2786 © 1991 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, ***64***, 2786—2791 (1991) [Vol. 64, No. 9

H-Aggregate of a Long-Chain Crystal Violet Dye in Langmuir-Blodgett Films[1)]

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(Received February 22, 1991)

The molecular orientation and aggregate formation in Crystal Violet (CV) dye monomolecular layers have been investigated by means of polarized reflection and absorption spectral measurements at an incident angle of 60°. A relatively sharp absorption band at 2.04 eV and a broad band around 2.23 eV assignable to the J-dimer and the H-dimer, respectively, were observed in the optical measurement geometry with polarized light either parallel(p) or perpendicular(s) to the incident plane. A sharp band at 2.61 eV, assigned to the H-aggregate (tetramer), was detected by p-polarized spectral measurement, but not s-polarized measurement. The J- and H-dimers have horizontal transition moments and the H-aggregate has a vertical transition moment. The H-aggregate peak shifted from 2.53 eV (10 mN m^{-1}) to 2.61 eV (40 mN m^{-1}) with increasing surface pressure. This is due to an increase in the slip angle between the transition dipole moments and their center-to-center lines because the chromophoric planes become to be gradually oriented normal to the water surface. The behavior of these aggregates is interpreted in terms of the extended dipole model.

Dye aggregates can easily be obtained in well-ordered layer structures using the Langumir–Blodgett (LB) method. Merocyanine,[2)] cyanine,[3)] and squarylium[4)] dyes form J- and H-aggregates and this has attracted much attention on account of their optical and electrical functions as photosensitizers. It is desirable to control the orientation and aggregation of the chromophores in layered structures with functions such as energy and electron transfer. Sugi et al. reported that J-aggregates in the merocyanine LB films show a high photoelectric conversion efficiency.[2)] In order to attain higher efficiency, several photoelectrical LB heterojunctions have been prepared.[5)] For example, the electrical and photoelectrical characteristics of organic p-n junction diodes consisting of an n-type Crystal Violet (CV) dye and a p-type merocyanine dye have been studied in comparison with homogeneous merocyanine LB films. Nakahara et al. reported that energy transfer occurred from the merocyanine J-aggregates to the CV dye in hetero-type LB films.[6)]

It is necessary to control the orientation and structure of dye aggregate in the monolayers for developing functional organic thin films with high quality and good structure. The molecular orientations in monolayers on water are determined by cohesive forces of chromophores, by hydrophobic interactions between long alkyl chains, and by adsorptive interactions between chromophores and the water surface. Möbius et al. reported that the orientation of chromophores and aggregates, i.e., dimer, J- and H-aggregates can be investigated by measurements of reflection spectra with linearly polarized light.[7–9)] The transition moments for a porphyrin, a cyanine dye, and an azo dye are oriented within the monolayer plane, with the exception of an azo dye H-aggregate which is oriented normal to the monolayer plane. In this paper we report the optical properties of the CV dye aggregates in the monolayer on water at various surface pressures and the LB films. The configuration of the dye aggregates are discussed in terms of Kuhn's extended dipole model.[10)]

Experimental

Materials. The Crystal Violet dye with a long alkyl chain was purchased from Nippon Kankoh-Shikiso Kenkyusho Co. and was used without further purificaiton. The chemical structure is shown in Fig. 1. Chloroform of spectroscopic grade was used for spreading the monolayers.

