01

Sulfaguanidine under UV irradiation in aqueous solution

© N.P. Bezlepkina, O.N. Tchaikovskaya, E.N. Bocharnikova¶, O.K. Bazyl'

Tomsk State University,
634050 Tomsk, Russia

¶e-mail: bocharnikova.2010@mail.ru

Received November 30, 2022
Revised January 11, 2023
Accepted April 05, 2023.

The phototransformation of sulfaguanidine in water under ultraviolet (UV) radiation was studied experimentally and theoretically. Absorption, fluorescence and fluorescence excitation spectra of the studied substance before and after irradiation were obtained. Under the influence of KrCl excylamp radiation, stained photoproducts were formed. Quantum-chemical analysis of the orbital nature and localization of electronic transitions of complexes of photoproducts with water 1:3 reveals great similarity with the spectrum of the complex of the parent compound. The energy of electronic transitions of primary photoproducts decreases that is there is a low-energy shift of transitions $S_0 \rightarrow S_1(\pi\pi)$ and $S_0 \rightarrow S_3(\pi\pi)$ of the original molecule to long-wave region of spectrum (260−315 nm) and decrease of intensity of transition $S_0 \rightarrow S_3(\pi\pi)$ of sulfaguanidine coplex. In the process of irradiation under the action of KrCl excylamp, the transformation of sulfaguanidine, its primary photoproducts and their subsequent interaction with each other and the solvent occur, which leads to the appearance of a colored photoproduct absorbing at $\lambda_{max} = 560$ nm.

Keywords: sulfaguanidine, sulfanilic acid, photolysis, UV irradiation, absorption, fluorescence, photodissociative states.

DOI: 10.61011/EOS.2023.04.56363.4388-22

Introduction

The widespread use of antibiotics in medicine and veterinary medicine, inefficient removal in treatment facilities result in the constant discharge of these substances into the environment. Among these compounds, sulfonamides, which are considered to be potent chemicals and widely used in large quantities in health systems and animal husbandry, are found in runoff and natural waters ranging from 2.4 to 146 ng/l [1]. Due to the ability of sulfonamides to act against the protozoan gram-negative and gram-positive bacteria, they are used to treat ear infections, bacterial meningitis, urinary tract infections, eye infections, chronic bronchitis, etc. In addition, sulfonamide residues penetrate into human biofluids and animal tissues [2], and then a large amount of them gets into surface and underground waters and penetrates into the food chain of non-specific organisms. Environmental pollution worldwide is a major problem and causes widespread concern. The history of medicinal compounds in the environment, the rate of their distribution and the ability to accumulate in the biosphere are different. The high biological activity of antibiotics indicates that these drugs, even in small amounts, can cause significant changes in the environment [3–7]. The studies have shown that sulfa compounds are present in the soil at concentrations up to 15 mg/kg [8]. The ecotoxicological effect of sulfonamides has been proven for aquatic organisms, especially for higher plants such as duckweed and algae [9]. It is known that biodegradation and photodegradation are among the ground transformation processes affecting the removal of these pollutants in natural waters. However, biological processes take a long time and a low degree of transformation due to the biological stability of many organic compounds and their by-products [10,11]. Direct photolysis can be considered as a potential method for the degradation [12] of organic compounds in aqueous solutions [13].

The photodegradation routes of most antibiotics are not fully studied. Transformation mechanisms include several specific steps such as desulfurization and photohydrolysis for sulfadiazine and sulfapyridine [14–16]. Other proposed transformation routes are rearrangement of the isoxazole ring and its hydroxylation to sulfamethoxazole, oxidation/reduction of nitrogen atoms for sulfadiazine and sulfamethazine [17].

The data of liquid chromatography in combination with triple quadrupole mass spectrometry (LC-MS/MS) determine the potential ways of fragmentation of the starting compound for further identification of photodegradation products [18–20]. New generations of high resolution mass spectrometers allow to unambiguously confirm the molecular structures of the transformation products and the recently discovered desulfurized sulfamethazine (PT 215), defluorinated and hydroxylated ciprofloxacin (PT 330) (Fig. 1). HPLC (High Performance Liquid Chromatography) analysis of an irradiated 20% conversion sulfaguanidine solution shows four primary photoproducts produced by sunlight [20]. The photoproduct with a retention time of 0.18 min was easily identified by the authors as sulfanilic acid (Fig. 1, № 2). This identification

