USE OF RAMAN SPECTROSCOPY FOR THE ESTABLISHMENT OF THE STRUCTURE OF PYRIMIDINE DERIVATIVES

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Intense bands of stretching vibrations are characteristic for the IR spectra of compounds of the pyrimidine series, whereas strong polarized bands of the radially symmetrical vibrations of the pyrimidine skeleton are characteristic for the Raman spectra. The band of the radially symmetrical vibration at ~1000 cm^{-1} is not observed in the Raman spectra of pyrimidines having a substituent in the 5 position.

The combined use of IR and Raman spectroscopies for a large set of compounds of the pyrimidine series with allowance for the available interpretation of the spectrum of unsubstituted pyrimidine and some of its derivatives [1-5] makes it possible to expose bands due to vibrations of the pyrimidine skeleton in the spectra of substituted pyrimidines and to establish correlations of the spectral characteristics with the structural features of pyrimidine derivatives.

According to the data in [3, 5], in substituted pyrimidines the ring stretching vibrations (ν_{8a}, ν_{8b}, ν_{19b}, and ν_{19a}, according to the Wilson numbering [2]) practically do not interact with the stretching vibrations of the C–X bonds, where X is a substituent. We examined the vibrational spectra of ~100 substituted pyrimidines differing with respect to the type and degree of substituion of the pyrimidine ring. Atoms and groups with various electronic effects and masses [F, Cl, Br, CH_3, C_6H_5, CCl_3, $COOC_2H_5$, SCH_3, CN, NO_2, NH_2, and $N(CH_3)_2$] were used as substituents. The analysis of the spectra of the compounds (see also [6]) showed that the bands corresponding to the above-indicated ring vibrations are observed at 1560-1620 (ν_{8a}), 1520-1575 (ν_{8b}), 1400-1480 (ν_{19b}), and 1330-1420 cm^{-1} (ν_{19a}) for the overwhelming majority of the pyrimidine derivatives. It should be noted that the bands corresponding to the 8a and 19a vibrations are among the most intense bands in the IR spectra of the pyrimidine derivatives and can be readily identified from the absence in this spectral region of bands due to vibrations of the substituents. These vibrations are usually weak in the Raman spectra, and only the 8a vibration appears in the form of a medium-intensity band. Moreover, one observes a qualitative correlation of the frequencies of the indicated vibrations within the noted intervals both with respect to the electronic nature of the substituents and with respect to their masses. Electron-donor substituents that display a considerable +M effect (NH_2 and F) raise the frequencies of the indicated vibrations somewhat whereas electron-acceptor and "heavy" (with masses greater than 25) substituents lower them. When several electron-acceptor and "heavy" substituents are present in the pyrimidine ring, the frequencies of the ring stretching vibrations are lowered even more significantly.

In the case of phenylpyrimidines one observes complication of the IR spectra in the region of the ring stretching vibrations. However, the absorption bands of the phenyl groups are of low intensity and have somewhat higher frequencies than the bands of the pyrimidine ring. The presence of a phenyl group in the pyrimidine ring can be detected from the Raman spectra, in which the 8a vibration of the phenyl group appears in the form of a very intense band at 1605 cm^{-1}. Thus the assignment of the bands at 1560-1620 cm^{-1} to the vibrations of benzene and pyrimidine rings in phenylpyrimidines seems unambiguous in the case of the combined use of IR and Raman spectroscopy.

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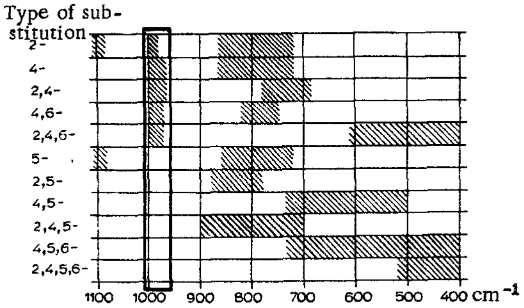

Fig. 1. Position of the intense polarized bands in the Raman spectra that characterize the type of substitution of the pyrimidine ring.

We have shown [7] that for monosubstituted pyrimidines the Raman spectra at 600-1300 cm^{-1}, over which range the radially symmetrical (the so-called "breathing") and deformation vibrations of the ring and the in-plane deformation vibrations of the C—H bonds appear, can be used to establish the position of the substituent in the pyrimidine ring. Moreover, two intense polarized bands at 1100 cm^{-1} (the ν_{9a} band of the C—H in-plane deformation vibrations) and $\sim$1000 cm^{-1} (the ν_{12} band of the radially symmetrical vibrations) are characteristic for 2-substituted pyrimidines. A strong polarized band at $\sim$1000 cm^{-1} (ν_{12}) is characteristic for 4-substituted pyrimidines, and a band at $\sim$1100 cm^{-1} (ν_{9a}) is characteristic for 5-substituted pyrimidines. In addition to the bands noted above, in the Raman spectra of all of the monosubstituted pyrimidines one observes an intense polarized band at 720-870 cm^{-1} (ν^*_1) due to interaction of the ν_1 vibrations and the ν_{C-X} stretching vibrations; its position depends on the electronic effects of the substituent and on its mass. All of these bands are the most intense bands in the Raman spectra, although their relative intensity may vary. The intervals over which the bands characteristic for each type of substitution appear are noted in Fig. 1.

