are essentially independent of this temperature change and the change in the alkali metal splitting.[15] This would therefore explain the agreement of the spectra even though a tight complex has been formed.

The question also arose as to whether a chemical reaction had taken place, such as a reduction of a nitro group. This seems implausible, first, because of the equivalence of the nitrobenzene negative ion hyperfine spectra, regardless of the method of preparation and secondly because the complete lack of any hyperfine interaction at·the position of the non-interacting nitro group does not indicate that any change of the nitro group has taken place.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

Nuclear Magnetic Resonance Spectra of Acrylonitrile and Mono-methyl Substituted Acrylonitriles[1]

BY G. S. REDDY, J. H. GOLDSTEIN AND LEON MANDELL

Complete analyses of the n.m.r. spectra of acrylonitrile and all the three monomethyl substituted products, *i.e.*, α-methacrylonitrile and *cis*- and *trans*-crotononitriles, were carried out and the shifts and coupling constants obtained at infinite dilution in tetramethylsilane which also served as an internal reference. The spectrum of acrylonitrile was very complicated and has been solved by preparing and analyzing the spectrum of α-D-acrylonitrile as an ABX system and converting the H–D couplings into H–H coupling by the factor of 6.5. The isotope effect both in coupling constants and resonance frequencies is within the limits observed by Gutowsky.[2a] The fact that the α-proton in acrylonitrile comes at higher field than the β-protons has been explained by estimating the diamagnetic anisotropic shielding due to the C≡N group on all the protons and making the corresponding corrections in their shifts. A linear relationship between the shifts of *cis*- and *trans*-protons in the series $\overset{\displaystyle H \qquad H}{\underset{\displaystyle H \qquad X}{C=C}}$ and the group dipole moment of X, with X = H, CH₃, C₆H₅, CN, Cl and OCH₃, was obtained only after making anisotropic corrections in H₂C=CHCN and H₂C=CHC₆H₅ due to C≡N and C₆H₅ groups, respectively.

Experimental

All the spectra were obtained at 21° on a Varian Model 4300B High Resolution Spectrometer equipped with a Flux Stabiliser operating at 40 mc./sec. Spinning 5 mm o.d. Pyrex glass sample tubes were used and the solvent in all the cases was tetramethylsilane purified by distilling over concentrated sulfuric acid to remove the traces of diethyl ether. Calibrations were done by the side band technique, using a Krohn–Hite Model 440B Push-Button Oscillator and Hewlett–Packard Model 522B frequency counter, with tetramethylsilane solvent as internal reference. A commercial sample of α-methacrylonitrile was fractionated and the portion boiling between 89 and 90°, which did not show any impurities in its n.m.r. spectrum, was used. *cis*- and *trans*-crotononitriles were obtained by separating a 70:30 *cis* to *trans* commercial mixture by gas chromatography using a Carbowax 20 M column at 100°. The acrylonitrile used was a commercial sample purified by distillation, the fraction boiling at 78 ± 0.5° being used. α-D-acrylonitrile was prepared by treating acrylonitrile with D₂O in presence of pure CaCl₂.[2]

All the frequencies are expressed in cycles per second with respect to the TMS solvent as internal reference. The coupling constants are given directly in c.p.s. The reproducibility in the calibrations of the frequencies is within ± 0.2 c.p.s. An uncertainty of ± 0.1 c.p.s. in the coupling constants is allowed. However, a margin of ± 0.5 c.p.s. should be left in the frequencies at infinite dilution obtained by extrapolation.

Analysis.—The analyses of the spectra of the three monomethyl substituted acrylonitriles, α-methacrylonitrile and *cis*- and *trans*-crotononitriles, were straightforward. These molecules constitute five-spin ABX₃ systems and their complete 32 × 32 matrices can be factored into submatrices, the largest of which is a 10 × 10 block, utilizing the eigen-

values of the total spin angular momentum. Assuming free rotation and using the symmetry properties of the methyl group around the C–C bond, further reduction in the size of the matrices was made possible leaving sixteen unconnected elements and eight 2 × 2 blocks, of which four are degenerate and in each case the off diagonal element is $^1/_2 J_{AB}$. It was thus necessary to solve only quadratic equations to obtain the eigenvalues and eigenfunctions. In all these compounds there was no overlap of the spectra of different protons (there is some overlap in the vinyl proton spectra of α-methacrylonitrile; however, the protons can easily be identified) and the appearance of the spectra was essentially first order. Thus, there was no difficulty encountered in identifying the protons and obtaining initial values of the coupling constants and resonance frequencies. The methyl group spectra were at much higher fields than those of the vinyl protons and provided good initial values for all the H–CH₃ coupling constants, as the second order corrections are quite small in these cases.

The spectra of α-methacrylonitrile and *cis*- and *trans*-crotononitriles are shown in Figs. 1–3. Allowed transitions and the corresponding frequencies and intensities for the ABX₃ system were worked out by Whipple, *et al.*[3] The agreement between the observed and calculated spectra, as shown in Tables I–III, is within the experimental uncertainty, estimated at ± 0.2 c.p.s.

