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TAUTOMERISM OF PYRIMIDYL-2-METHANE DERIVATIVES: MEDIUM EFFECTS, THERMODYNAMICS, KINETICS AND MECHANISM

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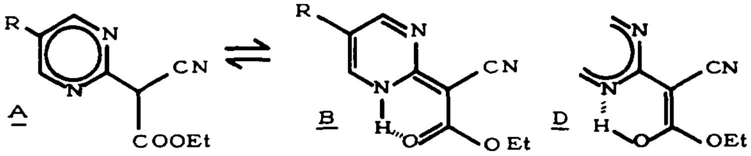
Abstract- The investigation of tautomeric equilibria among pyrimidyl-2-methanes has been undertaken. Pyrimidyl-pyrimidylidene equilibrium has been found in the case of 5-substituted 2-pyrimidyl-cyanoacetic esters. Unsymmetrically substituted pyrimidyl-2-methanes form two types (1-NH and 3-NH) of ylidene tautomers, which differ in ring proton spin coupling constants. The effect of substituents in the pyrimidine ring and of the solvent on tautomeric equilibrium are discussed. A drastic effect is produced by acids (CF_3COOH) which shift the equilibrium toward the ylidene tautomer of higher basicity. The thermodynamic and kinetic characteristics and the mechanism of the tautomeric equilibrium were examined.

Previously, we have found the first examples of pyrimidyl-pyrimidylidene tautomeric equilibria in the series of pyrimidyl-4-malonic, cyanoacetic esters and pyrimidyl-4-nitromethanes[1,2]. The purpose of the present work is the search for tautomeric compounds among pyrimidyl-2-methanes and the study of their tautomeric equilibria in various solvents.

Pyrimidylmethanes 1-16 were prepared by condensation of halogeno- or methylsulphonylpyrimidines with cyanoacetic and malonic esters, nitromethane or methylsulphonylacetic ester, respectively (Table 1).

For compounds 1-16, actually three tautomeric forms are possible (Schemes 1 and 2): the pyrimidine form A and two (1-NH and 3-NH) ylidene forms B and C. In basic solvents (DMSO), the formation of non-chelate analogues of ylidene tautomers B and C, stabilized by intermolecular hydrogen bond (HB) to the solvent, is possible. The specific indications of the ylidene forms are: a long wave maximum (300-400 nm) in the u.v. spectrum, an intense ν_{CN} band** at 2200 cm^{-1} in the i.r. spectra of 1-12 and $\nu_{C=O}$ band at 1650-1680 cm^{-1}. The A form is characterised by the presence in the p.m.r. spectrum of a signal of methine proton at ~5.1 ppm and of a band of non-conjugated ester group at 1750 cm^{-1}. There are some possibilities for the formation of the enol

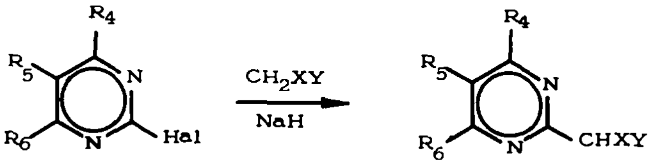


1:	R= H	5:	Br
2:	Me	6:	p-$NO_2C_6H_4$
3:	Ph	7:	OMe
4:	Cl	8:	NMe_2

Scheme 1

** For the A form, the ν_{CN}band practically is not observed.

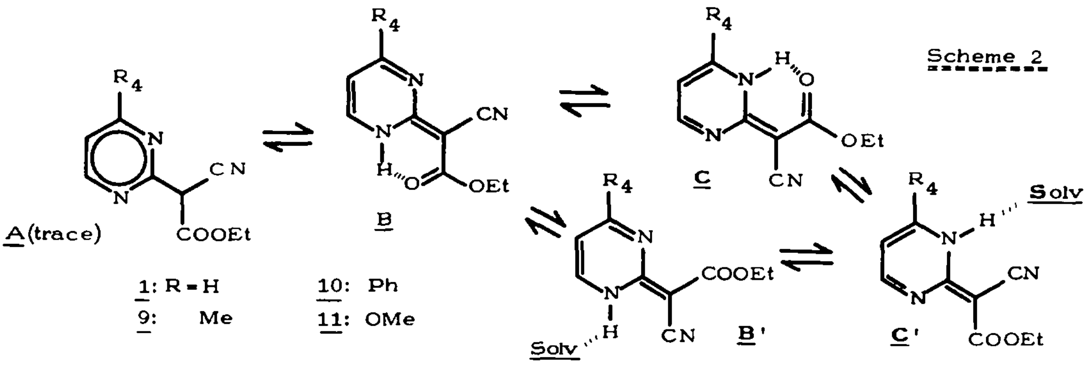
Table 1. Properties of pyrimidylmethanes 1-16.



