JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 81 OCTOBER 1, 1959 NUMBER 18

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, EMORY UNIVERSITY]

Proton Magnetic Resonance in Allene and Methylacetylene

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RECEIVED NOVEMBER 25, 1958

N.m.r. parameters for the protons in allene and methylacetylene have been determined both in the vapor and at high dilution in inert solvents, using C^{13}—H splittings to determine the allene coupling. Differences in shifts between vapor and solution are used to measure the medium effect in the solution state and indicate a non-vanishing, but approximately constant, medium shift for several proton types. The allene shift shows evidence of anisotropic shielding by the π-electrons on the sp carbon which is explicable in terms of a simple ring current model. The long-range coupling in allene, 7.0 c.p.s., is unusually large by comparison with other molecules. This is discussed in terms of delocalization of C–H bonding electrons and is related to the electronic structure of allene.

1. Introduction

The relative intramolecular magnetic shielding at the site of a particular nucleus i has been expressed in terms of the corresponding chemical shift in the n.m.r. spectrum of the compound by (1)

$$\sigma_i = 10^{-6}\,\delta_i - \frac{2\pi}{3} K - \beta_i \qquad (1)$$

where δ_i is the shift in p.p.m. against a common external reference, K is the magnetic susceptibility of the medium, and β_i includes any environmental effects other than the Lorentz cavity; *i.e.*, β_i is so defined that the shielding σ_i is expressed for the isolated molecule.[1] To the approximation that K and β_i are negligible in gases at moderate pressures (1–20 atm.), the relative shieldings may be expressed directly in terms of chemical shifts measured in the vapor phase.[2] More commonly, an infinite dilution reference state is adopted wherein δ_i values are extrapolated to infinite dilution in "inert" solvents.[3] To the approximation that $\sigma_i = 10^{-6}\,\delta_i^{v}$ in the vapor phase, (1) may be written for an infinite dilution reference state in the form (2)

$$\beta_i^{\infty} = 10^{-6}\,(\delta_i^{\infty} - \delta_i^{v}) - \frac{2\pi}{3} K_s \qquad (2)$$

where K_s is the solvent susceptibility. An ideal solvent is defined by $\beta_i^{\infty} = 0$, where an inert solvent is one for which $\Delta\beta_{ij}^{\infty} = 0$ for chemically different solute nuclei, i and j.

2. Experimental

Spectra were measured at 21° on the Varian Model 4300 B Super High Resolution System with a 40 megacycle RF system and 5 mm. spinning glass sample tubes. Calibration was effected by the side-band technique[4] using a Hewlett-Packard Model 200J oscillator, direct superposition of markers being used for single line spectra (reproducible to ±0.5 c.p.s.), while patterns showing fine structure were calibrated by interpolation and averaging in the manner described previously.[1] Calibration by the latter technique was reproducible to within ±0.1 c.p.s. except in the case of propyne vapor, where an error of ±0.2 c.p.s. is indicated. Coaxially sealed H_2O(liq.) reference capillaries were used for vapor standardizations, while solutions were calibrated off the solvent and converted by empirical solvent–H_2O corrections.[1]

Commercial C.P. grade reagents and solvents were used without further purification. Commercial "pure" grade tetramethylsilane (TMS) was redistilled from concd. H_2SO_4, and allene was synthesized from propargyl bromide according to the procedure described by Morse.[5] Solutions of about 5% vol. concentration were prepared in the sample tubes by dilution of the liquefied gases on a vacuum system, while gaseous samples were prepared by sealing the liquefied gas under vacuum and allowing to warm to room temperature, the amount having been adjusted so that evaporation was complete.

The methylacetylene spectrum falls into the general class of four nuclei of spin $^1/_2$ belonging to the symmetry group AB_3, the principles of analysis having been given by Mc-

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[1] E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy and G. R. McClure, THIS JOURNAL, **81**, 1321 (1959).

[2] W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

[3] A. A. Bothner-by and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

[4] J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[5] A. T. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1958).

