

## Nature of the electronic transitions in thiocarbocyanines with a long polymethine chain

Richard S. Lepkowicz<sup>a,\*</sup>, Olga V. Przhonska<sup>a,b</sup>, Joel M. Hales<sup>a</sup>,  
Jie Fu<sup>a</sup>, David J. Hagan<sup>a,c,1</sup>, Eric W. Van Stryland<sup>a</sup>, Mikhail V. Bondar<sup>b</sup>,  
Yuriy L. Slominsky<sup>d</sup>, Alexei D. Kachkovski<sup>d</sup>

<sup>a</sup> College of Optics and Photonics: CREOL & FPCE, University of Central Florida, Orlando, FL 32816, USA

<sup>b</sup> Institute of Physics, National Academy of Sciences, Prospect Nauki 46, Kiev 03028, Ukraine

<sup>c</sup> Physics Department, University of Central Florida, Orlando, FL 32816, USA

<sup>d</sup> Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya 5, Kiev 03094, Ukraine

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### Abstract

A detailed experimental investigation and quantum-chemical analysis of symmetric cyanines of different conjugation lengths have been performed with the goal of understanding the nature of the electronic transitions in molecules that possess a long chromophore. The nature of electronic transitions in cyanines with a relatively short chromophore (inside the cyanine limit) has already been investigated and many properties of these molecules are well understood. However, little is known about the nature of the transitions beyond the cyanine limit. Their unusual properties, which were proposed by Tolbert and Zhao to be connected with symmetry breaking, still remain unexplored. The analysis of the spectral data in various solvents and results of femtosecond pump-probe saturable absorption measurements enable us to conclude that an increase in the length of the chain leads to a symmetry breaking and the appearance of two forms with symmetrical and asymmetrical distributions of the charge density in the ground state. For thiocarbocyanines, symmetry breaking is predicted and observed for a pentacarbocyanine dye. Quantum-chemical calculations provide additional proof of this hypothesis. The excited-state absorption properties of a pentacarbocyanine in the visible region are also reported. For the first time we have observed an excited-state cross-section that is larger ( $\approx 3\times$ ) than the ground state cross-section at the peak spectral position.

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### 1. Introduction

Polymethine (or cyanine) dyes (PDs) of the general molecular structure **1** in Fig. 1 represent linear conju-

gated molecules that exhibit numerous unique electronic and spectral properties which are useful for a broad area of applications connected with light conversion, e.g., spectral sensitization, initiation of polymerization, molecular probes in polymer science and biology, active and passive components for tuneable lasers, nonlinear media exploiting excited-state absorption (ESA), etc. [1]. Polymethine molecules also serve as objects for developing new theoretical concepts and effective quantum-chemical models.

\* Corresponding author. Present address: Optical Science Division, Naval Research Lab, 4555 Overlook Avenue, SW Washington, 2037-55338, USA. Tel.: +1-2024043662; fax: +1-2024048114.

E-mail addresses: [lepkowicz@sisyphus.nrl.navy.mil](mailto:lepkowicz@sisyphus.nrl.navy.mil) (R.S. Lepkowicz), [dhagan@creol.ucf.edu](mailto:dhagan@creol.ucf.edu) (D.J. Hagan).

<sup>1</sup> Tel.: +1-407-823-6817; fax: +1-407-823-6880.

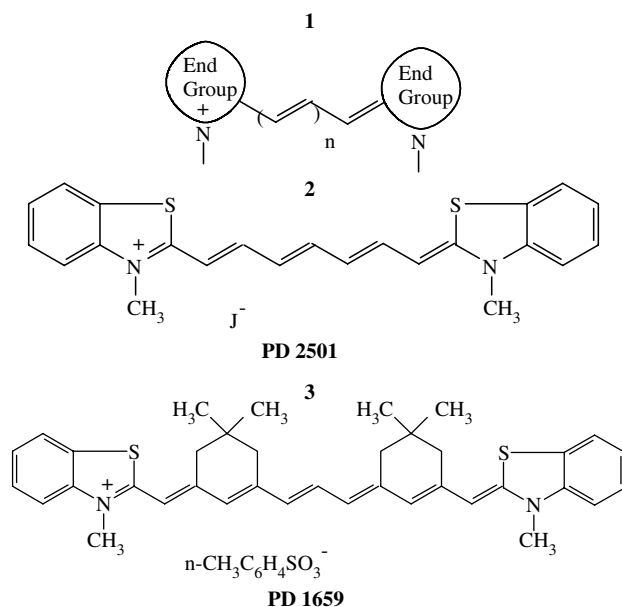


Fig. 1. Molecular structures of PDs.

In the past decades there have been several approaches developed to aid in the understanding of the nature of the electronic transitions in PDs. The first and simplest quantum-chemical theories, the Huckel molecular orbital method and the Kuhn free-electron or “metallic model”, were modified to explain the deep colour of PDs containing an extended chain of methine groups as the main component [2–5]. These theories were based on an alternation of the charge density along the chain, which was proposed by König [6]. The first experimental proof of this hypothesis was provided in 1963 by nuclear magnetic resonance spectroscopic measurements [7]. In 1966 all existing approaches were unified by Dahne [8–11] into a theoretical concept of the existence of three ideal states of unsaturated organic compounds, the so called triad principle. According to this principle, all conjugated organic compounds can be characterized by three ideal states: the aromatic, the polyene and the polymethine state.

It is known that polymethine molecules can be represented by two dominant resonance forms with positive charges at opposite ends of the chain. Therefore, each carbon–carbon (CC) bond can be characterized as a single bond in one form and a double bond in the other, which leads to the formation of a non-alternating structure in which each bond is considered a 1.5 instead of a 1 (single bond) or a 2 (double bond). Systematic X-ray structure analysis confirmed the predicted equalization of CC bond lengths [12,13]. According to the triad theory, there are two distinguishing properties of PDs: first of all, equalization of the single and double bond lengths and secondly the appreciable alternation of the positive and negative charges at the carbon atoms. Excitation leads to a substantial change of the atomic charges,

while the CC bond lengths remain practically unchanged. These structural features of the PDs are responsible for the strong first electronic transition  $S_0 \rightarrow S_1$ , which is accompanied by a considerable  $\pi$ -electron density transfer from the carbon atoms in odd positions to ones in the even positions. Therefore, PDs combine a maximum  $S_0 \rightarrow S_1$  transition probability with relatively low transition energy. The absorption and fluorescence bands of polymethines can be shifted from the visible to the IR-region by lengthening of the polymethine chain or by introducing specific terminal groups which possess their own large  $\pi$ -electron systems. Currently, the long wavelength limit for the peak of the absorption in PDs is approximately 1600 nm [14].

In contrast to PDs, the related neutral polyenes represent another type of linear conjugated system that is characterized by considerable alternation of the CC double and single bond lengths and an equalization of the  $\pi$ -electron density along the conjugated chain. Excitation leads to a substantial change of CC bond lengths, while the atomic charges remain practically unchanged. Therefore, lengthening of the chain in the polyenes is accompanied by a much smaller red shift of their spectral bands as compared to PDs, so that their spectral limit is  $\sim 700$ – $800$  nm, which depends slightly on the constitution of the terminal groups [15].

