SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

SOUTH. BRAZ. J. CHEM., Vol.4 N°4, 1996

CARBON-13 NMR OF ALIPHATIC TERTIARY AMIDES

Paulo Irajara Borba Carneiro*
Instituto de Química, Universidade Estadual de Ponta Grossa
Caixa Postal 1007
84.031.510 Ponta Grossa-PR - Brasil

Roberto Rittner
Instituto de Química, Universidade Estadual de Campinas
Caixa Postal 6154
13081 Campinas-SP - Brasil

ABSTRACT

This work presents unpublished Carbon-13 NMR data for eight aliphatic tertiary amides. The substituent chemical shifts of the **CONMe$_2$** and **CONEt$_2$** groups were determined and can be useful in correlation analysis.

RESUMO

O presente trabalho apresenta dados inéditos de deslocamentos químicos para oito amidas alifáticas terciárias. Os deslocamentos químicos do substituinte para os grupos CONMe$_2$ e CONEt$_2$ foram determinados e podem ser úteis em anáslise correlacional.

KEY WORDS: Carbon-13 NMR, chemical shifts, aliphatic tertiary amides.

INTRODUCTION

Recently, we have studied aliphatic compounds by Carbon-13 NMR spectroscopy[1,2]. Although aliphatic tertiary amides are easy to synthesize, there is a lack of NMR data in the literature[3]. We have synthesized several aliphatic tertiary amides of the type **R-Z** where **R** is a alkyl group containing two to six carbon atoms (Ethyl, propyl, butyl, amyl and hexyl groups), and **Z** represents the **CONMe$_2$** or **CONEt$_2$** groups. The purpose of this work was to sinthesize eight non-branched aliphatic tertiary amides with sp^3 hibridization, to record their Carbon-13 NMR data for their full characterization, and to determine the substituent chemical shifts (SCS) of the **CONMe$_2$** and **CONEt$_2$** groups. The chemical shifts are inedited and the SCS can be useful in correlation analysis.

---

* Author to whom correspondence should be addressed.

DOI: 10.48141/SBJCHEM.v4.n4.1996.94_1996.pdf

EXPERIMENTAL PROCEDURE

Materials: All compounds were prepared according to literature procedures[5]. The physical and spectral data are shown in Tables 1-3. Solvents were of spectroscopic quality and were used without further purification.

Spectra: the C-13 NMR spectra of 1,0 M solutions in CCl_4 with 5 % TMS as an internal reference in 10 mm o.d. sample tubes, were recorded at 25,2 MHz using a Varian XL-100 spectrometer in the FT mode. The conditions were as follows: pulse width, 20 µs; acquisition time, 0,67 s; spectral width, 6150 Hz; pulse repetition time, 0,4 s; temperature, 30 °C; internal lock, D_20; angle tumbling, 45°; number of transients, 6000; and number of data point, 8192. The C-13 NMR spectra were recorded in both the proton-noise decoupled and coupled modes. The H-1 NMR spectra of the solutions investigated, in 5 mm o.d. sample tubes, were recorded at 80 MHz using a Bruker AW-80 spectrometer in the FT mode.

RESULTS AND DISCUSSION

Table 1 shows the physical constants of these compounds. They agree whith published data. The H-1 NMR data are shown in Table 2 and Table 3 shows the C-13 NMR data. Table 4 shows the **SCS** of the dialkylamide groups. The synthesis of eight tertiary amides allow to amplify the C-13 NMR data of these amides and to estimate directly form the SCS of these groups. The four **SCS** α, β, γ and δ for the **$CONMe_2$** and **$CONEt_2$** groups are defined as follow: R-$^{\delta}CH_2$-$^{\gamma}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-**Z** where **Z** = **$CONMe_2$** or **$CONEt_2$**, and were estimated from the chemical shifts of the unsubstituted compounds [where Z = H]. The signals of aliphatic carbons were assigned by single-frequency off-resonance decoupling (SFORD) and proton noise decoupled (DFL) spectra and known chemical shifts rules[3]. We have determined the **SCS** of the **$CONMe_2$** and **$CONEt_2$** groups, wich were not been previously reported in the literature. These values can be useful in correlation analysis.

