Allyl *vs* ethyl substituted thioquinoline complexes with diiodine: Halogen bonds and iodocyclization

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A R T I C L E   I N F O

A B S T R A C T

A comparative analysis of 2-allylthioquinoline and 2-ethylthioquinoline interactions with diiodine in solutions was performed using UV/Vis spectroscopy and molecular modelling with a TD-DFT approach. The named compounds exhibit different reactivity: 2-allylthioquinoline participates in the iodocyclization reaction and 2-ethylthioquinoline forms molecular complexes with diiodine only. The emergences of iodocyclization products and diiodine complexes of alkyl- and alkeny lsubstituted thioquinolines on spectra allow us to enable process control of interactions with diiodine.

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1. Introduction

Alkenylthioquinolines react with an excess of iodine yielding iodocyclization products [1,2] containing tricyclic molecular systems. Tricyclic quinoline-based heterocycles are widely known as important broad-spectrum antibiotics [3]. It would be natural to assume that this reaction of alkenylthioquinolines passes through the stage of molecular complexes in which diiodine forms halogen bonds with electron-donating centers. For reaction control, it is important to estimate the mutual influence of the closely located donor centers (N and S), which determines the iodocyclization initial stages [4]. UV/Vis spectroscopy is the available method that yields useful information about the peculiarities of such processes [5,6]. In this context, it is obviously important to study the spectral characteristics of S-alkenyl substituted thioquinolines and the role of iodocyclization products in the process of iodine halogen bonds identification in the molecular complexes.

It should be noted that the state and spectra of molecular iodine (diiodine) and polyiodides in solutions was reasonably well investigated, both experimentally and by calculation methods. It has been detected that the absorption band of iodine develops a strong hypsochromic shift with increase in solvent basicity (according to Lewis): the maximum shifts from 520 nm in hexane down to 447 nm in methanol [7]. Besides, the intensive band appears in the range 290 … 300 nm [7,8] – in benzene, related to changes in the electron transition set on iodine interaction with a solvent. Drago et al. have investigated similar interactions and the iodine complex formation with various donor molecules with nitrogen [9] or sulfur atoms [10] in detail. We suggest that the halogen bonds are in the foundation of such complexes. The spectra of the solutions of compounds, formed on mixing of monoiodide with the diiodine, are characterized by disappearance of the 460-nm band and appearance of the maximum at 350 nm in water [11]. The presence of intensive narrow absorption bands in the spectrum ranges 287 … 290 and 350 … 355 nm [12,13] is also noted in other papers concerned with the study of polyiodides.

Experimental research [14,15] in various solvents and *ab initio* calculations of iodine interaction with 2,3-diaminopyridine has been carried out. It has been noted that such a reaction runs in several steps. First, the interaction of the diiodine with the nitrogen of amino group proceeds with the subsequent breakage of I–I bond and formation of monoiodide ion I^-. Then the interaction of monoiodide ion with the second molecule of iodine and formation of the ion pair, including triiodide anion I_3^-, takes place. The appearance of intensive absorption bands, typical for the triiodide ion, namely, 355 and 295 nm, is observed in the spectrum of the final product.

The interaction of 8-thioquinoline and pyrrolidine-2-thione with iodine [5,6] leads to formation of the molecular complexes. For the spectra, the appearance of the absorption band at 297 nm (in the former case) and two maxima of 289 and 362 nm (in the latter case) was observed, while the intensity of the diiodine band at ~500 nm simultaneously decreased. Those were the characteristics of polyiodide ions formation. The authors also noted that it was possible to reliably trace the degree of advancement of the reaction and the change in reagent concentrations with the help of UV/Vis spectra, as well as to determine the stability constants of complexes.

As a rule, in order to account for medium (solvent) influence on the electronic spectra features of the investigated compounds, refining models are used [16]. The precise numerical polarizable continuum

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model (PCM) [17,18] was developed in the past decade. In particular, the results of experimental investigation of 2-amino-5-bromobenzoic acid were in good approximation to calculations of the Raman and UV/Vis spectra in solutions [19], and the authors explained some features of spectra by the presence of conformers' differences.

Studies of theoretical electronic spectra of organic heterocycles with the use of time dependent density functional theory (TD-DFT) [20,21] are widely conducted at present. For example, in Ref. [22] the spectra of azoalkanes were observed, followed by the attempts to improve initial conditions of calculations and to explain the differences in theoretical and experimental data. In work [23] comprehensive experimental research of benzodithiazol derivatives initiated the calculations of electron density and spectra of the synthesized substances, which proved to be consistent with the measured data.

