CHARACTERISTIC VIBRATIONS OF 5-MONOSUBSTITUTED PYRIMIDINES

V. I. Berezin and V. V. Berezin

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The frequency intervals of localization of the bands of the characteristic and noncharacteristic vibrations of 5-substituted pyrimidines were determined on the basis of calculations and analysis of the experimental data. A theoretical interpretation of the bands with respect to the form of vibrations is given, and the groups of characteristic and noncharacteristic vibrations of the aromatic skeleton of 5-monosubstituted pyrimidines were established. Groups of substituents with different regions of localization of the frequencies of the aromatic skeleton were isolated for the noncharacteristic vibrations.

This paper is a continuation of our investigation of the distinctive character of the vibrations of nitrogen heterocycles that was begun in [1]. In evaluating the distinctive character of the vibrations of 5-monosubstituted pyrimidines we used the same criteria and methods as in the case of 2-monosubstituted pyrimidines [2]. In contrast to the latter, the experimental data on the spectra of 5-monosubstituted pyrimidines are extremely scanty, and there are virtually no assignments of the fundamental frequencies.

Theoretical calculations of the frequencies and forms of the vibrations for these substances, which contain NH_2, CH_3, CN, Cl, Br, and NO_2 substituents, constituted the foundation of the assignments. On the basis of such calculations we formulated the assignments of the fundamental frequencies of 11 5-monosubstituted pyrimidines. From these data we determined the intervals of changes in the frequencies of the vibrations for each of the bands and cal-

TABLE 1. Frequencies of the Bands of 5-Monosubstituted Pyrimidines and Their Interpretation

Type of symmetry	Vibration	Pyrimidine		5-Substituted pyrimidines*			
		ν, cm^{-1}	form of vibration	$\nu_{av} \pm \Delta\nu$, cm^{-1}	form of vibration	$(\nu_{d_0}-\nu_{av})/\nu_{d_0}$, %	$\Delta\nu/\nu_{av}$, %
A_1	20*a*	3074	q	1211±88	q_x, γ, β, Q	60,61	7,27
	8*a*	1564	β, Q, γ	1566±16	γ, Q, β, q_x	0,13	1,02
	19*a*	1397	β, γ, Q	1417±16	β, γ, Q	1,43	1,13
	9*a*	1139	β, Q, γ	1027±21	γ, Q, β	9,83	2,04
	12	1065	γ, β	1086±33	γ, Q	1,97	3,04
	1	991	Q, β, γ	795±62	γ, q_x, Q	19,78	7,80
	6*a*	678	γ, β	446±122	γ, q_x	34,22	27,35
B_1	8*b*	1568	β, Q, γ	1569±28	Q, γ, β	0,06	1,78
	19*b*	1466	β	1454±34	Q, β, γ	0,82	2,34
	14	1284	β	1296±30	β, Q	0,93	2,31
	3	1225	β, Q	322±69	β_x	73,71	21,43
	15	1159	β, Q	1170±23	Q, β, γ	0,95	1,97
	18*b*	1071	β, Q, γ	1088±36	Q, β, γ	1,59	3,31
	6*b*	623	γ, β	625±11	γ	0,32	1,76
B_2	5	980	$\rho, \varkappa$	960±37	ρ	2,04	3,85
	11	811	ρ	823±78	$\rho, \varkappa$	1,48	9,48
	10*b*	721	$\varkappa, \rho$	717±15	$\varkappa$	0,55	2,09
	4	708	$\rho, \varkappa$	233±29	$\varkappa, \rho$	67,09	12,45
	16*b*	344	$\varkappa$	397±67	$\varkappa, \rho$	15,41	16,88
A_2	17*a*	980**	ρ	970±3	ρ	1,02	0,31
	16*a*	398	$\varkappa$	400±10	$\varkappa$	0,50	2,50

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*Taken from [3, 6-9].

**A frequency that is repeated twice.

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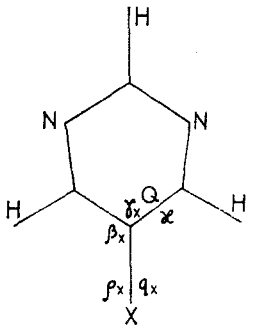

Fig. 1. Natural vibrational coordinates of a 5-monosubstituted pyrimidine.

