

CARBON-13 NMR OF SOME S-METHYLTHIOLESTERS

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ABSTRACT

H-1 and C-13 NMR chemical shifts for some alkyl-S-methylthiolesters (RCOSMe) are reported. The α -methylene and carbonyl carbons show lower field shifts when compared to analogous carboxylic acid derivatives. This behavior was explained by using charge densities and separation energies calculated by the AM1 MO-SCF semiempirical method.

KEYWORDS: C-13 NMR, Chemical Shifts, Alkyl-S-methylthiolesters.

RESUMO

O presente trabalho apresenta deslocamentos químicos de RMN de H-1 e C-13 para alguns ésteres de alquil-S-metiltiol (RCOSMe). Os carbonos do grupo α -metileno e carbonila exibem um deslocamento para campo mais baixo, quando comparados com derivados análogos de ácidos carboxílicos. Este comportamento foi explicado usando densidades de carga e energias de separação calculadas através do método semi-empírico AM1 MO-SCF.

INTRODUCTION

Although thiolesters (RCOSMe) are important starting materials for condensation and transference reactions of the acyl group in biological systems¹, there is a lack of NMR data in the literature for this type of compounds, particularly when R is a nonbranched alkyl group. The electronic structure of these compounds is well known.

C-13 NMR chemical shifts for the α -methylene and carbonyl carbons have been reported to show a lower field chemical shift in relation to analogous carboxylic acid derivatives.

This work describes the study of a closely related series of four alkyl-S-methylthiolesters that has also been investigated using the semiempirical AM1 MO-SCF calculations in order to check the generality of the observed behavior.

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EXPERIMENTAL PROCEDURE

Materials.

Solvents were of spectroscopic quality and were used without further purification. All compounds were prepared according to procedures described in the literature^{9,10}.

Spectra.

The C-13 NMR spectra of 1,0 M solutions in CHCl_3 , 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 $^\circ$ C; internal lock, D_2O ; angle tumbling, 45 $^\circ$; number of transients, 6000; and number of data points, 8192. The C-13 NMR spectra were recorded in both the proton-noise decoupled and coupled modes. The H-1 NMR spectra of the various solutions investigated, in 5 mm o.d. sample tubes, were recorded at 80 MHz using a Bruker Aw-80 spectrometer in the FT mode.

Computations.

Net charge densities and energy separations were obtained through the AM1 SCF-MO semiempirical method on an IBM computer with the AMPAC program.

RESULTS AND DISCUSSION

Table I summarizes the experimental C-13 chemical shifts obtained for the four alkyl-S-methylthioesters studied.

TABLE I. C-13 NMR CHEMICAL SHIFTS^a FOR ALKYL-S-METHYLTHIOESTERS^b.

Compounds	R—CH ₂ COSMe						
	C-1	C-2	C-3	C-4	C-5	C-6	C-1'
1 CH ₃ CH ₂ COSMe	198.1	35.5	9.1				10.7
2 CH ₃ CH ₂ CH ₂ COSMe	196.5	44.6	18.3	12.4			10.0
3 CH ₃ CH ₂ CH ₂ CH ₂ COSMe	197.6	42.8	27.1	21.5	13.0		10.5
4 CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COSMe	198.1	43.3	24.9	30.7	21.9	13.3	10.8

a: in ppm relative to TMS. b: Ref. 6 in HCCl_3 solutions.

Table II presents the boiling points and experimental H-1 NMR data obtained. The physical constants of compounds 1-4 agree with data published in the literature¹⁻⁴.

TABLE II. PHYSICAL AND SPECTRAL DATA FOR ALKYL-S-METHYLTHIOLESTERS^a.

Compound	bp (°C/Torr)	H-2 ^b	H-3	H-4	H-5	H-6	H-1'
<u>1</u>	60/110	2.60 ^q	1.20 ^t				2.30 ^o
<u>2</u>	55/40	2.50 ^t	1.70 st	0.95 ^t			2.25 ^o
<u>3</u>	70/30	2.55 ^t	1.10-1.90 ^m		0.90 ^t		2.25 ^o
<u>4</u>	70/20	2.50 ^t	1.65 ^m	1.10-1.45 ^m		0.90 ^t	2.25 ^o

a: ppm relative to TMS, in deuterated chloroform solutions. b: s = singlet; t = triplet; q = quartet; st = sextet and m = multiplet

The signals of these compounds were assigned by single-frequency off-resonance decoupling (SFORD), proton noise decoupled (DFL) spectra and known chemical shift rules⁵.

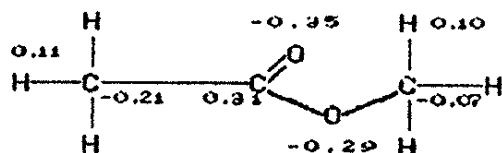
The chemical shifts of the carbonyl carbon were found in the 197,30±0,80 ppm band, next to analogous aldehydes and ketones. This values is about 15-20 ppm higher, when compared to analogous carboxylic acid derivatives.