It should be noted that functional B3LYP [24,25] and full-electron basis sets of the 6-311G family [26,27] are most frequently used at present for characterization of organic molecules. Comparative calculations of electronic spectra were also carried out [28,29] with the use of functional PBE0 [30] and similar basis sets. We have previously noted [31] that the electronic spectra, calculated with the use of functional B3LYP, better correspond to the experimental spectra of 2- and 8-thioquinoline, in comparison with PBE0. Moreover, the calculated lines, obtained with the use of B3LYP, reproduce the experimental absorption bands of phenothiazine in the best way [28]. On the contrary, the calculated lines, obtained with the use of PBE0, better reproduce the absorption bands of halogen-substituted azo-compounds [29]. The basic electronic transitions determining the absorption bands in the spectra of iodine complexes are presumably related to atomic orbitals (AO) of iodine. The correct determination of iodine contributions to molecular orbitals (MO) of the substituted 2-thioquinoline complexes with halogen bonds is important first and foremost. Therefore, the estimation of applicability of various combinations of functionals PBE0 and B3LYP and basis sets to the present task was carried out on the example of the triiodide ion. We found that the calculated oscillatory frequencies, closest to experimental ones, were obtained with the use of functional PBE0 and basis set 6-311G (d, p). Similarly, the calculation of electronic spectra showed, that the absorption lines, obtained with the use of PBE0, were particularly relevant to experimental bands 287 … 290 and 350 … 355 nm [12,13].

Note that conformity estimations of experimental UV/Vis spectra bands to the calculated electronic transitions have not been described in the literature, both for iodine complexes with halogen bonding as a whole and for polyiodides as components of solutions in particular. At the same time we consider that the understanding how the UV/Vis spectra change during reactions of diiodine with substituted thioquinoline heterocycles, which are rich in electron-donating centers, enables keeping track of the reaction path and simplifies the control of the following stages, for example the iodocyclization reaction. As a rule, in the iodocyclization reaction, the alkenyl derivatives of thioquinoline form tricyclic cations, which precipitate as salts – oligoiodides – in the traditionally used solvents (dichloromethane, benzene, etc.) [1]. At similar conditions, alkyl-substituted thioquinoline also interacts with diiodine, but iodocyclization does not proceed further. This fact allows using the comparison of spectral characteristics of alkenyl- and alkyl-substituted thioquinoline in order to study the complex formation with iodine and the iodocyclization reaction in detail.

The prime aim of the present work is the research of the characteristic features of allyl- and ethyl-substituted 2-thioquinoline complex formation with diiodine. It gives the possibility of reaction staging identification, with the use of UV/Vis spectra, under conditions of appearance of iodocyclization products in a reaction mixture. For this

purpose, the following objectives have been met:

- The analysis of experimental UV/Vis spectra of 2-allylthioquinoline and 2-ethylthioquinoline under conditions of interaction with diiodine in dichloromethane solution has been completed.
- The comparisons of experimental UV/Vis spectra of considered complexes with previously isolated iodocyclization products (thiazoloquinolinium monoiodide and thiazoloquinolinium triiodide) have been realized.
- The calculated spectral characteristics of the substituted 2-thioquinoline iodine complexes, containing iodine halogen bonds S … I, N … I, and C … I, have been investigated.

2. Materials and methods

2.1. Experimental

2-Allylthioquinoline and 2-ethylthioquinoline compounds were synthesized according to the technique described in Refs. [32,33] in order to investigate their spectral properties. In a typical experiment, 25 mL of 4 mmol/L or 0.06 mmol/L I_2 dichloromethane solution were mixed with 25 mL of 2-allylthioquinoline (0.8 mmol/L) or 2-ethylthioquinoline (0.06 mmol/L) dichloromethane solution, respectively. UV/Vis spectra were registered every 2–5 min during the first 30 min of the reaction, then every 30 min during 6 h.

UV/Vis spectra of 1-(iodomethyl)-1,2-dihydro [1,3]thiazolo[3,2-a]quinolinium monoiodide $C_{12}H_{11}INS^+I^-$ and triiodide $C_{12}H_{11}INS^+I_3^-$, synthesized according to [2] (Fig. 1), in dichloromethane solution (0.2 mmol/L) were recorded. All the initial solutions were prepared and diluted to the desired concentrations in volumetric flasks.