Table 1. Physical Constants of Aliphatic Tertiary Amides[4]

	Compounds	b.p (°C/Torr)	Yield (%)
1	N,N-Dimethyl-N-propanamide	70/20	90.0
2	N,N-Dimethyl-N-butanamide	80/20	93.8
3	N,N-Dimethyl-N-pentanamide	100/20	90.0
4	N,N-Dimethyl-N-hexanamide	115/20	80.0
5	N,N-Dimethyl-N-heptanamide	130/20	92.6
6	N,N-Diethyl-N-pentanamide	110/20	95.4
7	N,N-Diethyl-N-hexanamide	130/20	96.7
8	N,N-Diethyl-N-heptanamide	140/20	86.8

Table 2. H-1 NMR Chemical Shifts of Aliphatic Tertiary Amides in ppm Relative to TMS[4] (Solvent CCl_4)

Compounds	H-2	H-3	H-4	H-5	H-6	H-7	H-1'E	H-1'Z	H-1'	H-2'
1	2.20	1.00					2.90	2.80		
2	2.20	1.60	0.90				2.90	2.80		
3	2.20	1.10 to 1.80		0.90			2.90	2.80		
4	2.20	1.10	to	1.80	0.90		2.90	2.80		
5	2.20	1.10	to		1.80	0.90	2.90	2.80		
6	2.20	0.80 to 1.80		0.90					3,20	a
7	2.20	0.80	to	1.80	0.90				3.20	a
8	2.20	0.80	to		1.80	0.90			3.20	a

a: multiplet in 0,80-1.80 ppm. **E** (entgegen): NR_2 group *anti* to carbonyl oxygen. **Z** (zusammen): NR_2 group *syn* to carbonyl oxygen.

Table 3. C-13 NMR Chemical Shifts of Aliphatic Tertiary Amides in ppm Relative to TMS[4] (Solvent CCl_4)

Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-1'E	C-2'E	C-1'Z	C-2'Z
1	171.8	26.0	9.2					36.6		34.8	
2	171.0	34.7	18.3	13.9				36.7		35.2	
3	171.0	32.5	27.1	22.5	13.9			36.8		34.8	
4	171.1	32.7	24.6	31.6	22.5	14.0		36.7		34.8	
5	171.0	32.8	24.8	29.1	31.7	22.5	14.0	36.8		34.8	
6	170.1	32.3	27.3	22.5	14.0			41.6	14.6	39.7	13.2
7	170.1	32.6	24.9	31.6	22.5	14.0		41.5	14.6	39.7	13.2
8	170.0	32.6	25.1	29.1	31.7	22.5	14.1	41.5	14.6	39.7	13.2

E (entgegen): NR_2 group *anti* to carbonyl oxygen. **Z** (zusammen): NR_2 group *syn* to carbonyl oxygen.

Table 4. Substituent Chemical Shifts of Aliphatic Tertiary Amides in ppm[4]

group	α	β	γ	δ
$CONMe_2$	19.2	2.3	-2.7	-0.1
$CONEt_2$	19.2	2.3	-2.7	-0.1

ACKNOWLEDGMENTS

The authors thank the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) for financial support of this research and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships to R. R. and P. I. B. C.

REFERENCES

1. P. I. B. Carneiro et al., *South. Braz. J. Chem.*, 1(1): 5-9, (1993).
2. P. I. B. Carneiro; R. Rittner, *South. Braz. J. Chem.*, 3(3): 89-92, (1995).
3. E. Breitmaier and W. Voelter, "*Carbon-13 NMR Spectroscopy*", 3rd. edition, Weinheim, New York, USA, 1987.
4. P. I. B. Carneiro, *Tese de Doutorado*, UNICAMP, Campinas, S. P, Brasil, 1991.
5. B. S. Furniss et al. "*Vogel's Textbook of Practical Organic Chemistry*". 4th edition, London, 1978.