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IR SPECTRA AND STRUCTURE OF 6-METHYLMIDAZO[1,2-a]PYRIMIDINE-2,5-DIONE AND ITS 3-YLIDENE DERIVATIVES

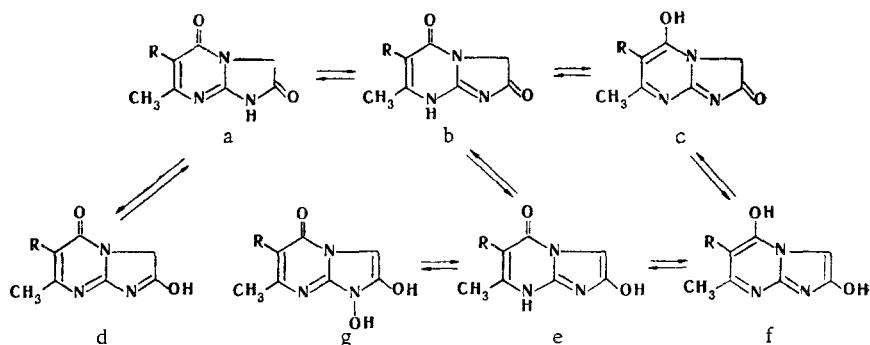
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The structures of 6-R-7-methylimidazo[1,2-a]pyrimidine-2,5-diones and their 3-alkylidene and 3-arylidene derivatives were studied by IR spectroscopy. It was established that these compounds exist in the solid phase in the form of a mixture of tautomers. The most probable tautomers were identified. It is shown that the $\nu_{C=O}$ band of the imidazole fragment correlates with the σ parameters of the substituents in the arylidene grouping. The geometry of this grouping is discussed.

Recently, one of us described the synthesis of imidazo[1,2-a]pyrimidine-2,5-diones [1] and 3-ylidene derivatives based on them [2]. In the present communication we set out to discuss the results of a study of the structure of these compounds by means of IR spectroscopy. The spectra of KBr pellets of the compounds (2 mg of the compound in 100 mg of KBr) were measured with a UR-20 spectrometer at 700-3700 cm^{-1} . The results are presented in Table 1.

A primary feature of this heterocyclic system is the possibility of its existence in the form of several tautomeric forms:

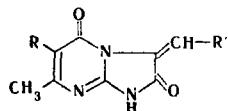


The literature does not contain information regarding the ratio of these forms. It is asserted in [3] on the basis of data on the acidities, behavior with respect to solvents, and hydrolysis that the labile hydrogen atom is attached to the nitrogen atom in the imid-

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TABLE 1. Frequencies (cm^{-1}) of the Characteristic Absorption Bands of Compounds of the General Formula



Compound	R	R'	$\nu_{2\text{-CO}}$	$\nu_{5\text{-CO}}$	$\nu_{\text{C-H}}$	Data for correlation	
						$\Delta\nu_{2\text{-CO}}$	σ^*
I	H	=CH-R' absent	1772 1752	1705 1690 1680	—	—	—
II	Br	The same	1776 1757	1692 1678 1666	—	—	—
III	NO ₂	" "	1786 1764	1712 1694 1684	—	—	—
IV	H	—C ₆ H ₅ †	1733	1689 1679	951	0	0
V	H	—C ₆ H ₄ CH(CH ₃) ₂ -p	1732	1689 1679	949	-1	-0.15
VI	H	—C ₆ H ₄ OCH ₃ -o	1724	1692 1679	941	-9	-0.39
VII	H	—C ₆ H ₄ OCH ₃ -p	1730	1689 1679	946	-3	-0.27
VIII	H	—C ₆ H ₄ OH-p	1726	1686 1671	952	-7	-0.37
IX	H	—C ₆ H ₄ N(CH ₃) ₂ -p	1719	1686 1678	952	-14	-0.83
X	H	—C ₆ H ₄ NO ₂ -o	1747	1686 1678	—	+14	+0.80
XI	H	—C ₆ H ₄ NO ₂ -m	1743	1706 1695	—	+10	+0.71
XII	H	—C ₆ H ₄ NO ₂ -p	1749	1688 1678	954	+16	+0.78
XIII	H	—CH=CH—C ₆ H ₅	1725	1690 1680	930	—	—
XIV	H	—C ₄ H ₃ O*	1739	1692 1682	923	—	—
XV	H	—CH ₂ CH ₂ CH ₃	1746	1710 1700	932	—	—
XVI	Br	—C ₆ H ₅	1740	1681 1671	957	—	—
XVII	Br	—C ₆ H ₄ OCH ₃ -p	1733	1680 1670	944	—	—
XVIII	Br	—CH=CH—C ₆ H ₅	1729	1681 1671	967	—	—