No.	X, Y	R_4	R_5	R_6	M.p., °C (solvent)	^{1}H n.m.r., 0,5-1% in $CDCl_3$ at 300 K, δ, ppm from Me_4Si					
						Chemical shifts				Content, %	
						CH	H-4	H-5	H-6	A	B(C)
1	CN COOEt	H	H	H	187-190 (ethanol)		7.85	6.43	8.71		100
2	CN COOEt	H	Me	H	217-219 (ethanol)		7.62		8.60		100
3	CN COOEt	H	Ph	H	200-202 (ethanol)		8.00		8.95		100
4	CN COOEt	H	Cl	H	198-206 (benzene)	5,09	8.72 (A) 7.90 (B)		8.72 (A) 8.58 (B)	9	91
5	CN COOEt	H	Br	H	185-193 (benzene)	5,08	8.81 (A) 7.90 (B)		8.81 (A) 8.60 (B)	5	95
6	CN COOEt	H	p-$NO_2C_6H_4$	H	249-250 (ethanol-DMF)	5,30	8.45 (A) 7.41 (B)		8.45 (A) 8.64 (B)	20	80
7	CN COOEt	H	OMe	H	176-185 (benzene)	5,03	8.27 (A) 7.16 (B)		8.27 (A) 8.66 (B)	35	65
8	CN COOEt	H	NMe_2	H	184-190 (ethanol)	5,00	8.26 (A) 7.14 (B)		8.26 (A) 8.47 (B)	40	60
9	CN COOEt	Me	H	H	139-143 (benzene-CCl_4)		8.52 (B) 7.75 (C)	6.65 (B+C)			50(B) 50(C)
10	CN COOEt	Ph	H	H	183-184 (benzene-CCl_4)	5.15	8.67 (B)	6.03 (C)		2	70(B) 28(C)
11	CN COOEt	OMe	H	H	164-168 (benzene)		7.66 (C)	6.02 (C)			100(C)
12	COOMe COOMe	H	H	H	oil	5.12	8.90	7.40	8.90	100	
13	COOMe COOMe	Ph	H	H	62-65 (ethanol)	5.13	8.70	7.56		100	
14	SO_2CH_3 COOEt	Ph	H	Ph	143-150 (ethanol)	5.12				100	
15	Ph COOEt	Ph	H	Ph	111-113 (CCl_4)	5.14		7.96		100	
16	H NO_2	Ph	H	Ph	132-134 (CCl_4)	5.83				100	

tautomer D, rapidly exchanging with the ylidene form B. Judging by the ^{14}N n.m.r. data, there is no evidence for any significant proportion of the enol tautomer. Thus, the spectra of compound 1 contain, along with broad signal of C=N and C≡N fragments (100±10 ppm from external nitromethane), a narrow signal at 220 ± 1 ppm. Location and width of the signal suggest the presence of the "amide" NH group, whereas for form D, a broad signal at 100-130 ppm could be expected [3].

Using all the above indications, we found in the case of 2-pyrimidylcyanoacetic esters 1-8 the first example of pyrimidyl-ylidene A⇌B equilibrium among pyrimidyl-2-methane derivatives (for the preliminary communication, see [1]). The position of the equilibrium strongly depends on the nature of R_5 substituent. Unexpectedly, the introduction of both electron-donating (compounds 7-8) and withdrawing (compounds 4-6) substituents results in a shift of equilibrium toward the aromatic A form. The first case might be explained in terms of the lowered acidity of the A tautomer, which is induced by the strong electron-donating effect of the methoxy- and dimethylamino groups [4]. As to the cyanoacetic esters 4-6, the acidity of the A form will be increased under the influence of substituents ($NO_2C_6H_4$-, Cl and Br), but that of the B tautomer will be increased still more , since the acidic centre of the B form (NH-group) is located closer to the acidifying substituent. Thus, the shift of the equilibrium toward A, observed in the case of 4-8, is induced by various effects. If R_5=Cl, Br, $NO_2C_6H_4$, the main effect is the destabilization of type B tautomer, while if R_5=OCH_3, $N(CH_3)_2$, it is stabilization of the tautomer of type A.


