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Chimica fisica. — *Vibrational effects of deuterium substitution on N.M.R. parameters of acetylene.* Nota di MASSIMO ROSSI (*), FLAVIANO COLETTA e GIORGIO RIGATTI, presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — La determinazione della variazione delle costanti N.M.R., nel caso delle molecole di acetilene ed acetilene monodeuterato, produce il valore di 0.02 *ppm* per la variazione dello spostamento chimico e praticamente di zero per le costanti di accoppiamento tra idrogeno e carbonio 13. Il comportamento di queste costanti nel caso dell'acetilene è posto in relazione all'influenza dell'atomo di deuterio nel modificare, attraverso il suo effetto sui moti di vibrazione torsionali, la distribuzione di carica π che nell'acetilene normale è simmetrica.

It has been shown experimentally [1] that in molecules like R—CH_3, the deuterium substitution of one proton produces a variation in $J_{^{13}C-H}$ of about 4 *cps*.

One of us [2] has given a theoretical explanation of this effect, in tetrahedrally hybridized carbon atoms, by invoking a change in the time averaged per cent "*s*" character in C—H bond after deuteration, due to the coupling of the bending vibrations.

The theory produces a $J_{^{13}C-H}$ increase of 2.5 *cps*, which is in good agreement with the experimental one, considering the approximations used.

Working along this line, we have applied the theory of the effects of the bending motions to the variation of N.M.R. parameters with the partial deuteration of the acetylene molecule.

We have also carried out the necessary experimental measurements.

The molecule H—C ≡ C—H belongs to the $D\infty_h$ point group, hence the electronic distribution is symmetric about the mirror plane perpendicular to C—C axis (Z axis) and bisecting it, the dipole moment is zero and the protons are magnetically equivalent.

On the other hand, the molecule H—C ≡ C—D (1) belongs to $C\infty_v$ point group and on symmetry grounds, the electron distribution can be asymmetric, the dipole moment can be different from zero and the proton can have shielding and coupling constants different from those of light acetylene.

In Table I the experimental results about the various isotopic species of acetylene are collected.

(*) Deceased in August 1971.

(**) Nella seduta del 15 gennaio 1972.

(1) Also the molecule in which one of the C–12 atoms is substituted with C–13, belongs to the $C\infty_v$ point group, but in this case the effect on the previous properties is probably negligible.

TABLE I.

NMR *parameters* (*) *of isotopic acetylenes.*

	δ_{H_1}	δ_{H_2}	J_{HH}	J_{HD}	$J_{^{13}C-H}$	$J_{^{13}C\equiv C-H}$
$H-{}^{12}C_2 \equiv {}^{12}C_1-H$	0.000	0.000	—	—	—	—
$H-{}^{12}C_2 \equiv {}^{13}C_1-H$	$+0.000_8$	-0.000	9.79	—	$\pm 248.7_7 \pm 0.07$	$\pm 50.0_8 \pm 0.08$
$D-{}^{12}C_2 \equiv {}^{12}C_1-H$	$+0.016 \pm 0.002$	—	—	1.44 ± 0.06	—	—
$D-{}^{12}C_2 \equiv {}^{13}C_1-H$	$+0.016 \pm 0.002$	—	—	1.44	$\pm 248.9_6 \pm 0.1$	—
$D-{}^{13}C_2 \equiv {}^{12}C_1-H$	$+0.016 \pm 0.002$	—	—	1.44	—	$\pm 50.3_3 \pm 0.1$

(*) The δ's are given in *ppm*, taking as zero the chemical shift position of the protons in light acetylene. Positive values of the δ's mean upfield shifts. Deuterated sample of acetylene prepared by reaction of CaC_2 with a mixture containing 50% in volume of deuterated water was dissolved in acetone, where the solubility is very high. The spectra were registered on a Varian A-56/60 spectrometer, at a temperature of —80 C°, equipped with the units for the sideband calibration. Each value, reported in Table I, is the mean over ten spectra or more. The values of the coupling constants in the light acetylenes are similar although the experimental conditions are different, to that found by Bell *et al.* (3).

DISCUSSION

To evaluate quantitatively the effect of the substitution of an hydrogen atom with a deuterium one on the electronic distribution of the acetylene molecule, we shall make the following simplifyng assumptions:

a) each hybrid atomic orbital of the carbon atom involved in the σ_{C-H} or σ_{C-D} localized molecular orbital " follows " the motion of the hydrogen or deuterium atom [2].

b) The " orbital following " affects mainly the π orbitals. When the C—H bond forms an angle θ with the Z molecular axis, owing to the bending motions in the Z—X plane, the σ_{C-H} molecular orbital must be transformed into:

$$(1) \qquad \sigma^{(\theta)}_{C-H} = \frac{1}{\sqrt{2}} \left\{ \left[\cos\left(\frac{\theta}{\sqrt{2}}\right) \left(\frac{s_c + p_{z_c}}{\sqrt{2}}\right) + \operatorname{sen}\left(\frac{\theta}{\sqrt{2}}\right) p_{x_c} \right] + s_H \right\}.$$

