of (I)-(III). Aband for the normal vibration with the participation of the Si \leftarrow 0 bond in the region below 200 cm⁻¹ can be expected in the IR spectra of compounds (I-III). In the case of a sufficient degree of localization of this vibration on the Si \leftarrow 0 bond its frequency must obey the equation $v = v_0 - \rho \sigma_p$.

CONCLUSIONS

1. In the spectra of (aroyloxymethyl)trifluorosilanes and methyl (aroyloxymethyl) fluorosilanes with the general formula $4-X-C_6H_4COOCH_2Si(Me)_{3-n}F_n$ (n = 1-3) the variation of the vC=0 frequencies with variation of the substituent X in the aromatic ring is significantly larger in the spectra of the cyclic molecules with an intramolecular Si \leftarrow 0 coordination bond than for the acyclic molecules containing a free C=0 group and a tetracoordinated silicon atom.

2. The frequencies for the stretching vibrations of the COC and SiF groups in the spectra of the molecules with the pentaccordinated silicon atom depend on the nature of the substituent X. Alternation between positive and negative values of the coefficient ρ is observed in the Hammett equations relating the frequencies and the σ_p values: $\rho > 0$ (vC=0, SiF_{ax}), $\rho < 0$ (vCoC).

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POLARITY AND POLARIZABILITY OF SOME 4,6-DIMETHYLPYRIMIDINE DERIVATIVES

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Pyrimidine derivatives play an important role in life processes and are widely used as drugs [1]. However, these compounds have been studied insufficiently by electric methods making it possible to obtain important information on the electronic and steric structure of molecules. In particular, there are practically no data on the polarizability anisotropy of pyrimidines.

In the present paper, by using the methods of dipole moments and birefringence in an electric field (Kerr effect) we investigated the following representatives of this class of compounds

(I) - (V) $R^2 = Cl$ (I), MeO (II), MeCOO (III), PhCOO (IV), p-MeC₆H₄SO₃.

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TABLE 1.	Experimental	Parameters	of	the	Investigated	Com-
pounds.						

Compound	$\Delta e \Delta w_2$	$\frac{\Delta n^{2}D}{\Delta w_{2}}$	$\frac{\Delta n_D}{n_1 \Delta w_2}$	$\frac{\Delta d}{d_1 \Delta w_2}$	$\frac{\Delta B}{B_1 \Delta w_2}$	μ, D	m ^{K.1012}
(I) (II) (III) (IV) (V)	$\begin{array}{r} 22,040\\ 11,816\\ 7,695\\ 4,432\\ 26,216\end{array}$	$\begin{array}{c} 0,250\\ 0,248\\ 0,225\\ 0,453\\ 0,401 \end{array}$	0,059 0,058 0,053 0,107 0,095	$\begin{array}{r} -0,316\\ -0,597\\ -0,053\\ -0,398\\ -0,377\end{array}$	708,762 242,442 107,346 48,161 83,434	4,02 2,88 2,54 2,16 6,11	747,1 246,7 130,9 81,0 150,8

The experimental parameters of compounds (I)-(V) are given in Table 1. A direct comparison of the dipole moments of 2-chloro-4,6-dimethylpyrimidine and 4,6-dimethylpyrimidine (2.65 D [2]) indicates that the dipole moment of the dimethylpyrimidine ring is directed toward the R substituent. If we accept for the dipole moment of the C_{sp2} -H bond the value 0.7 D [3], the dipole moment of the C-Cl bond in (I) can be evaluated as 0.67 D. Comparing this characteristic with the analogous ones for chlorobenzene (0.86 D) and 1-chlorocyclohexene (0.52 D), we can note its intermediate value, namely, (0.86 D + 0.52 D)/2 = 0.69 D \approx 0.67 D, which is possibly related to the less pronounced aromatic nature of the pyrimidine ring in comparison with the benzene ring.

