Nuclear magnetic resonance studies of hydrogen bonding in acetylenes containing oxygen functions¹

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Dilution shifts in carbon tetrachloride and cyclohexane solution have been obtained for the terminal acetylenic proton signals in the nuclear magnetic resonance (n.m.r.) spectra of some acetylenes. The presence of an oxygen atom results in a significant increase in the magnitude of the dilution shift, suggesting that oxygen is an important proton acceptor site in these compounds. Steric influences on the dilution shift and differences between the infinite dilution chemical shifts in the two solvents used, have been observed.

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It has been known for some time that compounds with terminal acetylene groups are capable of forming hydrogen bonds between the slightly acidic acetylenic hydrogen atom and electron donor groups. Weak hydrogen bonds of this type are amenable to study by nuclear magnetic resonance (n.m.r.) methods and several reports of work in this area have appeared (1).

Hatton and Richards (2) have examined the n.m.r. spectra of propargyl chloride, phenylacetylene (3), and benzoylacetylene in various solvents. They found that dilution with a poor electron donor solvent, such as cyclohexane, resulted in a small upfield shift of the acetylenic proton line position. It was assumed that, at infinite dilution in cyclohexane, acetylene-acetylene interactions were at a minimum. The lower field position of the acetylene proton resonance in the neat liquid was taken as evidence for deshielding produced by weak intermolecular hydrogen bonding between the acetylenic protons and the π -electron system. Whipple and co-workers (3) obtained comparable results when studying the spectrum of propargyl bromide in similar solvents.

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Elsakov and Petrov (4, 5) have studied the dilution shifts in carbon tetrachloride of a number of acetylenes, including one containing an ether oxygen atom. Their results suggested that hydrogen bonding may be more extensive in acetylenes containing oxygen than in the corresponding hydrocarbons.

In order to obtain more information on the

chemical shifts of acetylenic protons than has been available in the literature, we have undertaken a study to ascertain the extent to which the presence of an oxygen atom influences the magnitude of the dilution shift. Carbon tetrachloride was selected as the main solvent since it is a poor proton acceptor and it is a commonly used solvent for n.m.r. studies. However, in a study of the O-H stretching frequencies of a number of alcohols in several solvents, Allerhand and Schleyer (6) have found that $\Delta v = v_{\text{free}}$. $- v_{H-bonded}$ is larger in carbon tetrachloride than in cyclohexane. Since $v_{"free"}$ and $v_{H-bonded}$ were found to be shifted to different extents in going from cyclohexane to carbon tetrachloride, these authors concluded that the latter solvent must interact in some specific way with solute molecules, and thus is not a totally "inert" solvent. Schaefer et al. (7) have also reported results which they interpret as evidence for a solvent effect on proton chemical shifts by carbon tetrachloride as compared to cyclohexane. For these reasons we have also determined the dilution shifts of some of the acetylenes in the apparently "more inert" solvent cyclohexane. The chemical shifts of the acetylenic protons of a number of compounds, some with oxygen atoms and some without, were measured as a function of concentration in carbon tetrachloride and cyclohexane. Concentrations in both solvents ranged from almost neat liquids to the lowest mole fraction which yielded spectra that could be measured with tolerable accuracy. The dilution curves obtained in this way were extrapolated to mole fractions of 1.00 and 0.00 (see Fig. 1 for carbon tetrachloride dilution curves). Extrapolation error was small because in no case was

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FIG. 1. Chemical shift vs. concentration in carbon tetrachloride solution of acetylenic protons: (), compound 1; (), compound 2; (), compound 3; (), compound 4; (), compound 5; (), compound 6. See Table I.

the curvature of the plot very great. The chemical shifts of the neat liquids and of the infinitely dilute solutions in carbon tetrachloride and cyclohexane are shown in Table I. Some data from ref. 2 are included for comparison purposes. Internal references were used in all cases.

Measurement of Spectra

All samples were prepared by weighing an appropriate amount of the acetylene directly into the sample tube. Carbon tetrachloride samples were prepared by weighing a solution of 5 or 15% of tetramethylsilane in the solvent into the tube. Cyclohexane solutions of 6 (see Table I) were prepared similarly, while samples of 2 and 3 were prepared without the addition of tetramethylsilane. The weight of tetramethylsilane was taken into account in calculating the mole fractions, which were accurate to ± 0.003

or better. Analytical grade carbon tetrachloride and cyclohexane were dried by standing over Fisher type 4A molecular sieve before use.

