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CARBON-13 NMR OF ALIPHATIC TERTIARY AMINES

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ABSTRACT

There are few data for the tertiary aliphatic amines in the literature. Unpublished Carbon-13 NMR data for seven aliphatic tetiary amines are reported and are inedited. The empirical substituent effects of the NMe_2 and NEt_2 groups were determined and can be useful in correlation analysis.

RESUMO

O presente trabalho apresenta dados inéditos de deslocamentos químicos para sete aminas alifáticas terciárias. Os efeitos empíricos do sustituinte para os grupos NMe_2 e NEt_2 foram determinados e podem ser úteis em anáslise correlacional.

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

INTRODUCTION

Recently, we have studied aliphatic compounds by Carbon-13 NMR spectroscopy[1]. Although aliphatic tertiary amines are important starting material for some syntetic routes, there is a lack of NMR data in the literature[2]. We have synthesized several aliphatic tertiary amines of the type **R-X** where **R** is a alkyl group containing two to six carbon atoms (Ethyl, propyl, butyl, amyl and hexyl groups), and **X** represents the NMe_2 or NEt_2 groups. The purpose of this work was to sinthesized seven aliphatic tertiary non branched amines with sp^3 hibridization, to record their Carbon-13 NMR data for their full caracterization, and to determine the empirical effects of the NMe_2 and NEt_2 groups. The chemical shifts for these compounds have not been reported in the literature and the empirical effects can be useful in correlation analysis.

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EXPERIMENTAL PROCEDURE

Materials: All compounds were prepared by described in the literature procedures[4]. The physical and spectral data are shown in Tables 1-3. Solventes 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 several investigated solutions, 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 empirical effect theses dialkylamine groups. The synthesis of seven tertiary amines allow to amplify the C-13 NMR data these amines and to estimate in the straight form the empirical effect of these groups. The four empirical effects α, β, γ and δ are defined as follows. 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[2]. We have determined the empirical effects of the NMe_2 and NEt_2 groups, wich were not been previously reported in the literature. These values can be useful in correlation analysis.

Table 1. Physical Constantes of Aliphatic Tertiary Amines[3]

	Compounds	b.p (°C/Torr)	Yield (%)
1	N,N-Dimethyl-N-ethylamine	36/760	70
2	N,N-Dimethyl-N-propylamine	60/760	80
3	N,N-Dimethyl-N-butylamine	95/760	60
4	N,N-Dimethyl-N-pentylamine	120/760	60
5	N,N-Diethyl-N-propylamine	105/760	84
6	N,N-Diethyl-N-pentylamine	50/20	60
7	N,N-Diethyl-N-hexylamine	80/25	80

Table 2. H-1 NMR Chemical Shifts of Aliphatic Tertiary Amines in ppm Relative to TMS[3] (Solvent CCl_4)

Compounds	H-1	H-2	H-3	H-4	H-5	H-6	H-1'	H-2'
1	2.25	0.95					2.15	
2	2.26	1.85	1.00				2.06	
3	2.15	1.10 to 1.50		0.90			2.10	
4	2.35	1.10	to	1.50	0.90		2.12	
5	2.40	1.30	0.95				2.40	1.05
6	2.30	1.15	to	1.50	0.90		2.40	0.95
7	2.30	1.16		to	1.50	0.88	2.42	0.97

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

Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'
1	53.2	12.8					44.8	
2	61.5	20.8	11.7				45.2	
3	59.2	29.8	20.4	14.0			45.2	
4	59.5	27.2	29.6	22.6	14.0		45.2	
5	55.0	20.5	11.9				46.9	12.0
6	52.8	26.9	29.7	22.6	14.2		46.8	12.0
7	53.0	27.3	27.4	31.9	22.7	14.0	46.9	12.1

Table 4. Empirical Effects of Aliphatic Tertiary Amines in ppm[3]

group	α	β	γ	δ
NMe_2	46.1	4.8	-4.4	0.0
NEt_2	39.5	4.5	-4.5	0.0

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