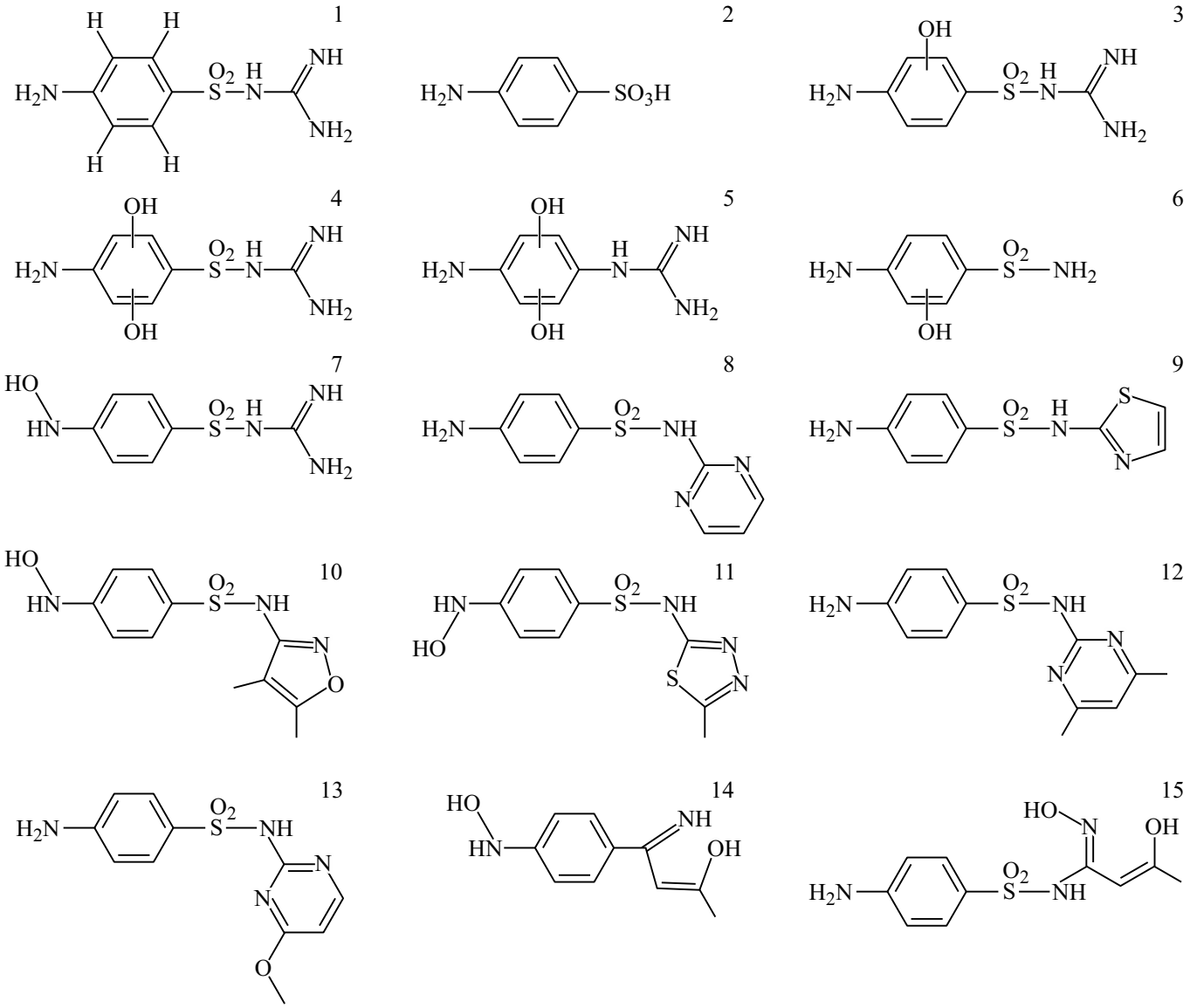

Figure 1. Structural formulas: 1 – sulfaguanidine, 2 – sulfanilic acid (SAA), 3 – P1, 4 – P2, 5 – P3, 6 – SND (PT 189), 7 – SGD (PT 231), 8 – SDZ, 9 – STZ, 10 – SFX (PT 284), 11 – SMT (PT 287), 12 – SMZ, 13 – SMP, 14 – SMX (PT 193), 15 – STZ (PT 272).

was based on a comparison with an authentic sample. The remaining products of sulfaguanidine photodegradation were detected and labeled in the order of increasing retention time from P1 to P3 (Fig. 1, № 3–5). At least 68 out of 102 photo products have been described for the first time [1]. Fig. 1 shows the potential transformation products of sulfanilamide drugs. Direct irradiation and hydrolysis in water resulted in the degradation of all substances and the detection of up to 17 degradation products for SMZ (sulfamethazine), 16 for SMX (sulfamethoxazole), 15 for SMP (sulfamethoxypyridazine), 13 for SDZ (sulfadiazine), 10 for STZ (sulfathiazole), 9 for SGD (sulfaguanidine), SFX (sulfisoxazole), and SMT (sulfamethizole), and 4 for SND (sulfanilamide) (Fig. 1).

The objective of this study — to study the photodegradation of sulfaguanidine under the action of KrCl excilamp radiation by spectroscopy and quantum chemistry methods.

Object under study

Sulfaguanidine (4– Amino–N– (aminoiminomethyl) benzenesulfonamide) — bacteriostatic antimicrobial drug, a derivative of guanidine and sulfanilamide with the chemical formula $C_7H_{10}N_4O_2S$. The structural formula of the molecule is shown in Fig. 1, № 1. The substance belongs to the pharmacological group of sulfonamides and is used to treat intestinal infections, including bacterial dysentery, and for preoperative prophylaxis [21]. Sulfaguanidine is usually presented in the form of a white, odorless, finely crystalline

powder. Slightly soluble in water, alkali solutions, ethanol and acetone.

Experimental methodology

To obtain a matrix solution with a $C = 10^{-3}$ mol/l concentration, 43 mg of dry sulfaguanidine was required, distilled water was used as a solvent. Since sulfaguanidine is poorly soluble in water, the solution was placed in an ultrasonic stirrer and heated to 45°C, after which it was left in a dark place until it cooled completely. The phototransformation solution was prepared by diluting to a concentration of $C = 5 \cdot 10^{-5}$ mol/l. The prepared solution of sulfaguanidine with a volume of 90 ml was irradiated in a glass beaker with a diameter of 4.6 cm on a magnetic stirrer at room temperature in a [22] stationary photoreactor. The source of UV irradiation was a KrCl excilamp with a radiation maximum at a wavelength of $\lambda = 222$ nm. The distance from the excilamp to the irradiated solution was 4 cm, the total irradiation time —64 min. During the irradiation, the maximum energy absorbed by the test solution did not exceed 10 J/cm^3. Irradiation control time: 0, 1, 2, 4, 8, 16, 32 and 64 min. In these time intervals, samples were taken and the absorption, fluorescence, and fluorescence excitation spectra were recorded on a SM2203 spectrofluorimeter (CJSC „SOLAR", Belarus), and the change in the pH index was recorded as well using a pH meter „Expert-pH". After the measurement, the sample was returned back to the beaker with the solution so as not to disturb the volume.

Quantum-chemical calculations of spectral-luminescent properties and photolysis of molecules

The absorption spectra of sulfaguanidine and its primary photoproducts were calculated using the intermediate neglect of differential overlap (INDO) method with the original parametrization [23] implemented in the software package developed at the Molecule Photonics Laboratory of Tomsk State University. The calculated wave functions of the investigated molecules make it possible to obtain electronic absorption spectra, fluorescence, induced absorption spectra, and physicochemical properties of molecules (electron density distribution on atoms and chemical bonds, dipole moment). The influence of the universal intermolecular interaction on the spectra of molecules is partially taken into account in the specified system of parameters, and specific intermolecular interactions, for example, H-bonds, are taken into account by calculating complexes with polar solvent molecules. For the reasonable construction of complexes with H-bonds, the method of molecular electrostatic potential (MEP) is used, which allows to calculate not only the proton-acceptor ability of a molecule in the ground and excited states, but also the places of the most probable attachment of solvent molecules [24–26] . An important feature of this software package is the ability to calculate the rate constants of intramolecular nonradiative processes of excitation energy conversion (internal and intercombination conversions).