UV/Vis spectra of prepared solutions were registered by means of a Shimadzu UV-2700 spectrophotometer in the range 220 … 850 nm at the recording speed 450 nm/min.

2.2. Calculation

Structures of 2-allylthioquinoline and 2-ethylthioquinoline complexes with diiodine, formed on different electron-donating centers S⋯I, N⋯I, C═C⋯I, were considered. Besides, the structures of ini-
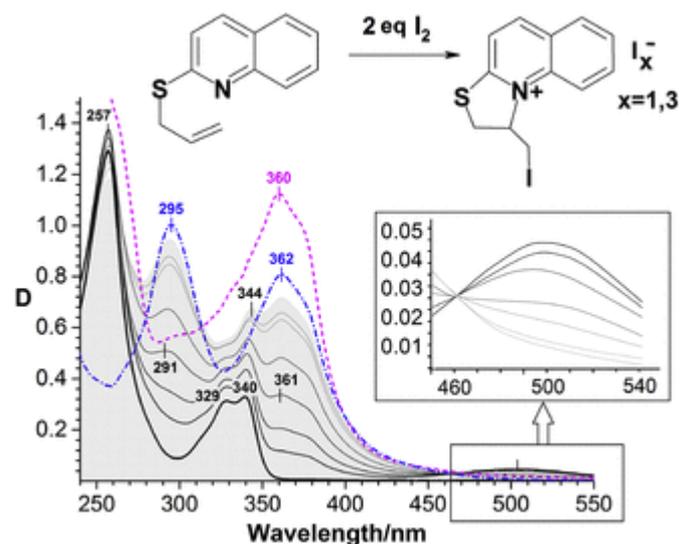

Fig. 1. 2-allylthioquinoline and iodocyclization products spectra.

tial compounds were taken in several conformational states [34]. We carried out the quantum chemical calculations of the optimized structures and their energy characteristics with the use of software package Firefly v.8 [35]. Optimized geometry of complexes with iodine halogen bonds was calculated at level PBE0/6-311G(d,p). Optimization of structures was performed in the necessary number of steps up to the stationary point with the greatest magnitude of the energy gradient, not more than 1×10^{-5} (in Hartree/Bohr units). There were no imaginary frequencies in the Hessians obtained for all structures.

We took account of the solvent influence with the use of model D-PCM (dielectric PCM) [17,18] in its basic variant with the following parameters: the same coefficient for all tesserae of a cavity, without calculation of energies of cavitation, repulsion and dispersion. All the calculations were carried out with allowance made for dichloromethane as medium.

Energies of excited states and the corresponding electronic spectra of the optimized structures were obtained by method TD-DFT [20,21] at the same level, also with allowance made for solvent influence. We carried out such calculation for 10–30 excited states with the necessary number of iterations and the convergence criteria in energy for each state (not more than 3×10^{-5} in Hartree/Bohr units), so that the spectrum range had the lower boundary of 250 nm.

Graphical representations of molecular structures and MO were obtained with the use of software package Chemcraft [36].

3. Results and discussions

The intensity and position of marked bands in the spectrum of 2-allylthioquinoline solution both change in time when the compound interacts with diiodine in dichloromethane medium, as is shown in Fig. 1. The final iodocyclization reaction products: 1-(iodomethyl)-1,2-dihydro [1,3]thiazolo[3,2-a]quinolinium monoiodide $C_{12}H_{11}INS^+I^-$ and triiodide $C_{12}H_{11}INS^+I_3^-$, which were previously synthesized in crystalline state and identified by XRD, have been used for control and comparison. The spectra of these products in pure form are shown in Fig. 1, too. The spectrum of the initial solution of 2-allylthioquinoline is added to Fig. 1 for comparison.

Experimental absorption spectra of 2-allylthioquinoline taken at various time intervals during the reaction with diiodine in dichloromethane solution and the spectra of iodocyclization products: 1-(iodomethyl)-1,2-dihydro [1,3]thiazolo[3,2-a]quinolinium monoiodide $C_{12}H_{11}INS^+I^-$ (dashed line) and triiodide $C_{12}H_{11}INS^+I_3^-$ (dash dotted line). The reaction time (in the ascending order of line transparency): 1; 4; 8; 20; 35; 60; 90 min. Bold line is the spectrum of pure 2-allylthioquinoline. The enlarged fragment of the absorption band about 500 nm are shown in the box. The iodocyclization reaction scheme are shown at the top. The value D is the optical density of solution.