Many experimental and theoretical studies have confirmed the triad theory which has led to a deeper understanding of the main photophysical and photochemical properties of unsaturated organic compounds, in particular PDs [16,17]. Also, this theory is the basis for studying structure-property relationships. However, the triad theory predicted for symmetric PDs with an infinite chain length that the bandgap should vanish and the molecules should exhibit metallic behaviour. The linear behaviour of the bandgap on the “effective” number of double bonds (including the influence of the terminal groups) has been demonstrated by Bredas et al. [18] and by Tolbert and Ogle [19] for short conjugated systems only. It was shown experimentally that by lengthening the polymethine chromophore the intensity of the  $S_0 \rightarrow S_1$  transition decreases regularly and the bandwidth increases progressively. This effect for cyanine dyes was first reported by Brooker [20]. The structureless shape of the broad absorption band for other long polymethines was described by Tolbert and Zhao [21]. They assumed that the properties of the long conjugated linear systems could not be extrapolated from the short analogues, and that this spectral phenomenon is connected with the collapse of ground-state symmetry. The fundamental quantum-chemical investigation of the symmetry breaking phenomenon was performed by Hush et al. [22,23] for the simplest cyanines, the so called Brooker ions. Their explanation was based on the formation of charged mobile defects (also referred to as solitons) in the doped linear conjugated polymers [24,25].

It was found by numerous investigators, both theoretically and experimentally, that the total charge (positive and negative) in the charged  $\pi$ -electron system is not delocalized uniformly along the polymethine chain, but instead is distributed at the  $\pi$ -centres as a wave of alternating positive and negative partial charges, i.e. as a soliton of the electron or hole type, respectively [22,23,26–30].  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy measurements confirmed the  $\pi$ -electron density localization in the centre of the chain with a decrease of the charges at the ends [27,28]. Quantum-chemical calculations performed for the linear conjugated molecules show that the width of the charge wave is of finite size, approximately 15–17 carbon atoms for an unsubstituted polymethine chain [22,23,26]. The peak of the soliton always corresponds to the region of equality of the CC bond lengths and is placed on this “geometrical” or “topological” defect. Under certain conditions, if the width of the  $\pi$ -conjugated chromophore of the real molecule becomes comparable (or longer) than the width of the soliton, the charge maximum of this molecule, accompanied by a geometrical defect, could be shifted to one of the terminal groups. As a result, a symmetry breaking occurs leading to dramatic changes in the absorption spectrum, such as band broadening and a decrease in the intensity of the transition [21]. Recently Tolmachev et al. [31] investigated this effect for a series of thiacyanines (from monomethine to hexamethine) and confirmed that the main reason for band broadening is the intramolecular charge transfer from one side of the dye molecule to the other.

Thus, there is not a simple correlation between the dependence of the spectral characteristics on the chain length. For a relatively short chromophore (inside of the cyanine limit) many properties of these molecules are well understood, but little is known about the nature of the transitions beyond the cyanine limit. Therefore, one of the goals of this article was to study the nature of the  $S_0 \rightarrow S_1$  electronic transitions for near-IR absorbing PDs. For this purpose we performed a detailed experimental investigation and quantum-chemical analysis of PDs with different chain lengths, in particular, the tri- and penta-thiacyanines.

The experimental techniques used to investigate the PD molecules are:

1. Linear absorption spectral measurements in solvents of different polarity.
2. Femtosecond tuneable pump–probe measurements – saturable absorption study.
3. ESA-spectrum and ESA-anisotropy measurements.

Experimental analysis and comparison of predictions from quantum-chemical modelling give us a clear picture of the nature of the transitions.

## 2. Materials

In order to study the nature of the  $S_0 \rightarrow S_1$  transitions experimentally, we selected from the series of thiacyanines with the benzothiazolium terminal groups two PDs with different lengths of the polymethine chromophore, and thus with different spectral properties: 3,3-dimethylthiatriacyanine *p*-toluenesulfonate (structure 2, Fig. 1), labeled as PD 2501, and 3,3-diethyl-0, 11,15,17-di ( $\beta,\beta$ -dimethyltrimethylene) thiapentacyanine iodide (structure 3, Fig. 1), labeled as PD 1659. These PDs were synthesized at the Institute of Organic Chemistry, Kiev, Ukraine. The molecular structures were confirmed by elemental analysis and nuclear magnetic resonance spectral measurements. It is known that lengthening the polymethine chromophore usually results in a decrease of the photochemical stability. Introduction of the polymethylene bridges into the chain results in substantial molecular stabilization, while only slightly changing the absorption spectra [14]. To improve the stability of the pentacyanine (3) two polymethylene bridges were included. The linear absorption spectra of the dyes were recorded with a Shimadzu UV-3100 spectrophotometer. Spectroscopic grade ethanol, methanol, acetonitrile, *o*-dichlorobenzene and methylene chloride (from Merck Company) were used as the solvents.

## 3. Experimental methods

### 3.1. Femtosecond pump–probe measurements

The laser system used for the experiments was a Clark-MXR 2001 Ti:sapphire regeneratively amplified frequency-doubled erbium-doped fiber ring oscillator system operating at 1 kHz ( $\sim 1$  mJ per pulse) followed by two optical parametric generator/amplifiers OPA (Light Conversion Ltd., model TOPAS), providing 100–120 fs pulses (FWHM) with independently tuneable wavelengths from 0.55 to 2.2  $\mu\text{m}$ . The basic experimental set-up is shown in Fig. 2. A more detailed description of this experiment can be found in [32]. The pump beam was the output of one of the OPA's, which has pulse energies of tens of microjoules. No focusing lens is required in the pump path, due to the large linear absorption of the polymethine molecules. The large spatial extent of the pump beam ensures a constant irradiance over the probe beam. The probe beam was a subpicosecond white-light continuum (WLC), generated by focusing a 1  $\mu\text{J}$  pulse from the other OPA at a wavelength of 1300 nm into a 2.5-mm thick calcium fluoride plate [33].

Measurements were made to determine both saturable absorption (SA) and ESA by monitoring the energy of a probe beam through a section of the

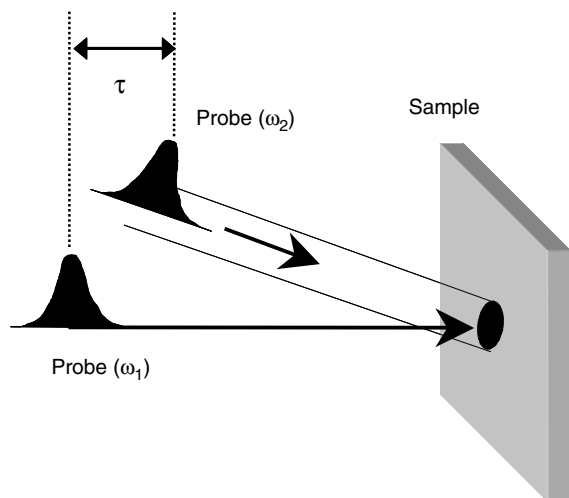


Fig. 2. Close up view of pump-probe setup. The delay between the pump and probe is given by  $\tau$ .

sample which overlaps with a pump beam (as shown in Fig. 2). A reference beam is used to monitor the linear transmittance. The transmitted light was collected with a fiber connected to a 1/4 m spectrometer coupled to a silicon dual photodiode array. For the SA and ESA pump-probe measurements large area (1-cm diameter) silicon photodiodes with wavelength filters with a bandwidth of  $\sim 10$  nm to select a portion of the transmitted WLC probe beam were used. The probe beam could be temporally delayed with respect to the pump beam by up to 1 ns and its irradiance was kept low so as not to induce any nonlinearity in the sample. The pump and the probe beams were overlapped at a small angle ( $\sim 5^\circ$ ) within the sample so the probe beam can be separated after the sample from the pump as shown in Fig. 2. For anisotropy measurements the polarization of the probe was fixed, while the pump polarization was adjusted with a half-wave plate and could be set to any angle with respect to the probe polarization.