Procedures. The subphase was water containing $NaHCO_3$ at pH 6.7—6.8 and at 20—21 °C. Monolayers were spread on the subphase from a 4×10^{-4} M (1 M=1 mol dm^{-3}) chloroform solution of the dye. The measurements of surface pressure-area (π–A) isotherms and preparations of monolayers for absorption spectra were carried out by means of a conventional Langmuir trough (Joyce Loebl Ltd., model IV) equipped with a Wilhelmy balance. The absorption spectra of monolayers at incident angles of 0° and 60° were measured using a multichannel spectrophotometer (Otsuka Electronics Co., model MCPD-200) as illustrated in Fig. 2. The incident plane was perpendicular to the direction of compression. For absorption spectra measurements, the photodetector was positioned to detect only the beam reflected from the mirror and not that from the water surface. After spreading the solution, the monolayer was compressed to a predetermined surface pressure and maintained there for 5 min before starting spectral measurements. The substrates for visible

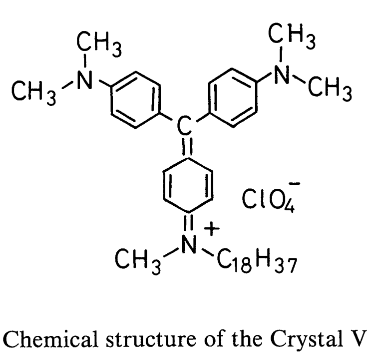

Fig. 1. Chemical structure of the Crystal Violet dye.

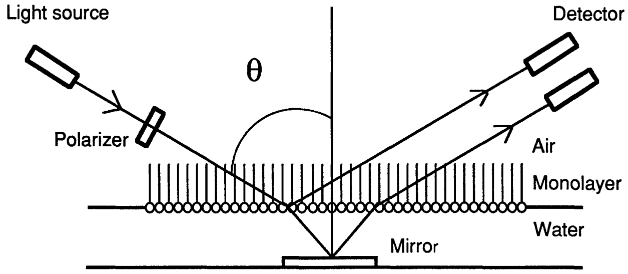

Fig. 2. Schematic diagram of polarized reflection and absorption measurements at an incident angle of 60°.

spectroscopic measurements were made fully hydrophilic by immersion in a 0.5 M KOH–ethanol solution. The monomolecular film was deposited onto a hydrophilic glass substrate by the vertical lifting method.

Results and Discussion

π–A Isotherm. Figure 3 shows a π–A isotherm for the monolayer of CV dye at the air–water interface. The CV dye gives a stable monolayer upto 50 mN m^{-1}. Various conformations of this dye can arise from free rotations of the phenylene rings and amino groups. The chromophore dimensions are about 13Å×14Å×5Å, and a planar close packed arrangement of the molecules on the water surface gives an area of about 120 Å^2 per molecule. The limiting area obtained by extrapolation of the linear portion in the π–A curve to π=0 is 50 Å^2 molecule^{-1}. This area is much too small to be consistent with the molecule lying flat on the water. Judging from this molecular area, the orientation of the chromophoric plane corresponds to lying horizontal on the water surface at 0—5 mN m^{-1}, and the molecules gradually overlap as the pressure increases and produces an upright structure at high surface pressures. For the mixed monolayer of the CV dye and cadmium arachidate, the π–A isotherms clearly gave two-step phase transitions from the expanded to condensed monolayers.[11] The marked two-step phase transitions are probably due to molecular reorientations, which did not depend on mixing ratios, but only on the change of surface pressures. It is possible that similar reorientation occurs in a neat dye monolayer.

Absorption Spectroscopy for Monolayer on Water. Figure 4 shows the normal incident absorption spectra at various surface pressures. An absorption band was observed at 2.04 eV at low surface pressures (0—5 mN m^{-1}). This 2.04 eV band is red-shifted from the monomer band (2.10 eV) in chloroform. The dye within the monolayer does not exist as isolated molecules but as a linear aggregate. The intensity of the 2.04 eV peak decreased with an increase in surface pressures from 10 to 40 mN m^{-1}, while that of the 2.24 eV peak increased. The 2.24 eV band is blue-shifted from the monomer band and assigned to an H-dimer. Its configuration is of a face-to-face structure consisting of two molecules oriented parallel to the water surface.