The spectra of compounds 1, 5, and 6 in carbon tetrachloride and 2, 3, and 6 in cyclohexane were determined using a JEOLCO 4H-100 spectrometer operating at 100 MHz. Line positions, accurate to ± 0.1 Hz, were measured directly from the recorded peak maxima using the internal frequency counter. The spectra of compound 2 in carbon tetrachloride were determined with a Varian HR-60 spectrometer and the spectra of compounds 3 and 4 in carbon tetrachloride with an A-60 spectrometer, both instruments operating at 60 MHz. Line positions were measured by the sideband method, using a Hewlett Packard 200 CD audio oscillator and a CMC 201 B frequency counter, to an accuracy of ± 0.2 Hz.

Results and Discussion

Weak hydrogen bonds of the type studied in this project must be considered as transient on the n.m.r. time scale. At a given instant some molecules will be bonded and some will be "free". When several electron donor sites exist (as many as three in the current series), acetylenic protons will be present in a number of hydrogen-bonded complexes as well as in the "free" or unassociated state. The observed timeaveraged chemical shift must be dependent on the chemical shift of protons in each of the environments, and on the relative numbers of protons in each state. If the chemical shift at infinite dilution is the true "free" chemical shift then the observed dilution shift (the difference between the chemical shift of the neat liquid and that of the infinitely dilute solution) will be a measure of the net effect of the factors which displace the chemical shift from its "free" value. If the solvent is not completely "inert", as may be the case with carbon tetrachloride. the chemical shift of acetylene molecules bonded to solvent molecules will also influence the resultant chemical shift. A change in molecular structure which alters the chemical shift of protons bound at a particular site, or which affects the relative numbers of molecules bound at that and other sites, may be expected to influence the resultant chemical shift.

Compounds 1-6 may be grouped into two distinct classes on the basis of their dilution

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No.	Compound	Solvent	Infinite dilution (\approx)	Neat liquid (t)	Dilution shift (Δτ, p.p.m.)
1	CH ₃ (CH ₂) ₅ C≡CH	CCl4	8.262	8.150	0.112
2	$CH_2 = C(CH_3)C \equiv CH$	CCl₄	7.290	7.162	0.128
	_ , ,,	C_6H_{12}	7.388	7.150	0.238
3	C ₆ H ₅ C=CH	CCl₄	7.115	6.950	0.165
		$C_{6}H_{12}$	7.203	6.935	0.268
		$C_{6}H_{12}$	7.26*	6.91*	0.35*
4	<i>cis</i> -CH₃OCH==CHC==CH	CCl_4	7.247	6.894	0.353
5	$CH_3OC(CH_3)_2C \equiv CH$	CCl₄	7.764	7.458	0.306
6	CH ₃ OCH ₂ C=CH	CCl ₄	7.750	7.388	0.362
		$C_{6}H_{12}$	7.870	7.387	0.483

TABLE I						
Acetylene	proton	dilution	shifts			

shifts in carbon tetrachloride solution. The hydrocarbons show dilution shifts of less than 0.2 p.p.m. whereas the compounds containing oxygen show dilution shifts greater than 0.3 p.p.m. (Table I). The magnitude of the dilution shift is an unreliable indication of the strength of the hydrogen bonds since the chemical shift of a bonded hydrogen atom is determined by magnetic anisotropy as well as by the electron polarization produced by bond formation. However, the greater dilution shift (by a factor of 2 to 3 or more) when an oxygen atom is present in the molecule suggests that this atom can be an important proton acceptor site in these compounds. The presence of an oxygen atom may also influence the extent of hydrogen bonding at other electron donor sites.

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Compounds 2, 3, and 6 were also examined in cyclohexane solution (Table I). Compounds 2 and 6 were selected for this study to determine whether or not the large difference in dilution shift between compounds with and without oxygen functions is also observable in this solvent. A logical choice for a non-oxygen containing acetylene would have been 1, but the acetylenic proton of this compound absorbs too close to the cyclohexane solvent line position for accurate analysis. Compound 3 was reinvestigated in this solvent because its dilution shift in cyclohexane reported by Hatton and Richards (2) was more than double that found in this laboratory for carbon tetrachloride solutions.

The dilution shifts of both 2 and 6 were found to be increased by approximately 0.12 p.p.m. in cyclohexane as compared to carbon tetrachloride. Compound 6 still shows a shift larger by a factor of 2 than that of 2, which supports the inference that the oxygen atom is a major electron donor in hydrogen bond formation in these compounds. In this respect, the results are the same in the two solvents. The dilution shift of 3 is also increased in cyclohexane compared to that in carbon tetrachloride. However, the shift was not found to be as large as that reported previously by Hatton and Richards.