In compounds (II)-(V), there is a common hydroxypyrimidyl fragment, $Me_2C_4HN_2O$ the dipole moment of which can be evaluated by using the experimental dipole moment of (II) and a group m(MeO) = 1.18D [4]. With a change of the valence angle of COC from 120 to 115°, the dipole moment of the fragment of interest to us assumes values from 3.28 to 3.18 D, and the dipole moment of C_{sp2} -O assumes the values from -0.07 to -0.17 D. In the series of structurally related phenols and anisoles, negative $m(C_{sp^2}-O)$ values are characteristic of planar structures in which there is bonding of the unshared electron pair of oxygen and the π system of the aromatic ring [5]. Thus, the fact that the dipole moment of the C_{sp2} -O bond in (II) is directed toward the pyrimidine ring suggests that in (II) by analogy with anisole all the heavy atoms lie in the same plane.

Esters with simple alkyl substituents have been studied repeatedly by dipole-moment methods [6], and the best results have been obtained when the group dipole moment of the RCOO fragment is used in the additive scheme. Its value and direction for benzoates can be determined, for example, by using the experimental values of the dipole moment of methyl benzoate and methyl p-chlorobenzoate (1.92 and 1.94 D [2]), an m(Me-O) value of 1.18 D, and a dipole moment of PhCl of 1.56 D. Assuming for these compounds a planar Z conformation with valence angles characteristic of esters (COC = 115, OCO = 125, OCC = 109° [7]), we find that in the system of coordinates in Fig. 1 for the PhCOO fragment $\mu_X = 0.92$, $\mu_Y = 0.0$, and $\mu_Z = 2.36$ D.

The dipole moments of methyl formate, methyl benzoate, and methyl acetate measured under identical conditions are close in value [8], which presupposes retention of the polarity characteristics of the RCOO fragment for R = H, Me, and Ph. Therefore, for the MeCOO fragment in (III) we used the above-presented values of the dipole-moment components of PhCOO.

The theoretical dipole moment of esters (III) and (IV) changes monotonically in relation to the dihedral angle of OCOC between the two extreme values attained for the planar structures (5.81 D for the E conformation and 2.38 D for the Z conformation). The experimental value of the dipole moment for (IV) (see Table 1) is lower than the lowest theoretical one; the experimental value for (III) corresponds formally to an 18° deviation from the planar Z conformation. Apparently, just as for most esters, (III) and (IV) have a planar Z conformation.

The data on the geometry of the MeC₆H₄SO₂O fragment and the value and direction of its dipole moment [9] made it possible to construct the theoretical relation of the dipole moment of (V) to the dihedral angle τ (τ =0 if the O-C bond shields the bisector of the angle of OSO in Fig. 1). Agreement of the experimental and theoretical values is attained when $\tau \approx 80^{\circ}$. In addition, the O-C bond shields one of the S=O bonds. The gauche conformation in the case of (V) can be considered typical for organic sulfonates [9].

To analyze the Kerr-effect data of compounds (I)-(V), it is necessary to have information on the value of the semiaxes of the polarizability ellipsoid of the pyrimidine ring. As yet, there has been no such information. According to the data for dilute solutions of (I) in CCl₄, we determined the values of the molecular refraction (35.61 Å³), dipole moment and molar



Fig. 1. System of coordinates accepted for compounds (III)-(V).

Kerr constant (see Table 1), and molecular anisotropy ($\gamma^2 = 84.88$ Å⁶ according to the depolarization of Rayleigh light scattering). The molecule of (I) has C_{2V} symmetry; therefore, for it, it is possible to determine the semiaxes of the polarizability ellipsoid [10, p. 46]: b₁ = 16.11, b₂ = 15.00, b₃ = 9.10 (here and subsequently the polarizability data are given in Å³). In addition, the b₁ axis coincides with the symmetry axis of the molecules and with the direction of the dipole moment, the b₂ axis is located in the plane of the pyrimidine ring, and the b₃ axis is perpendicular to them. If the contribution of the C_{arom}-CH₃ fragments and C_{arom}-Cl bond is taken into account according to an additive scheme [10, p. 94], the polarizability ellipsoid of the unsubstituted pyrimidine ring can be characterized by the following values of the semiaxes: b₁ = 9.16, b₂ = 8.92, b₃ = 4.97. Of interest is the closeness of the values of b₁ and b₂, which is characteristic of aromatic molecules. Thus, our data confirm Battaglia and Ritchie's [11] conclusion, based on a number of assumptions, concerning the symmetry of the polarizability ellipsoid of the pyrimidine ring with respect to the axis perpendicular to it.

