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High Polariton Reflectance in Heptamethinebis(dimethylamino)cyanine Chloride Crystal

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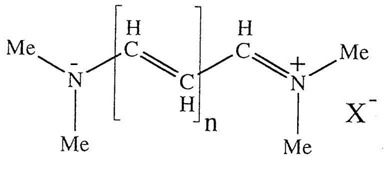
The reflection spectra of single crystals of bis(dimethylamino)heptamethinium chloride were measured with polarized light in the region from 500 to 38000 cm^{-1}. The Kramers Kronig transformation was calculated and the determined dielectric functions are discussed in terms of the polariton and molecular exciton theories. The highly anisotropic reflection band is caused by one narrow molecular transition, which is polarized parallel to the molecular chain. The bathochromic shift of the transition energy compared to the value in solution and the large splitting of transverse and longitudinal modes are explained by the molecular exciton theory. The expected charge resonance transition could not be found. That will be discussed in respect to the arrangement of the molecules in the crystal.

Since the discovery of the spectral sensitization of silver halides by polymethine dyes, a lot of interesting properties were found with this class of dyes, namely the formation of aggregates in solution,[1] the spectal sensitization of other semiconductors,[2] high optical nonlinearities[3] and the energy transfer[4] in J-Aggregates. Despite these exceptional properties the excited states in the crystalline state of dyes have hardly been characterized. One reason for this situation may be the difficulties in obtaining suitable dye crystals.[5]

Polariton reflectance was reported for crystals from 2,2′-(3-cyclopropylpentamethine)bis(1,3,3-trimethyl-3*H*-indole)cyanine tetrafluoroborate abbreviated PTIC)[6] and from a yellow form of pentamethinebis(dimethylamino)cyanine perchlorate (Fig. 1, (2) n=2, BDP).[7,8] The reflection bands are caused by coupling of light waves with the polarization of the medium induced by molecular exciton. In contrast to these results an orange form of the same dye BDP (2) shows an additional transition the direction of which deviates relating to the direction of the molecular exciton state.[8] This transition could not be explained by the Davydov splitting of the molecular exciton. One reasonable explanation may be to consider an additional charge-resonance state, which results from an intermolecular interaction of the polymethine chains arranged closely parallel to each other in stacks.[8] This is in accordance to the occurence of the J-band in aggregates formed by some polymethine dyes in solution.



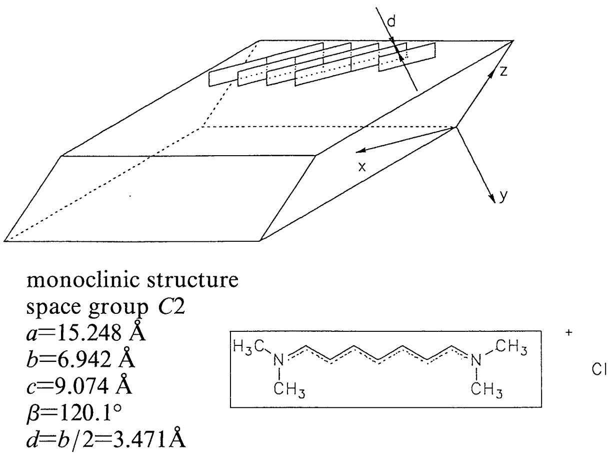
1 n=1 bisdimethylaminotrimethine,
2 n=2 bisdimethylaminopentamethine (BDP),
3 n=3 bisdimethylaminoheptamethine (BDH).

Fig. 1. Structure of the polymethinebis(dimethylamino)cyanine dyes.

In the simple streptocyanine dyes n=1—3 the tendency of aggregation increases with increasing length of the methine chain.[9] In accordance with the latter result, the crystal of trimethinebis(dimethylamino)cyanine salts (1) (n=1) shows neither a CR-band nor a polariton one.[10] These optical phenomena can be observed already in the two forms of BDP (2) (n=2).[8] Accordingly one can expect in crystals of heptamethinebis(dimethylamino)cyanine salts (3) (n=3, abbreviated BDH) more strong interactions. In this paper the reflection spectra of the BDHCl will be presented and a theoretical consideration of the band shape based on the molecular exciton and polariton theories will be discussed. We will also explain the absence of the CR-band by the specific arrangement of the molecules in the crystal.

