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Electronic Spectra of a Simple Trimethine Cyanine Dye Crystal. (3-Dimethylamino-2-propenylidene)dimethylammonium Perchlorate

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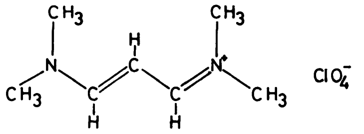
The electronic spectra of the simplest polymethine cyanine dye crystal were studied by measuring the reflection spectra of (3-dimethylamino-2-propenylidene)dimethylammonium perchlorate. The spectra consist of a single peak situated at 32400 cm^{-1} in solution. Davydov splitting is observed in the crystal spectra and it is explained by calculating the dipole–dipole interaction energy and the interaction energy between the transition densities with the Ewald sum method.

(3-Dimethylamino-2-propenylidene)dimethylammonium perchlorate (3-DMP) is the simplest polymethine cyanine dye so far studied. The spectral features and the crystal structure of 3-DMP were studied by Johnson *et al.*[1] and Matthews *et al.*[2] to investigate the orientation of the molecules in a crystal. In our laboratory we continued the study of the reflection spectra and the crystal structures of (5-dimethylamino-2,4-pentadienylidene)dimethylammonium perchlorate.[3,4] A comparative study regarding 3-DMP will be quite interesting.

The reflection spectra of 3-DMP were measured with several crystal faces and the absorption spectra and the optical constant of the crystals were obtained by Kramers-Kronig transformation of the reflectivity. The observed Davydov splitting can be explained by the dipole–dipole interaction energy calculated with the dipole approximation and the Ewald sum of the transition density. The results showed reasonable agreement between theory and experiment.



3-Dimethylaminopropenylidenedimethylammonium perchlorate (3-DMP)

Experimental

The material, 3-DMP, was synthesized from propalgyl alcohol. Propynal was obtained by the oxidation of the alcohol with CrO_3 and H_2SO_4.[5] Dimethylamine and the aldehyde reacted to form an adduct[6] and the obtained 3-dimethylamino-2-propenal was refluxed with dimethylammonium perchlorate to give 3-DMP.

Single crystals were obtained from a hot acetic anhydride solution under slow cooling. The crystalline faces are illustrated in Fig. 1. The reflection spectra of the crystals were measured with the (010), (1$\bar{1}$0), and (11$\bar{1}$) faces by a microspectrophotometer developed in this laboratory.

Results and Discussion

The absorption spectrum of 3-DMP measured in an aqueous solution is shown in Fig.2. It consists of a single peak centered at 32400 cm^{-1}. Its origin is considered to be a $\pi\pi^*$ transition of the polymethine chain. From the oscillator strength (f=0.97), the transition moment length is estimated as 1.66 Å. The f value given by Johnson *et al.*[1] is larger by a factor of 3 because of a difference in formulation.

On the (010) face shown in Fig. 3(a), all molecules are aligned along the same direction, and only a single excited state may be found if an intermolecular interaction such as a charge transfer is not concerned.

The reflection spectra were recorded along the

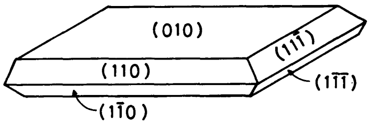


Fig. 1. Crystal habit of 3-DMP.

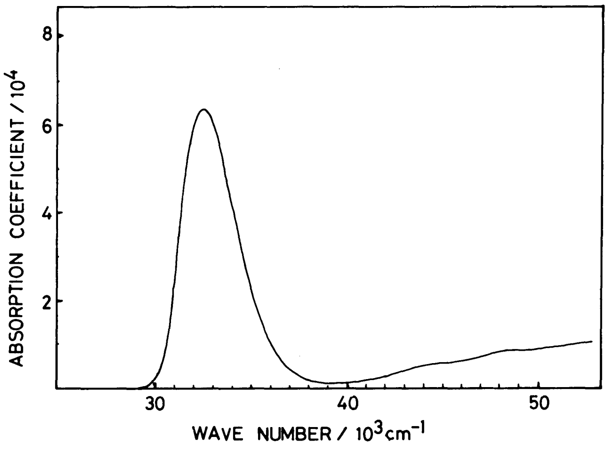


Fig. 2. Electronic absorption spectrum of 3-DMP in aqueous solution.