Table 1. Change in pH and temperature of the solution depending on the time of irradiation

Time of exposition, min	t, °C	pH			<pH>	σ
0	20.9	6.721	6.699	6.733	6.718	0.014
1	21.0	7.076	7.081	7.088	7.082	0.005
2	20.8	6.703	6.659	6.562	6.641	0.059
4	20.9	6.541	6.496	6.489	6.465	0.039
8	20.9	6.526	6.482	6.448	6.485	0.032
16	21.5	6.436	6.343	6.320	6.366	0.050
32	21.7	6.161	6.165	6.159	6.162	0.002
64	22.7	6.092	6.069	6.036	6.066	0.023

The paper [27] describes in detail the technique for studying the primary process of photodissociation of the chemical bond of a molecule based on the wave functions of the INDO method. Its main provisions are as follows. First, the rupture of a chemical bond implies the destruction of theσ-component of the bond; therefore, the rupture should be expected in the states of the $\pi\sigma$-, $\sigma\pi$- and $\sigma\sigma$-type states. Secondly, the ground state of the molecule is modeled by the Morse potential when using for its calculation the experimental characteristics of the bond under study for breaking: the equilibrium bond length (R_0), the natural vibration frequency of the bond (ω_0) and the breaking energy of the bond under study (D_0). The energy of electronically excited states is obtained by summing the value of the Morse potential and the energy of the excited state at each step of changing the length of the bond being investigated for breaking. The nature of the potential of the excited state indicates the opportunity of breaking or its absence: the presence of a minimum of potential curves corresponds to a strong bond, the absence of a minimum — the probability of breaking the bond under study. Thirdly, based on the analysis results of the constants values of nonradiative photophysical processes of the conversion of absorbed energy, the opportunity of populating a photodissociative state (singlet or triplet) is determined and a conclusion is made about the probability of bond breaking in one or another photodissociative state.

Results and Discussion

In order to study the effect of irradiation on the change in pH, appropriate measurements were made. For each

irradiation time, the experiment was repeated three times; the results are presented in Table 1. The mean <pH> and standard deviation σ were calculated. The measurement error did not exceed 1%. It can be seen from the obtained data that pH changes towards higher values after 1 min irradiation — from 6.7 to 7.08. When the solution is irradiated from 1 to 64 min, pH decreases to 6 (Table 1). The studies of the authors [20] showed that the efficiency of photodegradation of sulfaguanidine under irradiation at 254 and 302 nm depends on pH. Thus, it was found that photochemical transformation can occur under natural conditions (pH<7), but in an artificially created alkaline environment (pH>10) phototransformation is more efficient, since at high pH values the rate constant of sulfaguanidine degradation increases significantly[20].

Quantum-chemical study of the photolysis of sulfaguanidine in aqueous solutions

We carried out a detailed analysis of the calculated absorption spectrum of sulfaguanidine and its 1:3 complex with water earlier [28]. The spectrum of the complex of sulfaguanidine with water is given in Table 2 for the convenience of comparing the spectra of the initial molecule with the spectra of complexes of photoproducts.

Calculations showed that the intense absorption band $\lambda_{max} = 259$ nm of sulfaguanidine is formed by the electronic transition $S_0 \rightarrow S_3(\pi\pi)$ (Table 2). The $S_2(\pi\sigma)$ state, according to the calculation, is localized on the C_4-S_8 bond of the molecule, the population (P) of which in this excited state decreases from $P(S_0) = 0.592e$ to $P(S_2) = 0.244e$, which indicates its weakening upon excitation. As regards the bond between S_8-C_{11}, its strength upon excitation to the $S_3(\pi\pi)$ state practically does not change ($P(S_0) = 0.550e$, $P(S_2) = 0.527e$). Reducing the strength of the bond C_4-S_8 suggests the opportunity of breaking it. Fig. 2 shows potential curves of the ground and some excited states of the complex of sulfaguanidine with water of composition 1:3. When calculating the Morse potential of the ground state of the molecule for the bond C_4-S_8, the following experimental parameters were used: $\omega_0 = 600\ \text{cm}^{-1}$ [29], $D_0 = 29750\ \text{cm}^{-1}$ [30], $R_0 = 1.7418$ Å [31]. The potential state curve $S_3(\pi\pi)$ has a minimum, i.e. corresponds to a strong C_4-S_8 bond in this state, and the potential curves of the singlet and triplet electronically excited states localized on the C_4-S_8 bond correspond to its break. Thus, the absence of a minimum in the potential curves of the electronically excited states $S_{4-8}(\pi\sigma)$ and $T_{4-8}(\pi\sigma)$ indicates the opportunity of breaking this bond in both the singlet and triplet states (Fig. 2).

The route analysis of the fastest nonradiative processes in the sulfaguanidine complex (Fig. 3) showed that after excitation of the $S_3(\pi\pi)$ state, most of the absorbed energy deactivates to the $S_1(\pi\pi)$ state. Some of the excited molecules populate the $S_2(\pi\sigma)$ state, in which the strength of the C_4-S_8 bond decreases. Deactivation of the

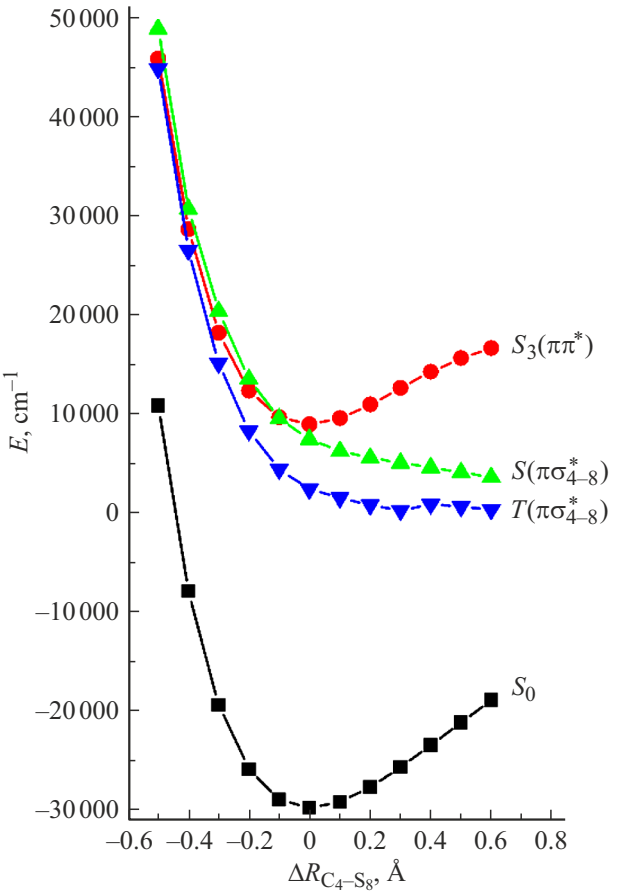

Figure 2. Potential curves of the ground and some excited states of the complex of sulfaguanidine with water.

absorbed energy into the channel of triplet states is not effective: the rate constants of the intercombination conversion $k_{ST}(S_3 \rightarrow T_5)$ and $k_{ST}(S_2 \rightarrow T_4) \sim 6 - 8 \cdot 10^8\ \text{s}^{-1}$ are much smaller than the rate constants of the internal conversion $k_{SS}(S_3 \rightarrow S_1) = 10^{12}\ \text{s}^{-1}$ (Fig. 3). It can be concluded from this relation that bond rupture C_4-S_8 is more probable in the singlet state, although the probability of photodissociation can be reduced by its shorter lifetime than for the triplet state.