A further study of the vibrational spectra of di-, tri-, and tetrasubstituted pyrimidines showed that regular changes in the spectra are observed for these derivatives and that both the degree of substitution of the pyrimidine ring and the mutual orientation of the ring substituents are of importance in this case.

2,4- and 4,6-Disubstituted and 2,4,6-Trisubstituted Pyrimidines.

An intense polarized band at $\sim$1000 cm^{-1} (ν_{12}) is characteristic in the Raman spectra of these compounds. In the spectra of phenyl-substituted pyrimidines this band is usually masked by a very intense band at 1000 cm^{-1} corresponding to the 12 vibrations of the benzene ring. Another band, which is evidently due to the manifestation of an interacting vibration (ν^*_1), is observed at 680-820 cm^{-1} in the Raman spectra of disubstituted pyrimidines, whereas it is observed at 400-600 cm^{-1} in the spectra of trisubstituted pyrimidines. In addition to the bands indicated above, a number of other appreciably less intense bands are observed in this region of the spectrum. Only the chloro derivatives have a very strong band at $\sim$400 cm^{-1}. The corresponding bands in the IR spectra of these compounds have variable intensities.

2,5- and 4,5-Disubstituted, 2,4,5- and 4,5,6-Trisubstituted, and Tetrasubstituted Pyrimidines.

All of the pyrimidines having a substituent in the 5 position of the pyrimidine ring are characterized by the absence in their Raman spectra of an intense polarized band at $\sim$1000 cm^{-1} (ν_{12}) (Fig. 1). Inasmuch as the radially symmetrical 12 vibration has trigonal symmetry and is associated in the case of the pyrimidine ring with the vibration of two ring nitrogen atoms and the carbon atom in the 5 position, the presence of a substituent in this position leads to a pronounced interaction of ν_{12} and the ν_{C-X} substituent stretching vibration [7]. The intense polarized bands observed in their Raman spectra which correspond to the radially symmetrical vibrations of the pyrimidine ring interacting with the stretching vibrations of the substituents, are observed in a lower-frequency region of the spectrum as compared with monosubstituted pyrimidines (Fig. 1). In this case, the qualitative dependence of the position of these bands in the indicated intervals on the electronic nature of the substituents and their mass is retained [7].

EXPERIMENTAL

The IR spectra of KBr pellets of the solids, CCl_4 solutions of the liquids, and of the liquids themselves were recorded with a Perkin-Elmer 180 spectrometer. The Raman spectra were recorded with a Coderg PH-1 spectrometer with a helium—neon laser without solvents. The compounds of the pyrimidine series were obtained by published methods (see [8] for details).

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RESEARCH IN THE PYRIMIDINE SERIES

XXV.* CALCULATION OF THE NORMAL VIBRATIONS OF BARBITURIC AND 2-THIOBARBITURIC ACIDS

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The frequencies and forms of the in-plane normal vibrations of the tricarbonyl forms of barbituric and 2-thiobarbituric acids and their tetradeutero derivatives were calculated. The calculations were made for the C_{2V} (or C_{2V} and C_s for barbituric acid) symmetry point group. The principal frequencies observed in the IR spectra of these compounds were assigned with respect to the types of vibrations on the basis of an analysis of the forms of the normal vibrations.

Continuing our investigation of the vibrational spectra of polyhydroxypyrimidines, we calculated the in-plane normal vibrations of barbituric and 2-thiobarbituric acids. The IR and Raman spectra of barbituric acid and its derivatives were investigated previously in [2-13]. Principal attention was directed to an interpretation of the spectra in the region of the stretching vibrations of the NH and C = O bonds. Two intense bands at ~3200 and ~3080 cm^{-1} are observed in the spectra of most of the investigated compounds in the ν_{NH} region (for example, see Fig. 1) [6]. The intensity of the first band is somewhat higher than that of the second. These same bands are also present in the spectra of the mono-N-methyl derivatives. For example, two intense bands at 3208, 3098, and 3230, 3130 cm^{-1} are observed in the spectra of 1-methylbarbituric acid and 1-methylbarbital [9]. These same bands were also detected in the spectra of other cyclic amides [14]. Miyazawa [14] feels that the band at 3200 cm^{-1} is due to ν_{NH} and that the band at 3080 cm^{-1} is due to a combination of $\nu_{C=O}$ and δ_{NH} and is reinforced by Fermi resonance. However, there are a number of examples [10] in which the intensity of the band at 3080 cm^{-1} is higher than that of the band at 3200 cm^{-1}. According to x-ray diffraction data [15], crystalline barbituric acid exists in the tricarbonyl form and only two of its carbonyl groups participate in the formation of hydrogen bonds. The $C_{(2)}=O$ carbonyl group forms a hydrogen bond with the NH group (R = 2.909 Å). Two acid molecules form a dimer by means of these hydrogen bonds, and the $C_{(4)}=O...H-N$ hydrogen bonds (r = 2.855 Å) crosslink the dimers in ribbons. The third $C_{(6)}=O$ carbonyl group does not participate in the formation of hydrogen bonds. Bolton [15] determined the bond lengths and the valence angles in the barbituric acid molecule.

The hydrogen bonds are also retained in solutions of barbituric acid and its derivatives in chloroform and dimethyl sulfoxide (DMSO), but a band at 3400 cm^{-1}, which can be assigned to the vibrations of

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*See [1] for communication XXIV.

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