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Reference Data

^{17}O NMR Studies on Dialkoxy Disulfides

Giovanni Cerioni[1]* and Antonio Plumitallo[2]

[1] Dipartimento di Scienze Chimiche,
Università di Cagliai,
Via Ospedale 72,
I-09124 Cagliari
Italy
[2] Dipartimento Farmaco Chimico Tecnologico,
Università di Cagliari,
Via Ospedale 72,
I-09124 Cagliari
Italy

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ABSTRACT: ^{17}O NMR spectra, at natural isotopic abundance, of dialkoxy disulfides are presented and β- and γ-SCS effects shortly discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{17}O NMR; dialkoxy disulfides; β- and γ-SCS effects

INTRODUCTION

Dialkoxy disulfides of the general formula RO—S—S—OR′ are a class of compounds that, although known[1] since the end of last century, have received little attention in the chemical literature.[2,3] Recently, we have exploited their ability[4] to generate alkoxy radicals and studied their structure and stereodynamics.[5] ^{17}O NMR is a powerful method for studying chemical bonds[6] and we have applied this technique to gain further knowledge about the title compounds.

RESULTS AND DISCUSSION

^{17}O NMR data are given in Table 1. To the best of our knowledge, there is only one report[7] on compound **1**. Notwithstanding the very different experimental conditions, there is good agreement between the two sets of data for δ(^{17}O) (14[7] *vs* 14.8 ppm).

Sulfur–oxygen bonds have been extensively studied by ^{17}O NMR spectroscopy,[8] but most of the efforts have been devoted to terminal S—O bonds and its has been recognized that, except for two classes of compounds,[9] such a bond does not have a 'double bond' character. A strong similarity of ^{17}O shifts between terminal and bridge oxygen, when bonded to sulfur, has also been observed.[10] In our case, there is a shielding of *ca.* 90–110 ppm in comparison with the shifts of bridge oxygens in arylsufinic[10] and arylsulfonic[10] esters. Comparison is made among **1** and the methyl esters, so that the substituent-induced chemical shift (SCS) effects are set aside. From these data, it appears that in dialkoxy disulfides oxygen bonds are truly single bonds.

SCS effects have been studied for both sulfinyl[11] and sulfonyl[12] groups and also for alcohols[13] and ethers,[13] but there is a lack of similar studies for oxygen as a bridge between sulfur and carbon. Table 2 shows a comparison of the β-effects in dialkoxy disulfides, ethers and alcohols.

The first methyl group causes similar downfield shifts for dialkoxy disulfides and aliphatic ethers and larger effects for alcohols as already observed[13] when comparing the last two classes of compounds. It can be seen that the effects of a second and a third methyl group decrease in all three classes of compounds but this decrease is smaller in the case of alkoxy disulfides, i.e. there is a difference of *ca.* 4 ppm *vs.* 10 ppm for the former compounds.

γ-Effects in dialkoxy disulfides can again be better compared with those of alcohols and ethers. Relevant data are summarized in Table 3.

It is interesting that whereas substitution by the first and third methyl groups induces larger upfield shifts than the introduction of a second methyl group for both alcohols and ethers, in the case of dialkoxy disulfides a steady decrease of the γ-effect is observed. As observed also for the β-effect, in the case of dialkoxy disulfides the overall effect is less pronounced.

EXPERIMENTAL

All compounds have been already reported; **1**, **2**,[1] **3**–**5** and **9**,[2b] **6**–**8**[4] and **10**, **11**.[5]

Fourier transform ^{17}O NMR spectra were recorded at a nominal frequency of 40.661 MHz on a Varian VXR 300 spectrometer equipped

Table 1. ^{17}O NMR data in MeCN solution for compounds ROSSOR′

Compound	R	R′	δ(^{17}O)(ppm)[a]	$\nu_{1/2}$ (Hz)
1	Me	Me	14.8	115
2	Et	Et	45.1	130
3	^{n}Pr	^{n}Pr	40.5	220
4	^{i}Pr	^{i}Pr	72.5	170
5	^{n}Bu	^{n}Bu	40.5	165
6	^{i}Bu	^{i}Bu	37.9	210
7	^{t}Bu	^{t}Bu	96.0	205
8	*neo*-Pt[b]	*neo*-Pt[b]	36.0	276
9	Bz[c]	Bz[c]	47.6	280
10	*p*-O_2N-Bz[d,e]	*p*-O_2N-Bz[d,e]	45.8	480
11	^{t}Bu	Me	96.0 (*O*^{t}Bu)	150
11	^{t}Bu	Me	15.5 (*O*Me)	135

[a] *T* = 65 °C.
[b] *neo*-Pentyl.
[c] Benzyl.
[d] *p*-nitrobenzyl.
[e] NO_2 575 ppm; 560 Hz estimated half-height linewidth.

Table 2. β-SCS(Me) effect (ppm) in ROSSOR, ROMe[13] and ROH[13]

R	ROSSOR	ROMe	ROH
Et	30.3	30	42.9
^{i}Pr	27.4	20.5	33.9
^{t}Bu	23.5	11.0	22.5

Table 3. γ-SCS(Me) effect (ppm) in ROSSOR, ROMe[11] and ROH[11]

R	ROSSOR	ROMe	ROH
^{n}Pr	−4.6	−6.5	−6.4
^{i}Bu	−2.6	−1.5	−1.5
neo-Pt	−1.9	−2.5	−4.8
Total γ-SCS(Me)	−9	−11	−13
γ-Me/Me	−3	−3.6	−4.3

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* *Correspondence to*: G. Cerioni, Dipartimento di Scienze Chimiche, Università di Cagliari, Via Ospedale 72, I-09124 Cagliari, Italy.
E-mail: cerioni@vaxcal.unica.it.

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with a Sun 3/60 computer and with a 10 mm broadband probe at 65 °C (probe temperature = 338 K) in MeCN solutions and at natural isotopic abundance. Concentrations were in the range 60–90 mg ml^{-1}. The signals were referenced to external deionized water via the spectrometer frequency setting. The instrumental settings were: spectral width 36 kHz, acquisition time 10 ms, preacquisition delay 100 μs, pulse angle 90° (pulse width 28 μs) and number of scans typically 10^5–2×10^5. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 30 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to 0.08 ppm by zero filling to 16 K data points. The reproducibility of the chemical shift data is estimated to be ±1 ppm.

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