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The J-aggregate 5,5′,6,6′-Tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl)-benzimidazolocarbocyanine Sodium Salt in Aqueous Solution

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The aggregation of the title dye in a dilute alkaline aqueous solution is investigated at 283—303 K by measuring the electronic absorption spectra. The association number is estimated to be 8, the heat of formation and the entropy change for the association are found as $\Delta H = -91.5$ kcal mol^{-1} (1 cal=4.184 J) and $\Delta S = -139.3$ cal K^{-1} mol^{-1}, respectively. The structure of the octamer is discussed from a view of spectral shift, intermolecular force and the crystalline structural data. The lifetimes, quantum yields and polarization of fluorescence are investigated on the monomeric and the J-aggregate state of the dye. The energy transfer between several J-aggregate units is indicated in the excited state.

The appearance of the J band is an extraordinary spectral phenomenon caused by molecular association. Since Jelly[1] and Scheibe[2] found the J band, its origin has been discussed by many people. Herz[3] has reviewed the aggregation of organic dyes in solution, but only a few dyes are known to form the J-aggregate in solution. The aggregation number of the J-aggregate is not firmly fixed; different numbers, $n=3$—7, have been proposed for 2,2′-cyanine chloride[4,5] and $n=4$ for the dye discussed in this paper.[3] 5,5′,6,6′-Tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl)benzimidazolocarbocyanine sodium salt is a good sensitizer for silver halide crystals and easily forms the J-aggregate in aqueous solution,[3] in a monomolecular film and on silver halide crystals.[6] We have investigated the equilibrium of the dye in a dilute alkaline aqueous solution and obtained the aggregation number, the equilibrium constant and the heat of formation. A model of the aggregate is suggested based on the crystal structural data and a theoretical calculation of the molecular interaction.

Experimental

The dyes used were gifted from Fuji Film Co. and were used without further purification. The water used for the solvent was twice distilled with potassium permanganate to remove oxidant and carbon dioxide. The dilute NaOH aqueous solution was prepared by carefully adjusting the pH of solution at 11.0. The dyes were dissolved immediately before experiment into the prepared solvent to attain the concentration to be measured. The temperature of the dye solution was kept constant with an accuracy of ±0.04 °C by circulating thermostated water around the cell compartment. The temperature was measured with a copper-constantan thermocouple by a Hewlett-Packard type 3465 B digital multimeter. The visible absorption spectra were recorded with a Cary 16 spectrophotometer. The fluorescence, the fluorescence excitation, and polarization spectra were measured with a Shimadzu spectrofluorometer RF-501. The band-width of the fluorescence was measured with a Spex double spectrometer under a narrow band excitation of the dye laser, Spectra Physics model 375 at the Institute of Molecular Science. The lifetime of fluorescence was measured by a HTV streak camera excited with a ps pulse of the second harmonics of YAG laser at the Institute of Molecular Science. The condition for the aggregation is dependent on several unexpected factors: *e.g.* a careful removal of the oxidant from the water is essential and the stability of the dye solution must be checked before each measurement.

Results and Discussion

A typical spectral change by the dye aggregation is shown in Fig. 1 for the concentration range of 10^{-7}—10^{-3} mol/dm^3 at 293 K. The monomer absorption peak was found at 19490 cm^{-1}, and a shoulder was observed at 20900 cm^{-1}. The peak of the J absorption band was observed at 17040 cm^{-1} with a half-band width of 240 cm^{-1}. An isosbestic point was found at 18590 cm^{-1}, and the tail of the absorption of the J-aggregate extended to 21000 cm^{-1} region (curve 9 of Fig. 1).