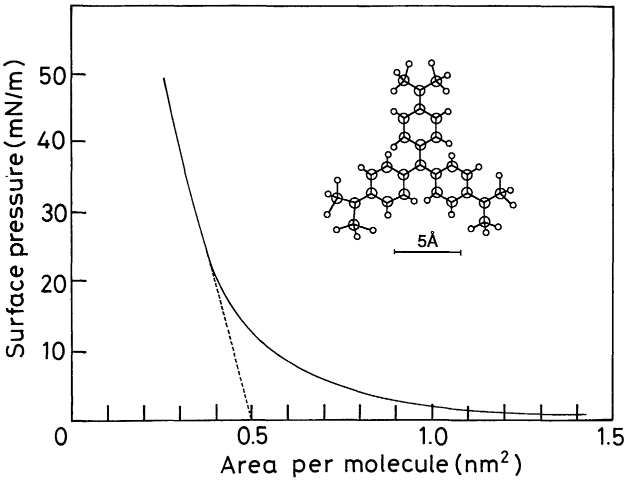

Fig. 3. Surface pressure-area isotherm for the monolayer of the CV dye.

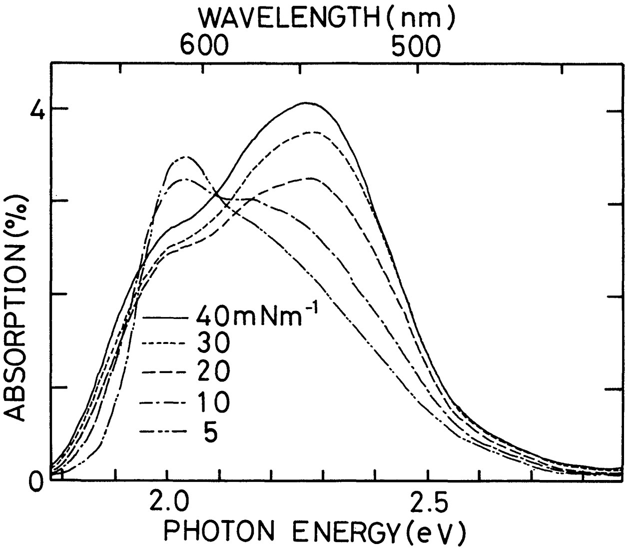

Fig. 4. Absorption spectra under normal incidence for the monolayer on water at various surface pressures.

The molecular orientation and arrangement were further studied by measuring the polarized absorption spectra with an incident angle of 60°. The broad band around 2.23 eV was observed with polarized light either parallel(p) or perpendicular(s) to the incident plane as shown in Figure 5(a) and (b). On the contrary, the isotropic and sharp absorption band at 2.61 eV, which can be assigned to an H-aggregate, was observed in the p-polarized spectra between 20 and 40 mN m^{-1}, but not in the s-polarized spectra. Figure 6 shows the H-aggregate band detected with p-polarized light after substraction of H-dimer absorption spectra. The peak shifted from 2.53 eV at 10 mN m^{-1} to 2.61 eV at 40 mN m^{-1}. This blue-shift is due to an increase in the slip angle between the transition dipole moments and their center-to-center

