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THE 13C ISOTOPE SHIFTS IN THE PROTON MAGNETIC RESONANCE SPECTRA OF DIMETHYL SULFOXIDE AND SOME OTHER SYMMETRICAL MOLECULES

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In connection with another study[1] we had the opportunity to examine the high resolution PMR spectrum of neat dimethyl sulfoxide (*1*) by means of the side band technique,[2] and in addition to the main signal given by the six chemically and magnetically equivalent protons, we observed the presence of satellite signals located at both higher and lower fields with respect to the main absorption signal and removed from it by about 69 Hz. The quartet nature of the satellite signals (Fig. 1), and the observations that the signals shifted proportionally with the magnitude of the applied fields (Table I) while the coupling constants remained constante (Table II), revealed the origin of the satellite bands. While the main signal is produced by the six equivalent protons of *1* in which both methyl groups contain ^{12}C atoms, the protons of the first methyl group that contains a ^{13}C atom (natural abundance 1.1%, spin $= 1/2$) originate two absorption signals which are split further into a quartet by long range interactions with the trio of hydrogen atoms in the second methyl group of *1* that contains the ^{12}C atom. The probability of finding *1* that contains ^{13}C in both methyl groups is insignificant. The relative peak intensities of the quartet are 1:3:3:1.

The isotope effect on magnetic shielding has been observed[3] for a number of different nuclei.

In their study of the spin coupling constants in ethane, ethylene, or acetylene containing one or two ^{13}C nuclei Lynden-Bell and Sheppard[4] noted rather small isotope shifts values. Also Graham and Holloway[5] reported the isotope shift in ethylene without offering a theoretical interpretation. The isotope shift is relatively pronounced in the case of the deuterium isotope effect on the magnetic resonance of protons or ^{19}F atoms (*ca.* 0.2 and 0.4 ppm, respectively, for one deuterium being present in the given molecule), but the effect of the ^{13}C isotope on the magnetic resonance of ^{19}F and especially that of protons is relatively small (*ca.* 0.2 and 0.007 ppm, respectively) and hence more difficult to observe. The magnitude of the isotope shifts in NMR is known[3] to depend on the proximity as well as the electronic nature of isotopic nuclei, and thus the magnitude of the resultant isotopic shifts is subject to significant variations.

The determination of the exact location of the ^{13}C satellites with respect to the main proton signal of *1* reveals a displacement in the direction of higher field strength. This is consistent with the usual direction of the isotope effect,[3] namely an apparent greater proton shielding by the heavier isotope. The displacement of the proton signals caused by the heavier isotope is referred to as the isotope shift ($\Delta\delta$)

and, as can be seen in Table I, it increases as the applied magnetic field is also increased. On the other hand, as can be seen from the result shown in Table II, the coupling constants are indifferent to the magnitude of the applied magnetic field.

TABLE I

Chemical and ^{13}C and ^{15}N Isotope Shifts ($\Delta\delta$) of Proton Resonance at 60 and 100 MHz.[a]

Compound	$\Delta\delta$ at 60 MHz.	$\Delta\delta$ at 100 MHz.
$(CH_3)_2SO$	0.33 ± 0.1	0.4 ± 0.1
$(CH_3)_2S$	0.22 ± 0.1	0.5 ± 0.2
$(CH_3)_2O$	0.35 ± 0.1	0.75 ± 0.2
CH_2Cl_2	0.22 ± 0.1	0.4 ± 0.1
$cis\text{-}C_2H_2Cl_2$	0.23 ± 0.1	(0.38 ± 0.16)[b]
$trans\text{-}C_2H_2Cl_2$	(0.21 ± 0.1)[b]	0.35 ± 0.2
NH_3	0.59 ± 0.2	

a All isotope shifts are expressed in Hz. The 60 MHz spectra were run at $44 \pm 1°C$ except in the case of CH_2Cl_2, where $T = 23 \pm 1°C$. All 100 MHz spectra were run at $33.5 \pm 1°C$, by courtesy of the Chemistry Department, Michigan State University.

b Calculated values assuming that $\Delta\delta$ values vary proportionally with the magnitude of the applied magnetic field.

