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Spectral Study of the Molecular Structure of Some 2-Methylthio-6-methyl-4-alkyl- and Alkylaminopyrimidines

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Abstract—A number of 2-methylthio-6-methyl-4-alkyl- and alkylaminopyrimidines, as well as their salts produced by the reaction with methyl *p*-toluenesulfonate and trifluoroacetic acid, were investigated. The quantum chemical and experimental IR and Raman spectral methods were used to determine the preferential isomeric forms of the molecules of studied compounds, whose convenient spectral markers were revealed. The starting pyrimidines and their salts were found to exist predominantly as an amino form. The salt formation proceeds via the methylation (protonation) of the N^1 atom of pyrimidine ring.

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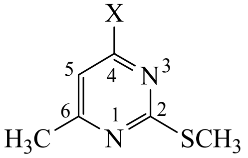
Pyrimidines and their derivatives are the nitrogen-containing compounds with high biological activity and extremely wide application fields. They play a great role in the life processes, and their functions and activity can vary considerably depending on such structural modifications as the introducing substituents into the molecule, tautomeric and even conformational transitions. Hence, there is the interest in the structural investigations of pyrimidines, including the methods of vibrational spectroscopy [1, 2].

The aim of this work is a study of the pyrimidines **I**–**VI** structure as well as the products of their reaction with methyl *p*-toluenesulfonate and trifluoroacetic acids using the IR and Raman spectroscopy combined with the quantum chemical calculations of the vibrational spectra. These compounds exhibiting diverse biological activities are also of interest as the starting material to obtain the macrocyclic and chelate molecular systems capable of selective binding of amines, amino acids, adenosine phosphates.

Various aspects of the electron shell mobility of the molecules of such compounds as well as their ability to structural transitions from one form to another, in particular the amine-imine tautomerism, have been previously discussed [3–12]. At the same time, there are little data on the theoretical analysis of the possible molecular forms and their spectral parameters, and also on the co-application of IR and Raman spectroscopy for this purpose.



X = CH_3 ($\mathbf{I}$, $\mathbf{I}^{k}$, $\mathbf{I}^{s}$); NH_2 ($\mathbf{II}_a$, $\mathbf{II}_a^{k}$, $\mathbf{II}_a^{s}$, $\mathbf{II}_i$, $\mathbf{II}_i^{k}$); $HNC_{10}H_{21}$ ($\mathbf{III}_a$, $\mathbf{III}_a^{k}$, $\mathbf{III}_a^{s}$, $\mathbf{III}_i$, $\mathbf{III}_i^{k}$, $\mathbf{III}'^{s}$); $H(CH_3)_2$ ($\mathbf{IV}$, $\mathbf{IV}^{k}$, $\mathbf{IV}^{s}$); HNC_2H_5 ($\mathbf{V}_a$, $\mathbf{V}_a^{k}$, $\mathbf{V}a^{S}$, $\mathbf{V}_i$, $\mathbf{V}_i^{k}$); HN-C_6H_{12}NH-Pm ($\mathbf{VI}_a$, $\mathbf{VI}_a^{k}$, $\mathbf{VI}_a^{S}$, $\mathbf{VI}_i$, $\mathbf{VI}_i^{k}$), (Pm) 2-methylthio-6-methyl-pyrimidine.

As an example, consider the results of the IR spectral experiment for compound **VI** and its corresponding salt $\mathbf{VI}^{s}$. The spectra of the starting compounds **VI** and methyl *p*-toluenesulfonate (TsOMe) are presented on Fig. 1.

The IR spectrum of the salt $\mathbf{VI}^{s}$ (Fig. 2, curve *1*) is very different from those of the starting compounds. In the spectrum the intense absorption bands at 1644 (CCN), 1221 and 1010 (SO_3^-) cm^{-1} appear [13, 14],