Absorption spectra of sulfaguanidine photoproducts in water

Fig. 4 shows the absorption spectra of sulfaguanidine in water before and after irradiation. The absorption spectra clearly show a decrease in optical density in the area of 259 nm and an increase in the range from 300 to 800 nm, which indicates the phototransformation of sulfaguanidine and the formation of absorbing photoproducts. The appearance of a broad band with a maximum in the area of 540 −550 nm indicates the formation of a colored photoproduct. This is also confirmed by the change in the color of the

Table 2. Calculated absorption spectra of complexes of sulfaguanidine and its photoproducts

Calculation*				Experiment	
State	E_i, cm^{-1}	λ, nm	f	E_i, cm^{-1}	λ, nm
sulfaguanidine+3H2O					
$S_1(\pi\pi)$	34930	286	0.050	34500	290
$S_2(\pi\sigma)$	37640	266	0.005		
$S_3(\pi\pi)$	38570	259	0.374	38600	259
$S_9(\pi\pi+\pi\sigma)$	47560	210	0.458		
$S_{10}(\pi\pi)$	47560	210	0.386	48100	208
$S_{11}(\pi\sigma)$	48960	204	0.480		
Sulfanilic acid $+3H_2O$					
$S_1(\pi\pi)$	34590	289	0.055		
$S_2(\pi\pi+\pi\sigma)$	37330	268	0.116	31750−38000	315−260
$S_3(\pi\pi+\pi\sigma)$	37580	266	0.182		
$S_4(\pi\sigma)$	41980	238	0.002		
$S_8(\pi\pi)$	46870	213	0.473		
$S_9(\pi\pi)$	47440	210	0.853		
Photoproduct P1$+3H_2O$					
$S_1(\pi\pi)$	33640	297	0.077		
$S_2(\pi\pi)$	36240	276	0.149	31750−38000	315−260
$S_3(\pi\sigma)$	36410	275	0.051		
$S_8(\pi\sigma)$	44630	224	0.416		
$S_9(\pi\pi)$	45130	222	0.328		
$S_{10}(\pi\pi)$	45880	220	0.651		
Photoproduct P2$+3H_2O$					
$S_1(\pi\pi)$	32580	307	0.022		
$S_2(\pi\pi)$	34800	287	0.164	31750−38000	315−260
$S_3(\pi\sigma)$	36020	278	0.005		
$S_4(\sigma\sigma)$	38000	263	0.002		
$S_7(\pi\pi)$	43010	232	0.621		
$S_8(\pi\pi)$	43470	230	0.813		
Photoproduct P3$+3H_2O$					
$S_1(\pi\pi)$	31900	314	0.040		
$S_2(\pi\pi)$	34190	293	0.205	31750−38000	315−260
$S_3(\pi\sigma)$	39180	255	0.007		
$S_6(\pi\pi)$	43090	232	0.422		
$S_9(\pi\pi+\pi\sigma)$	43670	229	0.215		
$S_10(\pi\pi)$	45450	220	0.303		

*E_i — transition energy, f — transition oscillator strength.

solution itself during irradiation. The solution acquires the most saturated color after 16 min of irradiation.

The study of changes in the experimental absorption spectra of aqueous solutions of sulfaguanidine upon excitation in the area of the long-wavelength absorption band ($\lambda_{max} = 259$ nm) clearly registered a significant transformation in the area from 200 to 700 nm (Fig. 4). The changes are characterized by a decrease in the absorption intensity at $\lambda = 259$ nm during irradiation, the appearance of absorption in the area from 260 to 400 nm, and a broad band with a maximum at $\lambda_{max} = 560$ nm. Such changes may indicate phototransformations of the sulfaguanidine molecule. Similar changes in the absorption spectrum are given in the paper [20], the authors of which, using high-resolution mass spectroscopy in combination with liquid chromatography, identified four primary sulfaguanidine photoproducts, the structural formulas of complexes with water of which are shown in Fig. 5. According to the authors [20], sulfaguanidine is almost completely destroyed and passes into the final product, which absorbs at $\lambda_{max} = 560$ nm, upon prolonged exposure to sunlight. Since the experimental studies were carried out for aqueous solutions, we calculated and analyzed the absorption spectra of the complexes of the identified primary photoproducts of sulfaguanidine (Fig. 5, Table 2). The sites of attachment of water molecules are determined by calculating the MEP potentials, as was done earlier for the sulfaguanidine molecule [28].

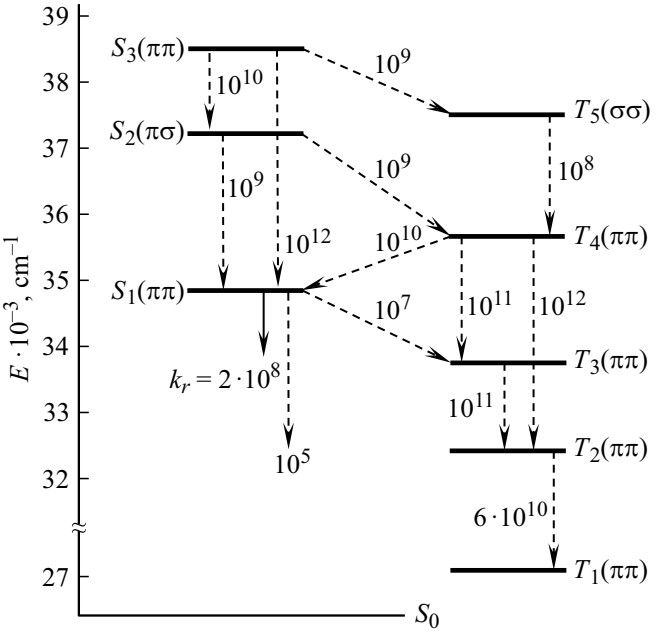

Figure 3. Energy scheme of electronically excited states of the complex of sulfaguanidine with water (geometry of the ground state).

