The chemical shifts were obtained by extrapolation to infinite dilution. The internal standards for the ^1H 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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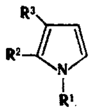
TABLE 1. List of the Investigated Pyrroles



Compound	R¹	R²	R³	Compound	R¹	R²	R³
I	H	CH_3	H	XXVII	$CH_2{=}CH$	$n\text{-}C_6H_{13}$	H
II	H	CH_3	CH_3	XXVIII	$CH_2{=}CH$	C_6H_5	H
III	H	C_6H_5	H	XXIX	$CH_2{=}CH$	C_6H_5	CH_3
IV	H	C_6H_5	CH_3	XXX	$CH_2{=}CH$	C_6H_5	C_2H_5
V	H	C_6H_5	C_2H_5	XXXI	$CH_2{=}CH$	C_6H_5	$n\text{-}C_3H_7$
VI	H	C_6H_5	C_6H_5	XXXII	$CH_2{=}CH$	C_6H_5	$i\text{-}C_3H_7$
VII	H	$-(CH_2)_4-$		XXXIII	$CH_2{=}CH$	C_6H_5	C_6H_5
VIII	H	$-(CH_2)_5-$		XXXIV	$CH_2{=}CH$	$p\text{-}C_2H_5-C_6H_4$	H
IX	C_2H_5	CH_3	H	XXXV	$CH_2{=}CH$	$p\text{-}Cl-C_6H_4$	H
X	C_2H_5	C_6H_5	H	XXXVI	$CH_2{=}CH$	$p\text{-}Br-C_6H_4$	H
XI	C_2H_5	C_6H_5	CH_3	XXXVII	$CH_2{=}CH$	$-(CH_2)_4-$	
XII	C_2H_5	C_6H_5	C_2H_5	XXXVIII	$CH_2{=}CH$	$-(CH_2)_3CH(CH_3)-$	
XIII	C_2H_5	C_6H_5	$n\text{-}C_3H_7$	XXXIX	$CH_2{=}CH$	$-(CH_2)_5-$	
XIV	C_2H_5	C_6H_5	$i\text{-}C_3H_7$	XL	$(CH_2)_2SC_2H_5$	C_6H_5	H
XV	C_2H_5	$-(CH_2)_4-$		XLI	$(CH_2)_2SC_3H_7\text{-}n$	C_6H_5	H
XVI	$CH_2{=}CH$	CH_3	H	XLII	$(CH_2)_2SC_4H_9\text{-}n$	C_6H_5	H
XVII	$CH_2{=}CH$	CH_3	CH_3	XLIII	$(CH_2)_2SC_2H_5$	$-(CH_2)_4-$	
XVIII	$CH_2{=}CH$	CH_3	$n\text{-}C_3H_7$	XLIV	$(CH_2)_2SC_3H_7\text{-}n$	$-(CH_2)_4-$	
XIX	$CH_2{=}CH$	CH_3	$i\text{-}C_3H_7$	XLV	$(CH_2)_2SC_3H_7\text{-}i$	$-(CH_2)_4-$	
XX	$CH_2{=}CH$	CH_3	$n\text{-}C_5H_{11}$	XLVI	$(CH_2)_2SC_4H_9\text{-}n$	$-(CH_2)_4-$	
XXI	$CH_2{=}CH$	C_2H_5	H	XLVII	$(CH_2)_2SC_4H_9\text{-}i$	$-(CH_2)_4-$	
XXII	$CH_2{=}CH$	C_2H_5	CH_3	XLVIII	$(CH_2)_2SC_2H_5$	$-(CH_2)_3CH(CH_3)-$	
XXIII	$CH_2{=}CH$	$n\text{-}C_4H_9$	H	XLIX	$(CH_2)_2SC_3H_7\text{-}n$	$-(CH_2)_3CH(CH_3)-$	
XXIV	$CH_2{=}CH$	$n\text{-}C_4H_9$	$n\text{-}C_3H_7$	L	$(CH_2)_2SC_3H_7\text{-}i$	$-(CH_2)_3CH(CH_3)-$	
XXV	$CH_2{=}CH$	$i\text{-}C_4H_9$	H	LI	$(CH_2)_2SC_4H_9\text{-}n$	$-(CH_2)_3CH(CH_3)-$	
XXVI	$CH_2{=}CH$	$t\text{-}C_4H_9$	H	LII	$(CH_2)_2SC_4H_9\text{-}i$	$-(CH_2)_3CH(CH_3)-$	

In the present research we made a detailed analysis of the IR spectra of 52 substituted pyrroles (primarily 1-vinylpyrroles) in order to fix the boundaries of the characteristic pyrrole and vinyl absorption, to ascertain the bands most suitable for the identification of the investigated compounds, and to detect the possible conformations relative to the N-vinyl bond. A list of the investigated pyrroles is given in Table 1, and their typical IR spectra are shown in Fig. 1.