As soon as the diiodine solution is added, the wide absorption band appears in the range 450 … 550 nm with the maximum about 500 nm (Fig. 1), which is assigned to absorption of diiodine. Eventually, the intensity of this band decreases naturally, this indicates the consumption of diiodine during its interaction with 2-allylthioquinoline. Together with it the band in the spectral range 355 … 400 nm appears, too. Approximately in 5 min after diiodine addition the new absorption band in the spectral range 280 … 315 nm is generated. Then the absorbance in these two ranges increases simultaneously. The maxima of absorption bands of the mixtures are about 362 and 294 nm, respectively. We can note that the first band slopes more gently towards long-wave side, which can occur due to the presence of the maximum of smaller intensity about 380 nm.

Absorption spectra of iodocyclization products, dissolved in dichloromethane, have shown the presence of wide, intensive absorption bands in the ranges 275 … 315 nm (the maximum at 295 nm, for triiodide only) and 330 … 385 nm (the maximum at 362 nm). The triiodide anion, which also has absorption bands in these ranges, can be formed in a solution only simultaneously with thiazoloquinolinium cation formation – one of the products of iodocyclization reaction. Therefore, the concentration of triiodide anion – the other product of this reaction – should match the concentration of the former product. According to the obtained data, the occurrence of iodocyclization products in the solution takes place in a few minutes of the reaction. The increase of corresponding bands' intensity is related to the increase of product concentration in the mixture. Hence, it is actually possible to monitor the course of iodocyclization with the use of UV/Vis spectra.

We have carried out similar measurements for the 2-ethylthioquinoline and diiodine solution to identify differences between the alkyl- and alkenyl-substituted thioquinolines. Here it is necessary to take into account that an alkyl-substituted compound cannot enter into an iodocyclization reaction, though formation of complexes with halogen bonds with the diiodine is probable, not less so than for alkenyl-substituted thioquinoline. The spectrum of 2-ethylthioquinoline solution is shown in Fig. 2, together with a characteristic spectrum accompanying the addition of diiodine solution. The wide absorption band about 500 nm, the intensity of which decreases in time, is observed here. Absorption bands of the initial compound with maxima 257, 328 and 340 nm significantly decrease in intensity with time, too. Within tens of minutes after iodine addition the absorption in the ranges 275 … 310 nm and 350 … 400 nm increases. We suppose that the spectrum-changing situation registers the formation of the 2-ethylthioquinoline molecular complex with diiodine.

Experimental absorption spectra of 2-ethylthioquinoline after the reaction with diiodine in dichloromethane: Solid line: pure 2-ethylthioquinoline; dashed line: in an 30 min after iodine addition.

The formation of complexes with iodine halogen bonds should be expected in the course of iodine interaction with alkenylthioquinolines. Such halogen bonds can be formed on electron-donating centers of 2-allylthioquinoline. Here, on the one hand, the complex of iodine with halogen bond C=C … I, in which the π-system of the allyl group acts as a donor center, immediately precedes the cyclization re-
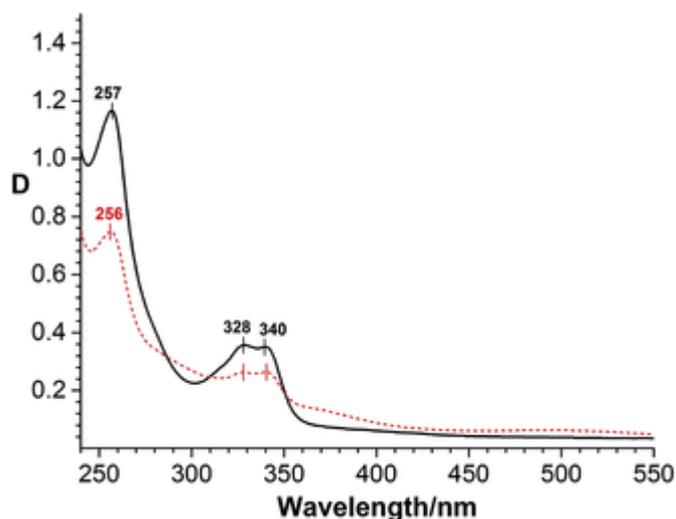

Fig. 2. 2-ethylthioquinoline spectra.

action of 2-allylthioquinoline and the formation of the covalent bond C–I. Let us describe such a complex as "C-complex". On the other hand, formation of the halogen bond of the iodine atom with the sulfur atom of 2-allylthioquinoline ("S-complex") is the more probable event (Table 1); this has been confirmed by our previous examinations [4]. Therefrom follows that the complexes with coordination of iodine on the double bond of the allyl group and on another electron-donating center – nitrogen of the quinoline ring ("N-complex"-1) – are less stable because of interaction energy [4]. The formation probability of halogen bond I … N also decreases due to conformational mobility of the alkenyl radical, which can set up the steric block and reduce the access of iodine to the nitrogen atom.

