which the mixture was cooled and dissolved in 50 ml of benzene. The benzene solution was washed with 5% aqueous KOH solution and water, dried with Na_2SO_4, and chromatographed on silica gel. The violet zone of X was eluted with benzene–hexane (1 : 1), and the eluate was evaporated to give 0.83 g (21%) of X in the form of violet-black needles with mp 178-179° (from benzene). UV spectrum (dioxane): λ_{max} 540 nm (log ε 3.2). Found: C 90.5; H 5.0%. $C_{30}H_{20}O$. Calculated: C 90.9; H 5.1%.

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INVESTIGATION OF THE CONDUCTIVITY OF ELECTRONIC EFFECTS BY THE AZIRIDINE RING

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UDC 547.717 : 543.422.25

Different degrees of conductivity of electronic effects through the aziridine ring in the direction of the C–C, C–N, and N–C bonds were observed for 1,2-diarylaziridines by ^1H and ^{19}F NMR spectroscopy.

Various researchers have shown [1-3] that a pronounced decrease in the algebraic value of the geminal spin–spin coupling constant (SSCC) occurs in aziridines as the electronegativity of the substituent in the 1 position increases. In order to study the relative effect of substituents in the 1 and 2 positions on $^2J_{HH}$ we synthesized two series of 1,2-disubstituted aziridines and studied their PMR spectra (Table 1).

The signs of the SSCC between the protons of the heteroring were determined by the INDOR method [4] (Fig. 1). The signs were found to be identical for the geminal and both vicinal SSCC, and they should therefore be considered to be positive ($^3J_{HH} > 0$ [5]).

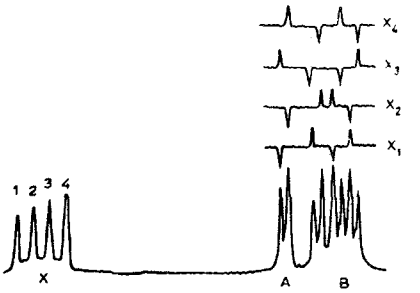
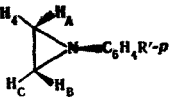


Fig. 1. INDOR spectra of the protons of the aziridine ring of 1,2-diphenylaziridine.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 906-909, July, 1977. Original article submitted October 11, 1976.

TABLE 1. Parameters of the PMR Spectra of 1,2-Diarylethyleneimines 

Compound	R	R′	τ, ppm					J, Hz		
			H_A	H_B	H_C	2-aryl	1-aryl	AB	AC	BC
I	H	H	7,01	7,64	7,74	2,80	2,8—3,3	6,22	3,15	1,51
II	OCH_3	H	7,03	7,67	7,79	2,84; 3,28; 6,38 (OCH_3)	2,8—3,3	6,22	3,20	1,56
III	F	H	6,98	7,63	7,77	2,82; 3,08	2,8—3,3	6,45	3,13	1,42
IV	Cl	H	7,00	7,61	7,76	2,80	2,8—3,3	6,26	3,04	1,37
V	Br	H	7,01	7,62	7,76	2,90; 2,70	2,8—3,3	6,34	3,07	1,38
VI	H	CH_3	7,06	7,69	7,79	2,83	3,24; 3,11; 7,76 (CH_3)	6,23	3,09	1,62
VII	H	OCH_3	7,05	7,68	7,78	2,82	3,24; 3,40; 6,43 (OCH_3)	6,33	3,13	1,53
VIII	H	F	7,01	7,67	7,73	2,81	3,22	6,09	3,18	1,42
IX	H	I	7,01	7,67	7,72	2,78	3,34; 2,61	5,80	3,27	1,36
X	H	Br	6,99	7,65	7,71	2,80	3,26; 2,82	6,27	3,47	1,38
XI	H	Cl	7,00	7,66	7,70	2,83	3,24; 3,00	6,27	3,24	1,37

TABLE 2. ^{19}F Chemical Shifts of 2-(p-Fluorophenyl)- and 2-(m-Fluorophenyl)-1-arylethyleneimines and Reaction Constants of the 1-Aryl-2-aziridinyl Group

Compound	R	δ_F^m	σ_I	Compound	R	δ_F^p	σ_C
XII	OCH_3	0,40	0,028	XIX	OCH_3	2,80	−0,081
XIII	CH_3	0,35	0,035	XX	CH_3	2,72	−0,080
XIV	H	0,22	0,054	XXI	H	2,50	−0,077
XV	F	0,16	0,62	XXII	F	2,40	−0,076
XVI	Cl	0,07	0,075	XXIII	Cl	2,20	−0,072
XVII	Br	0,06	0,076	XXIV	Br	2,19	−0,072
XVIII	I	0,04	0,079	XXV	I	2,17	−0,072

The geminal SSCC of 1,2-diarylethyleneimines are determined by the nature of the substituent in the aromatic ring and are related by means of linear equations to the Hammett σ constants of the latter.

