Tetrahedron Letters No.29, pp. 3311-3314, 1968. Pergamon Press. Printed in Great Britain.

HINDERED INTERNAL ROTATION IN METHYL N-METHYL-N-ARYLSULFONYLMETHYLCARBAMATES AND RELATED CARBAMATES. THE LONG-RANGE SHIELDING OF THE ESTER METHYL GROUP BY AN AROMATIC RING.

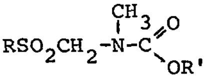
S. van der Werf and J.B.F.N. Engberts

Department of Organic Chemistry, The University,

Bloemsingel 10, Groningen, The Netherlands

(Received in UK 15 April 1968; accepted for publication 25 April 1968)

Recently we reported that the NMR spectra of the alkyl N-methyl-N-arylsulfonylmethylcarbamates I - III showed only temperature dependence of the signal of the ester alkyl group (1). It was suggested that the barrier to internal rotation merely involved the ester group itself since the data then available made amide resonance unlikely. However, further studies with related carbamates (2) now show, that these results may be explained by assuming hindered rotation about the carbonyl carbon to nitrogen bond (referred to as the amide bond) and by considering intramolecular shielding of the ester alkyl group by the aromatic ring.

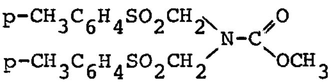


$RSO_2CH_2-N(CH_3)-C(=O)OR'$

I R = $p-CH_3C_6H_4$, R' = CH_3

II R = $p-CH_3C_6H_4$, R' = C_2H_5

III R = $p-NO_2C_6H_4$, R' = C_2H_5



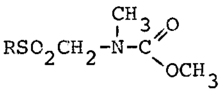
$(p-CH_3C_6H_4SO_2CH_2)_2N-C(=O)OCH_3$

IV

In compound IV, m.p. 140-141°, cis-trans isomerism within the ester function ought to be indicated by a broadening of the ester methyl absorption on lowering the temperature. However, if there were only hindered rotation about the amide bond, then the ester methyl signal should be temperature independent and should remain sharp since the nitrogen substituents in the carbamate are the same.

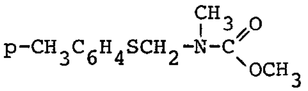
In fact, only broadening of the methylene signal (δ 5.1 ppm) was found down to -80°. This observation can only be reconciled with slow rotation about the amide bond (3). In agreement with this, a splitting (0.06 ppm) of the N-methylene group of I has now been found at 7° in deuterochloroform as the solvent. In hexadeuteroacetone as the solvent, the N-alkyl protons in I-III give signals which are temperature independent (1) and we attribute this to the fact that the chemical shifts of these groups in the different rotamers by chance happen to coincide (4).

It is noteworthy that the ester methyl group in IV absorbs at a higher field (δ 3.12 ppm) than is normally found (5) in methyl N,N-dialkylcarbamates (δ 3.6 - 3.8 ppm). On basis of electronic effects, a downfield shift would be expected due to the electronwithdrawing properties of the arylsulfonyl groups. One of the rotamers of I also shows (1) an ester methyl signal at rather high field (δ 3.17 ppm at 10°). Since these chemical shifts are almost concentration independent, we attribute these upfield shifts to intramolecular shielding of the ester methyl group by the aromatic ring. As can be seen from molecular models, this methyl group can be situated easily above the plane of the aromatic ring in an apparently favourable conformation. Results obtained with related compounds V - X are shown in the Table. Broadening or splitting into two unequally populated sites of the N-alkyl signals and the ester methyl signal is observed upon lowering the temperature owing to hindered rotation about the amide bond. In the carbamates V - VII and the thioncarbamate VIII a fairly large difference in chemical shift of the ester methyl group in the rotamers is interpreted as resulting from different intramolecular shielding by the aromatic ring. By contrast, the carbamates IX and X exhibited only slight broadening of the ester methyl proton absorptions down to -50°. No upfield shifts for these signals were found.



