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A Linear Dichroism Study of Pyrromethene-, Pyrromethenone- and Bilatriene-abc-Derivatives[1]

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The linear dichroism of several pyrromethene, pyrromethenone and bilatriene-abc derivatives embedded in a polyethylene film and oriented by stretching is investigated. On dissolving these pigments in the polymer matrix no changes in their conformations are observed, as compared to solutions in apolar solvents. Polarisation of the absorption bands of the pigments is deduced from the polarisation spectra. To enhance the solubility and orientation in the polymer, a pyrromethenone and a bilatriene-abc bearing a C_{18}-alkyl chain were synthesised for the first time.

(Keywords: Linear dichroism; Absorption band polarisation; Conformation; Pyrromethenes; Pyrromethenones; Bilatrienes-abc)

Zum Lineardichroismus von Pyrromethen-, Pyrromethenon- und Bilatrien-abc-Derivaten

Der Lineardichroismus einiger Pyrromethen-, Pyrromethenon- und Bilatrien-abc-Derivate, die in eine Polyethylenfolie eingebettet vorliegen, wird untersucht. Bei der Lösung dieser Pigmente in der polymeren Matrix wird keine Veränderung der Konformation im Vergleich mit Lösungen in apolaren Lösungsmitteln beobachtet. Aus den Polarisationsspektren wird die Polarisation der Absorptionsbanden dieser Chromophore abgeleitet. Ein Pyrromethenon und ein Bilatrien-abc mit C_{18}-Alkylseitenkette wurden zur Verbesserung der Löslichkeit und Orientierung in der Polymerfolie erstmals dargestellt.

Introduction

Bile pigments constitute the chromophoric group of several proteides which as antennas are responsible for harvesting light or as sensitive receptors for the photomorphogenesis in the plant kingdom[4]. These pigments are incorporated into the living system in a highly organised form as demonstrated by X-ray crystallography[5] and action dichroism[6] in case of phycocyanin and phytochrome, respectively. It therefore seemed to be of interest to investigate the light absorption properties of model pigments in an oriented system. This should yield informations on structural aspects of the pigments incorporated in an oriented phase as well as on the polarisation of their absorption bands. In this paper the synthesis of model pigments especially suited for incorporation in a nonpolar polyethylene film is reported and the linear dichroism of these compounds and several others in stretched polyethylene films is measured and discussed.

Materials and Methods

The following compounds were prepared and purified according to the literature: **1**[7], **2**[8], **3**[10], **4**[11] and **7**[12].

4-Ethyl-3-methyl-5-(3,5-dimethyl-4-stearoyl-pyrrolyl-2-methylidene)-3-pyrrolin-2-one [$C_{32}H_{52}N_2O_2S$]

267 mg $AlCl_3$ (2 mmol) are suspended in 20 ml dry CH_2Cl_2 and cooled to 0 °C. To this suspension 606 mg (2 mmol) stearoylchloride are added at 0 °C and after stirring for 0.5 h 230 mg (1 mmol) of 4-ethyl-3-methyl-5-(3,5-dimethyl-pyrrolyl-2-methylidene)-3-pyrrolin-2-one[13] are added at once. After stirring at 55 °C for 2.5 h the solution is poured on 50 ml H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, evaporated to dryness and crystallised from CH_3OH; yield 305 mg, i.e. 61%.

Mp.: 190–192 °C. MS: $m/e = 496$ (M^+).

^{1}H-NMR (360 MHz, δ, $CDCl_3$): 11.2 (s, NH), 10.6 (s, NH), 6.18 (s, =CH—), 2.74 (t-like, CH_2CO), 2.54 (q, $J = 7$ Hz, CH_2), 2.41 (s, CH_3), 1.98 (s, CH_3), 1.70 (q, $J = 7$ Hz, CH_2), 1.60 (s, CH_3), 1.30 (m, 28 H), 1.21 (t, $J = 7$ Hz, CH_3), 0.91 (t, $J = 7$ Hz, CH_3) ppm.

IR (KBr): $\nu = 1\,682, 1\,641, 1\,620\,cm^{-1}$.

