Computer simulation of band shapes in electronic absorption spectra of dimers of organic dyes

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The band shapes in the absorption spectra of dimers of cyanine dyes were simulated using a combination of an empirical molecular force field for the ground state with quantum-chemical calculations of the electron excitation energy as a function of normal nuclear coordinates. The shape and the width of an absorption band strongly depend on the mutual arrangement of the monomers. If the monomers are located one directly above the other, the sublevels arising from intramolecular vibrations disappear in the spectrum, and a large hypsochromic shift of the 0—0-transition band is observed, which results mainly from through-space interaction of monomer orbitals. If the monomers are strongly shifted relative to each other, the sublevels mentioned are also absent in the spectrum, but the bathochromic shift of the 0—0-transition band is small and results from interaction of dipole moments of electron transitions. A rather broad region of intermediate structures is found between these dimer forms, where the interaction of dipole moments of electron transitions in monomers is low, and the shapes of absorption bands are similar to those of the monomers.

Key words: cyanine dyes, dimers; electronic absorption spectra, computer simulation.

Many experimental studies in the field of molecular electronics and nanotechnology are connected with investigation of molecular organized organic systems including dimers, trimers, and aggregates of conjugated molecules.[1—3] It is known that the formation of associates or aggregates often determines both the structure and electronic properties of monomolecular layers.[4,5]

The formation of aggregates results in change in the positions and shapes of absorption bands. Theoretical interpretation of the experimental data on the change in the positions of bands is based on the results of known works.[6,7] The shifts of the absorption bands can be calculated using both the approximation of point dipoles[6,7] for the interaction energy and the scheme of space dipoles.[8,9] The version of point dipoles is based on the assumption that the lengths of dipoles are much less than the distance between them. However, monomers are actually large conjugated organic molecules, and the distances between them in an aggregate are much less than their sizes. In this connection, the approximation of point dipoles may result in an inadequate description of the influence of the mutual arrangement of the molecules in an aggregate on the electronic absorption spectra.

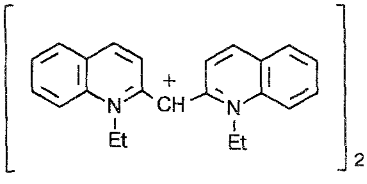
The approximation of space dipoles represents the dipole moment (M) as two point charges ($+q$ and $-q$) with the distance (l) between them so that the equality $ql = M$ is valid. The interaction of dipole moments of electron transitions of monomers is calculated as Coulombic, with two point charges located on each of them. However, this model is also rough, therefore, it often has to be modified and adapted for solving particular problems.[4,10]

The shapes of absorption bands of molecular aggregates were analyzed by many authors. However, the only problem concerning the forms of narrow bands of J-aggregates has been discussed. A detailed consideration of the transition from wide bands of monomers to narrow bands, which are observed in the spectra of many aggregates, has not been carried out so far.

The interaction energies of dipole moments of electron transitions and the shapes of absorption bands that depend on the geometry of an aggregate can be accurately calculated using the methods of quantum chemistry. We carried out semiempirical quantum-chemical calculations of electronic absorption spectra of dimers of cyanine dyes **1** and **2**.

$$[\mathrm{Me_2N{-}(CH{=}CH)_2{-}CH{=}NMe_2^+}]_2$$

1



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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1705—1710, September, 1995.

Calculation Methods

In the present work we used two methods for calculating the change in the energy of 0—0-transition due to the formation of dimers. The first method was based on a supermolecule approximation, where a dimer was treated as one large molecule. The corresponding calculations of dimers were made using the CNDO/S method,[11] taking into account the interactions of all the once excited electron configurations of $\pi\pi^*$-type. According to the second method, the wave functions of the ground and once electronically excited states of $\pi\pi^*$-type for a monomer were calculated by the CNDO/S method in the one-configurational approximation. Then, the electronic absorption spectrum of a dimer was calculated using the method of configurational interaction (CI) on the basis of the obtained multielectron wave functions of monomers.

