# PYRROLES FROM KETOXIMES AND ACETYLENE.

# 14.* QUANTITATIVE ESTIMATE OF THE EFFECT OF SUBSTITUENTS ON THE NH ACIDITIES OF PYRROLES

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The pK values of a series of substituted pyrroles and the $\Delta\nu_{NH}$ values (in dimethylformamide), which characterize their relative acidities were measured by the transmetallation method. It was established that the acidities of pyrroles are determined primarily by the inductive effect of the substituents and are virtually independent of the ability of the latter to enter into conjugation with the ring. This means that the electron pair of the anion that is set free in the ionization of pyrrole retains σ character. The linear dependences of the pK and $\Delta\nu_{NH}$ values on the inductive constants ($\sigma_I$) of the substituents can be used to estimate the pK values of various compounds that contain a pyrrole ring starting from the $\Delta\nu_{NH}$ and $\sigma_I$ values.

The unusual character of heterocycles of the pyrrole series is determined in many respects by their ability to undergo ionization at the N–H bond. However, the information available on the acidities of pyrroles is still scanty. It is limited to the $pK_a$ values of 15 NH acids of this type measured in aqueous alkaline solutions (see [2, 3] and the literature cited therein). The only conclusion that follows from these data is of qualitative character, viz., that electron acceptors increase the acidity of the NH group and that they are more effective from the α position than from the β position [3], whereas the quantitative relationships between the acidities of pyrroles and the structures of the substituents may substantially supplement our knowledge of the electron distribution in this important heteroaromatic system and open up another way to predict its reactivity.

The reaction of ketoximes with acetylene, which has made pyrroles with diverse substituents readily accessible, has become a reliable synthetic basis for the systematic quantitative analysis of structurally functional bonds in the pyrrole series [4-6]. We used this method to synthesize a series of substituted pyrroles (Table 1), and we measured the pK values in dimethyl sulfoxide (DMSO) by the transmetallation method [7] to study their NH ionization (Table 2); we also compared the acidities by characterizing the strengths of the hydrogen bonds with dimethylformamide (DMF) in $CCl_4$ from data from the IR spectra (Table 3).

The pK values of pyrrole and substituted pyrroles presented in Table 2 are relative: they were determined with respect to 9-phenylfluorene (pK 18.5) as the standard. Their difference from the absolute pK scale in DMSO [19] based on potentiometric measurements with a hydrogen electrode is 0.6 log units on the lower acidity side. The pK value that we found for pyrrole (I in Table 2) differs from the $pK_a$ value (17.51 ± 0.05) established by the method of the $H_-$ function in aqueous solution [3] (we obtained pK 17.6 ± 0.1 by the same method). The higher acidity of pyrrole in water is explained by stabilization of the N anion due to the formation of a hydrogen bond (see [10] for a more detailed discussion). The transmetallation method (with $Li^+$ as the gegenion) also gives a low pK value (18.2) for pyrrole in an aprotic solvent with a low dielectric permeability, viz., 1,2-dimethoxyethane (DME). The increase in the acidity as compared with the acidity in DMSO is due to

*See [1] for communication 13.

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TABLE 1. Physicochemical Constants and Results of Analysis of the Pyrroles