The p_x, a.c., to remain orthogonal to the σ_{C-H}, becomes

$$(2) \qquad P_x(\theta) = \cos\left(\frac{\theta}{\sqrt{2}}\right) p_x - \frac{1}{\sqrt{2}} \operatorname{sen}\left(\frac{\theta}{\sqrt{2}}\right) (s_c + p_{z_c}).$$

If α is the Hückel energy of an a.o., and since $\alpha_{p_x} = \alpha_{p_z} = \alpha_{s_c} + \Delta$, with $\Delta > 0$, in small angle approximation we have:

$$(3) \qquad \alpha^{(\theta)}_{P_x} = \alpha_{p_x} - \frac{\theta^2 \Delta}{4}.$$

The averaged value over this vibrational motion is:

$$\langle \alpha_p \rangle = \alpha_{p_x} - \frac{\Delta}{4} \langle \theta^2 \rangle = \alpha_{p_x} - \frac{\Delta}{4} \left(\frac{h}{4\pi^2 M \nu} \right) \frac{1}{R^2} \tag{4}$$

where R is the C—H distance, M is the mass of the bonded atom (H or D) and ν is the frequency of the bending motion.

For the molecule $H—C_1 \equiv C_2—D$, substituting in (4) the necessary values [4] we have

$$\langle \alpha_{P_1} \rangle - \langle \alpha_{P_2} \rangle = -4\,\Delta \cdot 10^{-3} \tag{5}$$

so that the Hückel coefficients are

$$c_1 = \frac{(1-t)^{-1/2}}{\sqrt{2}} \qquad c_2 = \frac{(1-t)^{1/2}}{\sqrt{2}}$$

where $t = (\Delta/\beta)\, 2 \cdot 10^{-3}$ and β is the resonance Hückel integral for the acetylenic π bond.

Finally, remembering that there are four π electrons on the π C—C bond, we obtain the increase δQ in the time averaged charge density on the atom C_1 in C_2HD, with respect to C_2H_2:

$$\delta Q = 2\,t \tag{6}$$

in electronic charge units.

It is known that the π charge density and proton chemical shift of a C—H group are related by the following relation [5]:

$$\Delta\sigma\,(ppm) = \delta Q\,(e) \cdot K \tag{7}$$

where K is a parameter which ranges between $7 \div 16$ *ppm*/electron. So, taking into account the experimental results about the difference between chemical shifts in normal and deuterated acetylene molecules, as given in Table I, we see that it is possible to reproduce the experimental difference by assuming the acceptable (2) value of —0.5 for Δ/β.

The change in the $J_{^{13}C-H}$ and $J_{^{13}C\equiv C-H}$ coupling constants

The variations in the $J_{^{13}C-H}$ coupling constants are usually related to changes in the per cent "*s*" character in the C—H bond. The theory [2] rationalizes the dramatic change of the coupling constants in the case of methanes when a proton is substituted by a deuteron. In the acetylene, the same theory predicts that the same substitution has a very small effect of the order of $2 \cdot 10^{-3}$ *cps*, on $J_{^{13}C-H}$ in agreement with the experiment.

(2) The value of Δ/β calculated with the parameters given by Hoffmann [6] is about–1.2 for the acetylenic case.

At difference with respect to the methane molecule, monodeuteration produces in acetylene also a small π charge asymmetry, which can in turn affect the carbon-hydrogen coupling constant. Such a possibility was first examined by Grant and Litchman [7]. They showed that $J_{^{13}C-H}$ in differently charged carbon atoms was proportional to the third power of the effective nuclear charge Z_{eff}, namely

$$\delta J_{^{13}C-H} = 3 J_{^{13}C-H} \frac{\delta Z_{eff}}{Z_{eff}} . \tag{8}$$

Following Coulson [8] we assume that

$$\delta Z_{eff} = -0.35\, \delta Q \qquad Z_{eff} = 3.25$$

With the same value of Δ/β which fits the change in chemical shift for deuterated and normal acetylenes, we obtain the magnitude of the variation in the coupling constants, due to this π charge asymmetry, which is of the order of 0.2 *cps* in agreement with the experimental results, as reported in Table I, in which we practically do not observe any variations in the $J_{^{13}C-H}$ coupling constants between normal and deuterated acetylene.

CONCLUSIONS

It is known that the isotopic shifts are usually interpreted in terms of the differences of the equilibrium distances along the bonds. A new way to explain the same effect, at least in the case of acetylenes or similar molecules, is the bending approach that can well explain the π charge density asymmetry and hence the variation in the chemical shift and also the much smaller effect, if any, on the $J_{^{13}C-H}$ coupling constant.

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