The procedure previously proposed by us,[12] involving the combination of empirical force field for the ground electron state of a molecule and the quantum-chemical calculations of the energy of transition (E_{0-e}) from the ground to the electronically excited state, was used for the simulation of the shape of the absorption bands. Such an approach allowed us to reduce significantly the volume of calculations. Within the framework of this approach one may write the following expression for the energy of an electronically excited state:

$$E_e(Q_n) = E_e(0) + \sum_n (0.5\omega_n^2 Q_n^2 + a_n Q_n) + 0.5\sum_{nm} b_{nm} Q_n Q_m, \qquad (1)$$

where $a_n = \partial E_{0-e}/\partial Q_n$; $b_{nm} = \partial E_{0-e}/\partial Q_n \partial Q_m$; $E_e(0)$ is the energy of the electronically excited state at vertical electron transition (with equilibrium geometry of the ground state); summation is carried out over all normal nuclear coordinates n and m; ω_n is the frequency of the corresponding vibration; and Q_n is the mass-weighted normal nuclear coordinate of the ground state.

The nondiagonal terms $b_{nm}Q_nQ_m$ in Eq. (1) are usually small for the majority of molecules[12] and can be neglected. Hence, we ignored the rotation of normal nuclear coordinates at electron excitation (the Dushinskii effect). In this approximation it is sufficient to minimize the function

$$E_e = \sum_n \left[0.5(\omega_n^2 + b_{nn})Q_n^2 + a_n Q_n\right], \qquad (2)$$

and to calculate the shifts along the mass-weighted normal nuclear coordinates for the minimum of the total energy at electron excitation using the following equation:

$$\Delta_n = a_n/(\omega_n^2 + b_{nn}). \qquad (3)$$

A small number of high-frequency intramolecular vibrations, which can be taken into account in an explicit form using Eqs. (1)—(3), makes the main contribution to the width of the absorption bands of monomers. All other effects are described in implicit form as nonuniform broadening using the Gaussian function. The shape of bands for dimers (or more complex aggregates) is simulated within the framework of this model in the same approximation, that is, we consider that the contribution of their intramolecular vibrations is always involved in the Gaussian term. This permits us not to take the changes in intramolecular geometrical parameters at excitation into account. In addition, the contribution of the above-mentioned high-frequency intramolecular vibrations of monomers along the width of the absorption bands depends substantially on the mutual arrangement of molecules in a dimer (aggregate) as a result of exciton effects. This determines the dependence of the shape of the absorption band on the geometry of an aggregate.

The dipole moment of the electron-vibrational transition 00—*en* for the symmetrically resolved electron transitions may be estimated in the Franck—Condon approximation:

$$M_{00-en} = M_{0-e}\langle 0|n\rangle, \qquad (4)$$

where M_{0-e} is the dipole moment of the electron transition calculated using only electronic wave functions; $\langle 0|n\rangle$ is the integral of overlapping of nuclear wave functions. The latter is easily determined using the harmonic approximation by integration of Hermitian polynomials. Using our designations, ω_n, $(\omega_n^2 + b_{nn})^{1/2}$, and Δ_n correspond to the vibrational frequencies of the ground and excited states and the shifts along the mass-weighted normal coordinates required for these calculations. The intensities (I_n) of vibrational sublevels are proportional to $(M_{00-en})^2 = (M_{0-e})^2 \langle 0|n\rangle^2$.

The molecules of organic substances in solutions at room temperature have very wide absorption spectra (up to 5000 cm^{-1}). The large width of bands results from the vibrational structure of electron transitions. Along with 0—0-transitions, the 0—1- and 0—2-transitions with the frequency of 1200—1500 cm^{-1} corresponding to the stretching vibrations of a system of conjugated bonds are observed in many molecules. Another factor that influences the width of spectral bands is non-uniform broadening resulting from fluctuations of solvation shells (phonons of the medium). In the present work, the non-uniform broadening (similar to all other vibrational effects mentioned above) is taken into account by the Gaussian function used for the approximation of the shape of the bands for individual electron-vibrational transitions. In this approximation, the shape of the absorption band for one electron transition may be calculated by summation over all vibrational sublevels n:

$$f(\gamma) = \sum_n (M_{00-en})^2 \exp[-(\gamma - \gamma_{00-en})^2 / \Gamma_{00-en}^2], \qquad (5)$$

