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Spectral Luminescent Properties and Nature of Electronically Excited States of Sulfaguanidine in Water

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The absorption and fluorescence spectra of sulfaguanidine, its complexes with hydrogen bonds, and doubly charged cationic forms have been studied experimentally and theoretically. The orbital nature of electronically excited states is established and a theoretical interpretation of the absorption and fluorescence spectra is given. It was shown that the main reason for the anomalously large Stokes shift of fluorescence is the rearrangement of the benzoid structure of the phenyl fragment of sulfaguanidine into a quasi-quinoid one. The influence of the formation of hydrogen bonds and the addition of a proton on the amount of charge transfer between weakly bound fragments of the molecule has been established

Keywords: sulfaguanidine, sulgin, absorption spectra, fluorescence, quantum chemical calculation.

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Introduction

Sulgin is a commercial name of an antibacterial agent with a broad spectrum of action, whose medicinal component is sulfaguanidine — an antibiotic belonging to the pharmacological group of sulfanilamides actively used for treatment and prevention of intestinal infections of humans and animals. The mechanism of action of sulgin refers to antagonism with para-aminobenzoic acid and viable suppression of dihydropteroate synthetase. Characteristic feature of sulfaguanidine is the presence of a molecule of functional groups — sulfonic and guanidine groups. Guanidine group is a cationic fragment that creates an active center in the form of positive charges in macromolecules. These groups are building blocks that are found from time to time in the molecules of strong drugs [1]. Unfortunately, the molecular structure of sulfanilamides and their ion forms, as well as the complex formation with biological systems are poorly studied. The authors of works [2,3] performed the conformational analysis of anion of methane sulfonamide and simulated various interactions between substituted sulfonamides and carbonic anhydrase by using *ab initio* a high-level method. As a result of theoretical study, stable conformations were determined, as well as reactivity and hydrophilic property in gaseous phase of eleven biologically active sulfanilamides.

The purpose of this work is the study of a molecular structure and spectral luminescent characteristics of sulfaguanidine, its complexes with hydrogen bonds and double-charged cationic forms by means of quantum-chemical calculations and experimental methods. For biological objects, such as antibiotics, first of all, the ground state characteristics matter, i.e. absorption spectra, since the interaction of antibiotic molecules with the cells of living organisms takes place in a dark mode. On the other hand, application of a photodynamic therapy requires knowledge of the properties of molecules in excited state. Moreover, it is also important to know the interaction of an antibiotic molecule with a solvent, because compounds of antibiotics usually get inside a living organism as a solution, in particular, as a water solution.

Study methodology

Experimental methods

The object of the study is *n*-aminobenzenesulphonylguanidine monohydrate (sulfaguanidine) synthesized by a commercial company Sigma-Aldrich (product ID Si-Al S8751-25G). The structural formulae of the studied object and its complexes are given in Fig. 1. A white fine-crystalline powder is poorly soluble in water. In order to produce a matrix solution of sulfaguanidine with the concentration of 1 mM a dry weighed quantity was solved in distilled water by means of ultrasonic agitator. The absorption and fluorescence spectra of the studied solutions were registered by means of the VARIAN Cary

5000 Scan UV-VIS-NIR spectrophotometer and the VARIAN Cary Eclipse spectrofluorometer (AgilentTech., USA–Netherlands–Australia) at indoor temperature within the spectral band of 200−800 nm. A quartz cell with the pathway of 10 mm was used for the measurement. By using the derivative spectrophotometry the stripes were obtained that are manifested only as latent maxima and unclear bends in the absorption spectrum. This method is based on the same principles as a conventional spectrophotometry, however, the analytical response is not absorbance, but its derivative of the order of n (usually, by the wavelength). The spectrum differentiation allows more clear determination of the position of the absorption stripe maximum, and narrows the stripes and allows to determine substances that absorb at similar wavelengths, whose initial spectra are partially overlapping each other. According to this procedure we succeeded in distinguishing electron transitions in the sulfaguanidine absorption spectra in water. The spectroscopic characteristics of sulfaguanidine in water are given in [4]. In order to study ion forms of sulfaguanidine in water, the pH value of the medium was modified from that of the acid region to alkali ones by adding HCl and NaOH. The error of measurement of the absorption and fluorescence wavelength is ±1 nm.

Quantum-chemical calculations of the spectral and luminescent properties, comparison with an experiment

In theoretical study of molecular systems in solutions, the absence of reliable data on the spatial structure of a molecular system is a significant challenge. For example, it is unclear how many molecules of a solvent are in the first coordination sphere of the solvation shell of the studied molecule. As a rule, specific intermolecular interactions (for example, H-bonds) that occur in the first coordination sphere of a molecule result in greater modifications in the spectra of studied molecules versus the registration of universal interactions between molecules and a solvent. We suppose that the closer is a selected geometry of the studied molecule, as well as the solvent molecules arrangement in the first coordination sphere to real one, the better is concordance between the calculated spectral and luminescent properties and the experimental data.