Table 1 shows the data of the calculated spectra of some iodine complexes with 2-allylthioquinoline, with coordination on sulfur, nitrogen and the double bond of the allyl group. Let us consider probable accordance of the calculated absorption lines with the experimental spectrum bands. Low-intensity lines of the calculated spectrum of "C-complex" – 490, 406 and 335 nm – are not observed in the experimental spectrum. The intensive line 302 nm finds its way into the experimental absorption band. The most intensive line about 275 nm is not observed or is masked by overlapping bands with maxima 257 and 295 nm. Besides, as follows from the calculations, the absorption line in the spectral range 270 … 280 nm is not specific for "C-complex"; it occurs in any calculated spectra. We have noted that the electron transitions in this range are determined by different MO for different complexes. Therefore, we cannot confirm the long-term presence of "C-complex" in a reaction medium during the experiment by the spectral data. It is probable, if such complexes are formed, they are fast consumed, turning into iodine-containing products of iodocyclization.

The calculated spectrum of "N-complex"-1 fits the experimental data to a lesser degree than the spectrum of "N-complex"-2, as one of its intensive lines (327 nm) is not observed in the solution spectrum or it is masked by absorption of the initial 2-allylthioquinoline. Other intensive lines (353, 300, 295 nm) are present in the calculated spectra of other structures. As to "N-complex"-2 (with the lowest value of interaction energy), it is impossible to exclude its existence in the solution, as the most intensive lines 313, 289 and 288 nm correspond to the wide absorption band 280–320 nm of the solution. However, the assignment of absorption bands to the calculated electron transitions in "N-complexes" seems less reliable than in the case of other structures, as the calculated oscillator strength of such transitions is less by several times, than in other complexes.

We can assign the appearance of the band 355 … 400 nm with absorption intensity gently sloping to the long-wave side at the start of the iodine reaction with 2-allylthioquinoline to the transition corresponding to the most intensive absorption line in the calculated spectrum of "S-complex" (352 nm, Fig. 3). The band spreading, observed in the experimental spectrum, is presumably caused by both the variety of conformers and the rather low stability of such complexes. Consequently, we do not observe the possible separation of calculated absorption lines of 352 and 391 nm in the experimental spectrum. Let us mention the results of the calculated spectra analysis, namely, that the absorption lines 352 and 391 nm correspond to the excited states that are possible only for the molecular complexes of alkenylthioquinolines with diiodine: they are determined by electron transitions HOMO-1→LUMO and HOMO→LUMO (Fig. 4). The general contribution to LUMO is focused on iodine atoms. In this case, the sulfur atom and atoms of the quinoline cycle contribute to occupied MO.

Calculated electronic spectra of "S-complex" and "N-complex"-2 of 2-allylthioquinoline with diiodine in dichloromethane compared to the experimental spectrum in a 1 min time after start of the reaction. The value f is the oscillator strength of the calculated absorption line.

Graphical representation of the MO that provide significant contributions to electron transitions in the complex of 2-allylthioquinoline with diiodine

The calculated absorption line 275 nm corresponds to electron transitions in the conjugate cycles of quinoline, affected by the sulfur atom. Though the iodine AO apparently do not participate in forming the MO that are active in the spectrum, the transitions referred to are under their influence; they essentially differ from the similar transitions observed in the spectrum of 2-allylthioquinoline. In the short-wave side of the experimental spectrum, the increasing absorption in the spectral region around the intensive calculated line 275 nm is observed in the course of the reaction with iodine. However, on the one hand, the right edge of the experimental absorption band of 2-allylthioquinoline is overlapped by the left edge of the experimental absorption band of the iodocyclization product. On the other hand, the absorption value of the reaction mixture at 275 nm is much greater than the separate absorption values of both compounds at comparable concentrations. Therefore, it is impossible to determine the partial contributions of different compounds into absorption in this spectral range, so the band in the range about 275 nm cannot indicate the presence or absence of 2-allylthioquinoline complex with iodine.

