Some Spectral Studies of *N*-Arylaziridines

RAY F. SEVERSON,[1] JAMES T. RUDESILL,[2] RICHARD G. ZAYLSKIE, and J. GEORGE POMONIS[3]
Metabolism and Radiation Research Laboratory, Agriculture Research Service, State University Station, Fargo, ND 58102

The proton magnetic resonance chemical shift of the methylene protons and the infrared ring breathing frequency of a series of 9 *p*-substituted *N*-arylaziridines have been measured. The carbon-hydrogen stretching frequency of the aziridine methylene moiety has been verified by means of the infrared spectrum of *N*-phenylaziridine-2-d_2. When the chemical shift at infinite dilution was plotted against σ_p^-, a good correlation was obtained. Similarly, the infrared ring breathing gave a linear relationship when plotted against chemical shift.

In a recent paper (*7*), we described the preparation of a series of *p*-substituted *N*-arylaziridines. In this communication, we are reporting the spectral behavior of the aziridinyl moiety of this series.

Since successful correlations have been made between substituents and chemical shifts of amino protons in anilines (*2*) and the *N*-methyl protons of dimethylanilines (*6*), one would predict that the resonance frequency of the methylene protons in a series of *N*-arylaziridines would also be a function of the ring substituent.

Carbon tetrachloride was chosen as the solvent for the nmr studies because solvent shift effects upon dilution of the compounds with this solvent are virtually independent of the aromatic substituent and because good correlations between chemical shift and substituent effects can be obtained (*3*, *8*). The very strong infrared absorption band (1250–1360 cm^{-1}) of *N*-substituted aziridine compound which Potts (*5*) and Spell (*10*) assigned to a symmetrical ring breathing vibration was also carefully measured for the series of compounds. The various empirically assigned infrared carbon-hydrogen vibrations were verified by using *N*-phenylaziridine-2-d_2.

EXPERIMENTAL

The preparation and physical constants of the *N*-arylaziridines used are exactly as given by Rudesill et al. (*7*).

NMR STUDIES

The nmr data were obtained on a Varian model A-60A spectrometer, using Mallinckrodt spectral AR-grade carbon tetrachloride as solvent and tetramethylsilane (TMS) as an internal standard. A constant level of TMS was maintained by the addition of 0.3 ml of TMS into a total volume of 100 ml of carbon tetrachloride. The solution was divided into small volumes, and the solvent from each container was used for only one day. The samples were prepared by serial dilutions from a stock solution of known concentration. The nmr tubes were filled with 0.3 ml of sample and sealed with pressure caps.

Frequency calibration was achieved by using the side-band technique analogous to that of Arnold and Packard (*1*). In this work, a 100-Hz scan was used (Figure 1). This allowed for the use of the parent peak of TMS and its first lower side band for calibration. The sample parent resonance is not recorded, but its position is known to be *F* Hz downfield from its first upper side band. The equation used to determine the