Experimental

Materials. The BDHCl was prepared by the method of Nikolajewski and Daehne.[11] After manifold recrystallisations the crystals were grown from a methanol solution including 10 percent water by slow evaporation. Prismatic



monoclinic structure
space group $C2$
a=15.248 Å
b=6.942 Å
c=9.074 Å
β=120.1°
d=b/2=3.471Å

Fig. 2. Schematic representation of the crystal structure and the arrangement of the chromophores of BDHCl$_3$ (rectangles).

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single crystals were obtained up to 30 mm in length. The faces had an excellent quality and could be used without further treatment. The crystals possess only two optically different faces (Fig. 2). The (001) face looks like a silvery mirror whereas the (110) face exhibits a dark blue reflectance. The two BDH-cations in the monoclinic unit cell are arranged parallel to the *a*-axis.[12] They form stacked layers along the [010] direction in which they are shifted by the translational operation (1/2, 1/2, 0). The perpendicular distance between the polymethine chains is only 3.48 Å while it is 3.64 Å in the orange form of BDP.[8]

The reflection spectra were measured over a range from 4000 cm^{-1} up to 38000 cm^{-1} by using microscopic reflection spectrophotometer equipped with a Wollaston prism. The polished surface of silicon carbide was used as reference. The spectra in the infrared region below 4000 cm^{-1} were investigated by an FTIR-microspectrophotometer. A gold mirror served as reference. The absorption spectrum of the monomer in solution was recorded on a Shimadzu UV-3101 PC-spectrophotometer. The real and imaginary parts of the dielectric constant and the absorption spectra of the crystals were calculated by Kramers–Kronig transformation of the reflection spectra. The computation program is based on the method of Ahrenkiel.[14] At the low energy side below 3000 cm^{-1} the reflectance was set to a constant value. This extrapolation has no influence on the calculated data in the visible region. The IR spectra will be discussed in a subsequent paper.

Results

Solution Spectrum. The spectrum of BDH in methanol is shown in Fig. 3. The absorption maximum lies at 19600 cm^{-1}. The half width amounts to 1335 cm^{-1}. The oscillator strength is determined as f=1.65 whereby the refractive index of the solvent is taken into account. The estimated transition dipole lengths has a value of μ=2.85 Å. Three additional weak bands with f<0.01 appear at higher energies.

Crystalline Reflection Spectra. The reflection spectra of the (001) face are shown in Fig. 4a. The molecular axis is exactly parallel to this face and gives therefore the largest projection of the transition moment.

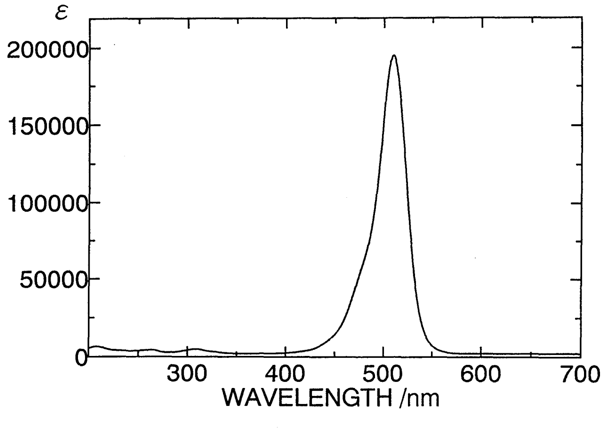


Fig. 3. Single molecule absorption of BDH in methanol.