The equilibrium between the monomer and the J-aggregate is described as

$$nM \rightleftharpoons J, \tag{1}$$

where the equilibrium constant, K, is given by

$$K = \frac{C_J}{(C_M)^n}. \tag{2}$$

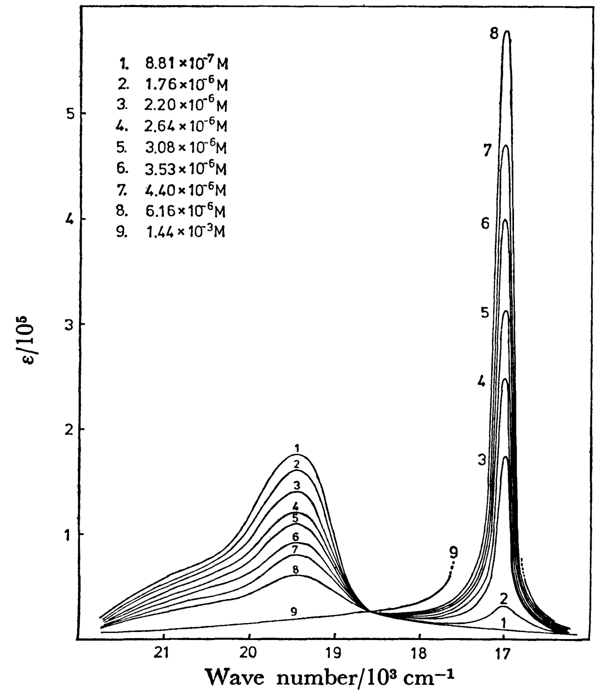

Fig. 1. Change of electronic absorption spectra with the concentration of the dye in a dilute alkaline aqueous solution (pH=11.0). (The concentrations are given in unit of monomer.)

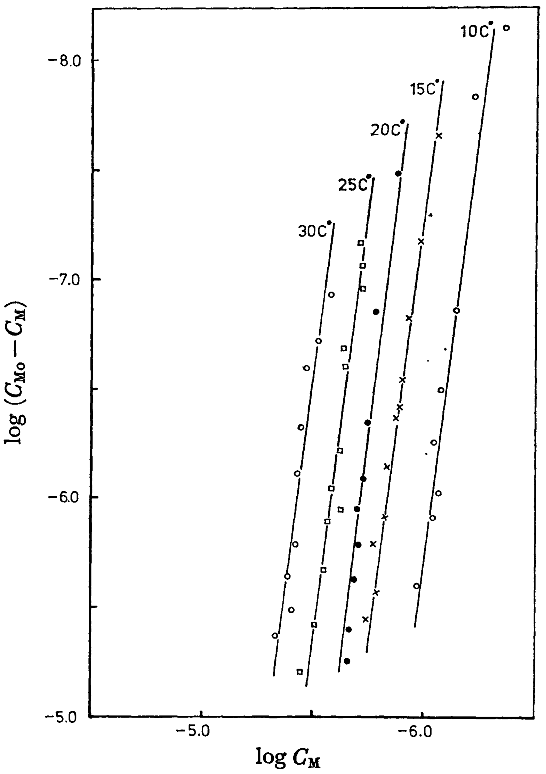

Fig. 2. Plots of $\log(C_{Mo}-C_M)$ against $\log C_M$.

Here C_J and C_M are the concentrations of the J-aggregate and the monomer, respectively. If the nominal concentration of the dye is shown by C_{Mo}, then

$$C_{Mo} = C_M + nC_J$$
$$= C_M + nK(C_M)^n. \qquad (3)$$

By taking the logarithms we obtain

$$\log(C_{Mo}-C_M) = n\log C_M + \log(nK). \qquad (4)$$

We have carefully measured C_M by using the monomer's molar absorption coefficient, $\varepsilon_M=175000$, at 19490 cm^{-1} and used them to obtain constants in Eq. 4. A plot of $\log(C_{Mo}-C_M)$ *versus* $\log C_M$ is shown in Fig. 2, where the contribution of the tail of the J-band to the absorption at 19490 cm^{-1} is estimated by the absorption spectrum of a high concentration solution, which indicated a slight absorption of the J-band as shown in curve (9) of Fig. 1. Although Herz[3] plotted $\log(nC_J)$ *versus* $\log C_M$ in his analysis, we used $(C_{Mo}-C_M)$ instead of nC_J, because the concentration of the J-aggregate at the initial stage of the aggregation is liable to experimental artifact. When we use the intensity of the J band for equilibrium measurements, the results were not quantitatively reproducible for small absorbance. It appears that the concentration of the residual monomer which does not aggregate in solution is more precisely determined than that of the aggregate in the early stage of aggregation.

The gradient of the straight lines drawn for these plots gives the association number $n=8$, which is different from the value $n=4$ reported by Herz.[3] Since the present experiment covers wider temperature and concentration ranges, we believe that 8 is more reliable. Actually the gradient of the plot is easily influenced by uncertain experimental conditions, and it has tendency to give rather larger value more than 8.