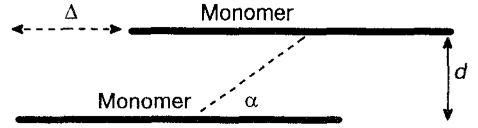
where γ_{00-en} is the frequency of the 00—*en* electron-vibrational transition, and Γ_{00-en} is the parameter characterizing its non-uniform broadening. We varied the value of Γ_{00-en} (calculations of the spectrum using several Γ_{00-en} parameters were carried out) and chose a value at which the calculated spectrum most closely fitted the experimental one.

The derivatives of the electron transition energy with respect to mass-weighted normal coordinates are determined within the framework of the CNDO/S approximation using numerical differentiation. The resonance integrals matching the π—π-type overlapping were decreased for the calculations[12,13] of cyanine dyes: $k_\pi = 0.5$ for **1** and 0.4 for **2**. Good agreement with the experiment is reached using these values, both for the position and shapes of the absorption bands of monomers (Fig. 1). Otherwise, the electron transition energies are greatly overestimated.

Dimer geometry. We placed the molecules in a dimer one above the other in parallel planes and then shifted one of them by different distances along the direction of the dipole moment of the electron transition in the monomer. The angle α between the vector connecting the mass centers of monomers and the axis of the dipole moment of the electron transition was used as a parameter that determines the mutual arrangement of the molecules (Scheme 1).

Effect of counterions. The considered monomers in dimers **1** and **2** are cations. Counterions play a decisive stabilizing role

Scheme 1



in the formation of such dimers. Therefore, we carried out calculations for model structures of the type

Cl^- Monomer

Monomer Cl^-

both taking into account the counterions and without taking them into account, and we compared the results obtained. The presence of counterions in the model systems appeared to have practically no effect on the calculated electronic absorption spectra of dimers **1** and **2**.

Results and Discussion

Table 1 presents the calculated splitting energies (δE_{dd}) for the long-wave electron transition of dimer **1**. These data show that the two approximations used (the supermolecule model and calculation by the CI method with wave functions of monomers) lead to noticeably different results for nonshifted structures (H-aggregates). This difference appears as a consequence of through-space interaction of monomer orbitals, which is taken into account only in the supermolecule approximation.

Table 1. Calculated splitting energies (δE_{dd}) of the long-wave electron transition in dimer **1**

d/Å*	δE_{dd}/eV supermolecule approximation	CI method with wave functions of monomers
	$\alpha = 90°$	
3.5	0.80	0.51
4.0	0.52	0.40
4.5	0.39	0.34
	$\alpha = 40°$	
3.5	0.05	0.05
4.0	0.00	0.01
4.5	0.02	0.02
	$\alpha = 30°$	
3.5	0.12	0.12
4.0	0.11	0.11
4.5	0.09	0.09

* Distance between the planes of monomers in dimer.

Hence, the commonly accepted electrostatic approach is not adequate for H-type structures. This conclusion is based on the calculations by the semiempirical CNDO/S method. To prove the validity of this method, we compared the values calculated for a formaldehyde molecule by this method and nonempirical methods using broadened bases.[14] As can be seen from the data in Table 2, the CNDO/S approximation and nonempirical calculations give the same results for π-orbitals.

The supermolecule model and the CI scheme with wave functions of monomers are equivalent for dimers with a strong shift, *i.e.* the splitting energy is determined by electrostatic interaction of dipole moments of electron transitions. The results of calculations of dimers **1** and **2** are given in Fig. 2 and 3 and in Table 3. These data show that the shape and position of absorption bands of dimers are very sensitive to the mutual arrangement of the molecules. If the molecules are strongly shifted relative to each other ($\alpha = 30°$ for **1** and 20° for **2**), a significant bathochromic shift of the position of 0—0-transition and substantial narrowing of the absorption band are observed in the spectrum, *i.e.*, a spectrum typical of J-aggregates is recorded.