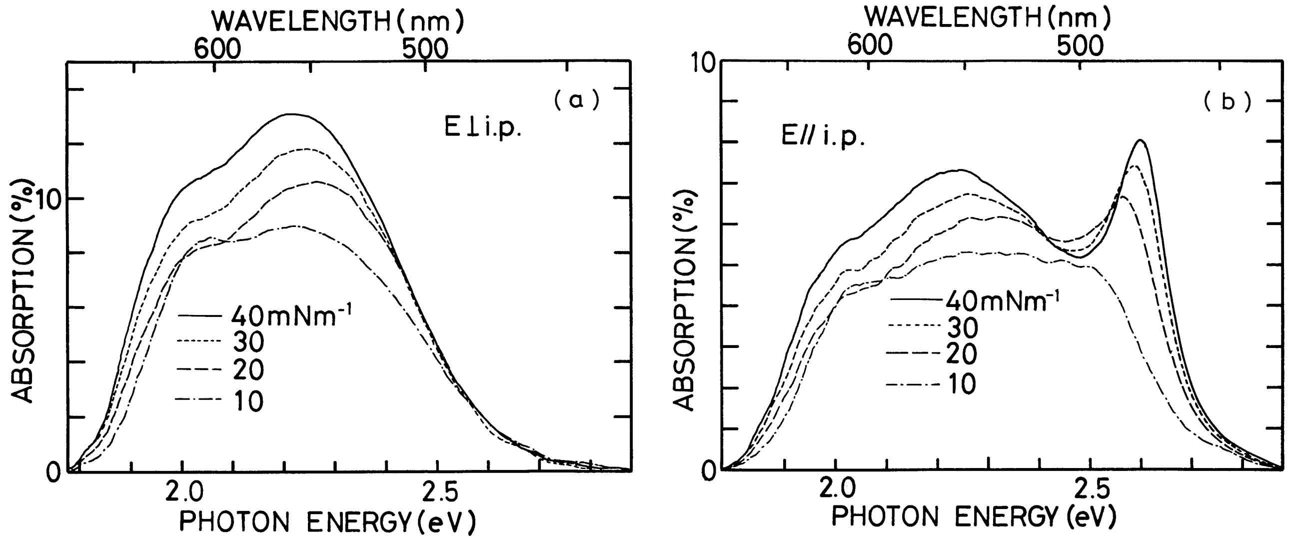

Fig. 5. Polarized absorption spectra for the monolayer on water at various surface pressures.; (a) perpendicular and (b) parallel to incident plane with polarized light of 60° incident angle.

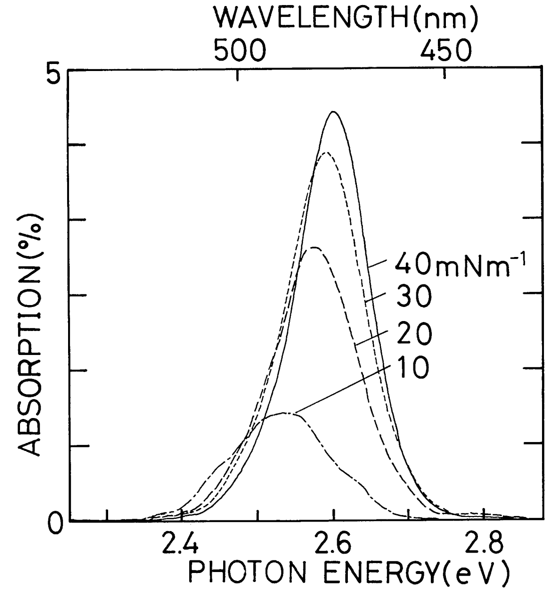

Fig. 6. Parallel polarized absorption spectra for H-aggregate band at various surface pressures.

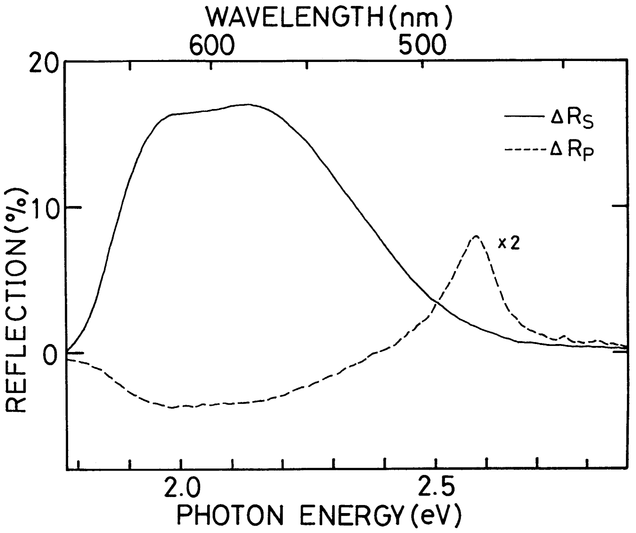

Fig. 7. Perpendicular and parallel polarized reflection spectra for the monolayer on water with 60° incident angle at a surfacce pressure of 40 mN m^{-1}.

lines with increasing surface pressures.