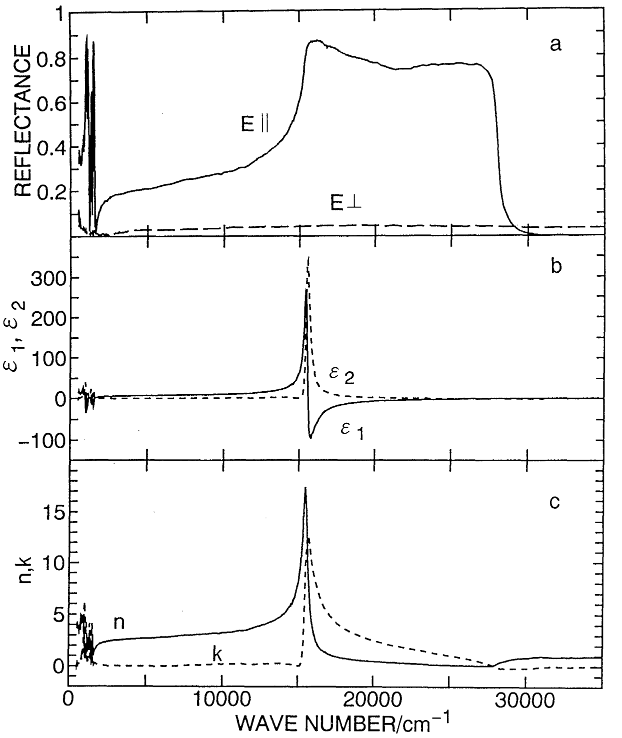


Fig. 4. Reflectance spectra of the (001)-face for light polarized parallel and perpendicular (dashed) to the *a*-axis.
b) ε_1 and ε_2 (dashed) obtained by Kramers–Kronig transformation from the above parallel spectrum.
c) Refractive index *n* and absorption coefficient *k* (dashed).

With light polarized parallel to the BDH-chain one can observe an extremely broad reflection band with a width of 13400 cm^{-1} and a reflectivity up to nearly 90 percent. With perpendicular light polarization the reflectivity is about 5 percent for the whole investigated range. The polarization ratio amounts to $R_{\parallel}/R_{\perp}$=17. Fig. 4b presents the dielectric functions obtained by Kramers–Kronig transformation of reflectance. The spectrum exhibits a typical polariton behavior which is given by [15]

$$\varepsilon_1(\omega) = \varepsilon' + \frac{4\pi\alpha_0\omega_t^2}{\omega_t^2 - \omega^2} = \varepsilon' \frac{\omega_l^2 - \omega^2}{\omega_t^2 - \omega^2}, \qquad (1)$$

where ω_t and ω_l are the resonance frequency for the transverse and longitudinal modes and ε' is the dielectric constant including the contribution from the higher excited states and α_0 is a measure of the strength of the interaction of the polarization oscillation with the electromagnetic field.

A strong narrow peak of ε_2 is found at the resonance energy of the transverse mode. The ε_1 spectrum shows negative values from the resonance position up to the level of the longitudinal mode at 27970 cm^{-1}. The ε_2 spectrum is directly related to the absorption spectrum of the crystal. It clearly demonstrates that the polariton

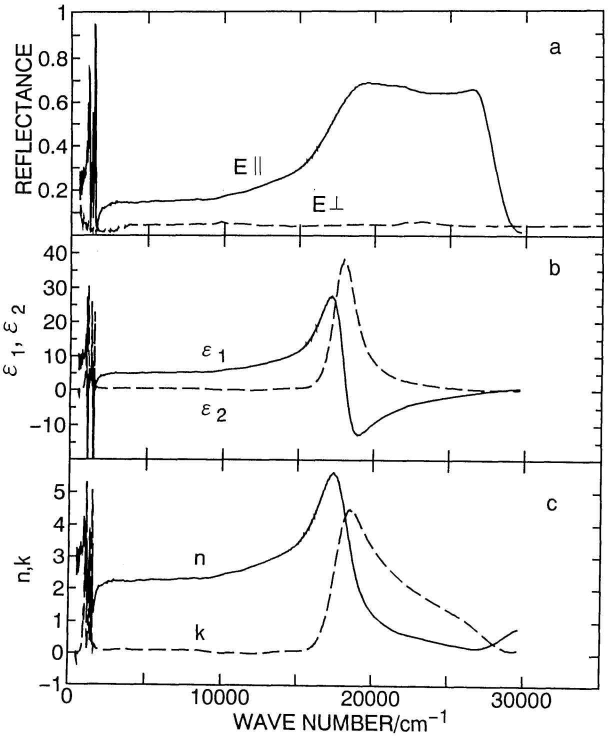


Fig. 5. a) Reflectance spectra of the (1 10) face for light polarized parallel and perpendicular (dashed) correspond to the projection of the *a*-axis onto this face.
b) ε_1 and ε_2 (dashed) from the parallel spectrum.
c) Refractive index *n* and absorption coefficient *k* (dashed).

band arised from only one strong molecular transition. One remarkable feature is the strong bathochromic shift of the resonance energy from 19600 cm^{-1} in the solution to 15560 cm^{-1} in the crystal. The shift is 4040 cm^{-1}, while it is 3090 cm^{-1} in the case of the yellow form of BDP and only 1533 cm^{-1} in PTIC.