In the theoretical study of the absorption and luminescence spectra we used quantum-chemical calculations performed by using the semi-empirical method of intermediate neglect of differential overlap with the original parametrization [5,6]. The use of this software tools package enables calculation of the electron spectra of singlet and triplet excited states, induced absorption spectra, fluorescence spectra, as well as physical and chemical properties of molecules (distribution of electron density on atoms and chemical bonds, dipole moment), as well as proton acceptor ability of the molecule in ground and excited states by using the method of molecular electrostatic potential [7,8]. The use of this package for calculation of the spectral and luminescent properties of organic molecules was successfully applied in the work [9].

In calculation of the geometry of the ground state X-ray diffraction data are generally used (chemical bond lengths, bond angles), as well as modern methods of the molecules geometry optimization [10]. For the sake of correct calculation of the emission spectrum it is required to know the geometry of a molecule in the excited state. We considered a partial modification of the molecule geometry in the fluorescent state in view of the modification of the chemical bond lengths of the molecule backbone in the state in question. Subject to the known linear dependence between the chemical bond length and its population density (according to Mulliken [11]), we can find the bond length modification in case of transition into excited state by using the formula

$$\Delta R^*_{\mathrm{AB}} = -k\Delta P^*_{\mathrm{AB}},$$

where ΔP^*_{AB} — is the bond population density A−B in case of excitation relative to the ground state, the coefficient $k = 0.46$ was obtained from modification of the bond length C−C in case of the $S_0 \rightarrow S_1$ transition in benzene [12]. All the properties of molecules listed in the software tool are calculated not only for neutral, but for charged molecules too. Correctness of calculations is assessed by concordance with the experimental data: the characteristics of the absorption and luminescence spectra.

Results and discussion

Electronic spectra of sulfaguanidine in water

According to the data from the referred publications, a long wavelength absorption stripe of sulfaguanidine in water was generated by one electron transition (259 nm), and a short wavelength — by two transitions (208 and 197 nm) [4,13]. For sulfaguanidine, the linear dependence of absorbance in the absorption spectra on the concentration preserves within the range from 0.005 to 0.2 mM. In the fluorescence spectra, the linear dependence of the sulfaguanidine intensity on the concentration has a linear nature within the range of 0.005−0.075 mM. It indicates that sulfaguanidine does exist in water generally in the monomeric form in the ground and excited states within the above mentioned intervals of concentration, accordingly. The sulfaguanidine fluorescence stripe maximum in water falls within the region 348 nm [4]. The structure of sulfaguanidine has many functional adsorption centers (NH_2-, SO_2- and NH-groups, O- and N-hetero atoms, aromatic rings) and is a highly basic, therefore, poorly soluble in water and easily soluble in an acid medium. Modification of pH medium in water with addition of NaOH does not result in increase of solubility and high modification of the stripes position in optic spectra versus a neutral form of sulfaguanidine (Fig. 2). A fall of intensity is recorded in the fluorescence spectra of sulfaguanidine in water-alkali solution (up to pH ∼ 11) versus a neutral form.