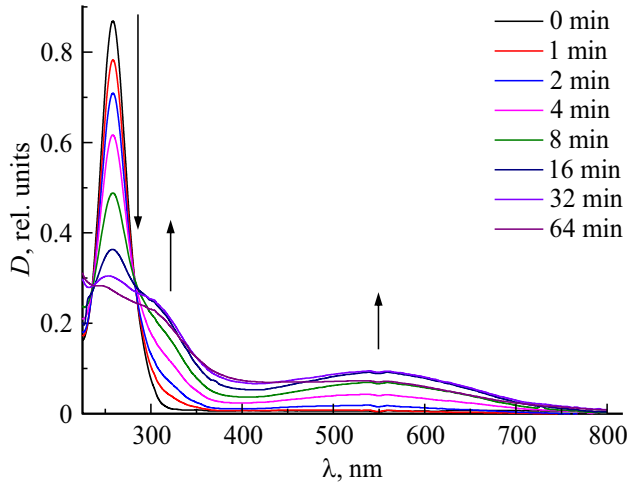

Figure 4. The absorption spectra of sulfaguanidine in water before and after irradiation. The arrows indicate the direction of change in the absorption intensity as a function of the irradiation time.

The presence of hydroxyl groups in the photoproducts P1 and P2 does not increase the number of water molecules in the complexes of these molecules, since the minimum of the electrostatic potential associated with the oxygen atoms of the OH groups is insignificant compared to the potential values near the oxygen atoms of the sulfo group and the nitrogen atom in >C=NH group. The dominant site for the formation of an H-bond in the P3 molecule is the nitrogen atom in the >C=NH group. The absence of a sulfo group in photoproduct P3 increases the value of the potential near the oxygen atoms of the OH groups, which allows to form H-bonds in this molecule with the oxygen atoms of the hydroxyl groups. Table 2 shows the results of calculating the spectra of the complexes of the investigated primary photoproducts of sulfaguanidine. The results of calculating the absorption spectra of photoproduct complexes are followed by this.

The absorption spectra of all studied photoproducts lie in the area 260–315 nm, which is formed and grows in intensity in the process of solution irradiation (Fig. 4).

The orbital nature and localization of electronic transitions in this area of the spectrum of complexes of photoproducts reveals a great similarity with the spectrum of the complex of the initial compound. Meanwhile, the energy of electronic transitions in primary photoproducts decreases; there is a long-wavelength shift of the $S_0 \rightarrow S_1(\pi\pi)$ and $S_0 \rightarrow S_3(\pi\pi)$ transitions of the initial molecule to the long-wavelength region of the spectrum (260–315 nm) and a decrease in the intensity of the $S_0 \rightarrow S_3(\pi\pi)$ transition of the sulfaguanidine complex (Table 2).

The absorption area from 200 to 240 nm, which arises upon irradiation of a solution of the initial product (Fig. 4, curves 32 and 64 min), includes electronic transitions to the states $S_4(\pi\sigma)$ of sulfanilic acid and $S_3(\pi\sigma)$ photoproducts P1 and P2, localized on the C_4-S_8 bond, which can be broken, and the state $S_3(\pi\sigma)$ of the photoproduct P3, localized on the C_4-N_{10} bond (Fig. 5,*e*). The presence of the photodissociative state of the complexes of photoproducts in the area from 200 to 240 nm suggests that further transformation of the primary photoproducts of sulfaguanidine with their subsequent destruction and the

