

The Use of ^{13}C N.M.R. Spectroscopy for the Characterization of Carbonates, Thiocarbonates, Dithiocarbonates and Trithiocarbonates

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Abstract

The ^{13}C nuclear magnetic resonance chemical shifts are reported for a variety of carbonates (δ 154), thiocarbonates (δ 193 for OCSO, δ 170 for SCO), dithiocarbonates (δ 215 for SCSO, δ 188 for SCOS) and trithiocarbonates (δ 224).

In the course of some recent work on thiocarbonates¹ we had occasion to collect the ^{13}C n.m.r. spectra of some carbonates, thiocarbonates, and dithiocarbonates. In particular, we were struck by the consistent chemical shift of carbon in each of the various types of carbonyl and thiocarbonyl groups investigated. In two instances, the structure elucidation of the product of a thiocarbonate/methyl iodide reaction was greatly aided by a knowledge of the carbonyl carbon chemical shift. This led us to make a detailed study of carbonates, thiocarbonates (OCSO and SCO), dithiocarbonates (SCSO and SCOS) and trithiocarbonates. Our results are summarized in Table 1.

The chemical shift of carbon (OCOO) in the carbonates (1)–(5) is centred at about 154 ppm, and this consistency in chemical shift has been noted previously.² For the thiocarbonates (6)–(10), the carbon (OCSO) resonance moves significantly downfield to around 193 ppm. This value is in good agreement with that reported by Krief (191.5 ppm),³ who studied a very closely related series of *O,O*-dialkyl thiocarbonates. The thiocarbonates (11)–(15) show a carbon resonance (SCO) at around 170 ppm. For the dithiocarbonates (16)–(20), a carbon resonance (SCSO) is observed around 215 ppm, and the related dithiocarbonates (21)–(23) show a carbon resonance (SCOS) centred at 188 ppm. The trithiocarbonates (24)–(26) show the lowest resonance for carbon here (SCSS), namely 224 ppm. From these results, two additivity relationships are obvious. The replacement of oxygen by sulfur of the type OCOO \rightarrow SCO results in a downfield shift of the carbon resonance by some 17 ppm, whereas the alternative replacement of oxygen by sulfur, e.g., OCOO \rightarrow OCSO, results in a much larger downfield shift, about 40 ppm.

Although the above empirical additivity relationships are easily discerned, it is not quite so simple to give a theoretical basis to the trends observed in chemical shift

¹ Patroni, J. J., Skelton, B. W., Stick, R. V., and White, A. H., *Aust. J. Chem.*, 1980, 33, 987.

² Levy, G. C., and Nelson, G. L., 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists' p. 126 (Wiley-Interscience: New York 1972).

³ Hevesi, L., Nagy, J. B., Krief, A., and Derouane, E. G., *Org. Magn. Reson.*, 1977, 10, 14.

Table 1. The ^{13}C chemical shifts for $\text{C}=\text{O}$ and $\text{C}=\text{S}$ in carbonates and thiocarbonates