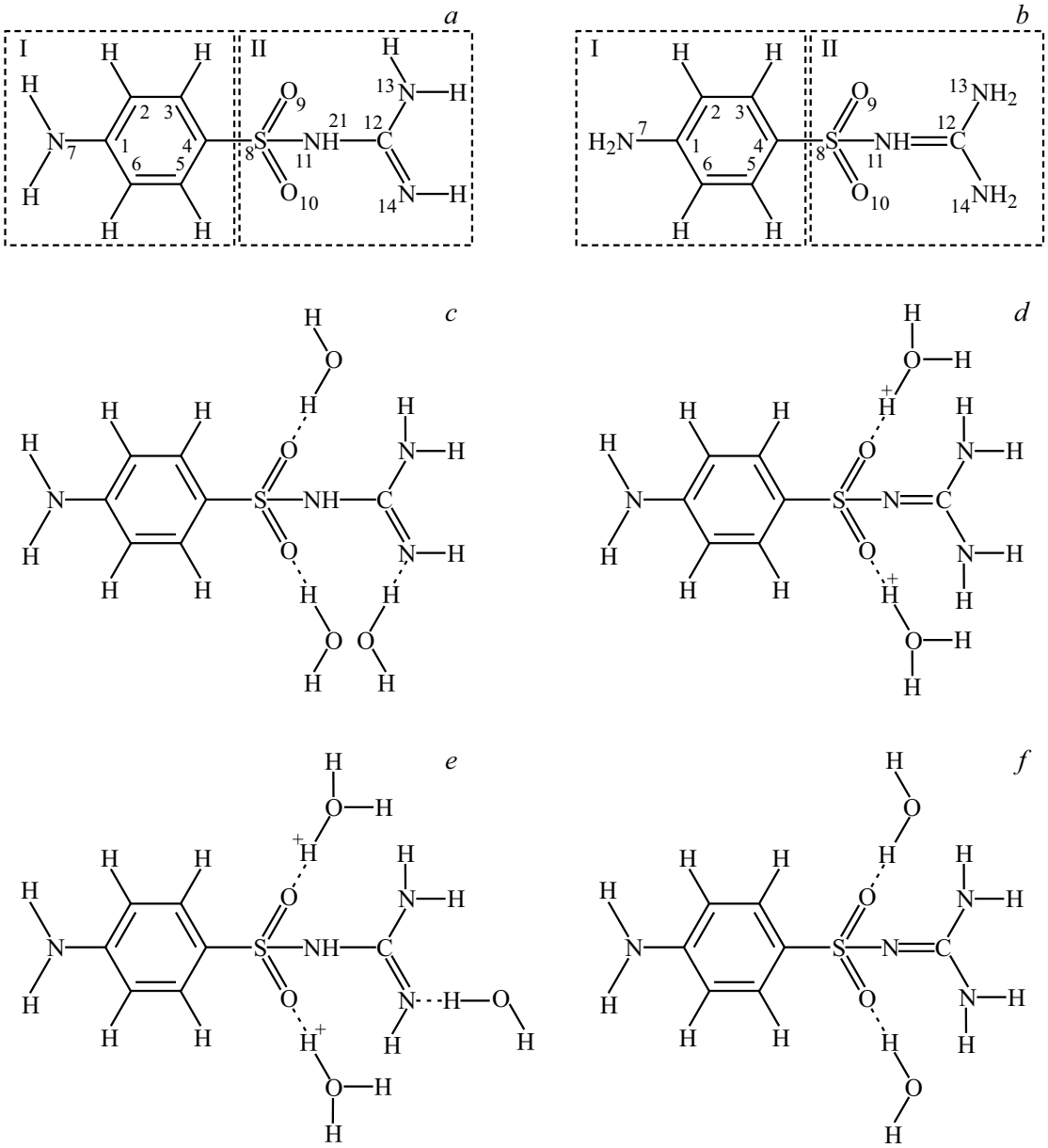

Figure 1. The structures of sulfaguanidine and its complexes: *a* — sulfaguanidine 1; *b* — sulfaguanidine 2; *c* — sulfaguanidine $1 + 3H_2O$; *d* — sulfaguanidine $2 + 2H^+H_2O$; *e* — sulfaguanidine $1 + 2H^+H_2O + H_2O$; *f* — sulfaguanidine $2 + 2H_2O$. I and II are aniline and sulfonic fragments of sulfaguanidine, accordingly.

The centers of interaction in sulfaguanidine and complexes building

There are two known structures of sulfaguanidine (Fig. 1). The structure of sulfaguanidine 2 is generated because of proton passage from the bond $N_{11}-H_{21}$ to the bond $N_{14}-H_{24}$ with subsequent formation of an amine group. We failed to distinguish the structures 1 and 2 of sulfaguanidine in experiments, nevertheless, we have separated these structures in the calculation in order to find distinctive features in generation of the absorption and fluorescence stripes. The possibility of intramolecular passage of proton in this case is caused by a high value of the minimum of the molecular electrostatic potential related with the atom N_{14} and decrease of the distance $N_{11}-N_{14}$ (the chemical bond length $R_{11-14} = 2.83$ Å), versus the van der Waals distance between two atoms of nitrogen N–N, varying within the limits of 3.16–3.0 Å [14,15]. Most likely, both structures are in equilibrium in the solution, it is impossible to distinguish them in the electronic spectrum of absorption.

When studying spectral and luminescent properties of sulfaguanidine we performed calculations of spectra of isolated molecules, their complexes with hydrogen bonds with the molecules of water, as well as double-charged (the charge value $q = +2e$) cations of both molecules. As a rule, position of electron states of isolated structures

of molecules in the calculation is compared with the absorption spectrum in a non-polar solvent. Sulfaguanidine is insoluble in a non-polar solvent, this is why Table 1 does not provide experimental data for the case of isolated molecules. A trial of comparison of the calculation results with the position of stripes in the absorption spectrum of sulfaguanidine in a weak acid water solution with addition of 0.01 M HCI increasing its solubility, failed to result in satisfactory concordance of the calculation with the experiment (Fig. 3, Table 1).

For description of behavior of the studied compound in water we studied the complexes of a molecule of sulfaguanidine with the molecules of water of the composition 1:3 (for sulfaguanidine 1) and of the composition 1:2 (for sulfaguanidine 2) (Fig. 1). The centers of a molecule with a high proton acceptor ability that determine the possibility of formation of H-bonds were obtained from the calculation of the value and coordinates of the minima of the molecular electrostatic potential. In sulfaguanidine 1 the atoms of oxygen of the sulfonic acid group ($U(O_9) = -604$ kJ/mol, $U(O_{10}) = -590$ kJ/mol) and the atom N_{14}, $U(N_{14}) = -380$ kJ/mol (Fig. 1) have the highest proton acceptor abilities, here U is the energy of electrostatic interaction of the studied molecule with a proton of a proton-donor solvent. In the structure of sulfaguanidine 2 the named proton acceptor centers of the oxygens of the sulfonic acid group are preserved, and these are added with the minimum of the electrostatic potential bound with the atom N_{11} ($U(N_{11}) = -450$ kJ/mol), however, the access to that center for a molecule of water during generation of the H-bond (moreover, for a solvated proton) is impeded. For that reason, a complex with H-bonds of sulfaguanidine 2 has the composition 1:2. A cation form of sulfaguanidine is represented by the complexes with hydrogen bonds with protons (H^+) solvated by a molecule of water (Fig. 1).