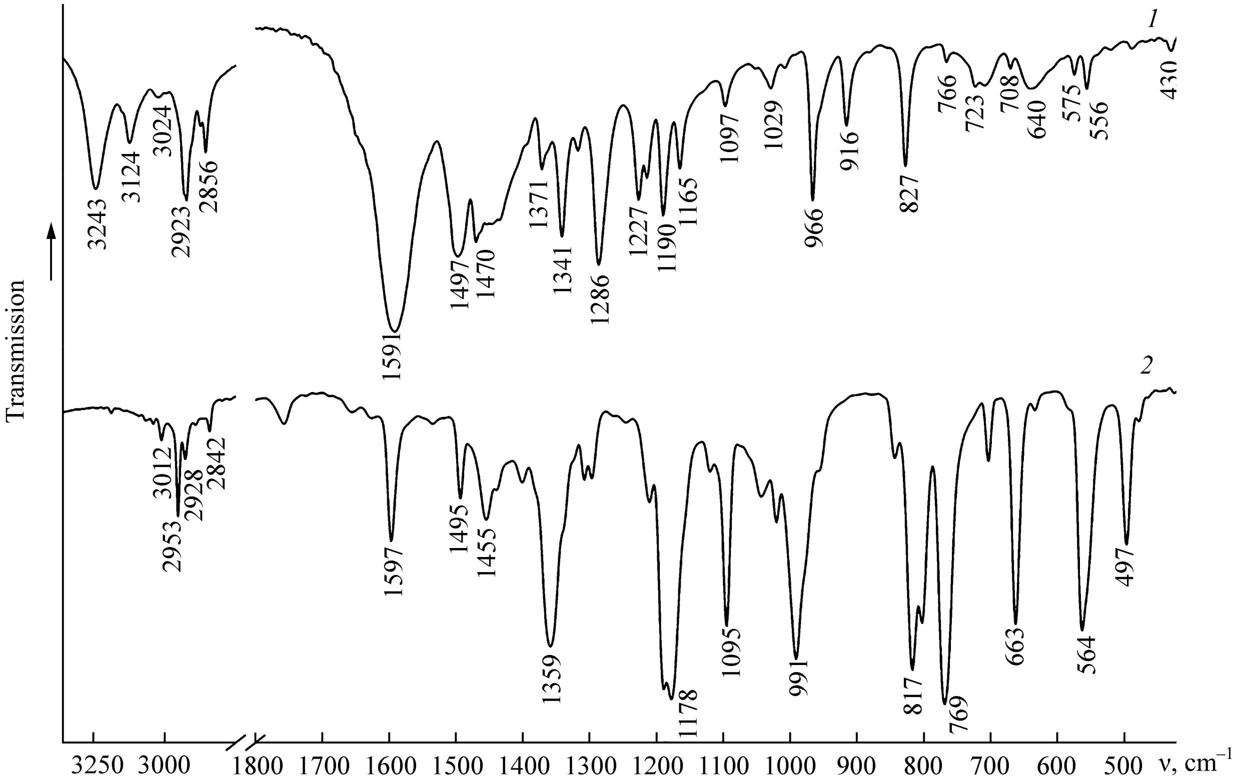


Fig. 1. The IR spectra of (*1*) compound **VI** and (*2*) methyl *p*-toluenesulfonate.

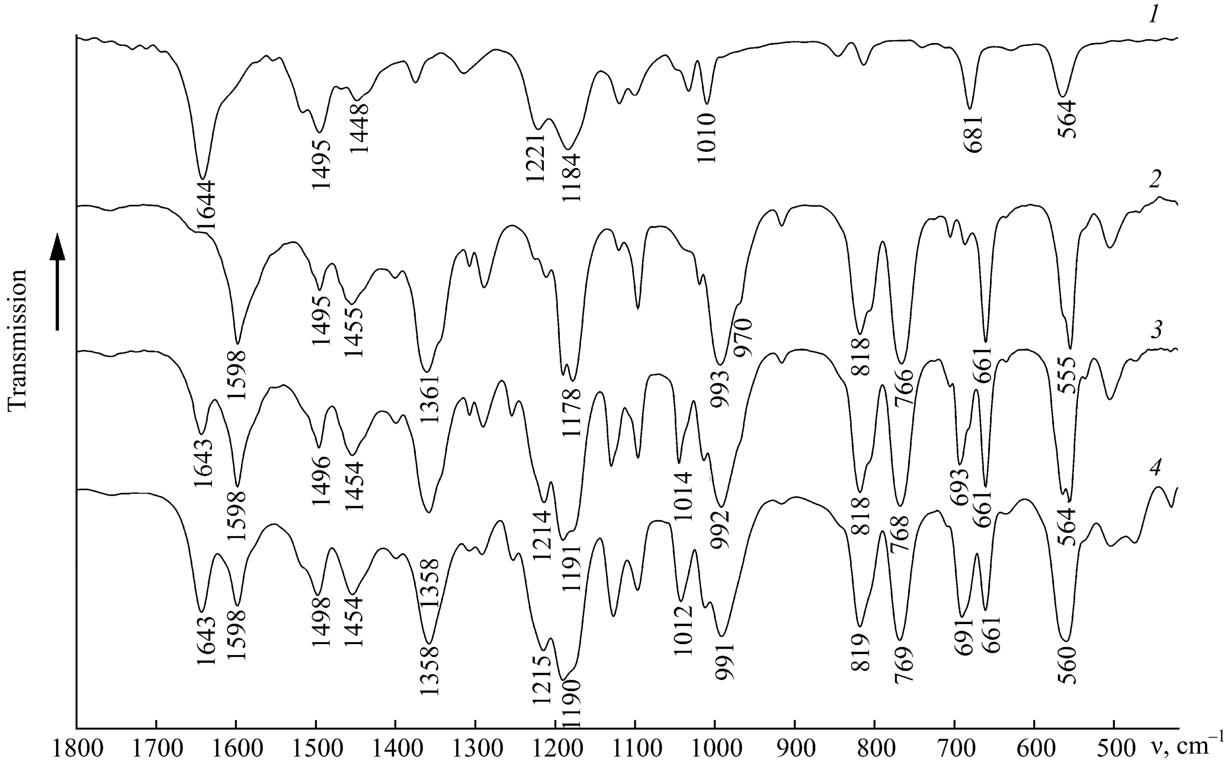
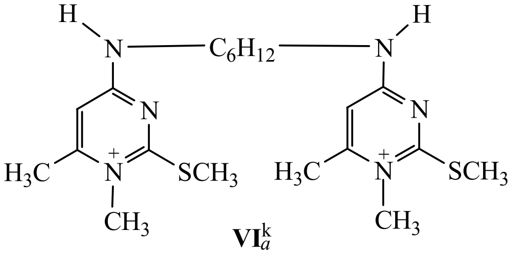
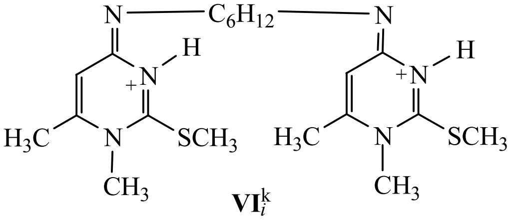