*The σ values were taken from [10].

†The phenyl ring is indicated by C₆H₅, and the α -furyl ring is indicated by C₄H₃O.

azolone fragment (form a). One should also bear in mind some general principles established for potentially tautomeric nitrogen-containing heterocyclic compounds [4, 5], according to which the keto forms predominate. This means that the probability of tautomeric forms c-g should be low.

A distinctly expressed doublet of bands at 1752-1786 cm^{-1} and a triplet at 1666-1712 cm^{-1} are observed in the IR spectra of I-III (see Table 1); the difference in the frequencies in the case of the doublet is $21 \pm 1 \text{ cm}^{-1}$, whereas it changes somewhat for the triplet as a function of substituent R. The electronic character of the latter has a substantial effect on the ratio of the intensities of the signals. Only the vibrations of the carbonyl group may show up in this region in the case of I-III,* and a large number of signals consequently constitutes evidence for the presence of a mixture of tautomers in the solid state.

A singlet and doublet, respectively, are observed in the spectra of the remaining compounds (IX-XVIII) in the region of carbonyl absorption, from which it follows that the number of tautomers is reduced.

It is known [6] that the frequency of absorption of the carbonyl group depends on the size of the ring in which this group is incorporated: it is considerably higher ($\sim 40 \text{ cm}^{-1}$) in the case of five-membered cyclic amides than in the case of six-membered amides. This makes it possible to assign the bands for the compounds that we investigated: the higher-frequency doublet (singlet for IV-XVIII) in our opinion, characterizes the imidazole keto group, whereas the low-frequency triplet (doublet for IV-XVIII) characterizes the pyrimidine keto group. This assignment is confirmed by the substituent effects. Thus, a substituent in the 6 position of the ring changes the frequencies of all of the peaks, whereas variation

*According to a great deal of data summarized in a monograph by Bellamy [6], the amide I band has a considerable amount ($\sim 80\%$) of carbonyl absorption character. As we will show below, this is also reflected in the spectra of the compounds in this study. Here and subsequently, we will therefore use the term "carbonyl absorption" instead of "amide I absorption."

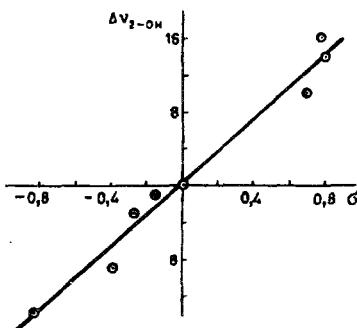


Fig. 1. Correlation of the $\Delta\nu_{C=O}$ values with the σ substituent parameters ($\rho = 0.055$, $r = 0.987$).

of the substituents in the ylidene grouping is reflected only in the carbonyl absorption of the imidazole ring.

As seen from the scheme presented on page 1053, six possible tautomers are peculiar to the keto group, and their electronic character and, consequently, their absorption frequencies should be different. The number of bands observed in the IR spectra is constant regardless of R and R': five for I-III, and three for IV-XVIII. These facts can be explained if one assumes for I-III increased percentages of tautomers a, b, and d in equilibrium (this thereby ensures an odd number of bands and a ratio of low-frequency to high-frequency bands of 3:2). In this case, form d should be preferred over e and g, since the latter are characterized by a more strained five-membered ring. Forms c and f are also unlikely, since their formation is possible only under the condition of migration of a hydrogen atom through four bonds of the pyrimidine ring.