In all cases the differences between the dilution shifts in the two solvents result from the infinite dilution chemical shifts in cyclohexane being at higher field than those seen in carbon tetrachloride. The small differences in the chemical shifts reported for the neat solutions in Table I reflect extrapolation errors. These results imply that carbon tetrachloride undergoes some type of specific association with the acetylene molecules, which causes a small downfield shift in the acetylenic proton signals.

Steric factors which hinder the approach of an acetylenic hydrogen atom to a donor site may be expected to reduce the magnitude of the dilution shift. This steric effect is likely to be particularly marked if a major bonding site which makes an important contribution to the total chemical shift is affected. This situation is well illustrated by a comparison of the dilution shifts in carbon tetrachloride of 3-methoxy-1-propyne (6), and 3-methyl-3-methoxy-1-butyne (5). These two compounds have the same carbon skeleton but differ in that 5 has two methyl substituents on C-3. Since the infinite dilution chemical shifts of these compounds are very similar, it is clear that the structural differences have little

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direct effect on the shielding of the acetylenic proton. The two methyl groups on the carbon bearing the oxygen atom in 5 should be expected to hinder the approach of another molecule of the acetylene, particularly to the bonding site on oxygen. It is found that the dilution shift of the more hindered compound, 5, is about 15%smaller than that of the less hindered compound 6, in accord with this prediction. The dilution shift of 5 is also substantially smaller than that of compound 4, which is relatively unhindered.

Introduction of a double bond has little effect on the dilution shift in carbon tetrachloride. Elsakov and Petrov have noted (4) that conjugation of a double bond with the acetylenic triple bond has only a small effect on the magnitude of the shift. The presence of the phenyl group conjugated with the triple bond in 3 results in a more marked increase in the magnitude of the dilution shift. Interpretation of the shift in this case is complicated by the effect of the anisotropy of the aromatic ring.

Elsakov and Petrov (4, 5) have reported dilution shifts in carbon tetrachloride for compound 2 $(\Delta \tau = 0.16 \text{ p.p.m.})$ and compound 4 ($\Delta \tau = 0.28$ p.p.m.), plus the additional compounds vinylacetylene ($\Delta \tau = 0.09$ p.p.m.) and 3-methyl-1butyne ($\Delta \tau = 0.07$ p.p.m.). The last compound would be expected to show a dilution shift similar to that observed for 1-octyne, (1), in this laboratory. The agreement is reasonable, but not excellent. While the reported dilution shifts for compounds 2 and 4 are in general agreement with our results, they differ somewhat in magnitude. Experimental data obtained at the lower concentrations contain the main source of the discrepancies. The dilution shift reported for compound 4 is smaller than we obtained and tends to de-emphasize the role of oxygen as a proton acceptor site. Data reported by these authors were obtained from a much smaller number of measurements than were made in the present study.

Jouve (8) has determined the chemical shifts at infinite dilution in carbon tetrachloride of a number of terminal acetylenes and has presented an explanation of these shifts in terms of the molecular environment of the acetylenic protons. The reported infinite dilution chemical shifts of several straight chain terminal acetylenes (C-3 to C-7) show close agreement with the value obtained in this laboratory for 1-octyne. From the information now available it may be concluded that the chemical shift at infinite dilution in carbon tetrachloride of the acetylenic proton in compounds of this type is likely to fall in the range τ 8.24–8.27. Jouve has also reported infinite dilution chemical shifts for compounds 2, 3, and 6 in carbon tetrachloride differing by no more than 0.04 p.p.m. from the values obtained in this laboratory. The experimental data now available are adequate to indicate the approximate range within which the acetylenic protons of a variety of compounds may be expected to absorb in carbon tetrachloride solution. By combining the infinite dilution chemical shifts given in ref. 8 with the dilution shifts of representative compounds given in Table I and in refs. 4 and 5, it should be possible to make a reasonably satisfactory prediction of the chemical shifts of the acetylenic protons of many compounds at typical concentrations in carbon tetrachloride solution.

Hatton and Richards (2) have observed that the methylene protons of propargyl chloride were shifted by 0.26 p.p.m. when this compound was diluted with cyclohexane. We have observed a similar effect when compound **4** is diluted with carbon tetrachloride, the lines arising from the protons on the double bond undergoing an upfield shift (Table II). The chemical shift of the protons of the methyl group in this compound is essentially independent of concentration.

Experimental

Boiling points are uncorrected.