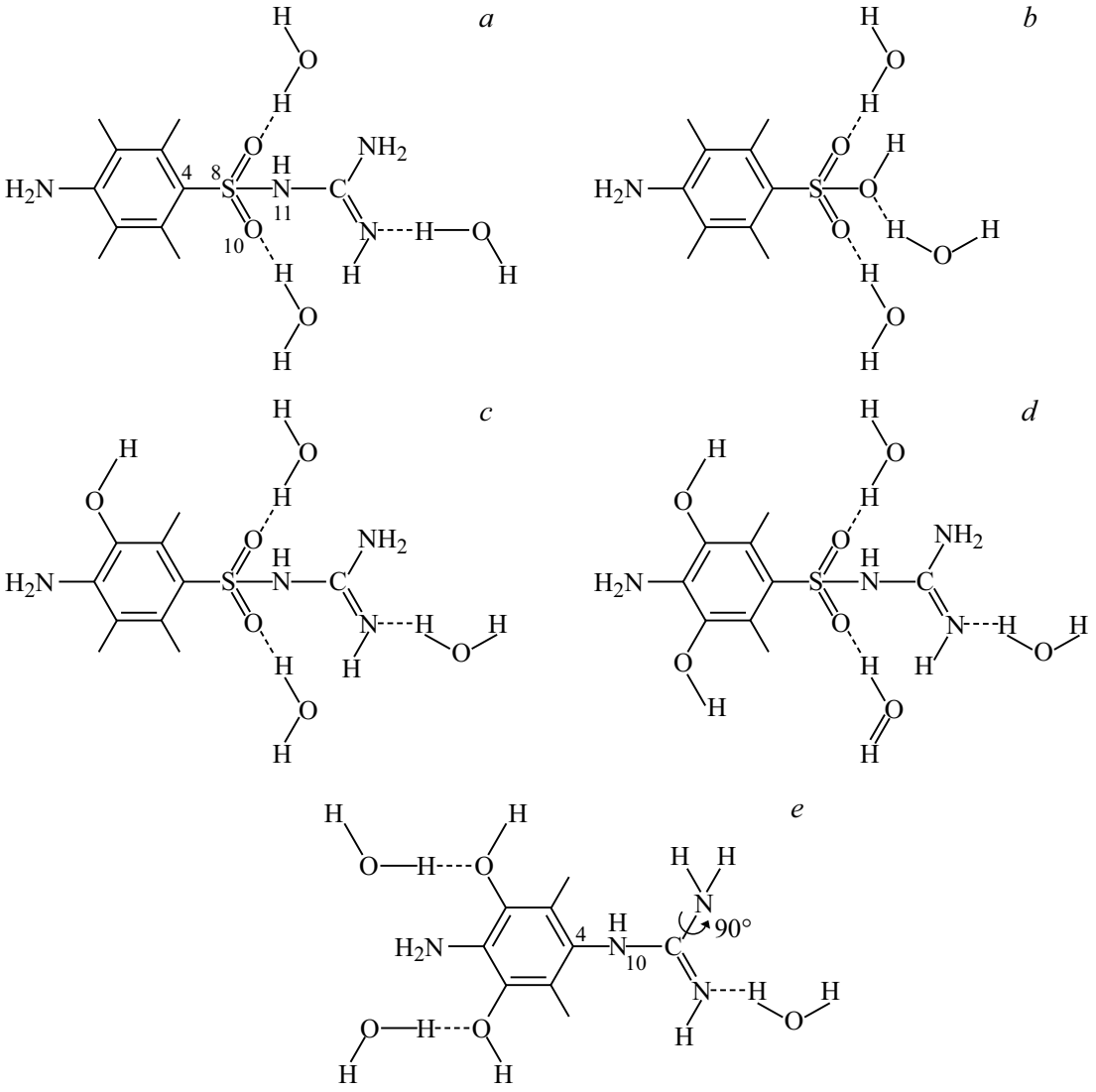

Figure 5. Structures of complexes of identified photoproducts of sulfaguanidine with water: *a* — sulfanidine $+3H_2O$, *b* — sulfanilic acid $+3H_2O$, *c* — photoproduct P1$+3H_2O$, *d* — photoproduct P2$+3H_2O$, *e* — photoproduct P3$+3H_2O$.

interaction of the formed secondary photoproducts with each other and with the solvent, leading to the appearance of a colored photoproduct absorbing at $\lambda_{max} = 560$ nm. With the help of quantum chemical calculation data, the fluorescence quantum yield was estimated according to the following formula:

$$\varphi_f = k_r/k_d, \qquad (1)$$

where φ_f — fluorescence quantum yield, k_r — radiative process rate constant, k_d — sum of radiative and nonradiative disintegration rate constants: $k_d = k_r + k_{ic} + k_{ST}$.

The fluorescence quantum yield of φ_f complexes of photoproducts is: 0.14 for sulfanilic acid$+3H_2O$ ($\lambda_{fl} = 306$ nm), 0.23 for P1$+3H_2O$ ($\lambda_{fl} = 317$ nm), 0.02 for P2$+3H_2O$ ($\lambda_{fl} = 325$ nm), 0.30 for P3$+3H_2O$ ($\lambda_{fl} = 338$ nm).

Fluorescence spectra of sulfaguanidine photoproducts in water

Fig. 6 shows the fluorescence spectra of sulfaguanidine in water before and after irradiation at fluorescence excitation wavelengths of 260 (Fig. 6, *a*) and 500 nm (Fig. 6, *b*) respectively. At excitation at 260 nm, similarly to the absorption spectra, a decrease in the fluorescence intensity in the 346 nm area (Fig. 6, *a*) is observed, which is also explained by the process of phototransformation of sulfaguanidine. An increase in the fluorescence intensity in the range 400– 500 nm after 8 min of irradiation indicates the formation of photoproducts that fluoresce in this area. The formation of a colored photoproduct, which was mentioned earlier, manifests itself in the fluorescence spectra upon excitation at 500 nm (Fig. 6, *b*). During the irradiation of a sulfaguanidine solution, efficient phototransformation occurs with the subsequent formation of various photoproducts.

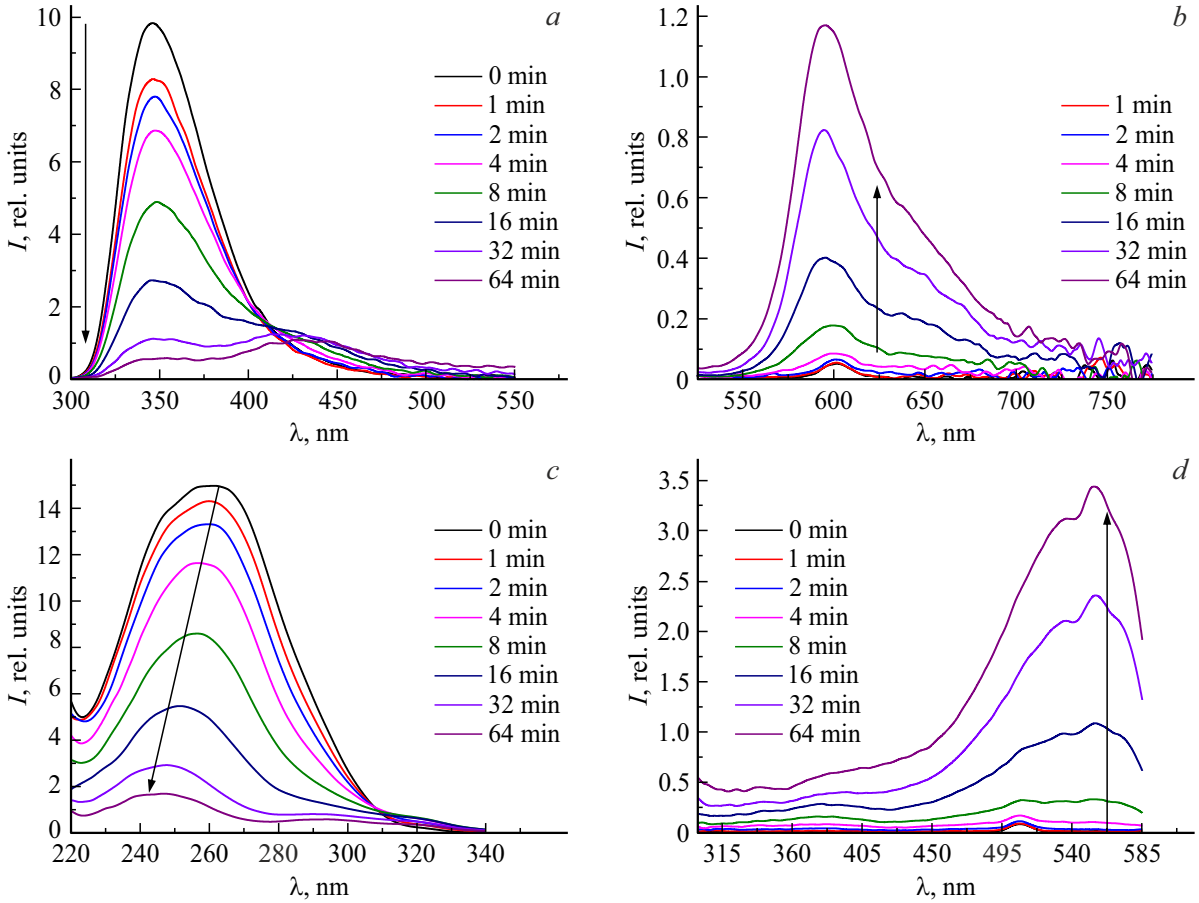

Figure 6. Fluorescence (*a*, *b*) and fluorescence excitation (*c*, *d*) spectra of sulfaguanidine in water before and after irradiation at (*a*) $\lambda_{ex} = 260$ nm, (*b*) $\lambda_{ex} = 500$ nm, (*c*) $\lambda_{em} = 360$ nm, (*d*) $\lambda_{em} = 610$ nm. The arrows show the direction of changes in the spectra upon irradiation.

