STRUCTURES AND REACTIVITIES OF COMPOUNDS THAT CONTAIN A PHENANTHRIDONE GROUPING

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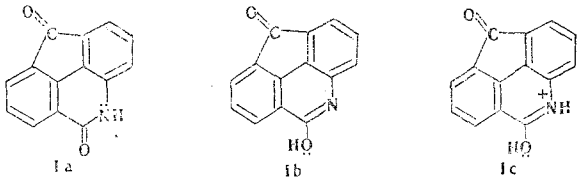
The structures of 4H-cyclopenta[k,l,m]phenanthridine-5,9-dione, phenanthridone, and 5,10-dioxo-4,5,9,10-tetrahydro-5-aza-9-oxapyrene were refined by IR and electronic spectroscopy and quantum-chemical calculations, and the order of aromatic substitution of the lactam form of the first compound was evaluated. It is shown that all three compounds exist primarily in the form of lactam tautomers. The long-wave transition in their absorption spectra was interpreted.

The 4H-cyclopenta[k,l,m]phenanthridine-5,9-dione (I) molecule, like lactams [1, 2], can exist in the following forms, depending on the state and the medium:

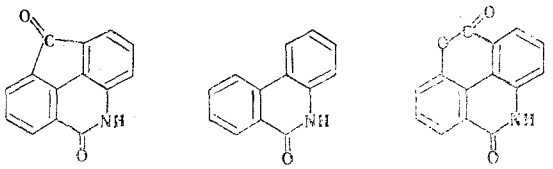


Ia Ib Ic

In [3, 4] it was pointed out that the molecule in the crystalline state exists in the Ia form. However, no detailed analysis has been made. The aim of the present research was to evaluate the probability of the existence of I in tautomeric forms Ia, b and to establish the relationship between the structures of these forms and the properties of the compounds.

Stabilities

To evaluate the stabilities of the lactam, lactim, and cationic forms (Ia-c) we used the calculated heats of atomization (ΔH) and the coefficients of solvation (M).



I II III

It is apparent from Table 1 that for II and III, according to the ΔH values, the lactam tautomers are the most stable forms in the gaseous state and that for I the stabilities of the lactim and lactam tautomers are identical. In solutions the stabilities of the lactam tautomers are higher than the stabilities of the lactim tautomers by a factor of 1.5 to two due to the energy of solvation in conformity with the M values. Consequently, in solutions and in the crystal state I-III should exist primarily in the lactam form; the energies of isomerization in accordance with $\Delta\Delta H = \Delta H_{\text{lactam}} - \Delta H_{\text{lactim}}$ in the gas phase for II and III are $\sim$1.05 eV, whereas $\Delta\Delta H = 0$ for I. The high stabilities pf lactams II and III are ensured due to the π-bond energy. According to the ΔH values, the protonated lactam tautomers for II and III have ΔH values that are close to the ΔH values for the lactam tautomers, but the coefficients of solvation for the latter are 30% higher. Consequently, the probability of protonation of II and III is low. For I the analogous gain in energy due to ΔH in the case

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TABLE 1. Energy Characteristics of the Compounds

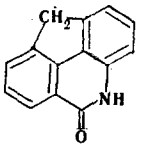
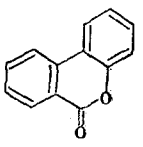
Compound*	Energy of the π bonds (E_π, eV)	Energy of the σ bonds (E_σ, eV)	Total energy (E_B, eV)	Heat of atomization (ΔH, eV)	Coefficient of solvation (M_{solv})
Ia	31,25	73,89	105,14	135,97	2,892
Ib	31,02	73,90	104,92	135,98	1,812
Ic	31,85	73,94	105,78	136,51	2,976
IIa	23,57	62,33	85,89	125,60	2,434
IIb	22,25	62,34	84,59	124,53	0,928
IIc	23,60	62,38	85,98	125,58	1,958
IIIa	29,57	77,94	107,50	138,33	4,364
IIIb	28,28	77,95	106,23	137,29	2,882
IIIc	29,62	77,99	107,61	138,33	3,904

*Symbols: a pertains to the lactam form, b pertains to the lactim form, and c pertains to the lactam form protonated at the ring nitrogen atom.