Fig. 2. The IR spectra of (*1*) compound **VI**^{S}, (*2*) melt of [**VI** + TsOMe] mixture at ~180°C, (*3*) the same mixture after 1 day at ~25°C, and (*4*) after 2 days at ~25°C.

while the absorption band of SO_2-group (1359 cm^{-1}) disappears. Similar changes are recorded in the Raman spectra: a peak ν(CCN) (1647 cm^{-1}) is of medium intensity. All this corresponds to the reaction scheme: **VI** + 2 TsOMe → $\mathbf{VI}^k$ + 2 TsO^-. The possible forms of the cation $\mathbf{VI}^k$ formed by the base **VI** are shown below:



$\mathbf{VI}_a^k$



$\mathbf{VI}_i^k$

The following notations were used for the studied objects: *a*/*i* is amine/imine form; k/s is cation/salt form. When a compound without specifying the tautomeric composition is discussed, the a/i notation is omitted.

Comparison of the IR spectra of [**VI** + TsOMe] mechanical mixture and the melt after keeping the latter between KBr plates at room temperature for 2 days, (Fig. 2) illustrates the transformation dynamics of [**VI** + TsOMe] mixture into a salt pair, occurring even without heating the mixture.

The spectra of compound **I** and all the starting aminopyrimidines **II**–**VI** are similar in the pyrimidine (Pm) ring vibrations field. The analogy of the spectra of the primary and secondary amines **II**, **III** and **VI** with those of compounds **I** and **IV**, for which the imine structure is not possible [7, 15], suggests the amine structure for the molecules of **II**, **III**, **VI,** in accordance with the many published data [3–12, 15].

Like the spectra of salt $\mathbf{VI}^s$, the IR/Raman spectra of the products of the reaction of pyrimidines **I**–**IV** with TsOMe contain the high-frequency peaks νCCN (cm^{-1}): 1618 v.s/1601 m ($\mathbf{I}^s$), 1655 v.s ($\mathbf{II}^s$), 1644 v.s/1632 m ($\mathbf{III}^s$), 1636 v.s/1639 m ($\mathbf{IV}^s$), and also absorption bands (cm^{-1}) ~1190/1120 v.s (SO_3^-), ~1030/1010 s, ~680 m, ~570 m, which are typical for the anions [13, 16–18]. In the spectra of the product of the reaction of compound **III** with trifluoroacetic acid the absorption band with a maximum at 1576 cm^{-1} [$\nu_{as}(CO_2)$] appears instead of the band 1800 cm^{-1} [ν(C=O)]. Thus, all the reactions yield the acids anions involving SO_3^- or $CF_3CO_2^-$ group. The formed Me^+ or H^+ fragment attached to the pyrimidine ring, causing an increase in the ν(CCN) frequency in the spectra of pyrimidine cations compared with those for the starting neutral structure. As shown in [7], the reaction of the studied aminopirimidine with methyl iodide proceeds via the transition of Mg^+-group of the latter to the nitrogen atom N^1 of the pyrimidine ring. This is logical to assume in our case, taking into account the maximal basicity of the N^1 atom relative to all other atoms of pyrimidine ring [15]. In [7] the rebuilding the original structure of the amine into the imine form assumed to be a result of methylation. According to the NMR spectra, the proton of trifluoroacetic acid by reacting with compound **III** also becomes attached to the N^1 atom of the pyrimidine ring [11].