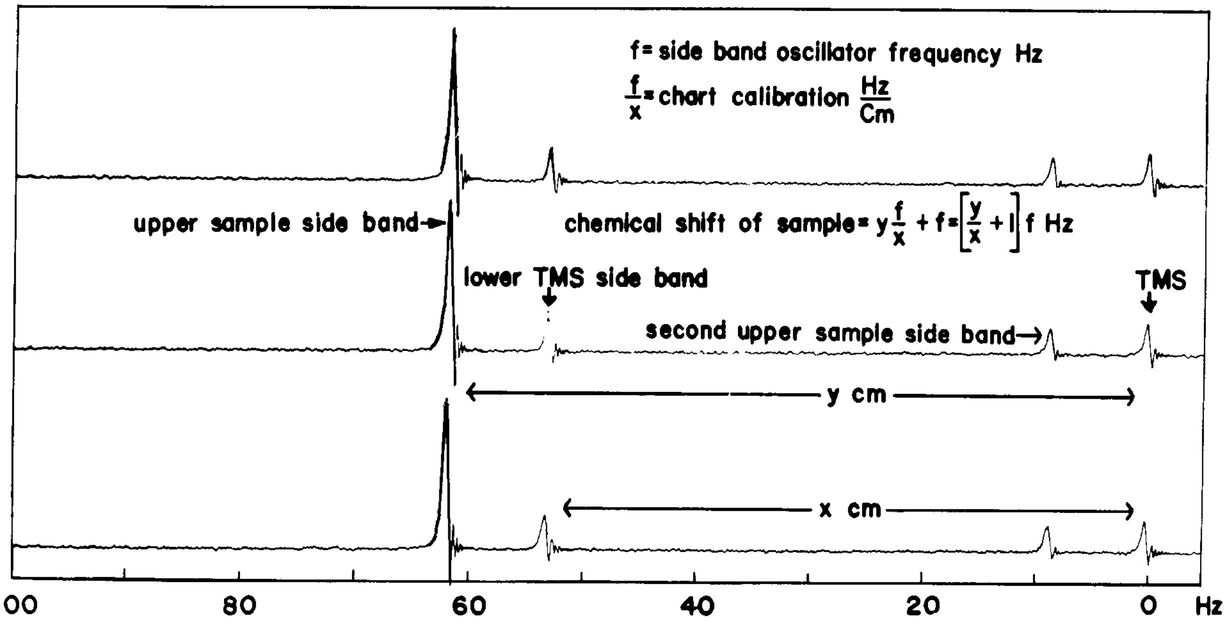

Figure 1. Side-band method for determination of chemical shifts

---

[1] Present address, Naval Stores Laboratory, USDA, Olustee, FL 32072.

[2] Present address, North Dakota State University, Department of Chemistry, Fargo, ND 58102.

[3] To whom correspondence should be addressed.

parent resonance of the sample is as follows:

$$\text{Chemical shift of sample} = (Y/X + 1)F \text{ Hz} \quad (1)$$

where F = side-band oscillator frequency, Hz
X = measured displacement of lower TMS side band from TMS parent resonance, cm
Y = measured displacement of sample upper side band from TMS parent resonance, cm

Each sample was scanned four to six times, and each point of Figure 2 is an average value for the chemical shifts as determined by Equation 1. The amplitude of the audio-frequency modulation was adjusted to yield a parent resonance and first side band of approximately equal intensity. The samples were allowed 10 min to equilibrate to the probe temperature (36.5°C), and the spectrometer was tuned before scanning each sample.

The side bands were imposed by means of a Hewlett-Packard model 200CD wide-range oscillator. The frequency of oscillation was measured by a frequency counter consisting of a Hickok model DMS-3220-A main frame with a Hickok model DP-150-A frequency-counter plug-in.

INFRARED STUDIES

The infrared data on the *N*-arylaziridines were obtained on a Beckman model IR-12 infrared spectrophotometer in double-beam mode, using Mallinckrodt spectra AR-grade carbon tetrachloride as solvent. The complete ir spectra were obtained in a 0.1-mm KBr liquid cell, using a scan speed of 40 cm^{-1} min^{-1} and a slit-gain program to allow at least an accuracy of 2 cm^{-1} in peak positions. The approximate value of the ring breathing frequency was determined and the spectrophotometer was then programmed to give a scan speed of 0.8 cm^{-1} min^{-1}, a chart speed of 2X, and a scan accuracy of 0.5 cm^{-1}. The area of the ring breathing frequency was scanned at least three times to determine accurately its position. Dilution effects were studied, using a Beckman micrometer variable path length cell (KBr).

RESULTS AND DISCUSSION

The effect of the *N*-arylaziridine concentration on chemical shift is shown in Figure 1. The p-OCH_3, p-CH_3, p-F, p-H, p-Cl, p-Br, and p-$COCH_3$ *N*-arylaziridines show about the same rate of change in chemical shift with dilution, while the p-CN and p-NO_2 compounds show an opposite effect (Table I). The shifts upon dilution can best be explained by a decrease in the intermolecular diamagnetic anisotropy (*8*) effect between solute molecules. In those compounds that have a downfield shift, the aziridine ring can be assumed to be associated with the π cloud of another solute molecule, while in those with upfield shifts, the substituent might be associated with the aziridine ring (or π-cloud) of another solute molecule.