Similar tendencies have been detected through interpretation of UV/Vis spectra of the mixture of 2-ethylthioquinoline with diiodine in dichloromethane. In this case, we can observe only the spectra of initial compounds and their iodine complexes with halogen bonds. During calculations for "N-complex" and "S-complex" of 2-ethylthioquinoline, significant differences have been found only for complexes differing in type, taking into account the conformational variety. Table 2 shows the data of the calculated spectra of the iodine complexes with 2-ethylthioquinoline, with coordination on sulfur and nitrogen atoms, and interaction energy in these complexes. The calculated spectrum of "S-complex" in comparison with an experimental spectrum is showed in Fig. 5. The position and small oscillator strength of the calculated absorption lines of "N-complex" against the intensive absorption of 2-ethylthioquinoline do not allow us to confirm its presence in the solution unambiguously. However, we can definitely interpret the absorption bands in the experimental solution spectrum within the ranges 270 … 310 nm and 350 … 400 nm and their profiles (Fig. 2) as evidence of the presence of "S-complex" in the solution. In the first range the absorption corresponds to the intensive calculated line 273 nm and the less intensive lines 283 and 298 nm; in the second range it corresponds to the intensive calculated line 357 nm and the less intensive one 388 nm. Also, interaction energy in "S-complex" is significantly more than in "N-complex".

Calculated electronic spectra of "S-complex" of 2-ethylthioquinoline with diiodine in dichloromethane compared to the experimental spectrum in a 30 min time after start of the reaction.

Notably, the spectral characteristics of diiodine complexes with 2-ethylthioquinoline practically copy the characteristics of similar complexes with 2-allylthioquinoline. The absorption in the range higher than 300 nm is also determined by transitions between MO, the basic contribution in which is made by AO of the carbon atoms of the quinoline rings, the sulfur and iodine atoms. Some differences are observed only in the range of wavelength lower than 280 nm, where the contribution of AO of the allyl group carbon atoms to MO, which are active in the spectrum, becomes essential. The experimental spectra do not reveal such differences, as there is the intensive absorption band of 2-ethylthioquinoline in this range.

Table 1
The intensive absorption lines (oscillator strength > 0.01) in the calculated spectra of 2-allylthioquinoline complexes with diiodine and the interaction energy in complexes (kJ/mol).
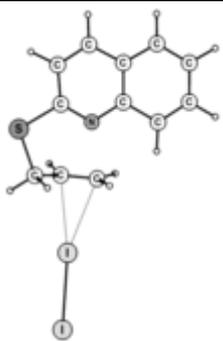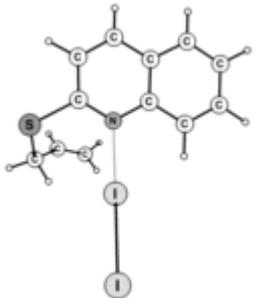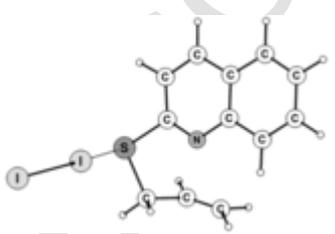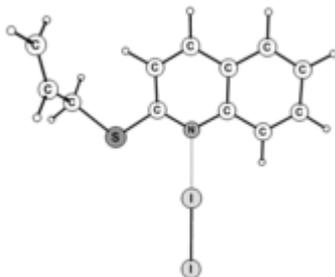
Complexes (interaction energy)	Structure of complexes	Absorption wavelength	Oscillator strength
«C-complex» (−25.6)		489.6	0.035
		406.2	0.022
		335.1	0.048
		302.2	0.208
		297.5	0.042
		295.7	0.017
		274.2	1.098
«N-complex » -1 (−27.8)		353.2	0.030
		326.7	0.065
		300.5	0.023
		295.6	0.071
		282.2	0.092
		270.3	0.110
«S-complex» (−38.1)		391.4	0.048
		352.0	0.558
		327.3	0.010

Table 1 (*Continued*)