### 3.2. ESA spectrum and ESA anisotropy measurements

To measure the ESA spectrum of PD 1659, the pump was set at 900 nm and the WLC was measured from 400–800 nm with (signal) and without (reference) the pump to determine the nonlinear absorption signal. The probe was set at approximately a 13 ps delay to that of the pump beam, which is longer than the vibrational relaxation time, but shorter than the excited-state lifetime. The analysis to extract the absolute cross-section and shape of the ESA spectrum from the continuum spectrum with and without the pump is given in [32], but will be reviewed here. The linear ( $T_L$ ) and nonlinear ( $T_{NL}$ ) transmittance of the continuum is given by the following equations:

$$T_L(\lambda) = \exp[-\sigma_{01}NL], \quad (1)$$

$$T_{NL}(\lambda) = \exp[-\sigma_{01}N_0L - \sigma_{1i}N_1L], \quad (2)$$

where  $L$  is the sample length and  $\sigma_{01}$  and  $\sigma_{1i}$  are the ground- and excited-state cross-sections, respectively.  $N$  is the total population, which is the sum of the ground ( $N_0$ ) and excited ( $N_1$ ) state populations. The absolute cross-section was determined near the peak of the ESA spectrum (630 nm) using the open aperture Z-scan technique [34] with a picosecond (24 ps FWHM) 10-Hz *EKSPLA* PL2143 Nd:YAG laser and an *EKSPLA* PG401/DFG optical parametric generator (OPG) tuneable from 0.42 to 2.3  $\mu\text{m}$ . This absolute cross-section can then be used to calibrate the ESA spectrum using the following equation:

$$\sigma_{1i}(\lambda) = \sigma_{01}(\lambda) - (\sigma_{01}(630 \text{ nm}) - \sigma_{1i}(630 \text{ nm})) \times \frac{\ln[T_{NL}/T_L]_{\lambda}}{\ln[T_{NL}/T_L]_{630 \text{ nm}}}, \quad (3)$$

where  $\sigma_{01}(\lambda)$  is the ground-state cross-section as a function of wavelength,  $\sigma_{1i}(630)$  is the excited-state cross-section obtained from the fitting of the open aperture Z-scan data. The ratio of the WLC measurements as a function of wavelength is  $\ln[T_{NL}/T_L]_{\lambda}$  and  $\ln[T_{NL}/T_L]_{630}$  is this ratio at 630 nm. Eq. (3) is derived by solving two forms of Eq. (2) simultaneously, the first as a function of wavelength and the second for the fixed wavelength of 630 nm (at which the Z-scan was taking) and solving for  $\sigma_{1i}(\lambda)$ .

The ESA anisotropy measurements were conducted with a fixed probe wavelength of 620 nm and the pump was tuned over the range of 560–960 nm. The purpose of this experiment is to determine the spectral position and orientation of the transition dipole moments from the ground to the first and higher excited states  $S_0 \rightarrow S_n$  ( $n = 1, 2, 3, \dots$ ). This information is commonly obtained using the fluorescence excitation anisotropy method [35]. The excitation anisotropy spectrum,  $R(\lambda)$ , is calculated as a function of the excitation wavelength  $\lambda$  at a fixed emission wavelength (usually near the fluorescence maximum) and is given as

$$R(\lambda) = \frac{I_{\parallel}(\lambda) - I_{\perp}(\lambda)}{I_{\parallel}(\lambda) + 2I_{\perp}(\lambda)}, \quad (4)$$

where  $I_{\parallel}(\lambda)$  and  $I_{\perp}(\lambda)$  are the polarized fluorescence intensities oriented parallel and perpendicular to the excitation wavelength polarization, respectively. The angle between the absorption and emission transition moments can be determined from the anisotropy  $R$  by

$$R = \frac{2}{5} \left( \frac{3\cos^2(\beta) - 1}{2} \right), \quad (5)$$

where  $\beta$  is the angle between the absorption transition dipole moment and the emission transition dipole mo-

ment [35]. However, for PD 1659 this is not possible due to the low fluorescence quantum yield. The lifetime of the first excited-state was measured with the femtosecond polarization-resolved pump-probe technique to be approximately 60 ps. Therefore, we have used a new approach, recently developed by us [36,37], which is based on decomposing the absorption of a weak probe into parallel ( $\Delta T_{\parallel}$ ) and perpendicular ( $\Delta T_{\perp}$ ) components and using this to determine the anisotropy. This means that in Eq. (4) the polarized fluorescence intensities ( $I_{\parallel}(\lambda), I_{\perp}(\lambda)$ ) are replaced by the change in absorption of a weak probe ( $\Delta T_{\parallel}, \Delta T_{\perp}$ ). In this case the anisotropy gives information about the angle between the pump and probe absorption transition dipole moments. We have previously shown [36,37] that this gives nearly identical results to the fluorescence anisotropy results for both the angle of orientation of the transition dipole moments and the spectral positions of excited-states.

## 4. Results

### 4.1. Absorption properties

Linear absorption spectra for PDs 2501 and 1659 in five solvents of different polarity: methanol, acetonitrile (ACN), ethanol, methylene chloride and *o*-dichlorobenzene are presented in Fig. 3(a), (b). As can be seen from this figure, PD 2501 (structure 2) exhibits a relatively narrow absorption band in all solvents, while the width of the band increases progressively as a function of polarity for PD 1659 (structure 3). This increase is mainly connected with the appearance of a broad shoulder on the short wavelength side of the absorption band. Also, the intensity of the long wavelength band decreases substantially with an increase of the chain length: extinction coefficients in ethanol are  $21.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (at peak position 761 nm) for PD 2501 and  $6.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (at 997 nm) for PD 1659. To exclude the possibility of aggregation for PD 1659, concentration dependences in ethanol were measured over the broad concentration range from  $5 \times 10^{-7} \text{ M}$  up to  $10^{-4} \text{ M}$ . All concentrations followed Beer's law and no changes in the shape of the absorption spectra were observed. Thus, the unusually broad absorption band of pentacarbocyanine PD 1659 cannot be connected with aggregation. Moreover, it is generally accepted that the solubility of cationic molecules increases in polar solvents, yet our experimental absorption spectra are the broadest in polar solvents. The polarity of the solvents can be characterized by their orientational polarizability, which is given by

$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1), \quad (6)$$

where  $\varepsilon$  is the static dielectric constant and  $n$  is the refractive index of the solvent [35]. Calculated  $\Delta f$  values

