it was cooled and chromatographed with a column (3.5 × 30 cm) packed with silica gel. The principal fraction was evaporated to dryness, the residue was refluxed in 50 ml of $CCl_4$ for 5 min, and the mixture was filtered. The solid material was dissolved in 10 ml of concentrated $H_2SO_4$; after 1 h, the mixture was poured over 100 g of ice, and the substance was extracted with three 50-ml portions of chloroform. The solvent was evaporated in vacuo to give 20 mg of a mixture of porphyrins XXIV and XXV containing, according to the mass-spectral data, 20-25% admixed porphyrin XXVI. To obtain a sample of XXIV/XXV that does not contain porphyrin XXVI a part of the product was chromatographed on plates with Silufol by elution with chloroform with ventilation of the plate with ammonia vapors. Porphyrin XXVI had $R_f$ 0.7, and XXIV/XXV had $R_f$ 0.5. Mass spectrum of XXIV/XXV: 502 ($M^+$, 100), 487 (37), 473 (10). UV spectrum, $\lambda_{max}$ (intensity ratio): 404 (14.4), 504 (1.0), 540 (0.37), 569 (0.43), 620 nm (0.28). PMR spectrum of XXIV/XXV ($CDCl_3$ + 1% $CF_3COOH$): 10.60 and 10.44 (meso-H, XXV); 10.53 (s, meso-H, XXIV); 5.70 (m, $5^1,15^1$-$CH_2$); 4.44 (m, $3^1,13^1,17^1$-$CH_2$); 4.18 and 4.17 (q, $CH_2CH_3$); 3.70 (s, $CH_3$, XXV); 3.73 (s, $CH_3$, XXIV); 2.0 and 1.77 (two t, $CH_2CH_3$, XXV); 1.98 and 1.80 (t, $CH_2CH_3$, XXIV); −4.43 ppm (s, NH).

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# Z,E ISOMERISM OF 1-FORMYL- AND 1-ACETYL-2-PYRAZOLINES

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The conformational equilibrium in the 1-acyl-2-pyrazoline series caused by retarded rotation about the $N_{(1)}$—CO bond in the case of protonation of the $N_{(2)}$ atom was studied by NMR spectroscopy.

It was previously established by measurement of the dipole moments and PMR spectroscopy that 1-acyl-2-pyrazolines in low-polarity solvents exist in the s-trans form relative to the $N_{(1)}$—Co bond (E isomers) because of repulsion of the like-charged nitrogen and oxygen atoms [1, 2]. It might be assumed that in solvents with high dielectric permeabilities, which partially compensate this effect, the probability of the existence of the Z conformer increases, particularly in the case of favorable steric factors. Precisely this principle is followed in related series of hydrazides [3], acylhydrazones [4], and acylamidrazones [5]. In addition, it has been shown [4] that 1-formyl-3,5,5-trimethyl-2-pyrazoline, which is the E isomer in $CCl_4$, is a mixture of the Z and E forms in aqueous solution. Taking this into account, we examined the phenomenon of Z, E isomerism for a series of 1-formyl- and 1-acetyl-2-pyrazolines (I-XIV) by means of $^1H$ and $^{13}C$ NMR spectroscopy (see scheme on following page).

The data from the PMR spectra of I-XIV in inert and low-polarity solvents are in complete agreement with the data presented in [1, 2] and indicate the existence of a single isomer.

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TABLE 1. Chemical Shifts of the Protons of the Acyl Substituent of 2-Pyrazolines

