Computer simulation of the shape of absorption bands in electronic spectra of *J*-aggregates

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The shape of absorption bands of aggregates formed by two, four, and nine molecules of a polymethine dye was calculated by the Monte-Carlo method. The energy of interaction of the molecules in the ground state was simulated using atom-atom potentials, and the energies of interaction between dipole moments of electronic transitions of the monomers were estimated by quantum-chemical methods. In the dimer aggregate the dipole moments of the electronic transitions in the monomers interact weakly; therefore, the electron absorption spectrum should be similar to that of the monomer. On going from the dimer to the aggregates consisting of four and nine monomers, the relative positions of monomers change and this, in turn, increases the energy of interaction between the dipole moments of their electronic transitions, resulting in a red shift characteristic of *J*-aggregates and narrowing of the absorption bands.

Key words: polymethine dye, *J*-aggregates; electronic absorption spectra; shape of absorption bands; computer simulation, AM1, Monte-Carlo method.

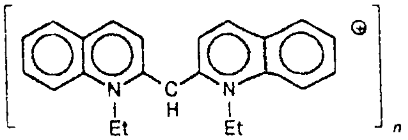
Much experimental research in molecular electronics and nanotechnology have been devoted to molecular organized organic systems, including *J*-aggregates of conjugated organic molecules.[1–3]

It is known that the formation of such ordered systems often defines the structure and electronic properties of monomolecular layers.[4,5]

The formation of *J*-aggregates results in essential changes in the electronic absorption spectra: there is a shift of the maximum to the long-wavelength region and a strong narrowing of the absorption band. A large number of theoretical papers on *J*-aggregates analyzing experimental data have been published. However, the use of analytical methods involves rather crude assumptions that limit the area of application of the theoretical results. In particular, the expressions obtained can be used only for aggregates consisting of a relatively large number of molecules. However, for many systems investigated, the *J*-aggregates contain a rather small number of monomers, no more than 10—15. Therefore, such important questions as the dependence of the shift of the absorption band of *J*-aggregates on the number of molecules and their mutual arrangement in the aggregate are still not clear. Nowadays, the so-called computer experiment is used to resolve such problems, based on the molecular simulation of real systems within the framework of the Monte-Carlo method or molecular dynamics.

The electronic absorption spectra of aggregates formed by two, four, and nine molecules of polymethyne dye 1 were calculated in the present work using the Monte-Carlo method.[6]

The choice of this dye was stipulated by its ability to form *J*-aggregates in solution even at very low concentration. The dependence of the electronic spectra of dye 1 on its concentration[7] is presented in Fig. 1; it reflects well the appearance of the *J*-aggregate band and a sharp growth of its intensity when the concentration of monomer 1 in solution is increased.



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n = 2, 4, 9.

Method of Calculations

At the first step of calculations the geometry of the aggregate corresponding to the minimum of the total energy was found. The structure of the monomers was previously calculated with the AM1 method[8] and was not changed during the optimization of the aggregate geometry. The energy of interaction between the monomers was estimated using two sets of atom-atom potentials (see Refs. 9, 10). The counterions were simulated by Cl^- anions. The point dipoles model[11] was used to take into account interaction with the environment. Because the potential energy surface of the

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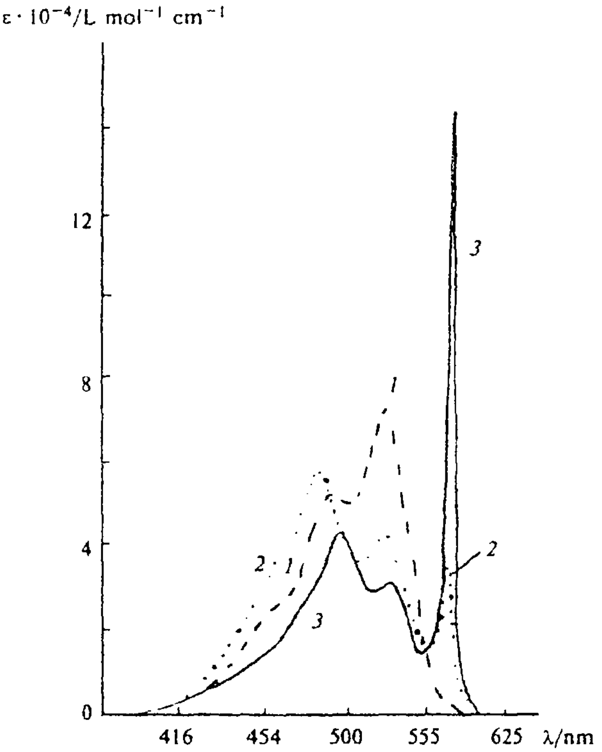

Fig. 1. Experimentally observed changes in the absorption spectrum of dye **1** upon formation of *J*-aggregates in water depending on concentration: [**1**] = $1 \cdot 10^{-5}$ (*1*), $5 \cdot 10^{-3}$ (*2*), and $3 \cdot 10^{-2}$ mol L^{-1} (*3*).[7]

considered aggregates has many local minima divided by activation barriers from 1 to 12 kcal mol^{-1} in height, the global minimum of the total energy can be found only with the help of the Monte-Carlo method.

The most stable structure found for the dimer can be presented by Scheme 1.

Scheme 1

Cl^- M
M Cl^- (M is a monomer)

For the aggregates consisting of four and nine molecules the most stable are similarly constructed brickwork-type structures (Scheme 2, *a* and *b*, respectively).

