TAUTOMERISM OF DERIVATIVES OF AZINES.

18.* EFFECT OF SOLVENTS ON INTRACHELATE TAUTOMERISM OF THE [1,5]-SIGMATROPIC TYPE IN THE ACYLMETHYLAZINE SERIES

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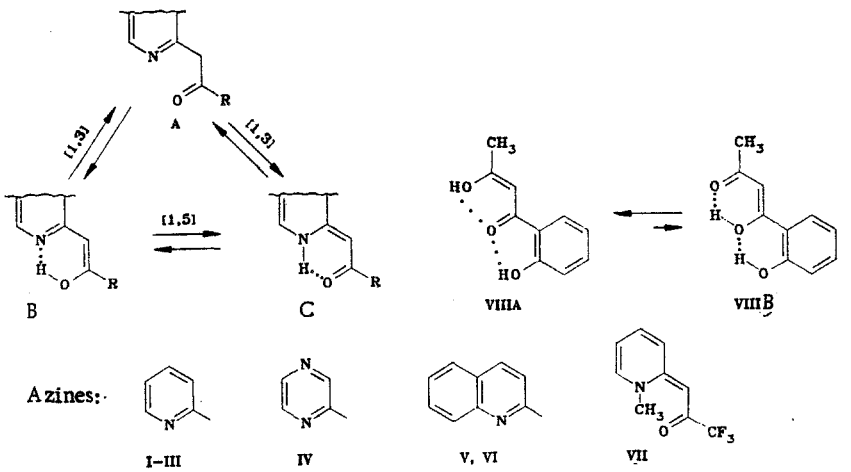
The constants of the intrachelate tautomeric equilibria of trifluoro- and trichloroacetonylpyridines in aprotic and hydroxy-containing solvents were determined by ^{1}H, ^{14}N, and ^{17}O NMR spectroscopy and UV spectrophotometry. It is shown that an increase in the polarity of the solvent and transition to hydroxy-containing solvents are accompanied by a shift of the intrachelate equilibrium to favor the ylidene tautomer.

Tautomeric equilibria with the participation of three forms — aromatic form A, enol form B, and ylidene form C (see the scheme) — are possible for acylmethylazines. An important factor that affects the ratio of tautomers is solvation. The effect of solvents on the azinyl—ylidene equilibrium of the A ⇄ C type has been previously examined [1, 2]; however, intrachelate tautomeric equilibria B ⇄ C remain little investigated. Until recently, the study of the effect of the medium on intrachelate tautomerism of the B ⇄ C type was hindered because of the lack of reliable data on the position of the "fast" tautomeric equilibrium. We recently obtained such data using ^{14}N and ^{17}O NMR spectroscopy [3, 4]; this makes it possible to pose the problem of the effect of the medium on the intrachelate tautomeric equilibrium B ⇄ C in the present paper.



I, IV R=CF_3, II R=CCl_3, III, VI R=*t*-Bu, V R=Ph

We studied the effect of solvents by means of UV spectrophotometry and ^{14}N and ^{17}O NMR spectroscopy in the case of I-VI, which differ with respect to the ratios of forms B and C. The method of determination of the tautomeric equilibrium constants (K_T), the principles of modeling, and the accuracy in the determination of K_T by ^{14}N and ^{17}O NMR methods were set forth in [3]. The ratios of the forms of acylmethylazines I, II, IV, and V in $CHCl_3$ obtained by means of ^{1}H, ^{14}N, and ^{17}O NMR spectroscopy are presented in Table 1. The existence of

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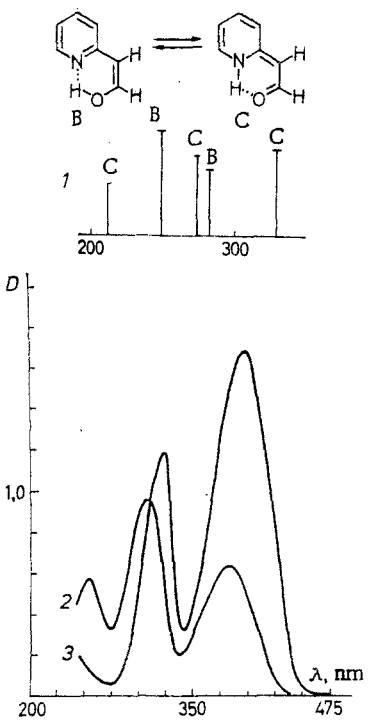

Fig. 1. UV spectra: 1) calculated spectrum of 2-pyridylacetaldehyde; 2) trifluoroacetonylpyridine (I) in $CHCl_3$; 3) 1-(1,2-dihydro-1-methylpyridylidene)-3,3,3-trifluoro-2-propanone (VII) in $CHCl_3$.

these data made it possible to reliably assign the absorption bands in the UV spectra of I-VI and to study the effect of solvents on the intrachelate tautomerism of acylmethylazines I-VI by UV spectrophotometry. This method is more accessible and makes it possible to obtain data for dilute solutions.

