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Use of Carbon-13-Proton Coupling Constants in the Assignment of Proton Signals in the N.m.r. Spectrum of S-Methyl Thioacetate¹

BY RICHARD L. MIDDAGH² AND RUSSELL S. DRAGO

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The use of coupling constants between directly bonded carbon-13 and protons for the assignment of the two proton magnetic resonance signals in S-methyl thioacetate is reported. The applicability of this technique to other systems is discussed.

Introduction

The proton magnetic resonance spectrum of S-methyl thioacetate, $\text{CH}_3\text{COSCH}_3$, consists of two closely spaced signals of equal intensity arising from the two nonequivalent methyl groups. The very small separation (0.03 p.p.m.) between the signals precludes their assignment by comparison with spectra of similar compounds. The assignment could be made by observing the decrease in intensity of the proton resonance signal that would result from partially deuterating one of the methyl groups, but this would involve the inconvenience of the preparation of the compound. We were able to make an unequivocal assignment by observing the small satellite signals in the n.m.r. spectrum caused by the splitting of the proton resonance by directly bonded carbon-13 ($I = 1/2$) present in natural abundance (1.1%).³

Experimental

Chemical shifts and coupling constants were determined from spectra recorded on a Varian Associates model A-60 high resolution nuclear magnetic resonance spectrometer. The carbon-13 present in natural abundance (1.1%) produces satellite side bands which are symmetrically disposed about the main proton signal. Coupling constants can be evaluated with an accuracy of at least ± 1 c.p.s. from these satellite bands. Their low intensity necessitates use of higher than normal spectrum amplitudes. The spectrum of pure S-methyl thioacetate reproduced in Fig. 1 was obtained using the following instrument settings: frequency response, 1 c.p.s.; radiofrequency field, 0.2 m.g.; sweep time, 250 sec.; sweep width, 500 c.p.s.; spectrum amplitude, 10. Spinning side bands, deleted from the figure, were identified by recording spectra at two different sample spinning speeds. The carbon tetrachloride solutions contained about 1% tetramethylsilane (TMS) as an internal standard.

The S-methyl thioacetate was prepared from acetyl chloride and methanethiol⁴ and was thrice distilled to give a colorless liquid, b.p. 96.5–97.0° at atmospheric pressure.

Results

It has been shown that solvent effects can cause the relative chemical shifts of the N-methyl protons in N,N-dimethylamides to change sign.⁵ Because chemical shifts are ordinarily determined in solutions too dilute to give favorable signal-to-noise ratios for the carbon-13 satellites, both the relative chemical shifts and the coupling constants were checked over the complete concentration range, from dilute solution in carbon tetrachloride to pure liquid. The data in Table I show no change in relative chemical shifts or coupling constants.

Figure 2 shows the spectrum of a solution, recorded at the low spectrum amplitude normally used for determination of chemical shifts. Figure 1 shows a spectrum recorded at a higher spectrum amplitude to facilitate accurate measurement of the coupling constants.

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TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF S-METHYL THIOACETATE

Concn., moles/l. in CCl_4	τ , p.p.m. ^a	$J_{\text{C}^{13}\text{-H}}$, c.p.s. ^b
0.55	7.70	...
	7.73	...
4.2	7.70	131
	7.73	143
7.4	7.69	131
	7.72	143
9.5	7.69	131
	7.72	143
11 (pure liq.)	Low field ^c	131
	High field ^c	143

^a Chemical shift relative to internal tetramethylsilane at 10.00 p.p.m. ^b Uncertainty less than 1 c.p.s. ^c Separation between low- and high-field signals of the two methyl groups is 0.03 p.p.m.

Coupling constants between directly bonded carbon-13 and protons in the methyl groups of a number of acetyl and S-methyl compounds are listed in Table II.

TABLE II

SPIN-SPIN COUPLING CONSTANTS BETWEEN CARBON-13 AND PROTONS IN ACETYL AND IN S-METHYL COMPOUNDS

Compound	$J_{\text{C}^{13}\text{-H}}$, c.p.s. ^a
$(\text{CH}_3)_2\text{CO}$	127 ^b
$\text{CH}_3\text{COC}(\text{CH}_3)_3$	127
CH_3CHO	127 ^{7a}
$\text{CH}_3\text{CON}(\text{CH}_3)_2$	128, 138(N-methyl)
$\text{CH}_3\text{CONHCH}_3$	128, 137.5(N-methyl)
CH_3CONH_2	129
$\text{CH}_3\text{COOCH}_3$	130, 146(O-methyl) ⁸
$\text{CH}_3\text{COOC}_2\text{H}_5$	130 ⁸
$(\text{CH}_3\text{CO})_2\text{O}$	130 ± 5^{3a}
CH_3COOH	130 ^{7a}
CH_3SH	138 ^{7b}
$(\text{CH}_3)_2\text{S}$	138 ^{7b}
$(\text{CH}_3)_2\text{SO}$	138 ^{7a}
$\text{CH}_3\text{SC}_6\text{H}_5$	139
$(\text{CH}_3)_2\text{SO}_2(\text{aq.})$	140 ^{7b}

^a Uncertainty is ± 1 c.p.s., except as noted.

