1	0.1513 ± 0.0015	0.2092 ± 0.002
34.2 ± 0.1	0.0635 ± 0.0006	0.0842 ± 0.0007
40.5 ± 0.1	0.0359 ± 0.0002	0.0486 ± 0.0003
49.1 ± 0.2	0.0184 ± 0.0002	0.0251 ± 0.0003

All measurements were carried out using a Varian A-60 instrument with a V-6040 variable temperature accessory. The temperature was determined in the spinning sample by means of a thermocouple before and after running a spectrum. Details will be published in a subsequent paper. The calculations were performed on a Telefunken TR 4 computer of the Rekencentrum, Groningen. Copies of the computer program NMREX are available on request.

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