Scheme 2

For pyrimidylcyanoacetic esters 9-11, unsymmetrically substituted in the pyrimidine ring, two different tautomers B and C of pyrimidylidene structure are possible (Scheme 2). The analysis of spin-spin coupling constants (SSCC) of the ring protons in the p.m.r. spectrum provides a clear-cut differentiation of these forms and, as a consequence, the simple tool for determination of the ratio of A, B and C (Table 1). Modelling of the initial spectra (Fig. 1) has shown that the long-range coupling constant J_{14} is very small, while the SSCC J_{61} and J_{65} are comparable, which is responsible for the triplet character of H^6 and H^5 signals. The pulse mode double resonance study of compound 1 showed that magnetic saturation in the H_4 absorption range results in a decreased intensity of the H_6 signal (and vice versa).

Further experiments with the inverted pulse (180°) have shown that the decreased intensity of the signals results from the transfer of "saturation label" [5] in the degenerate tautomeric interconversion 1B ⇌ 1C.

A careful examination of the data collected in Table 1 suggests that the tautomeric equilibrium is considerably affected by various substituents on the pyrimidine nucleus. Concerning the effect of α-substituents (compounds 9-11), one could expect (by analogy with 2-hydroxypyridines [6]) that the B form would be destabilised by substituents with

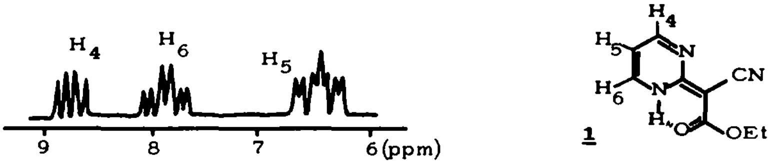


Fig. 1. The p.m.r. spectrum of 2-pyrimidylcyanoacetic ester 1 (ring protons).

-I effect. There are two alternatives for the pyrimidine derivatives: a shift of equilibrium either toward the A form or toward the second ylidene form with the 3-NH group located far from the substituent. The experimental data show that the latter alternative is realised, i.e. introduction of α-substituents affects the equilibrium between the ylidene tautomers more than the equilibrium A / (B+C).

In contrast to the previously studied 4-pyrimidyl-nitromethanes and -malonic esters [1], 2-pyrimidylnitromethane 16, 2-pyrimidylmalonic esters 12-13, and compounds 14, 15 do not show tautomeric properties. In $CHCl_3$ or CCl_4 solutions they exist in the pyrimidine form A. This is indicated by the absence of a long-range maximum (~350 nm) in the u.v. spectrum, typical of the tautomers of the ylidene type.

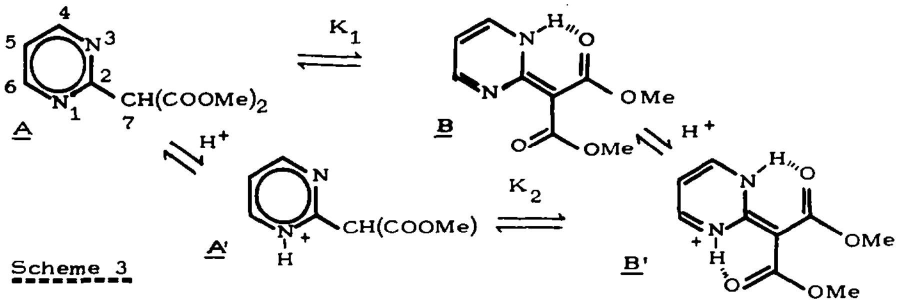
Since the tautomeric equilibrium strongly depends on the nature of the medium, we studied the behaviour of 2-pyrimidylmethanes in various solvents, including those of basic and acidic character. The decreased polarity of the medium raises the content of the aromatic form. Thus, according to the u.v. spectral data for 4, changing the solvent from $CHCl_3$ to the heptane-$CHCl_3$ mixture (49:1), results in the increase of the content of the A form from 9 to 50%. Destabilisation of the ylidene forms by non-polar solvents has also been observed before for other types of azinyl-ylidene equilibrium [6].