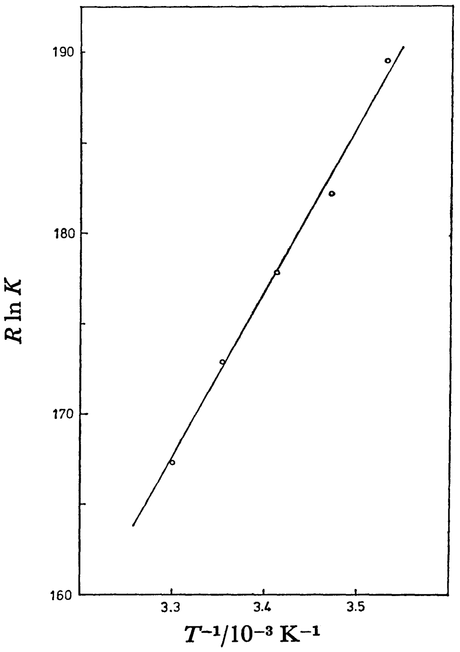

Fig. 3. A plot of $R\ln K$ against T^{-1}.

Table 1. Equilibrium constants and free energies of association

Temp K	Association number	$10^{-4}\varepsilon_J/8$	$\log K$	$-\Delta G$ (kcal mol^{-1})
283	8	85.3	41.4	53.7
288	8	85.3	39.8	52.5
293	8	85.2	38.8	52.0
298	8	78.7	37.8	51.5
303	8	75.9	36.6	50.7

By using this number, the equilibrium constants K were determined at several temperatures (Table 1). In the Table the molar absorption coefficients of the octamer are shown confirming that the values are reasonably constant. The plot of $R\ln K$ against $1/T$ gives the heat of formation and entropy change for the aggregation. The values are $\Delta H=-91.5$ kcal mol^{-1} and $\Delta S=-139.3$ cal K^{-1} mol^{-1} for the octamer. These values are much larger than those of dimerization ($\Delta H=-3$—-8 kcal mol^{-1}, $\Delta S=-10$ cal K^{-1} mol^{-1})[7–11] and of trimerization ($\Delta H=-11$ kcal mol^{-1})[11] for other dyes. This result indicates that the octamer is formed concertedly without an intermediate stage as is consistent with the appearance of the isosbestic point in Fig. 1.

The J type absorption band was found in the crystal of5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide solvated with two molecules of methanol,[12] and it was realized that the intermolecular arrangement and contact is very important for the appearance of the J band. It seems certain that the J-aggregate in solution takes a similar conformation as was seen in the crystal structure determined by Smith and Luss.[13]

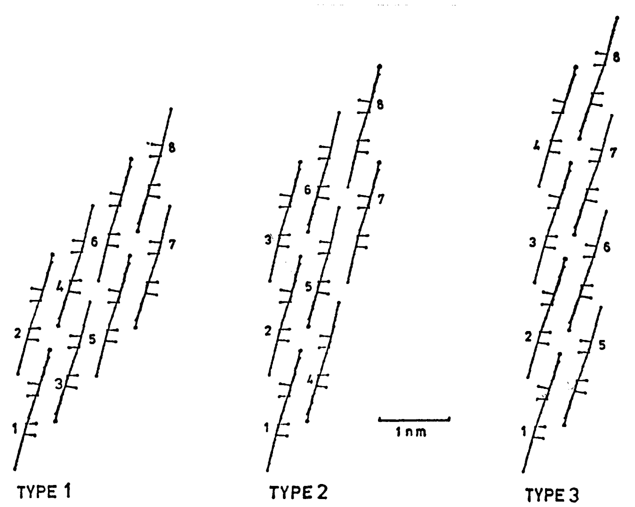

Fig. 4. Three types of model of J-aggregate

We have tried to correlate the observed J band shift with the calculated band shift in the models of the octamer. The calculation is not merely to evaluate the spectral shift by a theoretical calculation, but to estimate the magnitude of the intermolecular attraction by a dispersive and charge transfer forces.

Now we assume three models of the J-aggregate as shown in Fig. 4, where the dyes are placed face to face on a sheet as in the crystal of the dye solvated with two methanol molecules.[13] Eight dye molecules are arranged as in the crystalline bc plane; the choices of lateral displacement are different for three kinds of models. The exciton states are presumed for the octamer; the wavefunction of the ground and the excited states are written as

$$\Phi_G = \prod_{i=1}^{8} \phi_i^{o}$$
$$\Phi_E = \sum_{j=1}^{8} \Big(\prod_{i\neq j}^{8} \phi_i^{o}\Big)\phi_j^{e} \tag{5}$$

where ϕ_i^o and ϕ_j^e mean the ground and the excited states of the i-th and the j-th molecules. The calculation of the energy shift is carried out for the allowed in phase state given by Eq. 5 by a dipole-dipole approximation and by a somewhat rigorous transition density method.[14] In the dipole-dipole approximation the length of the transition dipole was estimated as 2.42 Å from the solution spectral oscillator strength of the monomer absorption band. Here we take the strong coupling model for the aggregate, in which all transition intensities are concentrated in the 0-0 band. In the transition density model we take it as $\pm 0.32\,e$ charges separated by 7.54 Å in the molecular plane based on the MO calculation. The results of calculation is shown in Table 2, and it is found that the type 1 model gives the largest stabilization of the excited state and the two methods give identical results. Experimentally the observed shift is $-2460\ \mathrm{cm}^{-1}$, hence the magnitude of the shift is well explained by these models. So far no rigorous proof for the in-phase Φ_E to be real eigenstate of the system is given. However, the 8-th order eigenvalue problem was solved for the type 1 model, and the result gave practically