We initially conducted our investigation of the effects of solvents in the case of 2-trifluoro- and 2-trichloroacetonylpyridine (I and II), for which comparable amounts of chelate tautomers B and C are present in $CHCl_3$, whereas aromatic tautomer A is virtually absent in aprotic solvents. In addition to weak absorption at 250 nm, two long-wave bands at 307 and 383 nm are observed in the UV spectrum of I in $CHCl_3$ (Fig. 1). Since absorption of aromatic form A at $\lambda > 300$ nm is absent, the long-wave absorption bands correspond to forms B and C and bear information regarding the position of intrachelate tautomeric equilibrium B $\rightleftarrows$ C.

For the assignment of the absorption bands of the enol (IB) and ylidene (IC) tautomers we used the CNDO/S method [5], taking into account 50 singly excited states, to calculate the UV spectra for the B and C tautomers of 2-pyridylacetaldehyde, which models tautomeric acylmethylazines I-III (Fig. 1). According to the results of the calculations, absorption bands at 280 (f* 0.28) and 245 nm (f 0.51) should be observed in the UV spectrum for enol tautomer B, while absorption bands at 330 (f 0.36), 275 (f 0.39), and 207 nm (f 0.11) should be observed for ylidene tautomer C. All of the bands are related to transitions of the $\pi-\pi^*$ type. These results make it possible to assign the longest-wave absorption band (λ_{max} 383 nm) in the UV spectrum of I to the absorption of ylidene tautomer C, while both tautomeric form B and form C may contribute to the absorption at λ_{max} 307 nm. Confirmation for this was found on comparing the UV spectra of I with the spectrum of 1-(1,2-dihydro-1-methylpyridylidene)-3,3,3-trifluoro-2-propanone (VII) (Fig. 1), which models form IC. The character of the spectrum of a close analog of I — 2-trifluoroacetonylpyrazine (IV) — indicates the absence of absorption of the enol tautomeric form at 383 nm (Fig. 2). According to the data in [6], tautomeric equilibrium B $\rightleftarrows$ C for IV in $CHCl_3$ is shifted completely to favor the B form, and only one long-wave maximum at 325 nm is observed in the UV spectrum of this compound.

To establish the ratio of forms B and C in dilute solutions by UV spectrophotometry it was necessary to determine the coefficients of extinction of the absorption bands of tauto-

*Oscillator force f [5].

TABLE 1. Data from ^1H,* ^{14}N, and ^{17}O** NMR Spectroscopy of Acylmethylazines I, II, IV, and V

Compound	Solvent	^{14}N NMR		Compound	Solvent	^{14}N NMR	
		CS, ppm	K_T ([C]/[B])			CS, ppm	K_T ([C]/[B])
I	Cyclohexane	—	—	II	Chloroform	−195*4	4,8±1,0
I	Chloroform	−177	2,0±0,3	II	Chloroform–ethanol (1:1)	−200	6,7±1,8
I	Methylene chloride	—	—				
I	Acetonitrile	—	—	II	DMSO	−205	11±4
I	DMSO	−195	4,8±1,0	IV	Chloroform	—	—
I	Methanol	−188*3	3,3±0,5	V	Chloroform	−225 [3]	>20

*According to the ^1H NMR data, the percentage of the A form is 30% for I (in methanol) and 5% for V (in chloroform), as compared with 0% in the remaining cases.

**^{17}O NMR: for IV, according to the data in [6], CS 108 ppm, and K_T ([C]/[B]) < 0.03; for the model compound benzoylacetic ester, according to the data in [3], CS 109 ppm (enol oxygen). For V, according to the data in [3], CS 326 ppm, and K_T ([C]/[B]) > 5.7; for model compound acetonylquinoline, according to the data in [3], CS 365 ppm.

*3For the model compound 2-pyridylcyanoacetic ester, according to the data in [3], CS − 215 ppm.