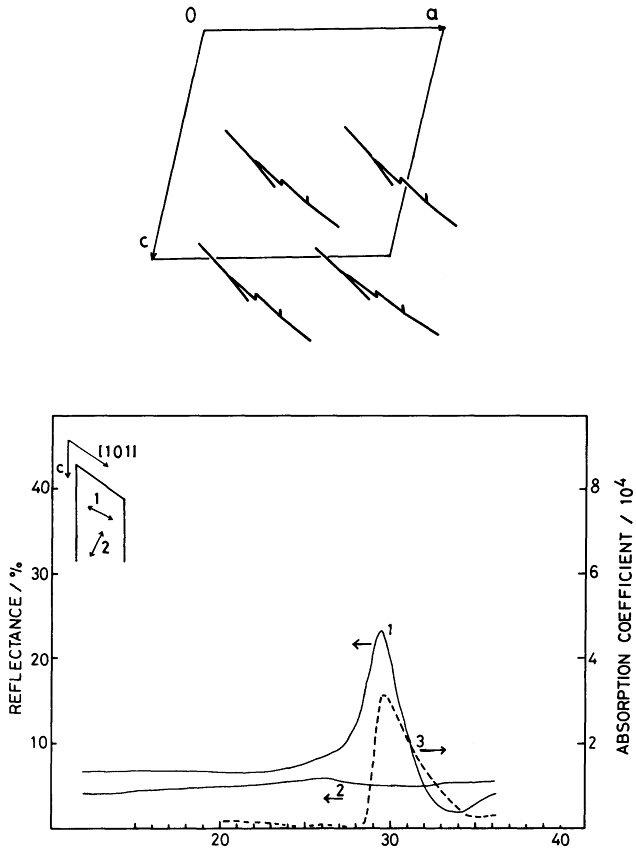


Fig. 3. (a): Projection of molecules onto the (010) face. (b): Crystal reflection spectra parallel to the [101] axis (1) and perpendicular to it (2) and absorption spectrum obtained by K-K transformation for the [101] direction with the (010) face (3).

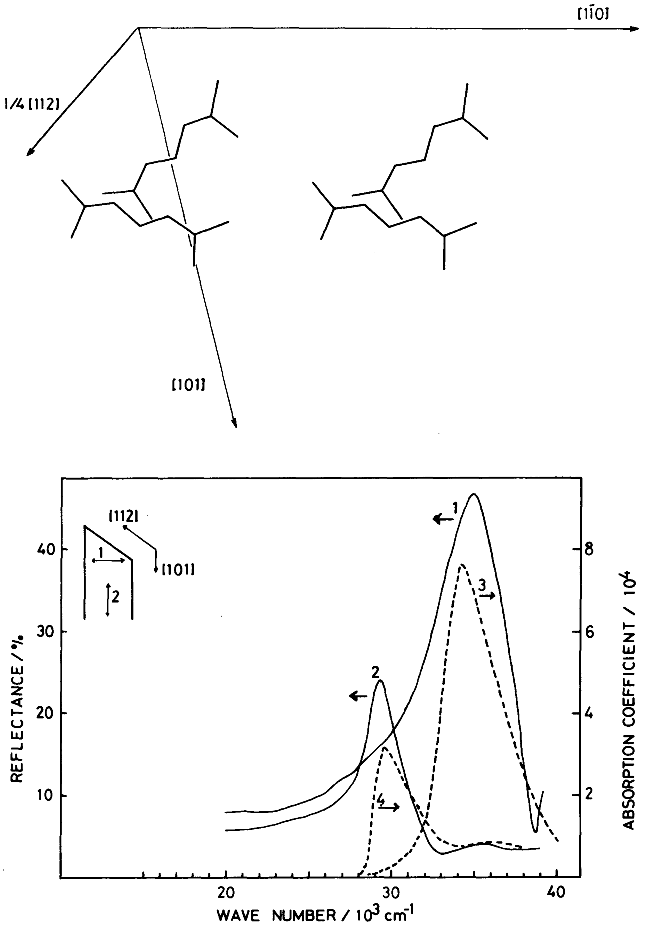


Fig. 4. (a): Projection of molecules onto the (11$\bar{1}$) face. (b): Crystal reflection spectra measured for perpendicular (1) and parallel (2) direction to the [101] axis and absorption spectra obtained by K-K transformation for perpendicular (3) and parallel (4) direction to the [101] axis with the (11$\bar{1}$) face.

molecular axis and perpendicular to it (Fig. 3(b)). A strong peak was found at 29000 cm^{-1} but nothing was found along the perpendicular direction. The K-K transformation gives a single peak situated at 29600 cm^{-1} (Fig. 3(b)).