| Compound | Pyrrole, substituents | bp, °C (mm), mp, °C | $d_4^{20}$ | $n_D^{20}$ | Found, % | | | Empirical formula | Calc., % | | | UV spectrum[a], $\lambda_{max}$, nm (log ε) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | | C | H | N | |
| I | 2-Me | 75—76 (50) | 0,9426 | 1,5010 | 74,0 | 8,6 | 17,1 | $C_5H_7N$ | 74,0 | 8,7 | 17,3 | 217 (3,91) |
| II | 2-Me, 3-Me | 69—70 (30) | 0,9322 | 1,4990 | 75,8 | 9,5 | 14,6 | $C_6H_9N$ | 75,7 | 9,5 | 14,7 | 212 (3,89) |
| III | 2-Me, 3-Et | 71—72 (13) | 0,9223 | 1,4990 | 76,7 | 9,9 | 12,4 | $C_7H_{11}N$ | 77,0 | 10,0 | 12,8 | 213 (3,95) |
| IV | 2-Me, 3-*n*-Pr | 71—72 (5) | 0,9071 | 1,4935 | 78,1 | 10,6 | 11,2 | $C_8H_{13}N$ | 78,0 | 10,6 | 11,4 | 213 (3,90) |
| V | 2-Et, 3-Me | 60—61 (4) | 0,9206 | 1,5010 | 77,3 | 9,9 | 12,9 | $C_7H_{11}N$ | 77,0 | 10,2 | 12,8 | 224 (3,83) |
| VI | 2-*i*-Pr, 3-Me | 69—70 (5) | 0,9240 | 1,4910 | 78,3 | 10,5 | 11,2 | $C_8H_{13}N$ | 78,0 | 10,6 | 11,4 | — |
| VII | 2-*n*-Pr, 3-Et | 84—85 (3) | 0,8365 | 1,4950 | 79,3 | 11,0 | 10,4 | $C_9H_{15}N$ | 78,8 | 11,0 | 10,2 | 222 (3,87) |
| VIII | 2-*n*-Bu, 3-Pr | 90—91 (1) | 0,8800 | 1,4860 | 80,0 | 11,6 | 8,6 | $C_{11}H_{19}N$ | 79,9 | 11,6 | 8,5 | 222 (3,89) |
| IX | 2-*t*-Bu | 32 | — | — | 78,3 | 10,5 | 11,2 | $C_8H_{13}N$ | 78,0 | 10,6 | 11,4 | — |
| X | 2,3-$(CH_2)_4$-(4,5,6,7-Tetrahydroindole | 50 | — | — | 79,2 | 8,9 | 11,3 | $C_8H_{11}N$ | 79,3 | 9,1 | 11,6 | 222 (3,87) |
| XI | 2,3-Pentamethylene-pyrrole | 102 | — | — | 79,8 | 9,4 | 10,4 | $C_9H_{13}N$ | 80,0 | 9,5 | 10,4 | 224 (3,89) |
| XII | 2-*t*-Bu, 5-$COCF_3$ | 106 | — | — | 54,6 | 5,4 | 6,4 | $C_{10}H_{12}F_3NO$[b] | 54,8 | 5,5 | 6,4 | 253 (3,63) 310 (4,36) |
| XIII | 2-Ph | 129 | — | — | 83,6 | 6,8 | 9,6 | $C_{10}H_9N$ | 84,0 | 6,3 | 9,8 | 205 (4,32), 219 (4,06) 222 (4,04), 237 (3,97) 287 (4,46), 305 (4,21) |
| XIV | 2-Ph, 3-Et | 121—122 (1) | 1,0467 | 1,5950 | 84,1 | 7,8 | 7,8 | $C_{12}H_{13}N$ | 84,2 | 7,7 | 8,2 | — |
| XV | 2-Ph, 3-Ph | 127 | — | — | 87,1 | 5,9 | 6,2 | $C_{16}H_{13}N$ | 87,6 | 5,9 | 6,3 | 202 (4,31), 242 (4,08) 248 (4,04), 297 (3,95) |
| XVI | 2-Ph, 5-Ph | 143 | — | — | 88,1 | 5,9 | 6,2 | $C_{16}H_{13}N$ | 87,7 | 5,9 | 6,3 | 208[c] (4,13), 232 (4,05) 327 (4,48) |
| XVII | 2-Ph, 5-$COCF_3$ | 158—159 | — | — | 60,4 | 3,5 | 5,9 | $C_{12}H_8F_3NO$[d] | 60,5 | 3,4 | 5,9 | 235 (4,10), 341 (4,52) |
| XVIII | 2-(4′-PhO)Ph | 152—154 | — | — | 81,6 | 5,4 | 5,6 | $C_{16}H_{13}ON$ | 81,4 | 5,5 | 5,9 | — |
| XIX | 2-(2′-$C_4H_4S$), Thienyl | 62 | — | — | 64,6 | 4,7 | 9,1 | $C_8H_7NS$[e] | 64,4 | 4,7 | 9,4 | — |
| XX | 4,5-Dihydrobenzo[g]-indole | 109 | — | — | 84,9 | 6,9 | 8,1 | $C_{12}H_{11}N$ | 85,2 | 6,6 | 8,3 | — |

[a]In hexane. [b]Found: F 26.0%. Calculated: F 26.0% [c]In alcohol. [d]Found: F 24.1%. Calculated: F 24%. [e]Found: S 21.6%. Calculated: S 21.5%.