*4For the model compound o-hydroxyphenylpyridine CS − 100 ppm.

mer B at 307 nm (ε_V^{307}) and tautomer C at 307 (ε_C^{307}) and 383 nm (ε_C^{383}). Although fixed models are also useful in the assignment of absorption bands, the error in estimating ε when they are used may reach 50% [7]. In this connection the molar coefficient of extinction of the enol tautomeric form (ε_B^{307}) of I was determined by extrapolation [2, 8]. The results obtained for two systems of solvents (hexane–methylene chloride and hexane–dichloroethane) coincide (ε_B^{307} = 7700 ± 100 cm/mole-liter). The molar coefficients of extinction of ylidene tautomeric form C at 307 and 383 nm were determined in DMSO using UV and ^{14}N NMR spectroscopic data (ε_C^{307} = 12.400 ± 250 and ε_C^{383} = 16.100 ± 800 cm/mole-liter). The coefficients of extinction for II were similarly obtained (ε_B^{318} = 10,700 ± 400, ε_C^{318} = 9800 ± 100, and ε_C^{395} = 17,000 ± 1100 cm/mole-liter).

The constants of the intrachelate tautomeric equilibria of the [1,5]-sigmatropic type of trifluoro- and trichloroacetonylpyridine (I and II) found by means of UV spectrophotometry are presented in Table 2. An examination of these data shows that a general tendency is observed: ylidene tautomeric form C becomes more stable with an increase in the polarity of the solvent. Good correlation of the ln K_T value with the polarity parameter in the Kirkwood–Onsagar equation [9] $(\varepsilon - 1)/(2\varepsilon + 1)$, which describes the effect of nonspecific solvation, is observed for hexane–methylene chloride (Table 2).

$$\ln K_T = -(5,9 \pm 0,1) + (13,2 \pm 0,3)(\varepsilon - 1)/(2\varepsilon + 1);$$
$$G_T^0 = (14,4 \pm 0,2) - (32,1 \pm 0,7)(\varepsilon - 1)/(2\varepsilon + 1) \text{ (kJ)};$$
$$T = 293 \text{ K}; \; r = 0,998; \; s = 0,07; \; n = 7.$$

One's attention is drawn to the marked shift of equilibrium B ⇄ C to favor ylidene form C on passing to hydroxy-containing solvents. This is possibly associated with the greater ability of form C to form an intermolecular hydrogen bond (IHB), since the carbonyl group (form C) usually forms a stronger IHB as compared with the IHB of the oxygen atom of the OH group (form B) [10]. This is in good agreement with a recent observation [11] regarding the effect of an IMHB on the position of the intrachelate tautomeric equilibrium of β-diketones. According to the data in [11], the stronger IMHB with the C=O group leads to stabilization of tautomer A of VIII.

A substantial dependence of the intrachelate equilibrium on the solvents is also displayed for other acylmethylazines. In the case of IV-VI (Figs. 2 and 3) it is apparent that a change in the character of the medium not only affects the ratio of the forms that are present but also may give rise to the development of another chelate tautomer. Judging from

TABLE 2. Optical Densities at the Absorption Maxima (D_{max}) in the UV Spectra and Constants of the Intrachelate Equilibria B ⇄ C (K_T = [C]/[B]) of Trifluoro- and Trichloroacetonylpyridine (I and II) in Various Solvents at 20°C

Solvent	Compound I		Compound II	
	λ_{max}, nm (D_{max})	K_T	λ_{max}, nm (D_{max})	K_T
Pentane	303 (0,79); 383 (0,04)	0,03±0,03		
Hexane	303 (0,77); 383 (0,04)	0,03±0,03		
Heptane			316 (1,11); 392 (0,24)	0,15±0,03
CCl_4	304 (0,80); 387 (0,13)	0,09±0,03	319 (0,98); 396 (0,44)	0,37±0,04
Hexane–CH_2Cl_2 (9:1)	307 (0,79); 384 (0,28)	0,09±0,03		
Hexane–CH_2Cl_2 (7:3)	307 (0,85); 384 (0,28)	0,21±0,04		
Benzene	306 (0,85); 387 (0,37)	0,31±0,05		
Hexane–CH_2Cl_2 (1:1)	307 (0,87); 384 (0,41)	0,35±0,05		
Hexane–CH_2Cl_2 (3:7)	307 (0,91); 384 (0,52)	0,49±0,07		
Chloroform	307 (0,95); 383 (0,62)	0,63±0,08	318 (1,03); 393 (1,09)	1,62±0,24
Hexane–CH_2Cl_2 (1:9)	307 (0,94); 384 (0,62)	0,64±0,08		
CH_2Cl_2	307 (0,99); 382 (0,70)	0,74±0,09		
1,2-Dichloroethane	306 (0,98); 382 (0,68)	0,72±0,09	317 (1,02); 391 (1,19)	2,1±0,4
Acetonitrile	303 (1,04); 378 (0,95)	1,46±0,18	315 (0,99); 388 (1,43)	4,3±1,0
DMF			316 (1,01); 392 (1,42)	4,2±1,0
DMSO	308 (1,01); 382 (1,09)	3,0±0,5	318 (0,97); 395 (1,48)	7±2
Ethanol (95%)	301 (0,93); 375 (0,94)	2,2±0,4	310 (1,07); 386 (1,59)	6±2
Methanol	299 (0,74); 374 (0,78)	2,7±0,4		