A comparison of the spectra of 1-vinylpyrroles XVI-XXXIX with the spectra of pyrroles I-VIII, IX-XV, and XL-LII, which do not have a vinyl group attached to the nitrogen atom, makes it possible to reliably isolate the absorption bands related to the double bond. Of greatest analytical value are the five that are characterized by high or medium intensity and constancy of position: H—C=C—H fan vibrations (ω_{CH}) at 582 ± 4 (m); CH_2= fan vibrations ($\omega\omega_{CH_2}$) at 859 ± 5 (s) (the band appears as a doublet or is appreciably broadened; the low-frequency component is presented); H—C=C—H twisting vibrations (τ_{CH}) at 946 ± 6 (s); and C=C stretching vibrations ($\nu_{C=C}$) at 1585 ± 5 (m) and 1642 ± 2 (s). All of these bands are absent in the spectra of nonvinyl compounds I-VIII, IX-XV, and XL-LII.

The following bands are common to the spectra of all of the pyrroles without exception: 708 ± 4 (s), pyrrole ring C—H deformation vibrations, which in many cases show up as a narrow doublet or triplet with ~10 cm^{-1} between the maxima; ~1380 cm^{-1} (s) (more often a doublet with 10-20 cm^{-1} between the maxima, and less frequently a doublet with up to 30 cm^{-1} between the maxima); 1490 ± 4 (s) and ~1540 (usually a weak doublet with a difference in frequencies of 10-20 cm^{-1}). The last three bands (~1380, ~1490, and ~1540 cm^{-1}) are assumed to be related to the stretching vibrations of the pyrrole skeleton [10]. The band at ~1300 cm^{-1} (s) (sometimes a doublet) is characteristic only for N-substituted pyrroles and is probably related to C—N stretching vibrations [4]. This band is at 1330 cm^{-1} in the spectra of 1-ethyl-2-phenylpyrroles X-XIV. Additional bands (~1500 s, 1575-1585 w, and 1605-1612 m) related to the benzene ring vibrations appear in the spectra of 2-phenyl-substituted pyrroles III, VI, X, XI, XIII, XXVIII, XXIX, and XXXIII at 1490 and 1600 cm^{-1}. At 3090-3140 cm^{-1} (primarily at 3100 cm^{-1}) the spectra of all of the pyrroles contain a weak, poorly resolved multiplet, which is of little use for identification purposes.

Unsymmetrical 1-vinyl-2-substituted pyrroles may have three conformations relative to the N-vinyl bond (Fig. 2): two planar syn and anti conformations (the angle between the planes of the ring and double bond $\alpha \cong 0°$) and one nonplanar gauche conformation ($\alpha \cong 90°$). A certain population of the planar conformations of 1-vinylpyrroles is evidenced by, for example, an analysis of their NMR spectra [11]. The two planar conformations have similar geometries (they degenerate to one conformation when R = H) and approximately equal

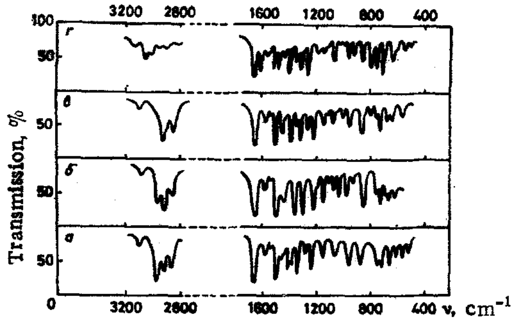


Fig. 1

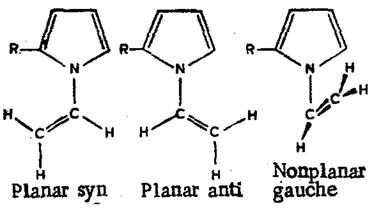


Fig. 2

Fig. 1. Typical IR spectra of 1-vinylpyrroles: a) 3-methyl-2-ethyl-1-vinylpyrrole; b) 7-methyl-1-vinyl-4,5,6,7-tetrahydroindole; c) 2,3-pentamethylene-1-vinylpyrrole; d) 1-vinyl-2,3-diphenylpyrrole (films).