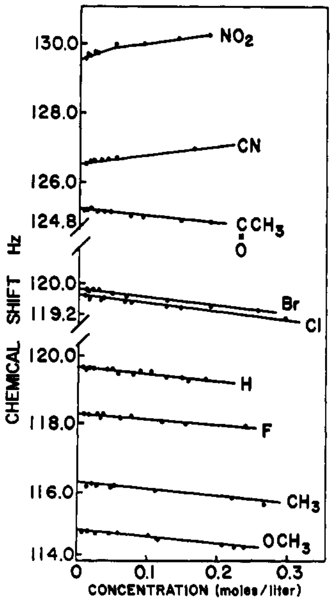

Figure 2. Effect of *N*-arylaziridine concentration on chemical shift. Carbon tetrachloride solutions

The chemical shifts of the aziridinyl methylene protons in carbon tetrachloride did not show a good correlation with σ (correlation coefficient = $\bar{r}$ = 0.0985). When σ^- values were used for those substituents which are capable of a $-R$ resonance interaction with the aziridinyl group, a good linear correlation was obtained (Figure 3, $\bar{r}$ = 0.996; omitting the phenyl data). The degree of dependence of the aziridinyl methylene protons on changes in electron density of the aromatic ring is approximately the same as that observed for the *N*,*N*-dimethylaniline series (*6*).

Table I. Effect of Concentration of Chemical Shift of Methylene Protons of N-Arylaziridine in Carbon Tetrachloride Solution

N-Aryl-aziridine	Concn, mol/l.	Chemical shift, Hz
p-OCH_3	0.235	114.43
	0.230	114.48
	0.206	114.59
	0.118	114.63
	0.115	114.69
	0.103	114.76
	0.059	114.81
	0.0514	114.76
	0.426	114.81
	0.030	114.81
	0.018	114.83
	0.0092	114.86
p-CH_3	0.264	115.68
	0.218	115.89
	0.109	116.07
	0.054	116.17
	0.047	116.16
	0.027	116.22
	0.021	116.23
	0.014	116.23
	0.011	116.18
p-H	0.176	119.23
	0.156	119.22
	0.102	119.44
	0.088	119.48
	0.078	119.40
	0.059	119.45
	0.051	119.51
	0.044	119.54
	0.025	119.53
	0.020	119.54
	0.012	119.53
	0.0097	119.62
p-F	0.239	117.85
	0.154	117.97
	0.120	118.12
	0.077	118.17
	0.060	118.13
	0.038	118.22
	0.030	118.19
	0.019	118.24
	0.015	118.23
	0.0097	118.24
p-Cl	0.296	118.98
	0.148	119.30
p-Cl *Contd.*	0.127	119.33
	0.074	119.45
	0.063	119.48
	0.037	119.57
	0.018	119.56
	0.016	119.59
	0.092	119.63
p-Br	0.254	119.23
	0.187	119.34
	0.127	119.50
	0.094	119.36
	0.047	119.71
	0.032	119.72
	0.023	119.80
	0.016	119.70
	0.012	119.78
P-$COCH_3$	0.029	124.68
	0.181	124.93
	0.145	125.00
	0.091	125.09
	0.072	125.12
	0.045	125.22
	0.036	125.21
	0.023	125.23
	0.018	125.29
	0.014	125.27
	0.009	125.25
p-CN	0.163	126.98
	0.053	126.76
	0.041	126.73
	0.027	126.68
	0.020	126.69
	0.013	126.65
	0.0096	126.62
p-NO_2	0.185	130.17
	0.145	130.10
	0.093	130.00
	0.058	129.96
	0.029	129.75
	0.022	129.78
	0.014	129.73
	0.011	129.68
	0.0065	