Scheme 2

a

Cl^- M Cl^-
M Cl^- M
M Cl^-

b

Cl^-M Cl^-
M Cl^-M Cl^-
M Cl^-M Cl^-M
M Cl^-M
Cl^-M Cl^-

Further calculations were carried out using the following procedure:

(1) structures for calculations of the band shape in the absorption spectrum (the technique is described below) were selected using the Monte-Carlo method;

(2) for each selected structure the energies and the oscillator strengths of vibronic transitions were calculated in the exciton approximation by quantum-chemical methods described previously;[12,13]

(3) an absorption spectrum of the aggregate was obtained by a superposition of bands of all vibronic transitions of each selected structure with subsequent averaging over these structures on the assumption that the absorption band of any such transition has a Lorentzian shape with half-width of 5 cm^{-1}.

The selection of structures by the Monte-Carlo method was carried out using the following procedure:

(1) the aggregate with the geometry corresponding to the global minimum of the total energy was taken as the initial structure;

(2) for each parameter determining the mutual arrangement of molecules in the initial structure, a random number δ in the interval from -1 to $+1$ was generated, and the quantity $\Delta_{max}\delta$ was added to the value of this parameter, $\Delta_{max} = 0.5$ Å and 1° for the parameters describing the position of the center of mass of the monomer and its relative orientation, respectively;

(3) the relative energy (E) of such a structure (the energy of the global minimum was taken as a zero) was calculated with the atom-atom potential method;

(4) a random number δ from the interval [0, 1] was calculated; if $\delta < \exp[-E/(kT)]$, then the aggregate with this geometry was included in the number of structures selected and the calculation continued, using this structure as initial, otherwise it was rejected;

(5) when the number of selected structures was large enough the calculation was stopped, otherwise it was switched back to the second step to continue the sampling. It was found that 2000—3000 structures of several millions tested give the shape of the absorption band that did not vary with a further increase in the number of sampled structures.

The calculations were carried out in parallel using two force fields specified above. The results obtained (the position and the shape of the absorption bands) were virtually independent of the force field used. Typical calculated absorption spectra are presented in Fig. 2.

Results and Discussion

According to the results of the recent work,[12] the shape and width of the absorption band of the aggregate depend strongly on the mutual arrangement of molecules in the aggregate. If the molecules are situated one above the other, a considerable blue shift of the absorption band is observed in the spectrum, *i.e.*, the so-called H-aggregates are formed. If the molecules are strongly displaced from each other, the red shift of the absorption band is observed in the spectrum, *i.e.*, the *J*-aggregates are formed. Between them there is a rather large manifold of intermediate structures in which the interaction of the dipole moments of electronic transitions in the monomers is weak and the shape of the absorption band is almost the same as in the monomer spectra.

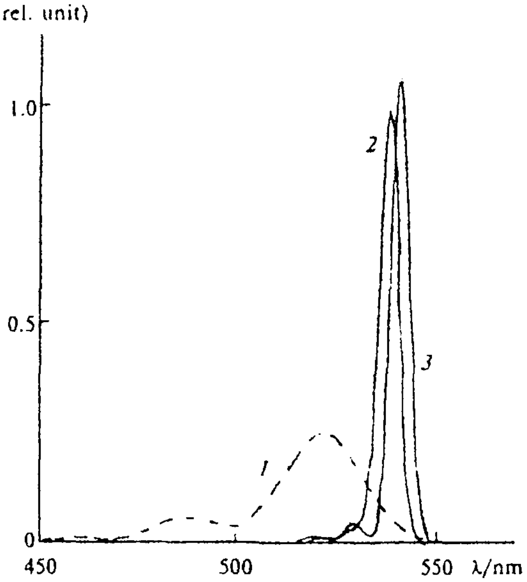

Fig. 2. The calculated absorption spectra of dye **1**: *1*, the monomer and the dimer; *2*, the aggregate of four molecules; *3*, the aggregate of nine molecules.

According to our calculations the dimer (irrespective of the force field used) is just in this intermediate area; therefore, its electronic absorption spectrum should be the same as that of the monomer. On going from the dimer to the aggregates of four and nine molecules the displacement of the monomers from each other increases and brickwork-type structures (see the Scheme 2, *a*, *b*) are formed. Therefore, the calculations predicted a red shift of the maximum characteristic for *J*-aggregates and the narrowing of the absorption band (see Fig. 2).

The spectra presented were calculated at $T = 300$ K. The decrease in temperature caused a small narrowing of the absorption band of the aggregate and a dramatic growth of the computational time (because the program overcame activation barriers more slowly).

On going from the aggregate of four molecules to that of nine molecules an insignificant (less than expected) shift of the absorption band to the long-wavelength region takes place, compared to the shift of the maximum on going from the monomer to the aggregate of four molecules. We have analyzed the origin of this effect. The significant red shift of the maximum on going from the monomer to the aggregate of four molecules is apparently explained by a superposition of two effects: the disappearance of the vibrational structure (only the 0—0 transition is observed) and the displacement of the absorption band due to the interaction between the dipole moments of electronic transitions of the monomers, with the first factor dominating. Therefore, with an additional increase of the second effect on going from aggregates of four to nine molecules, the red shift increases insignificantly. At the same the half-width of the absorption band decreases by ~10%.

A comparison of Figs. 1 and 2 shows that the calculations of the shape of the absorption band of the aggregates studied provide a good description of the experimental spectral changes upon an increase in the concentration of monomer **1** in solution, when dimers and then aggregates of larger size appear. At very low concentrations of dye **1** only monomers and dimers occur in solution, and the peak of the 0—0 transition is nearly absent. Upon an increase in concentration of monomer **1** in solution, aggregates of larger size appear, which results in the formation and fast growth of the 0—0 transition peak.

Thus, the computational scheme used allows us to describe satisfactorily the shape of the absorption spectra observed experimentally and their dependence on the size of *J*-aggregates of the cyanine dye studied.

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