Fig. 2. Conformations of 1-vinyl-2-substituted pyrroles.

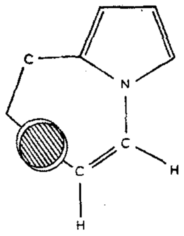


Fig. 3

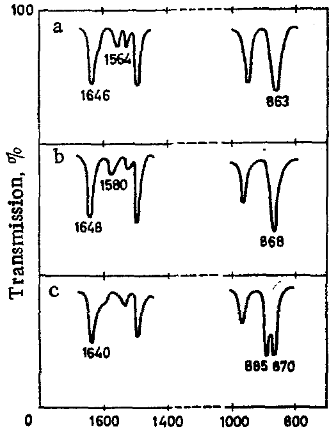


Fig. 4

Fig. 3. Steric hindrance of the planar syn conformation of 2-tert-butyl-1-vinylpyrrole (XXVI) (an interaction radius of 0.6 Å was used for the hydrogen atoms [14]).

Fig. 4. IR spectra at 1400-1650 cm^{-1} and 800-1000 cm^{-1}: a) 1-vinylpyrrole; b) 2-methyl-1-vinylpyrrole; c) 2-tert-butyl-1-vinylpyrrole.

conditions for conjugation of the double bond with the ring π system exist in them. The IR frequencies of these conformations therefore should not differ appreciably. Conjugation is "disconnected" in the gauche conformation, and, in addition, it has a fundamentally different geometry, and some of the frequencies of its vinyl grouping may consequently also change.

The energy barrier between the planar and nonplanar conformations may be due to repulsion of the π-electron clouds of the vinyl and pyrrole systems during rotation about the $C_{sp^2}-N$ bond to certain (critical) angles, after which the planar conformation is fixed by the developing $>\overset{+}{N}{=}CH{-}\overset{-}{C}H_2$ π bond.

The presence of two $\nu_{C=C}$ bands (~1590 and ~1640 cm^{-1}) and the doublet character of the ω_{CH_2} band (~860 and ~875 cm^{-1}) actually indicates the conformational heterogeneity of 1-vinylpyrroles. A close analogy with vinyl ethers, the conformations of which are most distinctly distinguishable in the same spectral regions [12, 13], is observed. It is apparent from Fig. 3 that in 1-vinylpyrroles with branched chains in the 2 position realization of the planar syn conformation should be particularly hindered (this primarily pertains to the 2-tert-butyl- and 2-phenyl-substituted compounds). An analysis of the spectra shows that as in the case of vinyl ethers, the intensity of the doublets is redistributed in favor of the high-frequency components as the condi-

TABLE 2. Integral Intensity (A) of the High-Frequency Component of $\nu_{C=C}$ of Some 1-Vinylpyrroles

Compound	$A \cdot 10^{-4}$, $mole^{-1} \cdot liter \cdot cm^{-2}$	$\nu_{C=C}$, cm^{-1}
N-Vinylpyrrole	0,85	1646
XVI	1,19	1648
XXII	1,20	1642
XXIII	1,18	1642
XXIV	1,16	1643
XXV	1,22	1640
XXVI	1,20	1642
XXVII	1,21	1642
XXIX	1,35	1640
XXXIII	0,30	1642
XXXVII	1,18	1639
XXXVIII	1,29	1640
XXXIX	1,27	1642