Narrowing of the absorption band of dimers with such structure results from delocalization of electron excitation over two molecules and, as a consequence, the shifts along the normal nuclear coordinates (Δ_n)

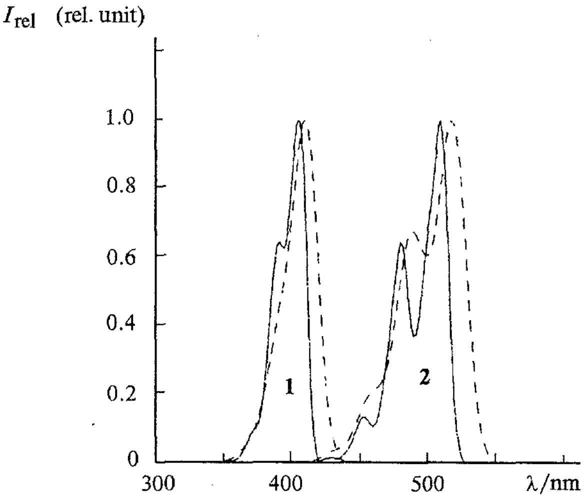


Fig. 1. Calculated (solid lines) and experimental (dashed lines) absorption spectra of monomers **1** and **2**.

Table 2. Splitting energies (δE_{dd}/eV) of π- and n-orbitals in formaldehyde dimer

Orbital	Parallel dimer CNDO/S	Parallel dimer *ab initio**	Antiparallel dimer CNDO/S	Antiparallel dimer *ab initio**
		$d = 3.5$ Å		
n_-	0.0464	0.0496	0.0311	0.0561
π	0.5290	0.5268	0.5302	0.5268
n_+	0.0561	0.0613	0.0345	0.0476
		$d = 4.5$ Å		
n_-	0.0061	0.0052	0.0041	0.0079
π	0.0535	0.0838	0.0532	0.0871
n_+	0.0078	0.0065	0.0064	0.0054

* 6-311G basis.[14]

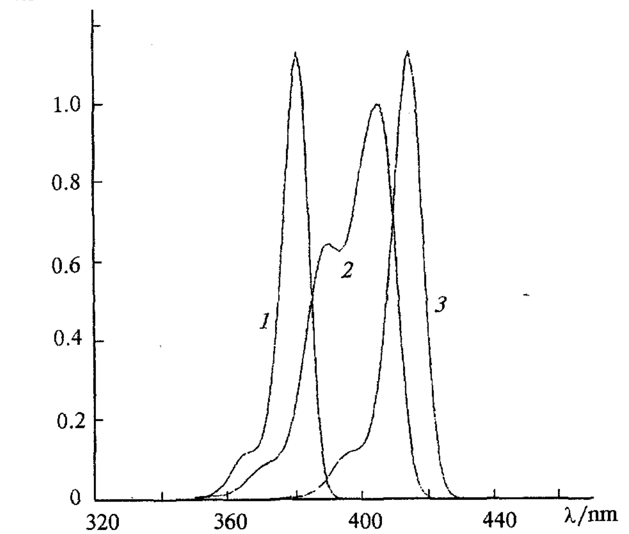


Fig. 2. Calculated absorption spectra of dimer **1** with different mutual arrangements of the monomers: α = 90° (*1*), 40° (*2*), and 30° (*3*).

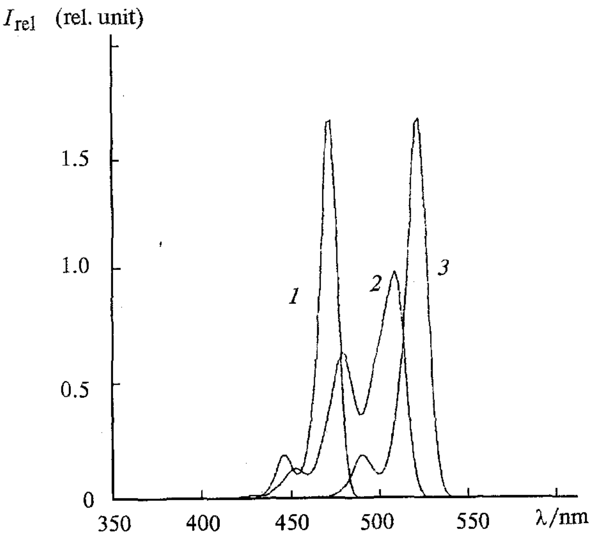


Fig. 3. Calculated absorption spectra of dimer **2** with different mutual arrangements of the monomers: α = 90° (*1*), 30° (*2*), and 20° (*3*).