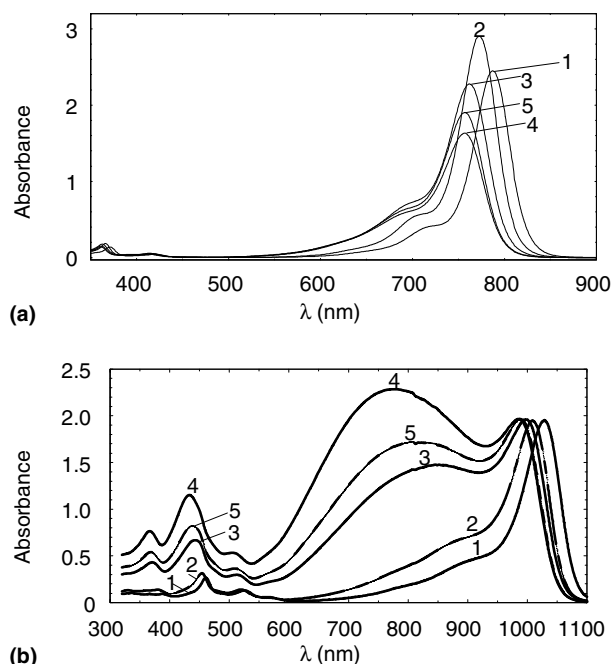


Fig. 3. Absorption spectra for PD 2501 (a); PD 1659 (b) in *o*-dichlorobenzene (1), methylene chloride (2), ethanol (3), acetonitrile (4) and methanol (5).

range from 0.208 for *o*-dichlorobenzene to 0.308 for methanol. It is well known that relatively short wavelength absorbing PDs exhibit classic nonpolar solvatochromism, which is consistent with a symmetrical ground and excited state charge distribution and small permanent dipole moments [35]. In contrast, absorption spectra of PD 1659 (Fig. 3(b)) demonstrates a strong dependence on solvent polarity. An increase in solvent polarity leads to a substantial band broadening represented by the growth of the short wavelength shoulder. This is a strong indication of polar solvatochromism, which is typical for dyes that exhibit charge localization and a large ground-state permanent dipole moment [38]. From the analysis of the spectral data we were able to conclude that PDs with a polymethine chain containing at least five methine groups may exist in the ground state in two charged forms with symmetrical and asymmetrical distributions of the charge density. Quantum-chemical calculations presented in Section 5.2 validate this conclusion.

Based on this hypothesis of the coexistence of two charged forms in the ground state, we separated the absorption spectra of PD 1659 into two bands and compared the dependence of the peak spectral position of each form as a function of the solvent polarity. In order to separate these two forms, we first fit the absorption spectra for PD 2501 in different solvents making the assumption that the shape of the spectrum is that of the symmetric form of PD 1659. Secondly, this function was then used in the fitting procedure for PD 1659 to

determine the asymmetric form. The result for the polar solvent ACN is shown in Fig. 4(a). In this case, the integral ratio between the absorption of the asymmetric and symmetric forms is 5 to 1. Quantum-chemical calculations show that the  $S_0 \rightarrow S_1$  transition dipole moments for both forms are comparable. Therefore, we can assume that the absorption bands integral ratio approximately corresponds to their concentration ratio. Inhomogeneity in the solvent shell distribution around dye molecules may be connected with the different permanent ground-state dipole moments for symmetric (0.7 D) and asymmetric (17.5 D) forms.

The dependences of the peak spectral position as a function of solvent polarity for PD 2501 and for both forms of PD 1659 are shown in Fig. 4(b). As can be seen, for the symmetric form the spectral shift is only 300–500  $\text{cm}^{-1}$  and for the asymmetric form is much larger, up to 1600  $\text{cm}^{-1}$ . This solvent dependency reinforces the hypothesis that the absorption spectrum of PD 1659 consists of two charged forms with a symmetrical and asymmetrical charge distribution.

However, these measurements do not rule out the possibility that the short wavelength shoulder could be connected with a higher excited-state transition, for example the  $S_0 \rightarrow S_2$  transition. The following sections discuss experiments which show that the broad absorption band in the range 600–920 nm is connected with only the  $S_0 \rightarrow S_1$  transition.

#### 4.2. Excited-state absorption and anisotropy properties

This method of determining the spectral position of the excited-states using a pump-probe method is based

on the understanding that in polymethine molecules the ESA transition dipole moments (in particular, the most intense  $S_1 \rightarrow S_5$  transition) can be used for determining the orientation of the  $S_0 \rightarrow S_n$  transitions instead of the fluorescence transition dipole moment ( $S_1 \rightarrow S_0$ ) [37].

Fig. 5 shows the ground state and ESA spectrum which was obtained with a 120 fs (FWHM) excitation pulse at 900 nm and a 117 fs (FWHM) white-light probe pulse, delayed by 13 ps with respect to the excitation pulse, over the spectral range of 400–800 nm. For the first time we have observed an excited-state cross-section that is larger ( $\approx 3\times$ ) than that of the ground state cross-section at the peak spectral position, while the integrated areas of their absorption bands are nearly the same. This result needs additional investigation due to the fact that the oscillator strength in the excited-state is nearly equivalent to that in the ground state, and its implications for nonlinear optical applications such as optical limiting. Also, it is important to note that the excited-state cross-section is  $6.3 \times 10^{-16} \text{ cm}^2$  at 615 nm (peak ESA position), which is comparable to the largest measured results obtained by us [39] and described in the literature [40]. Fig. 5 also shows the ESA anisotropy spectrum which gives us information about the orientation of the ESA transition dipole moment relative to the polymethine chromophore (or  $S_0 \rightarrow S_1$  transition). As seen from the figure, the anisotropy value  $R = (0.32 \pm 0.07)$  and is approximately constant (within experimental errors) over the spectral range of 600–920 nm. This indicates that there are no transitions oriented at a large angle ( $>20^\circ$ ; typically for polymethines the  $S_0 \rightarrow S_2$  transition is oriented at an angle of greater than