Acrylonitrile is a three-spin ABC system, the analysis of which has been reported previously.[4] The complete 8 × 8 matrix of this system consists of two 1 × 1 and two 3 × 3 blocks, with no further factorization possible because of lack of symmetry in the molecule. The coupling constants are large compared to the differences in the frequencies and hence reduction of the size of the matrix using perturbation methods is not possible. There are six unknowns: three frequencies and three coupling constants, hereafter referred to as ω's and J's. The observed spectrum is so compli-

(1) This research was supported in part by grants from the National Institutes of Health [Research Grant A-2397 (C2)] and Schering Corporation, Bloomfield, N. J.

(2) (a) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959). (b) L. C. Leitch, *Canad. J. Chem.*, **35**, 345 (1957).

(3) E. B. Whipple, J. H. Goldstein and Leon Mandell, THIS JOURNAL, **82**, 3010 (1960).

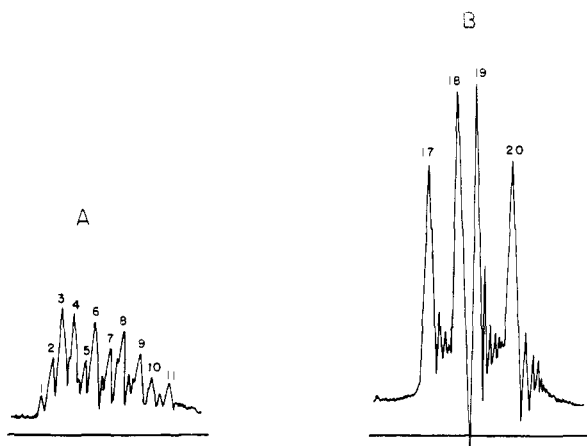(4) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).

Fig. 1.—Nuclear magnetic resonance spectrum of α-methacrylonitrile: A is vinyl group and B the methyl group; peak 2 is overlap of calculated peaks 2 and 3; peak 3 is overlap of calculated peaks 4 and 5; peak 4 is overlap of calculated peaks 6, 7 and 8; peak 5 is overlap of calculated peaks 9 and 10.

cated (Fig. IV) that identification of the protons is practically impossible and none of these six parameters can be obtained directly from the observed spectrum. Polar solvents like acetone and benzene were tried with the idea that the protons might be better separated in these solvents

TABLE I

OBSERVED AND CALCULATED SPECTRUM OF α-METH-
ACRYLONITRILE

Peak no.	Frequency[a] Obsd.	Calcd.	Relative intensity Obsd.[b]	Calcd.
1	−227.0	−227.1	0.8	0.8
2	−226.0	−226.2	3.2	1.2
3		−225.9		2.4
4	−224.85	−225.0	5.5	3.6
5		−224.7		2.4
6	−223.6	−223.8	5.2	3.6
7		−223.5		0.8
8		−223.4		1.2
9	−222.5	−222.6	2.2	1.2
10		−222.5		0.8
11	−221.85	−221.8	3.9	3.6
12	−220.8	−220.85	2.6	2.4
13	−220.1	−220.1	3.8	3.6
14	−219.2	−219.2	2.5	2.4
15	−218.5	−218.3	1.3	1.2
16	−217.5	−217.4	0.8	0.8
17	− 77.1	− 77.15	12.0	12.0
18	− 75.95	− 75.95	12.0	12.0
19	− 75.45	− 75.45	12.0	12.0
20	− 74.2	− 74.25	12.0	12.0

[a] In cycles per second relative to solvent tetramethylsilane as internal reference. [b] The estimated uncertainty in the observed intensities is ± 5%.

but these did not help in the identification of the protons. Methods described by previous workers for treating the ABC systems[5] were of no value in this case as there is no way to identify three quartets as a first order approximation in the spectrum. It is very tedious and impractical to try to fit the spectrum numerically by trial and error methods without having initial estimates for the six parameters. Deuterium substitution at the α-position (unfortunately this appears to be the only position where D-substitution can be carried out by presently known methods[2]) reduced

(5) W. Anderson and H. M. McConnell, J. Chem. Phys., 26, 1498 (1957).

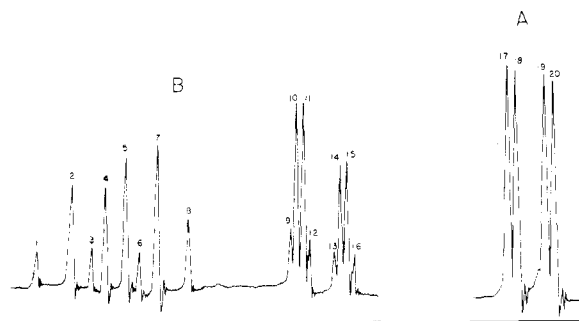Fig. 2.—Nuclear magnetic resonance spectrum of cis-crotononitrile: A, methyl group; B, vinyl group.
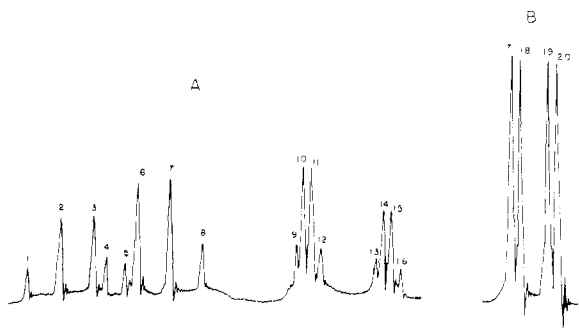

