INVESTIGATION OF AZLACTONES AND AZLACTAMS BY IR SPECTROSCOPY

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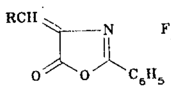
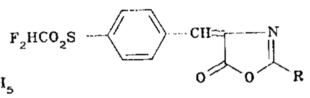
The IR spectra of a number of azlactones and their structural analogs, viz., azlactams, in solutions in carbon tetrachloride and in chloroform and in the solid phase were obtained. The character of the interaction of the carbonyl group of the heteroring with substituents with different electronic natures has a substantial effect on the frequencies of the stretching vibrations of the carbonyl group and the azomethine and ethylene bonds. The carbonyl frequencies were subjected to correlation analysis, and high conductivity of the electronic effects of substituents in the 2-phenyl-4-arylideneoxazol-5-one series was ascertained.

Some derivatives of azlactones and azlactams are effective organic luminophores that emit light both in solutions and in the crystalline state. A study of the spectral-luminescence properties of I-IV enabled us to observe a relationship between the structure and behavior of the molecules in the excited state [1, 2].



I



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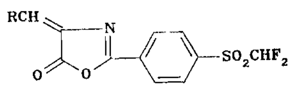
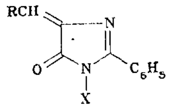
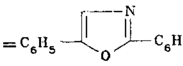
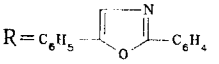


III



IV

I a $R=C_6H_5$; b $R=4\text{-}Cl—C_6H_4$; c $R=4\text{-}Br—C_6H_4$; d $R=4\text{-}NO_2—C_6H_4$; e $R=4\text{-}CN—C_6H_4$; f $R=4\text{-}CH_3O—C_6H_4$; g $R=4\text{-}(CH_3)_2N—C_6H_4$; h R=  ; i R=H; II a $R=C_6H_5$; b $R=4\text{-}NO_2—C_6H_4$; c $R=4\text{-}Cl—C_6H_4$; d $R=C_6H_5—C_6H_4$; e $R=1\text{-}C_{10}H_7$; III a $R=C_6H_5$; b $R=4\text{-}CH_3O—C_6H_4$; c $R=4\text{-}(CH_3)_2N—C_6H_4$; d $R=4\text{-}NO_2—C_6H_4$; e $R==4\text{-}Cl—C_6H_4$; f $R=4\text{-}Br—C_6H_4$; g $R=4\text{-}C_6H_5—C_6H_4$; h $R=1\text{-}C_{10}H_7$; IV a $R=C_6H_5$, X=H; b $R=4\text{-}CH_3O—C_6H_4$, X=H; c $R=4\text{-}(CH_3)_2N—C_6H_4$, X=H; d $R=4\text{-}C_6H_5—C_6H_4$, X=H; e R=  X=H; f $R=C_6H_5$, $X=CH_3$

In order to investigate the mutual effect of the structural fragments of the molecules of these substances in the ground state we studied their IR spectra. The data obtained make it possible to state some ideas regarding the character of the interaction of the C=O, C=N, and C=C bonds with substituents with different electronic natures, which is manifested in a change in the corresponding frequencies of the stretching vibrations. The literature data on this problem are extremely limited [3].

The frequencies of some characteristic vibrations of the investigated substances are presented in Table 1.

It is apparent from an examination of the spectra obtained that a number of characteristic absorption bands, the highest-frequency band of which (1790-1800 cm^{-1}) was assigned to the stretching vibrations of the carbonyl group [3], appear distinctly at 1580-1850 cm^{-1}.

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TABLE 1. Spectral Characteristics of I-IV

Compound	$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	$\nu_{C=N}$, cm^{-1}	Compound	$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	$\nu_{C=N}$, cm^{-1}
Ia	1793	1770	1654	IIIa	1795	1770	1651
Ib	1797	1767	1656	IIIb	1792	1771	1657
Ic	1798	1772	1657	IIIc	1790	1770	1644
Id	1800	Inflection	1657	IIId	1798	1775	1661
Ie	1798	1765	1658	IIIe	1797	1775	1656
If	1789	1770	1654	IIIf	1796	1771	1644
Ig	1785	1764	1650	IIIg	1794	1774	1652
Ih	1797	1775	1655	IIIh	1794	Inflection	1652
Ii	1818	—	1658	IVa	1704	1699	1642
IIa	1796	1775	1653	IVb	1703	1698	1640
IIb	1800	1775	1658	IVc	1703	1697	1638
IIc	1792	1766	1656	IVd	1703	1697	1638
IId	1795	1764	1655	IVe	1703	1699	1635
IIe	1795	1774	1656	IVf	1742	1710	1640