For 1-phenyl-2-arylaziridines (I-V)

$$^2J_{HH} = 1.48 - 0.385\sigma, \qquad r = 0.966, \tag{1}$$

whereas for 1-aryl-2-phenylaziridines (I, VI-XI)

$$^2J_{HH} = 1.49 - 0.623\sigma, \qquad r = 0.967. \tag{2}$$

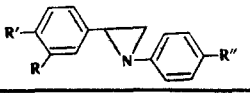
Judging from the regression equations, the conductivity of the electronic effect of substituent R by the system of $-C_6H_4-N-C-$ bonds is more effective in arylaziridine molecules than the conductivity observed for the $-C_6H_4-C$ fragment. The changes in the $^2J_{HH}$ values of 1,2-diarylaziridines may be due, first, to the change in the effective electronegativity of the substituent attached to the β atom [6]. However, its effect on the $^2J_{HH}$ values of both compounds should be identical. Second, a change in the state of the unshared electron pair of the nitrogen atom has an additional effect on the $^2J_{HH}$ values of 1-aryl-2-phenylaziridines. In qualitative molecular orbital theory this effect is explained by transfer of the electron pair to the antisymmetrical bonding orbital of the CH_2 fragment [6, 7]. In 1-aryl-2-phenylaziridines, as competitive delocalization of the electron pair on the benzene ring increases (under the influence of substituent R), its contribution to $^2J_{HH}$ evidently decreases; this decrease in the geminal SSCC takes place more rapidly than in 1-phenyl-2-arylaziridines.

In order to study the observed (by means of PMR spectroscopy) difference in the conductivity of the electronic effects of substituent R we investigated the ^{19}F NMR spectra of 2-(p-fluorophenyl)- and 2-(m-fluorophenyl)-1-arylaziridines and 1-(p-fluorophenyl)-2-arylaziridines (Tables 2 and 3). The ^{19}F chemical shifts were used for the calculation from the known [8] equations of the reactivity constants of the 1-aryl-2-aziridinyl group (Table 2). One is easily persuaded that the resonance constants of these groups are determined by a combination of the inductive and mesomeric effects of the R substituent of their 1-aryl fragment. This follows automatically from the linear dependence of the ^{19}F chemical shifts on the σ constants of substituent R in both series of 1-aryl-2-fluorophenyl- [Eqs. (3) and (4)] and 1-(p-fluorophenyl)-2-arylaziridines [Eq. (5)].

TABLE 3. ^{19}F Chemical Shifts of 1-(p-Fluorophenyl-2-arylethyleneimines

Compound	R	δ_F^p
XXVI	OCH_3	8,88
XXVII	H	8,67
XXVIII	F	8,37
XXIX	Br	8,20
XXX	Cl	8,23
XXXI	I	8,20

TABLE 4.



Compound	R	R′	R″	bp, °C (0.05 mm)	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
XII	F	H	OCH_3	78	74,2	6,1	6,1	$C_{15}H_{14}FNO$	74,0	5,8	5,8	47
XIII	F	H	CH_3	72	79,6	6,4	6,4	$C_{15}H_{14}FN$	79,3	6,2	6,2	43
XIV	F	H	H	63	77,3	5,5	6,9	$C_{14}H_{12}FN$	77,6	5,6	6,8	55
XV	F	H	F	53	73,0	4,8	6,3	$C_{14}H_{12}F_2N$	72,7	4,7	6,1	45
XVI	F	H	Cl	110	68,2	4,6	5,8	$C_{14}H_{11}ClFN$	67,9	4,5	5,6	53
XVII	F	H	Br	124	57,9	4,0	5,0	$C_{14}H_{11}BrFN$	57,5	3,9	4,8	51
XVIII	F	H	I	126	49,7	3,5	4,5	$C_{14}H_{11}FIN$	49,4	3,3	4,1	52
XIX	H	F	OCH_3	78	74,3	5,4	5,4	$C_{15}H_{14}FNO$	74,0	5,8	5,8	43
XX	H	F	CH_3	74	79,7	6,2	6,3	$C_{15}H_{14}FN$	79,3	6,2	6,2	50
XXI	H	F	H	87	77,3	5,5	6,8	$C_{14}H_{12}FN$	77,6	5,6	6,8	57
XXII	H	F	F	77	72,9	4,5	5,6	$C_{14}H_{11}F_2N$	72,7	4,7	6,1	49
XXIII	H	F	Cl	115	67,4	4,1	5,2	$C_{14}H_{11}ClFN$	67,9	4,5	5,6	47
XXIV	H	F	Br	131	56,8	3,5	4,4	$C_{14}H_{11}BrFN$	57,5	3,9	4,8	54
XXV	H	F	I	135	49,2	3,0	3,8	$C_{14}H_{11}FIN$	49,4	3,3	4,1	54
XXVI	H	OCH_3	F	75	74,3	5,9	6,0	$C_{15}H_{14}FNO$	74,0	5,8	5,8	47
XXVII	H	H	F	61	77,4	5,4	6,6	$C_{14}H_{12}FN$	77,6	5,6	6,8	55
XXVIII	H	F	F	59	72,6	4,6	5,9	$C_{14}H_{11}F_2N$	72,7	4,7	6,1	48
XXIX	H	Br	F	105	57,3	3,6	4,5	$C_{14}H_{11}BrFN$	57,5	3,9	4,8	53
XXX	H	Cl	F	97	68,0	4,6	5,8	$C_{14}H_{11}ClFN$	67,9	4,5	5,6	45
XXXI	H	I	F	113	49,7	3,6	4,4	$C_{14}H_{11}FIN$	49,4	3,3	4,1	52