Fig. 3.—Nuclear magnetic resonance spectrum of trans-crotononitrile: A, vinyl group; B, methyl group.
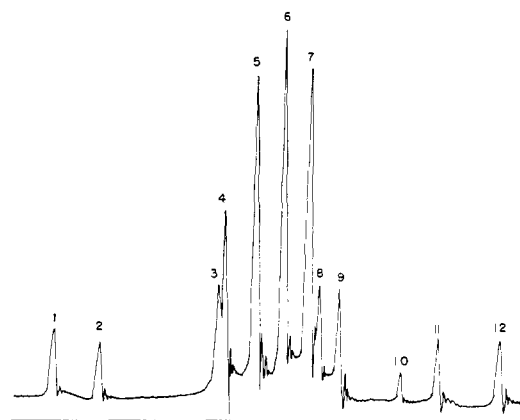

Fig. 4.—Nuclear magnetic resonance spectrum of acrylonitrile.

this complicated ABC system to the much simpler ABX system. From the analysis of α-D-acrylonitrile (Fig. 5) three J's (J_{AB}, J_{AX} and J_{BX}) and two ω's ($ω_A$ and $ω_B$) were obtained. On the assumption that isotopic substitution would not substantially affect the ω's and J's,[5,6] these five parameters obtained from α-D-acrylonitrile were used as the initial values for the corresponding parameters in acrylonitrile after converting the H–D couplings into H–H couplings by the factor of 6.5, still leaving the problem of obtaining an initial value for the third frequency, $ω_C$. Comparison with similar compounds such as vinyl chloride,[7] styrene,[8] methyl vinyl ether,[9] etc., indicates that $ω_C$ should be at lower field than $ω_A$ and $ω_B$. On the other hand, close examination of the observed spectrum and the values for $ω_A$ and $ω_B$ from α-D-acrylonitrile suggests that $ω_C$ must be

(6) George Van Dyke Tiers, ibid., 29, 963 (1958).

(7) E. B. Whipple, Ph.D. Dissertation, Emory University, 1959.

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(9) G. S. Reddy, unpublished results.

TABLE II
Observed and Calculated Spectrum of cis-Crotononitrile

Peak no.	Frequency[a] Obsd.	Calcd.	Relative intensity Obsd.[b]	Calcd.
1	−271.3	−271.3	0.8	0.78
2	−264.5	−264.55	2.3	2.34
3	−260.6	−260.5	1.0	1.22
4	−257.9	−287.85	2.3	2.34
5	−253.8	−253.75	3.2	3.66
6	−251.2	−251.1	0.8	0.78
7	−246.95	−246.95	2.3	3.66
8	−240.25	−240.3	1.0	1.22
9	−215.9	−215.9	1.2	1.22
10	−214.35	−214.3	3.4	3.66
11	−212.8	−212.85	3.4	3.66
12	−211.3	−211.3	1.2	1.22
13	−205.1	−205.1	0.8	0.78
14	−203.6	−203.55	2.3	2.34
15	−202.0	−202.05	2.3	2.34
16	−200.5	−200.5	0.8	0.78
17	− 82.2	− 82.15	12.0	12.0
18	− 80.65	− 80.6	12.0	12.0
19	− 75.4	− 75.4	12.0	12.0
20	− 73.85	− 73.85	12.0	12.0

[a] In cycles per second relative to solvent tetramethylsilane as internal reference. [b] The estimated uncertainty in the observed intensities is ± 5%.

TABLE III
Observed and Calculated Spectrum of trans-Crotononitrile

Peak no.	Frequency[a] Obsd.	Calcd.	Relative intensity Obsd.[b]	Calcd.
1	−281.3	−281.3	0.50	0.71
2	−274.8	−274.8	2.00	2.13
3	−268.2	−268.2	2.00	2.13
4	−265.4	−265.3	1.20	1.30
5	−261.6	−261.7	0.50	0.71
6	−258.7	−258.8	3.00	3.87
7	−252.1	−252.2	3.00	3.87
8	−245.5	−245.7	1.30	1.30
9	−219.0	−219.0	1.50	1.30
10	−217.4	−217.4	3.90	3.87
11	−215.8	−215.7	3.90	3.87
12	−214.2	−214.0	1.40	1.30
13	−203.0	−203.0	0.80	0.71
14	−201.4	−201.4	2.20	2.13
15	−199.7	−199.7	2.20	2.13
16	−198.1	−198.0	0.70	0.71
17	− 76.6	− 76.6	12.0	12.0
18	− 75.0	− 75.0	12.0	12.0
19	− 70.0	− 70.0	12.0	12.0
20	− 68.4	− 68.4	12.0	12.0

[a] In cycles per second relative to solvent tetramethylsilane as internal reference. [b] The estimated uncertainty in the observed intensities is ± 5%.