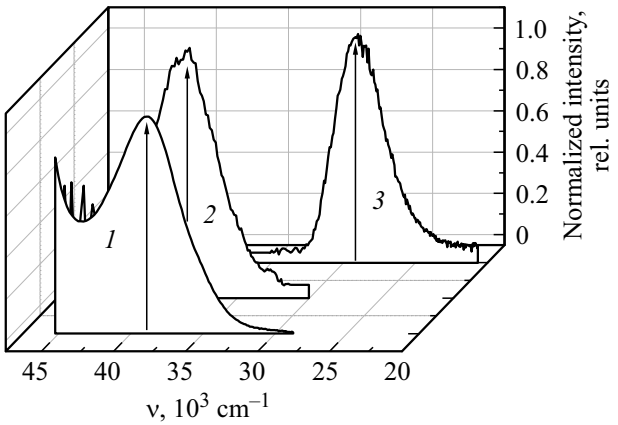

Figure 2. The rated intensity of sulfaguanidine in water solution of 0.4 M NaOH: *1* — absorption ($\nu_{max} = 50000$, 48300 and 39100 cm^{-1}); *2* — fluorescence excitation spectrum ($\nu_{max} = 38300\,cm^{-1}$), emission wavelength 342 nm; *3* — fluorescence ($\nu_{max} = 29000\,cm^{-1}$), $\lambda_{excit} = 250$ nm. The arrows indicate the stripe maxima: *1* — 39100 cm^{-1}, *2* — 38300 cm^{-1}, *3* — 29000 cm^{-1}.

Table 1. Experimental and calculated absorption spectra of sulfaguanidine 1 and 2, their complexes with water and cation forms

Calculation				Experiment	
State	E_i, cm^{-1}	λ, nm	f	ν_{max}, cm^{-1}	λ_{max}, nm
Sulfaguanidine 1, isolated					
$S_1(\pi\pi^*)$	35250	284	0.045	Insoluble	
$S_2(\pi\sigma^*)$	38390	260	0.035	in a non-polar	
$S_3(\pi\pi^*)$	38770	258	0.307	solvent	
$S_9(\pi\pi^* + \sigma\sigma^*)$	47060	212	0.357		
$S_{10}(\pi\pi^* + \sigma\sigma^*)$	47160	212	0.287		
$S_{11}(\pi\pi^* + \sigma\sigma^*)$	48020	208	0.220		
$S_{12}(\pi\pi^*)$	48699	206	0.564		
$S_{16}(\pi\pi^* + \sigma\sigma^*)$	52180	192	0.148		
Sulfaguanidine 2, isolated					
$S_1(\pi\pi^*)$	35220	284	0.050	Insoluble	
$S_2(\pi\sigma^*)$	38800	258	0.019	in a non-polar	
$S_3(\pi\pi^*)$	38990	256	0.364	solvent	
$S_9(\pi\pi^* + \sigma\sigma^*)$	47080	212	0.948		
$S_{10}(\pi\pi^*)$	47540	210	0.336		
$S_{11}(\sigma\sigma^* + \pi\pi^*)$	47930	209	0.198		
$S_{13}(\pi\pi^* + \sigma\sigma^*)$	49570	202	0.078		
Sulfaguanidine $1 + 3H_2O$					
$S_1(\pi\pi^*)$	34930	286	0.050	34500	290
$S_2(\pi\sigma^*)$	37640	266	0.005		
$S_3(\pi\pi^*)$	38570	259	0.282	38600	259
$S_9(\pi\pi^* + \pi\sigma^*)$	47560	210	0.458	48100	208
$S_{10}(\pi\pi^*)$	47670	210	0.386		
$S_{11}(\pi\sigma^*)$	48980	204	0.480		
$S_{14}(\sigma\sigma^*)$	52420	191	0.224	50800	197
Sulfaguanidine $2 + 2H_2O$					
$S_1(\pi\pi^*)$	35240	284	0.050	34500	290
$S_2(\pi\sigma^*)$	38450	260	0.004		
$S_3(\pi\pi^*)$	39110	256	0.393	38600	259
$S_9(\pi\pi^* + \sigma\sigma^*)$	47330	211	1.004		
$S_{10}(\pi\pi^*)$	47830	209	0.438	48100	208
$S_{11}(\sigma\sigma^*)$	48269	207	0.101		
$S_{13}(\pi\pi^* + \sigma\sigma^*)$	49760	201	0.110		
Sulfaguanidine $1 + 2H^+H_2O + H_2O$ (cation, $q = +2e$)					
$S_1(\pi\pi^*)$	34690	288	0.050	39100	256
$S_2(\pi\sigma^*)$	35210	285	0.007		
$S_3(\pi\pi^*)$	37870	264	0.430		
$S_8(\pi\pi^*)$	46800	214	0.475	48300	207
$S_9(\pi\pi^*)$	48590	206	0.906		
$S_{11}(\sigma\sigma^*)$	50070	200	0.059	50000	200
$S_{14}(\pi\pi^* + \sigma\sigma^*)$	52400	191	0.058		