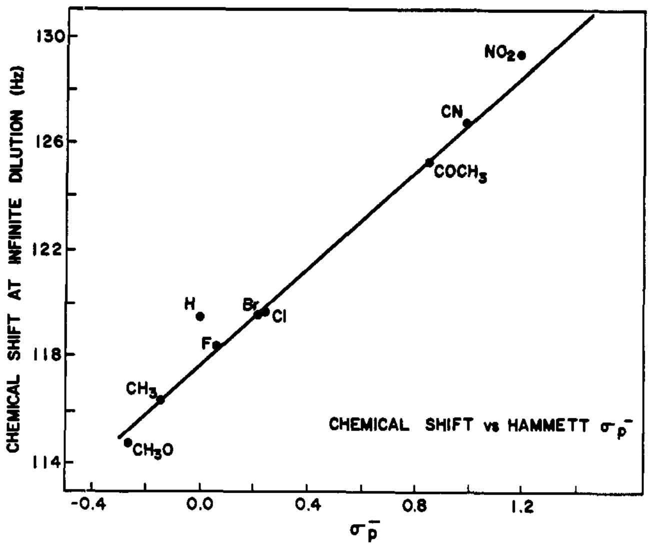

Figure 3. Relationship of Hammett σ_p^--constants with chemical shift (3)

The relationship expressed by Equation 2 was determined by a least-squares treatment of the data.

$$\text{Chemical shift (Hz)} = 9.24\,\sigma^- + 117.6 \qquad (2)$$

The chemical shifts of the eight p-substituted N-arylaziridines are predicted by Equation 2 with an average deviation of 0.3 Hz. The phenyl data showed a deviation of about 2.0 Hz. Large deviations of phenyl data have also been observed in other nmr Hammett correlations (*4, 11*).

The good correlation obtained from σ^- indicates that the resonance interactions with the aromatic ring are important. Correlations of chemical shift with σ_p^- constants of 0.1M solutions (a concentration recommended by many workers) show a significant deviation from linearity from the nitro and nitrile substituents (Figure 4). Because the deviation obtained from more dilute solutions (Figure 3) is significantly less, the authors suggest that one should obtain chemical shift data at infinite dilution whenever possible.

The symmetrical ring breathing frequency of each N-arylaziridine in carbon tetrachloride was independent of the concentration of the aziridine. Some of the infrared absorption frequencies of the N-arylaziridines studies are recorded in Table II. The observed ring breathing frequencies were plotted vs. both σ and σ^-. The best linear correlation (omitting the p-OCH$_3$ data) was obtained by using the σ^- values $(\sigma^- \bar{r} = 0.98)$. The relationship expressed by Equation 3 was determined by a least-squares treatment of the data.

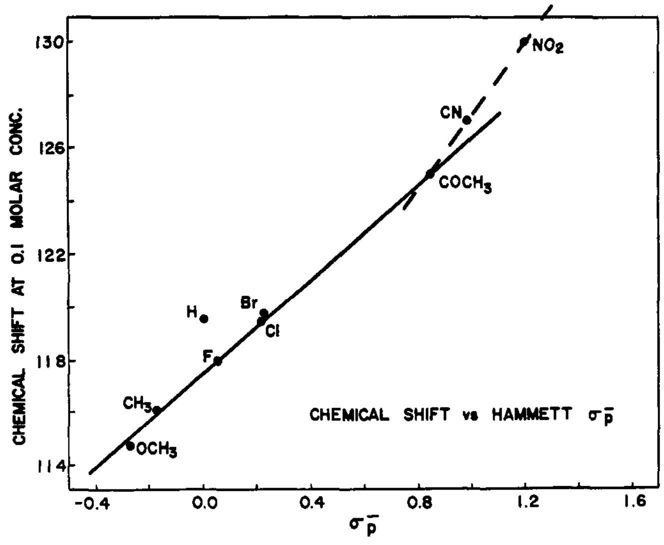

Figure 4. Effect of small concentration range of solute on relationship of Hammett σ_p^--constants (3) with chemical shift

$$\text{Ring breathing frequency (cm}^{-1}) = 16.2\,\sigma^- + 1317.8 \qquad (3)$$

The ring breathing frequencies of the N-arylaziridine are predicted by Equation 3 with an average deviation of 2.4 cm^{-1} (omitting the p-OCH$_3$). The p-OCH$_3$ data showed a deviation of about 18 cm^{-1}. No reasonable explanation for this large deviation can be found.