TABLE 2. Equilibrium NH Acidities of Pyrroles in DMSO (298°K)

| Compound | Pyrrole, substituents | Indicator[a] | $K_{eq}$ | n[b] | pK[c] | $\Sigma\sigma_I$[d] |
|---|---|---|---|---|---|---|
| I | Unsubstituted | Fluorene (22.9) | 0,41±0,03 | 4 | 23,3[e] | 0 |
| II | 2-Me | 9-tert-Butylfluorene (24.6) | 1,2±0,2 | 3 | 24,5 | −0,08 |
| III | 2-Me, 3-Me | " " | 0,47±0,06 | 3 | 24,9 | −0,12 |
| IV | 2-Me, 3-Et | " " | 0,26±0,06 | 4 | 25,2 | −0,11 |
| V | 2-Me, 3-*n*-Pr | Tetraphenylpropene (26.2) | 6,8±1,2 | 3 | 25,4 | −0,11 |
| VI | 2-Et, 3-Me | 9-tert-Butylfluorene | 0,26±0,04 | 3 | 25,2 | −0,09 |
| VII | 2-*n*-Pr, 3-Et | " " | 0,24±0,03 | 4 | 25,2 | −0,08[f] |
| VIII | 2,3-$(CH_2)_4$-(4,5,6,7-Tetrahydroindole) | " " | 0,41±0,04 | 3 | 25,0 | −0,03[f] |
| IX | 2-*t*-Bu | " " | 1,0±0,1 | 4 | 24,6 | −0,07 |
| X | 2-*t*-Bu, 5-$COCF_3$ | 4-Nitrobenzanilide (15.4) | 0,34±0,06 | 6 | 15,9 | 0,41 |
| XI | 2-Ph | 9-Benzylfluorene (21.8) | 1,7±0,2 | 6 | 21,6 | 0,08 |
| XII | 2-Ph, 3-Ph | " " | 4,1±0,4 | 5 | 21,2 | 0,12 |
| | | 3,5-Dimethylpyrazole (22.0) | 0,8±0,1 | 3 | 21,1 | |
| XIII | 2-Ph, 5-Ph | 9-Phenylfluorene (18.5) | 0,029±0,002 | 3 | 20,0 | |
| | | Pyrazole (20.4) | 2,3±0,1 | 3 | 20,0 | 0,16 |
| XIV | 2-Ph, 5-$COCF_3$ | Ethyl 4-nitrophenylacetate (15.1) | 18,2±0,6 | 5 | 13,8 | 0,56 |
| XV | 2-(4′-PhO)Ph | Fluorene | 2,5±0,5 | 5 | 22,5 | 0,09[g] |
| XVI | 2-(2′-$C_4H_4S$), Thienyl | 9-Benzylfluorene | 16,5±2 | 6 | 20,6 | 0,17[h] |
| | | Pyrazole | 0,41±0,3 | 3 | 20,8 | |
| XVII | 4,5-Dihydrobenzo[g]-indole | 9-Benzylfluorene | 0,42±0,04 | 3 | 22,2 | 0,06[f] |

[a]The pK values of the indicator acids (hydrocarbons [7], ethyl 4-nitrophenylacetate [8], 4-nitrobenzanilide [9], and azoles [10]) are indicated in parentheses. [b]This is the number of determinations of the $K_{eq}$ value. [c]$pK = pK_{initiator} - \log K_{eq}$. [d]In the case of 2,3-disubstituted pyrroles (II-VIII, XII, and XVII) it was assumed that: $\Sigma\sigma_I = \sigma_{I(2-R)} + 0.5\sigma_{I(3-R)}$ (see the text); the $\sigma_I$ values of substituents R, except for those noted in footnotes f and h, were taken from a handbook [11]; on the basis of the closeness of the σ* values for Et, n-Pr, and n-Bu (see [11]) it was assumed that $\sigma_I(n\text{-Pr}) \simeq \sigma_I(n\text{-Bu}) \simeq \sigma_I(Et)$. [e]In 1,2-dimethoxyethane (DME) pK = 18.2 for protonation of $Li^+$ (with 2-cyanofluorene as the indicator, pK 18.3 [7], $K_{eq} = 1.3 \pm 0.6$, and n = 6) and pK = 22.0 for protonation of $Cs^+$ (with benzanthrene as the indicator, pK 21.3 [12], $K_{eq} = 0.2 \pm 0.02$, n = 4). [f]The $\Sigma\sigma_I$ values were calculated for both 2,3-diethylpyrrole and 3-ethyl-2-phenylpyrrole. [g]Assumed as for the 4-$MeOC_6H_4$ grouping, the $\sigma_I$ value of which was calculated from the equation in [13] from the $pK_a$ of 4-$MeOC_6H_4CH_2COOH$ (4.36) [14]. [h]Calculated by an additive scheme as for MeCH=C(SMe) with the use of the σ* values from [13]: 0.34 for MeCH=CH, and 1.44 for SMe; according to [13, 15], $Z_{sp^2} = 0.5$ (it was assumed [11] that $\sigma^* = 6.2\sigma_I$).