Connell, McLean and Reilly.[6] An example of this type has been reported by Abraham, *et al.*,[7] and for the sake of brevity we use the notation employed by these authors. The coupling constant J is given conveniently by the 3,5-splitting, so that when these lines are resolved the analysis proceeds straightforwardly in terms of the single adjustable parameter $\nu_0\delta$. The spectrum in TMS solution, shown in Fig. 1, does not permit such simple analysis, however.[8] Rather than proceed by adjusting $J/\nu_0\delta$ to match the observed spectrum, and thereby introduce uncertainties in J comparable to those in $\nu_0\delta$, we use a result previously noted that medium effects can substantially perturb δ without appreciably changing the coupling constant J, as illustrated by the data in Table I. The methylacetylene spectrum in benzene solution, shown in Fig. 2, is accordingly simplified and permits accurate determination of $J = 2.8 \pm 0.1$ c.p.s. from either the (3,5)-splitting or from $^1/_2[(2,1) + (6,4)]$. The calculated spectrum with $\nu_0\delta = -10.0$ c.p.s. ($\delta_a < \delta_b$) is shown in Fig. 2 for comparison with the observed. Using the value $J = 2.8$ c.p.s. thus obtained, and taking $\nu_0\delta = +5.0$ c.p.s., the calculated spectrum in Fig. 1 for propyne in TMS is obtained. In terms of the internal solvent reference, $\nu_0\delta_a = -61.6$ c.p.s. and $\nu_0\delta_b = -66.6$ c.p.s., and converting to standard shifts through the correction 201.5 c.p.s., the shifts listed in Table II are obtained.

TABLE I

N.M.R. PARAMETERS OF PROPARGYL BROMIDE IN DIFFERENT SOLVENTS

Solvent	$\nu_0\delta^a$	J
TMS	57.7	2.70 ± 0.1
CCl_4	56.7	2.66 ± .1
Benzene	48.0	2.75 ± .1
Liquid	51.4	2.60 ± .1

^{a} $\nu_0 = 40 \times 10^6$ sec.$^{-1}$; $\delta = \delta(\equiv C—H) - \delta(CH_2)$.

TABLE II

N.M.R. PARAMETERS OF HYDROCARBONS IN LIQUID AND VAPOR REFERENCE STATES

Compound	Group	$\delta^{\infty\,a}$	δ_v	β^∞	J
Methane	CH_4	4.85	6.42	−0.29	
Allene	$=CH_2$	0.49	2.08	− .31	7.0 ± 0.1
Propyne	$\equiv C—H$	3.50	5.12	− .34	2.9 ± 0.2
Propyne	$-CH_3$	3.38	4.90	− .24	

^{a} The standard chosen for chemical shifts is the infinitely dilute solution in cyclohexane against an H_2O(liq.) external reference.

The methylacetylene vapor spectrum shown in Fig. 3 is directly analyzed with $J = 3.0$ c.p.s. obtained from the (3,5)-splitting. It is noted, however, that calibration errors are greater; *e.g.*, $J = 2.85$ c.p.s. is obtained from $^1/_2[(2,1) + (6,4)]$. These errors in calibration arise from poorer sensitivity and the necessity for interpolation over a wider frequency range (~20 c.p.s.) than in the solution spectra. The coupling constant is taken as $J = 2.9 \pm 0.2$ c.p.s. for both solution and vapor, since the differences observed could conceivably arise from calibration errors. The chemical shifts relative to the H_2O(liq.) reference are listed in Table II.

The allene resonance consists of a single line at $\delta^v = 2.08$ and δ^∞ +0.49 for vapor and solution, respectively. Using a pure liquid sample, weak multiplets arising from the approximately 2% abundant $H_2C{=}C{=}C^{13}H_2$ could be detected.[9] The patterns correspond to an A_2B_2 system[10] with a single J_{AB} coupling of 7.0 c.p.s. and a chemical shift equal to one-half the C^{13}–H coupling constant of 168.2 c.p.s. The J_{AB} coupling is confirmed by measurements of the H–D interactions in allene 1,1-d_2, which give a value of 7.1 ± 1.0 c.p.s.