4-Ethyl-3-methyl-5-(3,5-dimethyl-4-octadecyl-pyrrolyl-2-methylidene)-3-pyrrolin-2-one [**5**; $C_{32}H_{54}N_2O$]

248 mg (0.5 mmol) of the stearoyl derivative described above are dissolved in 30 ml dry tetrahydrofurane and cooled to 5 °C. Addition of 38 mg (1 mmol) $NaBH_4$ is followed by addition of 142 mg (1 mmol) $BF_3 \cdot C_2H_5O$ dissolved in 5 ml dry tetrahydrofurane during 10 min at 10 °C. After stirring for 1 h at 20 °C 5% HCl is added dropwise. The reaction mixture is poured on water and extracted with $CHCl_3$. After drying with Na_2SO_4 and evaporation the residue is chromatographed on SiO_2 using toluene: diethylether = 2 : 1 as the solvent. Yield 318 mg, i.e. 66%.

Mp.: MS: $m/e = 482$ (M^+).

UV ($CHCl_3$): $\lambda = 409$ nm ($\varepsilon = 32\,700$).

^{1}H-NMR (360 MHz, δ, $CDCl_3$): 11.2 (s, NH), 10.3 (s, NH), 6.20 (s, =CH—), 2.57 (q, $J = 7$ Hz, CH_2), 2.43 (s, CH_3), 2.17 (s, CH_3), 1.98 (s, CH_3), 1.28 (m, 34 H), 1.20 (t, $J = 7$ Hz, CH_3), 0.90 (t, $J = 7$ Hz, CH_3) ppm.

IR (KBr): $\nu = 1\,685\,cm^{-1}$.

3-Methyl-4-ethyl-2-methoxy-5-(3,4-dimethylpyrrolyl-2-methylidene)-5H-pyrrole [**6**; $C_{15}H_{20}N_2O$]

6 is prepared by methylation of **4** with trimethyloxoniumtetrafluoroborate in analogy to Ref.[14] in 88% yield as an amorphous powder. Its spectroscopic properties are in accord with its structure and comparable to the 3-methyl derivative of Ref.[14].

3,17-Diethyl-2,7,13,18-tetramethyl-8,12-dioctadecyl-1,19,22,24-tetrahydro-21H-bilin-1,19-dione [**8**; $C_{63}H_{99}N_4O_2$]

Two molecules of **5** were condensed by means of trifluoroacetic acid and dichlorodicyanobenzoquinone in analogy to Ref.[12] in 56% yield. Mp.: 88–89 °C.

UV-VIS ($CHCl_3$): $\lambda = 366$ (13 700), 618 (4 600), nm (ε).

IR (KBr): $\nu = 1\,680, 1\,626, 1\,588\,\mathrm{cm}^{-1}$.

MS (FD): $m/e = 943$ (M^+).

^{1}H-NMR (360 MHz, δ, $CDCl_3$): 6.63 (s, =CH—), 5.87 (s, 2=CH—), 2.5 (m, 2 CH_2), 2.03 (s, CH_3-7, 13), 1.84 (s, CH_3-2, 18), 1.18 (broad s, 34 CH_2), 0.83 (t-like, 2 CH_3) ppm.

The polyethylene used was Suprathen 200 (0.2 mm thickness) from Kalle and Co. AG.

The ^{1}H-NMR-, IR-, UV-Vis- and M-spectra were recorded using the Bruker WM-360-, Zeiss-IMR-, Perkin-Elmer-330- and Finnigan-MAT-115-spectrometers. The UV-VIS-linear dichroism was measured on a CARY-118 instrument using the polarised non polarised technique described in Ref.[15], in which two successive scans are taken of the stretched film: one uses light polarised parallel to the stretching direction and another uses depolarised light, by insertion of a depolariser in front of the polariser used for the first scan. A separate baseline is fixed for each polarisation by inserting sample free references in both the reference and the sample compartments. Very accurate measurements are obtained with this method since no turning of the sample film is required, thus the same sample population is measured with each scan. The dichroic ratio is calculated using equation (1).

$$d_0 = OD_{\parallel}/(OD - \log(1 + 10^{-\Delta} - 10^{OD - OD_{\parallel} - \Delta})) \qquad (1)$$

OD is the optical density from the depolarised measurement $OD_{\parallel}$ from the parallel polarised measurement, and Δ is a wavelength dependent correction factor for the UV-dichroism of the polyethylene matrix.