Discussion

The value of $J_{\text{C}^{13}\text{-H}}$ depends primarily on the s-character at the carbon atom in the orbital bonding the proton.^{3c,9} For monosubstituted methanes, CH_3X , it has been shown that $J_{\text{C}^{13}\text{-H}}$ is proportional both to the electronegativity of the substituent and to the C-X bond distance.^{7,8} Thus for methyl groups attached to atoms which have similar electronegativities but which are in different periods of the periodic table, the value of $J_{\text{C}^{13}\text{-H}}$ will be related to the C-X bond distance. This has been observed for the group IV tetramethyl com-

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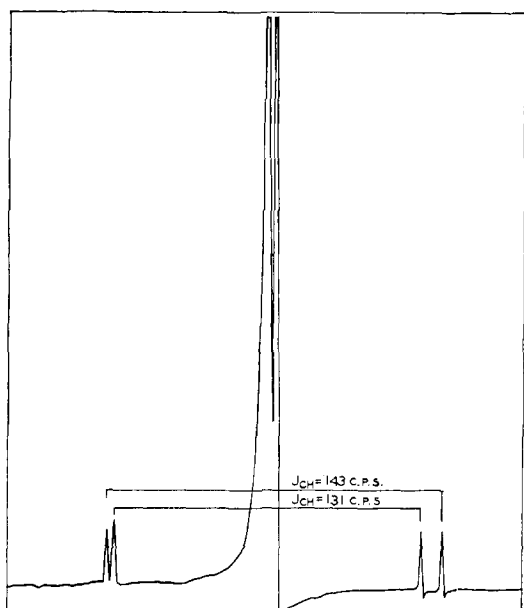


Fig. 1.—Proton n.m.r. spectrum of S-methyl thioacetate at high spectrum amplitude showing satellites arising from C^{13} .

pounds $(CH_3)_4M$, where M is Si, Ge, Sn, and Pb.¹⁰ The central atoms, M, have similar electronegativities, but the C–M bond distances increase as the size, or atomic number, of M increases. The change in bond distance is reflected in the values of $J_{C^{13}-H}$, which increase from 119 c.p.s. for M = Si to 134 c.p.s. for M = Pb. The dependence of the C–H coupling constant on the C–X bond distance in CH_3X compounds is explained by consideration of overlap in the C–X bond. The overlap integral and consequently the bond energy for a hybrid orbital on carbon and an orbital on X will in general be larger for a carbon hybrid with more s-character.¹¹ Thus the substituent X competes with the protons for carbon s-character. When the orbital on X is large and diffuse, the overlap in the C–X bond is less, and the total bond energy in the molecule is less sensitive to changes in s-character in the C–X bond. The C–H bonds are strengthened by increasing the s-character in the C–H bonds, so that the total bond energy is maximized by increasing the s-character in the C–H bonds rather than in the C–X bond.¹⁰

Since carbon and sulfur have similar electronegativities but rather different sizes, it is not surprising that

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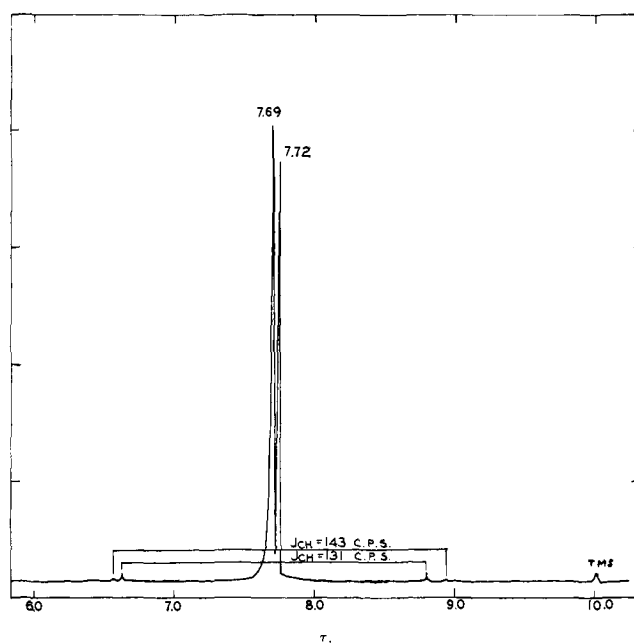


Fig. 2.—Proton n.m.r. spectrum of S-methyl thioacetate at normal spectrum amplitude.

methyl groups attached to carbon show different values of $J_{C^{13}-H}$ from those attached to sulfur. It can be seen from the data in Table II that the values of $J_{C^{13}-H}$ for methyl groups attached to carbonyl functional groups lie in the range 127 to 130 c.p.s., and that the values for methyl groups attached to sulfur lie in the range 138 to 140 c.p.s. The values $J_{C^{13}-H} = 131$ c.p.s. for the low-field signal and $J_{C^{13}-H} = 143$ c.p.s. for the high-field signal in S-methyl thioacetate enable us to assign the signals to the acetyl and S-methyl groups, respectively.

This technique should be useful in many organic and inorganic systems to distinguish between possible structures containing methyl groups attached to atoms of different size and for assigning n.m.r. signals in the spectra of molecules containing methyl groups bonded to atoms in different periods of the periodic table.

The requirement that the atoms or groups X have similar electronegativities should be emphasized. As X becomes more electronegative, there is more s-character in the C–H bonds and the coupling constant increases. In the series of methyl halides, CH_3F , CH_3Cl , CH_3Br , and CH_3I , the decrease in electronegativity of the heavier halides is offset by the increase in size, and nearly identical values of $J_{C^{13}-H}$ are observed^{7a} (149, 150, 152, and 152 c.p.s., respectively).