Based on the literature data [3–12, 15], for the salts $\mathbf{II}^s$, $\mathbf{III}^s$, $\mathbf{V}^s$ and $\mathbf{VI}^s$ can be expected the both amine (*a*) and imine (*i*) forms of the pyrimidine cation as shown above for the dication $\mathbf{VI}^k$.

In the spectra of the pyrimidinium salts the stretching vibrations ν(C=N) of the cation are known to be usually manifested in the frequency range above 1600 cm^{-1} [13–18], while the vibrations of the neutral pyrimidine ring appear at about 1600 cm^{-1} and below. This increase in the ν(C=N) frequency compared with the spectra of the starting bases **I**–**VI**, is observed in the spectra of their salts resulting from the methylation. For example, in the IR spectrum of the salt $\mathbf{VI}^s$ the ν(C=N) band (1644 cm^{-1}, Fig. 2) coincides practically with the corresponding bands in the IR spectrum of 1,2-dihydro-2-imino- and l,4-dihydro-4-imino-l-methylpyrimidines (1645, 1648 cm^{-1}) described in [7]. All this may testify in favor of imine forms of the salts $\mathbf{II}^s$, $\mathbf{III}^s$, and $\mathbf{VI}^s$. But at the same time, in the spectra of the dimethylamino derivative salt $\mathbf{IV}^s$, where the fragment with imino-pyrimidine structure is impossible, an intense high-frequency peak with a maximum at 1638 cm^{-1} also presents. According to [15], pyridinium cation Py^+ formation is indicated by the IR spectra as a high frequency shift of the stretching vibrations bands of pyridine ring from

~1600 to ~1640 cm^{-1}. Thus, the observed increase in the ν(C=N) frequency up to ~1645 cm^{-1} in the spectra of pyridinium salts may be a result of the pyrimidine ring ionization, rather than its transformation into the imino form.

To obtain the additional data, we investigated the IR spectra of diluted chloroform and ethanol solutions of the starting bases **III**, **IV**, **VI** and **V** [19] and their salts at various concentrations. In all cases the IR spectra of the salts at ~1650 cm^{-1} remains the same, pointing to the absence of tautomeric transformations under the experimental conditions.

In the spectra of the diluted solutions of the starting bases **III**, **V**, **VI** ($CHCl_3$, $CDCl_3$ ~10^{-3} mol l^{-1}) the broad band at ~3000–3400 cm^{-1} belonging to the NH involved into a hydrogen bonding (νNH^b), being typical for the polycrystalline amines [13, 16–18], are replaced by a high-frequency narrow doublet νNH at ~3440/3430 cm^{-1}. The doublet structure of the vibrational bands of free N–H bonds [$\nu(NH^f)$] is characteristic for the secondary amines and explainable by the coexistence of N–C–NH *cis*- and *trans*-structures in solution [13, 16, 17]. In the IR spectrum of the base **II** solution there are two $\nu(NH^f)$ bands at 3531 [$\nu_{as}(NH_2)$] and 3412 cm^{-1} [$\nu_s(NH_2)$]. All this indicates clearly the available hydrogen bonds breakage [$\nu(NH^b)$] followed by their replacing with $\nu(NH^f)$ according to the molecular structure of the amine bases.

In the spectra of solutions of the corresponding salts, when diluting, the contours of the $\nu(NH^b)$ absorption bands are only a little changed, but do not disappear. The high-frequency bands $\nu(NH^f)$ do not appear, i.e., the NH-groups are involved into the very strong intermolecular hydrogen bonding, in particular with TsO^-. In addition, in the case of imine salts structure one can also expect the appearance of the low-frequency bands of stretching vibrations of exocyclic N^+–H bonds [$\nu(N^+H)$] in their spectra. Thus, in the spectra of a $PyH^+SnCl_6^-$ system the $\nu(N^+H)$ frequency is 3260/3240, 3188 cm^{-1} [15], i.e., very close to the frequencies recorded in the spectra of the salts **III**^{s}, **VI**^{s}. There are other examples of similar $\nu(N^+H)$ frequency [16].

Thus, the described analysis confirms the salt formation and provides arguments both in favor of the amine and imine structures of the methylated (protonated) pyrimidinium cation in these salts **I**^{s}, **III**^{s}, and **VI**^{S}. In this connection the task of establishing the structure of the obtained salts can not be completely solved within the framework of a purely empirical approach based on comparison of spectra with the previously published spectra of similar compounds and the use of well-known spectral-structural correlations.