1-Octyne (1)

1-Octyne was obtained from Chemical Procurement Laboratories. Before use it was distilled twice, yielding a colorless liquid, b.p. 125–127°, n_D^{26} 1.4165. Samples with mole fractions of 0.056–0.920 were prepared in carbon tetrachloride and the chemical shift of the acetylenic proton from an internal TMS lock was measured. The position of the center peak of the triplet arising from the acetylene proton was taken as the chemical shift.

TABLE II

Vinyl proton chemical shifts of *cis*-methoxy-1-butene-3yne (4) (carbon tetrachloride solutions)

Proton	Infinite dilution (7)	Neat liquid (τ)	Dilution shift (Δτ, p.p.m.)
С ₂ -Н	5.647	5.558	0.089
С ₁ -Н	3.824	3.616	0.208

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2-Methyl-1-butene-3-yne (2)

Compound 2, obtained from the Aldrich Chemical Company, was distilled before use. The colorless distillate, b.p. $33-34^\circ$, n_p^{25} 1.4123, was used to prepare samples with mole fractions of 0.060-0.908 in carbon tetrachloride. The chemical shift from TMS of the broad acetylenic singlet was measured. Samples of mole fraction 0.084-0.897 were prepared using cyclohexane as solvent. The position of the broad acetylenic singlet relative to cyclohexane was determined. This shift was then added to the slightly concentration dependent cyclohexane-TMS separation for the concentration in question in order to obtain the chemical shift relative to TMS.

Phenylacetylene (3)

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This compound was obtained from Eastman Organic Chemicals Company and was distilled before use, yielding a colorless distillate, b.p. 138.5-139.5°, $n_{\rm D}^{26}$ 1.5461. Samples with mole fractions of 0.048-0.980 were prepared with carbon tetrachloride as solvent. The position of the acetylenic proton singlet relative to TMS was measured. Samples with mole fractions of 0.086-0.964 were prepared in cyclohexane. In this case the acetylenecyclohexane separation was measured. This was then added to the concentration dependent cyclohexane-TMS separation to obtain the acetylene-TMS separation.

cis-1-Methoxy-1-butene-3-yne (4)

This compound was obtained from the Aldrich Chemical Company as an 80% solution in methanol. Fractional distillation in small quantities immediately before use yielded a colorless liquid, b.p. 59-61° (60 mm), $n_{\rm D}^{24}$ 1.4789. Samples with mole fractions of 0.066-0.975 in carbon tetrachloride solution were analyzed. The position of the highest field member of each acetylenic and olefinic proton quartet was measured with respect to TMS. Chemical shifts for each proton were taken to be the centers of the respective quartets.

3-Methoxy-3-methyl-1-butyne (5)

This compound was prepared in a manner similar to that of Kreevoy et al. (9). The entire reaction was carried out at 0 °C. 48 ml (0.15 mole) of dimethyl sulfate (Eastman Organic Chemicals practical grade) were added with stirring to a mixture of 42 g (0.50 mole) of 2-methyl-3-butyne-2-ol (Eastman Organic Chemicals practical grade), 53 ml of water, and 5 g of 50% sodium hydroxide solution. To this an additional 50 g of 50% sodium hydroxide solution (a total of 0.69 mole) were added slowly over a period of several hours. The upper layer of the resulting two phase system was extracted with cold water and dried over MgSO₄. The

dried material was fractionally distilled, the fraction boiling at 70-87° being collected. This fraction was then redistilled using an 18 in. spinning band column. The desired material (8.6 g, 8.8%) was collected at 77-78.5°, n_D^{22} 1.3988. Samples with mole fractions of 0.054–0.956 in carbon tetrachloride were prepared and the position of the acetylenic proton singlet measured. The singlet at 1.385 p.p.m. from TMS arising from the geminal dimethyls was used as the lock signal. It was found that the position of this signal was independent of concentration.

3-Methoxy-1-propyne (6)

This compound was prepared from 3-hydroxy-1-propyne, obtained from Eastman Organic Chemicals Company, by the method of Reppe (10) yielding 41% of the desired product, b.p. $57-61^\circ$, n_D^{25} 1.3931. Samples with mole fractions of 0.057-0.993 were prepared in carbon tetrachloride, while cyclohexane was used to prepare samples of mole fractions 0.115-0.993. In both solvents the slightly concentration dependent methoxyl singlet at approximately 3.3 p.p.m. from TMS was used as the lock signal. The methoxyl-acetylene and methoxyl-TMS separations were measured for each sample. Subtraction of the former from the latter yielded the acetylene-TMS separation.

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