Table 3. Spectral parameters of dimers calculated using CI method with wave functions of monomers (d = 4 Å).

α/deg	Δ/Å*	λ_{0-0}/nm**	δE_{dd}/eV
		Dimer **1**	
90	0	438 (0), 382 (1.96)	0.41
70	1.46	434 (0), 386 (1.94)	0.34
60	2.31	428 (0), 392 (1.90)	0.27
50	3.36	419 (0), 400 (1.87)	0.15
45	4.0	414 (0), 404 (1.94)	0.08
40	4.77	409 (0), 409 (1.85)	0.00
35	5.71	413 (1.82), 406 (0)	0.06
30	6.93	416 (1.82), 401 (0)	0.11
		Dimer **2**	
90	0	556 (0), 474 (2.90)	0.39
60	2.31	549 (0), 482 (2.80)	0.31
50	3.36	541 (0), 490 (2.74)	0.24
40	4.77	529 (0), 502 (2.67)	0.13
35	5.71	520 (0), 508 (2.66)	0.06
30	6.93	515 (0), 512 (2.65)	0.01
25	8.58	522 (2.67), 502 (0)	0.09
20	10.99	525 (2.71), 499 (0)	0.12

* Shift of monomers in the dimer. ** Wavelength of 0—0-transition (the oscillator force is given in parentheses).

which determine the change of monomer geometry due to excitation, are reduced by half. The large width of the absorption bands of the monomers results from intramolecular stretching and bending vibrations.[12] As Δ_n is reduced by half, the vibrational structure of the aforementioned vibrations disappears. This effect is the reason for the narrowing of absorption bands when passing from monomers to a J-aggregate.

If the molecules are located one above the other (α ≅ 0°), a strong hypsochromic shift of the position of the 0—0-transition occurs in the absorption spectrum, *i.e.*, a spectrum typical of H-aggregates is observed. One peculiarity of the results obtained should be noted: the experimental spectra of H-aggregates are usually wide whereas calculations result in rather narrow bands. This fact may be due to the contribution of through-space orbital interaction to the energy of spectral transition. This interaction is rather strong in the studied geometry of dimers and depends very strongly (exponentially) on the distance between the molecules (see Table 1), which is reflected in the similar dependence of 0—0-transition energy. Therefore, intermolecular vibrations in dimer, which change the mentioned distance, should lead to a significant widening of the absorption band.

In addition to J- and H-aggregates, we found the existence of a large intermediate region (35° < α < 45° for **1** and 25° < α < 35° for **2**). The characteristic feature of this region is that the position and shape of the absorption bands for dimers are quite similar to those of monomers. For these dimers, the geometry of only one of the two molecules is changed upon electron transition, and electron excitation is localized, to a large extent, on this molecule. Intermediate structures occupy a part of the region that should belong to J-aggregates, according to calculations using the point dipole approximation. According to our calculations, this part is rather long (its length reaches 3 Å). Therefore, such complexes with J-aggregate structure and wide absorption spectra can really exist.