This assignment is in agreement with the literature data for such compounds [4] and is confirmed by Bellamy's method, which consists in comparison of the IR spectra of the investigated compounds in solutions in carbon tetrachloride and chloroform. A shift of the absorption bands of the C=O group to lower frequencies ($\Delta\nu_{C=O}$ = 4-5 cm^{-1}) is observed on passing from solutions in carbon tetrachloride to solutions in chloroform as a consequence of the formation of a hydrogen bond between this group and the solvent molecules; the $\nu_{C=N}$ and $\nu_{C=C}$ bands were insensitive to the effect of the solvents. The small $\Delta\nu_{C=O}$ values are associated with the low basicities of azlactones (thus $pK_a < 4$ for Ia in acetonitrile and nitromethane). This is also confirmed by the relatively small shift of the frequency of the stretching vibrations of the hydroxy group of phenol ($\Delta\nu_{OH}$) when the latter forms hydrogen bonds with the investigated compounds. Thus $\Delta\nu_{OH}$ is 130 cm^{-1} for Ia, which is much lower than the corresponding values for α,β-unsaturated carbonyl compounds [5].

The high $\nu_{C=O}$ value (1800 cm^{-1}) for I-III can be explained by the effect of the following factors: the negative inductive effect of the ester oxygen atom, the strain in the five-membered heteroring, the s-cis orientation of the C=C and C=O bonds, and the electron-acceptor effect of the C=N group.

It should be noted that the frequency of the stretching vibrations of the C=O bond decreases relatively little ($\Delta\nu_{C=O}$ = 3-6 cm^{-1}) on passing from solutions in carbon tetrachloride to the solid phase (KBr pellets). This is probably associated with the relatively low polarity of this bond due to the factors indicated above.

The absorption band at 1770 cm^{-1} can be assigned to the stretching vibrations of the exocyclic C=C bond. The validity of this assignment is confirmed by the absence of corresponding absorption for oxazolone, which does not contain a C=C bond (Table 1, Ii). As regards the high frequency of the indicated vibration, it is probably associated, as in the case of $\nu_{C=O}$, with the acceptor effect of the C=O and C=N groups, the s-cis conformational structure, and the ring strain. The relatively low intensity of the absorption band of the C=C bond (in the case of s-cis conformers of α,β-unsaturated ketones its intensity is almost equal to or even higher than the intensity of the absorption band of the carbonyl group [6]) is associated with strain in the oxazolone ring [7].

The rather intense absorption at 1650-1660 cm^{-1} is due to the stretching vibrations of the C=N bond, and the absorption at ∿1660 cm^{-1} is due to vibrations of aromatic rings.

A number of bands that are characteristic for a five-membered heteroring are observed in the spectra of azlactam derivatives IVa-f at 1600-1734 cm^{-1}.

The highest-frequency band, which was assigned to the absorption of a carbonyl group, is appreciably lower (1703 cm^{-1}) in the solid phase (KBr pellets) than in solutions in carbon tetrachloride and chloroform (1734 and 1720 cm^{-1}, respectively). This is associated with the formation in the solid phase of a rather strong C=O...H—N intermolecular hydrogen bond, which is absent in dilute solutions. Broadening and a low-frequency shift of the corresponding band constitute evidence for participation of the N—H bond in an H complex. In the case of the N-methyl derivative (IVf) the $\nu_{C=O}$ bands in the solid phase and in carbon tetrachloride are found at 1742 and 1750 cm^{-1}, respectively, which also confirms the pres-

TABLE 2. Data from the Correlation Analysis of the $\nu_{C=O}$ Values for I and III*

Compound	Equation: y = mx + b	r	S	n
I	$\nu_{C=O} = 9{,}64\sigma_p + 1793{,}0$	0,96	1,74	7
	$\nu_{C=O} = 6{,}2\sigma^+ + 1796{,}1$	0,94	2,40	7
III	$\nu_{C=O} = 5{,}30\sigma_p + 1795{,}2$	0,97	0,98	7
	$\nu_{C=O} = 3{,}20\sigma^+ + 1795{,}1$	0,85	1,03	7

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*Symbols: r is the correlation coefficient, S is the overall dispersion, and n is the number of points.