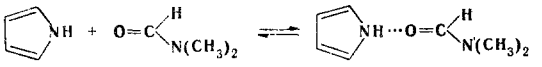
additional stabilization of the N anion as a consequence of interionic interaction (see [7-10] regarding this). When $Li^+$ is replaced by a cation with a large radius ($Cs^+$) the ionic interaction becomes appreciably weaker, and in this case the pK value in DME is much closer to the value established in DMSO, although it does differ by 1.3 log units (see the pK value for I in Table 2 and footnote e). A similar situation was also previously noted in the case of NH acids of a different type, viz., N-phenylcarbamates [20]. It follows from the above information that the pK values of pyrrole and substituted pyrroles determined in DMSO (Table 2) reflect to a lesser degree the effect of external factors on the stabilities of the N anions in solution and are therefore more suitable for comparison of the structural effects than the results of measurements in water and DME.

TABLE 3. Relative NH Acidities of Pyrroles According to the IR Spectroscopic Data (the Shifts of the Bands of the Vibrations of the N–H Bonds and the Enthalpies of Formation of the Hydrogen Bonds)

| Compound | Pyrrole, substituent | ν, cm$^{-1}$ [a] | | $\Delta\nu_{NH}$, cm$^{-1}$ | $n$ [b] | ΔH, kcal/mole [c] | | |
|---|---|---|---|---|---|---|---|---|
| | | I | II | | | III | IV | V |
| I | Unsubstituted | 3498 | 3358 | 140±2 | 4 | 3,5 | 3,7 | 3,7 |
| II | 2-Me | 3492 | 3360 | 132±2 | 3 | 3,4 | 3,5 | 3,6 |
| III | 2-Me, 3-Me | 3497 | 3368 | 129±1 | 3 | 3,4 | 3,5 | 3,6 |
| IV | 2-Me, 3-Et | 3495 | 3369 | 126±2 | 3 | 3,4 | 3,4 | 3,6 |
| V | 2-Me, 3-*n*-Pr | 3495 | 3367 | 128±2 | 3 | 3,4 | 3,5 | 3,6 |
| VI | 2-Et, 3-Me | 3491 | 3367 | 124±3 | 2 | 3,3 | 3,4 | 3,5 |
| VII | 2-*n*-Pr, 3-Et | 3492 | 3366 | 126±2 | 3 | 3,4 | 3,5 | 3,6 |
| VIII | 2-*i*-Pr, 3-Me | 3500 | 3367 | 123±3 | 2 | 3,3 | 3,4 | 3,5 |
| IX | 2-*n*-Bu, 3-*n*-Pr | 3490 | 3365 | 125±2 | 3 | 3,3 | 3,4 | 3,5 |
| X | 2,3-$(CH_2)_4$ | 3493 | 3366 | 127±2 | 3 | 3,4 | 3,5 | 3,6 |
| XI | 2,3-$(CH_2)_5$ | 3490 | 3364 | 126±2 | 2 | 3,4 | 3,5 | 3,6 |
| XII | 2-*t*-Bu | 3499 | 3369 | 130±3 | 3 | 3,4 | 3,5 | 3,6 |
| XIII | 2-*t*-Bu, 5-$COCF_3$ | 3460 | 3200 | 260±5 | 3 | 5,0 | 5,1 | 5,1 |
| XIV | 2-Ph | 3496 | 3340 | 156±2 | 2 | 3,7 | 3,9 | 3,9 |
| XV | 2-Ph, 3-Et | 3490 | 3340 | 150±1 | 3 | 3,6 | 3,8 | 3,9 |
| XVI | 2-Ph, 3-Ph | 3487 | 3322 | 165±2 | 5 | 3,8 | 4,0 | 4,1 |
| XVII | 2-Ph, 5-Ph | 3488 | 3330 | 158±2 | 3 | 3,7 | 3,8 | 4,0 |
| XVIII | 2-Ph, 5-$COCF_3$ | 3450 | 3175 | 275±5 | 3 | 5,2 | 5,3 | 5,2 |
| XIX | 2-(4′-PhO)Ph | 3495 | 3340 | 155±3 | 3 | 3,7 | 3,9 | 4,0 |