The appearance of non-chelated NH-tautomer of the B type has been reported [7] *for* pyridyl-2-cyanoacetic ester in $CHCl_3$. The experimental data for 9 and 10 showed that the appearance of non-chelated tautomers B′(C′) is possible only in the presence of highly basic solvents capable of forming a strong HB with the NH-group. The following observations indicate the formation of non-chelated forms. Addition of dimethylsulphoxide to $CHCl_3$ solutions of 9 or 10 results in a 2-4 ppm upfield shift of the COOR signal in the ^{13}C n.m.r. spectrum, which is observed in the case of disrupting of the intramolecular HB by solvents [8]. In addition, the presence of DMSO and DMF induces a considerable shift of equilibrium for 9 and 10 toward the 3-NH-tautomer, which may be easily explained by the fact that the3-NH-group is more available for HB formation (Scheme 2). Increase of the content of DMSO up to 100% results in partial or complete ionisation of pyrimidylcyanoacetic esters 1-13, which is obvious from the comparison of the u.v. spectra of these compounds in DMSO with the spectra of their sodium salts.

Probably, the most significant effect upon the tautomeric equilibrium of heterocycles is produced by strong acids [9,10], which are able to protonate compounds 1-16.

Therefore we studied the tautomeric equilibria of compounds 13-16 (which exist in the A form and do not show tautomeric properties in neutral solvents of $CHCl_3$ type) in the presence of trifluoroacetic acid. Addition of the latter to chloroform solutions of 13-14 resulted in the appearance of a specific maximum at 300-400 nm in the u.v. spectra of these compounds, probably indicating a considerable shift of the equilibrium toward the ylidene form. For a rigorous proof of this, we used indications of the appearance of cations of A′, B′ types (Scheme 3), which had been found earlier as a result of the investigation of the corresponding cations [10] of pyridyl- and pyrimidylcyanoacetic esters.

In the p.m.r. spectrum of 13-14 in CF_3COOH, the proton signal of CH (the A form)



Scheme 3

at 5 ppm is absent. In the ^{13}C n.m.r. spectra in trifluoroacetic acid, instead of the C^7 signal of the aromatic tautomer (60 ppm, $CDCl_3$), a C^7 signal appears at 80 ppm. The off-resonance spectrum shows that this signal cannot be the C^7 signal of the aromatic tautomer (the $J\,^{13}C_{C-H}$ splitting constant is absent) but corresponds to the tautomer of the ylidene type. The chemical shift of the ring carbon atoms $C^{4,6}$ and C^5 (155 and 110 ppm) indicates the existence of the protonated ylidene form B (cf. 13). Thus, the ^1H and ^{13}C n.m.r. data are consistent with the u.v. spectral data, showing a practically complete shift of the equilibrium toward the ylidene tautomer B in acid solution. As follows from the expression [9] $K_2 = K_1 \frac{K_B}{K_A}$, (where K_2 and K_1 are the constants of tautomeric equilibrium of protonated and non-protonated forms and K_A and K_B are the basicity constants of the A and B tautomers), such a great shift of tautomeric equilibria is caused by the greater basicity of the ylidene tautomers as compared to the aromatic ones. It should be noted that dissolution of compounds 15 and 16 in CF_3COOH does not lead to the ylidene tautomer. This seems to result from the decreased number of electron-withdrawing substituents at the CH fragment, which diminishes the relative stability of the ylidene form [1,2].

Thus comparison of the tautomeric forms of pyrimidyl-2-methanes with their 4-analogues [1] shows the lower ability of 2-derivatives to convert to the NH form. The structure of pyrimidyl-2-methanes and their tautomeric equilibrium depend considerably both on substituents in the heterocyclic part of a molecule and at the CH fragment, and on the solvent. In the case of 4-derivatives, basic solvents lead to the appearance of quinoid NH-forms, whereas in the case of 2-derivatives they lead to non-chelated ylidene tautomers or to ionisation of molecules. A strong effect is produced by acids which shift the equilibrium toward the ylidene tautomer.