In the alkyl-S-methylthiolesters $\left[\overset{2}{\text{R}}-\overset{1}{\text{CH}_2}-\overset{1'}{\text{COSMe}} \right]$, C-1 and C-2 show paramagnetic chemical shifts. On the other hand, the C-1' carbon showed diamagnetic chemical shifts, when compared to analogous carboxylic acid derivatives.

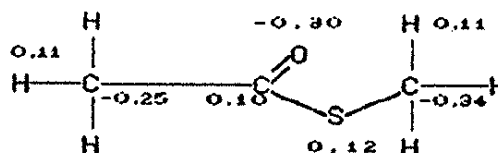
Comparison between the thiolesters and analogous carboxylic acid derivatives showed that the C=O bond length is shorter than the C-S bond. This is the case because the oxygen atom is more electronegative than the sulfur atom. The magnitude of the $\text{p}\pi-\text{p}\pi$ or $\text{p}\pi-\text{d}\pi$ conjugation is inversely proportional to the core length and is more pronounced in the C=O bond. This reduces the carbonyl withdrawing effect in the alpha carbon. In the oxygenated esters the carbonyl carbon is more shielded than in the thiolesters analogues.

The inductive effect of the oxygen atom deshields the methyl carbon (C-1') and its resonance appears in a lower field. The chemical shift differences between these compounds is thus caused by the differences in size between the two heteroatoms and the differences in their electronegativities, polarizabilities and energy of the atomic lone pair orbitals⁷.

Making use of the AM1 MO-SCF semiempirical calculations, we computed the charge densities of the carbon atoms in compounds 5 and 6 and also determined the energy separation (ΔE).

5

$$\Delta E = 12,51 \text{ ev}$$

6

$$\Delta E = 10,37 \text{ ev}$$

According to Equation (I) the paramagnetic constant, derived by Karplus and Pople⁸, shows that the higher ΔE and Q_i , the higher the shielding observed in the carbon atom. Our experimental results and the values computed for ΔE and Q_i are in agreement with these observations.

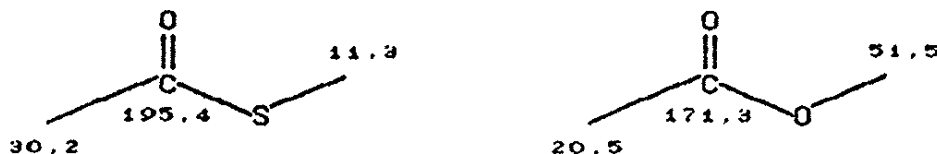
$$\sigma_p = - \frac{e^2 h^2}{m^2 c^2} \Delta E^{-1} \langle r^{-3} \rangle_{2p} [Q_i + \sum Q_j] \quad (I)$$

The charge densities show that in the methyl ester (C-1) the carbonyl carbon is more shielded ($Q_{C-1} = 0,31$) than in the thiolester analogue ($Q_{C-1} = 0,10$).

Our calculations show that the energy separation and charge of the C-1 of the thiolester are smaller. This corresponds to higher polarizability and chemical shifts of the alpha and carbonyl carbons of these compounds.

These observations can explain the principal properties of the thiolesters: C-1 and C-2 have resonance in a lower field when compared to analogous oxygenated esters (C-1 $\Delta\delta \approx 15-20$ ppm, C-2 $\Delta\delta \approx 10$ ppm). They also explain the higher reactivity of thiolacetates to alkaline hydrolysis when compared to analogous acetates². The lower electronegativity of the sulfur atom results in a lower inductive effect in C-1'. In fact, C-1' is more shielded in these compounds in the C-13 NMR spectra. C-1' appears in an even higher field ($\Delta\delta \approx 40$ ppm) when compared to alkyl esters analogues.

These observations are confirmed by the chemical shifts of S-methylethanethioate and methyl acetate shown on the following page.

C-13 NMR of S-Methylthioesters

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REFERENCES

1. C. M. Hall and J. Wemple, *J. Org. Chem.*, 42, 2118-2123 (1977).
2. J. P. Idoux, P. T. R. Hwang and C. K. Hancock, *J. Org. Chem.*, 38, 4239-4243 (1973).
3. J. Obermeyer, *Ber.*, 20, 2918-2928 (1887).
4. V. A. Vinkurov and E. G. Gaevoi, *J. Org. Chem. USSR*, 23, 1990-1991 (1987).
5. E. Breitmeier and W. Voelter, *"Carbon-13 NMR Spectroscopy"*, 3rd edition, Weinheim, New York, USA, 1987.
6. P. I. B. Carneiro, *"Tese de Doutorado"*, UNICAMP, Campinas, São Paulo, 1991.
7. F. Bernardi, I. G. Csizmadia, H. B. Schlegel and S. Wolfe, *Can. J. Chem.*, 53, 1144-1153 (1975).
8. M. Karplus and J. A. Pople, *J. Chem. Phys.*, 38, 2803 (1963).
9. D. J. Dagli, P. S. Yu and J. Wemple, *J. Org. Chem.*, 40, 3173-3178 (1975).
10. P. N. Rylander and S. Tarbell, *J. Amer. Chem. Soc.*, 72, 3021-3025 (1950).