- (1) Diethyl carbonate (ref. 2).
- (2) Propane-1,3-diyl carbonate (ref. 2; Carothers, W. H., and Van Natta, F. J., *J. Am. Chem. Soc.*, 1930, **52**, 314).
- (3) *o*-Phenylene carbonate (Copeland, C., and Stick, R. V., *Aust. J. Chem.*, 1979, **32**, 637).
- (4) Methyl 2,3-*O*-carbonyl-4,6-*O*-isopropylidene- α -D-mannoside (ref. 1).
- (5) Methyl 2,3-*O*-carbonyl-6-deoxy-6-iodo- α -D-mannopyranoside (ref. 1).
- (6) *O,O*-Diethyl thiocarbonate (Staab, H. A., and Walther, C., *Justus Liebigs Ann. Chem.*, 1962, **657**, 98).
- (7) *O,O*-cis-Cyclohexane-1,2-diyl thiocarbonate (Barton, D. H. R., and Stick, R. V., *J. Chem. Soc., Perkin Trans. 1*, 1975, 1773).
- (8) *O,O*-trans-Cyclohexane-1,2-diyl thiocarbonate (as for compound (3)).
- (9) Methyl 4,6-*O*-isopropylidene-2,3-*O*-thiocarbonyl- α -D-mannoside (ref. 1).
- (10) Methyl 2,3-*O*-thiocarbonyl- α -D-mannopyranoside (ref. 1).
- (11) *O,S*-Diphenylthiocarbonate (Schönberg, A., and Vargha, L. v., *Ber. Dtsch. Chem. Ges.*, 1930, **63**, 178).
- (12) 1,3-Benzoxathiol-2-one (Greenwood, D., and Stevenson, H. A., *J. Chem. Soc.*, 1953, 1514).
- (13) 5,6-*O*,*S*-Carbonyl-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-thio- α -D-glucose (Barton, D. H. R., and Subramanian, R., *J. Chem. Soc., Perkin Trans. 1*, 1977, 1718).
- (14) Methyl 3-deoxy-3-iodo-4,6-*O*-isopropylidene-2-*O*-(methylthio)carbonyl- α -D-altroside (ref. 1).
- (15) Methyl 3,6-dideoxy-3,6-diiodo-2-*O*-(methylthio)carbonyl- α -D-mannopyranoside (ref. 1).
- (16) *O*-Ethyl *S*-phenyl dithiocarbonate (Rivier, M. H., *Bull. Soc. Chim. Fr.*, 1907, **1**, 733).
- (17) *O*-Cyclohexyl *S*-methyl dithiocarbonate (Taguchi, T., and Nakao, M., *Tetrahedron*, 1962, **18**, 245).
- (18) Benzyl 2-acetyl-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-(methylthio)thiocarbonyl- α -D-glucoside.
- (19) 1,2,5,6-Di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl- α -D-glucose (Barton, D. H. R., and McCombie, S. W., *J. Chem. Soc., Perkin Trans. 1*, 1975, 1574).
- (20) 1,2,5,6-Di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl- β -D-altrose (Fuller, T. S., and Stick, R. V., *Aust. J. Chem.*, 1980, **33**, 2509).
- (21) *S,S*-Diphenyl dithiocarbonate (Heine, H.-G., and Metzner, W., *Justus Liebigs Ann. Chem.*, 1969, **724**, 223).
- (22) *S,S*-Dibenzyl dithiocarbonate (Bulmer, G., and Mann, F. G., *J. Chem. Soc.*, 1945, 666).
- (23) *S,S*-Dibutyl dithiocarbonate (Little, L. H., Poling, G. W., and Leja, J., *Can. J. Chem.*, 1961, **39**, 745).
- (24) Diphenyl trithiocarbonate (Schönberg, A., Nickel, S., and Černík, D., *Ber. Dtsch. Chem. Ges.*, 1932, **65**, 289).
- (25) Dibenzyl trithiocarbonate (Runge, F., El-Hewehi, Z., Renner, H.-J., and Taege, E., *J. Prakt. Chem.*, 1960, **11**, 284).
- (26) Dibutyl trithiocarbonate (as for compound (25)).

OCOO	OCSO	SCOO	SCSO	SCOS	SCSS
(1) 155.7	(6) 195.9	(11) 168.5	(16) 213.3	(21) 187.5	(24) 224.4
(2) 155.2	(7) 192.8	(12) 168.8	(17) 214.8	(22) 188.4	(25) 222.7
(3) 151.3	(8) 193.1	(13) 172.3	(18) 217.6	(23) 189.7	(26) 224.7
(4) 153.3	(9) 189.9	(14) 170.5	(19) 214.6		
(5) 154.1	(10) 192.0 ^a	(15) 170.7	(20) 214.4		

^a In $(\text{CD}_3)_2\text{CO}$.

for the six different types of carbonyl group here. For example, the replacement of oxygen by sulfur ($\text{OCOO} \rightarrow \text{SCOO}$ and OCSO) results in moderate and large downfield shifts for the carbon resonance, respectively, and this is opposite to the upfield shift expected based on the electronegativity of the atoms concerned. Demarco⁴ has given an explanation for the lower field resonance of thiocamphor ($\text{C}=\text{S}$) relative

⁴ Demarco, P. V., Doddrell, D., and Wenkert, E., *Chem. Commun.*, 1969, 1418.

to camphor (C=O) in terms of the contribution of the mean excitation energy, ΔE , to the paramagnetic screening term, σ_p . A smaller value of ΔE (as expected for thio-camphor) gives rise to a larger magnitude of σ_p , and a lower shielding and chemical shift value. A similar explanation has been proposed for the lower chemical shift of carbon in carbon disulfide as compared with carbon dioxide.⁵ In our case, the proposal by Demarco adequately explains the OCOO \rightarrow OCSO transformation, and begs the statement that the alternative transformation, OCOO \rightarrow SCOO, also lowers the value of ΔE for the carbonyl group, but by a lesser amount. This seems to be the case when one compares the ultraviolet spectra for 5,6-*O*-carbonyl-1,2-*O*-isopropylidene-3-*O*-methyl- α -D-glucose⁶ and the thiocarbonate (13) in diethyl ether, with the thiocarbonate (13) showing an absorption band at longer wavelength (246 nm, ϵ 3200) than the carbonate (212 nm, ϵ 600).