The transition forms with wide absorption bands owe their origin to the weak interaction of dipole moments of electron transitions of monomers in a dimer. Two contributions to reducing the dimer energy in electronically excited state compete in the intermediate region. One contribution results from the mentioned interaction (ΔE_{dd}), while the second one arises from geometric relaxation (δE_r). The maximum contribution of ΔE_{dd} is observed for an equal change in geometry of both monomers, and δE_r has the highest value when excitation is localized on one of the monomers, the value of δE_r being proportional to Δ_n squared:

$$\delta E_r \approx \sum 0.5h\omega_n\Delta_n^2 . \qquad (6)$$

Summation is carried out over all nuclear normal vibrations; $h\omega_n$ is the energy of vibrational quantum; Δ_n is the shift along the mass-weighted normal nuclear coordinate (in dimentionless units). When excitation is delocalized on two monomers and their geometry is changed uniformly, the value of δE_r is half as much as that in the case of localization on one of the monomers. Therefore, if the contribution of δE_{dd} is small, localization of electron excitation on one of the monomers is more energetically favorable.

Table 4 presents the values of δE_{dd} calculated using the models of point and broadened dipoles. The comparison of these values with the data of Table 3 shows that point dipole approximation gives incorrect results for both dimers. The model of broadened dipoles appears to be satisfactory if the distance between the charges is chosen accurately. According to our calculations, l = 5.4 Å for **1** and 8.5—10.0 Å for **2**.

For such large values of l, the method of broadened dipoles also predicts the existence of an extended transition region where the interaction of dipole moments of electron transitions is low and a dimer should have a wide unshifted spectrum similar to that of a monomer. If the point charges are brought together, this region is reduced and becomes very narrow in the point dipole model. Hence, large sizes of the intermediate region result from the inadequate point dipole approximation, because the distance (d) between monomers in real systems is less than the monomer length.

Hence, the present work shows that the calculated form and width of the bands in the spectra of dimers of cyanine dyes depend strongly on the mutual arrangement of molecules. If the monomers are located one above the other, electron excitation is delocalized on both molecules, and so vibrational structure is absent from the spectrum. In addition, a strong hypsochromic shift of the position of 0—0-transition is observed, *i.e.*, the spectrum has a form typical of H-aggregates. The width of the absorption band in such structures is determined by the through-space interaction of monomer orbitals. If the molecules are strongly shifted towards each other, the sublevels of intramolecular vibrations are absent from the spectrum for the same reason; however, a large narrowing of the absorption band and a small bathochromic shift of the position of 0—0-transition are observed, *i.e.*, a spectrum typical of J-aggregates appears. A rather large intermediate region exists between these structures. According to the generally accepted concept, J-aggregates should exist in this region, but the interaction of dipole moments of electron transitions of monomers in this form are actually low. Therefore, as a result of geometrical relaxation, electron excitation is localized practically on one of the monomers, and, as a consequence, the form of the absorption band of these dimers is almost similar to that of monomers.

Table 4. Splitting energy (δE_{dd}/eV) of long-wave electron transition in dimers **1** and **2** calculated using broadened dipole approximation (d = 4 Å)

α/deg	Dimer **1**				
	0*	1.0 Å*	3.0 Å*	5.4 Å*	7.0 Å*
90	0.92	0.88	0.65	0.41	0.30
70	0.49	0.49	0.45	0.33	0.26
60	0.15	0.16	0.24	0.24	0.21
50	−0.10	−0.09	0.01	0.11	0.13
45	−0.16	−0.15	−0.08	0.04	0.08
40	−0.19	−0.18	−0.14	−0.03	0.03
35	−0.18	−0.17	−0.16	−0.09	−0.03
30	−0.14	−0.14	−0.14	−0.12	−0.08
α/deg	Dimer **2**				
	0*	3.0 Å*	6.0 Å*	8.5 Å*	10.0 Å*
90	1.32	0.98	0.54	0.35	0.28
70	0.74	0.68	0.46	0.31	0.25
60	0.22	0.35	0.34	0.26	0.21
50	−0.15	0.01	0.19	0.18	0.16
40	−0.28	−0.21	−0.01	0.08	0.09
35	−0.26	−0.24	−0.11	0.02	0.05
30	−0.21	−0.43	−0.16	−0.06	−0.01
25	−0.15	−0.16	−0.16	−0.12	−0.07
20	−0.09	−0.09	−0.10	−0.11	−0.10

* Distance (l) between the charges; l = 0 corresponds to point dipole approximation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-08539) and the International Science Foundation (Grant M1Z 000).

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Received December 21, 1994