Encouraged by the observation of the [13] C isotope effects on the PMR spectrum of *I* we examined the spectra of several other symmetrical molecules (Tables I, II).

The PMR spectra of dimethyl sulfide and oxide resemble the spectrum of DMSO in line with the similar symmetry of the structures except that the quartet of the ether is broadened beyond recognition. It is of interest to note that the relative magnitude of the isotopic shifts (Table I) suggests that the distance that separates the different methyl groups in $H_3\,^{12}C\text{-}X\text{-}^{13}CH_3$ varies as a function of X in the following manner $S > SO > O$. The separation in question depends on both the bond lengths and bond angles, and while the C-S bond lengths are

greater than the C-O bonds length, the C-S-C bond angles, on the other hand, are usually smaller than the C-O-C bond angles. The calculated distances between the carbon atoms of the three C-X-C systems under discussion are shown in Table III and they are consistent with the observed variation in the magnitude of the isotopic shifts. The effect of molecular geometry on the magnitude of the isotope shift is also clearly demonstrated in the case of the *cis* and *trans* 1,2-dichloroethylenes in which the greater proximity of the protons in $\begin{smallmatrix}C = {}^{13}C\\H \qquad H\end{smallmatrix}$ results in larger isotope shift.

TABLE II

Heteronuclear Coupling Constants ($J_{^{13}C\text{-}H}$) and Long Range Coupling Constants ($J_{H\text{-}H}$) at 60 and 100 MHz.[a]

Compound	$J_{^{13}C\text{-}H}$ (60 MHz)	$J_{^{13}C\text{-}H}$ (100 MHz)	$J_{H\text{-}H}$ (60 MHz)	$J_{H\text{-}H}$ (100 MHz)
$(CH_3)_2SO$	137.55 ± 0.1	137.3 ± 0.2	0.44 ± 0.1 quartet	0.43 ± 0.1 quartet
$(CH_3)_2S$	137.56 ± 0.1	137.3 ± 0.2	0.28 ± 0.1 quartet	0.3 ± 0.1 quartet
$(CH_3)_2O$	139.55 ± 0.1	139.5 ± 0.2	broad	0.5 ± 0.1
CH_2Cl_2	178.21 ± 0.1	177.9 ± 0.2	none	none
$cis\text{-}C_2H_2Cl_2$	197.90 ± 0.1	198.1 ± 0.2	5.3 ± 0.1 doublet	5.2 ± 0.1 doublet
$trans\text{-}C_2H_2Cl_2$		199.0 ± 0.2		12.1 ± 0.1 doublet

a All coupling constants are expressed in Hz. Experimental condition as described in Table I.