Reflection Spectroscopy. In order to confirm whether the chromophore lies flat or edge-on, reflection spectra were measured with an incident angle of 60°. Figure 7 shows the polarized reflection spectra of the monolayer on water at 40 mN m^{-1}. According to the Möbius' theory,$^{9)}$ when the transition moment of the dye molecule lies within the surface water, s-polarized reflection (ΔR_s) with an incident angle of 60° should always be positive, and p-polarized reflection (ΔR_p) should be negative. If the transition moment is oriented normal to the water surface, ΔR_s is positive and ΔR_p cannot be observed. In the ΔR_s spectra (Fig. 7), a broad band around 2.15 eV, which is likely assigned to the H-dimer, is positive, while a sharp band assigned to the H-aggregate is almost absent. In the ΔR_p spectra, the broad H-dimer band is negative, while the H-aggregate band at 2.59 eV is positive. This result therefore supports our view that the transition moment for the H-dimer is oriented parallel to the surface plane, while that for the H-aggregate lies normal to the water surface.

Absorption Spectroscopy for Monomolecular Films on Substrate. Polarized absorption spectra were measured in order to examine whether the H-aggregates form in the LB film. The monomolecular LB film was

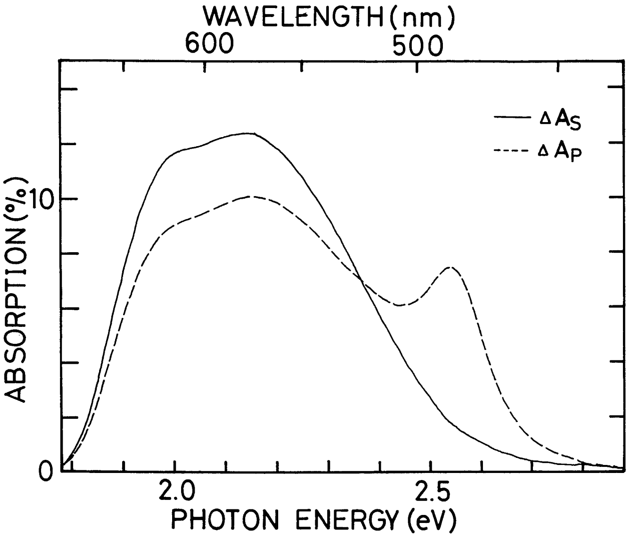

Fig. 8. Absorption spectra of perpendicular and parallel polarized light with an incident angle of 45° for the LB film at a deposition pressure of 40 mN m^{-1}.

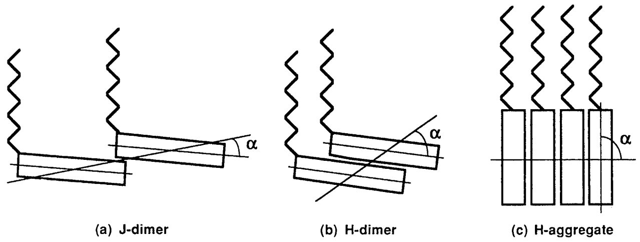

Fig. 9. Model of molecular configurations.

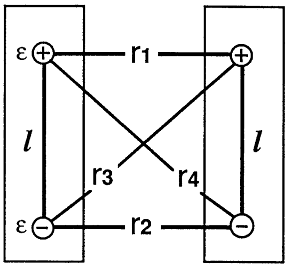

Fig. 10. An arrangement of two extended dipoles of charge ε and length l for calculation of the energy shift $\Delta E'$.

deposited at a surface pressure of 40 mN m^{-1} and a dipping speed of 6 mm min^{-1} under the same conditions for forming H-aggregate in monolayer on water. Figure 8 shows typical polarized absorption spectra of the LB film. The polarized absorption spectra of the LB film is similar to those of the monolayer on water. The H-aggregate band was observed at 2.55 eV. The red-shift from 2.61 eV (monolayer on water) to 2.55 eV indicates that the LB is in a more disordered state than the monolayer on water, and some fluctuations of the chromophores occurred during deposition process.