The incorporation of the substrates **1**–**8** into the polyethylene films is carried out as follows: Firstly the substrate is dissolved in $CHCl_3$ filtered through basic Al_2O_3 before use (in case of **1**, a trace of diisopropylamine was added to prevent protonation). Then a 2.5 × 5.0 × 0.02 cm polyethylene film is immersed in the $CHCl_3$ solution contained in a narrow glass test tube which contains a glass rod to minimise the free volume. The test tube is purged with argon and heated to 50 °C for 12–48 h in the dark. Then the film is removed from the solution, rinsed with $CHCl_3$ at 50 °C, dried in hot air and stretched in a line draw, approximately 500–600% to its yield point. The reference films are prepared in the same manner.

Results and Discussion

1. Pyrromethenes and Pyrromethenones

There is no indication of a different light absorption between nonpolar solvents, and solutions of the derivatives **1**–**6** incorporated in

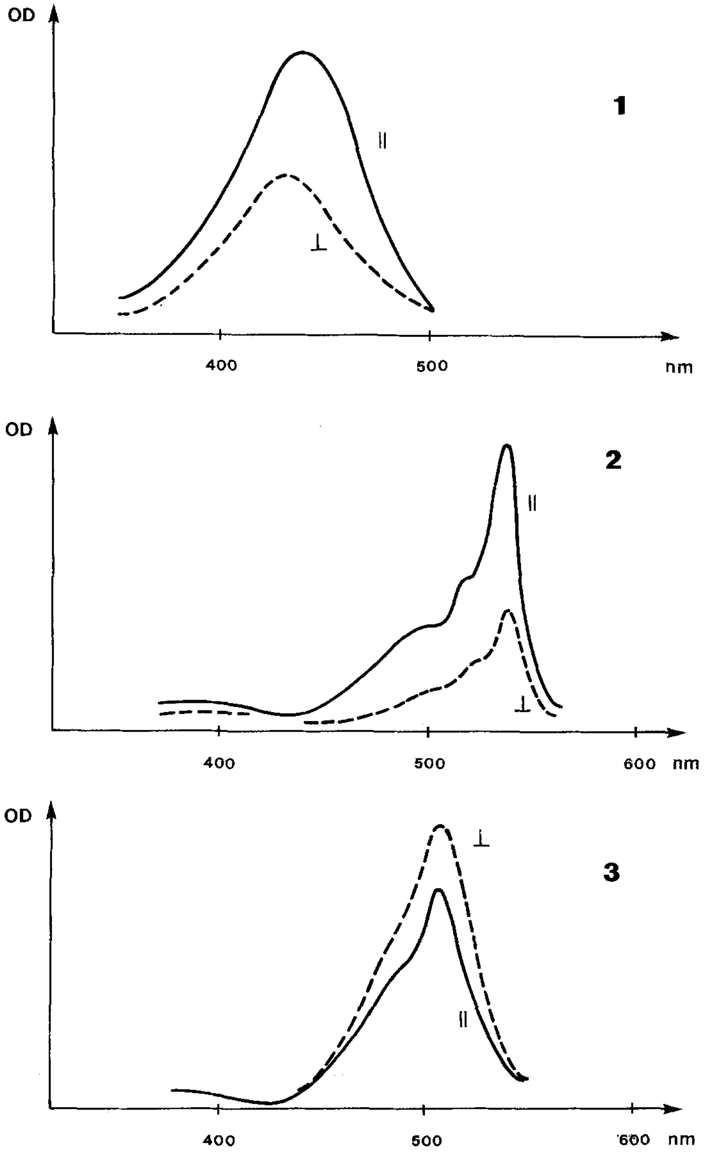


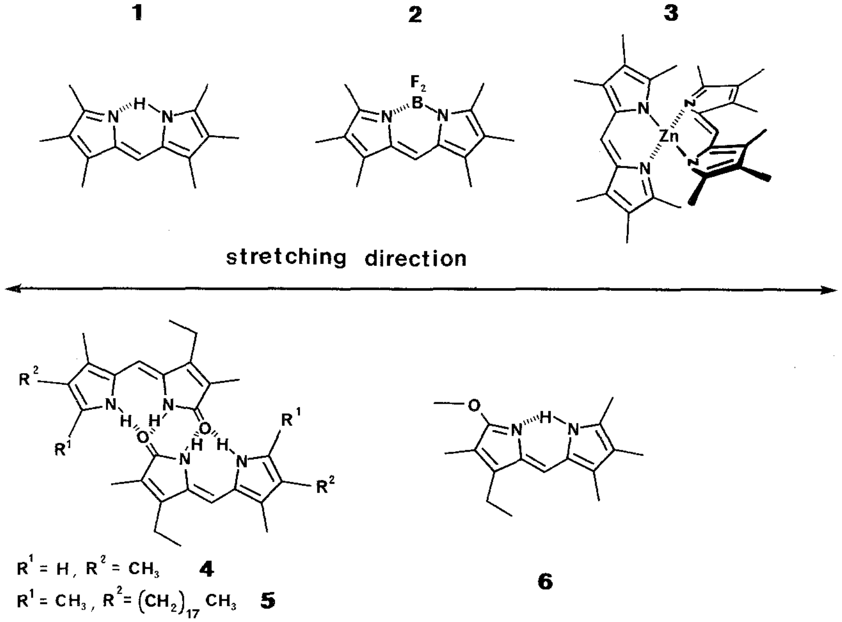
Fig. 1. Polarisation spectra of **1**–**3**. || . . . the curve obtained by light polarised in the direction of film stretching; ⊥ . . . the curve obtained by light polarised perpendicular to the film stretching

polyethylene film. This shows that there is no difference between the stereochemical features of these compounds in solutions and embedded in the polymer film.

The polarised spectra of **1** and **2** (Fig. 1) clearly reveal that these pyrromethene derivatives, oriented on film stretching along their longest molecular dimension (Scheme 1), exhibit a parallel polarisation of the main absorption band, which is in agreement with quantum mechanical calculations[16]. Compound **2** shows a practically constant dichroic ratio ($d_0 = 2.5$) throughout the absorption band. Therefore, the shoulders of this band can be interpreted as vibrational structure of its main transition, due to the planar and conformational rigid chelate system.