[a] Compound I is free pyrrole, and II is pyrrole tied up in an H complex. [b] Number of measurements. [c] Calculated from the formulas: $-\Delta H = (0.0123 \pm 0.0006)\Delta\nu_{NH} + (1.8 \pm 0.1)$ (III) [16], $\Delta\nu_{NH} - 20 = 9(\Delta H)^2$ (IV) [17], and $\Delta\nu_{NH} = 10(\Delta H)^2$ (V) [18].

The ability of pyrroles to form hydrogen bonds was estimated from the shift of the band of the stretching vibrations of the N–H bond ($\Delta\nu_{NH}$) under conditions that exclude intermolecular association of pyrroles (see the experimental section). These stretching vibrations are displayed in the IR spectrum as two bands: a narrow weak band (free pyrrole) and a broad intense band (pyrrole participating in the formation of an H complex with DMF). Some typical IR spectra of pyrrole–DMF systems in the $\nu_{NH}$ region are shown in Fig. 1. According to [16], as in other similar cases, the difference $\Delta\nu_{NH} = \nu_{NH}^{free} - \nu_{NH}^{assoc}$ is proportional to the enthalpy (ΔH) of the reaction to form the H complex:



The ΔH values calculated on the basis of $\Delta\nu_{NH}$ from independent empirical formulas [16–18] (Table 3) are in good agreement with one another and can be regarded as reliable.

The relationship between the pK and $\Sigma\sigma_I$ (the sum of the inductive constants of the substituents) values is shown in Fig. 2 (line 1); in the case of 2,3-disubstituted compounds the $\Sigma\sigma_I$ value is understood to be the sum $\sigma_{I(2\text{-}R)} + 0.5\sigma_{I(3\text{-}R)}$, which takes into account (see [15]) the fact that the inductive effect of the substituents in the 3 position and in positions more remote from the NH group than the substituents in the 2 position is weaker by a factor of approximately two. A good correlation between the pK and $\Sigma\sigma_I$ values that encompasses all of the data in Table 2 is available:

$$pK = (23.4 \pm 0.1) - (17.4 \pm 0.5)\Sigma\sigma_I, \quad (1)$$
$$r = 0.994;\ S_0 = 0.37;\ n = 17$$

The analogous correlation (Fig. 2, line 2) for the shifts of the band of the vibrations of the NH bond, $\Delta\nu_{NH} - \Sigma\sigma_I$, is poorer (in the case of XI in Table 3 the $\Sigma\sigma_I$ value was calculated as for 2-ethyl-3-propylpyrrole; see footnote e in Table 2):

$$\Delta\nu_{NH} = (144 \pm 2) + (229 \pm 12)\Sigma\sigma_I, \quad (2)$$
$$r = 0.976;\ S_0 = 9.7;\ n = 19$$

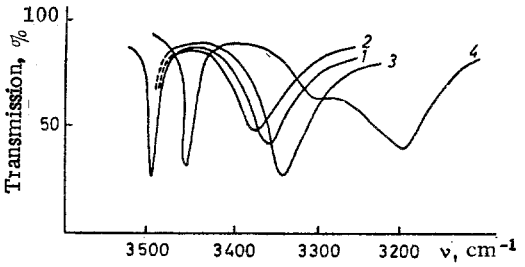



Fig. 1. IR spectra of pyrroles in the presence of DMF: 1) pyrrole; 2) 2-tert-butylpyrrole; 3) 2-phenylpyrrole (the high-frequency maxima of spectra 1-3 coincide); 4) 2-tert-butyl-5-trifluoroacetylpyrrole (the maximum at 3320 $cm^{-1}$ is the residual absorption of the intermolecular associate) (pyrrole concentration 0.01 M, DMF concentration 0.1 M, $CCl_4$).

