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 $\nu_{OH}$ 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 $\sim 25\%$ 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 heterocyclic 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 $\sim 250$ 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 substituent 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 $\Delta \nu_{OH}$ 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
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 CCl₄).

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 conformation. 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) (XXI) clearly gives the opposite effect. Pronounced anomalies are observed for this compound during a study of the UV [5]