Table 1. The calculated electron energy difference Δ*E* (kcal mol^{-1}) for the most favorable conformers of amino and imino forms of the neutral starting molecules and their cations

Compound	Amino form (*a*)	Imino form (*i*)
II	0	16.9
II^k	0	25.4
V [19]	0	15.2
V^k	0	26.3

For further clarification, we performed the quantum chemical calculations of possible structures and their spectra. All they are similar to those calculated for the compound **V** in [19]. The calculated theoretical energy difference between the optimized conformers with the S–CH_3 fragment *anti*-arranged relative to C^2=N^1 bond of amino- and imino-forms of neutral molecules and cations of the pyrimidine compounds is presented in Table 1 by an example of compounds **II**, **II**^{k}, **V** and **V**^{k}.

As mentioned above, in the reaction of aminopyrimidines **I**–**VI** with methyl *p*-toluenesulfonate and, consequently, the formation of salts **I**^{s}–**VI**^{s}, the most likely methylation position is the N^1 atom of pyrimidine ring owing to its greater basicity compared with the N^2 atom. The quantum chemical calculations of the two variants of the structure **IV**^{k} (with Me^+ bonded with the N^1 atom in the first case and with N^3 atom in the second) confirm this assumption: the energy of the first structure (N^1–Me^+) is by 12.1 kcal mol^{-1} lower than of the second structure (N^2–Me^+).

According to the calculations, the amine form of the isolated cations is energetically more favorable in comparison with the imine tautomers (Table 1). Nevertheless, we performed calculation of IR and Raman spectra for both the amino- and imino-forms of the neutral molecules of the starting bases and the corresponding cations. In all cases, the calculations show that the ν(C=N) frequency of the imino-form is higher (~1670 cm^{-1} in the neutral molecule, ~1700 cm^{-1} in the cation) compared to the amino-form (~1590 cm^{-1} in the neutral molecule, ~1650 cm^{-1} in the cation). This fact can be explained by the difference in the form of the discussed vibrations. In the case of imines the main contribution is from the exocyclic C=N bond, along with some participation of pyrimidine ring, while in the amines from the ordinary C–N bond with a much smaller force constant. In the spectra of the cations these differences between the tautomers are more pronounced (Table 2): the calculations for the structures of $\mathbf{III}^{k}$ predict an increase beyond 1600 cm^{-1} of two frequencies (1712, 1642 cm^{-1}) for imino-form, while for the amino cation of one frequency (1634 cm^{-1}).

As mentioned above, the quantum-chemical calculations for the two variants of the structure $\mathbf{IV}^{k}$ indicate the preference for the methylation of pyrimidine core on the N^1 atom. The comparison of the theoretical IR and Raman spectra of compound $\mathbf{IV}^{k}$ with the experimental data confirm this conclusion: the calculated frequencies ν_{ring}(C=C, C=N) 1633 cm^{-1} and ν(C–N) 1582 cm^{-1} for the molecule of $\mathbf{IV}^{k}$ containing Me^+, attached to the N^1 atom, are close to the corresponding experimental frequencies (1636 and 1592 cm^{-1} in the IR and 1639 and 1599 cm^{-1} in the Raman spectra). At the same time, the calculations for the structure $\mathbf{IV}^{k}$ with an ion Me^+, attached to the N^2 atom, predict the corresponding vibrations the frequencies 1601 and 1531 cm^{-1}, which are not consistent with the experimental spectra.

Thus, the intense infrared bands and Raman lines associated with the vibrations of C=N, C–N and C=C groups, manifested in the spectral region where they are not overlapping with the bands of pyrimidine ring and exocyclic groups are useful for the study of amine-imine tautomerism. According to the calculations, the appropriate frequencies for the amino forms of the starting bases should be observed in the range of ~1574–1596 cm^{-1}, for the imine at ~1668–1673 cm^{-1}, for the amine tautomers of the salt cations at ~1603–1641 cm^{-1} and for the imine tautomers of the salt cations at ~1709–1713 cm^{-1}. In the spectra of compounds $\mathbf{I}_{a}$, $\mathbf{I}_{a}^{s}$, $\mathbf{IV}_{a}$, $\mathbf{IV}_{a}^{s}$ of amine structure (due to the lack of labile protons) the experimental frequencies are actually within the range predicted by the calculation for the amines. In the spectra of compounds **III**, $\mathbf{III}^{s}$, **VI**, $\mathbf{VI}^{s}$ (compound **II** will be discussed below) the corresponding peaks are recorded at 1574–1592 cm^{-1} for the bases and at 1632–1655 cm^{-1} for the salt, i.e., all the studied compounds are predominantly in amine form. However, in the Raman spectra of compounds $\mathbf{II}^{s}$ and $\mathbf{III}^{s}$ were recorded weak peaks in the imine region (~1703–1715 cm^{-1}). Therefore, the presence of the small amounts of imine tautomers in these cases can not be excluded.