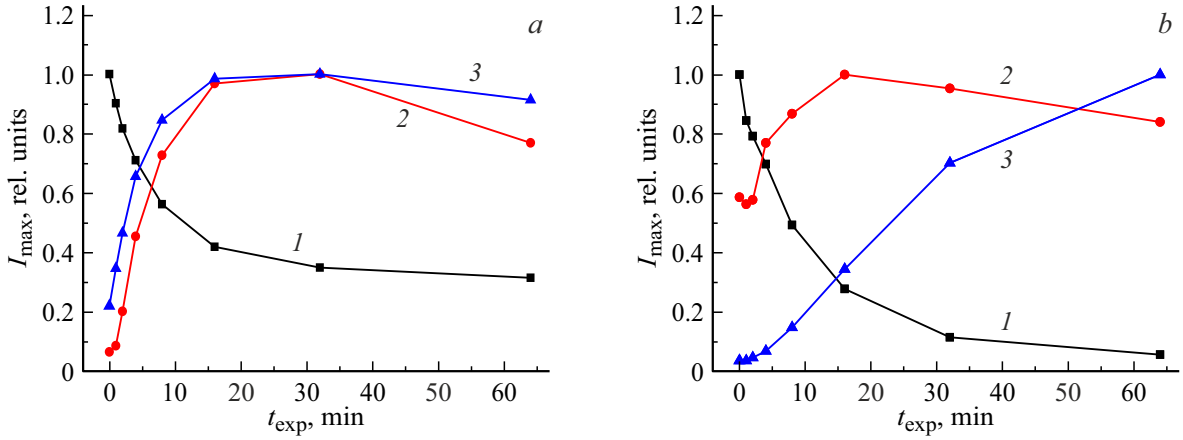

Figure 7. The decrease in sulfaguanidine and the increase in the content of photoproducts depending on the time of irradiation according to the absorption (*a*) and fluorescence (*b*) spectra: *1* — sulfaguanidine loss curve, *2* — photoproduct 1 formation curve, *3* – photoproduct 2 formation curve.

This is evidenced by an increase in the fluorescence intensity with an increase in the irradiation time from 0 to 64 min. According to the obtained experimental data, curves of the dependence of the decrease in sulfaguanidine and the growth of photoproducts on the time of irradiation were plotted (Fig. 7). Analyzing this dependence, it can be concluded that during irradiation from 0 to 16 min (Fig. 7, *a*, curve *1*), an effective phototransformation

occurs, resulting in a sharp decrease in sulfaguanidine. Simultaneously with this, active formation of primary and secondary photoproducts occurs during irradiation from 0 to 32 min (Fig. 7, *a*, curves *2* and *3*), after which a decrease is observed upon irradiation up to 64 min, which indicates a decrease in the photoproducts formed earlier (Fig. 7, *a*, curve *2*). Similar conclusions can be drawn for the dependence shown in Fig 7, *b*. Special attention should be paid to the fact that during irradiation from 0 to 64 min, the growth of one of the photoproducts does not stop (Fig. 7, *b*, curve *3*), which indicates the accumulation of this photoproduct and its resistance to irradiation.

Fig. 6, *c* and 6, *d* show the fluorescence excitation spectra of sulfaguanidine in water before and after irradiation. It can be seen from Fig. 6, *c* that the maximum shifts to the shortwave area, and the intensity decreases with increasing irradiation time. In addition, after 8 min of irradiation, several bands appear in the 280 −340 nm range, which indicates the phototransformation of sulfaguanidine and the formation of various photoproducts that appear in the fluorescence spectra (Fig. 6, *a*) . An increase in intensity is observed in the 450−585 nm range (Fig. 6, *d*), which corresponds to the absorption of the photoproduct, which possibly fluoresces in the 560−600 nm area, which is consistent with the spectra fluorescence upon excitation at 500 nm (Fig. 6, *b*).

It can be concluded that the fluorescent photoproduct with a band in the 596−650 nm area has absorption bands in the 245, 300, 380, and 540 nm areas. The fluorescent product in the 420 nm area has absorption bands in the 245, 300, and 320 nm areas.

Conclusions

Based on the results of the study the following conclusions were made:

1. In the process of irradiation, pH changes towards lower values.

2. Analysis of the experimental data showed that during the irradiation of an aqueous solution of sulfaguanidine, phototransformation occurs with the formation of several colored photoproducts. After irradiation, a colored photoproduct remains in the solution, which fluoresces in the 596 nm area.

3. The data of quantum-chemical calculations showed that the absorption spectra of all primary photoproducts lie in the middle part of the spectrum, which is formed and grows in intensity in the process of irradiation of the solution, namely, in the area from 260 to 315 nm.

4. An analysis of the orbital nature and localization of the electronic transitions of photoproduct complexes reveals a great similarity with the spectrum of the complex of the initial compound. Meanwhile, the energy of electronic transitions of primary photoproducts decreases relative to the electronic transitions of the initial molecule, i.e. there is a long-wave shift of the transitions $S_0 \rightarrow S_1(\pi\pi)$ and $S_0 \rightarrow S_3(\pi\pi)$ of the initial molecule to the long-wavelength area of the spectrum (260−315 nm) and a decrease in the intensity of the transition $S_0 \rightarrow S_3(\pi\pi)$ of the sulfaguanidine complex.

5. The absorption area of 200−240 nm, which arises upon irradiation of a solution of the initial product, includes an electronic transition to the states $S_4(\pi\sigma)$ of sulfanilic acid and $S_3(\pi\sigma)$ of photoproducts P1 and P2 localized on the C_4-S_8 bond, which can be broken, and into the state $S_3(\pi\sigma)$ of the P3 photoproduct, localized in the C_4-N_{10} bond. The latter circumstance suggests that in the process of the irradiation, the primary photoproducts of sulfaguanidine undergo further transformation, and the subsequent interaction of the final photoproducts with each other and with the solvent leads to the formation of a colored photoproduct that absorbs at $\lambda_{max} = 560$ nm.

6. The short-wavelength region of the spectrum has not been studied experimentally, but calculations allow us to speak of a decrease in the energy of one-electron transitions responsible for absorption in this region of the spectrum, while maintaining their intensity.