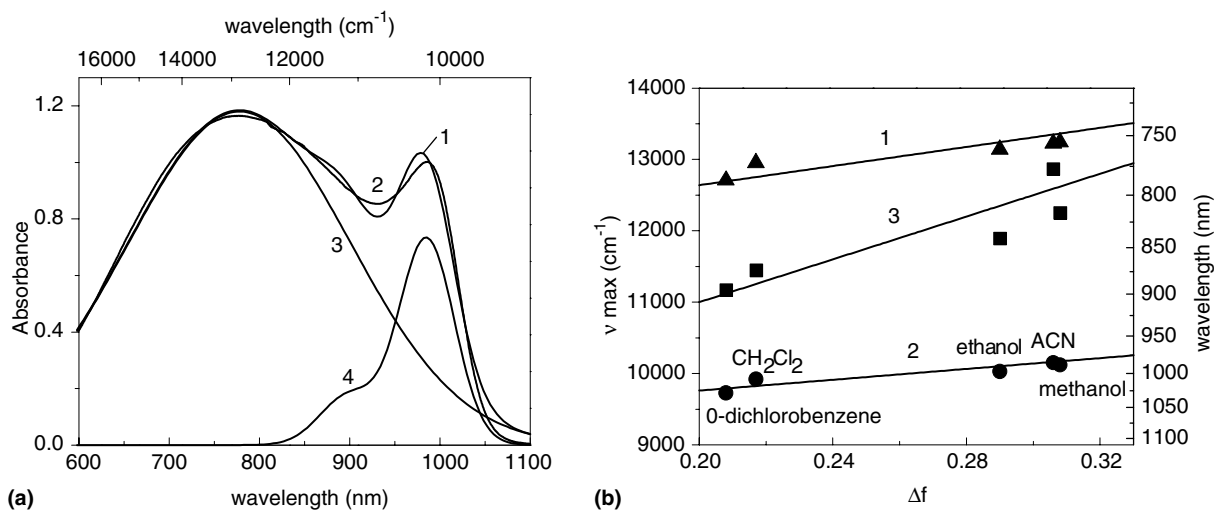


Fig. 4. (a) Separation of the absorption spectra of PD 1659 in ACN on two absorption bands: 2, experiment; 1, fitting curve:  $y = 1.18 \exp[-0.0000331(x - 778)^2] + 0.73 \exp(-0.000531(x - 985)^2) + 0.175 \exp[-0.00049(x - 899)^2]$ ; 3, asymmetric form  $y = 1.18 \exp[-0.0000331(x - 778)^2]$  and 4, symmetric form  $y = 0.73 \exp[-0.000531(x - 985)^2] + 0.175 \exp[-0.00049(x - 899)^2]$ . (b) Dependences of peak positions on solvent polarity for PD 2501 (curve 1) and for both forms of PD 1659: symmetric form (curve 2) and asymmetric form (curve 3).

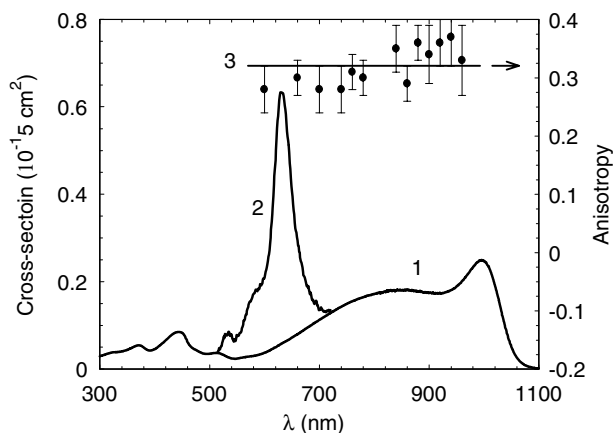


Fig. 5. Ground state absorption (1), ESA-spectrum (2) and ESA-excitation anisotropy spectrum (3) for PD 1659 in ethanol.

50° [36,37]) to the polymethine chromophore within this spectral range. Therefore, we can assume that this broad absorption band is connected with the  $S_0 \rightarrow S_1$  transition oriented along the molecular backbone.

#### 4.3. Saturable absorption measurements and the nature of the ground state of PD 1659

Nonlinear absorption measurements were performed to determine whether or not the broad ground-state absorption band for PD 1659 in the polar solvents is inhomogeneous and includes the absorption of two forms with symmetrical and asymmetrical charge distri-

butions. For this purpose we selected two pump wavelengths 760 and 955 nm, which are close to the two absorption peaks observed in ethanol solution (see Fig. 3(b)). The probe wavelengths were selected at 850 and 1000 nm. If the absorption spectrum is homogeneous and connected with the absorption of one form only, the change in optical density under strong pump irradiation should be identical across the entire spectrum. If, on the contrary, the absorption spectrum represents a mix of two independent forms, the two probe wavelengths should experience quite different transmittance changes. The results of these experiments for PD 1659 in ethanol together with a simplified schematic potential energy diagram are presented in Fig. 6.

As can be seen from the SA curves 1 and 2 (Fig. 6(a)), pumping at 955 nm strongly saturates the long wavelength region of the absorption band (probe 1000 nm), whereas the saturation effect at the short wavelength peak (probe 850 nm) is very small. From these results we can conclude that the absorption spectrum is inhomogeneous, consisting of absorption of two forms of the molecule. The results for pumping at 760 nm with the same probe wavelengths 1000 nm (curve 3) and 850 nm (curve 4) are presented in Fig. 6(a). Coincidentally, curves 2 and 4 strongly overlap in Fig. 6(a), so in Fig. 6(b), we show these same curves on a magnified transmittance scale.

The different kinetics shown in curves 1 and 3 may be connected with the change in ground state equilibrium. Depletion of the ground state population of the asymmetrical form produced by the 760 nm pump leads to

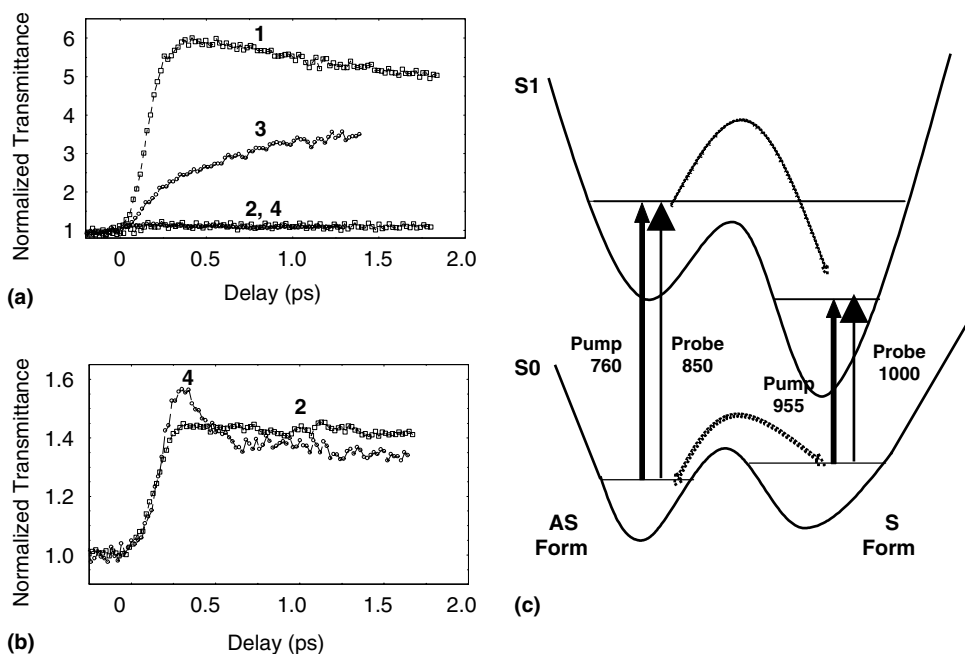


Fig. 6. (a) and (b) Saturable absorption of PD 1659 in ethanol at pump 955 nm, probes 1000 nm, curve 1 and 850 nm, curve 2, and at pump 760 nm, probes 1000 nm, curve 3 and 850 nm, curve 4; (c) Simplified schematic model of electron transitions for PD 1659.

either a transfer from the symmetrical to the asymmetrical form while in the ground state, or a transfer from the asymmetrical to the symmetrical form while in the excited state. Both processes lead to an increase of SA in the symmetrical form. A simplified schematic model of the possible transitions in PD 1659, presented in Fig. 6(c), is consistent with all experimental results.