Thermodynamic Parameters of Equilibria. Tautomeric equilibria 1-8 appeared to be very sensitive to temperature. Thus at 238 K, 5-dimethylaminopyrimidyl-2-cyanoacetic ester in $CHCl_3$ contains 5% of the aromatic tautomer, while at 370 K it contains 75% of this tautomer. Parameters ΔH $(H_B - H_A)$ and ΔS $(S_B - S_A)$ have been obtained from the temperature dependence of equilibrium constants $K^t = \frac{B}{A}$ (Table 2). In the case of compounds 7 and 8, an exceedingly high entropy difference is observed, which is generally not typical of the prototropic tautomeric equilibria [11,12]. The values of

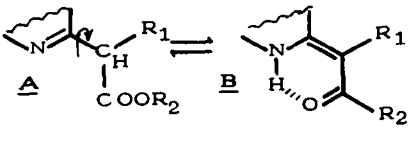


Table 2

			$-\Delta H$	$-\Delta S$
7:	Az*=5-OMe-pyrimidyl-2;	R_1, R_2=CN, Et	21.1	62
8:	5-NMe_2-pyrimidyl-2;	CN, Et	23.2	71
17:	6-OMe-pyridazinyl-3;	CN, Et	12.2	38
18:	Pyridazinyl-3;	COOMe, Me	4.7	24
19:	2-Me-pyrimidyl-4	COOMe, Me	7.9	47
			kJ/mol (±0.8)	J/mol·K (±3)

* Az: azine fragment

$\Delta S = 60-70$ J mol^{-1}K^{-1}, determined for compounds 7 and 8, are comparable only with the entropy difference for the azide-tetrazole equilibrium[13] which, however, does not refer to the prototropic one. Such an unfavourable entropy change on passing to the ylidene tautomer of pyrimidylcyanoacetic esters seems to be due to the restriction of rotation around the exocyclic C=C bond. This was confirmed by the results of the measurement of the ΔS value for pyridazinyl-3-cyanoacetic ester 17. The presence of a more bulky $-CH(COOR)_2$ fragment makes rotation in the A tautomer also difficult; this is expected to result in a smaller entropy difference between A and B. Experimental data confirm this suggestion (Table 2).

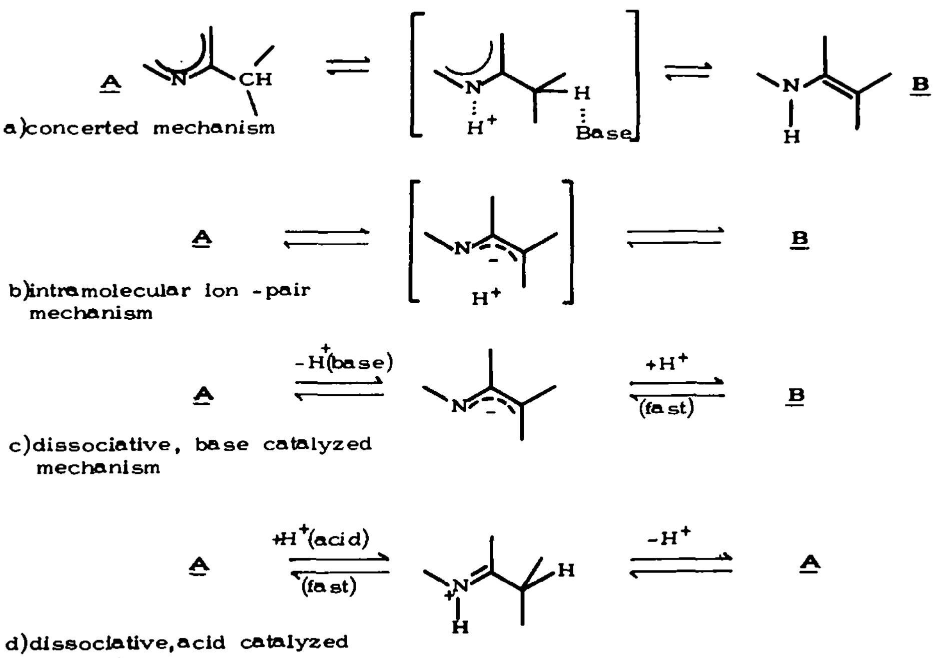
Kinetics and Mechanism. In the previous studies of the kinetics of tautomeric interconversions of the type $A \rightleftharpoons B$ on azinylmalonic esters, some arguments in favour of the ionic mechanism of the tautomeric process have been found[14].