As shows Table 2, in almost all cases there is good agreement between the calculated and experimental vibrational frequencies with the participation of C=N, C–N and C=C groups for the amino tautomers. However, for the structure **II** a deviation of the corresponding theoretical values from the experimental frequencies of the solid samples is observed. This fact is explained by involvement of NH_2 groups into the $NH_2\cdots X$ hydrogen bonding in the condensed state. According to calculations, the deformations $\delta(NH_2)$ contribute significantly to the potential energy of the discussed vibrations with the frequencies 1596 and 1569 cm^{-1} (34 and 45%, respectively). Therefore, the formation of the strong hydrogen bonds increasing $\delta(NH_2)$ leads to a high-frequency shift of the corresponding bands in the experimental spectra of the solid samples. Thus, these calculated frequencies for compound **II** should be compared with the spectra of the diluted solutions of these compounds in neutral solvents, which are unable to form the hydrogen bonds (Table 2).

To check the universality of the above spectral-structural correlations, we recorded the IR spectra of the salt $\mathbf{III}'^{s}$ formed by the reaction with trifluoroacetic acid in $CDCl_3$ solution. According to the published NMR data [11], in the $CDCl_3$ medium this salt exists as an amino-form, and the formed pyrimidinium cation is protonated at the N^1 atom. In this case, in the IR spectrum of the salt $\mathbf{III}'^{s}$ solution one should expect the appearance of a strong band in the range of ~1600–1655 cm^{-1}, which was experimentally observed (1653 cm^{-1}).

Thus, the calculation of all the molecules of the studied series showed that the chosen method B3LYP/6-31G* predicts correctly the frequencies of the experimental spectrum and reproduces all the effects associated with the charge state of the molecule, tautomeric changes in the structure, as well as the position of the methyl group or proton in the formed pyrimidinium cation. The used scaling factors can significantly improve the quality of the calculations. Good agreement between the theoretical and experimental frequencies confirms the ability to transfer the working set of scaling factors in the studied series of compounds.

Thus, the methods of quantum chemistry and the experimental IR and Raman spectroscopy were used to

Table 2. Assignement of the calculated and experimental vibration frequencies ν_{ring}(C=C,C=N), ν(C–N)

Compound	Calculation		Experiment	
	ν, cm^{-1}	IR (Raman) intensity	IR, ν, cm^{-1} in vaseline oil (in $CHCl_3$)	Raman, pure substance, ν, cm^{-1}
I	1574	237 (8)	1582 v.s	1582 v.w
	1545	245 (39)	1543 s	1539 w
$\mathbf{I}^k$	1603	308 (22)	1618 v.s	1601 m
	1537	319 (42)	1542 m	1546 v.w
$\mathbf{II}_a$	1596	347 (10)	1665 s (1612 v.s)	1674 v.w
	1569	246 (8)	1592 v.s (1581 s)	1594 w
$\mathbf{II}_a^k$	1641	806 (18)	1637 m (1655 v.s)	1635 v.w
	1606	44 (12)	1600 v.w (1603 v.w)	1602 m
$\mathbf{II}_i$	1669	554 (82)	1665 s (1612 v.s)	1674 v.w
	1580	54 (11)	1592 s (1581 s)	1594 w
$\mathbf{II}_i^k$	1709	436 (153)	–	1715 v.w
	1634	19 (19)	1637 m (1655 v.s)	1635 v.w
$\mathbf{III}_a$	1587^a	710^a	1592 v.s (1588 v.s)	1580 m
	1555^a	151^a	1554 sh (1550 m)	1533 v.w
$\mathbf{III}_a^k$	1634	993 (30)	1645 s (1644 v.s)	1632 m
	1576	158 (47)	1579 w (1586 v.w)	1598 m
$\mathbf{III}_i$	1668^a	797^a	–	–
	1585^a	52^a	1592 v.s (1588 v.s)	–
$\mathbf{III}_i^k$	1712	472 (430)	1708 v.w (1703 v.w)	1712 v.w
	1642	55 (24)	1645 s (1644 v.s)	1632 m
IV	1582	683 (16)	1584 v.s	1579 w
	1536	164 (22)	1535 sh	1533 sh
$\mathbf{IV}^k$	1633	806 (38)	1636 v.s	1639 m
	1582	116 (45)	1592 m	1599 s
$\mathbf{VI}_a$	1589	179 (15)		
	1587	1400 (4)	1592 v.s (1587 v.s)	1574 m
	1569	131 (25)		
	1568	147 (24)	1542 sh (1551 m)	1536 v.w
$\mathbf{VI}_a^k$	1635	0 (75)		
	1632	1644 (0)	1644 v.s (1646 v.s)	1647 m
	1587	0 (90)		
	1585	704 (0)	1623 sh (1615 w)	1624 m
$\mathbf{VI}_i$	1673	318 (468)		
	1669	1269 (106)		
	1604	49 (7)		
	1602	51 (7)	1592 v.s (1587 v.s)	1574 m
$\mathbf{VI}_i^k$	1713	1 (1050)		
	1711	1268 (0)		
	1653	10 (30)		
	1653	36 (9)	1644 v.s (1646 v.s)	1647 m