Table 2. Shift of absorption spectra calculated by exciton type interactions

Model	Dipole-dipole approximation	Transition density method
1	-3000 (cm^{-1})	-2800 (cm^{-1})
2	-2700	-2650
3	-2500	-2400

Table 3. Overlap integrals between dye molecules

Overlap types	A	B	C
Overlap integrals S	-0.0003	-0.0036	0.0074

Table 4. Comparison of overlap index

Model	Overlap index
1	24.6×10^{-5}
2	19.1×10^{-5}
3	22.0×10^{-5}

the same energy ($-2950\ \mathrm{cm}^{-1}$) and the intensity of 84% as given by in-phase Φ_E. The lowest energy state has the largest transition dipole, and the wavefunction shows that the excitation distributes more in the middle of the aggregate.

The stabilization energy of the aggregate by the dispersion force in the ground state may be estimated by the perturbation theory as follows. The van der Waals force (dispersion force) for the pair-wise molecules i and j will be given by

$$E_{\mathrm{v.d.W}} = \sum_{e} \frac{|\langle \phi_i^{e}\phi_j^{e}|V|\phi_i^{o}\phi_j^{o}\rangle|^2}{E_{ei}+E_{ej}-E_{oi}-E_{oj}} \tag{6}$$

where the values of matrix element are the same for the calculated ones given in Table 2. Therefore the larger the shift the greater will be the dispersion force, and the type 1 model seems to be most stable from this point of view.

The charge transfer force between the dye pair may be estimated by the following formula

$$E_{CR} = \frac{4\beta_{ij}^2}{E_{CT}-E_0} = \frac{4(kS_{ij})^2}{E_{CT}-E_0} \tag{7}$$

where the dye molecules are presumed to play roles of both the electron donor and acceptor. Here β_{ij} is Mulliken's charge transfer integral approximated by the overlap integral between the HOMO and LUMO of the paired dye molecules, i and j. There are three types of overlap of dye molecules, A, B, and C in the order of increasing overlap integrals in the crystal of the dye with two methanol molecules.[13,15] The numerical calculation of the overlap integrals will be published in a separate paper and only the values are shown in Table 3. For three types of models we evaluate the overlap index given by $\sum_{ij} S_{ij}^2$ as shown in Table 4. The result of the calculation shows that type 1 is most stable from a view of the charge resonance interaction.

One more important force for the molecular association in aqueous solution is hydrophobic force which is produced by the surface tension of water.[16)

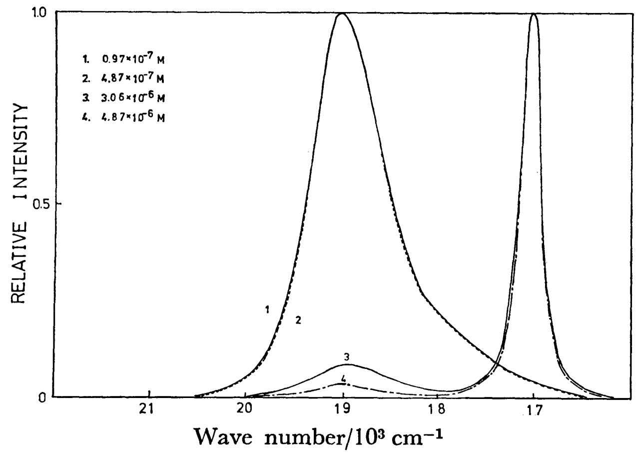

Fig. 5. Change of fluorescence spectra with the concentration of the dye.

The force will be greatest if the surface area of the aggregate is smallest and the type 1 model is most favorable from this point. On these grounds we may guess that the shape of the J-aggregate in aqueous solution correspond to type 1 model.