Complexes (interaction energy)	Structure of complexes	Absorption wavelength	Oscillator strength
		309.9	0.047
		300.6	0.086
		283.6	0.023
		275.0	0.224
N-complex » -2 (−41.0)		313.3	0.155
		289.5	0.010
		289.2	0.060
		287.7	0.072
		279.7	0.031
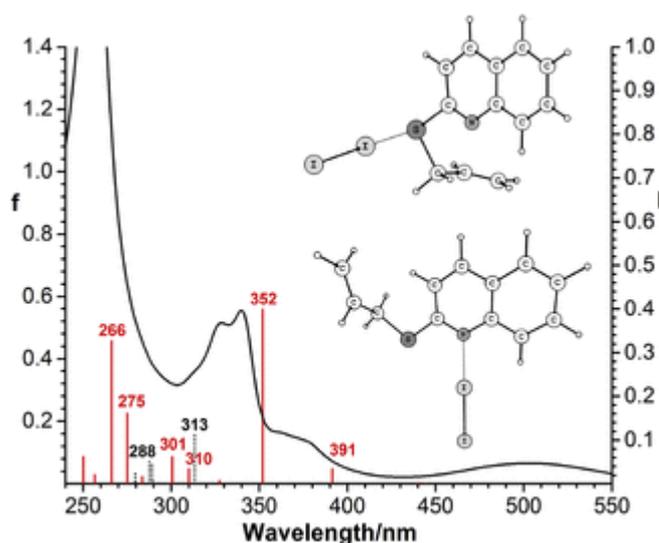
Fig. 3. S- and N- complexes of 2-allylthioquinoline spectra.

4. Conclusions

We have shown that the analysis of 2-allylthioquinoline and 2-ethylthioquinoline UV/Vis spectra, when they interact with diiodine, opens the possibilities of detailed study of iodocyclization reaction and the properties of iodine complexes with halogen bonds.

Special attention has been paid to the detailed spectra of 2-allylthioquinoline and 2-ethylthioquinoline complexes with diiodine. The full set of halogen bonds in substituted thioquinoline compounds with various electron-donating centers (S … I, N … I, C═C … I) has been considered. In the case of 2-ethylthioquinoline complex with diiodine the absorption increase in the ranges 275 … 310 nm and 350 … 400 nm is primarily the consequence of the "S-complex" emergence. The calculated absorption lines in these ranges are in good agreement with the experimental observations. Alkenyl-substituted thioquinolines, in contrast to the alkyl derivatives, participate in the iodocyclization reaction, still, they are characterized by similar electron transitions in the halogen-bonded complexes with diiodine. At the start of the reaction of 2-allylthioquinoline with iodine the absorption increase in the range 355 … 400 nm is observed, which corresponds to appearance of the absorption lines of "S-complex". However, we have found that at the next step of the reaction the complexes with halogen bonds are masked by the products of iodocyclization reaction with more intensive absorption.
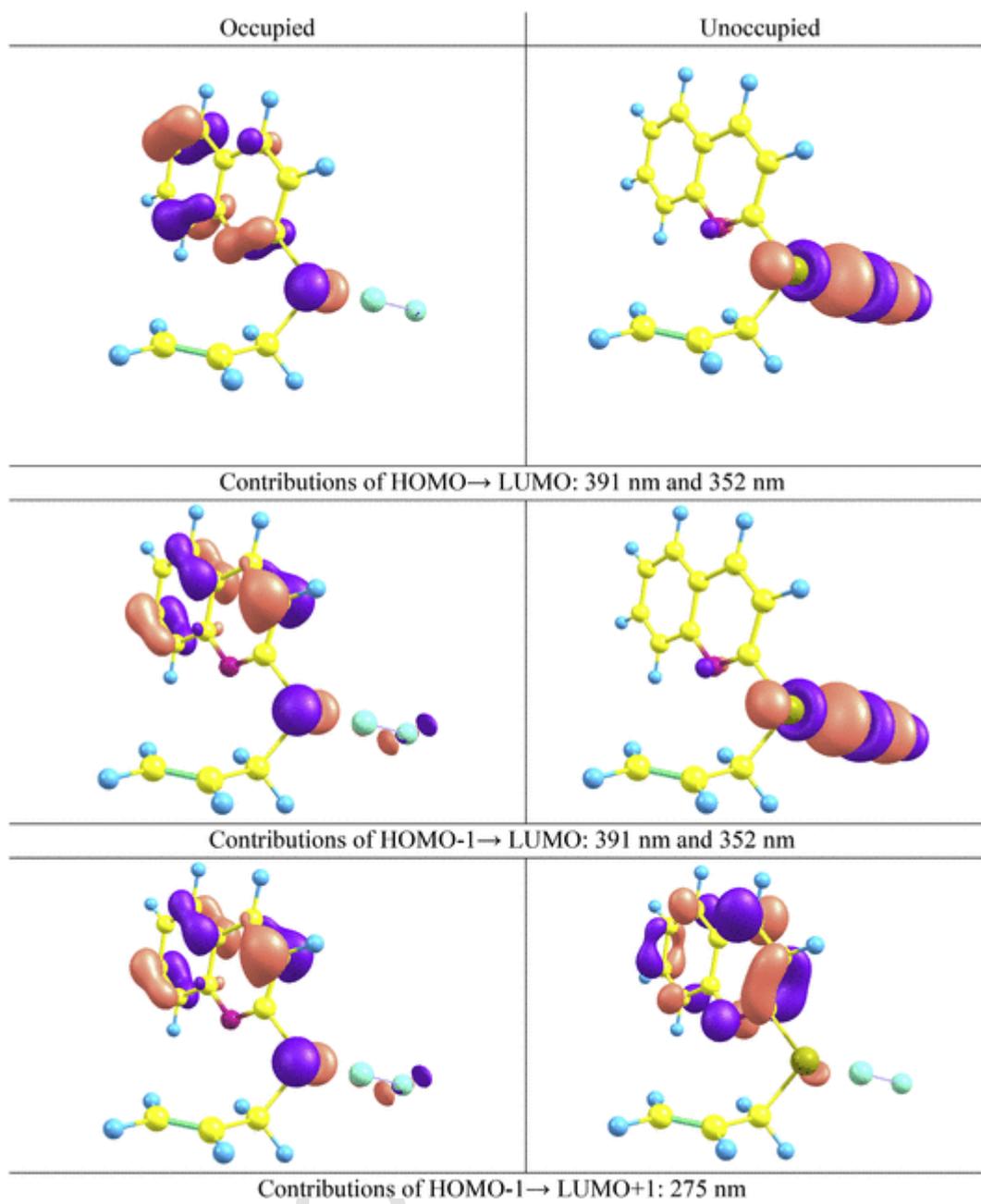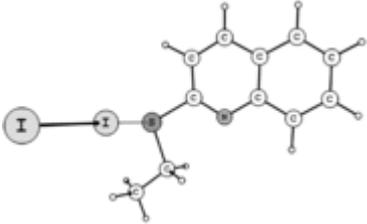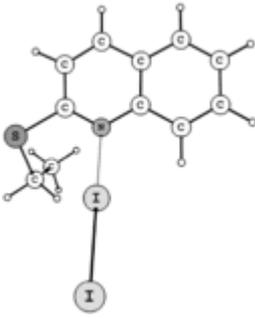
Fig. 4. Transitions.