In general, both structures 1 and 2 of sulfaguanidine are non-planar because of the presence of the groups $-SO_2-$ and $-HNC(NH_2)_2$ [16]. The work [17] studied theoretical parameters of neutral and cation forms of sulfanilamide compounds by using DFT- and semi-empirical methods. The authors also noted non-planar

Table 1. *continued*

Calculation				Experiment	
State	E_i, cm^{-1}	λ, nm	f	ν_{max}, cm^{-1}	λ_{max}, nm
Sulfaguanidine $2 + 2H^+H_2O$ (cation, $q = +2e$)					
$S_1(\pi\pi^*)$	34680	288	0.055	39100	256
$S_2(\pi\sigma^*)$	35300	283	0.007		
$S_3(\pi\pi^*)$	38300	261	0.467		
$S_8(\pi\pi^*)$	47230	212	0.509	483500	207
$S_9(\pi\pi^* + \sigma\sigma^*)$	47780	209	0.970		
$S_{10}(\pi\pi^* + \sigma\sigma^*)$	50060	200	0.120	50000	200
$S_{17}(\sigma\sigma^*)$	53850	186	0.141		

Note. E_i is the energy of electron transition, ν is the wave number, λ is the wavelength corresponding to the electron transition, f is the electron transition oscillator force.

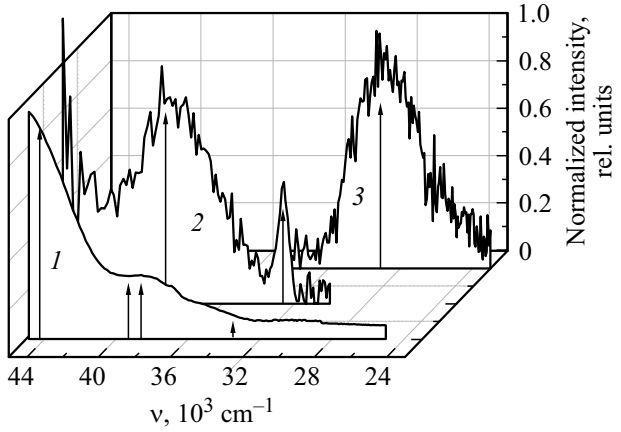

Figure 3. The rated intensity of sulfaguanidine in water solution of 0.4 M HCl: *1* — absorption ($\nu_{max} = 43500$, 38500, 36400 and 32200 cm^{-1}); *2* — fluorescence excitation spectrum ($\nu_{max} = 38400$ and 32200 cm^{-1}), emission wavelength 342 nm; *3* — fluorescence ($\nu_{max} = 29300\,cm^{-1}$), fluorescence excitation wavelength $\lambda_{excit} = 250$ nm. The arrows indicate the positions of the electron stripe maxima (curve *1*) determined by means of the derivative spectrophotometry.

structure of sulfaguanidine. Every of the molecules can be notionally separated into 2 parts: a planar one — benzene ring with NH_2-group (fragment I) and a non-planar one with the groups $-SO_2-$ and $-HNC(NH_2)_2$ (fragment II). Optimization of the geometry of the structures of sulfaguanidine 1 and 2 was performed by using the method of molecular dynamics MM2 ChemOffice [10] in the AM1 version. Note that the calculated spectra with completely optimized geometry for the studied molecule failed to give satisfactory results for the experiment description. This is why we used a „hybrid" geometry, at which the aniline part of molecules (fragment I) was within the plane XY of the molecular system of coordinates with averaged geometrical parameters [18], and the geometry of the part of a molecule with sulfonic and guanidine groups (fragment II) was taken according to the optimized geometry.

Notional separation of the molecule of sulfaguanidine into planar and non-planar fragments is caused by a considerable length of the chemical bond between the fragments ($R_{4-8} = 1.78$ Å), which resulted in decrease of the energy of interaction between them. It is also confirmed by the results of calculation of the lengths of bonds of the molecules backbone in excited states forming a long wavelength stripe of absorption. As an example, Table 2 provides the lengths of chemical bonds of the molecules backbones in electronically excited states of sulfaguanidine 1 $S_1(\pi\pi^*)$ and $S_3(\pi\pi^*)$, calculated according to the formula given above.

The nature of electronically excited states

According to the results of calculations, the electronically excited states $S_1(\pi\pi^*)$ and $S_3(\pi\pi^*)$ form long wavelength stripes of absorption in all molecular structures under study (Table 1).