the ^{17}O NMR spectra of trifluoroacetonylpyrazine (IV) in chloroform, only one of the possible chelate forms – enol form B – is realized [6]. The absorption band with λ_{max} 325 nm in the UV spectra of solutions in $CHCl_3$ and CCl_4 corresponds to it (Fig. 2). When a polar solvent – acetonitrile – is added, a long-wave absorption band at 410 nm, which corresponds to ylidene form C, develops in the UV spectrum and its intensity increases regularly. A similar effect is manifested when alcohols are added. We observed the opposite effect – the development of a significant percentage of the enol tautomer – in the case of phenacylquinoline (V) on passing from $CHCl_3$ to pentane. Judging from the ^{14}N NMR spectrum [6], in $CHCl_3$ this compound exists completely in the ylidene form. The band of complex form with λ_{max} 417, 430, and 460 nm in the UV spectrum corresponds to it. The transition to low-polarity solvents (CCl_4, pentane) is characterized by a marked decrease in the intensity of the long-wave absorption (a decrease in the percentage of the C form) and by the development of an enol band at ∿390 nm (Fig. 3). Thus [1,5]-sigmatropic equilibrium B ⇄ C is extremely sensitive to the effects of solvents; polar and hydroxy-containing solvents favor ylidene form C.

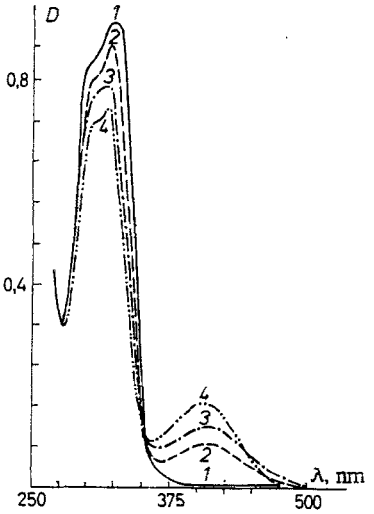

Fig. 2. UV spectra of trifluoroacetonylpyrazine (IV): 1) in CCl_4 (1:3); 3) in 2) in acetonitrile–CCl_4 (1:3); 3) in acetonitrile–CCl_4 (1:1); 4) in acetonitrile.

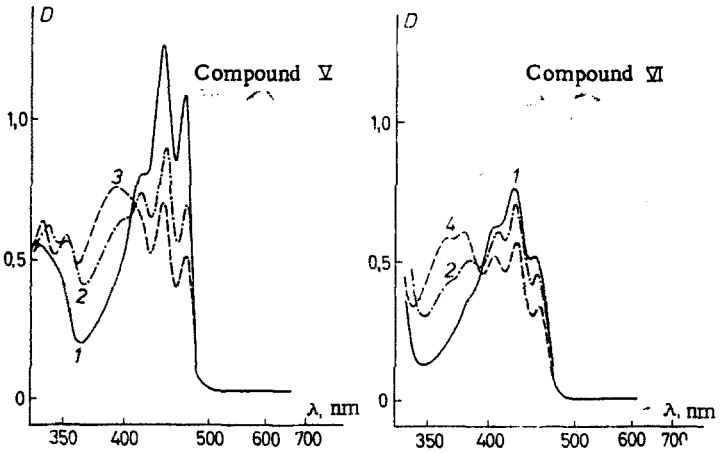

Fig. 3. Absorption spectra of phenacylquinoline (V) and pivaloylmethylquinoline (VI): 1) in $CHCl_3$; 2) in CCl_4; 3) in pentane; 4) in heptane.

