RELATIVE BASICITIES OF N-VINYLPYRROLES

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The relative basicities of a series of N-vinylpyrroles and some of their analogs with saturated substituents attached to the nitrogen atom were investigated (the $\Delta\nu_{OH}$ shifts in the IR spectrum of phenol were measured). The ν_{OH} values were measured in the interval 100-150 cm^{-1}. Alkyl substituents in the 2 and 3 positions raise the basicity of the pyrrole ring, while a phenyl substituent in the 2 position lowers it. N-Vinyl-pyrroles are ~25% less basic than their limiting analogs—N-ethyl- and N-(2'-alkylthioethyl)pyrroles. The inductive effect of the substituent makes the major contribution to the basicities of the investigated pyrroles. The $\Delta\nu_{OH}$ values for N-vinyl-2,3-diphenylpyrrole are not in conformity with the general tendencies and constitute evidence for the appreciable contribution of continuous conjugation through the double bond, the pyrrole ring, and the benzene ring in the 3 position.

It is known [1, 2] that pyrroles are weak bases; however, the effect of substituents on their basicities has not been studied. Of particular interest in this respect are pyrroles with unsaturated substituents that are capable of entering into conjugation with the heteroaromatic system. An analysis of the changes in the basicities in a series of compounds of this type may give new information regarding the mechanisms of transmission of the effect through the pyrrole ring and regarding the degree and character of its aromaticity.

In order to study the effect of a vinyl group attached to the pyrrole ring through the nitrogen atom on the donor properties of the system, we measured the relative basicities of a series of N-vinylpyrroles with alkyl and phenyl substituents in the 2 and 3 positions. For comparison we also investigated the basicities of some pyrroles that have saturated substituents attached to the nitrogen atom (ethyl and alkylthioethyl). The shift of the O—H stretching vibrations in the IR spectrum of phenol ($\Delta\nu_{OH}$) due to the formation of a hydrogen bond with the pyrrole base served as a measure of the relative basicity.

The result of the measurements are given in Table 1, and typical contours of the bands observed at 3300-3620 cm^{-1} are shown in Fig. 1.

All of the investigated pyrroles form an extremely weak hydrogen bond with phenol ($\Delta\nu_{OH}$ = 90-150 cm^{-1}), inasmuch as they are even less basic than aliphatic ethers [3] and sulfides [4]. Additional bands of an H-bonded hydroxyl group with $\Delta\nu_{OH}$ = 55 and ~250 cm^{-1} (broad shoulder), which are related to H complexes with the benzene ring and the sulfur atom, are observed in the spectra of systems made up of 2-phenyl- and 1-(2'-alkylthioethyl)-substituted pyrroles and phenol. It follows from the data in Table 1 that the vinyl group appreciably lowers the basicities of pyrroles as compared with the N-alkyl-substituted analogs — saturation of the double bond increases $\Delta\nu_{OH}$ by 30-35 cm^{-1} (compare XIV, XXIII, and XXIV; XVII and XX; XVIII and XXI). Alkyl substituents in the pyrrole ring somewhat increase its basicity. For example, replacement of the hydrogen in the 3 position by an alkyl group leads to an increase of 5-10 cm^{-1} in the Δ_{OH} value (compare II and III; VII and VIII; IX and XII, XVII and XVIII; XX, XXI, and XXII). A methyl group in the 2 position increases the basicity of pyrrole by 20 cm^{-1} (compare I and II). However, a direct relationship between $\Delta\nu_{OH}$ and the electron-donor strength of the alkyl group (on the Taft scale is not observed (for either 2- or 3-alkyl-substituted compounds); this is completely understandable if one takes into

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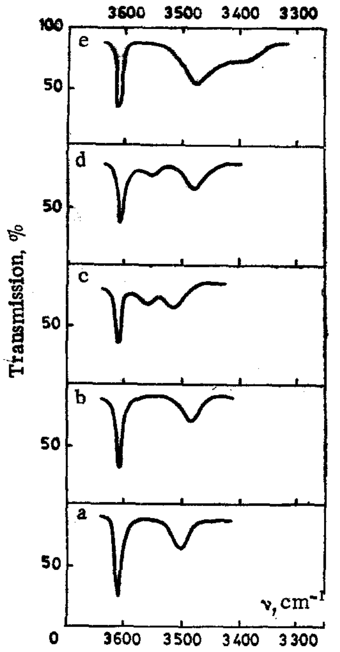


