High Sensitivity Linear Dichroism Spectrum of Tetraphenylporphyrin in Stretched Polyethylene

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In a recent study [1] of linear dichroism in planar molecules of high symmetry, viz. certain triphenylmethane derivatives, different degrees of polarisation for different transitions were distinguished. This was possible because of the high orientation achieved, and the strong chromophores present in the oriented molecules. In that favourable case a conventional method could be used, i.e. separate absorption spectra were recorded for two orthogonal polarisations of the electric vector of incident light, one of the directions being parallel to the direction of orientation (= stretch) of polymer film.

This method is, however, difficult, to apply in cases where one of the three factors necessary to obtain linear dichroism is weak even if the others are strong. These factors are (1) the orientation of the chromophore (i.e. the non-isodimensional shape of the molecule); (2) optical anisotropy (i.e. non-spherical polarisation of the transition moment); (3) high absorption intensity (i.e. non-zero transition probability).

However, recently one of us (B.N.) [2] has developed a method of high sensitivity for the study of linear dichroism for exactly such cases.

In the present investigation we have used this method to directly measure, with high amplification, the differential absorption, $A(\parallel) - A(\perp)$ ($\parallel$ denotes light vector parallel to stretch, $\perp$ perpendicular) of neutral tetraphenylporphyrine. The planar shape and the large dimension of the molecule guarantee a high degree of orientation, and its symmetry (D_{4h}) implies that any transition will be either polarized in the molecular plane (xy) or perpendicular to it

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(z), except for perhaps intermediate polarisation originating from the phenyl rings if these are not exactly perpendicular to the porphyrin plane.

From the model of orientation of a planar molecule with high symmetry, we know [1,3] that $A(\parallel) > A(\perp)$ means that the transition is polarised mainly in the molecular plane while $A(\perp) > A(\parallel)$ implies an out of plane polarisation. This follows from the fact that the molecules will be oriented in the stretched film with their z-axes perpendicular to the stretch direction. Thus, in the present case, we expect for an xy-polarised transition $A(\parallel) - A(\perp)$ to be positive; for a z-polarised it should be negative. As the effects may be partially cancelled by similar effects with opposite sign originating from neighbouring transitions, they may be recorded only as a positively and negatively directed peak, respectively, on the $A(\parallel) - A(\perp)$ curve.

The ordinary absorption spectrum (Fig. 1) shows from low to high energy, transitions at the following wavelengths (in nm, wavenumbers in kK in parenthesis): 650(15.4), 591(16.9), 547(18.3), 514(19.5), 480(20.8), 417(24.0), ca. 400[s](25), ca. 370[s](27), ca. 350[s](28), ca. 310[s](32), ca. 280(36), s = shoulder. From the polarised differential spectrum, it is obvious that the first five transitions are perfectly xy-polarised (the wavelengths of the extrema correspond perfectly to the maxima of the ordinary absorption spectra). The Soret band with major xy-polarisation then follows, but with a z-polarised transition on the high energy side (arrow). Because of the shift in apparent position of the extrema of components of opposite sign,* the z-polarised "trough" can probably be traced to a transition at about 400 nm. In this region one actually expects [5] an $n \rightarrow \pi^*$ transition with weak intensity. It has, however, never before been resolved from the predominating Soret band. The bands at shorter wavelength appear all to be xy-polarized except for a possibly z-polarized contribution at very short wavelength, which according to the above can be assigned to the transversal transitions of the benzene rings.

The polyethylene film was soaked in a chloroform solution of tetraphenylporphyrin (at 60° for 20 h); solid substance was washed from the film surface and the film was stretched to 3.00 times its original

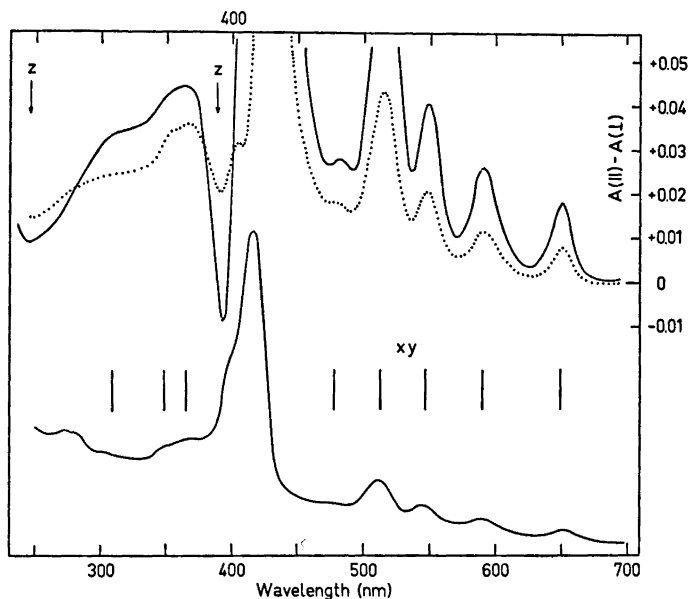* For a discussion of Gaussian curves with opposite, signs see Ref. 4.

Fig. 1. Above: Linear dichroism, $A(\text{II}) - A(\perp)$, of tetraphenylporphyrin, dissolved in polyethylene film (thickness 0.02 mm, R = 3.00),[3] $\cdots$ low concentration. Arrows denote out-of-plane transitions, vertical lines denote in-plane transitions. Below: Absorption spectrum (arbitrary units) in polyethylene solution. A solution in chloroform gave a very similar spectrum (d = 0.01 cm).

length. The fact that $R_D = A(\text{II})/A(\perp)$ for the xy-polarized transitions takes values $2.0 - 2.4$, indicates about 100 % orientation ($f = 1$) according to our outline[1] on linear dichroism of planar "circular" molecules. (With $\beta = 0$, $f = 1$ is $R_D = 2$.[1])

Measurements (to be published in detail later on) have also been performed on polyethylene solutions of iron(III) tetraphenylporphyrin. As expected from theory, no z-polarized component in the Soret region was observed.

The data from the present study show that the so called "Longo" band,[6] which has been interpreted as a new $\pi \rightarrow \pi^*$ band,[6] has the proper polarization for that assignment. The z-polarized band in the Soret region is at energies consistent with the $n \rightarrow \pi^*$ transitions calculated by Sundbom.[4,5]

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