The higher dichroic ratio of **2** ($d_0 = 2.5$) as compared to that of **1** ($d_0 = 1.5$) reflect its higher rigidity. It is interesting to note that in the zinc chelate **3** (Fig. 1), the sign of the polarisation "inverts", the absorption of light perpendicular to the film stretching being higher than that of light parallel to the stretching ($d_0 = 0.8$). This closely resembles the effect observed on comparing the dichroism of fluorene and vespirene[17]. The effect can be interpreted as follows: planar molecules incorporated in stretched polyethylene film tend to orient with their planes parallel to the

Scheme 1



stretching direction[3]. Therefore, zinc chelate **3** will be preferentially oriented with its two planar "halves", parallel to this direction. Accordingly, the long axes of the separate pyrromethene units will be oriented perpendicular to the stretching direction.

The polarisation results obtained with the liquid crystal induced circular dichroism of pyrromethenes[9] are in full agreement with those of the present linear dichroism study. However, the liquid crystal induced circular dichroism method was not applicable to the study of bile pigments due to their limitated solubility in the cholesteric mesophase.

The light absorption of **4** embedded into the polyethylene matrix closely resembles its spectrum in non-polar solvents such as tetrahydrofurane or chloroform in which pyrromethenones are associated in form of dimers[18], resembling the dimeric entities in the crystalline state[19]. Such dimers were also found in solutions of pyrromethenones in cholesteric mesophases[18]. Dimers of this type are oriented in the stretched matrix in the same manner as pyrromethenes **1** and **2**, as shown by a d_0-value of 2.4 for **4** and 2.0 for **5** (Fig. 2).