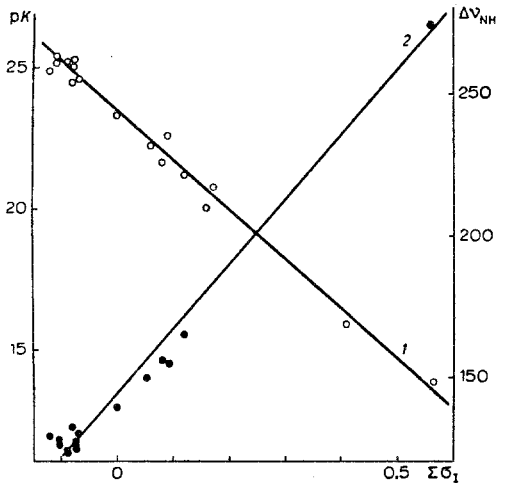



Fig. 2. Dependence of the pK (1) and $\Delta\nu_{NH}$ (2) values of pyrroles on $\Sigma\sigma_I$.

The points for two disubstituted pyrroles, viz., XIII and XVII (Table 3), deviate significantly (by 21-23 $cm^{-1}$) from this line in opposite directions. A comparison of dependences (1) and (2) shows that 2,5-disubstituted pyrroles behave anomalously only when a hydrogen bond is formed with DMF.

A possible reason for the depression of the acidity of 2,5-diphenylpyrrole as compared with the $\Delta\nu_{NH}$ valuepredicted from Eq. (2) is steric hindrance on the part of both phenyl groups to drawing together of a DMF molecule and the NH group of pyrrole. The decrease in the acidity of pyrrole XIII (Table 3) is evidently due to the presence in it of an intramolecular hydrogen bond. In any case, when one compares the data on the acidities of substituted pyrroles that were established by two methods, it is expedient to exclude 2,5-disubstituted compounds from consideration.

A good linear dependence exists between the pK values of pyrroles that contain substituents in the 2 and 3 positions and the corresponding $\Delta\nu_{NH}$ values:

$$pK = (38.4 \pm 0.8) - (0.105 \pm 0.006)\Delta\nu_{NH}, \quad (3)$$
$$r = 0.985;\ S_0 = 0.27;\ n = 12$$

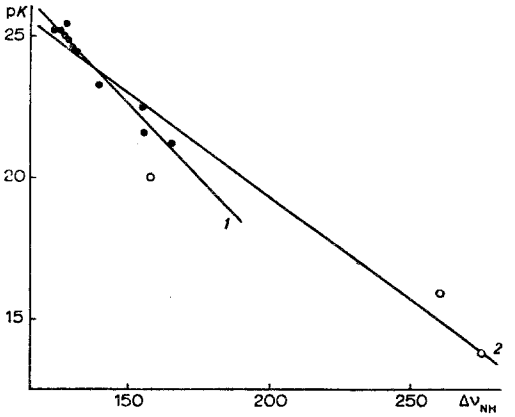



Fig. 3. Relationship between the pK and $\Delta\nu_{NH}$ values of pyrroles: line 1 corresponds to Eq. (3), line 2 corresponds to Eq. (4), and O pertains to 2,5-disubstituted pyrroles.

Thus, the two methods for estimation of the acidities of substituted pyrroles in general give similar results. In this connection, it is interesting to note that the exclusion of only 2,5-diphenylpyrrole from consideration makes it possible to obtain an extremely good linear relationship between the pK and $\Delta\nu_{NH}$ values:

$$pK = (34.1 \pm 0.5) - (0.072 \pm 0.003)\Delta\nu_{NH}, \quad (4)$$
$$r = 0.990;\ S_0 = 0.51;\ n = 14$$

It turns out to be even somewhat better than expression (3) with respect to the correlation coefficients and the errors in the regression coefficients; however, its standard of regression is almost double the value in (3), which is associated with the significant scatter of some of the points relative to the corresponding line (Fig. 3).