TABLE 2. Reactivity Indexes of I in the Lactam Form: L_r^+ Is the Electrophilic Localization Energy, L_r^- Is the Nucleophilic Localization Energy, F_r^+ Is the Free Valence Index, and Q_r Are the Charges on the Atoms

Atom No.	L_r^+, β	L_r^-, β	F_r^+	Q_r
1	2,15	2,59	0,431	−0,021
2	2,50	2,47	0,405	0,017
3	2,05	2,41	0,471	−0,028
6	2,57	2,42	0,426	0,061
7	2,48	2,50	0,414	0,000
8	2,49	2,31	0,412	0,058

TABLE 3. Frequencies of the Stretching Vibrations of the C=O, NH, and C=C Groups in the IR Spectra (in the crystalline state)

Compound	ν(C=O)*, cm⁻¹	ν(C=C), cm⁻¹	ν(NH), cm⁻¹
I	1723 (C=O), 1668 (NC=O) (24,0)	1622	2800—3200, 2900, 3135, 3165
II	1670	1635	2800—3330, 3100, 3175
III	1748 (OC=O), 1666/1685 (NC=O)	1628	2800—3300, 2900, 3260, 3280
 IV	1675/1660 (22,0)	1630	2900—3200, 3120, 3145, 3180
Fluorenone V	1720	1610	—
 VI	1738	1617	—
Quinolone VII [5]	1651 (13,8) } $CHCl_3$	1616	—

*The integral intensities of the bands in practical units (10^4 kg/mole·cm²) are given in parentheses.

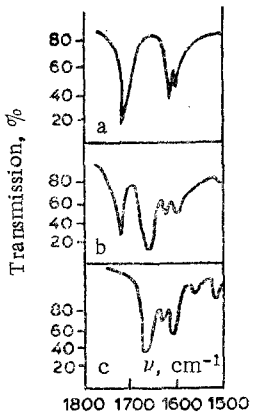
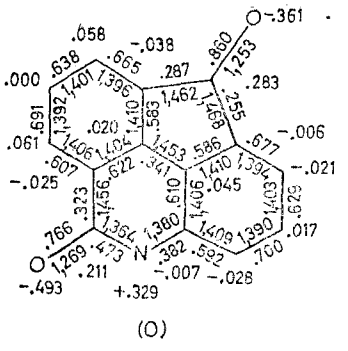


Fig. 1



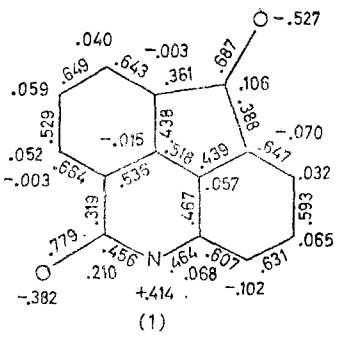


Fig. 2

Fig. 1. IR absorption spectra in the crystalline state: a) fluorenone; b) 4H-cyclopenta[k,l,m]phenanthridine-5,9-dione; c) phenanthridone.

Fig. 2. Molecular diagram of the lactam form of I in the ground (O) and first excited (1) states.