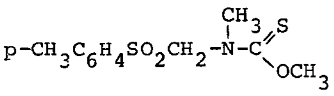
$RSO_2CH_2\text{-}N(CH_3)\text{-}C(=O)OCH_3$

V R = 2-naphtyl
VI R = 2-thienyl
IX R = CH_3
X R = $C_6H_5CH_2$



$p\text{-}CH_3C_6H_4SCH_2\text{-}N(CH_3)\text{-}C(=O)OCH_3$

VII



$p\text{-}CH_3C_6H_4SO_2CH_2\text{-}N(CH_3)\text{-}C(=S)OCH_3$

VIII

TABLE

Chemical shifts of the ester methyl group
in the carbamates V-X in $CDCl_3$ solution

Compound	m.p. (^oC)	Temp. (^oC)	δ_{OCH_3} * (ppm)
V	106.2-107.2	10	3.40 (44%); 2.87 (56%)
VI	97.9-98.6	10	3.59 (45%); 3.31 (55%)
VII	**	10	3.65 (40%); 3.35 (60%)
VIII	93-94	37	3.92 (38%); 3.49 (62%)
IX	63-64	-50	3.82
X	94-95	-50	3.79

* Rotamer population indicated between brackets
** b.p. 118°/3 mm

In comparison with I - VIII, IX lacks an aromatic ring and consequently the difference in magnetic environment of the ester methyl group in both rotamers is almost completely eliminated. In the carbamate X, the additional flexibility of the molecule as compared to I, resulting from the introduction of a methylene group between the aromatic ring and the sulfonyl group, apparently also eliminates the shielding effect.

Some additional evidence for the proposed intramolecular shielding effect in I - VIII was obtained from solvent effects. Intermolecular association (6) of the OCH_3 group in these carbamates with benzene as the solvent will be reduced when intramolecular shielding is present. This is confirmed by the observed shifts of the ester methyl signal when deuterochloroform is replaced by benzene as the solvent. The upfield shifts of the high-field signals of I and V (10°; I, 0.27 ppm; V, 0.28 ppm) are smaller than those of the low-field signals (10°; I, 0.34 ppm; V, 0.38 ppm) and those of the ester methyl signals of IX (0.47 ppm) and X (0.39 ppm).

Quantitative thermodynamic data obtained by complete line shape analysis (1) and further studies on structurally related carbamates and thiocarbamates will be published in due course.

The authors are indebted to Professor J. Strating and to Professor H. Wynberg for their encouragement and interest.

REFERENCES

1) S. van der Werf, T. Olijnsma and J.B.F.N. Engberts, Tetrahedron Letters, 689 (1967).

2) The NMR spectra were recorded using $CDCl_3$ as the solvent and TMS as internal reference. The carbamate concentrations amounted to 15-20% by weight. The new compounds IV - X had the requisite spectral properties and microanalyses. Compound IV was synthesized from $(p\text{-}CH_3C_6H_4SO_2CH_2)_2NH$ and methyl chloroformate. The carbamates V - X were prepared by the method of J.B.F.N. Engberts and J. Strating, Rec.Trav.Chim., **84**, 942 (1965).

3) Presumably the ester group retains the cis-conformation; see C.M. Lee and W.D. Kumler, J.Amer.Chem.Soc., **83**, 4596 (1961).

4) In N,N-dialkylcarbamates cross-conjugation tends to decrease the difference in magnetic environment for the same alkyl group in different rotamers. See: E. Lustig, W.R. Benson and N. Duy, J.Org.Chem., **32**, 851 (1967); M.T. Rogers and J.C. Woodbrey, J.Phys.Chem., **66**, 540 (1962).

5) E.H. White, M.C. Chen and L.A. Dolak, J.Org.Chem., **31**, 3038 (1966).

6) T. Ledaal, Tetrahedron Letters, 1683 (1968) and references cited therein.