tions for realization of coplanarity become worse (as the volume of group R^2 in the 2 position increases). When R^2 = tert-C_4H_9 (XXVI) and C_6H_5 (XXVIII, XXIX), this redistribution is expressed particularly distinctly: the maximum at 1590 cm^{-1} in the spectra of these compounds (Fig. 4) degenerates to two appreciable shoulders on the band at ~1640 cm^{-1}, and the ω_{CH_2} absorption is split into peaks at 870 (s) and 885 (s) cm^{-1} (XXVI) and 885 (m sh), 870 (s), and 880 (m sh) cm^{-1} (XXVIII). (The appearance of an additional ω_{CH_2} band in the spectrum of XXVIII is evidently associated with hindrance of rotation about the C_2–phenyl bond.*) Thus the high-frequency components of $\nu_{C=C}$ and ω_{CH_2} may be tentatively assigned to the unconjugated gauche conformation. The increase in the $\nu_{C=C}$ frequency as the conjugation in compounds of one series becomes weaker is a regular tendency that reflects the shortening of the C=C bond because of an increase in the s character of the carbon atoms.

If the noted doublet character of the bands is associated with the presence of two planar conformations, it should not be observed in the spectrum of unsubstituted N-vinylpyrrole ($R^2 = R^3$ = H), since there can be only one planar form for this compound. In fact, its spectrum is very similar to the spectrum of 2-methyl-1-vinylpyrrole (Fig. 4) and also contains a distinctly expressed $\nu_{C=C}$ doublet (1564 and 1646 cm^{-1}), whereas the ω_{CH_2} band at 863 cm^{-1} is markedly broadened.

Table 2 shows that the frequency and integral intensity of the high-frequency component of $\nu_{C=C}$ depend little on the structure and position of the alkyl groups in the pyrrole ring. The decreased intensity of the double bond in the spectrum of unsubstituted N-vinylpyrrole can be interpreted as the result of a change in the inductive effect of the ring in favor of weakening its donor character. It is interesting that even the introduction of a phenyl substituent in the 2 position of the pyrrole ring (XXIX) increases the intensity of $\nu_{C=C}$ only slightly. All of this confirms the conclusion that in the preferred conformation of 1-vinylpyrroles the double bond is to some extent conjugationally "disconnected" from the ring π system. The manifestations of conjugated interaction of the double bond with the ring that are observed in the UV spectra of 1-vinylpyrroles [14] are evidently related to the higher energy levels that are not affected by vibrational excitation. In addition, these manifestations may be associated with the presence of less populated planar conformations. The fact that the intensity of the C=C band of the preferred conformation (~1640 cm^{-1}) practically does not increase even in the case of almost complete disappearance of the planar conformations at 1590 cm^{-1}, as one observes in the spectra of XXVI, XXVIII, and XXIX, also constitutes evidence for a considerably lower percentage of the latter. On the basis of this it can also be assumed that the molar extinction coefficients of the $\nu_{C=C}$ bands of the planar (conjugated) conformations are considerably higher.

It can be seen from the sharp decrease in the intensity of the $\nu_{C=C}$ band (1642 cm^{-1}) of 1-vinyl-2,3-diphenylpyrrole (XXXIII) that the second phenyl substituent in the 3 position of the ring very substantially changes the electronic arrangement in the N-vinylpyrrole framework (the fraction of the unconjugated conformation decreases considerably); this is in complete agreement with the UV spectral data [14].

EXPERIMENTAL

Pyrroles I-VIII and 1-vinylpyrroles XVI-XXXIX were synthesized by reaction of the appropriate ketoximes with acetylene [1-3, 15], unsubstituted 1-vinylpyrrole ($R^2 = R^3$ = H) was synthesized by vinylation of

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* The above-noted multiplicity of some of the pyrrole bands (for example, at ~710 and ~1300 cm^{-1}) is evidently also due to rotational isomerism of the groupings.

pyrrole with acetylene, and 1-ethyl- and 1-(2'-alkylthioethyl)pyrroles IX-XV and XL-LII were obtained by selective hydrogenation [16] and thiylation [17] of 1-vinylpyrroles.

The purity of all of the samples, except 1-vinyl-2,3-diphenylpyrrole XXXIII, was monitored by gas-liquid chromatography (GLC) and was no less than 99%. Pyrrole XXXIII was purified by recrystallization from ethanol; the purified product had mp 112°, and one spot was observed when it was subjected to thin-layer chromatography (TLC) on Al_2O_3 [elution with heptane–ether (1:2)].

The IR spectra of liquid films and CCl_4 solutions of the compounds were recorded with a UR-20 spectrometer. The integral intensities of the absorption bands were measured by the method in [18].

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