TABLE 3. Characteristics of the Synthesized Compounds

Compound	Solvent for purification	mp, °C	N found, %	Empirical formula	N calc., %	Yield, %
Ie	Benzene	220—221	9,9	$C_{17}H_{10}N_2O_2$	10,2	60
IIb	Acetic acid	198	6,8	$C_{17}H_{10}F_2N_2O_6S$	6,8	63
IIc	Acetic acid	271—272	3,6	$C_{17}H_{10}F_2ClNO_4S$	3,5	65
IIId	Benzene	273—274	7,1	$C_{17}H_{10}F_2N_2O_6S$	6,8	70
IIIe	Acetic acid	216—217	3,5	$C_{17}H_{10}F_2ClNO_4S$	3,5	50
IIIf	Acetic acid	265—266	3,0	$C_{17}H_{10}BrF_2NO_4S$	3,1	48
IVc	Toluene	285—286	14,3	$C_{18}H_{17}N_3O$	14,4	30
IVd	Toluene	301—302	8,8	$C_{22}H_{16}N_2O$	8,9	45
IVe	Chlorobenzene	338	11,1	$C_{25}H_{17}N_3O$	11,2	60

ence of a hydrogen bond in the N–H derivatives. The lower-frequency and intense band at 1697-1699 cm^{-1} is due to vibrations of the C=C bond; as in the case of azlactones, the high value of the corresponding frequency can be explained by the strain in the five-membered ring, the electron-acceptor effect of the adjacent C=O and C=N groups, and the s-cis orientation of the C=C and C=O bonds. The high intensity of the band under discussion is also associated with this. A similar regularity was also observed for I-III. The absorption at 1635-1642 cm^{-1} is due to vibrations of the C=N bond.

However, in assigning the bands associated with the vibrations of the various fragments of the investigated five-membered heterocyclic systems one should bear in mind that the vibrations under consideration are close in frequency to symmetry of the n type and, consequently, should interact strongly with one another. Only a calculation of the vibrational spectrum can provide an answer to the question of the contribution made by the individual fragments to one or another vibration.

As expected, the effect of the electronic nature of substituent R on the spectral characteristics of the investigated compounds is manifested in the fact that electron-donor substituents decrease the $\nu_{C=O}$ value, whereas electron-acceptor substituents increase it. The absorption of the C=N bond behaves similarly, but the substituent effect is manifested more weakly. In the case of the $\nu_{C=C}$ values this dependence is not regular in character.

In order to quantitatively evaluate the effect of substituents introduced into the benzylidene part of the I and III series of azlactones, which include a sufficient number of compounds, we performed a correlation analysis with the aid of the Hammett substituent constants (σ_p) and electrophilic constants (σ^+) [8]. Good correlation with the σ_p constants is observed; the reaction constants show that in the first of the examined series the electronic effects of the substituents in the benzylidene fragment are transmitted to the carbonyl group considerably more effectively. A strong electron-acceptor substituent, viz., the difluoromethylsulfonyl group in the 2 position evidently depolarizes the carbonyl group and decreases its sensitivity to the effects of substituents. This is confirmed by the increase in the $\nu_{C=O}$ values and the increase in the reaction constant in the III series as compared with the I series.

The reaction constant in the I series (m = 9.6) is somewhat higher than for series of s-cis-benzylideneacetones (m = 8.3) [9], which model the cinnamoyl fragment of the investigated compounds. Thus fixing of the s-cis conformation of the cinnamoyl grouping by means of the rigid system of the oxazole ring favors transmission of the electronic effects of substituents to the carbonyl group to a certain extent.

EXPERIMENTAL

Azlactone derivatives I-III were synthesized by the Erlenmeyer—Plochl reaction by condensation of the corresponding aromatic or heterocyclic aldehydes with hippuric acid or substituted hippuric acids in acetic anhydride in the presence of anhydrous sodium acetate [10, 11]. Azlactams IV were obtained by reaction of azlactones with ammonia in the presence of sodium carbonate under pressure for 30 h by the method in [12]. The characteristics of the new compounds are presented in Table 3.

The IR spectra of KBr pellets and solutions of the compounds in CCl_4 and $CHCl_3$ (c = 0.01 mole/liter) at 700-1900 cm^{-1} were recorded with a UR-20 spectrometer in cuvettes with NaCl windows and a layer thickness of 0.1 cm.

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REACTION OF 2-CYCLOPROPYLTHIOPHENES WITH MERCURIC ACETATE

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The reaction of 2-cyclopropylthiophene with mercuric acetate in methanol takes place only in the thiophene ring. 5-Methyl-2-cyclopropylthiophene undergoes mercuration in both the heterocyclic ring and in the three-carbon ring (the Levina reaction).

It is known [1, 2] that 4-substituted 2-nitrophenylcyclopropanes (Ia-c) readily undergo rearrangement ot the corresponding o-nitrosopropiophenones under the influence of concentrated sulfuric acid. At the same time, a similar rearrangement cannot be realized in the case of 3-nitro-2-cyclopropylthiophenes (IIa-c) even under more severe conditions [3].*

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*Compounds IIa-c did not undergo rearrangement under the influence of sulfuric acid even at 20-25°C (the starting compounds were recovered), whereas nitrophenylcyclopropanes Ia-c undergo rearrangement at −30 to −10°C.

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