The analysis of data of Table 2 shows that in excited states $S_1(\pi\pi^*)$ and $S_3(\pi\pi^*)$ the lengths of chemical bonds of the fragment I of sulfaguanidine 1 and 2 vary differently, but are highly differed from the length of bonds of that fragment of sulfaguanidine in the ground state of the molecule, meanwhile, the fragment II has minor or no such variations. This result indicates that the long wavelength stripe in the absorption spectra is generally formed with participation of the fragment I with minor participation of the fragment II.

A non-planar structure of the molecule of sulfaguanidine in general impedes determination of orbital nature of the excited states. Therefore one should take into account that the orbital nature of excited states given in Table 1 indicates only a predominant contribution of such type configuration of molecular orbitals.

The results of calculation of the sulfaguanidine absorption spectrum give a higher number of electron transitions that have impact to the intensity of the absorption stripes, than it is distinguished in the experiment. Thus, a long wavelength stripe of absorption of sulfaguanidine, according to the calculations, includes three one-electron transitions with different intensity and orbital nature (Table 1). However, the most intensive part of that stripe is formed mainly by the transition $S_0 \rightarrow S_3(\pi\pi^*)$, which corresponds to the stripe maximum in the experimental spectrum, with some participation of less intensive transition $S_0 \rightarrow S_1(\pi\pi^*)$. All three electron transitions of the long wavelength absorption stripe, independently on their orbital nature, are localized on a benzene fragment of sulfaguanidine with participation of the atom N_7 of amine group or without it.

It is known that the effect of medicinal substances in a living organism, their metabolism, as well as hydrophilic and hydrophobic interactions between membranes of cells and a medicinal compound at the first stage of interaction are determined by electrostatic interactions [19]. Therefore, pharmacological activity of medicinal compounds depends

Table 2. Lengths of chemical bonds (R, Å) in the ground and some of excited electronic states of sulfaguanidine 1. Number of atoms in the calculations according to Fig. 1

Rs_i	Fragment I							Fragment II						
	Numbers of atoms in bonds													
	1–2	2–3	3–4	4–5	5–6	1–6	1–7	4–8	8–9	8–10	8–11	11–12	12–13	12–14
R_{S0}	1.40	1.40	1.40	1.40	1.40	1.40	1.409	1.783	1.479	1.479	1.742	1.454	1.453	1.260
Sulfaguanidine, isolated														
R_{S1}	1.428	1.458	1.431	1.424	1.455	1.428	1.390	1.786	1.479	1.479	1.750	1.453	1.453	1.260
R_{S3}	1.466	1.390	1.489	1.493	1.393	1.470	1.402	1.806	1.481	1.481	1.762	1.455	1.454	1.260
Sulfaguanidine $1 + 3H_2O$														
R_{S1}	1.429	1.458	1.429	1.426	1.457	1.430	1.397	1.786	1.480	1.480	1.747	1.455	1.454	1.260
R_{S3}	1.463	1.388	1.480	1.487	1.382	1.470	1.397	1.794	1.480	1.481	1.744	1.459	1.454	1.260
Sulfaguanidine $1 + 2H^+H_2O$														
R_{S1}	1.421	1.446	1.446	1.428	1.455	1.420	1.390	1.786	1.479	1.479	1.750	1.456	1.453	1.260
R_{S3}	1.460	1.390	1.464	1.497	1.397	1.465	1.397	1.803	1.480	1.480	1.760	1.458	1.454	1.260

on the distribution and modification of charges in the molecules of medicinal compounds. For that reason the analysis of the results of calculation of efficient charges of sulfaguanidine fragments and their modifications in the complexes and charged forms will be very useful. Table 3 provides calculated efficient charges in sulfaguanidine fragments, its complexes and charged forms.

According to the calculation, the fragment I in the ground state is a donor of electron density and the fragment II is an acceptor. At the same time, in the ground state, in the complexes and cation forms of sulfaguanidine, the value of charge transferred between the fragments is higher than in isolated molecules. It should be noted that in excited states creating the intensity of a long wavelength absorption stripe of different structures of sulfaguanidine, the donor and acceptor properties of the ground state fragments are preserved (Table 3).

Having analyzed the value of efficient charges of fragments of different structures of the sulfaguanidine molecules and water molecules participating in the complexes formation we conclude on the following. In the ground state the molecules of water in the complex carry a negative charge, weakly modified in case of electronic excitation, as well as not modifying proton acceptor ability of the molecule fragments. In other words, during formation of H-bonds, own charge of water molecules is weakly participating in the electron charge exchange process between the fragments of sulfaguanidine molecule. However, formation of H-bonds contributes into increase of efficient charge carried between the fragments of different structures of sulfaguanidine in case of excitation in all regions of the spectrum.