TABLE 2. Characteristic Vibrations of the Aromatic Skeleton of 5-Monosubstituted Pyrimidines

Type of symmetry	Vibration	Pyrimidine			5-Substituted pyrimidines		
		ν, cm^{-1}	intensity*		$\nu_{av}\pm\Delta\nu$, cm^{-1}	intensity*	
			IR	Raman		IR	Raman
A_1	8*a*	1564	—	p, vs	1566±16	s, vs	p, w, m
	19*a*	1397	vs	p, vw	1417±16	vs	p, w
	9*a*	1139	m	p, s	1027±21	var	w
	12	1065	w	p, vs	1086±33	var	s, vs
B_1	8*b*	1568	vs	dp, wing	1569±28	s, vs	—
	19*b*	1466	s	dp, w	1454±34	m, s	p, vw
	14	1284	w	—	1296±30	w	—
	15	1159	s	Wing	1170±23	m,s	vw
	18*b*	1071	s	—	1088±36	w	—
	6*b*	623	s	dp, m	625±11	s	vw
B_2	5	980	Wing	Wing	960±37	w, m	—
	10*b*	721	s	dp, w	717±15	s	—
A_2	17*a*	980	Wing	Wing	970±3	w, m	—
	16*a*	398	—	dp, m	400±10	—	vw

*Arbitrary symbols: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, p is polarized, dp is depolarized, and var is variable intensity.

culated the average values of the frequencies and the deviations from them in series of 5-monosubstituted pyrimidines (Table 1). The form of the vibrations is given in natural coordinates (see Fig. 1), in which the vibration is primarily localized. On the basis of the cited data we determined the characteristic and noncharacteristic vibrations of the pyrimidine skeleton in the case of 5-monosubstitution; these vibrations are presented in Tables 2 and 3, respectively.

CHARACTERISTIC VIBRATIONS

Ten in-plane vibrations – 8*a*, 19*a*, 9*a*, 12, 8b, 19b, 14, 15, 18b, and 6b – and four out-of plane vibrations – 5, 10b, 17*a*, and 16*a* – are characteristic vibrations (Table 2). Of these, 8*a*, 19*a*, 8b, 14, 15, 18b, 6b, 5, 10b, 17*a*, and 16*a* prove to be virtually insensitive to substitution. With respect to form and frequency they are localized in the same way as in unsubstituted pyrimidine. The 19b vibration, which in unsubstituted pyrimidine is the deformation vibration of the C–H bond, in the case of 5-monosubstitution takes on the traits of a group deformation-stretching vibration of the skeleton, undergoing almost no change in frequency. The 9*a* vibration, while retaining its form, decreases in frequency in the case of substitution, but in the series of 5-substituted compounds the frequencies of this vibration remain virtually constant; this makes it possible to regard it as a characteristic vibration.

The three stretching vibrations of the C–H bonds of the pyrimidine skeleton, which are not included in Tables 1 and 2, are also characteristic. The frequencies of these vibrations lie at 3000-3100 cm^{-1} and do not change in the case of 5-monosubstitution.

The experimental data on the intensities of 5-monosubstituted pyrimidines are insufficient, and one can therefore give only an approximate qualitative evaluation of the intensities in the IR and Raman spectra that coincides with that presented in [4, 5].

TABLE 3. Noncharacteristic Vibrations of the Aromatic Skeleton of 5-Monosubstituted Pyrimidines $C_4H_3N_2X$*

Type of symmetry	Vibration	Pyrimidine			5-Substituted pyrimidines			
		ν, cm^{-1}	intensity		$\nu_{av}\pm\Delta\nu$, cm^{-1}	intensity		compound
			IR	Raman		IR	Raman	
A_1	20*a*	3074	Wing	p, wing	1257±41	m, s	vw	I—VI
					1141±18	var	vw	VII—XI
	1	991	m	p, vs	829±28	w	w, s	I, II, IV, V
					764±14	w, m		III, VI—VIII, X
					730±4	w	w	IX, XI
	6*a*	678	m	s	535±35	var	vw	I—VI, IX
					450±39	var	w	VII, VIII, X
					313	v, w	s	XI
B_1	3	1225	s	dp, w	353±37	var	var	I, IV, VI, VII, X
					269±16	w	vw	VIII, XI
B_2	11	811	vs	dp, vw	880±20	var	—	I—V, VII—IX, XI
					752±7	m, s		VI, X
	16*b*	344	s	dp, w	461±2	w	—	I—III, IV, VII, VIII
					416±22	w		VI, IX, XI
					351±20	m		V, X
	4	708	m	dp, w	260±2	—	vw	VI, X
					211±7		vw	I, IV, VIII
					160**			XI

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*I X = NH_2, II X = OCH_3, III X = $N(CH_3)_2$, IV X = CH_3, V X = CN, VI X = C_6H_5, VII X = SCH_3, VIII X = Cl, IX X = NO_2, X X = $OSCH_3$, XI X = Br.