A projection of the dye molecules onto the (11$\bar{1}$) face is shown in Fig. 4(a). The reflection spectra were measured along the directions parallel and perpendicular to the [101] zone axis. The [101] direction is perpendicular to the b axis, and it has only an ac component. Therefore, a Davydov splitting between the [101] direction and the direction perpendicular to it is expected, and it was actually found. Along the [101] zone axis, a peak was found at 29200 cm^{-1} that is almost coincident with the peak found with the (010) face at 29000 cm^{-1}. A very strong reflection peak was found for the direction perpendicular to the [101] direction at 34800 cm^{-1}. The K-K transformation of the reflectance shows an absorption peak at 34500 cm^{-1} for the perpendicular to the [101] direction which includes the b-axis transition and 29500 cm^{-1} for the [101] zone axis. A large Davydov splitting of 5000 cm^{-1} was found between the ac and b axes components.

The projection of the molecules onto the (1$\bar{1}$0) face is shown in Fig. 5(a). The reflection spectra were measured along the c axis and perpendicular to it parallel to the [110] direction. Along the c axis, no strong peak was detected since the transition moment on the molecule is almost perpendicular to this axis. For the [110] zone axis, both the b and ac axes components were expected and were clearly found at 35300 cm^{-1} and 30200 cm^{-1}. The K-K transformation of these spectra gives absorption maxima at 34600 cm^{-1} and 30000 cm^{-1}.

Using the K-K transformation, the real and imaginary parts of the dielectric constants were estimated (Fig. 6) for the [101] direction and its perpendicular. Large dispersions of the real and imaginary parts were found in the region of a strong absorption band.

The transition moments on the respective faces were estimated from the intensities of these absorption bands. (Table 1)

A crystal of 3-DMP has four molecules in a unit cell; the crystal symmetry is Cc[2] and the coordinates of these molecules are given by (x,y,z), $(x, -y, 1/2+z)$, $(1/2+x, 1/2+y,z)$ and $(1/2+x, 1/2-y, 1/2+z)$. The molecular exciton state of the crystal is considered to have symmetry of A′ or A″ in the irreducible representation of Cs group. The A′ state is allowed for the ac axis, and the A″ state is active for the b axis direction.

$$\mathrm{A}' \quad \Psi(ac)=\frac{1}{\sqrt{N}}\sum_{i=1}^{n}(\phi_{1i}+\phi_{2i}+\phi_{3i}+\phi_{4i})e^{i\boldsymbol{K}\cdot\boldsymbol{R}_i}$$

$$\mathrm{A}'' \quad \Psi(b)=\frac{1}{\sqrt{N}}\sum_{i=1}^{n}(\phi_{1i}-\phi_{2i}+\phi_{3i}-\phi_{4i})e^{i\boldsymbol{K}\cdot\boldsymbol{R}_i}$$

where ϕ_{1i} represents the molecule in the 1-st site of the i-th unit cell being excited while all other molecules are in the ground state. The summation over i is extended ideally to all N molecules in a cell; however, it is limited in order to give a convergent result. Here $\boldsymbol{R}_i$ is the lattice vector and $\boldsymbol{K}$ is the reciprocal lattice vector.

The calculation of the Davydov splitting was performed using two methods. One was a dipole-dipole approximation to calculate the interaction energy on a particular crystalline surface for molecules with a limited depth and area; namely the summation is taken for molecules within a 20-Å depth and a 100-Å radius. The calculated splitting is shown in Table 1, where the calculated values are compared with the observed ones. Tendencies in the calculated shift are in good agreement with the observed