Proper choice of the polarizability characteristics of the C-O bond is important in constructing the polarizability ellipsoid of the Me₂C₄HN₂-O fragment. The use of the values $b_L = 0.89$ and $b_T = b_V = 0.46$ describing ethers satisfactorily, causes the theoretical values of the Kerr constants for (II) to be much too low in comparison with the experimental values for any geometry. On the other hand, the use of the effective polarizability ellipsoid of the C_{sp2}-O bond ($b_L = 1.83$, $b_T = -0.92$, $b_V = 0.80$), determined from the experimental data for anisole [12] give too high theoretical values of the Kerr constant for (II). In what followsfor the semiaxes of the polarizability ellipsoid of MeC₄HN₂-O, we use the values $b_L = 13.26$, $b_T = 12.84$, $b_V = 2.85$; we used the arithmetic means between the above-presented values as additive components of the C-O bond. In this case, the calculated value of the Kerr constant for the planar conformation of methoxypyrimidine (II) (235.4 esu) differs by less than 5% from the experimental value.

In a Kerr-effect analysis of the steric structure of (III) and (IV), we assumed that in accordance with the dipole-moment data the ester fragment of the molecules has a planar Z conformation. The angle of rotation of the 4,6-dimethylpyrimidine ring about the C-O bond (φ) was considered as the unknown characteristic. Agreement of the theoretical values of the Kerr constant with the experimental ones was attained when $\varphi \approx 35^{\circ}$ for the acetate (III) and when $\varphi \approx 70^{\circ}$ for the benzoate (IV). The latter figure can be compared with the value of 70° obtained for the analogous angle in the phenyl benzoate molecule [8]. The good agreement of the structural characteristics for structurally close molecules attests to the validity of the electrooptical parameters of the pyrimidine ring that we found. The decrease

of the effective angle φ for (III) in comparison with (IV) can be related to the increased degree of interaction of the π system of the pyrimidine ring with the unshared electron pair of the oxygen of the ester fragment in the case of the acetate because in the acetate there is no competing phenyl substituent.

In an analysis of the steric structure of (V) on the basis of dipole-moment data, we assumed the dihedral angle of COSC to be equal to $100^{\circ} (180^{\circ} - \tau)$. The polarizability parameters of the sulfonate fragment were taken as in [9]. It is known that inp-toluenesulfonates the plane of the MeC₆H₄ ring shields one of the S=0 bonds [9]. For (V) there are two possibilities: shielding of the same S=0 bond in the shielding with which is the C-0 bond of the fragment and shielding of the other S=0 bond.

An investigation of the theoretical relation of the Kerr constant of (V) to the angle of emergence of the plane of the pyrimidine ring from the plane of the valence angle of COS (θ) shows that agreement with the experimental value for the first case is attained in the narrow region of $\theta = 0 \pm 5^{\circ}$. For the second, less sterically hindered case, $\theta = 70 \pm 5^{\circ}$. The latter value is closer to those in the esters, which makes it possible to choose this conformation for (V).

EXPERIMENTAL

Compounds (I) and (II) were obtained according to [13] and [14].

<u>2-Acyloxy-4,6-dimethylpyrimidines (III)-(V)</u>. To a mixture of 0.1 mole of 4,6-dimethyl-2-dihydropyrimidine and 0.1 mole of $Et_{\$}N$ in 50 ml of MeCN was added dropwise at 20-25°C 0.1 mole of the acyl halide. The whole was stirred for 0.5 h at 20°C, the precipitate was filtered, and the solvent was removed in vacuo.