**Calculated.

NONCHARACTERISTIC VIBRATIONS

Four in-plane vibrations – 20*a*, 1, 6*a*, and 3 – and three out-of-plane vibrations – 11, 4, and 16b – are noncharacteristic vibrations (Table 3). These vibrations are localized on the group of atoms adjacent to the C–X bond, and the forms of these vibrations are localized primarily in the coordinates of the substituent. Let us isolate the 20*a* vibration, which in unsubstituted pyrimidine is the stretching vibration of the C–H bond. Like the analogous 13 vibration in 2-monosubstituted pyrimidine [1], in the case of 5-substitution it becomes a group deformation-stretching vibration.

Compounds for which the regions of localization of the frequencies of the noncharacteristic vibrations are not overlapped within the limits of one type of vibration are presented in Table 3 (see the last column). It is precisely with respect to these regions that one can distinguish groups of molecular compounds from the vibrational spectra. The difference within the limits of one group can be established from the noncharacteristic frequencies of several types of vibrations. The composition of the groups changes on passing from one noncharacteristic vibration to another, but the lower boundary of the frequency for each noncharacteristic vibration is determined, as a rule, by the high-mass substituent. The 6*a* and 16b vibrations, which are related to 5-bromopyrimidine, were isolated in an independent group.

It is of interest to compare the distinctive character of the vibrations of 2- and 5-monosubstituted pyrimidines. The 8*a*, 19*a*, 12, 8b, 19b, 14, 15, 6b, 5, 17*a*, and 16*a* vibrations are always characteristic, regardless of the type of substitution. The localization of these vibrations with respect to form and frequency is identical with the exception of the localization of the 15 vibration. For it the average values of the frequencies of localization of the band in the case of 2- and 5-monosubstitution differ by almost 80 cm^{-1}, chiefly due to the decrease in its frequency in the case of 2-monosubstitution. The distinctive character of this vibration for 2-monosubstitution was discussed in [2].

The 6*a*, 11, and 16b vibrations are always noncharacteristic in the case of 2- and 5-monosubstitution. The frequency intervals of their localization vary over a wide range, but with respect to form they are, as a rule, associated with the coordinate of the substituent.

The 20*a*, 13, 9*a*, 1, 3, 18b, 10b, and 4 vibrations display variable distinctive character. For example, the 20*a*, 1, 3, and 4 vibrations are characteristic in the case of 2-monosubstitution [2] and noncharacteristic in the case of 5-substitution, while the 13, 9*a*, 18b, and 10b vibrations, which are noncharacteristic in the case of 2-substitution, become characteristic in 5-monopyrimidines. It is precisely owing to these vibrations that one can distinguish the spectra of 2- and 5-monosubstituted pyrimidines from one another. However, the most characteristic feature of the spectra of 5-monosubstituted pyrimidines is the absence in them of an intense band at ~980 cm^{-1} in the Raman spectra, which was validly pointed out in [4]. Another difference between the spectra of 5-monosubstituted pyrimidines and 2-monosubstituted pyrimidines is the appearance of an intense band at 1170 cm^{-1} in the IR spectra.

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SYNTHESIS OF 2,5'-BIPYRIMIDINES FROM SUBSTITUTED 5-CYANOPYRIMIDINES

V. P. Mamaev,* M. A. Mikhaleva,
and A. I. Shadrina

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The Pinner method was applied to substituted 5-cyanopyrimidines to obtain 5-aminopyrimidines, which were condensed with acrolein derivatives to synthesize compounds that contain a 2,5-bipyrimidine fragment.

The study of biazines, of which 2,2'-bipyridine is of greatest interest [1], involves primarily their complexing properties [2]. Of the isomeric bipyrimidines, more study has been devoted to 2,2'-bipyrimidines (conformations [3] and complexes [4]) and substituted 4,5'-bipyrimidines as analogs of phleomycin [5] and dimers formed in the irradiation of DNA [6, 7]. The properties of all of the previously synthesized isomeric bipyrimidines, with the exception of the undescribed 2,5'-bipyrimidine system, were examined in [8, 9]. Japanese patent applications [10, 11] in which the use of 2',5-substituted 2,5'-bipyrimidines in liquid-crystal compositions was described were just published in 1986.

Continuing our research on the synthesis and study of the properties of pyrimidine derivatives [12] we have independently obtained a number of 2,5'-bipyrimidine derivatives. Their synthesis can be accomplished in conformity with the general principles of the construction of a pyrimidine ring from both 2- and 5-substituted pyrimidines. As starting compounds we used 5-cyanopyrimidines I [13], which were converted to amidines II; the latter were subsequently used to construct the pyrimidine ring.

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*Deceased.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630,090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3 pp. 371-375, March, 1988. Original article submitted October 16, 1986; revision submitted February 24, 1987.