The preferential orientation of the longest molecular axes of the two latter compounds and their dichroic spectra indicate that their main transitions are polarised along the longitudinal axis of the chromophore, in accord with quantum mechanical calculations[18] (Scheme 1). The dichroic ratio of lactim ether **6** ($d_0 = 1.6$) is similar to that of **1**, but it is smaller than the dichroic ratios of the dimers **4** and **5**. This lower value of 1.6 for **6** indicates a lower orientation in the film, which is due to its higher flexibility, similar to that of pyrromethene **1**. The dimers **4** and **5**, on the other hand, held together by an efficient hydrogen bonding system, have more planar and rigid structures and therefore higher orientations in the film.

2. *Bilatrienes-abc*

The bilatriene **7** strongly resists incorporation into the polyethylene film due to its very small solubility in this phase. Only very faintly colored films could be obtained and therefore stacks of such films had to be used. The absorption spectrum of **7** in polyethylene is comparable to its solution spectrum indicating that the circular helical solution conformation of this chromophore[20] remains unchanged in the polymeric phase. The weak dichroic signals for both the short and the long wavelength band ($d_0 = 1.3$ and 1.05, respectively, points to an orientation typical for disc shaped molecules as has been observed for coronene or the helicenes[21] (Scheme 2).

Solubility in the polymeric phase and orientation of the chromophore in the stretching process is enhanced by attaching long alkyl side chains in positions 8 and 12 of **7**, forming bilatriene **8**. Again, there is no change in its absorption spectrum in the polyethylene film, as compared to that in

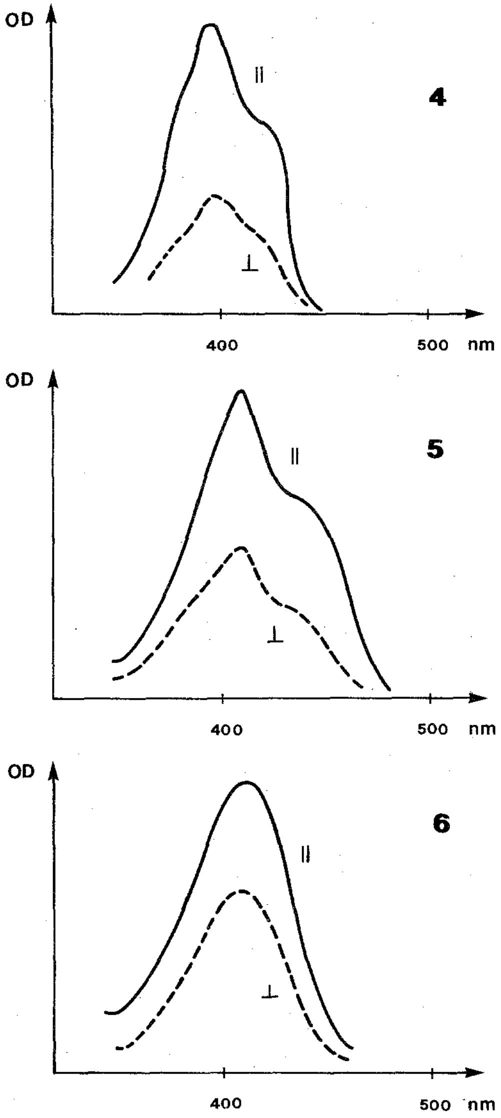
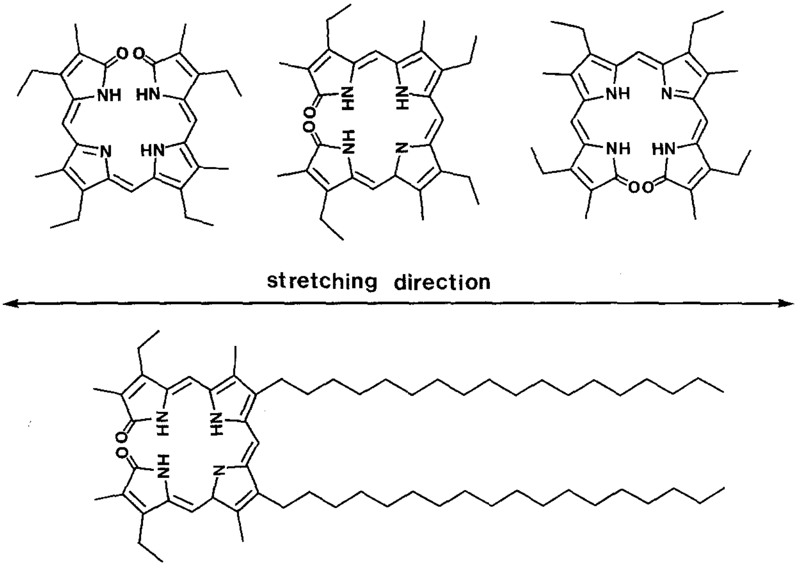


