Pressure-induced Proton NMR Chemical Shift of Some Simple Hydrocarbon Molecules in Hexane Solution. Marked Low Field Shift of Ethynyl Proton Resonance

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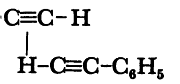
Synopsis. Pressure dependence of the ethynyl proton chemical shift of phenylacetylene was studied in comparison with some simple hydrocarbons. The pronounced low field displacement is interpreted taking account of a geometric feature of the ethynyl group, where the terminal hydrogen atom is exposed to a closer contact with solvent molecules.

High-pressure high-resolution NMR spectroscopy represents one of the promising new area of research at high pressure.[1] Considerable efforts with use of this technique have been devoted to the investigation of high pressure effect on the rate process and chemical equilibrium. However, little is known about the pressure sensitivities of the NMR chemical shifts.

In preceding paper, we reported a notable pressure dependence of the ethynyl proton chemical shift of neat phenylacetylene.[2] The result was interpreted in terms of the increased effect in the solvent magnetic anisotropy, σ_a, which is caused by the intensified intermolecular hydrogen bonding (I) at high pressure.



$$\begin{array}{l} C_6H_5\text{-}C{\equiv}C\text{-}H \\ \quad\quad\quad\quad\quad\; | \\ \quad\quad\quad\quad\quad H\text{-}C{\equiv}C\text{-}C_6H_5 \end{array}$$

(I)

We have now made a re-examination of phenylacetylene in a hexane solution in comparison with some simple hydrocarbons and have found a recurrence of the low field pressure shift of the ethynyl proton resonance. Since hexane behaves as a magnetically isotropic solvent, an interpretation of the low field shift can no longer be sought in the solvent magnetic anisotropy effect. The present paper attempted to offer a preliminary account of this anomalous pressure shift.

Experimental

High-pressure NMR experiment was conducted on a Jeol PS-100 spectrometer (ν_0=100 MHz) using a thermal expansion type high-pressure cell with sample spinning conditions.[3] Most measurements were carried out with 5 mol% solutions in hexane. The temperature of the sample under the NMR conditions was maintained at 35.0±0.2 °C. At least ten measurements were made at a fixed pressure. The standard deviation of the chemical shift was ±0.1—0.2 Hz.

Results and Discussion

Observed relative pressure shifts $\delta\Delta(150)$[4] are presented in Table 1. The ethynyl proton resonance, as compared with the other hydrocarbon resonances, evidently exhibits a marked low field displacement by the application of hydrostatic pressure.

It might be possible that the self association of the type (I)[5] still exists in the 5 mol% solution. In this association mode, both the hydrogen-bonding shift σ_H and the magnetic anisotropy shift σ_a, caused by $\Delta\chi_{C\equiv C}$ of another molecule, contribute to down field displacement of the ethynyl proton signal. Therefore, if the association mode (I) is favored at high pressure, a negative pressure shift, $\delta\Delta(150)<0$ would be induced. In order to examine this possibility, concentration dependence of the relative pressure shift was carefully measured for phenylacetylene. As shown in Fig. 1, no significant change was observed in the pressure shift upon dilution of the solution. On this basis, we consider that the contribution of the self association effect to the pressure shift is negligibly small at 5 mol% concentration. It is also approximated that the data for the other hydrocarbons, being based on the 5 mol% solution, represent the pressure shifts which are free from self association effects.

TABLE 1. RELATIVE PRESSURE SHIFTS,[a] 5 mol% IN HEXANE, ν_0=100MHz, 35.0 °C

Compounds	$\delta\Delta(150)$/Hz	Compounds	$\delta\Delta(150)$/Hz
Ph_3CH[b]	+1.9	H_2CCl_2	+0.1
$(CH_2)_6$	+1.5	$CH_3(CH_2)_4CH_3$	0.0
$HCCl_3$	+1.2	$PhCH_3$	−0.7
$CH_3(CH_2)_4CH_3$	+1.0	$Ph_2C{=}CH_2$	−1.9
Ph_2CH_2	+0.5	$PhC{\equiv}CH$	−5.3

a) Relative to the hexane CH_3 pressure shift. b) Because of the poor solubility, a 1 mol% solution was used.

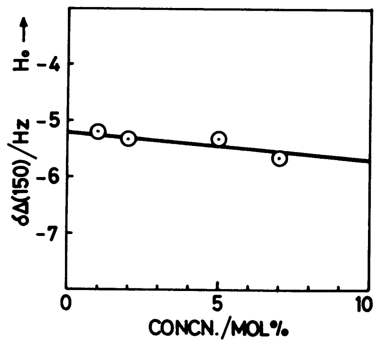


Fig. 1. Concentration dependence of the ethynyl proton relative pressure shift. For a 95 mol% solution, $\delta\Delta(150)=-7.7$ Hz.

Under the present experimental conditions, the solvent effect on the proton chemical shift can be divided into two kinds of main contribution:[6] (i) The σ_E effect which is related to the C–H bond polarization induced by so-called reaction field;[7] This should be mainly governed by the polarity of the solute molecule and the dielectric constant of the medium. (ii) The σ_w contribution arising from the weak van der Waals interaction between the resonating proton and solvent molecules;[6,8] When the resonating proton is more strongly subject to the van der Waals contact with medium molecules, a greater σ_w contribution (*i.e.*, a pronounced low field shift) should be expected.[9] Since the pressurization produces an increase in the dielectric constant of the medium and also intensifies the intermolecular van der Waals contacts, both the effects, (i) and (ii), would be amplified at high pressure, giving rise to a possible low field contribution to the pressure shift.

In an attempt to evaluate the contribution of the effect (i), the data were examined in connection with polar properties of the solute molecule. Although the examinations are only qualitative, several interesting points arise. For example, the pressure shifts for chloroform (μ=1.2 D) and phenylacetylene (μ=0.5 D, with a negative end directing toward the ethynyl group) exhibit a trend evidently opposite to that expected from the reaction field consideration. Furthermore, toluene shows a larger negative pressure shift relative to triphenylmethane, whereas, considering acidities of these hydrocarbons (pK_a=41, 32, respectively), one would predict the opposite. On these grounds, we conclude that the effect (i) cannot be a main contributor to the pressure shift.

We may now turn to the effect (ii). In Table 1, it will be noticed that the steric environment near the resonating proton is playing a dominant role in determining the pressure shift. For instance, a regular trend toward larger negative pressure shift can be seen as the steric overcrowding is liberated in the order of triphenylmethane, diphenylmethane, and toluene. In this view, the pronounced negative pressure shift of the ethynyl proton seems to be best rationalized on the basis of the geometric feature of the ethynyl group where the proton is located at the end of a rod shaped C≡C bond and, in the absence of a geminal hydrogen, it is well exposed to the van der Waals contact with solvent molecules. Axially symmetric electronic environment around the ethynyl proton should also lead to pronounced susceptibility to the σ_w effect.[6] Present result indicates that the previously observed pressure shift, −9 Hz, for neat phenylacetylene[2] could largely be interpreted as being due to this van der Waals contact effect rather than the σ_a effect.

This study has shown that a protrusion of a C≡C bond out of the molecule plays an important role in causing the marked low field pressure shift of the ethynyl proton. It should be pointed out that this stand out in sharp contrast to the ring proton of 1,4-di-*t*-butylbenzene,[10] which, being located in a cavity in the molecule, has proved to give a considerable high field pressure shift.

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