TABLE 4. Electronic Absorption Spectra in Ethanol

Compound	λ_{max}, nm		Intensity		Eigenvectors of the configuration interaction matrix (CIM)
	exptl.	calc.	exptl., ε_{max}, liters/mole·cm	calc., f	
I	342	365,9	7500	0,173	0,94 (9—10)
	328	310,2	7298	0,040	0,75 (8—10)
	312 sh		4194		
	287 sh	298,3	9677	0,012	0,68 (7—10)
	280 sh		12096		
	267	255,3	20161	0,229	0,71 (9—12)
	251	250,3	28225	0,680	0,61 (9—11)
	239	235,0	57278	0,224	0,56 (8—12)
	218	222,2	67742	0,328	0,68 (8—11)
		216,5		0,631	0,69 (6—10)
II	337	341,7	5800	0,170	0,86 (8—9)
	323	305,2	5400	0,128	0,81 (8—10)
	270 sh	291,9	6400	0,024	0,58 (8—11)
	259	261,8	12000	0,96	0,66 (7—10)
	250	244,9	9800	0,377	0,73 (8—11)
	237,5	238,1	25400	0,623	−0,56 (7—9)
	230,8	231,8	26800	0,224	−0,55 (8—12)
	225	222,7	23000	0,203	0,56 (8—12)
	208,6	214,9	11200	0,111	0,67 (7—11)
III	364	366,6	6779,6	0,319	0,90 (10—11)
	347	311,4	6949,2	0,165	0,88 (10—12)
	306	305,3	5254,2	0,002	0,65 (9—11)
	285	271,2	10678	0,081	−0,57 (9—11)
	276	258,5	10169,5	0,194	−0,65 (10—13)
	239	246,4	30084,7	0,426	0,57 (10—14)
	232	227,5	29872,9	0,088	0,63 (9—13)
	223	224,4	25847,5	0,148	0,59 (8—13)
	210,0	210,3	26271,2	0,396	0,65 (9—14)

of protonation is 0.5 eV, which constitutes evidence for the significant probability of protonation of I.

Reactivities

The chemical properties and structures of I should be determined by interaction of the benzene rings with the exocyclic keto and lactam groups; the keto group is an electron acceptor, while the lactam group is an electron donor. The distribution of the electron density in the benzene rings under the influence of the C=O and NC=O groups will be the determining factor in the orientation of aromatic substitution in the I molecule. To evaluate the direction of substitution we calculated the reactivity indexes (Table 2).

It is apparent from Table 2 that, according to the calculated localization energies (L_r^+), the free valence indexes (F_r^+), and the charges on the atoms (Q_r), the order of electrophilic

substitution is as follows: $C_3>C_1>C_7>C_8\geqslant C_2>C_6$. This order of substitution is in good agreement with the experimental data, according to which primary substitution in the case of nitration takes place in the 3 position, after which the 1 and 7 positions are substituted [4]. In the case of nucleophilic substitution the L_r^-, Q_r, and F_r values indicate that the 8 position should be substituted initially, after which the 3 position undergoes substitution (Table 2).

IR Spectra and the Structures

Information regarding the structural peculiarities of I were obtained from an analysis of the parameters of the characteristic absorption bands of the stretching vibrations of the >C=O and HNC=O functional groups in the IR spectra. With this in mind we measured the frequencies (ν_{xy}) and integral intensities (A_{xy}) of the bands of these groups in the IR spectra of I and in the IR spectra of the corresponding model molecules (Table 3). A band at 1723 cm^{-1}, which is related to the stretching vibrations of an exocyclic keto group, is observed in the IR spectrum of I. This is confirmed by the coincidence of the indicated frequency with the frequency of the IR spectra of fluorenone (Table 3). The band at 1668 cm^{-1} in the spectrum of I with an integral intensity of $\sim 24.0\cdot 10^4$ kg/mole·cm^2 is related to the stretching vibrations of the NC=O group, which is in agreement with the presence in the spectra of II and IV in this region of bands at 1670 and 1675/1660 cm^{-1} (the latter has an intensity of $22.0\cdot 10^4$ kg/mole·cm^2). Bands of vibrations of OCO (ν = 1748 cm^{-1}) and NC=O (ν = 1666/1685 cm^{-1}) bonds are similarly observed in the spectrum of III. The ν (OCO) value in the spectrum of III is somewhat higher than the ν (OCO) value in the spectrum of model compound VI. Thus the presence of characteristic stretching vibrations in the IR spectra of I constitutes evidence for its existence in the crystalline state primarily in lactam form Ia. The molecules are joined by a strong hydrogen bond, as evidenced by the markedly shifted bands of stretching vibrations of the NH bond (Table 3). One can form a judgment regarding the significant interaction of the lactam group with the benzene rings from the presence in the IR spectra of I and the model compounds of intense bands at 1617-1635 cm^{-1}.