Fig. 2. Polarisation spectra of **4**–**6**. || . . . the curve obtained by light polarised in the direction of film stretching; ⊥ . . . the curve obtained by light polarised perpendicular to the film stretching

Scheme 2



7

8

solutions (i.e. the optical densities of the short versus the long wavelength bands remain at a constant ratio and the absorption wavelengths are not significantly different in the two phases). However, the polarisation spectrum of **8** oriented in the stretched film as indicated in Scheme 2, reveals a perpendicular polarisation of the long wavelength band and a parallel polarisation of the short wavelength band (both with respect to the orientational axis). The dichroic ratios of 1.47 and 0.85 for the short and long wavelength bands, respectively, compare favourable with the results obtained for pyrromethene **1** and pyrromethenones **4** and **5**. The long wavelength band of **8** is polarised along the main axis of the pyrromethene moiety whereas the short wavelength band is polarised in the direction of the pyrromethenone fragment. This result is also in agreement with quantum mechanical calculations[22]. The linear dichroism of biliverdin incorporated in stretched polyvinyl alcohol films have been reported previously[23]. It was suggested on the basis of these measurements and quantum mechanical calculations, that biliverdin in this film has a partially uncoiled conformation. It should be pointed out, however, that the orientation, as well as conformation of substrates in polyvinyl alcohol can be changed considerably by hydrogen bonding with the polymer.

Our results, however, reveal clearly that these compounds have similar conformations in both matrices. There is ample evidence that this conformation is helical.

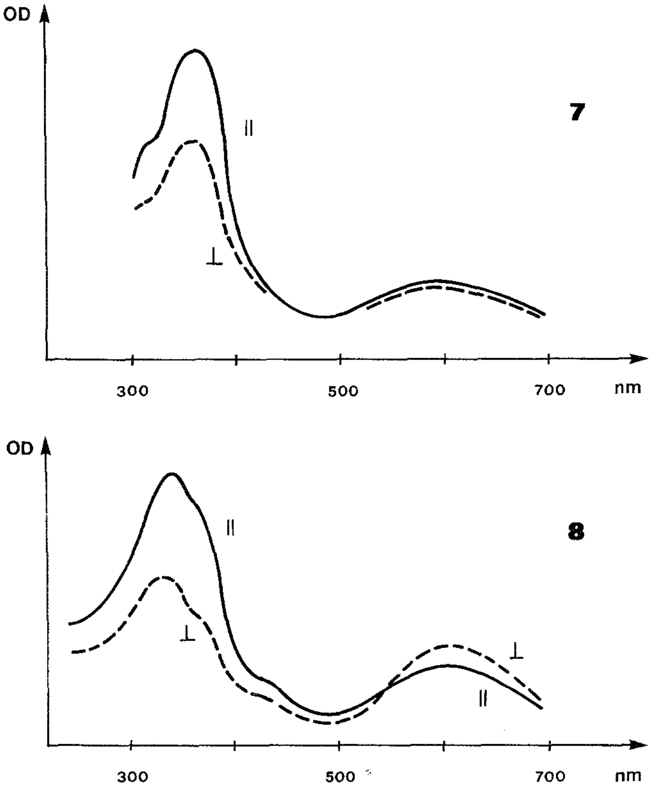


Fig. 3. Polarisation spectra of **7** and **8**. || . . . the curve obtained by light polarised in the direction of film stretching; ⊥ . . . the curve obtained by light polarised perpendicular to the film stretching

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