TABLE IV
Observed and Calculated Spectrum of α-D-Acrylonitrile

Peak no.	Frequency[a] Obsd.	Calcd.	Relative intensity Obsd.[b]	Calcd.
1	−243.57	−243.60	3.4	3.5
2	−242.47	−242.56	4.2	4.4
3	−240.82	−240.83	3.3	3.4
4	−239.78	−239.79	4.3	4.5
5	−238.14	−238.06	3.0	3.3
6	−237.08	−237.02	4.4	4.6
7	−235.44	−235.44	3.8	4.4
8	−234.32	−234.40	3.4	3.5
9	−233.64	−233.61	4.4	4.5
10	−232.46	−232.57	3.2	3.4
11	−231.80	−231.78	4.4	4.6
12	−230.71	−230.74	3.0	3.3

[a] In cycles per second relative to solvent tetramethylsilane as internal reference. [b] The estimated uncertainty in the observed intensities is ± 5%.

TABLE V
Observed and Calculated Spectrum of Acrylonitrile

Peak no.	Frequency[a] Obsd.	Calcd.	Relative intensity Obsd.[b]	Calcd.
1	−255.0	−255.0	1.3	1.3
2	−251.0	−251.2	1.0	1.0
3	−239.0	−239.0	2.5	2.1
4	−238.4	−238.4	3.5	3.7
5	−235.1	−235.0	8.5	8.6
6	−231.8	−231.9	9.7	10.0
7	−228.9	−229.0	8.5	8.8
8	−227.8	−227.9	2.0	1.9
9	−225.5	−225.7	2.4	2.3
10	−218.3	−218.6	0.6	0.8
11	−213.0	−212.8	1.3	1.4
12	−202.3	−202.3	0.6	0.8

[a] In cycles per second relative to solvent tetramethylsilane as internal references. [b] The estimated uncertainty in the observed intensities is ± 5%.
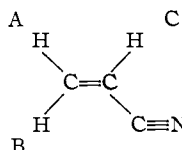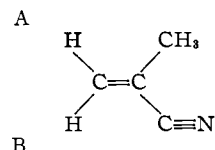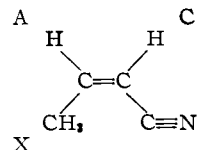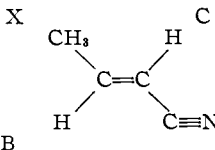
TABLE VI
Spectral Parameters for Acrylonitrile and α-D-Acrylonitrile[a]

	Acrylonitrile	α-D-Acrylonitrile
ω_A	−239.0 ± 0.5	−238.7 ± 0.5
ω_B	−232.3 ± 0.5	−231.6 ± 0.5
ω_C	....	−219.0 ± 0.5
J_{AB}	1.0 ± 0.1	1.0 ± 0.1
J_{AC}	11.4 ± 0.6	11.4 ± 0.1
J_{BC}	17.6 ± 0.6	18.2 ± 0.1

[a] All values are expressed in cycles per second. The shifts are relative to solvent tetramethylsilane as internal reference.

at higher field than ω_A and ω_B. (This point will be clarified later.) Accordingly ω_C was taken at higher field initially and the spectrum was calculated by varying each parameter until the agreement between the calculated and observed spectrum was within the experimental uncertainty of ± 0.2 c.p.s. as in the previous cases (Table V, Fig. 4).

Assignments.—Preliminary experiments on these compounds showed that concentration has no effect on coupling constants but that there is a small high field shift in the resonance frequencies of all protons with dilution in spite of the fact that tetramethylsilane is an almost isotropic and inert solvent. This might possibly be due to weak intermolecular association between the solute molecules. These shifts are small and almost linear with concentration at high dilutions. Moreover the dilution shift is nearly the same for all the vinylic protons within experimental error and the shifts in the methyl group frequencies are much smaller than those of the vinyl protons. The frequencies in Table VII are the values obtained by extrapolation

TABLE VII

NUCLEAR MAGNETIC RESONANCE SPECTRAL PARAMETERS IN ACRYLONITRILE, α-METHACRYLONITRILE AND cis AND trans-CROTONONITRILES[a]

	A H C H C=C H C≡N B	A H CH₃ X C=C H C≡N B	A H C H C=C CH₃ C≡N X X	X CH₃ C H C=C H C≡N B
$\omega_A^{\infty b}$	−231.6	−221.6	−251.0	...
ω_B^∞	−238.7	−225.8	...	−261.3
μ_C^∞	−219.0	...	−206.6	−208.7
ω_X^∞	...	− 75.7	− 78.1	− 72.2
J_{AB}	1.0	0.9	...	...
J_{AC}	11.4	...	11.0	...
J_{BC}	18.2	...	...	16.0
J_{AX}	...	1.7	6.8	...
J_{BX}	...	1.2	...	6.7
J_{CX}	...	...	1.4	1.5
$\Delta\omega_A^c$	− 15.1	− 15.1	− 15.1	...
$\Delta\omega_B$	− 11.5	− 11.5	...	− 11.5
$\Delta\omega_C$	− 45.3	...	− 45.3	− 45.5
$\Delta\omega_X$	...	− 19.8	+ 0.1	− 9.8
ω_A^{0d}	−246.7	−236.7	−266.1	...
ω_B^0	−250.2	−237.3	...	−272.8
ω_C^0	−264.3	...	−251.9	−254.0
ω_X^0	...	− 95.5	− 78.0	− 82.0

[a] All values are in cycles per second; the shifts are relative to solvent tetramethylsilane as internal reference. [b] Superscript ∞ denotes infinite dilution. [c] Δω's are the diamagnetic anisotropy corrections. [d] Superscript '0' denotes frequency corrected for diamagnetic anisotropy of the nitrile group.

to infinite dilution. In the case of acrylonitrile each peak was extrapolated to zero concentration and from these shifts the resonance frequencies at zero concentration were compiled. In all other cases analyses were made at each concentration and the actual resonance frequencies of each proton were extrapolated.