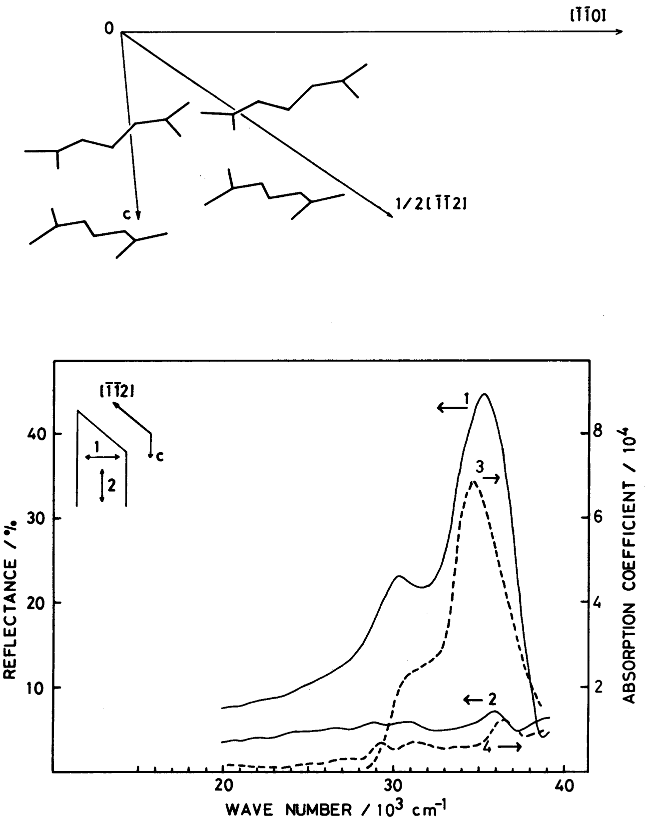


Fig. 5. (a): Projection of molecules onto the (1$\bar{1}$0) face. (b): Crystal reflection spectra measured for perpendicular (1) and parallel (2) to the c axis and absorption spectra obtained by K-K transformation for perpendicular (3) and parallel (4) to the c axis with the (1$\bar{1}$0) face.

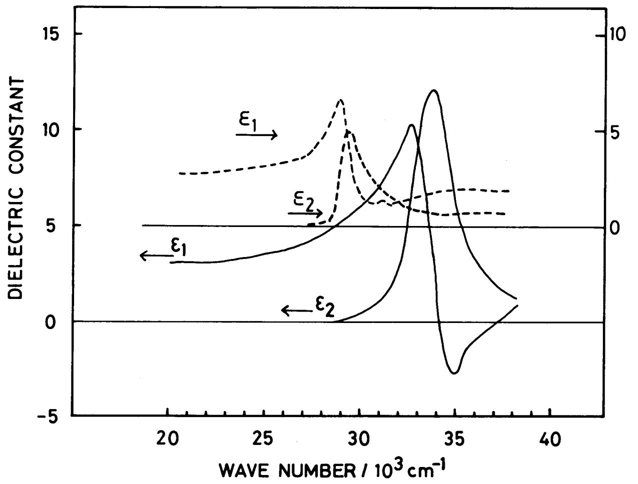


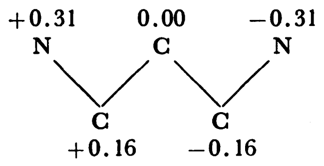
Fig. 6. Real and imaginary parts of dielectric constants for the direction parallel (----) and perpendicualr (——) to the [101] axis on the (11$\bar{1}$) face.

TABLE 1. OBSERVED EXCITED STATE AND CALCULATED ENERGY LEVELS BY DIPOLE-APPROXIMATION

		Energy levels of crystal excited states/10³ cm⁻¹		Shift of energy level/10³ cm⁻¹		f	Transition moment/Å	
Crystal face	Optically active axes	Observed value	Calculated value	Observed value	Calculated value	Observed value	Observed value	Calculated value
(010)	ac	29.6	28.6	−2.8	−3.8	0.40	0.63	0.67
(11$\bar{1}$)	ac	29.5	28.6	−2.6	−3.8	0.42	0.64	0.69
	b	34.5	37.3	+2.1	+4.9	1.77	1.26	1.33
(1$\bar{1}$0)	ac	29.5	28.6	−2.9	−3.8	0.31	0.55	0.22
	b	34.6	36.5	+2.2	+4.1	1.17	1.03	1.03
Free molecule		32.4	(34.1)	—	—	0.97	1.66	(1.50)

values; however, the magnitude is larger by a factor of 1.5~2.3.

It is well known that the dipole approximation exagerates the electrostatic Coulomb interaction, particularly at short distance. In order to more accurately estimate the interaction, the Ewald sum of the Coulomb energies for the transition densities on a molecule was calculated using a program written by Mrs. S. Akhtar of our laboratory. The molecular orbitals concerning the electronic transition were calculated by the Pariser-Parr-Pople method, and the transition densities estimated for a one-electron transition was multiplied by a factor of $\sqrt{2}$ as shown below,



This was because the excited state is described by a linear combination of two one-electron excited configurations. Moreover, these values were multiplied by a factor of 1.12 in order to scale the observed transition moment with the observed value in for a solution. The calculation was performed at the Nogoya University computation center. The result gives a much smaller value compared to the dipole–dipole approximation; the splitting being 3000 cm^{-1} as compared to the observed value of 5000 cm^{-1}.

The oscillator strengths for these crystal transitions were calculated by the oriented gas model and compared with observed values (Table 1). The agreement between theory and experiment is quite reasonable in spite of the simple approach.

The crystal reflection spectra of 3-DMP are characterizad by a single band and its behavior on several crystalline surfaces can be explained well by the excited state of the crystal; the selection rule, the energy shift and the intensities are all explained by the oriented gas model interacting through the electrostatic interaction in the excited state. The results provide a simple example of crystal excited state where no other complication due to a charge transfer or mixing with other highly excited states is significant.

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