Further information concerning tautomerisation kinetics and mechanism was obtained by using 5-methoxypyrimidyl-2-cyanoacetic ester 7, which has comparable amounts of both A and B tautomers in chloroform solution (Fig. 2).

We considered possible ionic type mechanisms of tautomerisation (Scheme 4).

Due to the high temperature dependence of the equilibrium, it was possible to apply *the temperature jump method, when the direct observation of time-dependent populations* of equilibrating tautomers allows the determination of the rate constant and their temperature dependence. As isomerisation $7A \rightleftharpoons 7B$ was slow, there was no need for any special equipment. Thus after equilibration of a sample in dried $CDCl_3$ at 50-60° and its subsequent cooling to -30°, the time of further equilibration was about three hours. The rates of tautomeric conversions were determined from the time-dependent change of relative intensity of signals at 3.8 and 3.95 ppm in the p.m.r. spectrum, corresponding to the methoxy groups of tautomers B and A, respectively (Fig. 2).

It has been found that, like the previously studied azinylmalonic esters[14], the $A \rightleftharpoons B$ interconversion in $CDCl_3$ is defined by the kinetic equation of the reversible first-order reaction. Rate constants and activation parameters, found according to the Arrhenius



Scheme 4

equation, are listed below:

	T, K	k^1(A→B)	k^{-1}(B→A)
$k \cdot 10^4 sec^{-1}$	240	0.81±0.04	0.04±0.002
	248	1.17±0.05	0.08±0.003
	263	3.8±0.4	0.4±0.04
	274	4.8±0.5	1.0±0.1
$\Delta H^{\ddagger}$, kJ/mol		26.7±2	50.0±2
$-\Delta S^{\ddagger}$, J/mol·K		200±10	138±10

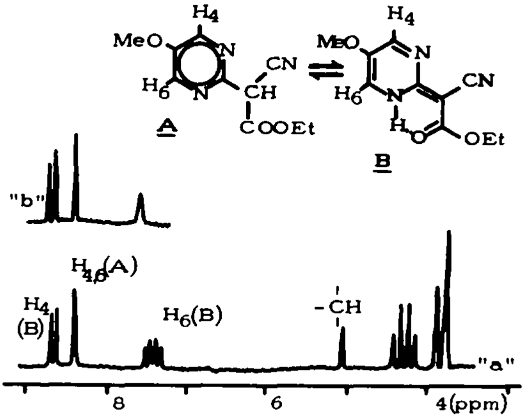


Fig. 2. The PMR spectrum of cyanoacetic ester 7 in $CDCl_3$ at 260 K(a) and 303 K(b).

With the temperature changed from − 33° to 97°, only the character of H_6(B) and NH proton signals is changed (see Fig. 2). It has been shown by the double resonance method that the broadening is related to the disappearance of spin-spin coupling of H^6 and NH protons. This indicates that the rate of rupture of the NH bond significantly exceeds the rate of the tautomerisation A⇄B, which permits us to leave out of consideration the synchronous mechanism (a), in which the rupture and the formation of the C−H and NH bonds must proceed simultaneously.

According to Bell[16] and Reutov with co-workers[17], the possibility of tautomerisation via the tight ion pair is especially high in the case of weakly polar aprotic solvents. In our case this mechanism is hardly possible, as the addition of deuteromethanol to chloroform solutions of compound 7 results in a fast isotope exchange. As shown above, the N−H bond cleavage rate exceeds by far the tautomerisation rate. Therefore, in the case of the two remaining mechanisms "c" and "d", the rate determining step should involve formation (or cleavage) of C−H bond. In order to confirm this suggestion, we have studied the kinetic isotope effect. As the tautomerisation rate is extremely sensitive to concentration of a compound and the solvent purity, we have developed a procedure for measuring the kinetic isotope effect on the basis of the method of competitive rate determination. The measuring of the rates of tautomerisation was performed by the p.m.r. method in a tube with the solution of pyrimidylcyanoacetic ester and its deutero-analogue (1:1) in $CDCl_3$. After the equilibrium had been disturbed by a temperature jump, the relaxation process was observed by p.m.r. spectroscopy. As the signals at 5.1 ppm (CH) and at 14 ppm (NH) respond only to the proton migration, while other signals respond to proton and deuterium migrations, there is the possibility of simultaneous measurement of tautomerisation rates for compound 7 and its deuterated analogue. The analysis of the kinetic equations provides additional simplifications. As shown above, the tautomerisation[18] rate is defined by the kinetic equation for the first order reversible reaction (eq. 1, Fig.2):

$$k^{obs} = k^1 + k^{-1} = \frac{1}{t} \ln \frac{A^o - \bar{A}}{A - \bar{A}}, \qquad /1/$$

where $\bar{A}$ − equilibrium concentrations of the tautomeric A form, A^o − concentration at the start of measurement, A − concentration of the A form during measurement, t − time.