Unequivocal assignments of shifts to specific protons in these compounds, especially in methacrylonitrile, is difficult to achieve. In vinylic compounds, such as acrylonitrile, it is well established that trans H–H couplings will be greater than cis H–H couplings. No exception has been reported to this yet, and it has been verified in the case of cis and trans-crotononitriles, the long range H–H coupling in the trans isomer being 16.0 c.p.s. while it is only 11.0 c.p.s. in the cis isomer. The energy eigenvalues and the transition frequencies obtained for acrylonitrile give no idea of the assignments as it does not make any difference even if two protons are exchanged, provided the corresponding coupling constants also are exchanged. In α-D-acrylonitrile the proton which couples more strongly, presumably that which is trans with respect to deuterium, comes at lower field (Fig. 5) and accordingly the cis proton in acrylonitrile was taken to be at lower field than the trans. For the reasons given in the previous section, the α-proton was taken to be the highest field proton. The assignments in cis and trans-crotononitriles are based on the same reasoning and also on the fact that in the compounds of this type the short range H–CH₃ couplings are greater (of the order of 5–7 c.p.s. in most cases) than long range H–CH₃ couplings (1–2 c.p.s. in most cases). Some support for this is obtained from methacrylo-

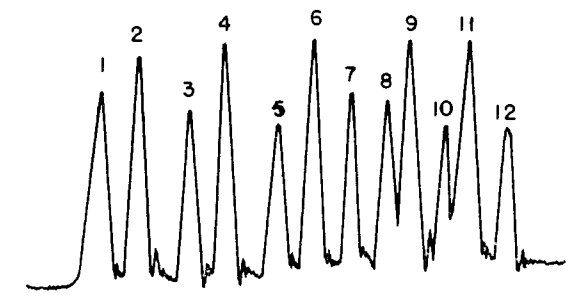nitrile where the H–CH₃ couplings are 1.7 c.p.s. for cis and 1.2 c.p.s. for trans couplings.

Fig. 5.—Nuclear magnetic resonance spectrum of α-D-acrylonitrile.

The assignments in α-methacrylonitrile are somewhat uncertain. Mortimer has measured the coupling constants in a number of chloropropenes[10] and concluded that in these compounds the 1,3 long-range couplings are greater in trans than in cis compounds. Also Fraser showed in tiglic and angelic acids[11] the long-range H–CH₃ coupling constants are greater in trans than in cis compounds. On the other hand Alexander[12] reported that in butenes the cis couplings are greater than the trans couplings. Whipple and Goldstein[13] analyzed the spectrum of 2-chloropropene and with additional observations based on solvent effect work, they agreed with

(10) F. S. Mortimer, J. Mol. Spec., 3, 340 (1959).
(11) Robert R. Fraser, Canad. J. Chem., 38, 549 (1960).
(12) S. Alexander, J. Chem. Phys., 28, 358 (1958).
(13) E. B. Whipple and J. H. Goldstein, Symposium on Molecular Spectroscopy and Structure, 1959, Ohio State University.
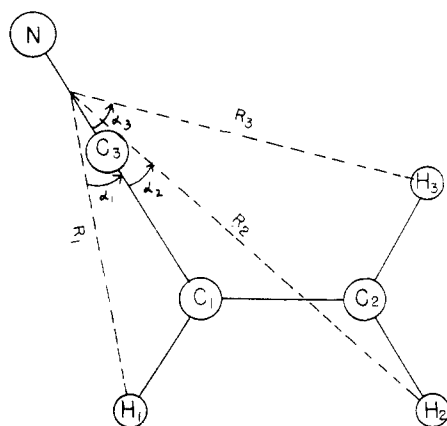
Fig. 6.—Structure used for calculating diamagnetic aniso-tropy effects in acrylonitrile: $C_1-C_2 = 1.339$, $C_3-N = 1.164$, $C-H = 1.086$ and $C_1-C_3 = 1.426$ Å.; $\angle C_2C_1C_3 = 122°37'$; $\angle C_2C_1H_1 = 121°44'$; $R_1 = 2.667$, $R_2 = 3.987$ and $R_3 = 3.027$ Å.; $\alpha_1 = 21°30'$; $\alpha_2 = 16°$ and $\alpha_3 = 43°15'$.

Alexander.[12] In α-methylstyrene, a greater *cis* H–CH$_3$ coupling has been observed.[14] In the present investigation it has been assumed that in α-methacrylonitrile the *cis* H–CH$_3$ coupling is greater than the *trans*. The H–CH$_3$ coupling constant is 1.5 c.p.s. in *cis* crotonitrile and 1.4 c.p.s. in *trans* crotonitrile. This provides some support for the assignments made in α-methacrylonitrile. The observed spectrum shows that the high-field proton couples more strongly with the methyl group than the low-field proton and accordingly the proton *trans* to the nitrile group (*cis* to the methyl group) is at higher field.