Although carbonates themselves are easily identified by infrared spectroscopy (C=O generally above 1740 cm⁻¹),⁷ the replacement of oxygen by sulfur makes assignment more difficult. Indeed, for thiocarbonates containing the thiocarbonyl grouping (OCSO), the assignment may not even be possible.⁷ It is in such cases that ¹³C chemical shifts are clearly a useful alternative.

Experimental

Experimental details have been given previously.¹ The ¹³C n.m.r. spectra were obtained on a Bruker WP-80 spectrometer operating at 20.1 MHz, with samples 0.5 M in deuteriochloroform as normal solvent and tetramethylsilane as internal standard (δ 0.0). Each spectrum was obtained by using a 2.2- μ s pulse, corresponding to a tilt angle of 30°. For a spectral window of 9 MHz over 8192 data points, an acquisition time of 0.43 s per pulse was used for 3000–5000 pulses. The delay time between pulses was 2–5 s. Spectra were obtained in the temperature range 30–35°.

Benzyl 2-Acetylamino-4,6-O-benzylidene-2-deoxy-3-O-(methylthio)thiocarbonyl- α -D-glucoside (18)

To benzyl 2-acetylamino-4,6-*O*-benzylidene-2-deoxy- α -D-glucoside⁸ (4.4 g, 11 mmol) in dimethylformamide (40 ml, 50°) was added sodium hydride (700 mg, 30 mmol) and imidazole (60 mg), and the mixture stirred under nitrogen (2 h), cooled (20°), carbon disulfide (1.0 ml, 16 mmol) added and stirring continued (2 h). Methyl iodide (1.0 ml, 16 mmol) was then added; the mixture was stirred overnight and poured onto ice-water. Filtration gave crude (18) which was dried and recrystallized to give the pure *dithiocarbonate* (18) as pale yellow needles (4.8 g, 85%), m.p. 184–185° (EtOH), $[\alpha]_D^{20} +25^\circ$ (Found: C, 58.9; H, 5.7; N, 3.0; S, 13.1. C₂₄H₂₇NO₆S₂ requires C, 58.9; H, 5.6; N, 2.9; S, 13.1%). ¹H n.m.r. (270 MHz) δ 1.88, s, COMe; 2.55, s, SMe; 3.78, apparent t, $J_{5,6a}$ 10.0, $J_{6,6e}$ 10.3 Hz, H 6a; 3.90, t, $J_{3,4} = J_{4,5}$ 9.3 Hz, H 4; 4.0, apparent td, $J_{5,6e}$ 4.5 Hz, H 5; 4.25, dd, H 6e; 4.53, 4.73, ABq, J 11.9 Hz, CH₂Ph; 4.54, ddd, $J_{1,2}$ 3.8, $J_{2,NH}$ 9.7, $J_{2,3}$ 10.4 Hz, H 2; 4.95, d, H 1; 5.56, s, CHPh; 5.89, d, NH; 6.35, dd, H 3; 7.3–7.5, m, 10H, Ph. ¹³C n.m.r. δ 18.9, 23.0, SMe, COMe; 52.7, 63.3, 78.5, 79.4, C2,3,4,5; 68.7, 70.1, CH₂, C6; 97.6, 101.4, CHPh, C1; 126.1, 128.1, 128.6, 129.0, 10C, =CH–; 136.7, 137.0, =C–; 169.8, CO; 217.6, CS.

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⁵ Maciel, G. E., and Beatty, D. A. *J. Phys. Chem.*, 1965, **69**, 3920.

⁶ Shasha, B. S., Doane, W. M., Russell, C. R., and Rist, C. E., *J. Org. Chem.*, 1965, **30**, 2324.

⁷ Bellamy, L. J., 'The Infrared Spectra of Complex Molecules' p. 143 (CO), p. 399 (CS) (Chapman & Hall: London 1975).

⁸ Liav, A., Hildesheim, J., Zehavi, U., and Sharon, N., *Carbohydr. Res.*, 1974, **33**, 217.