The N-(p-cyano)phenylaziridine showed two absorption maxima in the ring breathing region. Dilution failed to resolve the peaks. The lower value gave the best correlation, and it was used to determine Equation 3. The ring breathing vibration of the p-nitro compound appeared very close to the strong symmetric stretching valence vibrations of the nitro group (*8*), and its frequency could not be accurately determined.

A linear correlation was obtained when the nmr aziridinyl chemical shift values at infinite dilution were plotted against the corresponding ring breathing frequencies (Figure 5). This indicates that the substituent effects causing the spectral changes in one system can be used to predict the effects of that substituent in the other.

The correlation of the ring breathing frequencies with σ^- again illustrates that resonance interactions between the aziridine nitrogen and the aromatic rings are important.

Table II. Infrared Absorption Frequencies of Aziridine Ring in N-Arylaziridines (Cm^{-1})

Aryl-aziridine	CH$_2$ stretching Asym	CH$_2$ stretching Sym	Sym-ring breathing	CH$_2$ wagging	CH$_2$ rocking
p-OCH$_3$	3066	2993	1294	1180	906
p-CH$_3$	3065	2993	1316.7	1162	907
p-H	3066	2992	1320.6	1162	905
p-H-2-d_2	3060(H) 2310(D)	2990(H) 2170(D)	1320	1170(H) 834(D)	898(H) 660(D)
p-F	3062	2992	1317.0	1165	908
p-Cl	3067	2997	1326.2	1162	904
p-Br	3067	2995	1323.6	1162	905
p-COCH$_3$	3068	2976	1333.1	1162	909
p-CN	3071	2994	1336.1 1339	1160	908
p-NO$_2$	3075	3000	1340	1162	910

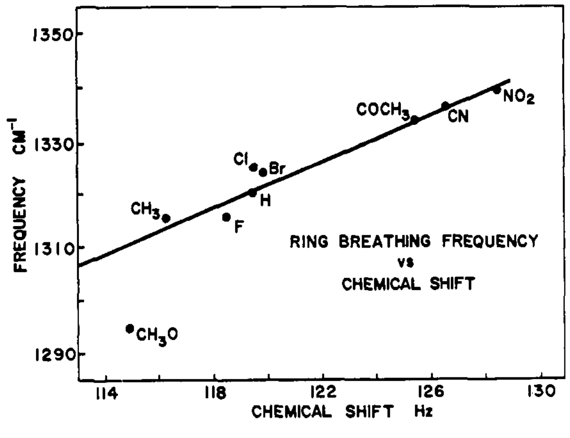

Figure 5. Ring breathing frequency vs. chemical shift

VERIFICATION OF INFRARED VIBRATIONAL FREQUENCIES ASSOCIATED WITH AZIRIDINE RING

The characteristic infrared frequencies of *N*-substituted aziridines were summarized by Spell (*10*) as follows: ring C—H stretching; 3040–3090 cm^{-1} (asymmetrical stretching vibrations), 2979–3005 cm^{-1} (symmetrical stretching vibrations); symmetrical-ring breathing vibration; 1250–1360 cm^{-1}; ring CH_2 wagging; 1150–70 cm^{-1}; ring deformation and CH_2 rocking modes; 745–860 cm^{-1}. Because data from deuterated aziridines and vibrational analyses of *N*-substituted aziridines were previously not available, some of these assignments are strictly empirical.

Applying Hooke's law (*9*) and assuming that a C—H bond and a C—D bond have the same force constant, the ratio of the C—H to C—D frequency can be calculated to be 1.38. Thus *N*-phenylaziridine-2-d_2 can be used to verify the various carbon-hydrogen vibrations.

The following infrared data in cm^{-1} were obtained from *N*-phenylaziridine-2-d_2:

	CH_2 stretching			
Methylene group	Asym	Sym	CH_2 wag	CH_2 rock
CH_2	3060	2890	1170	898
CD_2	2310	2170	834	660
rCH/rCD	1.33	1.38	1.40	1.36

The rCH/rCD ratios are all in very good agreement with those calculated by Hooke's law. Therefore, the empirically assigned CH_2 stretching, CH_2 wagging, and CH_2 rocking vibrational frequencies of the aziridine ring have now been verified by isotopic data. The fact that the ring breathing vibrations were correlated with Hammett sigma values also verifies their assignments.