The data in [12] regarding the development of appreciable amounts of the ylidene tautomer of pivaloylmethylpyridine (III) in a low-polarity solvent such as carbon disulfide (PMR data) are in poor agreement with this conclusion. In fact, the UV spectrum of III in CS_2 that we obtained does not contain the absorption band of ylidene tautomer C at 390 nm. Let us note that equilibrium IIIB $\rightleftarrows$ IIIC is shifted virtually completely to favor enol form B also in a more polar solvent — chloroform [2]. Moreover, one must reckon with the possibility of the formation of the ylidene tautomer in polar solvents. For example, the NH tautomeric form is not taken into account in [2] for III in strongly polar solvents, including DMSO, whereas a long-wave absorption band corresponding to tautomer C (λ_{max} 390 nm) is present in the UV spectrum of III in DMSO. In the case of another compound [2] — pivaloylmethylquinoline (VI) — the possibility of the formation of an enol tautomer in nonpolar solvents was not taken into account. However, as demonstrated by the UV spectroscopic data for quinoline VI in nonpolar solvents, the percentages of tautomers B and C may become comparable (Fig. 3). It is evident that, because of the lack of data on the true ratio between tautomers of the B and C type, a certain degree of indeterminacy is inherent in the conclusions drawn in [2].

It has previously been shown that ylidene tautomer C is destabilized with a decrease in the polarity of the medium in the case of [1,3]-sigmatropic tautomerism of hydroxy-, amino- [13], and methylazines [4]. In conjunction with the above-presented results regarding tautomerism of the [1,5]-sigmatropic type one can formulate a general tendency for prototropy of the azinyl—ylidene type: the transition to nonpolar solvents is accompanied by destabilization of the tautomer of the ylidene type. This conclusion can evidently also be extended to nonprototropic tautomeric equilibria of the azinyl—ylidene type. Thus in the case of the electrocyclic tautomerism of azides (azido-tetrazole tautomerism) the transition of nonpolar solvents is accompanied by destabilization of the tautomer of the ylidene type (the tetrazole form [14]). On the whole, it may be hoped that the proposed correlation will be fulfilled at least as a tendency for the family of tautomeric equilibria of the azinyl-ylidene type as a whole.

EXPERIMENTAL

The UV spectra of the compounds at 20°C were reported with a Beckmann DU-8 spectrophotometer; $c = 1 \cdot 10^{-4}$ M, and the layer thickness was 1 cm. The PMR spectra of 1% solutions at 20°C and 5% solutions at 40°C were recorded with Bruker WP-200SY and Varian A-56/60 spectrometers, respectively. The ^{14}N and ^{17}O NMR spectra were recorded with a Bruker CXP-300 spectrometer (at 40.69 MHz for the oxygen nuclei and at 21.68 MHz for the nitrogen nuclei) at 25°C (10-15% solutions). The chemical shifts are presented relative to standards: hexamethyldisiloxane (^1H NMR) as the internal standard and NO_3^- (^{14}N NMR) and H_2O (^{17}O NMR) as external standards. The solvents used in the UV spectrophotometry were purified and dried in conformity with the methods in [15]. Compounds I-VI were synthesized by the methods in [2, 3, 6, 16, 17]; the spectral characteristics and melting points of the compounds that we obtained coincided with the data presented in these papers.

1-(1,2-Dihydro-1-methylpyridylidene)-3,3,3-trifluoro-2-propanone (VII). This compound was obtained by the method in [18]. A 0.18-g (1.24 mmole) sample of methyl iodine, 0.14 g (1.24 mmole) of potassium tert-butoxide, and 0.04 g (0.1 mmole) of 18-crown-6 ether were added to 0.2 g (1.06 mmole) of trifluoroacetonylpyridine (I) in 30 ml of absolute ether in an argon atmosphere, and the mixture was stirred at room temperature for 8 h. The course of the reaction was monitored by TLC. At the end of the reaction 20 ml of distilled water was added, the aqueous part was neutralized with concentrated aqueous HCl, and the ether layer was separated. The aqueous layer was extracted with ethyl acetate. The ether layer and the ethyl acetate extracts were combined and dried with anhydrous $MgSO_4$, and the drying agent was removed by filtration. The solvent was removed by distillation, and the residue was separated by preparative TLC with collection of the yellow zone with R_f 0.2-0.4 (elution with ethyl acetate). The yield of VII was 0.18 g (67%); the product had mp 109-111°C [heptane–benzene (2:1)]. Found: C52.9; H 4.0; F 28.3; N 6.7%. $C_9H_8F_3NO$. Calculated: C 53.2; H 3.9; F 28.3; N 6.9%.