| Compound* | $R^3$ | $R^4$ | Chemical shift, ppm (J, Hz) | | | Relative amt. of the Z form, % |
|---|---|---|---|---|---|---|
| | | | $CDCl_3$, E form | $CF_3COOH$ | | |
| | | | | E form | Z form (s) | |
| I | H | $CH_3$ | 8,74 t (0,9) | 8,58 t (1,1) | — | — |
| II | $CH_3$ | H | 8,78 d (0,9) | 8,68 d (1,1) | 8,08 | 10 |
| III | $CH_3$ | $C_6H_5$ | 8,85 d (0,8) | 8,65 d (1,1) | —** | 20 |
| IV | $C_6H_5$ | H | 8,87 d (0,9) | 8,65 d (1,0) | 7,68 | 25 |
| V | $C_6H_5$ | $CH_3$ | 8,72 d (0,9) | 8,42 d (1,2) | 7,68 | 30 |
| VI | $C_6H_5$ | $C_6H_5$ | 8,93 d (0,9) | 8,68 d (1,0) | 7,72 | 40 |
| VII | $CH_3$ | $CH_3$ | 8.65 s | 8,53 s | 7,92 | 35 |
| VIII | H | $C_6H_5$ | 2,33 s | 2,42 s | 2,14 | 15 |
| IX | $CH_3$ | H | 2,27 s | 2,25 s | — | — |
| X | $CH_3$ | $C_6H_5$ | 2.32 s | 2,43 s | — | — |
| XI | $C_6H_5$ | H | 2,22 s | 2,21 s | 1.72 | 20 |
| XII | $C_6H_5$ | $CH_3$ | 2,25 s | 2,27 s | 1,75 | 30 |
| XIII | $C_6H_5$ | $C_6H_5$ | 2.28 s | 2.41 s | 1,87 | 30 |
| XIV | $CH_3$ | $CH_3$ | 2,20 s | 2,30 s | — | — |

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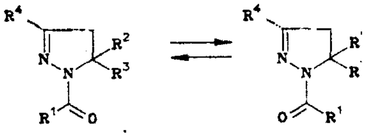
*I-VII $R^1$ = h, VIII-XIV $R^1$ = $CH_3$; I-VI, VIII-XIII $R^2$ = H, VII, XIV $R^2$ = $CH_3$.

**Covered by the signal of the aromatic protons. The isomer ratios were estimated from the doublet signals of the 5-$CH_3$ groups (1.16 ppm for the E form, and 1.25 ppm for the Z form).



E- I-XIV Z-

Let us note that spin-spin coupling (J = 0.8-0.9 Hz) is observed between the formyl and 5-H protons in the spectra of I-VI; this is yet another indication that pyrazolines I-VI have an E conformation. Similar long-range coupling is manifested between the formyl proton and the α protons of the N-alkyl substituents in the case of their trans orientation in N-alkylformamides [6]. As one should expect, a long-range spin—spin coupling constant (SSCC) is absent in the case of VII.

When 1-acylpyrazolines I-XIV are dissolved in trifluoroacetic acid, doubling of the number of signals in the $^1H$ and $^{13}C$ NMR spectra is observed in most cases. It should be noted that trifluoroacetic acid protonates these compounds at the $N_{(2)}$ atom (see below), and the results discussed in this paper pertain to the protonated state of 1-acyl-2-pyrazolines.* The doubling of the signals [precisely those that are most sensitive to a change in the orientation of the carbonyl group ($R^1$, $C_{(3)}$, $C_{(5)}$)] that is observed in the spectra is evidently due to development of the Z isomer.

In fact, a long-range SSCC for the signal of the formyl proton of the minor Z form is absent in the PMR spectra of formyl derivatives II and IV-VI, while the signal of the preponderant E isomer of II-VI is split due to coupling with the 5-H proton, as in the case of I. This, on the one hand, makes it possible to realize the assignment of the signals and, on the other, to estimate the relative percentages of the Z and E forms from their intensities. Additional confirmation of the correctness of the proposed assignment is provided by the fact that the signals of the formyl proton in the PMR spectra, which we ascribe to the E isomer, lie at weaker field, like the signals of the formyl carbon atom of this isomer in the $^{13}C$ NMR spectra. Just the reverse is observed for the signals of the $C_{(3)}$ and $C_{(5)}$ atoms. The same peculiarities are also characteristic for the spectra of the s-trans conformers of acid hydrazides and their derivatives [3-5].

Reliable criteria for the assignment of the signals are not available in the case of 1-acetylpyrazolines VIII-XIV. However, in analogy with the chemical shifts in the spectra of

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*The use of trifluoroacetic acid as the solvent was due to the fact that not all of the investigated substances are sufficiently soluble in $D_2O$ and $CD_3OD$.