Tautomers of the e-g type become unrealizable for IV-XVIII. Only the equilibrium of two tautomers, a and d, can correspond to the above-indicated number and ratio of carbonyl bands, since the direct equilibrium b \rightleftharpoons d is unlikely. Tautomers b and c of IV-XVIII would have a very strained five-membered ring; this is probably also the reason they are absent.

The high-frequency peaks of the carbonyl doublets and triplets of I-III most likely correspond to tautomer b; they vanish on passing to IV-XVIII. The bands adjacent to them belong to tautomer a. The regularity in the change in the intensities of these bands is interesting. In the case of I the intensities of the peaks under discussion are practically equal in each group of bands. The introduction of a bromine atom in the 6 position (II) causes an appreciable decrease in the intensities of the bands of tautomer a. This effect is even greater for the 6-nitro derivative (III); the peak intensity of the bands of form a is halved. Consequently, the equilibrium a \rightleftharpoons b is shifted to favor the latter as the electron-acceptor character of the substituent in the 6 position of the two-ring system increases (a stronger interaction of the electron-donor secondary nitrogen atom with acceptor 5-carbonyl and 6-nitro groups corresponds to form b). The solubilities of the investigated compounds in water increased in the same order; this is evidently due to an increase in the probability of the tautomeric transition b \rightleftharpoons c and b \rightleftharpoons e.

The $\nu_{C=O}$ band of the pyrimidine ring in the spectra of tautomers a of IV-XVIII are retained in analogy with the $\nu_{C=O}$ band of I, whereas the high-frequency absorption of the C=O groups of the imidazole fragments is, on the average, reduced substantially. The latter fact is undoubtedly due to the electronic effect of the introduced ylidene grouping.

The better conformity of the low-frequency band of the doublet (average 1679 cm^{-1}) in the spectra of IV-XV with the peak at 1680 cm^{-1} in the spectrum of I (a similar pattern is also observed for 6-bromo derivatives if one compares the spectra of XVI-XVIII with the spectrum of II) makes it possible to assume that this band belongs in all cases to one tautomer d.

Thus, one may arrive at the conclusion that, at least in the solid phase, 7-methylimidazo[1,2-a]pyrimidine-2,5-dione and its derivatives exist primarily in the form of tautomers of the keto type. In this case the point of view [3] that the probability of the location

of the labile proton in the imidazole ring is considerably higher than its location in the pyrimidine ring is confirmed.

In the characterization of ylidene compounds IV-XVIII, one should bear in mind not only the tautomeric equilibrium discussed above but also geometrical cis-trans isomerism.* Chromatographic analysis of IV-XVIII showed their individuality, but we were unable to ascertain their structures from their chemical properties.

The use of the band of out-of-plane deformation vibrations of hydrogen atoms for the establishment of the geometry of a vinylene group is well-known [7]. One of us [8] has shown that in the case of α,β -unsaturated ketones with a fixed s-cis structure, achieved by inclusion of an α -carbon atom in the ring (for example, α -benzylidenecycloalkanones), the absorption of the remaining protons is retained at $940-950\text{ cm}^{-1}$ as a band of medium intensity if the geometry of the propenone fragment has a trans structure. Returning to the IR spectra of IX-XVIII, it must be noted that extremely characteristic absorption in this region is observed on most of the spectrograms (see Table 1). Nitro derivatives X-XII, in the spectra of which several weak absorption bands are observed in each case at $900-1000\text{ cm}^{-1}$, constitute an exception to this. The strong deshielding effect of the nitrophenyl group on the β proton is probably operative here. It is extremely important that appreciable absorption is not observed in the spectra of I-III in this region. These data make it possible to assign the investigated compounds to the trans series.