Method of Determination of the B $\rightleftarrows$ C Equilibrium Constants (KT = [C]/[B]) of Trifluoro- and Trichloroacetonylpyridine (I and II). The optical densities at the absorption maxima (D_{max}) for I and II with an accuracy of ±0.02 are presented in Table 2 and for I are described by equations of system (1) ([7], p. 45):

$$\begin{aligned} &D_{307}=\varepsilon_B^{307}c_B l+\varepsilon_C^{307}c_C l;\\ &D_{383}=\varepsilon_C^{383}c_C l;\\ &c_B+c_C=c_0=\text{const};\\ &\varepsilon_C^{383}=(\varepsilon_C^{307}-\varepsilon_B^{307})/0{,}29, \end{aligned} \tag{1}$$

where c_B and c_C are the concentrations of tautomers B and C, l is the layer thickness, and $c_0 = 1\cdot10^{-4}$ M. The last equation was obtained in the determination of ε_B^{307} by the method in [2]. Solution of the system relative to ε_C^{383} leads to the expression

$$\varepsilon_C^{383}=\varepsilon_B^{307}\cdot\frac{1+1/K_T}{D_{307}/D_{383}-0.29}. \tag{2}$$

To exclude possible errors in the determination of ε_C^{307} and ε_C^{383} because of a difference in the ratio of the optical densities (D_{307}/D_{383}) in solutions that differ markedly in concentration we obtained the UV spectra of I in DMSO over the concentration range $1\cdot10^{-4}$ to $1.5\cdot10^{-1}$ M; the (D_{307}/D_{383}) ratio changed from 0.93 at a concentration of $1\cdot10^{-4}$ M to 0.88 at a concentration of $1.5\cdot10^{-1}$ M. To find ε_C^{307} and ε_C^{383} we adoted the ratio D_{307}/D_{383} = 0.87 (extrapolation to the ^{14}N NMR concentration) and the value K_T = 4.8 ± 1.0 of the B $\rightleftarrows$ C equilibrium of I in DMSO (Table 1). Similarly, from D_{318}/D_{395} = 0.62 and K_T = 11 ± 4 in DMSO for acylmethylazine II we obtained ε_{CV}^{318} and ε_C^{395} (see the text). The corresponding K_T values were then found by substitution of the ratios of the optical densities in various solvents into expression (2) (Table 2).

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TAUTOMERISM OF DERIVATIVES OF AZINES.

19.* EFFECT OF SOLVENTS ON THE o,p-QUINOID EQUILIBRIA OF THE YLIDENE FORMS OF 4-PYRIMIDINYLCYANOACETIC ACID ESTERS

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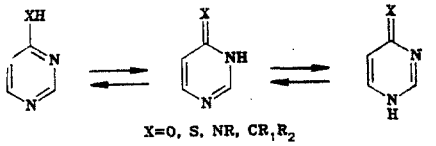
The effect of solvents on the tautomeric equilibria of the ylidene forms of 4-pyrimidinylcyanoacetic acid esters with o- and p-quinoid orientations of the double bonds in the heteroring was determined. The relative stability of the p-quinoid tautomer increased markedly on passing to polar solvents due to non-specific solvation and the formation of hydrogen bonds.

Annular tautomerism is an important type of tautomeric equilibrium in series of pyrimidine derivatives. In the case of 4-substituted pyrimidines the formation of two NH forms (B and C) with o- and p-quinoid orientations of the double bonds in the heteroring is possible.



X=O, S, NR, CR_1R_2

Tautomeric equiilibia of the B ⇄ C type can be observed for various derivatives of azines. In addition, little study has been devoted to o,p-quinoid tautomeric equilibria, evidently because of the difficulty involved in recording the tautomeric forms. We have previously established [2] that equilibria with the participation of aromatic tautomer A and o-quinoid tautomer B, which is stabilized by an intramolecular hydrogen bond (IHB), are characteristic for substituted 4-pyrimidinylmethanes. "Rare" p-quinoid tautomer C can be stabilized by solvents such as DMSO and HMPT [3, 4], and this makes it possible to investigate the effects of the medium on o,p-quinoid equilibrium B ⇄ C, which is the aim of the present research.

We selected 4-pyrimidinylcyanoacetic acid ester (I) and 2-methyl-4-pyrimidinylcyanoacetic ester (II), for which the observation of tautomeric equilibrium B ⇄ C is not complicated by the presence of tautomer A [4]. The UV spectra of I and II in various solvents are

*See [1] for Communication 18.

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