As the replacement of hydrogen by deuterium had a small effect on the tautomeric equilibrium[19], i.e., $K^t_H = K^t_D$ and $k^1 = \frac{k^{obs}}{1 + K_t}$, then

$$k_H/k_D = k^1_H/k^1_D = k^{obs}_H/k^{obs}_D. \qquad /2/$$

By substituting k^{obs} in eq. 2 for their value, determined from eq. 1, we obtain:

$$k_H/k_D = \frac{\ln(A_H^o - \bar{A}_H)/(A_H - \bar{A}_H)}{\ln(A_D^o - \bar{A}_D)/(A_D - \bar{A}_D)} , \qquad /3/$$

where $\bar{A}_H$, $\bar{A}_D$ - equilibrium concentrations of the tautomeric A form (containing proton A_H and deuterium A_D), A_H, A_D - concentrations of the A form and its deuterium analogue during measurement; A_H^o, A_D^o - concentrations of these forms at the start of measurement. The concentrations were determined from the integral intensities of the signals at 5.1 ppm (-CH-, form A_H), 3.95 ppm (OCH_3, form A_{H+D}), and 3.8 ppm (OCH_3, form B_{H+D}).

In equation 3, time (t) is absent, as all measurements for the H- and D-containing samples are carried out simultaneously. This allows the use of Fourier transform p.m.r. spectroscopy with signal accumulation, which affords increased accuracy of k_H/k_D determination. Measurements performed at - 4° revealed the primary kinetic isotope effect equal to 3.5 ± 0.5. These data conform to intermolecular ion-dissociative mechanisms "c" and "d", whose limiting stage is cleavage (or formation) of the C-H bond. Obviously, depending on the acid/base character of medium and compound, either of the two mechanisms may take place. In neutral solvents, the base-catalysed one seems to be more likely, as the strong CH-acids are more sensitive to base catalysis[16].

EXPERIMENTAL

The i.r. spectra were recorded on a UR 20 spectrophotometer, the u.v. spectra - on a UV-VIS Specord instrument. The ^1H and ^{13}C n.m.r. spectra were obtained with concentrations of 0.1-1%($CDCl_3$) in the Fourier transform mode with a Bruker WP 80 spectrometer. The ^{14}N n.m.r. spectra were measured on a Bruker WH 400 instrument. The ^{14}N chemical shifts were determined relative to the signal of external nitromethane (at ambient temperature), the ^{13}C chemical shift - relative to the signal of internal $CDCl_3$ and then it was converted to TMS-scale. The tautomer ratios were determined from the integral intensities of ring protons. To ensure accuracy, 10 to 100 scans were effected with a 20 s pulse delay, which is considerably greater than the proton relaxation time.

The kinetic measurements were carried out on a Bruker WP 200 and HX-90 instruments. Measurements of the kinetic isotope effect were conducted for 0.3% solution of compound 7 in $CDCl_3$, which had been dried just before the preparation of the solution. The solution was placed in a tube, which was then flushed with argon and sealed. The ampoule was kept for about 1 h at 60° (equilibration), then placed into the n.m.r. spectrometer sensor, which had been cooled to the required temperature. Measurements were started within five minutes.

To estimate the thermodynamic parameters, the equilibrium constants were measured for $CHCl_3$ solutions of compounds 7 and 8 (the tubes were sealed) in the range of 240 to 367 K, for compound 17 - in the range of 227 to 303 K.

Compounds 1-17 were synthesized from chloro- (1-5, 9-12, 15-17), fluoro- (7, 8, 14) and methylsulphonylpyrimidines (6,13), as described earlier[1]. Chromatographically purified and recrystallised compounds were identified by the t.l.c. and p.m.r. methods. The correct results of elemental analyses for carbon, hydrogen and nitrogen were obtained for all the compounds. The melting points and the p.m.r. data for the compounds are listed in Table 1.

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