Electronic Structures and the Absorption Spectra

A characteristic feature of 2-pyridones is the presence of markedly localized bands (r C_3C_4 = 1.37, r C_2C_3 = 1.44, and r C_4C_5 = 1.42 Å) [6] and pronounced polarization of the lactam grouping [5]. As in the case of pyridones, according to the calculation of I, the C—C bonds in the rings are markedly localized, and the dipole moment is 2.51 D (Fig. 2). The experimental and calculated electronic spectra and the characteristics of the compounds are in satisfactory agreement with one another (Table 4). According to the calculations, the long-wave band in the spectrum of phenanthridones is attributable to the extent of 72-86% to transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) due to transfer of 0.4e from the atoms of the lactam group (NC=O) to the ring C—C atoms (Table 4). Consequently, the amide group is a rather strong electron donor. The long-wave transition is accompanied by an increase in the dipole moment to 8.62 D and delocalization of the C_2—C_3 and C_4—C_5 bonds to the extent of 20-40%. The second band corresponds to a complex transition: 50% through the $E_{m-1,n}$ orbitals and 25% through the $E_{m,n+1}$ orbitals, where m is the HOMO, and n is the LUMO. The transition is localized in the benzene rings. The assignment of the remaining bands is given in Table 4.

EXPERIMENTAL

The synthesis of the investigated compounds was carried out by known methods [3, 7]. The purity and individuality of the compounds were monitored by thin-layer chromatography (TLC). The calculations were made by the Pariser—Parr—Pople (PPP) method [8] by means of the program in [9]. In the calculation of the electronic spectra we took into account the interaction of 25 singly excited configurations. The orbital ionization potentials, the one-center integrals of interelectronic repulsion (for the calculation of the excited states), and the variation parameters were adopted from Nishimoto and Forster [10]. The IR spectra were recorded with a UR-20 spectrometer. The electronic spectra were measured with a Specord UV-vis spectrophotometer.

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SYNTHESIS OF ISOMERIC SPIRO[AZAFLUORENEOXIRANES] FROM 3-METHYL-2-AZAFLUORENE AND 4-AZAFLUORENE

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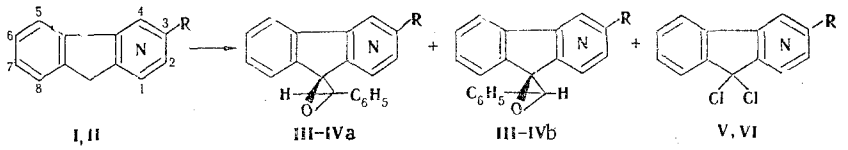
Compounds that belong to the class of new spiran heterocyclic systems that contain azafluorene and oxirane fragments were obtained from the corresponding azafluorenes and benzaldehyde under interphase-catalysis conditions. The Z and E isomers of 3-methyl-3'-phenylspiro(2-azafluorene-9,2'-oxirane) and 3'-phenylspiro(4-azafluorene-9,2'-oxirane) were isolated, and their configurations were established by NMR spectroscopy.

It has been established by means of the PMR spectra that 3'-phenylspiro[fluorene-9,2'-oxirane], which could not be isolated since it is converted to 9-methoxy-9-(α-hydroxybenzyl)-fluorene during crystallization from methanol, is formed in the reaction of fluorene with benzaldehyde, carbon tetrachloride, and 50% aqueous sodium hydroxide in the presence of triethylbenzylammonium chloride (TEBA) — reaction under interphase-catalysis (IPC) conditions [1].

We subjected 3-methyl-2-azafluorene (I) and 4-azafluorene (II) to a similar reaction. In the case of conversion of these heterocyclic compounds to stable spirans with azafluorene and oxirane fragments one had to expect the formation of compounds that are isomeric with respect to the position of the phenyl substituent in the oxirane ring relative to the pyridine ring of the azafluorene fragment.

3-Methyl-3'-phenylspiro[2-azafluorene-9,2'-oxirane] (III) was obtained from I in 25% yield. Its Z (IIIa) and E (IIIb) isomers were isolated by chromatography. The Z (IVa) and E (IVb) isomers of 3'-phenylspiro[4-aza-fluorene-9,2'-oxirane] were obtained from 4-azafluorene (II) in an overall yield of more than 50%. Spiro compounds III and IV are stable crystalline substances and were purified by crystallization from heptane.



I, III, V —2-aza, R=CH_3; II, IV, VI —4-aza, R=H

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