TABLE 2. $^{13}C$ NMR Spectra of 1-Formyl and 1-Acetyl-2-pyrazolines in $CF_3COOD$ at 30°C

| Compound | Chemical shift, δ, ppm (J, Hz) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C=O | | $C_{(3)}$ | | $C_{(4)}$ | | $C_{(5)}$ | |
| | E | Z | E | Z | E | Z | E | Z |
| I | 157,4 d (186,3) | — | 160.8 m | — | 31,9 t (133,5) | — | 38,6 t (147,6) | — |
| II | 160.7 d (204,7) | 159.4 d (206,4) | 154,2 d (198,3) | 157,0 d (201,0) | 40,0 t (138,0) | 41,0* | 49,3 d (150,0) | 50,5* |
| III | 163,0 d (201.4) | —** | 165,1 m | — | 41,7* | 43,3* | 54,3* | 55,7* |
| IV | 161.7 d (202,5) | 158.4 d (204,7) | 152,7 d (195,0) | 153,8* | 42,7 t (141,0) | | 56,3 d (150,0) | 58,2 d (150,6) |
| V | 159.2 d (206,7) | 156.4 d (204,0) | 165,0 m | 166,0 m | 44.9 t (138,6) | | 57,4 d (148,5) | 59,2 d (143,2) |
| VI | 159.9 d (206.7) | 157.2* | 160.5 m | 161,3 m | 40,3 t (138,0) | | 57,6 d (148,5) | 59,8 d (143,2) |
| VIII | 169.6 q (6,9) | —** | 166.0 m | —** | 30,4 t (138,0) | 31,8* | 43,4 t (154,5) | 45,4* |
| IX | 171,5 q (6.8) | — | 155,0 d (195,0) | — | 40,4 t (136,5) | — | 51,2 d (150,0) | — |
| X | 173.5 q (6.9) | — | 167.0 m | — | 42,0 t (135,0) | — | 56,3 d (153,0) | — |
| XI | 171.1 q (7,7) | 169.0 q (7,7) | 153.2 d (193,2) | —** | 41,9 t (125,7) | 43,1* | 57,2 d (151,5) | 58,6 d (153,0) |
| XII | 171.1 q (6.9) | 169.0* | 169.7 m | 170.1 m | 45,8 t (138,0) | 47,0 t (141,0) | 61,6 d (151,5) | 62,3 d (151,5) |
| XIII | 166.4 | 168,6 | 170,0 | 171,1 | 41,5* | 43,2* | 61,8* | 63,0* |
| XIV | 169.4 q (7,5) | — | 159,3 m | — | 50,4 t (135,0) | — | 62,4 s | — |

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*The SSCC was not determined because of the low intensity of the signal in the monoresonance spectrum.

**The signal was not localized.

the formyl derivatives, one may assume that the E isomers also predominate here. Evidence for the validity of this is provided by the fact that the positions of all of the signals in the PMR spectra of solutions in $CF_3COOH$ of the preponderant isomer of these compounds differ little from the corresponding signals of the single isomer in $CDCl_3$. We observe the same in the spectra of formyl derivatives I-VII. The isomer ratios in the case of VIII-XIV were determined from the integral intensities of the signals of the protons of the acetyl groups.

It is known from data for N-alkylamides [6], 1-alkyl-1-acetylhydrazines [3], and 1-alkyl-1-acetylamidrazones [5] that the percentage of the stereoisomer with a trans orientation of the alkyl group with respect to the oxygen atom in the case of formyl derivatives and with a cis orientation for acetyl derivatives increases with an increase in the steric volume of the alkyl group. The same peculiarity is observed in our case when methyl substituents are introduced into the 5 position of the pyrazoline ring; more precisely, the percentage of the Z isomer increases for the formyl derivatives (I-III, VII), whereas it decreases for the acetyl derivatives (VIII-X, XIV). However, the anomalous percentage of the Z form for IV-VI, which is close to the percentage for XI-XIII, cannot be explained only by steric factors. The introduction of a phenyl substituent into the 5 position in the case of these compounds evidently partially destabilizes the E form due to electronic interactions of the aromatic ring with the oxygen atom.

In a study of solutions of 1-acyl-2-pyrazoline hydrochlorides by means of PMR spectroscopy it was also established that the conformation of the five-membered ring does not change in this case, since the multiplicities of all the groups of signals are completely retained, and the SSCC of the coupling protons of the pyrazoline ring have the same values as in the case of the bases, as well as solutions in $CF_3COOH$. The data from the PMR spectra provide evidence that the hydrochlorides of V, VII, XII, and XIV in $CDCl_3$ exist in the Z form, since, in addition to coincidence of the chemical shifts when one compares them with the spectra of solutions in trifluoroacetic acid, a constant of long-range spin-spin coupling with the 5-H proton is absent in the spectra. These data constitute evidence that protonation of 1-acyl-2-pyrazolines does not occur at the $N_{(1)}$ and $C_{(3)}$ atoms, since otherwise a change in the conformation of the pyrazoline ring and, as a consequence, a change in the form of the PMR spectra should have occurred.