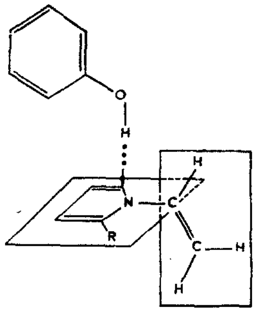


Fig. 1 Fig. 2

Fig. 1. Typical contours of the phenol O–H bands in the presence of substituted pyrroles: a) 2-methyl-N-vinylpyrrole (II); b) N-vinyl-4,5,6,7-tetrahydroindole (XIV); c) N-vinyl-2-phenylpyrrole (XVII); d) N-ethyl-2-phenylpyrrole (XX); e) N-(2'-ethylthioethyl)-4,5,6,7-tetrahydroindole (XXIII) (~ 0.4 M pyrrole and 0.02 M phenol in CCl_4).

Fig. 2. Probable orientation of the H bond between phenol and N-vinyl-2-phenyl-substituted pyrrole in the gauche conformation.

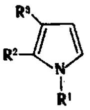
account the fact that the alkyl substituent in this case may affect the formation of an H bond not only via an inductive mechanism but also via steric and hyperconjugation mechanisms.

Replacement of a methyl group in the 2 position by a phenyl group makes a negative contribution of 10 cm^{-1} to the basicity of pyrrole (compare II and XVII and III and XVIII). A further comparison makes it possible to conclude that the character of the empirical effect of both the N-vinyl and 2-phenyl group bears little resemblance to conjugation, since their contributions to the basicity practically do not change, despite the very different geometrical conditions for the realization of coplanarity in the investigated series [5, 6]. Thus, for example, in N-vinyl-2-phenylpyrroles the planar conformations relative to the N-vinyl bond are sterically hindered, and the same is also valid for 2-tert-butyl-N-vinylpyrrole (XI).

The steric interaction of the N-vinyl group with the substituent in the 2 position may be a factor that promotes a shift in the equilibrium to favor the gauche conformer. This assumption is in agreement with the results of an analysis of the IR spectra of N-vinylpyrroles [6]. Thus the N-vinyl and 2-phenyl groups in this case act primarily as inductive acceptors of the electrons of the pyrrole ring.

Since the upper filled molecular orbital of pyrrole is a π orbital and its first ionization potential (8.20 eV) corresponds to the removal of a π electron [7], it may be assumed that the bond with the phenolic hydroxyl group is not localized on the nitrogen atom. This sort of directed character of the H bond is even less likely for the gauche conformation of N-vinylpyrroles because of the additional steric hindrance created by the vinyl group hanging over the ring. Being an analog of electrophilic attack and protonation, the H bond is most likely localized in the 2 and 5 positions of the pyrrole ring, whereas in N-vinyl-2-substituted pyrroles it is probably localized in the 5 position (Fig. 2).

Instead of the expected decrease in the basicity, a second phenyl group (in the 3 position) (XIX) clearly gives the opposite effect. Pronounced anomalies are observed for this compound during a study of the UV [5]

TABLE 1. Relative Basicities of Pyrroles  in Phenol $\Delta\nu_{OH}$ Units

Compound	R¹	R²	R³	$\Delta\nu_{OH}$, cm^{-1}
I	$CH_2{=}CH$	H	H	90
II	$CH_2{=}CH$	CH_3	H	110
III	$CH_2{=}CH$	CH_3	CH_3	117
IV	$CH_2{=}CH$	CH_3	C_3H_7-*n*	120
V	$CH_2{=}CH$	CH_3	C_3H_7-*i*	120
VI	$CH_2{=}CH$	CH_3	C_5H_{11}-*n*	120
VII	$CH_2{=}CH$	C_2H_5	H	119
VIII	$CH_2{=}CH$	C_2H_5	CH_3	126
IX	$CH_2{=}CH$	C_4H_9-*n*	H	120
X	$CH_2{=}CH$	C_4H_9-*i*	H	118
XI	$CH_2{=}CH$	C_4H_9-*t*	H	120
XII	$CH_2{=}CH$	C_4H_9-*n*	C_3H_7-*n*	125
XIII	$CH_2{=}CH$	C_6H_{13}-*n*	H	121
XIV	$CH_2{=}CH$	$-(CH_2)_4-$		120
XV	$CH_2{=}CH$	$-(CH_2)_3CH(CH_3)-$		120
XVI	$CH_2{=}CH$	$-(CH_2)_5-$		124
XVII	$CH_2{=}CH$	C_6H_5	H	100
XVIII	$CH_2{=}CH$	C_6H_5	CH_3	107
XIX	$CH_2{=}CH$	C_6H_5	C_6H_5	120
XX	C_2H_5	C_6H_5	H	135
XXI	C_2H_5	C_6H_5	CH_3	143
XXII	C_2H_5	C_6H_5	C_3H_7-*n*	145
XXIII	$(CH_2)_2SC_2H_5$	$-(CH_2)_4-$		150
XXIV	$(CH_2)_2SC_4H_9$-*n*	$-(CH_2)_4-$		150