## 5. Discussion

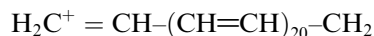
### 5.1. Methodology of quantum-chemical calculations

Quantum-chemical calculations were performed with the goal of understanding the main features of the electron density distribution in the ground and excited states for the thiocarbocyanines of different chain lengths.

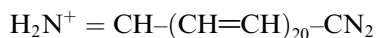
The equilibrium molecular geometry in the ground state and the charge distribution for the dyes in the ground and excited states is performed employing the semi empirical AM1 method (MOPAC package, gradient  $<0.01$  kcal/mol). Additionally, the charge distribution and electron transition energies were calculated in INDO/S and PPP (Parr–Pariser–Pople) approximations (with spectral parameterization) using the 100 lowest singly excited configurations. It was found that the calculated amplitudes of the charge waves are different for different methods (AM1, ZINDO/S or PPP). However, all methods predict similar trends for the behaviour of the charge waves as described below.

### 5.2. Quantum-chemical calculations for the model chromophore and the simplest polymethine molecule

In this section we describe the quantum-chemical calculations on the ground state electronic properties for the model chromophore and the simplest polymethine molecule (Brooker ion). This is done for two reasons. First of all, we wanted to compare our quantum-chemical calculations to previous published results. Secondly, the results from the model chromophore provide information about the width of the solitonic wave as described below. By comparing the width of the solitonic wave to the width of the charge distribution in the carbocyanine molecules we can determine if symmetry breaking will occur. The model structure is given as:



and the simplest PD, the so called Brooker ion, with the same chain length



It is seen in Fig. 7(a), that there is a considerable alternation of the charge magnitudes at the neighbouring atoms for both the model structure and the Brooker ion. The amplitude of the alternation for the model

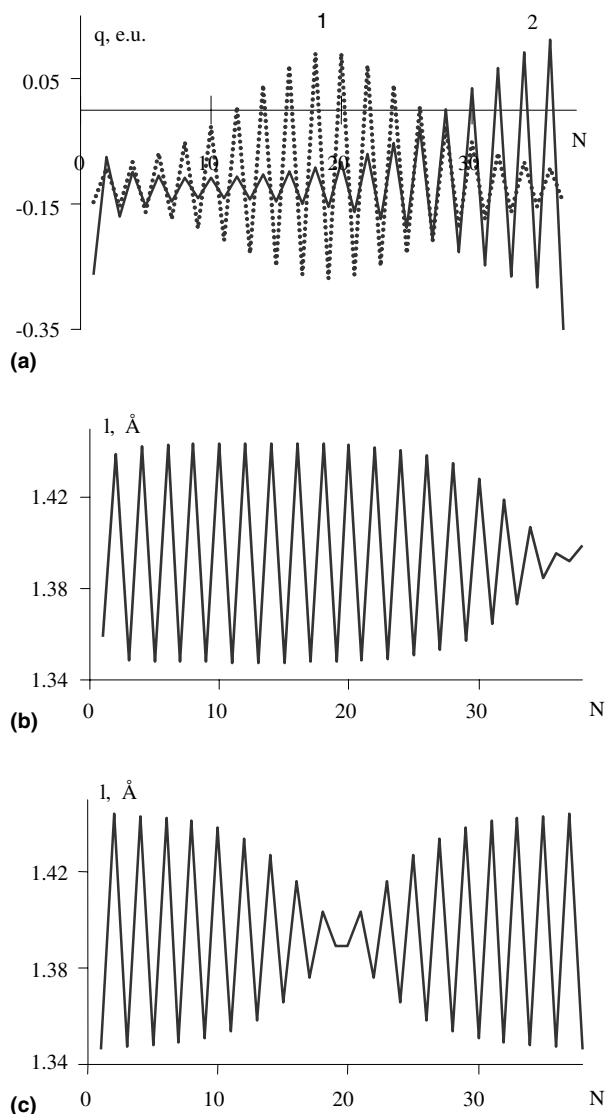


Fig. 7. (a) Charge magnitudes at carbon atoms for the model (1) and Brooker (2) ions. (b) Bond length alternation for the Brooker ion. (c) Bond length alternation for the model ion.

chromophore increases regularly from the chain ends to the middle of the chain (curve 1). It has already been shown that the peak of this solitonic wave always corresponds to the region of equality of the CC bond lengths and is placed on this “geometrical” or “topological” defect [22]. Fig. 7(c) shows that the minimum of the bond length alternation is also placed at the middle of the chain and coincides with the maximum of the solitonic wave. This is a general rule for the model chromophore with an arbitrary total length in the ground state global energy minimum [22,23]. Introduction of the terminal groups into the chromophore (Brooker ion) can lead to a substantial change in the amplitude of the charge alternation, see Fig. 7(a) (curve 2). For the long  $\pi$ -conjugated chain in the Brooker ion, the length of this chain becomes comparable (or longer) than the length of the



soliton (15–17 carbon atoms [22,23,26]) leading to a symmetry breaking effect. In this case the charge maximum accompanied by a geometrical defect could be shifted to one of the terminal groups. These shifts are shown in Fig. 7(a) (curve 2) and Fig. 7(b). As can be seen, the minimum of bond length alternation always coincides with the maximum of the corresponding charge wave.

### 5.3. Quantum-chemical calculation for thiocarbocyanines

#### 5.3.1. Ground-state

In this section we present our approach for the explanation of the specific features in the electronic structure and spectral properties of the series of thiocarbocyanines which have different chain lengths from monomethine ( $n = 1$ ) to hexamethine ( $n = 6$ ). Our approach is based on the previously mentioned concept that for the long IR dyes in the ground state there is a coexistence of two charged forms with symmetrical and asymmetrical charge distributions. We assume that if the length of the solitonic wave (15–17 carbon atoms) exceeds the dimension of the dye molecule which possesses a relatively short polymethine chain, only one symmetric charge distribution can be detected. In this case, PDs will show typical spectral behaviour such as narrow and intensive absorption bands, nonpolar solvatochromism, etc. If the length of the soliton becomes comparable to the length of the polymethine chain in the physical molecule, both the symmetrical and asymmetrical forms of the charge distribution can be detected. This leads to the dramatic changes in the spectral characteristics of the IR dyes.

It was shown in Section 4.1 that the absorption spectrum of PD 1659 strongly depends on the solvent polarity. The less polar solvent *o*-dichlorobenzene stabilizes the symmetric form only, whereas the more polar solvent ACN leads to the co-existence of both asymmetric and symmetric forms in the ratio of 5 to 1. In order to model the coexistence of two forms in the quantum-chemical analysis, we used the following procedure. First, the optimization process was performed for all the dyes of various chain lengths at gradient values  $< 0.01$  kcal/mol starting from the initial ideal molecule with equalized CC-bonds. This gives a single solution having only one form with the symmetrical distribution of the electron density for molecules up to tetracarbo-cyanine ( $n = 1-4$ ). For the longer PDs ( $n = 5, 6$ ) this procedure led regularly to the formation of a more stable form of the electron density, which was asymmetrical. Secondly, in order to model the formation of the symmetric form for PDs with  $n = 5, 6$  the optimization process was performed with a relatively large gradient values of 2–3 kcal/mol. This allowed us to get a solution for the symmetrical charge distribution form for the long PDs.