The nature of medium and short wavelength regions of absorption of sulfaguanidine 1 and 2 is more complicated. It should be noted that Table 1 provides only those electronically excited states with electron transitions from the ground state that form intensity of the absorption stripes in the experimental spectrum. Absorption in the medium and short wavelength regions of the spectrum is formed by several electron transitions of a mixed nature $\pi\pi^*$-, $\sigma\pi^*$- and $\sigma\sigma^*$-types. At the same time, electron transitions of $\sigma\sigma^*$- and $\sigma\pi^*$-types are localized on different parts of a non-planar fragment of the molecule and are related both with redistribution of electron density inside that fragment, and with its carrying between planar and non-planar fragments of molecules (Table 3). According to the calculations, in the medium part of the absorption spectrum, electron transitions into the states within the range S_8-S_{11} modify donor and acceptor properties of the fragments of the sulfaguanidine 1 and 2 molecules: in these excited states the fragment I acquires acceptor properties, and the fragment II becomes a donor most of all because of the atoms of oxygen of the sulfonic acid group and the atoms of nitrogen N_{11} and N_{14}.

Note that for the structures in question the electron transition $S_0 \rightarrow S_3(\pi\pi^*)$ is virtually constant in terms of the energy in all of the structures, modifying within $500-700\,\mathrm{cm}^{-1}$ according to the calculations. It is also illustrated by the position of the maxima of a long wavelength stripe in the experimental spectra of absorption of water solutions of sulfaguanidine and its ionic forms (Figs 2 and 3). This fact is clear, if a low interaction between the fragments I and II is taken into account, as well as that modifications of the structure in complexes and cations are relevant only for the fragment II, meanwhile a long wavelength stripe of the absorption spectrum is localized on the fragment I.

Comparison of calculated spectra of absorption of sulfaguanidine 1 and 2 demonstrates similar values of the energies of electronically excited states in the medium and short wavelength regions. At the same time, electron

Table 3. Modification of efficient charges (q_{ef}, e) in sulfaguanidine fragments 1 and 2, their complexes with water and cations in various electron states S_n

Fragment of molecule	q_{ef}					
	Absorption					Fluorescence
Sulfaguanidine 1						
	S_0	S_1	S_3	S_9	S_{11}	S_{fl}
I	0.084	0.051	0.084	−0.315	−0.147	0.289
II	−0.084	−0.050	−0.084	0.316	0.147	−0.290
Sulfaguanidine 2						
	S_0	S_1	S_3	S_9	S_{10}	S_{fl}
I	0.082	0.051	0.430	−0.096	−0.051	0.232
II	−0.080	−0.049	−0.425	0.096	0.054	−0.233
Sulfaguanidine $1 + 3H_2O$						
	S_0	S_1	S_3	S_9	S_{11}	S_{fl}
I	0.114	0.095	0.114	−0.330	0.062	0.223
II	0.019	0.039	0.016	0.453	0.064	−0.097
$3H_2O$	−0.134	−0.134	−0.130	−0.121	−0.125	−0.128
Sulfaguanidine $2 + 2H_2O$						
	S_0	S_1	S_3	S_9	S_{10}	S_{fl}
I	0.092	0.068	0.075	−0.120	0.049	0.283
II	−0.016	0.018	0.009	0.200	0.032	−0.224
$2H_2O$	−0.087	−0.086	−0.085	−0.079	−0.083	−0.073
Sulfaguanidine $1 + H_2O + 2(H^+H_2O)$						
	S_0	S_1	S_3	S_8	S_9	S_{fl}
I	0.177	0.189	0.292	0.250	0.153	0.371
II	−0.150	−0.171	−0.273	−0.232	−0.131	−0.353
$2H^+H_2O$	1.983	1.981	1.981	1.981	1.980	1.982
Sulfaguanidine $2 + 2H^+H_2O$						
	S_0	S_1	S_3	S_8	S_9	S_{fl}
I	0.170	0.210	0.340	0.313	0.067	0.735
II	−0.155	−0.190	−0.325	−0.295	−0.045	−0.719
$2H^+H_2O$	1.998	1.983	1.983	1.983	1.983	2.002

transitions in the medium and short wavelength parts of the spectrum of sulfaguanidine 2 are higher in terms of intensity than for sulfaguanidine 1. It is because of increase of symmetry of the structure of sulfaguanidine 2 relative to the structure 1. The same is observed for spectra of the complexes of sulfaguanidine, and in cation form the intensities of electron transitions in the medium and short wavelength regions are virtually the same.

Therefore, data in Table 1 have shown that formation of complexes and cation forms of sulfaguanidine 1 and 2 does not modify dramatically the form of absorption spectra versus the isolated molecules spectra, moreover, the calculated absorption spectra of the complexes and cation forms provide a satisfactory description of the experiment (Table 1).

Spectra of fluorescence of sulfaguanidine 1 and 2, their complexes and cation forms

According to the experiment, the maximum of the fluorescence spectrum of sulfaguanidine solutions in water is at 348 nm ($28740\,cm^{-1}$) [4]. In order to confirm the fact of relevance of the observed sulfaguanidine fluorescence, we obtained the fluorescence excitation spectrum, which in terms of the position and shape completely coincides the spectrum of a long wavelength stripe of sulfaguanidine absorption in water (Fig. 3, Table 1).