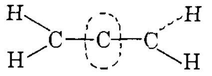
The methane spectrum consists of a single line and has been reported elsewhere.[2]

3. Discussion

The range of β_i^∞ values in Table II of 0.1 p.p.m. (4 c.p.s. at 40 megacycles) includes prototypes of the C–H bond in the systems R–H, $=CH_2$, $\equiv C—H$ and R–X and is barely outside the estimated accuracy of the measurements. The conclusion indicated is that while saturated hydrocarbons are not ideal solvents in the sense that β_i^∞ vanishes, they are inert to the extent that meaningful comparisons of $\Delta\sigma_{ij}$ can be inferred from shifts measured at high dilution in these media. The value of the interaction term agrees quite well with the empirical correction $\beta_i^\infty = 0.5K_s$ noted by Bothner-By[11] and could arise either through magnetic anisotropy[12] or electrical polarizability[13] of the solvent. In view of a previously cited parallel between infrared and n.m.r. medium shifts[1,2] which extends to the vapor–solution results above, the latter effect seems more likely.

Comparison of the vapor shifts in Table II with values reported by Schneider[2] for a number of gaseous hydrides reveals several interesting features. We may use the CH_4(g)–H_2O(liq.) shift in Table II to convert Schneider's values to our reference, obtaining $\delta^v = 1.24$ and $\delta^v = 5.07$ for ethylene and acetylene, respectively. The slight shift to higher field of the $\equiv C—H$ proton in propyne relative to acetylene is in accord with expectations based on its dipole moment of 0.80 D, coupled with Pople's estimate of the $—C{\equiv}C—$ anisotropic shielding.[14]

The shift of the vinyl protons in allene to higher field than the $=CH_2$ shift in non-cumulative alkenes provides evidence for long-range anisotropic shieldings associated with the π-electrons on sp hybridized carbon atoms.[15] If we assume the short-range effects to be largely cancelled by taking the difference in shifts between allene and ethylene, a contribution of 0.84×10^{-6} to the allene proton shielding is attributed to the sp hybridized carbon. This could arise largely from diamagnetic circulation in the cylindrically symmetrical π-electron distribution in the vicinity of the diagonally hybridized central atom. An equivalent



magnetic shell expansion based on the semiclassical ring current model[16] with two electrons localized in 2p orbitals whose effective radius is estimated from Slater functions[17] accounts for $^2/_3$ of the observed difference. The effects of neglecting the increased electronegativity of the

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[6] H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[7] R. J. Abraham, J. A. Pople and H. J. Bernstein, *Canad. J. Chem.*, **36**, 1302 (1958).

[8] The 3,5-splitting in Fig. 1 does not give a correct value for J due to interference between lines 3 and 4 from a weak line 60 c.p.s. removed from the intense solvent peak. The latter is at the position expected for $C^{13}H$ coupling in TMS. See P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

[9] A. D. Cohen, N. Sheppard and J. J. Turner, *J. Chem. Soc.*, 118 (1958).

[10] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

[11] A. A. Bothner-By and R. E. Glick, *ibid.*, **26**, 1647 (1957).

[12] (a) A. A. Bothner-By and R. E. Glick, *ibid.*, **26**, 1651 (1957); (b) A. A. Bothner-By and C. Naar Colin, THIS JOURNAL, **80**, 1728 (1958).

[13] H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958).

[14] J. A. Pople, *Proc. Roy. Soc.* (*London*), **A239**, 541 (1957).

[15] J. A. Pople, *ibid.*, **A239**, 550 (1957).

[16] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

[17] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

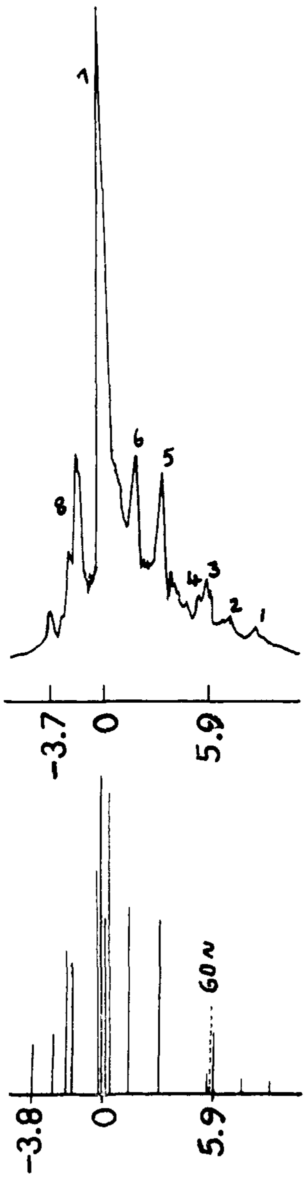

Fig. 1.—Methylacetylene in dilute tetramethylsilane (TMS) solution.[8]