The nitrile group is quite electronegative and the α-proton on the carbon bearing the nitrile group is expected to be less shielded and hence should occur at lower field than the β-protons. This has been reported by Meyer and Gutowsky in the case of halogen substitution.[15] However, the analyses show that the α-protons in all these compounds lie at higher field than the β-protons (Table VII). This cannot be explained by the resonance structures of the type I ⟷ II[16]

$$-C\equiv N \longleftrightarrow \overset{+}{-C}=\overset{-}{N}$$
$$\text{I} \qquad\qquad \text{II}$$
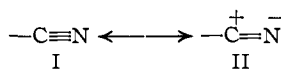
whose effect would be to shift the α-proton to even lower fields. In propargyl bromide[17] and other acetylenic compounds,[18] the acetylenic proton, contrary to naïve expectations, comes at much higher field than the methylene protons, and this has been adequately explained on the basis of diamagnetic anisotropic shielding[18] due to the acetylenic triple bond. The effect due to this additional shielding from diamagnetic anisotropy

(14) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Ch. 6.

(15) L. H. Meyer and H. S. Gutowsky. J. Phys. Chem., 57, 481 (1953).

(16) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca. N. Y., 1948.

(17) E. B. Whipple, J. H. Goldstein, Leon Mandell, G. S. Reddy and George McClure. THIS JOURNAL, 81, 1321 (1959).

(18) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

will be such that the corrected resonance frequencies of the protons will be shifted to lower field, and this correction will be greatest for the protons closest to the C≡C bond. It is expected that a similar situation also exists in these nitriles due to the anisotropy of the C≡N bond which has four π electrons capable of undergoing diamagnetic precession around the C≡N bond axis as in the C≡C bond. This diamagnetic anisotropy gives rise to additional shieldings on all the protons in the molecule and the correction due to this will bring the protons to lower field depending on their distance from the center of the C≡N bond and the angle between the line joining the center of the C≡N bond and the proton and the C≡N bond axis. Estimates of these diamagnetic shieldings were made for all the protons including methyl groups in all these compounds by taking the C≡N bond as a superconducting loop with four electrons located midway between the atoms of the C≡N bond. A small shift of the loop toward the more electronegative nitrogen will not seriously affect the calculated shieldings.

The diamagnetic shielding is given by

$$\Delta\omega = \frac{1}{3}\,\Delta\chi\,(3\cos^2\alpha - 1)R^{-3} \qquad (1)$$

where $\Delta\chi$ is the anisotropy in the molecular magnetic susceptibility of the group[19] under consideration (in this case the nitrile group) measured along the symmetry axis, α is the angle between the group symmetry axis and the line joining the proton under consideration and the center of the diamagnetic anisotropy, and R is the distance between the proton and the center of the loop. In all these calculations we have used the structural values of acrylonitrile reported by Costain and Stoicheff.[20] The value for $\Delta\chi$ for C≡C in methylacetylene was calculated by Whipple[7] and the same value was adopted for the C≡N bond. As an example, the complete structure showing the angles and distances required to calculate the $\Delta\omega$'s in acrylonitrile is shown in Fig. 6. The resulting diamagnetic anisotropic shieldings in c.p.s. at 40 mc. for all the protons in all these compounds are given in Table VII.

Discussion

In acrylonitrile, the *cis* proton is at lower field by 3.5 c.p.s. than the *trans* proton. Comparison of *cis* and *trans*-crotononitriles indicates that the β-proton in the *trans*-isomer (*cis* proton to C≡N) lies 6.7 c.p.s. below that in the *cis*-isomer (*trans* proton). The same situation exists in the case of α-methacrylonitrile where the *cis* proton is slightly below the *trans* proton. These differences between *cis* and *trans* protons are not great in light of the approximations involved in the estimations of diamagnetic anisotropy. However, the deviations from the plot of group dipole moments *vs.* proton shifts (see below) are not more than ± 4 c.p.s. which we assume as the value of the uncertainties in the corrected proton shifts. Apart from these uncertainties, the *cis* proton consistently falls below the *trans* in this group of compounds as well as in the series used for dipole moment correlation. A com-

(19) J. A. Pople, J. Chem. Phys., 24, 111 (1956).

(20) C. C. Costain and B. P. Stoicheff, ibid., 30, 777 (1959).

parison of the shifts in propylene[21] with this group of compounds strongly indicates that all the protons in the latter are much less shielded than those in the former. For example the methyl group frequency in propylene is -66.3 c.p.s. from the TMS reference while it is -95.5 c.p.s. in α-methacrylonitrile, -78.0 c.p.s. in cis-crotononitrile and -82.0 c.p.s. in $trans$ crotonitrile. Similar differences are noticed in the vinyl proton shifts (Table VII). Apparently the highly electronegative $C\equiv N$ group withdraws electrons from all the protons with the result that the protons in these nitriles are less shielded than in propylene or other similar molecules. The protons at the α-position should be affected more than those at the β-position, and this is borne out by the results in Table VII. The methyl group frequency is lowest in α-methacrylonitrile. Also, in complete agreement with this, the α-proton in acrylonitrile, after correcting for anisotropy of the nitrile group, is at much lower field than the β-protons and is hence less shielded. C^{13}–H couplings can be of help in verifying this statement. The C^{13}–H coupling constant of the methyl group in α-methacrylonitrile is 132 c.p.s. and that in cis-crotononitrile is 128 c.p.s. indicating that the α-methyl group is less shielded than the β-methyl group.[22] (The C^{13}–H coupling constants could not be obtained for the other protons because of the low natural abundance of C^{13} and complications in the spectra.) In other words, the electronegative group exerts a greater electron withdrawing effect on the α-proton than on the β-protons, if there are no other groups in the molecule which can act as electron withdrawing or releasing groups.