The Molecular Configuration Model. Figure 9 shows the models for molecular configuration to account for the present observations. Because the charged amino groups linked with three phenyl rings are anchored to the water surface, the dyes tend to assume a flat orientation at low surface pressures (0—5 mN m^{-1}). In view of the red-shifted absorption from the monomer band, dyes form a linear aggregate structure in model **a**. α is the slip angle between the transition dipole moments and their center-to-center lines. In this case the slip angle is small. At intermediate surface pressures (10—30 mN m^{-1}) the chromophores lie flat on the water surface or have an orientation with a relatively small angle between the chromophoric plane and the water surface. The dye molecule slips on the top of another adjacent molecule during film compression. The chromophoric planes are oriented parallel to each other and the dyes have a tace-to-face structure in model **b**. At high surface pressures (20—40 mN m^{-1}) the chromophoric planes are forced into an edge-on position and stack next to each other. In this case α is close to a right angle. The H-aggregate is indicated in model **c**. The appearance of this stacking structure is due to the strong dye–dye interaction between chromophoric planes with an edge-on position.

The Extended Dipole Model. Kuhn and associates proposed an extended dipole model to account for molecular arrangements in the blue- and red-shifted aggregates.$^{10)}$ The interaction integrals between dye molecules in the aggregation are given by varying a series of parameters, i.e., the number of aggregate molecules, the dipole length, the slip angle α and the distance between the centers of dipoles. In Fig. 10, the molecules are replaced by extended dipoles of length l between two charges $+\varepsilon$ and $-\varepsilon$. The energy shift ($\Delta E'$) of two molecules is obtained by

$$\Delta E' = \frac{2\varepsilon^2}{D}\left(\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{r_3}-\frac{1}{r_4}\right),$$

where D is the dielectric constant of the medium (D=2.5 for hydrocarbons) and r_i is the distance between two charges. The charge ε and the length l are assumed to be related to the transition moment μ by $\mu=\varepsilon\times l$.

Thus, the transition energy ΔE_{agg} of a dye aggregate is represented with the excitation energy of the dye monomer, ΔE_{m}, and the interaction integral $\Delta E'$ approximated by

$$\Delta E_{\mathrm{agg}} = \Delta E_{\mathrm{m}} \pm \Delta E'.$$

In the case of an aggregate containing n molecules, the intensity of the dipole–dipole interaction between ith and jth molecules is expressed as follows:

$$\Delta E' = \frac{2\varepsilon^2}{D}\sum_{i\neq j}^{n}\left(\frac{1}{|r_i^+ - r_j^+|} + \frac{1}{|r_i^- - r_j^-|} - \frac{1}{|r_i^+ - r_j^-|} - \frac{1}{|r_i^- - r_j^+|}\right),$$

where $|r_i^+ - r_j^+|$ and $|r_i^- - r_j^-|$ are the distance between positive charges and both negative charges of *i*th and *j*th molecule, respectively. $|r_i^+ - r_j^-|$ and $|r_i^- - r_j^+|$ are the distance between opposite charges of *i*th and *j*th molecule.