It has been proposed [23] to describe the charge wave by the amplitude of charge alternation:  $\Delta q = |q_n - q_{n+1}|$ , where  $q_n$  and  $q_{n+1}$  are the charges at two neighbouring atoms,  $n$  and  $n + 1$ . Similar to the charge distribution, the geometric deformation of the molecule can be estimated quantitatively by the differences in the lengths of the neighbouring CC-bonds:  $\Delta l = |l_{n,n+1} - l_{n+1,n+2}|$ , where  $l_{n,n+1}$  is the bond length between  $n$  and  $n + 1$  carbon atoms [22]. Fig. 8 presents the ground-state  $\Delta q$ - and  $\Delta l$ -functions for the series of the thiocarbocyanines with different chain lengths. It is seen from Fig. 8(a) that the calculated magnitudes of the charges,  $\Delta q$ , behave symmetrically up to tetracarbo-cyanines ( $n = 4$ ). Optimization of the electron density for penta- ( $n = 5$ ) and hexacarbo-cyanines ( $n = 6$ ) results in the formation of the asymmetrical forms. Thus, for the thiocarbocyanines containing benzothiazolium terminal groups, the symmetry breaking occurs at  $n = 5$ . For the Brooker ion, the calculations show the appearance of the asymmetrical form only when  $n \geq 8$ , i.e. symmetry breaking depends not only on the chain length itself, but on the total “effective” length of the chromophore, including the  $\pi$ -electron systems of both the terminal groups.

For the symmetric forms, the minimum amplitude of the charge is observed at the pairs of carbon atoms near the chain ends (see Fig. 8(a)), while the next pair of atoms shows the maximum of the  $\Delta q$ -function magnitude. This effect is connected with the donor influence of the terminal groups. For the longer molecules, the shape of the  $\Delta q$  function in the middle of the chain

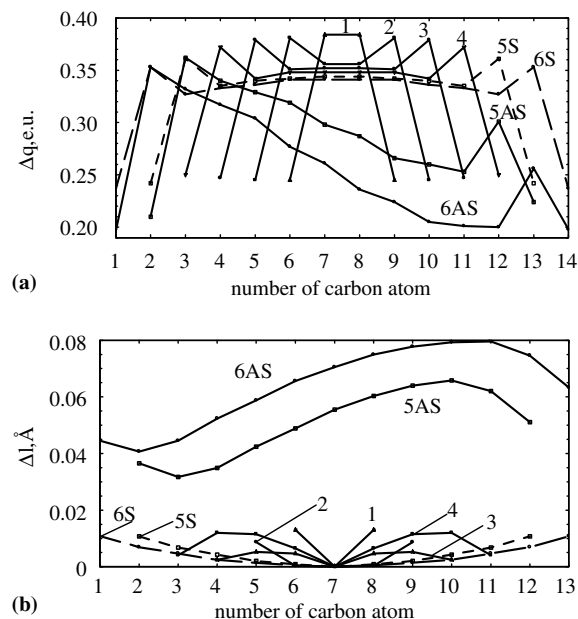


Fig. 8. Ground state  $\Delta q$ , (a) and  $\Delta l$ , (b) functions for the series of the thiocarbocyanines with the different length of the chain ( $n = 1-6$ ). S and AS are related to symmetrical and asymmetrical forms.

shows a typical shape of the solitonic wave with a nearly constant alternation of the charges. For the asymmetric forms of the thiocyanines ( $n = 5, 6$ ), the maximum amplitude is shifted to one of the chain ends similar to the behaviour of the asymmetric form in the Brooker ion (Fig. 7(a)); only the last two pairs of atoms disrupts this regularity.

Fig. 8(b) shows the calculated values of the  $\Delta l$  functions. It is seen that the shape of the bond alternation is substantially distorted when  $n \geq 5$ . It is necessary to note that the  $\Delta l$  functions for the asymmetric forms can reach a considerable magnitude ( $\approx 0.08 \text{ \AA}$ ), which is close to the amplitude of the bond length alternation in polyenes [29]. It is also seen that the shape of the symmetric  $\Delta l$  functions for the shortest molecules ( $n = 1, 2$ ) differs somewhat from the  $\Delta l$  functions for the cyanines with  $n = 3, 4$ , which is similar to the behaviour of the corresponding charge wave functions. This feature is also connected to the influence of the terminal groups.

### 5.3.2. Excited-state calculations and the nature of $S_0 \rightarrow S_1$ transitions in PD 1659

In this paper we only consider the Franck–Condon electron transitions with the unchanged equilibrium geometry in the excited state. Therefore, only the change in the  $\pi$ -electron density is examined in this section.

It is well known that the ground state  $\pi$ -electron density distribution at the carbon atoms within the polymethine chromophore changes substantially in the excited state [10,30]. Quantum-chemical calculations performed in the framework of the different quantum-chemical methods (the simplest Huckel, Parr–Pariser–Pople, all-valence semiempirical methods as well as in *ab initio*) results in the reverse of the  $\pi$ -electron density at the carbon atoms, i.e. the sign of the charge in the excited state is opposite to that of the ground state. The calculated  $\Delta q$ -functions for the series of thiocyanines in the first excited state are presented in Fig. 9(a) ( $n = 1–4$ ) and Fig. 9(b) ( $n = 5, 6$ ). First of all, the magnitude of the amplitudes of  $\Delta q$  in the excited state is appreciably lower than in the ground state (compare with Fig. 8(a)) for the entire series including the asymmetric forms. Secondly, the influence of the terminal groups is a crucial factor in the alternation of charge for the shortest PDs. The magnitudes of the order of alternation at the chain ends in the ground state is opposite to that in the excited-state for the short molecules ( $n = 1–3$ ), while this order is the same for longer molecules, for both the symmetrical and asymmetrical forms. Fig. 9(a), (b) shows an interesting feature in the behaviour of the symmetric  $\Delta q$  function: an increase of chain length leads to an appearance of two minima in the central part of the chromophore localized on the 5th and 10th carbon atoms. In the ground state (Fig. 9(a)) this central part becomes broader in width with an increase of  $n$ . For example, the central part of the symmetric

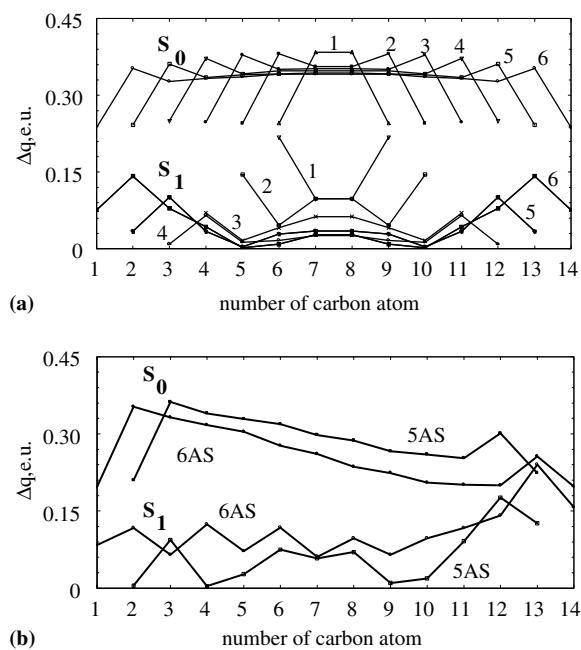


Fig. 9. (a) Ground- ( $S_0$ ) and excited-state ( $S_1$ )  $\Delta q$ -functions for the series of the thiocarbocyanines with the different length of the chain ( $n = 1–6$ ), symmetric forms only. (b) Ground- ( $S_0$ ) and excited-state ( $S_1$ )  $\Delta q$ -functions for the thiocarbocyanines with the chain length  $n = 5–6$ , asymmetric forms only. S and AS are related to symmetric and asymmetric forms.

form for hexacarbocyanine ( $n = 6$ ) is placed between the 3rd and 12th atoms. The chain sections in this region (between the 3rd and 12th atoms) for the ground state are characterized by nearly constant  $\Delta q$  values of 0.32–0.33 e.u. In the excited state between the two  $\Delta q$  minima are practically equalized, i.e.  $\Delta q \approx 0$  (Fig. 9).