The experimental spectrum of fluorescence of water solutions of sulfaguanidine has two features: 1) the energies of fluorescent state of water solution of sulfaguanidine and its cation forms are poorly differed (Figs 2 and 3,

Table 4. Characteristics of fluorescence of sulfaguanidine 1 and 2, their complexes and cation forms

Calculation*		Experiment	
E_{fl}, cm^{-1} (nm)	$\Delta\nu_{st}$, cm^{-1}	E_{fl}, cm^{-1} (nm)	$\Delta\nu_{st}$, cm^{-1}
Sulfaguanidine 1, isolated		28570 (350)	9800
28910 (346)	9860		
Sulfaguanidine 2, isolated			
29070 (344)	9830		
Complex of sulfaguanidine $1 + 3H_2O$			
28380 (352)	9430		
Complex of sulfaguanidine $2 + 2H_2O$			
28330 (353)	10020		
Sulfaguanidine $1 + H_2O + 2(H^+H_2O)$, $q = +2e$			
28330 (353)	10020		
Sulfaguanidine $2 + 2(H^+H_2O)$, $q = +2e$			
28380 (342)	10020		

Note. *$\Delta\nu_{st}$ is the Stokes shift, E_{fl} is the energy of fluorescent state.

Table 4); 2) the Stokes shift ($\Delta\nu_{st}$) of sulfaguanidine is reaching $\sim 10000\,cm^{-1}$, which indicates significant reconfigurations in the molecule during transition from ground state to fluorescent one.

One of the reasons of such a high value $\Delta\nu_{st}$ could be the differences of the molecule geometry in excited and ground states. Since the observed fluorescence belongs to sulfaguanidine and is excited in a long wavelength stripe of the absorption spectrum ($\lambda_{ex} = 250\,nm$), it is reasonable to consider modifications of geometrical parameters of the molecule in excited states forming that stripe (Table 2). We can partially consider modifications of the molecule geometry in case of excitation through the modification of the length of chemical bonds of the molecule backbone under study. Analysis of the lengths of bonds in the state $S_3(\pi\pi^*)$ has shown that the geometry of the fragment I is close to that of a quinoid structure: the bonds 1–2, 1–6, 3–4 and 4–5 are elongated in case of excitation, while the bonds 2–3 and 5–6, oppositely, are shortened (Table 2). In the state $S_1(\pi\pi^*)$ it does not occur.

The values of lengths of chemical bonds of the sulfaguanidine backbone in two excited states given in Table 2 have shown that the most radical modifications of geometrical structure of sulfaguanidine take place in the states $S_3(\pi\pi^*)$. The spectrum of sulfaguanidine fluorescence is obtained in case of excitation into a long wavelength stripe of absorption, which, according to calculations is formed mainly by the electron transition $S_0 \rightarrow S_3(\pi\pi^*)$. According to [20,21], reconfiguration of the molecule structure in an excited state occurs for the time $\sim 10^{-12-13}\,s$, by forming a non-equilibrium structure that is fast relaxing into a fluorescent state. Calculation of the energy of a fluorescent state with quasi-quinoid structure of the state $S_3(\pi\pi^*)$ results in the energy similar to the experimental one (Table 4).

The value of Stokes shift $\Delta\nu_{st}$ is experimentally determined as the difference of the energies of the maxima of absorption and fluorescence spectra stripes. Given the absorption stripe maximum in the calculation forms $S_0 \rightarrow S_3(\pi\pi^*)$ transition, whose energy in the structures in question is modified within the limits from 37870 to $39110\,cm^{-1}$ (Table 1), and the geometry of a fluorescent state is similar to quinoid one, the value $\Delta\nu_{st}$ becomes close to the experimental one ($\sim 10000\,cm^{-1}$). Note that the calculated characteristics of fluorescence are virtually the same for isolated molecules of sulfaguanidine, its complexes and cation forms (Table 4).

Theoretical calculation of efficient charges in fragments of sulfaguanidine 1 and 2 has shown that donor and acceptor properties of fragments I and II in fluorescent state are similar to the properties of the ground state, but the value of carried charge is increased versus the state S_0 (Table 3).

Conclusions

Summarizing the results of the study, we conclude on the following.

1. A long wavelength stripe of the absorption and fluorescence spectrum of sulfaguanidine, its complexes with water and cation forms is mainly formed by molecular orbitals localized on an aniline fragment of the molecule, and the atoms of the groups $-SO_2-$ and $-HNC(NH_2)_2$ virtually do not participate in formation of the molecular orbital of $\pi\pi^*$-type of low electronically excited states.

2. Formation of H-bound complexes and charged forms of sulfaguanidine have impact to the value of carried charge between planar and non-planar fragments of molecules.

3. A higher value of the Stokes shift $\Delta\nu_{st}$ is caused by reconfiguration in aniline fragment of sulfaguanidine: transition of benzenoide structure of phenyl into quasi-quinoid one.

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Conflict of interest

The authors declare that they have no conflict of interest.

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