The refractive index *n* and the absorption coefficient *k* are shown in Fig. 4c. The half band width of *k* is 1400 cm^{-1} which is exactly the same as the half band width in solution. Figure 5a shows te reflection spectra of the (110) face. The molecular axis is inclined towards this face by an angle of 24.8°. The edge on the low energy side is shifted to higher energy and doesn't rise up so sharply as in the case of the (001) face. This gives a blue color of this face. The high energy cut off lies at nearly the same energy. Perpendicular to the molecular axis the reflectivity lies also below 5 percent. The corresponding ε_1 and ε_2 spectra are shown in Fig. 5b and the *n* and *k*-spectra in Fig. 5c. On this face the resonance energy is shifted to 17970 cm^{-1} and the half width amounts to 2044 cm^{-1} which is broader than that in solution.

Discussion

The observed reflection spectrum parallel to the *a*-axis is typical for a polariton band. The broad high reflectance over 13400 cm^{-1} wide is extraordinary and this characteristics can be explained by the molecular exciton and polariton theories. The origin of high refectance is the strong absorption band of the BDH molecules which are arranged in the crystl parallel to each other (Fig. 2). The intensity of the crystal band is estimated by

$$f=\frac{2mc^2}{e^2N}\int \nu\varepsilon_2(\nu)d\nu, \tag{2}$$

where N is the number of molecules in unit volume. By this formula f is calculated as 5.04 and μ is 3.16 Å. These values are slightly larger than those in solution where μ is 2.85 Å.

The parameter fitting of ε_1 and ε_2 curves of Fig. 4b by Eq. 1 yields also the f-value, since

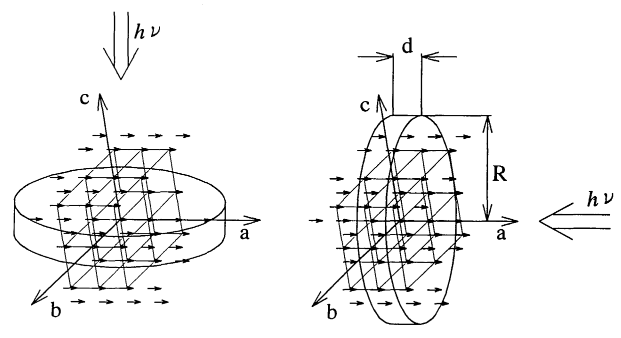
$$f=\frac{m\omega_t^2\alpha_0}{Ne^2}. \tag{3}$$

In fact the parameters of Eq. 1 are estimated as $\alpha_0=0.38$ with $\omega_t=15560$ cm^{-1}. The oscillator strength is estimated from Eq. 3 as 5.1, which is consistent with the previous value from Eq. 2. The transverse–longitudinal splitting of the polariton band is also calculated with the above parameters as 12600 cm^{-1} in good agreement with the observed value.

In order to study the microscopic origin of the polariton band splitting, we will use the molecular exciton theory. The energy levels of the transverse and the longitudinal excitons are calculated by the slab sum method[5] describing the excitonic dipole dipole interactions (Fig. 6).

Assuming that the light is incident normal to the (001) or the (100) faces, the transition dipole sum V is calculated by

$$V=\sum_j \frac{e^2\mu^2}{\varepsilon' R_{ij}^3}\left(p_i\cdot p_j-\frac{3(p_i\cdot R_{ij})(p_j\cdot R_{ij})}{R_{ij}^2}\right), \tag{4}$$



(a) (b)

Fig. 6. Calculation of dipole sum by a slab method; the direction of the incoming light is shown by a large arrow; the transition dipoles are drawn by arrows; the range of summation of a) transverse and b) longitudinal modes is defined by *R* (radius) and *d* (thickness).