In addition to the [13] C satellites, we also examined the proton spectrum of a mixture of exhaustively dried $^{14}NH_3$ and $^{15}NH_3$. The spectral center of a doublet for $^{15}NH_3$ did not coincide with the center peak of a triplet for $^{14}NH_3$ and thus yielded the greatest value for isotope shift observed in this study (Table I). Appleman[7] recently extended Ermler and Kern's work[8,9] to evaluate the zero-point vibrational effect of the paramagnetic contribution to proton and oxygen shielding constants in several isotopic species of the water molecule by using SCF MO wavefunction constructed from the Slater type minimal basis set. His results indicate that the proton isotope shift for $H_2\,^{16}O$ and $H_2\,^{17}O$ is in the order of 0.01 ppm. It is noteworthy that our value for ammonia is of the same order of magnitude.
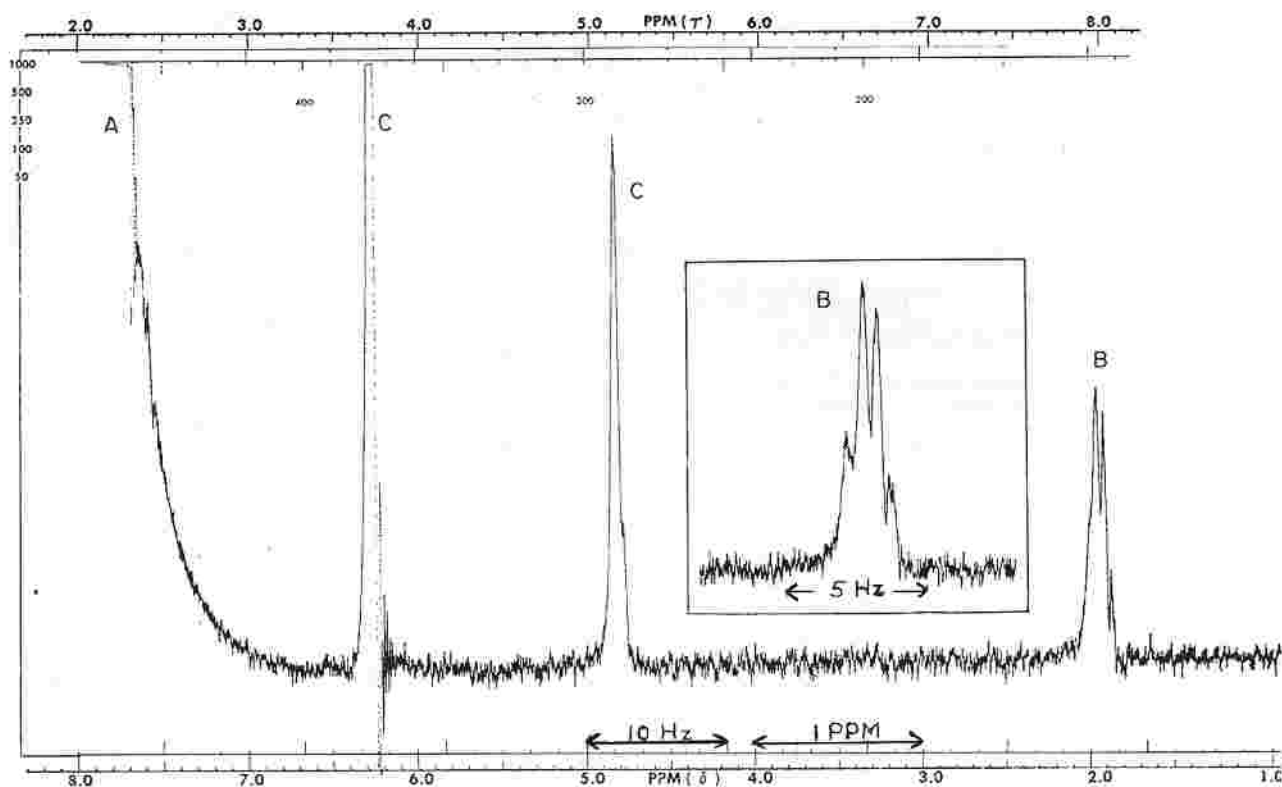
Fig. 1
Satellite NMR signals in DMSO.
The intense main signal (A) of the DMSO protons is accompanied by the satellite bands (B) at both higher and lower (not shown) magnetic fields. The spinning side band signals appear at C.

TABLE III

Calculated Separation between Carbon Atoms

in $H_3C-X-CH_3$

X	C-X (°A)	C-X-C (°)	d_{c-x-c} (°A)
S	1.802[a]	98.86[a]	2.737
S(O)	1.79[b]	96.9[b]	2.679
O	1.410[c]	111.71[c]	2.334

a L. Pierce and M. Hayashi, **J. Chem. Phys.,** 35, 479 (1961).

b Average values from those reported by H.H. Szmant in "Dimethyl Sulfoxide," S. W. Jacob, E. E. Rosenbaum and D. C. Wood, Editors, Marcel Dekker, New York, 1971, pp.3-6.

c Average values from K. Kimura and M. Kubo, **Nature,** 533 (1959); P. H. Kasai and R. J. Myers, **J. Chem. Phys.,** 30, 1096 (1959), and U. Biukis, and M. Hayashi, **J. Chem. Phys.,** 35, 479 (1961).