[a] The reported values are the frequencies and intensities of the compounds $\mathbf{V}_a$ and $\mathbf{V}_i$ taken from [19], since the replacement of the C_2H_5 alkyl chain (**V**) with $C_{10}H_{21}$ (**III**) does not affect much the bands ν(C=N), ν(C–N); these values in the table are compared with the experimental values for compounds $\mathbf{III}_a$ and $\mathbf{III}_i$.

investigate a number of 2-methylthio-6-methyl-4-alkyl- and alkylaminopyrimidines and their salts formed by the reaction of pyrimidines with methyl *p*-toluenesulfonate and trifluoroacetic acid. The predominant isomeric forms of the compounds were determined, for which the convenient spectral markers were revealed. Both the original pyrimidines and their salts were shown to exist predominantly in the amino form. The salt formation takes place through the methylation (protonation) at the N^1 atom of pyrimidine ring, resulting in a marked increase in the frequency of the stretching vibrations of the pyrimidine core in the IR and Raman spectra, up to ~1650 cm^{-1}. In the spectra of the starting bases the corresponding peaks are grouped in the range of ~1600 cm^{-1} and below.

EXPERIMENTAL

The synthesis procedure for compound **I** is given in [20], compounds **III**, **III**^{s} and **IV**^{s} in [21], compounds **II**, **III**$'^s$, **VI**, and **VI**^{s} in [11], compound **IV** in [22]. The salts **I**^{s}, **II**^{s}, and **V**^{s} were prepared by the procedure [21]. Synthesis of compound **V** is described in [23].

The IR spectra were recorded in the range of 4000–400 cm^{-1} on a Tensor 27 (Bruker) IR Fourier-spectrometer with an optical resolution of 4 cm^{-1} with accumulation of 64 scans. The samples were prepared as KBr pellets, emulsions in vaseline oil and solutions in $CHCl_3$, $CDCl_3$, CCl_4, MeOH, EtOH (c 10^{-3}–10^{-4} mol l^{-1}, l 1.02 and 0.176 mm). The solvents were previously distilled and dehydrated.

The Raman spectra were recorded on a Vertex 70 (Bruker) spectrometer with an infrared laser Nd:YAG CrystaLaser IRCL-XXX-WL (λ 1064 nm, 200 mW) in the range of 3600–100 cm^{-1} with an optical resolution of 2 cm^{-1} and the accumulation of 256 scans.

The calculations method. All calculations were performed within density functional theory using the Gaussian-03 software package [24]. The Becke's three-parameter exchange functional [25] in conjuncttion with the Lee–Yang–Parr correlation functional [26] (B3LYP) was used. The standard basis set 6-31G* was applied. The correspondence of the calculated stationary points to the potential energy surface minima was checked by computing the Hessian matrix and analyzing the obtained frequencies for the absence of imaginary ones. To correct the systematic errors caused by the limited size of the basis set functions and implementation of the harmonic approximation for computing vibration frequencies [27], and by the incomplete accounting for the electron correlation, the force constants were multiplied by the correction scaling factors s: $F_{ij}^{\mathrm{scal}} = (s_i s_j)^{1/2} F_{ij}$, where F_{ij} are the force constants in the dependent natural coordinates [27]. The conversion of the force fields, calculated in the Cartesian coordinates, to natural coordinates and the scaling with use of the known scaling factors [28, 29] were performed using the software [30].

In the calculations of the molecular structure and spectra of the salts their anionic components were not taken into account, since the anion variation in such cases does not affect the position of the spectral bands of the cations, i.e., analyzing their spectra, the effect of the counterions can be not taken into account.