Funding

The work was supported by the Ministry of Education and Science of the Russian Federation as part of the state assignment № FSWM-2020-0033 for 2020−2024 .

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R.M. Baena-Nogueras, E. Gonzalez-Mazo, P.A. Lara-Martín. Environ. Sci. Technol., **51**, 3148 (2017). DOI: 10.1021/acs.est.6b03038

[2] A. Gentili, D. Perret, S. Marchese. Trends in Analyt. Chem., **24** (7), 704 (2005). DOI: 10.1016/j.trac.2005.04.013

[3] S. Rafqah, M. Sarakha. J. Photochem. Photobiol. A., **316**, 1 (2016). DOI: 10.1016/j.jphotochem.2015.10.003

[4] R. Rosal, A.G. Rodriguez, J.A. Perdigón-Melón, A.L. Petre, E. García-Calvo, M.J. Gómez, A. Agüera, A.R. Fernández-Alba. Water Research, **44** (2), 578 (2010). DOI: 10.1016/j.watres.2009.07.004

[5] E. Zuccato, S. Castiglioni, R. Bagnati, M. Melis, R. Fanelli. J. Hazard. Mater., **179** (1−3), 1042 (2010). DOI: 10.1016/j.jhazmat.2010.03.110

[6] M. Gros, M. Petrović, A. Ginebreda, D. Barceló. Environ. Int., **36** (1), 15 (2009). DOI: 10.1016/j.envint.2009.09.002

[7] J. Fick, H. Söderström, R. Lindberg, C. Phan, M. Tysklind, D. Larsson. Environ. Toxicol. Chem., **28**, 2522 (2009). DOI: 10.1897/09-073.1

[8] A. Białk-Bielińska, J. Maszkowska, W. Mrozik, A. Bielawska, M. Kołodziejska, R. Palavinskas, P. Stepnowski, J. Kumirska. Chemosphere, **86** (10), 1059 (2012). DOI: 10.1016/j.chemosphere.2011.11.058.

[9] O. Zielinski, J. Busch, A. Cembella, K. Daly, J. Engelbrektsson, A. Hannides, H. Schmidt. Ocean Sci. Discuss., **5**, 329 (2009). DOI: 10.5194/OS-5-329-2009
[10] C.G. Daughton, T.A. Ternes. Environ. Health Perspectives, **107**, 907 (1999). DOI: 10.1289/ehp.99107s6907
[11] T.A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.-J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert. Environ. Sci. Technol., **36**, 3855(2002). DOI: 10.1021/es015757k
[12] H.D. Burrows, M. Canle L, J.A. Santaballa, S. Steenken. J. Photochem. Photobiol. B, **67** (2), 71 (2002). DOI: 10.1016/s1011-1344(02)00277-4
[13] A. Lin, Y. Lin, W. Lee. Environ. Pollution, **187**, 170 (2014). DOI: 10.1016/j.envpol.2014.01.005
[14] J. Xu, Z. Hao, C. Guo, Y. Zhang, Y. He, W. Meng. Chemosphere, **99**, 186 (2014). DOI: 10.1016/j.chemosphere.2013.10.069
[15] S. Chiron, C. Minero, D. Vione. Environ. Sci. Technol., **40** (19), 5977 (2006). DOI: 10.1021/es060502y
[16] P. Sukul, M. Lamshöft, S. Zühlke, M. Spiteller. Chemosphere, **71** (4), 717 (2008). DOI: 10.1016/j.chemosphere.2007.10.045
[17] J. Niu, L. Zhang, Y. Li, J. Zhao, S. Lv, K. Xiao. J. Environ. Sci., **25** (6), 1098 (2013). DOI: 10.1016/s1001-0742(12)60167-3
[18] U. Hubicka, P. Zmudzki, P. Talik, B. Zuromska-Witek, J. Krzek. Chemistry Central J., **7** (1), 133 (2013). DOI: 10.1186/1752-153X-7-133
[19] N.D. Khaleel, W.M. Mahmoud, G.M. Hadad, R.A. Abdel-Salam, K. Kümmerer. J. Hazard. Mater., **244**, 654 (2013). DOI: 10.1016/j.jhazmat.2012.10.059
[20] L. Mersly, M. Mouchtari, M. Zefzoufi, M. Sarakha, M. Haddad, S. Rafqah. J. Photochem. Photobiol. A, **430**, 113985(2022). DOI: 10.1016/j.jphotochem.2022.113985
[21] C.J. Smyth, M.B. Finkelstein, S.E. Gould, T.M. Koppa, F.S. Leeder. J. Amer. Med. Assoc., **121** (17), 1325 (1943).
[22] O.N. Tchaikovskaya, E.N. Bocharnikova, I.A. Lysak, T.D. Malinovskaya, G.V. Lysak, I.V. Plotnikova, S.E. Sakipova. Micro and Nanosystems, **12** (3), 345 (2020).
[23] V.Ya. Artyukhov, A.I. Galeeva. Soviet Physics J., **29**, 949 (1986). DOI: 10.1007/BF00898453.
[24] E. Scroco, J. Tomasi. Adv. Quant. Chem., **11**, 115 (1978). DOI: 10.1016/S0065-3276(08)60236-1
[25] V.Ya. Artyukhov. J. Struct. Chem., **19** (3), 364 (1978). DOI: 10.1007/BF00753260
[26] O. Rinco, M.H. Kleinman, C. Bohne. Langmuir., **17**, 5781 (2001). DOI: 10.1021/la010526c.
[27] G.V. Maier, O.K. Bazyl, V.Ya. Artyukhov. Opt.Spectrosc., **82** (6), 767 (1992).
[28] O.K. Bazyl, O.N. Chaikovskaya, V.S. Chaidonova, E.N. Bocharnikova, G.V. Mayer. Opt. i spektr., **130** (5), 627 (2022). (in Russian). DOI: 10.21883/OS.2022.11.53768.3721-22
[29] L. Bellami. *Infrakrasnyye spektry slozhnykh molekul* (Izdatel'stvo inostrannoy literatury, M., 1957)(in Russian).
[30] B.R. Eggins. *Khimicheskaya struktura i reaktsionnaya sposobnost' tverdykh veshchestv* (Khimiya, M., 1976) (in Russian).
[31] A.I. Kitaigorodskiy, P.M. Zorkiy, V.K. Belskiy. *Stroenie organicheskogo veshestva* (*dannye strukturnykh issledovaniy* 1929–1970) (Nauka, M., 1980) (in Russian).

Translated by E.Potapova