Compounds XIII and XVIII, which include a vinylene grouping in their molecules, have an intense band at 1000 cm^{-1} in their IR spectra, in addition to a band at 930 (967 cm^{-1}), from which it can be concluded that this grouping has trans geometry. As seen from Table 1, the polarity of the carbonyl group of the imidazole ring depends substantially on the electronic character of the ylidene fragment. Moreover, the correlation (see Fig. 1) between $\Delta\nu_{C=O}$ and the σ parameters of the substituent introduced in the aromatic ring in conformity with the following equation is followed satisfactorily for arylidene derivatives of IV-XII:

$$\Delta\nu_{2\text{-CO}} \frac{hc}{2.3KT} = \rho\sigma,$$

where $\Delta\nu_{2\text{-CO}} = \nu_{2\text{-CO}}^{\text{V-XII}} - \nu_{2\text{-CO}}^{\text{IV}}$ (see Table 1). Similar correlations have been noted for α,β -unsaturated ketones of the chalcone type [9]. In all likelihood, this constitutes evidence for the considerable carbonyl character of the "amide I" band under discussion and, consequently, for the validity of the terminology adopted here. The ρ value found (0.055) characterizes the high electronic conductivity of the fixed trans-s-cis-propenone grouping; this is most likely a consequence of the coplanarity of the arylidene grouping and the two-ring system.

Lengthening of the conjugated chain (compare XIII with IV and XVIII with XVI) or shortening of the conjugated chain (compare XV with IV) gives rise to a regular decrease or increase, respectively, in the $\nu_{2\text{-CO}}$ band.

The effect of a substituent in the 6 position is somewhat anomalous. As seen from Table 1, the effect of a substituent is more substantial for a remote imidazole keto group than for an adjacent pyrimidine keto group. This is probably due to the fact that interaction with the adjacent $C=O$ groups is realized inductively, whereas interaction with the imidazole $C=O$ group is possible via a conjugation mechanism. In conclusion it should be noted that absorption of the stretching vibrations of the $C=N$ and $C=C$ bonds of the two-ring system is observed in the form of broad mutually overlapped bands at $1580-1630\text{ cm}^{-1}$, and this hinders their identification. There is a broad low-intensity absorption band characteristic for associated hydroxyl groups at $3450-3550\text{ cm}^{-1}$. Its presence may be due to tautomer d. The substantial increase in the intensity of this band in the IR spectrum of III should be noted; this corresponds to the above conclusions regarding the shift of the tautomeric equilibria as the electron-acceptor character of the substituent in the 6 position increases. Bands of stretching vibrations of free $N=H$ groups are absent in all of the spectrograms.

*Here we refer to the propenone $\text{--CO} \begin{array}{c} \text{c}=\text{c}^{\text{R}'} \\ \text{H} \end{array}$ fragment of the molecule for the concept of "cis-trans isomerism."

The band of an associated group is shifted to 3000-3200 cm^{-1} and is overlapped by absorption of the stretching vibrations of the C-H bonds.

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NEW METHOD FOR THE PREPARATION OF CONDENSED IMIDAZOLONES

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Condensed imidazolones were obtained by the action of diethyl pyrocarbonate on aromatic o-diamines.

Condensed imidazolones (I) are obtained mainly by reaction of aromatic diamines with urea [1], phosgene [2], carbonyldiimidazole [3], or diethylcarbamoyl chloride [4]. The first method is the simplest and most widely used, but requires the use of excess urea, which sometimes hinders the isolation and purification of the imidazolones. In this respect, our method [5] for the synthesis of I by the action of aromatic o-diamines (II) with diethyl pyrocarbonate (DEPC) is more convenient. We used this method (method A) to obtain benzimidazolones (Ia,b), imidazo[4,5-b]-2-pyridones (Ic-g), and imidazo[4,5-c]-2-pyridones (IIh-q). The reaction of DEPC with diamines commences in the cold, but heating to 150-180°C is required to complete the process. The evolution of carbon dioxide and alcohol vapors that accompanies the reaction can be used to monitor the completeness of the conversion of diamines II. Practically pure imidazolones I containing a small amount of DEPC, which is removed by vacuum distillation or washed out with petroleum ether, are obtained at the end of the reaction. (See scheme on following page.)

In contrast to urea [4], DEPC reacts with N,N'-dimethyl-o-phenylenediamine (IIb). The described reaction probably proceeds in two steps. Initially one of the amino groups of diamine II reacts with the reagent, which can be considered to be the anhydride of carbonic acid monoester. The urethane derivative formed in this way is subsequently cyclized to imidazolone I as a result of intramolecular reaction of the carbethoxy group with the second

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