The results make it possible to conclude that the acidities of the investigated pyrroles are determined primarily by the inductive effect of the substituents and are almost independent of the ability of the latter to enter into conjugation with the ring. In the light of the generally accepted concept of resonance stabilization of the pyrrole anion [3], this conclusion seems as much unexpected as it is fundamental. It means that, with respect to its electronic structure, the pyrrole anion is identical to pyrrole, i.e., the electron pair of the anion that is set free by detachment of a proton retains $\sigma$ character. Inasmuch as it is located in the nodal plane of the ring $\pi$ electrons, it is naturally incapable of interacting with it via a conjugation mechanism but rather senses the effect of the substituents primarily along the $\sigma$ skeleton. The results of a correlation treatment of the literature [2, 3] $pK_a$ values (in aqueous solutions), for which we found the relationship

$$pK_a = (16.5 \pm 0.8) - (10.6 \pm 1.2)\Sigma\sigma_I, \quad (5)$$
$$r = 0.95;\ S_0 = 1.3;\ n = 12$$

constitute evidence in favor of this conclusion. If one takes into account the fact that the correlated $pK_a$ values were taken from various studies and were obtained by various methods, the very fact of satisfaction of this dependence is noteworthy, especially since correlation (5) encompasses primarily pyrroles that have several substituents such as CHO, $CO_2C_2H_5$, $NO_2$, and halogens, which are known for their high tendency for conjugation interactions of a different type. The exclusion from the correlation of the point for 2-carbomethoxy-4-nitropyrrole, which deviates markedly from the regression line, leads to an equation with substantially better criteria of linearity:

$$pK_a = (16.6 \pm 0.6) - (10.5 \pm 0.9)\Sigma\sigma_I, \quad (6)$$
$$r = 0.97;\ S_0 = 1.0;\ n = 11$$

The noncoincidence of the regression coefficients of (1) and (6) is explained by the difference in the pK scales for solutions in DMSO and water.

Thus the linear dependence of the acidities of pyrroles on the inductive constants of their substituents should be regarded as a general principle. The (1)-(6) dependences found can, with allowance for the stipulations stated above, be used to estimate the pK values of the most diverse compounds that contain a pyrrole ring starting from the $\Delta\nu_{NH}$ or $\sigma_I$ values of the substituents.

## EXPERIMENTAL

The substituted pyrroles (Table 1) were synthesized by the reaction of ketoximes with acetylene under the conditions in [5, 6], while the 5-trifluoroacetyl derivatives were obtained by acylation of the corresponding 5-unsubstituted pyrroles with trifluoroacetic anhydride in the presence of pyridine [21]. The purity of the compounds was monitored by gas–liquid chromatography (GLC) and PMR and IR spectroscopy and in most cases was 98-99%. Analysis by GLC was carried out with a Khrom-4 chromatograph with a catharometer as the detector; the column was 2.5-m long and had a diameter of 3 mm, the solid phase was Chromaton N-AW-DMCS, the liquid phase was 15% DS-550 silicone, and the carrier gas was helium.

The DMF and $CCl_4$ were purified by the method in [22]. The IR spectra were recorded with a UR-20 spectrometer at room temperature; the concentration of the pyrroles ranged from 0.01 to 0.1 M, the DMF concentration ranged from 0.1 to 1.0 M, and the thickness of the absorbing layer ranged from 0.01 to 0.1 cm. Different rates of recording the spectra were used, and a solution of DMF in $CCl_4$ of the same concentration as in the cuvette containing the pyrrole was placed in the reference beam.

The method for the spectrophotometric (with an SF-4A spectrophotometer) determination of the $K_{eq}$ values in thoroughly purified DMSO with the use of a seamless-soldered evacuable apparatus was similar to the method used in [7-10]. The residual absorption of the UV band (the maximum was generally located below 340 nm) of the spectra of the N anions of the pyrroles was taken into account in the calculation of the concentration equilibrium constants (the reagent concentrations ranged from $10^{-4}$ to $10^{-3}$ M). The maxima in the near-UV region (>340 nm) were recorded for a number of the N anions: 350 (XVI), 360 (XII), and 385 nm (XIII) (the numbers of the compounds correspond to the numbers indicated in Table 2).

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