As can be seen from a comparison of the corrected shifts, ω^0, in Table VII, the substitution of a methyl group at any of the three positions in acrylonitrile is accompanied by a definite increase in the shielding of the protons β to the methyl group. However, in the crotonitriles ω^0 for the protons α to methyl are smaller than the corresponding value in acrylonitrile. A similar decrease in shielding for the proton adjacent to methyl has been observed in propylene. It seems evident, then, that electron release by the methyl group is involved in modifying the shieldings, with possibly an additional small effect due to anisotropy in the methyl group. The consistent increase in shielding for protons β to methyl can be rationalized by hyperconjugative electron release, but the decreased shielding in the α-position remains unexplained. A clearer understanding of these data will require comparisons with an enlarged series of compounds studied under uniform conditions. Further work on this phase of the problem is in progress.

Mayer and Gutowsky[15] showed that the shielding of the proton decreases as the number of halogens on the proton-bearing carbon is increased. Also, Bothner-By and Naar-Colin[23] have reported a linear relation between the shieldings of the α-protons and the dipole moment of the molecule in a series of haloalkanes. It is expected that a similar relation exists between the proton shifts and group moments

(21) A. A. Bothner-By, private communication.

(22) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

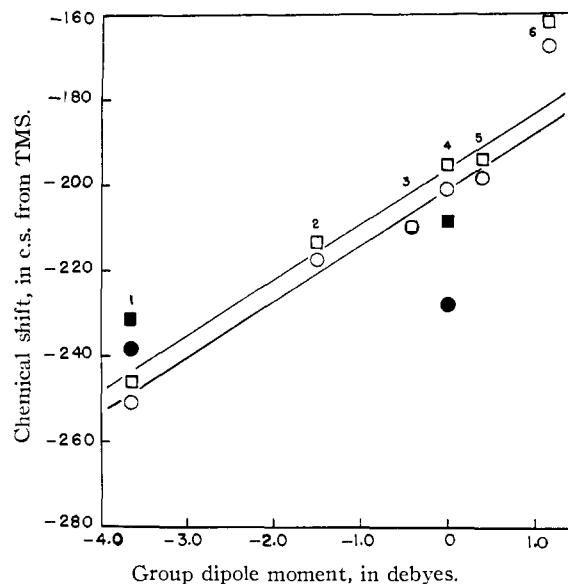(23) A. A. Bothner-By and C. Naar-Colin, THIS JOURNAL, **80**, 1728 (1958).

Fig. 7.—Plot of group dipole moments $vs.$ resonance frequencies, with respect to TMS internal reference, of the β-protons in the series $H_2C=CHX$. The substituents and their group dipole moments are: 1, $C\equiv N = -3.6$; 2, Cl $= -1.5$; 3, H $= -0.4$; 4, $C_6H_5 = 0.0$; 5, $CH_3 = +0.4$; 6, $OCH_3 = +1.16$. These were calculated by Dr. C. E. Boozer from values listed in C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

of the substituent group "X" in the series of compounds $H_2C=CHX$. We studied the series of compounds with X $=$ H, CH_3, Cl, $C\equiv N$, C_6H_5 and OCH_3. The shifts of vinyl chloride, vinyl cyanide and methyl vinyl ether were obtained from their complete analysis in these Laboratories with TMS as solvent and internal reference. The others were taken from published data and converted to the same reference by the difference of $+211.0$ c.p.s. which is the TMS shift with respect to H_2O external reference at $21°$.[7] The shifts of β-protons (cis and $trans$ protons to X) as obtained from the analyses do not show any linear relation with the group moment as expected. However, when the corrections due to diamagnetic anisotropy of phenyl and nitrile groups in styrene and acrylonitrile, respectively, were applied the plot is a straight line, that for the cis protons being lower and parallel to the one for the $trans$ protons. The anisotropy corrections due to the phenyl group were estimated on the basis of the decrease in shielding of the protons of benzene due to the ring current as determined by previous workers.[24] Fig. 7 shows the plot of cis and $trans$ proton shifts $vs.$ group dipole moments. The circles are cis proton shifts and the solid circles in the case of acrylonitrile and styrene are the shifts before making the corrections due to anisotropy of the nitrile and phenyl groups, respectively. The squares are those of the $trans$ protons, the solid squares again being uncorrected values. It is evident from the plot that the relation is linear and the cis proton is always at lower field than the $trans$. In propylene, as previous workers have reported,

(24) Kazuo Ito, *ibid.*, **80**, 3502 (1958).

the *trans* proton is at lower field and this is the only compound in this series which has reversed the *cis-trans* order. On the basis of this plot, the assignments in propylene by the previous workers were considered to be in error. However, in a recent communication, Bothner-By[21] made the assignments in propylene from its complete analysis and according to his results the *cis* proton is at lower field which is in complete agreement with these predictions.