LITERATURE CITED

(1) Arnold, J. T., Packard, M. E., *J. Chem. Phys.*, **19**, 1608 (1951).
(2) Dyall, L. K., *Aust. J. Chem.*, **17**, 419 (1964).
(3) Heathcote, C., *Can. J. Chem.*, **40**, 1965 (1962).
(4) Klinck, R. E., Strothers, J. B., *ibid.*, p 1071.
(5) Potts, W. J., *Spectrochim. Acta*, **21**, 511 (1965).
(6) Rae, I. D., Dyall, L. K., *Aust. J. Chem.*, **17**, 1419 (1964).
(7) Rudesill, J. T., Severson, R. F., Pomonis, J. G., *J. Org. Chem.*, **36**, 3071 (1971).
(8) Saito, H., Nukada, K., Kobyaski, T., Morita, K., *J. Amer. Chem. Soc.*, **89**, 6605 (1967).
(9) Silverstein, R. M., Bassler, G. C., "Spectrometric Identification of Organic Compounds," p 50, Wiley, New York, NY, 1963.
(10) Spell, H. L., *Anal. Chem.*, **39**, 185 (1967).
(11) Yamemoto, T., Reynolds, W. V., Hutton, H. M., Schaefer, T., *Can. J. Chem.*, **43**, 2668 (1965).

RECEIVED for review October 8, 1971. Accepted April 6, 1972. Mention of a proprietary product or company name in this paper does not constitute an indorsement by the U. S. Department of Agriculture.

Preparation and Physical Properties of Some Methoxy- and Ethoxyacetates

HENRY F. LEDERLE[1] and DAVID A. CSEJKA
Olin Corp., New Haven, CT 06504

Esters of methoxy- and ethoxyacetic acid with glycols or glycol ethers were prepared and evaluated. The physical properties determined were viscosities (212°, 122°, 100°, and —40°F), ASTM viscosity slopes, pour points, effect on rubber, and hygroscopicity. The effect of molecular structure on physical properties is discussed.

Conventional brake fluids are largely formulated from alkylene glycols and their ethers. Being hygroscopic, they soon deteriorate because of moisture absorption (*3*). Even small amounts of moisture can lower the boiling point of a brake fluid to an extent where under severe usage, vapor lock with loss of braking action may result. Moisture also increases the low-temperature viscosities and causes sluggish brake response at low temperatures.

Two approaches to overcome the problem of hygroscopicity have recently been used. The first uses fluids which are less hygroscopic than glycols and glycol ethers (*2*). In the second approach the moisture is chemically removed by reaction with the base fluid (*5*). A new approach based on esters of methoxy- and ethoxyacetic acids is presented here.

EXPERIMENTAL

Where available, reagent-grade chemicals were used for the ester syntheses. All other chemicals were high-quality commercial products. Starting materials were used as received Stoichiometric amounts of alkoxyacetic acid and glycol or glycol ether were refluxed in toluene using sulfuric acid as catalyst. After water no longer azeotroped in the Dean-Stark trap, calcium oxide or hydroxide sufficient to neutralize the sulfuric acid was added to the cooled product. After filtration, the product was stripped and distilled in vacuo through a vacuum-jacketed Vigreux column, 5.5 in. long. Elemental analyses (C, H) in agreement with the theory were obtained and submitted for review.

Physical properties were determined by ASTM methods except as follows: In the pour point determination only one cooling bath, Dry Ice–acetone, was used. Reflux boiling point (Table IV) and effect on rubber were determined by SAE procedures (*4*). Briefly, the effect on rubber (rubber swell) was determined as the diameter increase of a standard SBR wheel cylinder cup (original diameter 1.1 in.) after heating to 120°C for 70 hr. For automotive brake fluids, the Society of Automotive Engineers specifies the following limits for the properties tested here: kinematic viscosities at 212°F, 1.5 cSt minimum; at 122°F, 3.5 cSt minimum; at −40°F, 1800 cSt maximum; and rubber swell, 0.006-0.055 in. The hygro-

---

[1] To whom correspondence should be addressed