and IR [6] spectra. All of the available data indicate the existence in pyrrole XIX of strong continuous conjugation encompassing the vinyl group, the pyrrole ring, and the phenyl substituents (evidently primarily the phenyl group in the 3 position). Thus the increased basicity of this pyrrole is probably due to the particular mobility of its π system. Specifically, this is expressed in the sharp decrease in its ionization potential, as one can conclude from an analysis of the UV spectra [5]. In good agreement with this interpretation are the fact of the absence in the spectrum of the XIX–phenol system of resolved bands related to the H bond of phenol with the benzene rings and the assumption that the H bond is not formed with the nitrogen atom but rather with the π system of pyrrole in the region where the best distribution of the positive charge is ensured, i.e., in the vicinity of the 2 and 5 positions.

EXPERIMENTAL

1-Vinylpyrroles II-XIX were obtained from the appropriate ketoximes and acetylene in accordance with the method in [8-10], N-ethylpyrroles XX-XXII were obtained by hydrogenation of the N-vinylpyrroles under the conditions in [11], and 1-(2-alkylthioethyl)pyrroles XXIII and XXIV were obtained by homolytic addition of mercaptans to the N-vinylpyrroles by the method in [12]. The purity of the compounds was monitored by PMR and IR spectroscopy and gas–liquid chromatography (GLC) (with a Khrom-4 chromatograph with a catharometer detector; the column was 2.5 m long and 3 mm in diameter, the solid phase was Chromaton N-AW-DMCS, the liquid phase was 15% DS 550 silicone, the thermostat temperature was 100-200°, and the carrier gas was helium); in most cases the purity was no less than 99%. Thin-layer chromatography (TLC) on Al_2O_3 [elution with heptane–ether (1 : 2)] was used to verify the purity of the high-boiling N-vinyl-2,3-diphenylpyrrole. The samples were purified particularly thoroughly to remove traces of the accompanying N-substituted impurities: the complete absence of absorption in the region of N–H stretching vibrations (3300-3600 cm^{-1}) was achieved for 0.3-0.4 M solutions in CCl_4 at an absorbing-layer thickness of 5 mm. The IR spectra of 0.3-0.4 M pyrrole and 0.01-0.02 M phenol solutions in CCl_4 were recorded with a UR-20 spectrometer at layer thicknesses of 4.5-5 mm.

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PORPHYRINS

VI.* ABSORPTION SPECTRA AND ASSOCIATION OF METAL COMPLEXES OF meso-FORMYLETIOPORPHYRIN

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A magnesium complex of meso-formyletioporphyrin I (FEP) was obtained by reaction of FEP with methylmagnesium iodide. The electronic and IR spectra of FEP and its complexes with copper, zinc, nickel, cobalt, and magnesium in solutions and crystalline films were investigated. It is shown that the changes in the electronic spectra as the temperature of the solutions is lowered are due to association of the molecules of the metal complexes (M–FEP) of the metal–formyl type. Association of the molecules in solid films is accomplished through $\pi-\pi$ electron interaction of the porphyrin rings. The Mg–FEP complex, the molecules of which associate through a metal–formyl interaction both in solution and in films, constitutes an exception to this.

meso-Formylporphyrins have weaker reactivities with respect to the carbonyl group than the sterically unhindered β-formylporphyrins or aromatic aldehydes. For example, the formation of Schiff bases, oximes, hydrazones, and other carbonyl-group derivatives proceeds only at high temperatures [2-5].

During a study of the reaction of meso-formyletioporphyrin I (FEP) with a Grignard reagent in ether we observed that the reaction product has an unusual electronic spectrum in which the α and β bands in the visible region of the spectrum that are characteristic for metal complexes were practically absent and an intense broad band at 650-670 nm was present. Treatment of this substance with trifluoroacetic acid gave FEP, and this unambiguously indicated retention of the meso-formyl group in the reaction of porphyrin with methylmagnesium iodide and the formation of only Mg–FEP as a result of the reaction. Attempts to obtain Mg–FEP in the crystalline state were unsuccessful, since a polymeric dark-green film, which sub-

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* For communication V, see [1].

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