Table 1. Calculated Values of the Transverse and Longitudinal Modes in Crystals of BDHCl by the Slab Sum Method Compared with Experimentally Obtained Results

Mode	Face	Calcd	Calcd	Obsd
		$\Delta\tilde{\nu}/\mathrm{cm}^{-1}$	$E_0+\Delta\tilde{\nu}/\mathrm{cm}^{-1}$	$\Delta\tilde{\nu}/\mathrm{cm}^{-1}$
Transverse	(001)	−4045	15556	15560
Transverse	(110)	−1832	17768	17900
Longitudinal	(100)	9333	28934	27900

$E_0=19600\ \mathrm{cm}^{-1}$, $R=300$ Å, $d=20$ Å, $\mu=3$ Å, $\varepsilon'=2.1$.

where p_i is the direction cosine of the transition moment of the i-th molecule, which is taken at the center, p_j is the direction cosine of the transition moment of the j-th molecule, R_{ij} is the vector connecting the center of the i-th and the j-th molecules, ε' is the dielectric constant estimated by Eq. 1 and μ is the size of the transition moment. The slab sum is evaluated by varying the depth d and the radius R on the (001), (100), and (110) faces as shown in Fig. 6 and Table 1. The calculated results are almost convergent for $R=300$ Å and $d=20$ Å. The transition dipole length is found as $\mu=3.16$ Å from the crystal spectra and $\mu=2.85$ Å from the solution spectra. Taking $\mu=3.0$ Å for the dipole sum calculation, the shifts of the allowed transverse mode on the (001) and (110) faces and the longitudinal mode are calculated as shown in Table 1. The agreement between the calculated and experimental result is satisfactory in view of a simple and straightforward approach. Here the origin of the band is set equal to the value found in solution. The shift of the center of energy levels of the crystal compared to that in solution is not large for molecular crystals. The bathochromic shift of the resonance energy of the transverse mode in the crystal arises mainly from the large splitting of the molecular exciton band.

Especially attention should be paid to the appearance of charge transfer process in these crystals. The expected intensities of such states are usually very small in homomolecular crystals ($f<10^{-2}$)[16,17] except the case of 9,10-dichloroanthracene.[18] However in the orange BDP[8] the charge resonance transition can appear with a sharp band shape and fairly strong intensity of $f=0.13$.

If the charge transfer takes place between the nitrogen atoms of two adjacent molecules[8] the distance between them should be small and their electronic structure must be different, since one nitrogen atom acts as the donor and the other nitrogen atom behaves as the acceptor. This particular condition is not fulfilled in the BDHCl crystal since the dye molecules are situated symmetrically in the crystal with the two-fold molecular axis coinciding with the crystallographic two-fold symmetry axis.[12] Accordingly the environment around the two nitrogen atoms is exactly the same. Therefore, no charge resonance transition between the nitrogen atoms can be found in the crystals. The charge transfer interaction between the dye molecules may occur by the HOMO-LUMO overlap extending over the whole molecule but the overlapping is not so significant in the present crystal.

A well-known concept on the J band of cyanine dye crystals and aggregates is that a molecular broad absorption band changes to a sharp and red-shifted intense band in the aggregates. We proposed in the previous paper[8] that the charge resonance transition between the nitrogen atoms plays an important rolé for appearance of the J band. This argument was not supported in the present work, since no charge resonance band could be found. Moreover, the absorption spectra of strong polariton band is fairly sharp although its tail extends for the whole polariton reflection band. (Fig. 4c) Further study will be required to find the relation between the charge resonance band and the J band.

Summary

The crystals of BDHCl show a strong polariton resonance which is caused by the exciton interaction of molecular π–π^* transition. The large energy splitting of the transverse and longitudinal modes is accounted for by the strong excitonic dipole interactions between the molecules in the crystalline state. That could be confirmed by the good agreement of the calculated values of the dipole interaction, obtained by the slab sum method, and the experimental results. The BDHCl crystal is an exceedingly nice example to understand for polariton resonances in organic molecular crystals, because of their simple crystal structure and simple electronic transition. Therefore the microscopic origin of this phenomena is well explainable without further assumptions or approximations. Despite the strong excitonic dipole interactions the BDHCl crystals do not show any other transition like the orange form of BDP. The reason may be the high symmetry of the dye molecules in this particular crystal. Further investigations on other crystals are necessary in order to find the conditions which lead to strong charge resonance transitions in homomolecular crystals.

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