(III). Yield of 68%, bp 70° (0.2 mm), $n_{D}^{2^{\circ}}$ 1.4885, $d_{4}^{2^{\circ}}$ 1.1204. IR spectrum (v, cm⁻¹): 1100 (COC), 1780 (C=0). Found,%: C 57.46; H 6.02; N 16.86%. C₈H₁₀N₂O₂.Calculated,%: C 57.15; H 6.24; N 16.94%.

(IV). Yield of 75%, mp 103-104° (Et₂0). IR spectrum (v, cm⁻¹): 1100 (COC), 1730 (C = 0). Found,%: C 68.12; H 5.44; N 12.32%. $C_{13}H_{12}N_2O_2$. Calculated,%: C 68.41; H 5.30; N 12.28%.

<u>(V)</u>. Yield of 79%, mp 96-97° (Et₂0). IR spectrum (ν , cm⁻¹): 1190 and 1380 (SO₂), the C = O line was absent. Found, %: C 56.18; H 4.94; N 10.12%. C₁₃H₁₄N₂O₃S. Calculated, %: C 56.10; H 5.07; N 10.06%.

The dipole moments and molar Kerr constants for the dilute solutions in CC14 were measured according to [15]. The experimental parameters are given in Table 1.

CONCLUSIONS

1. The group dipole moments of fragments of substituted 4,6-dimethylpyrimidines and the polarizability ellipsoid of the pyrimidine ring were determined.

2. Esters of 4,6-dimethyl-2-hydroxypyrimidine have a planar Z conformation of the COC-O fragment.

3. The angles of rotation of the heterocycle in 4,6-dimethyl-2-acyloxypyrimidines were determined.

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OPTIMIZATION OF THE CHROMATOGRAPHIC PROCESS IN LIQUID CHROMATOGRAPHY

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Three varieties of optimization related to improvement of the units of the chromatograph, selection of the sorbent, and determination of the optimum mode for the desired parameter, can be distinguished in liquid chromatography. The last variety of optimization for the isocratic chromatographic process is examined in the present article, assuming that the first two types have already been performed. It is possible to distinguish optimization with respect to the rate, efficiency, and sensitivity of the analysis. Optimization with respect to the rate and efficiency of the analysis were examined in detail in [1-5]. This article represents the further development of these studies which will permit standardizing the optimum conditions of the chromatographic process, identifying their physical essence, and representing them in a more convenient form.

The variant of optimization examined only involves a decrease in the wash-out of the zone with fixed selectivity. It is possible to differentiate four types of processes by the characteristic hydrodynamic traits and resistance to mass transfer. Two of them concern a column variant, also examined in this article: chromatography in packed and open columns. Two other types of processes concern the thin-layer variety (chromatography on filled thin layers and porous films). The chromatographic processes in packed columns and filled layers connect the dependence of their hydrodynamics and mass transfer on the paricle size of the sorbent and the low pereability of the layers. The permeability of the layers is very high in capillary columns and porous films, the hydrodynamics of the process is determined by the size of the capillaries, and mass transfer makes an insignificant contribution to wash-out [6].

In all four types of chromatographic processes, wash-out of the eluted zone can be described uniformly, but it is necessary to use the time-averaged elution characteristics in the case of the thin-layer variety, and to use the size of the mobile phase channels and not the sorbent grain size in the capillary and film varieties.

The distinctive features of the chromatographic process are closely correlated with such characteristics of the chromatographic system as the selectivity S, efficiency N, and resolution KR on one hand, and on the other hand, with a set of three groups of operating parameters: intensity, economic, and technical. The first group of parameters includes the efficiency of the analysis N/t, at the time of the analysis t, and the sensitivity δ . They determine the intensity of the process. The column length L, pressure differential ΔP , and sorbent grain diameter d_p are in the second group. These parameters determine the economy of the process and the cost of the analysis. The third group consists of technical parameters: the column diameter \emptyset , the viscosity of the solvent n, the experimental temperature T, the column permeability k_0 , the capacity coefficient k', the diffusion coefficient of the test substance D, etc.

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