Table 2

The intensive absorption lines (oscillator strength > 0.01) in the calculated spectra of 2-ethylthioquinoline complexes with diiodine and the interaction energy in complexes (kJ/mol).

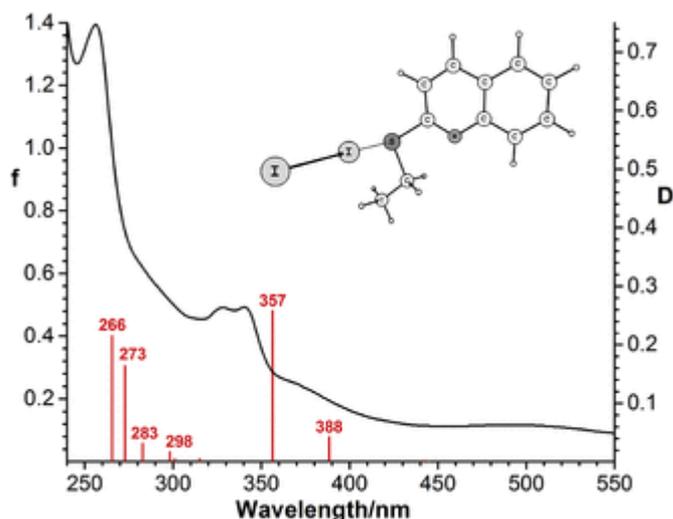| Complexes (interaction energy)	Structure of complexes	Absorption wavelength	Oscillator strength
«S-complex» (−37.7)		388.4	0.078
		356.4	0.481
		298.2	0.031
		282.8	0.058
		272.8	0.305
		265.6	0.400
«N-complex» (−24.3)		356.8	0.032
		323.4	0.086
		301.0	0.019
		293.7	0.069
		282.0	0.062

Fig. 5. S-complex of 2-ethylthioquinoline spectrum.

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