$$\delta_F^p = 2.48 - 1.23\sigma, \quad r = 0.997, \tag{3}$$

$$\delta_F^m = 0.22 - 0.68\sigma, \quad r = 0.997, \tag{4}$$

$$\delta_F^p = 8.54 - 1.36\sigma, \quad r = 0.967. \tag{5}$$

To estimate the relative contribution of the inductive effect to the conductivity of the effect of aryl substituent R [9] through the aziridine ring we calculated the equations of the pair correlations for 1-aryl-2-(p-fluorophenyl)aziridines [Eq. (6)] and 1-(p-fluorophenyl)-2-arylaziridines [Eq. (7)]:

$$\delta_F^p = 2.384 - 1.255\sigma_I - 1,782\sigma_C, \quad r = 0.988; \tag{6}$$

$$\delta_F^p = 8.654 - 1,704\sigma_I - 1.558\sigma_C, \quad r = 0.999. \tag{7}$$

In conjugated systems the $\lambda = \rho_C/\rho_I$ coefficient is greater than unity, whereas in compounds that are incapable of effective transmission of conjugation [9], $\lambda < 1$. The results obtained in this study constitute evidence that the conjugation effects are conducted quite well [$\lambda = 1.42$, Eq. (6)] in the direction of the N–C bond of the aziridine ring, whereas the inductive effect has the best conductivity in the direction of the C–N bond [$\lambda = 0.91$, Eq. (7)].

EXPERIMENTAL

The ^1H NMR spectra of the CCl_4 solutions of the compounds were obtained with a Tesla BS-487-C spectrometer (80 MHz): the ^{19}F NMR spectra were obtained with a Perkin–Elmer R 12A spectrometer (60 MHz).

The chemical shifts were obtained by extrapolation to infinite dilution. The internal standards for the ^{1}H and ^{19}F spectra were, respectively, tetramethylsilane and fluorobenzene. The INDOR spectra were obtained with a Tesla spectrometer. The ABC PMR spectra of 1,2-diarylaziridines I-XI were analyzed in accordance with the method in [10].

Compounds XII-XXXI were obtained from methylenedimethylsulfurane and the appropriate Schiff bases [11].

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IR SPECTRA OF SUBSTITUTED PYRROLES

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UDC 547.74:543.422.4

The IR spectra of 52 substituted pyrroles, including 24 1-vinylpyrroles, were thoroughly analyzed. The principal analytical bands of the pyrrole ring and the vinyl group were isolated. Doublet character of the bands of the stretching vibrations of the double bond ($\nu_{C=C}$) and the C–H (CH_2=) out-of-plane deformation vibrations, which indicates the presence of rotational isomerism relative to the N-vinyl bond, was detected. The integral intensity of the principal component of the $\nu_{C=C}$ doublet was measured for 12 of the 1-vinylpyrroles, and it is shown that it is practically independent of the structure of the alkyl substituents in the ring. Proof for the existence of a nonplanar gauche conformation for the 1-vinylpyrroles was obtained.

A new synthesis of pyrroles [1-3] has made many previously unknown or little-studied compounds of this series, including 1-vinyl-substituted compounds, which are interesting subjects for the study of the effects of conjugation, problems of aromaticity, and the influence of unsaturated groupings attached to the nitrogen atom, accessible. The vibrational spectra of pyrroles have not been studied systematically. There are only disconnected data available on the IR spectra of 1-methyl-, 1-phenyl- 2,5-dimethyl-, and 2,5-diphenylpyrroles [4], 1-, 2-, and 3-alkylpyrroles and 2,3,5-trialkylpyrroles [5-7], and 1- and 2-allylpyrroles [8]. The Raman spectrum of pyrrole has been studied [9], and the force constants of pyrrole and its deuterated and methyl derivatives have been calculated [10].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 910-914, July, 1977. Original article submitted May 18, 1976; revision submitted December 3, 1976.