No attempt has been made to correlate the shifts of the α-proton since, besides anisotropy, other effects will be large and difficult to evaluate. Further work is being carried out for similar correla-tions between Hammett's σ-constant, bond moments and other bond properties in related systems.

The Nuclear Resonance Spectra of Allyllithium and Vinyllithium[1]

By C. S. Johnson, Jr.,[2] M. A. Weiner, J. S. Waugh[2,3] and Dietmar Seyferth

Received July 22, 1960

Nuclear magnetic resonance has been used to investigate the structures of allyllithium and vinyllithium in diethyl ether solution. Preparation of solid allyl- and vinyllithium by the lithium–tin exchange reaction in pentane is described, and the results of spectral analysis are reported and discussed.

Nordlander and Roberts[4] have reported that the n.m.r. spectrum of allylmagnesium bromide in diethyl ether consists of a doublet and a quintet, consistent with a structure in which all four methylene hydrogen atoms are magnetically equivalent: that is, the spectrum is of the AX₄ type.[5] We have observed the spectrum of a dilute ether solution of the related compound allyllithium and found a similar result. We also wish to report the spectrum of the simpler compound vinyllithium, which shows no such time-average symmetry.

Experimental

Vinyllithium[6] and allyllithium[7] can be prepared conveniently by the exchange reaction between phenyllithium and tetravinyltin and tetraallyltin in ether solution. However, the resulting solutions of these reagents contain significant amounts of lithium bromide (from the preparation of phenyllithium from bromobenzene) and low concentrations of tetraphenyltin. In order to obtain uncontaminated vinyl- and allyllithium solutions, a modification of our method was used.

In the system

$$(CH_2=CH)_4Sn + BuLi \xrightarrow{\text{pentane}}$$
$$CH_2=CHLi + BuSn(CH=CH_2)_3$$
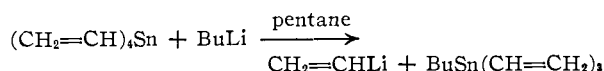
vinyllithium is the least soluble species, all organotin compounds, as well as butyllithium, being quite soluble.[8] This

allowed the preparation of an ether solution containing only vinyllithium by the procedure to be described.

To a solution of 2 g. (0.0088 mole) of tetravinyltin in 2 cc. of pentane under an atmosphere of prepurified nitrogen was added 25 cc. of 0.35 N solution of butyllithium in pentane. The resulting solution was concentrated by blowing a brisk stream of prepurified nitrogen across the surface of the solution. After the mixture had been left standing for several minutes, solid vinyllithium precipitated as an amorphous white powder. The solid was filtered under nitrogen using a sintered glass filtering apparatus and washed well with pentane. Dry vinyllithium is violently pyrophoric in air, and its properties and an alternate method of preparation will be reported elsewhere.[9] The sample of vinyllithium prepared as described above was dissolved in 2 cc. of diethyl ether immediately after its isolation.

Solid allyllithium was prepared in the same manner by the reaction of tetraallyltin and butyllithium (1:1 molar ratio) in pentane at room temperature.

Samples of the ether solutions of both compounds were sealed in 5 mm. Pyrex sample tubes and spectra were taken using a Varian Associates V-4300B spectrometer. Spectra of vinyllithium were obtained and analyzed at both 40 mc. and 60 Mc. Only 60 Mc. spectra were taken with allyllithium. The spectra were calibrated by the use of audio-frequency sidebands.

Results and Discussion

The spectrum of allyllithium showed the well-separated doublet and quintet typical of spectra of the AX₄ type, from which the parameters were derived by a first order analysis.

$$\delta_A = -5.52 \pm 0.05 \text{ p.p.m.}$$
$$\delta_X = -1.35 \pm 0.05 \text{ p.p.m.}$$
$$|J_{AX}| = 12 \pm 1 \text{ c.p.s.}$$

(1) This work was supported in part by the U. S. Army (Signal Corps), the U. S. Air Force (Office of Scientific Research, Air Research and Development Command) and the U. S. Navy (Office of Naval Research) and in part by the National Science Foundation.

(2) Laboratory for Chemical and Solid State Physics and Research Laboratory of Electronics.

(3) Alfred P. Sloan Fellow.

(4) J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

(5) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill Book Company, New York, N. Y., 1959, Chapter 6.

(6) D. Seyferth and M. A. Weiner, *Chem. and Ind. (London)*, 402 (1959).

(7) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

(8) A complete discussion of the exchange reaction which gives vinyl- and allyllithium will be given in later publications. It should be pointed out, however, that while practically complete exchange between tetravinyltin and butyllithium (1:1 molar ratio) is observed in ether, in pentane these reagents react in 1:4 molar ratio to give a mixture of Bu₃SnCH=CH₂ and Bu₂Sn(CH=CH₂)₂ and a correspondingly lower yield of vinyllithium.

(9) E. C. Juenge and D. Seyferth, *J. Org. Chem.*, **26**, 563 (1961).