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HIGH-PRESSURE HIGH-RESOLUTION N.M.R. PRESSURE DEPENDENCE OF THE PROTON CHEMICAL SHIFTS OF PHENYLACETYLENE AND CHLOROFORM

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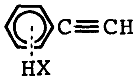
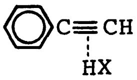
The acetylenic proton, in a striking contrast to the chloroform proton, exhibited a marked low field shift upon pressurization. Dissimilarity in the molecular shape between phenylacetylene and chloroform is considered to give rise to a difference in the high pressure association mode.

The phenylacetylene molecule in solution at ordinary pressure has received a great deal of attention, with interest focused on the effects of intermolecular interactions and solvent anisotropy on the acetylenic proton chemical shift.$^{1)}$ It seemed of interest to us to examine the nature of the pressure effect on the interaction between the weakly dipolar solute molecule and the solvent molecule which contains a dual proton-accepting site:


(I)


(II)

HX = $HCCl_3$, $HC\equiv C\text{-}C_6H_5$

The h.p.h.r.-n.m.r. experiment$^{2)}$ has been conducted on a 100 MHz spectrometer at 35°. In order to study the pressure behavior of chloroform and phenylacetylene in a common solvent, phenylacetylene, a sample solution containing 95 mol% of phenylacetylene, 4 mol% of chloroform, and 1 mol% of cyclohexane was used.

Figure 1 shows the pressure dependence of the proton chemical shifts relative to internal cyclohexane. The pressure dependence of the ring protons (not shown) was also estimated from the displacement of the ring proton multiplets: relative pressure shift,$^{3)}$ $\delta\Delta(1500) \fallingdotseq -3$ Hz for the ortho protons (a low field multiplet) and $\delta\Delta(1500) \fallingdotseq -2.5$ Hz for the meta and para protons (a high field multiplet).

One notable feature of the present observations is that the chemical shift of the acetylenic proton of phenylacetylene is displaced to lower field ($\delta\Delta(1500) = -9.0 \pm 0.1$ Hz), while the chemical shift of chloroform proton remains nearly unaffected ($\delta\Delta(1500) = +0.2 \pm 0.2$ Hz). This cannot be accounted for by the reaction field effect at high pressure$^{4)}$; for example, since a negative end of the phenylacetylene dipole is toward the acetylenic group,$^{5)}$ the high pressure reaction field would lead to a positive (high field) relative pressure shift of the acetylenic proton.

The shape and size of the molecules should govern the mode of association. Hence, the marked difference observed under pressure is considered to be caused from molecular characteristics of chloroform and phenylacetylene. Since the acetylenic group protrudes out of the molecule, its hydrogen tends to approach the triple bond of another molecule more closely than the chloroform hydrogen does so

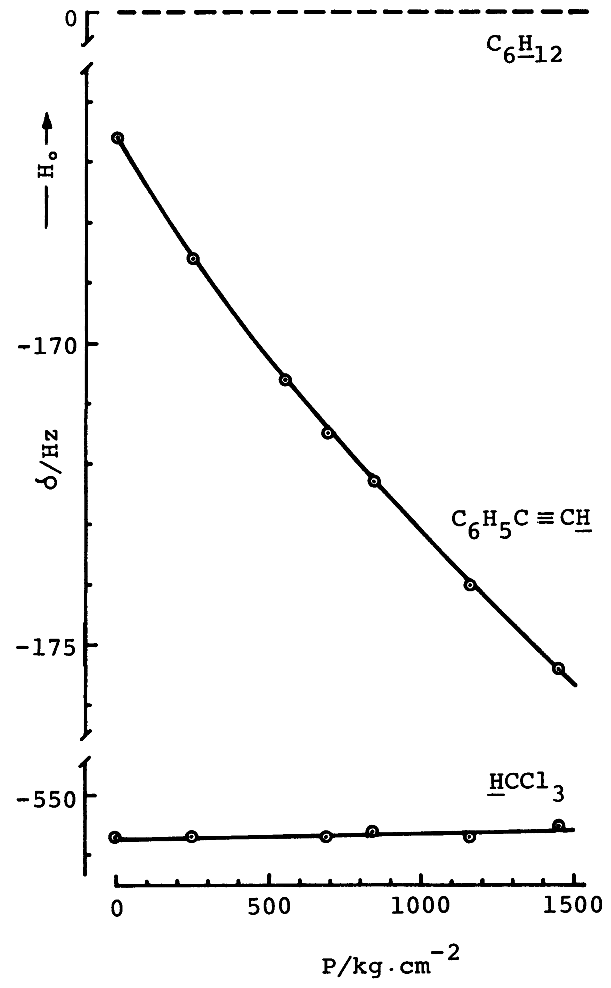


Fig.1. Effect of the increased pressure on the proton chemical shift, δ, relative to internal cyclohexane.

that the association of the type (II) allows the molecules to be packed together more tightly. On the same ground, the acetylenic proton is expectedly exposed to closer van der Waals contact with the surrounding molecules. Thus, the observed low field shift of the acetylenic proton may be understood in terms of the increased effect in the solvent magnetic anisotropy, $\Delta\chi(C\equiv C)$, as well as the increased σ_w contribution,$^{6)}$ at high pressure. Some evidence for this suggestion is provided by measurement of the pressure shift of phenylacetylene (4 mol%) dissolved in 2,4,6-trimethylphenylacetylene, whose acetylenic group is blocked by two methyl groups. The observed smaller pressure dependence of the acetylenic proton (-7.4 Hz) supports the present interpretation.

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1) a) N.Nakagawa and S.Fujiwara, Bull. Chem. Soc. Jpn,, 33, 1634 (1960);
b) S.Castellano and J.Lorenc, J. Phys. Chem., 69, 3552 (1965).

2) H.Yamada, Rev. Sci. Instrum., 45, 640 (1974).

3) $\delta\Delta(P)\equiv\delta(P) - \delta(1)$, displacement of the chemical shift relative to that of the chemical shift of internal cyclohexane, caused by pressurization of the sample up to P $kg\cdot cm^{-2}$.

4) H.Yamada, C.Itani, and K.Otsuka, J. Am. Chem. Soc., 99, 3572 (1977).

5) C.P.Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York 1955, p 317.

6) Even in a dilute hexane solution, the acetylenic proton exhibited a prominent pressure shift ($\delta\Delta(1500)=-6\sim-7$ Hz). This indicates the strong possibility that the σ_w effect also contributes to the acetylenic proton pressure shift. The importance of the σ_w effect on the pressure shift has been discussed in ref. 4).

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