Significant weak-field shifts of the chemical shifts of the $sp^2$-hybridized carbon atoms are observed for the $^{13}C$ NMR spectra of the above-indicated compounds obtained in ethanol and in ethanol saturated with dry hydrogen chloride (see Table 3). This shift is substantially greater for the $C_{(3)}$ atom than for the carbonyl carbon atom of the acyl substituent (the Δδ values are, respectively, 6.9-23.7 and 1.2-5.0 ppm). These data constitute evidence that the $N_{(2)}$ atom rather than the oxygen atom of the carbonyl group is protonated, since in the latter case the signals of the carbonyl carbon atom and the $C_{(3)}$ atom of the pyrazoline ring should have experienced a substantially greater weak-field shift [6].

The changes in the chemical shifts of the atoms on protonation are manifested even more graphically in the recording of the $^{15}N$ NMR spectra of 1-acetyl-5-methyl-2-pyrazoline. Thus

TABLE 3. Chemical Shifts of the Carbon Atoms of Solutions of 1-Acyl-2-pyrazolines*

| Compound | C=O | $C_{(3)}$ | $C_{(4)}$ | $C_{(5)}$ | Other signals |
|---|---|---|---|---|---|
| V | 170,1 | 157,3 | 54,2 | 64,3 | 26,8 (5-$CH_3$), 23,5 ($CH_3CO$), 16,3 (3-$CH_3$) |
| | [171,3] | [164,2] | [54,5] | [64.6] | [26,8] [22,4] [17,3] |
| VII | 160,5 | 158,5 | 53,4 | 62,5 | 25,5 (5-$CH_3$), 15,4 (3-$CH_3$) |
| | [161,9] | [180,7] | [51,9] | [65,4] | [24,5] [14,1] |
| XII | 169,0 | 158,1 | 46,6 | 60,0 | 142,3** 21,3 ($CH_3CO$), 15,5 (3-$CH_3$) |
| | [171,6] | [168,2] | [47,7] | [62,3] | [139,4]** [19,3] [16,3] |
| XIV | 157,0 | 156,5 | 46,5 | 58,5 | 140,8** 14,8 (3-$CH_3$) |
| | [162,0] | [180,2] | [45,3] | [61,8] | [133,0]** [14,2] |

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*The chemical shifts were obtained from the spectra of solutions in ethanol; the chemical shifts obtained from the spectra in ethanol saturated with HCl are given in brackets.

**The chemical shift of the quaternary carbon atom of the phenyl substituent is presented.

in the spectrum of the base the $N_{(1)}$ and $N_{(2)}$ atoms have chemical shifts of −170.2 and −44.9 ppm relative to $H^{15}NO_3$ as the external standard. The shifts for a saturated solution of the corresponding hydrochloride in methylene chloride are, respectively, −115.1 and 49.6 ppm, i.e., the change in the chemical shift of the $N_{(1)}$ atom is 55.1 ppm, and the change in the shift of the $N_{(2)}$ atom is 93.5 ppm. The assignment of the signals in both cases was accomplished on the basis of the known values of the chemical shifts of the $^{15}N$ nuclei in the acylhydrazone series [8] and the constant of spin-spin coupling of the $N_{(2)}$ atom with the 3-H proton in the hydrazone fragment of the pyrazoline ring [9]. In the case of the base this value is −20.5 Hz, while in the case of the salt it is −10.0 Hz. This increase in the SSCC is in agreement with the data known for hydrazones on its increase with a decrease in the s character of the hybridization of the nitrogen atom on protonation [9].

## EXPERIMENTAL

Compounds I-XIV and 1-acetyl-5-methyl-2-pyrazoline were obtained by acylation of the corresponding bases with formic acid or acetic anhydride [2]. The PMR spectra of 10% solutions of the compounds were recorded with a Tesla BS-497 spectrometer (100 MHz). The $^{13}C$ NMR spectra of concentrated (~3 moles/liter) solutions in $CF_3COOD$, $C_2H_5OH$, and $C_2H_5OH$ saturated with dry hydrogen chloride were recorded with Varian CFT-20 and FT-80 spectrometers under pulse conditions and also under conditions of complete or partial noise decoupling of the protons. The internal standard was tetramethylsilane (TMS). The $^{15}N$ NMR spectra of ~3 M solutions in methylene chloride were obtained with Varian FT-80 and Brucker WP-200 spectrometers.

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