As a rule, the appearance of two minima in the symmetric molecular form should lead to instability in the charge wave and could cause symmetry breaking at a relatively short chain length as compared to the ground state symmetry collapse. As seen in Fig. 9(b) the lengthening of the chain in the asymmetric form results in a distortion of the regularity of the  $\Delta q$  function. Calculations showed an unusual pulsation of charge amplitudes from one atom to the next within the polymethine chromophore, especially for hexacarbocyanine ( $n = 6$ ), which needs additional studies.

The difference between the charge distribution under the Franck–Condon  $S_0 \rightarrow S_1$  electronic transition for the symmetric and asymmetric forms of PD 1659 is shown in Fig. 10(a). It is clearly seen that if the nature of the transition for the symmetric form is connected with the charge transfer between neighbouring atoms in the chain, the nature of the same transition for the asymmetric form is different. Because of the charge localization, it is connected mostly with a charge transfer process from one part of the chromophore to an-

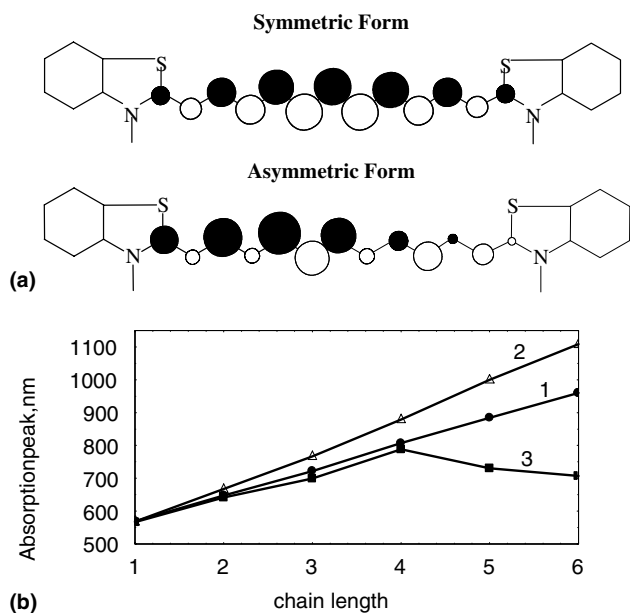


Fig. 10. (a) Electron energy redistribution on transitions  $S_0 \rightarrow S_1$  for symmetric and asymmetric forms in the model PD 1659 (without bridges in the chain). Dark circles correspond to an increase of electron density due to a transition, while the white circles correspond to a decrease. The diameters of the circles reflect the values of electron density change. (b) Calculated dependences of the absorption maxima for symmetric form in AM1 (1) and PPP (2) approximations, and asymmetric form in AM1 (3) on the length of the chain ( $n = 1-6$ ).

other. This leads to a saturation of the spectral position of the absorption maxima as the chain is lengthened. Fig. 10(b) shows the calculated dependence of the absorption peaks as a function of the chain length for the symmetric (curve 1 – AM1 approximation and 2 – modified by Fabian and Zahradnic [41] PPP approximation) and asymmetric (curve 3, AM1). For simplicity, the calculations were performed for the model structure of PD 1659 (without bridges in the chromophore). The most important point is that the symmetric form does not show a saturation effect even for hexacarboyanine ( $n = 6$ ), while the asymmetric form saturates at  $n = 4$ . These calculations show the trend which was observed experimentally.

## 6. Conclusion

We have performed a detailed experimental investigation and quantum-chemical analysis of PDs with different chain lengths, in particular, the tri- (PD 2501) and penta- (PD 1659) thiocarbocyanines. It is found that the relatively short wavelength absorbing PD 2501 exhibits classic nonpolar solvatochromism, consistent with symmetric ground and excited state charge distributions and small permanent dipole moments. In contrast, the absorption spectrum of PD 1659 demonstrates a strong solvent dependence. An increase

in solvent polarity leads to substantial band broadening represented by the growth of the short wavelength shoulder. This is a strong indication of polar solvatochromism, which is typical for dyes that exhibit charge localization and a large permanent ground-state dipole moment. Excited-state anisotropy measurements confirmed that this broad absorption band is connected with only the  $S_0 \rightarrow S_1$  transition. For the first time we have observed an excited-state cross-section that is larger ( $\approx 3\times$ ) than the ground state cross-section at the peak spectral position.

The analysis of the spectral data and femtosecond pump-probe saturation experiments enabled us to conclude that the PDs with the long polymethine chain exist in two charged forms in the ground state with symmetrical and asymmetrical distributions of the charge density. Quantum-chemical calculations presented in Section 5.2 gave an additional basis for this hypothesis. Experiments show that the less polar solvent, *o*-dichlorobenzene, primarily stabilizes the symmetric form. An increase of solvent polarity leads to an increase in the concentration of the asymmetric form. In the polar solvent ACN, both the asymmetric and symmetric forms can co-exist in the concentration ratio of 5 to 1.

We have performed a detailed quantum-chemical analysis with the goal of understanding the main features of the electron density distribution in the ground and excited states for the thiocarbocyanines with different chain lengths. We have come to the conclusion that an increase in the length of the polymethine chromophore leads to symmetry breaking and the appearance of an asymmetric form. For thiocarbocyanines the symmetry breaking effect was predicted and observed at  $n = 5$ . Our explanation is based on the previously proposed theoretical concept of the formation of a solitonic wave in the linear conjugated polymethine chromophores. We assume that if the width of the solitonic wave (15–17 carbon atoms) exceeds the dimensions of the dye molecule, then only the symmetric charge distribution can be detected. In this case, PDs show the typical spectral behaviour such as a narrow and intense absorption band, nonpolar solvatochromism, a red shift of the band with lengthening of the chain, etc. If the width of the soliton becomes comparable to the length of the polymethine chain then both the symmetrical and asymmetrical charge distribution can be detected as a function of the solvent properties. This leads to dramatic changes in the spectral characteristics of the IR dyes. The nature of the  $S_0 \rightarrow S_1$  transition for the symmetric form is connected with the charge transfer between neighbouring atoms in the chain. The nature of the same transition for the asymmetric form is different; due to charge localization it is connected mostly with the transfer process from one part of the chromophore to another and these dyes show limitations in the peak absorption positions.

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