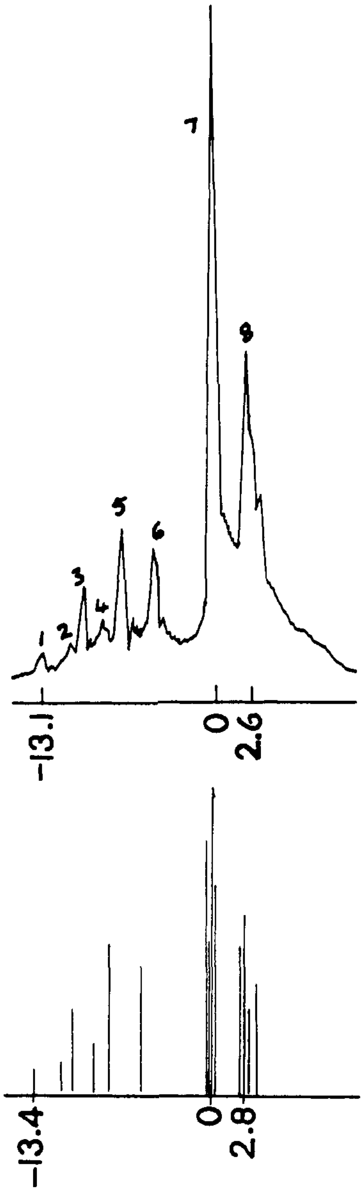

Fig. 2.—Methylacetylene in benzene solution.

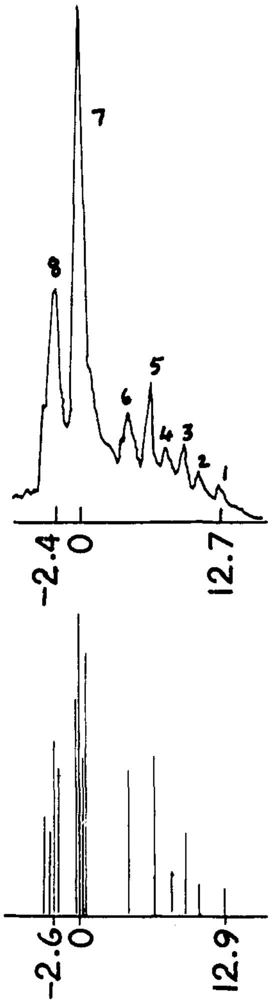

Fig. 3.—Methylacetylene vapor.

sp carbon and localizing the ring at the center of the symmetry axis both tend to make the calculated shielding too small.

The effects of halogen substitution on the chemical shifts of methylacetylene in the solution reference state are shown by the data in Table III. Shifts previously reported[12b] by Bothner-By for a corresponding series of bromomethyl halides are included in order to estimate the inductive effect of the acetylenic group, based on the observation that bromoacetylene has a vanishing dipole moment.[18] The differences in corresponding methylene shifts may be taken as a rough approximation of the anisotropy of the H—C≡C— group in excess of the anisotropic contribution from the Br atom, noting from the table that this difference is in each case constant where the acetylenic proton shift does not vary. By this argument the decrease of about −0.71 p.p.m. in the acetylenic shielding produced by halogen substitution in methylacetylene is accompanied by an effective increase in the anisotropic shielding of the methylene

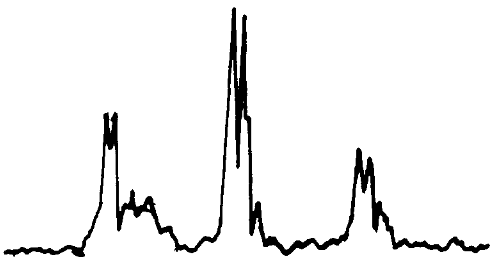

Fig. 4.—$=C^{13}H_2$ spectrum of allene (field increases from left to right).

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[18] L. O. Brockway and J. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938). This may not be a true measure of inductive effects, however, due to π-overlap with the non-bonding 3p orbitals on the Br.