Fluorescence Spectra. The fluorescence spectra at various concentration of the dye measured by the excitation at 21740 cm^{-1} is shown in Fig. 5. The monomer fluorescence band shows a Stokes shift of 620 cm^{-1}, while the sharp J-band emission shows no Stokes shift. The band shape of the J-emission band was measured by a sharp dye laser excitation at 17340 cm^{-1} and 17182 cm^{-1} for the solution of 2.14×10^{-6} mol/dm^3, but it did not show any shift or broadening by changing the excitation energy. The band-width of the emission was only 150 cm^{-1}, which is smaller than the absorption band-width. Anomalous sharpening and zero-Stokes shift by aggregation are quite unusual as a complex organic molecule. An importance of charge resonance effect on the excitation transfer is discussed on various crystals as is discussed in separate papers.[12)]

The excitation spectra for this sharp fluorescence band was in perfect agreement with the absorption spectra of the J-aggregate, and a long tail of absorption extended into the 22000 cm^{-1} region. The excitation profile of the J-emission was completely different from that of the monomer emission, therefore a possibility of energy transfer from the monomer to the J-aggregate may be rejected.

The quantum yields of fluorescence were measured relative to that of rhodamine B (0.97) in ethanol:

Monomer $\Phi^M = 0.03 \pm 0.006$

Aggregate $\Phi^J = 0.25 \pm 0.05$.

The lifetimes were measured at ambient temperature by a ps YAG laser as follows;

Monomer $\tau^M = 0.12 \pm 0.03$ ns

Aggregate $\tau^J = 0.062 \pm 0.01$ ns.

The lifetime of emission is correlated to the absorption oscillator strength f and fluorescence quantum yield. The natural lifetime is approximately given as

$$\tau_0 = 1.500/\bar{\nu}^2 f$$

and the fluorescence lifetimes are

$$\tau^M = \Phi^M \cdot \tau_0(\mathrm{M})$$

$$\tau^J = \Phi^J \cdot \tau_0(\mathrm{J}).$$

The oscillator strength of the aggregate absorption is conserved as compared to the monomer absorption, *i.e.* $f(\mathrm{M})=1.02$ and $f(\mathrm{J})=8.16$, from these and observed quantum yields we obtain $\tau^M=0.12$ ns and $\tau^J=0.16$ ns as calculated values. The agreement is excellent for the monomer and is not good for the J-aggregate.

The radiative (k_r) and non-radiative (k_{nr}) decay rates of the excited state are related to the quantum yield of fluorescence Φ and fluorescence life time τ as follows.

$$\Phi = \frac{k_r}{k_r + k_{nr}}$$

$$\tau = \frac{1}{k_r + k_{nr}}.$$

By using the observed values, these rates are evaluated for the monomer and the J-aggregate as

	$k_r[s^{-1}]$	$k_{nr}[s^{-1}]$
Monomer	2.5×10^8	8.1×10^9
Aggregate	4.0×10^9	1.2×10^{10}.

It is apparent that the J-aggregate has 16 times larger radiative rate as compared to the monomer. A most plausible explanation for this enhancement is that the fast excitation transfer takes place between more than two J-aggregate units within the life time of the excited state, and the coherent excited state has a larger radiative transition probability than the value expected for the octamer ($f(\mathrm{J})=8.16$). The extent of the excitation transfer might be more than two units, because two is an ideal number expected for the parallel arrangement which will be never realized in solution. Therefore the delocalization of the excited energy between several J-aggregate is the most acceptable reason for the discrepancy between τ^J (calcd) and τ^J (obsd).

Further support for the fast excitation transfer between the J-aggregate is given by the polarization measurement. The polarization of the emission bands were measured at different temperatures; the p-values were

$p(\text{monomer}) = 0.40\pm0.04$ for 275—303 K

$p(\text{aggregate}) = 0.20\pm0.02$ at 303 K

$p(\text{aggregate}) = 0.23\pm0.02$ at 275 K

in dilute alkaline solution. The relation given by Perrin[17,18)] on the rotational relaxation of the chromophore and the p-value is

$$p = p_0\left[1+\left(1-\frac{p_0}{3}\right)\left(\frac{\tau_{fl}}{\tau_{rot}}\right)\right]^{-1}$$

where p_0 is an ideal polarization value for rigid chromophore, τ_{fl} and τ_{rot} are the fluorescence and rotational relaxation lifetimes. From this equation and putting $p_0=0.45$ we may estimate the rotational relaxation times for the monomer to be 1.18 ns, while that of the J-aggregate is 0.04 ns. If we assume the excitation of the J-aggregate is confined within octamer, this result is quite unreasonable since the large aggregate has a much shorter rotational time constant than a small monomer. If the energy transfer between several J-aggregate is very efficient, the low *p*-value is reasonably accepted as a polarization quenching by a fast energy transfer.

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