The transition dipole moment μ used in our calculation is indicated in the inset of Fig. 11. The positive charge of nitrogen N_1 of the octadecylmethylamino group is assumed as $+\varepsilon$ and each of negative charges of N_2 and N_3 atom as $-0.5\,\varepsilon$. The dipole length is l=8.4 Å. The values of $\Delta E'$ can be calculated by the dipole length and also by estimating the distance between the adjacent transition moments to be about 5 Å, which corresponds to the molecular model and the transition moment μ=9.98 Debye from the chroloform solution spectrum. In correspondence to the face-to-face arrangement, the blue-shift value of the H-aggregate band is considered to be most significant. The calculated values $\Delta E'$ for various arrangements are indicated in Fig. 11. The observed shift −0.06 eV of the J-dimer was fitted to the calculated value $\Delta E'$ of −0.05 eV with n=2 and a minimum slip angle α of 26°. For the observed value between 0.12 and 0.14 eV for the H-dimer, it was calculated to be 0.12 and 0.14 eV with n=2 and slip angles between 72° and 90°. The broadness of the H-dimer band is probably due to containing the coexistence of several kinds of dimers with various slip angles. For the red shift value of 0.43 eV (10 mN m^{-1}) and 0.51 eV (40 mN m^{-1}) of the H-aggregate, it was calculated to be 0.43 eV (α=72°) and 0.49 eV (α=90°) with n=4.

In conclusion, it was found that an H-aggregate assignable to a tetramer of CV dye forms in a close-packed monomolecular layer at high surface pressures. Since the H-aggregate band is present in the p-polarized spectra and absent in the normal incident and s-polarized spectra, its chromophoric planes must be oriented normal to the monolayer. The results of polarized absorption spectral measurements indicated that a well-ordered arrangement of H-aggregate was indeed present in the monolayer on water rather than in the LB film. The H-aggregates having a vertical transition moment observed here are of much significance as optical information storage media that work with a linearly polarized light at an oblique incidence.

The authors are grateful to Dr. David Heard of Sharp Corporation and Professor Akihiko Yamagishi of College of Arts and Sciences, University of Tokyo for valuable discussions.

This work was performed under the management of the FED (the R & D Association for Future Electron Devices) as a part of the R & D of Basic Technology for Future Industries supported by NEDO (New Energy and Industrial Technology Development Organization).

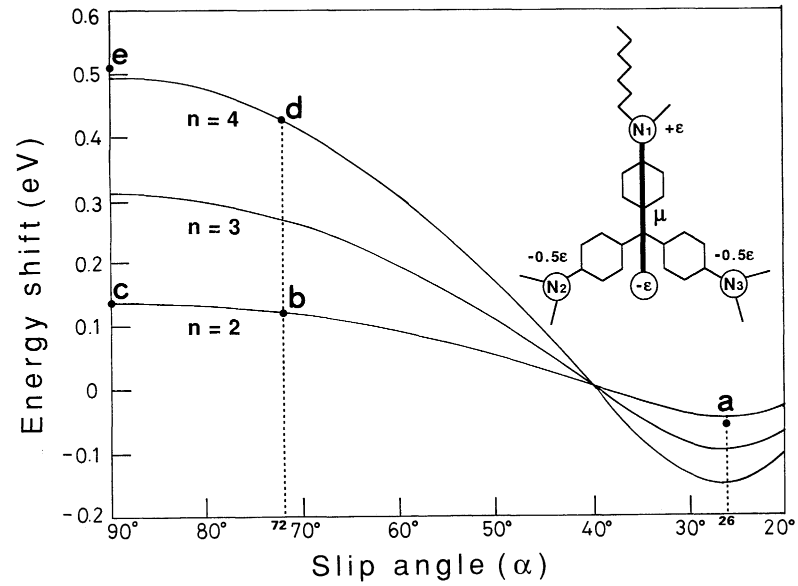

Fig. 11. The calculated energy shifts $\Delta E'$ are indicated; n is the number of molecules, the transition dipole moment μ (9.98 Debye) is charge ε and length l=8.4 Å; point a (−0.06 eV), 26° J-dimer; point b (0.12 eV), 72° H-dimer; point c (0.14 eV), 90° H-dimer; point d (0.43 eV), 72° H-aggregate (10 mN m^{-1}); point e (0.51 eV). 90° H-aggregate (40 mN m^{-1}).

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