TABLE III

CHEMICAL SHIFTS IN PROPARGYL AND BROMOMETHYL HALIDES

Substituent	Methylene shift, δ^{∞} Br-CH_2X[a]	Methylene shift, δ^{∞} $HC{\equiv}C{-}CH_2X$	$\Delta\delta^{\infty}$	Acetylenic shift $H{-}C{\equiv}C{-}CH_2X$
H	2.37	3.38	1.01	3.50
I	..	1.51	..	2.83
Br	0.05	1.34	1.29	2.79
Cl	−0.22	1.09	1.31	2.79

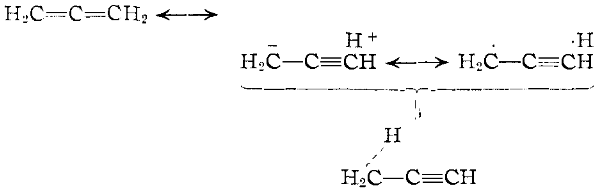
[a] Values reported by Bothner-By and C. Naar Cohen, THIS JOURNAL, **80**, 1728 (1958), in cyclohexane solution. The empirical correction +3.59 has been entered to convert to an H_2O(liq.) external reference.

protons of about 0.3 p.p.m. Both effects may be qualitatively accounted for by assuming a polarization of the π-electrons toward the methylene group in propargyl halides.

The long-range coupling observed in allene, 7.0 c.p.s., is considerably larger than any yet reported for protons separated by four bonds. We cite, for comparison, some typical couplings observed or estimated in various systems for the same proton–proton separation: alkanes, and derivatives, ~0; propylene derivatives, 0.3–3 c.p.s.; methylacetylene and propargyl halides, ~3 c.p.s. The allene value is, in fact, comparable to many couplings transmitted through one less bond, *e.g.*: acetylene, 9.1 c.p.s.[19]; ethylene and derivatives ~8(*cis*) and ~15(*trans*); and ethane and derivatives, 2-4(*gauche*) and 6-9(*trans*).[9] The sign of these couplings, including allene, is not yet known.

The theory of long-range spin–spin coupling has been treated by McConnell[20] from the MO standpoint and by Karplus, *et al.*,[19] using a valence bond approach. The former treatment relates couplings to bond-order between the corresponding protons, while the latter links the couplings to deviations from perfect pairing. In both approaches, therefore, the magnitude of J emerges as a criterion of the extent to which the C–H bond electrons have been delocalized in the molecule.

A comparison of the couplings for allene and for the systems cited above would appear to suggest that the unusual value in allene is at least qualitatively related to its cumulated double-bond structure. Hyperconjugation in allene provides a plausible mechanism for at least part of the extensive delocalization implied by the large coupling, and a recent molecular orbital calculation indicates that hyperconjugation is quite appreciable in this molecule.[21] The situation in allene can also be expressed in terms of valence structures



$$H_2C{=}C{=}CH_2 \longleftrightarrow \underbrace{H_2\bar{C}{-}C{\equiv}\overset{H^+}{CH} \longleftrightarrow H_2\dot{C}{-}C{\equiv}\overset{\cdot H}{CH}}_{\overset{H}{H_2C{-}C{\equiv}CH}}$$

The high degree of symmetry in allene permits multiplication of such structures, with the usual attendant stabilization. Another interesting and relevant observation is that substitution of one proton by a halogen in allene produces a decrease of 0.7–0.9 c.p.s. in J, whereas the coupling in the propargyl halides is only slightly smaller than that in methylacetylene, 2.6–2.8 and 2.9 c.p.s., respectively. The differences in haloallene couplings for X = Cl, Br, I, correspond to those in propargyl halides, however.[22]

Without denying the possibility that other factors may be involved, our comparisons suggest to us that the π-electron system may be rather important in augmenting the coupling in allene. Previous estimates[20b] that transmission of couplings through π-electron systems should be weak are not entirely applicable to allene because of its nonplanar structure. It would, of course, be instructive to compare the present results with couplings in the higher cumulenes and we hope to do this in the near future.

Acknowledgments.—We gratefully acknowledge the support given this work by the National Institutes of Health and by Schering Corporation. We are indebted to Dr. L. Mandell for many stimulating and helpful discussions during the course of this investigation.

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(20) (a) H. M. McConnell, *ibid.*, **24**, 460 (1956); (b) H. M. McConnell, *J. Mol. Spec.*, **1**, 11 (1957).

(21) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.* (*London*), **A235**, 136 (1956).

(22) E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959).