REFERENCES

1. Jayanth, N., Ramacandran, S., and Puranik, M., *J. Phys. Chem. A*, 2009, vol. 113, p. 1459.
2. Gerega, A., Lapinski, L., Nowak, M.J., Furmanchuk, A., and Leszczynski, J., *J. Phys. Chem. A*, 2007, vol. 111, p. 4934.
3. Brownlie, I.A., *J. Chem. Soc*., 1950, p. 3062.
4. Marshall, J.R. and Walker, J., *J. Chem. Soc*., 1951, p. 1004.
5. Whittaker, N., *J. Chem. Soc*., 1951, p. 1565.
6. Short, L.N. and Thompson, H.W., *J. Chem. Soc*., 1952, p. 168.
7. Brown, D.J., Hoerger, E., and Mason, S.F., *J. Chem. Soc*., 1955, p. 4035.
8. Lord, R.C., Marston, A.L., and Miller, F.A., *Spectrochim. Acta*, 1957, vol. 9, no. 2, p. 113.
9. Ivashchenko, A.V., Goricheva, O.N., Shmelev, L.V., and Ryabokobylko, Yu.S., *Khim. Getrotsikl. Soedin*., 1980, no. 8, p. 1114.
10. Inuzuka, K. and Fujimoto, A., *Bull. Chem. Soc. Japan*, 1990, vol. 63, no. 4, p. 971.
11. Kozlov, A.V., Semenov, V.E., Mikhailov, A.S., Aganov, A.V., Smith, M.B., Reznik, V.S., and Latypov, S.K., *J. Phys. Chem. B*, 2008, vol. 112, no. 10, p. 3259.
12. Ten, G.N., Nechaev, V.V., Zotov, N.B., and Baranov, V.I., *Opt. i Spektr.*, 2009, vol. 107, no. 1, p. 62.
13. Bellamy, L., *New Data on IR Spectra of Complicated Molecules*, Moscow: Mir, 1971.
14. Kuptsov, A.Kh. and Zhizhin, G.N., *Fur'ye-KR i Fur'ye-IK spektry polimerov* (Fourier-Raman and Fourier-IR Spectra of Polymers), Moscow: Fizmatlit, 2001.
15. *Physical Methods in Heterocyclic Chemistry*, Katritzkii, A.R., Ed., Leningrad: Khimiya, 1966.

16. Colthup, N.B., Daly, L.H., and Wiberley, S.E., *Introduction to Infrared and Raman Spectroscopy*, New York: Academic Press, 1964.
17. Rao, C.N.R., *Chemical Applications of Infrared Spectroscopy*, New York: Academic Press, 1963.
18. Kizel', V.A., *Prakticheskaya molekulyarnaya spektroskopiya* (Practical Molecular Spectroscopy), Moscow: MFTI, 1998.
19. Shagidullin, R.R., Chernova, A.V., Bazhanova, Z.G., Lii, J.-H., Kataev, V.E., Katsyuba, S.A., and Reznik, V.S., *J. Mol. Struct*., 2004, vol. 707, nos. 1–3, p. 1.
20. Hunt, R.R., McOmie, J.F.W., and Sayer, E.R., *J. Chem. Soc*., 1959, p. 525.
21. Kozlov, A.V., Semenov, V.E., Mikhailov, A.S., Il'yasov, A.V., Reznik, V.S., and Latypov, Sh.K., *Izv. Akad. Nauk SSSR*, *Ser. Khim.,* 2009, no. 1, p. 51.
22. Arutyunyan, E.A., Gunar, V.I., Gracheva, E.P., and Zav'yalov, S.I., *Izv. Akad. Nauk SSSR*, *Ser. Khim.,* 1969, no. 3, p. 655.
23. Shagidullin, R.R., Chernova, A.V., Doroshkina, G.M., Kataev, V.E., Bazhanova, Z.G., Katsyuba, S.A., Raznik, V.S., Mikhailov, A.S., Ganiyatullin, R.Kh., Pashkurov, M.G., Efremov, Yu.Ya., and Nafikova, A.A., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 10, p. 1725.
24. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Vreven, T., Jr., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *GAUSSIAN 03,* Revision, B.05; Gaussian, Inc., Wallingford CT, 2004.
25. Becke, A.D., *Phys. Rev. A*, 1988, vol. 38, no. 6, p. 3098.
26. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*, 1988, vol. 37, no. 2, p. 785.
27. Vol'kenshtein, M.V., *Stroenie i fizicheskie svoistva molekul* (Structure and Properties of The Molecules), Moscow: Akad. Nauk SSSR, 1955.
28. Baker, J., Jarzecki, A., and Pulay, P., *J. Phys. Chem. A*, 1998, vol. 102, no. 8, p. 1412.
29. Katsyuba, S.A. and Vandyukova, E.E., *Chem. Phys. Lett*., 2003, vol. 377, nos. 5–6, p. 658.
30. Sipachev, V.A., *J. Mol. Struct*., 2001, vol. 67, p. 567.