It is apparent that the isotope shift arises from a subtle difference in molecular electronic wavefunctions caused by changes in the vibrational motions of nuclei upon isotopic substitution. Concerning this effect Kern and Matcha[8] have recently developed successive order perturbation equations for nuclear wavefunctions and thus obtained the corresponding nuclear contributions to the expectation values for arbitrary operators over electronic wavefunctions. Ermler and Kern[9] applied this theory to the water molecule and found that the electronic expectation values typically needed to be corrected by about 1% of the equilibrium values, but the corrections could be as large as 20% in some cases. It was also found that the zero-point vibrational effect was the dominant cause for this correction.[8],[9]

EXPERIMENTAL

High resolution NMR spectra were taken by means of Varian A60A and HA100 spectrometers[10] and the frequency was determined

using the side band technique.[2] The molecular species containing one [13]CH_3 group in neat dimethyl sulfoxide, dimethyl sulfide, and dimethyl ether, the ^{13}C satellites of proton NMR spectra were analyzed as a heteronuclear A_2B_2X system, where A and B refer to the protons attached to ^{13}C and ^{12}C, respectively, and X stands for the ^{13}C nucleus. For these molecules the magnitude of the internal chemical shift $|\delta_A - \delta_B|$ is comparable to the long range spin coupling constant $|J_{AB}|$ and the heteronuclear coupling constant J_{BX} is identically zero. In a similar manner, the isotopic species containing one [13]CHCl group in *trans* and *cis*-dichloroethylene were treated as a heteronuclear ABX system. The values of isotope shifts were then calculated by subtracting the frequency of the main peak in the normal isotopic species from the value for $|\delta_A - \delta_B|$ obtained above (Table I). The values of the heteronuclear coupling constant J_{13} C-H (J_{AX}) and the long range coupling constant J_{H-H} (J_{AB}) were also obtained and are given in Table II.

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ESPECTROMETRIA DE MASAS DE LACTONES SESQUITERPENICAS DE LA SERIE DE LOS PSEUDOGUAYANOLIDOS. I*

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ABSTRACT. The mass spectra of several sesquiterpene lactones of the guaianolide series have been studied. The fragmentation patterns and mechanisms postulated have been confirmed by the determination of the mass spectra of deuterium labeled derivatives.

El estudio por espectrometría de masas de los patrones de fragmentación de compuestos orgánicos bajo impacto electrónico, puede proveer de una información fundamental y básica para el estudio estructural de compuestos semejantes. Las lactonas sesquiterpénicas de la serie de los pseudoguayanólidos, cuyos espectros han sido anteriormente poco estudiados,[1-7] constituyen una extensa serie de compuestos relacionados y semejantes, muy apropiados para estos estudios.

En este trabajo se estudian pseudoguayanólidos isómeros que poseen un grupo cetónico en C_4, cierres lactónicos en C_6 y C_8 y que difieren en uno o varios de sus centros asimétricos. También se estudian pseudoguayanólidos que difieren en la posición de una o dos dobles ligaduras.

Los compuestos del I al XII analizados, así como sus correspondientes derivados deuterados (Id-XIId) están dados en el esquema de fórmulas.

En todos los espectros de los compuestos analizados* (Tabla I) se encontró que seguían un patrón de fragmentación muy semejante, con diferencias notables en la abundancia relativa de los fragmentos iguales o semejantes, así como en la formación de distintos picos bases. Estas dife-

* Todos los mecanismos han sido elucidados complementando el estudio con los espectros de los derivados deuterados; y debido a la no observación de picos metaestables en las condiciones experimentales utilizadas en el espectrómetro no se cuenta con esta ayuda.