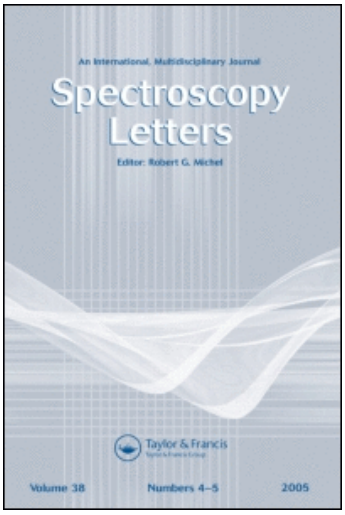

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Orientation and Transition Moment Directions of Small Planar Molecules in Stretched Polymer Films

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ORIENTATION AND TRANSITION MOMENT DIRECTIONS OF SMALL PLANAR MOLECULES IN STRETCHED POLYMER FILMS

KEY WORDS: Linear dichroism, transition moment directions, pyrimidines.

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We are concerned with the determination of electronic transition moment directions in molecules of low symmetry, purines and pyrimidines in particular, by the use of dichroic spectra in stretched polymer films.

We express our results in terms of a dichroism of absorbance defined by $R_Z = A_Z/(A_Z+2A_Y)$, where YZ is the plane of the film and Z is the direction of stretch.[1] For a particular transition i in a planar molecule, R_Z^i is given by

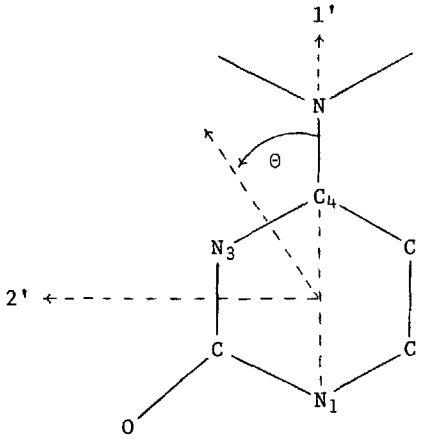
$$R_Z^i = K_1 \cos^2\theta_i + 2K_{1,2} \cos\theta_i \sin\theta_i + K_2 \sin^2\theta_i$$

$$= K_1 \cos^2(\theta_i - \theta_{OA}) + K_2 \sin^2(\theta_i - \theta_{OA})$$

where the K_j's are molecular orientation parameters, θ_i is the angle between the transition moment and axis 1' of an arbitrary molecule-fixed coordinate system (1',2',3') and θ_{OA} is the angle

between the axis 1' and axis 1, the orientation axis in that molecule-fixed system (1,2,3) where $K_{12}=0$.

Consider the pyrimidine derivative cytosine; the molecule-fixed (1',2',3') system is chosen as indicated below with the 3' axis perpendicular to the molecular plane.



We measure the ultraviolet dichroism of stretched films in cytosine in poly(vinyl alcohol), PVA, as well as the infrared dichroism R_Z^{CO} of the carbonyl stretching vibration[2] at 1660 cm^{-1} where the absorption of PVA itself is not excessive. Θ_{CO} is known, which still leaves three unknowns, K_1, K_2 and Θ_{OA} to be determined from just one equation. However, one may set up the following additional inequalities.

$$0.34 \leq K_2 \leq R_Z^{min};\ R_Z^{max} \leq K_1 \leq 0.54;\ K_1 + K_2 \leq 0.85$$

where R_Z^{min} and R_Z^{max} are minimal and maximal values, respectively,

of *all* transitions measured for the given polymer/solute system. The numerical limits are based on results pertaining to a number of other pyrimidines and small molecules whose orientation characteristics are similar.[3] These inequalities impose sufficient restrictions to enable meaningful values for the orientation parameters and for Θ_{OA} to be obtained. We shall discuss elsewhere the fact that for purines and pyrimidines the orientation axis is close to the principal polarisability axis.[3] However, this information cannot be used to choose between the two calculated orientation axes in this case because the principal polarisability axis of cytosine subtends an angle[4,5] of about 30° with axis 1', midway between Θ^1_{OA} and Θ^2_{OA}. The orientation parameters for a given film and both of the calculated orientation axes are thus used in conjunction with the data for the three ultraviolet transitions[6], R_Z^I, R_Z^{II} and R_Z^{III}, to obtain four possible moment angles for each of the transitions; these are shown in table 1.

Table 1 - Cytosine

i	Θ^i_{OA}	*j*	Θ^i_{Ij}	Θ^i_{IIj}	Θ^i_{IIIj}
1	59° ± 9°	1	90° ± 7°	68° ± 16°	-76° ± 4°
		2	27° ± 14°	48° ± 20°	12° ± 14°
2	4° ± 9°	1	35° ± 14°	15° ± 20°	-43° ± 4°
		2	-28° ± 7°	-6° ± 16°	50° ± 14°

We have also measured the dichroism of cytidine and of 5'-cytidine monophosphate and used procedures similar to those described for cytosine to obtain the sets of results shown in tables 2 and 3.

Table 2 - Cytidine

i	θ^i_{OA}	j	θ^i_{Ij}	θ^i_{IIj}	θ^i_{IIIj}
1	-80° ± 11°	1	-65° ± 5°	-45° ± 5°	3° ± 17°
		2	85° ± 27°	65° ± 18°	19° ± 20°
2	-38° ± 11°	1	-53° ± 5°	-73° ± 5°	43° ± 20°
		2	-23° ± 27°	-3° ± 18°	60° ± 17°

Table 3 - 5'-CMP

i	θ^i_{OA}	j	θ^i_{Ij}	θ^i_{IIj}	θ^i_{IIIj}
1	-81° ± 9°	1	-70° ± 6°	-42° ± 6°	-8° ± 22°
		2	87° ± 21°	62° ± 17°	29° ± 28°
2	-38° ± 9°	1	-49° ± 6°	-76° ± 6°	33° ± 28°
		2	-25° ± 21°	0° ± 17°	70° ± 22°

On the basis of crystal polarised absorption[7] and specular reflectance[8] measurements the transition moment directions for transitions I and II should be approximately parallel to axis 1'. Using this criterion the correct choice appears to be i=2 in each of the three compounds studied and j=2 for cytidine and 5'-CMP.

The choice of the value of j for cytosine is ambiguous, however; Θ^2_{I2} is closer to the results for the other two compounds while Θ^2_{I1} is closer to the crystal result. Comparison of the results for transition III, on the other hand, supports a value of 50° ± 14° for cytosine.

In these experiments ultraviolet spectra were measured in a special attachment to a Zeiss PMQ II spectrophotometer[9] which minimises scattering corrections. Infrared spectra were determined with a Perkin-Elmer Model 457 spectrophotometer using matching grid polarisers in both beams. Base-lines were determined by removing the solutes from the film with ethanol-water mixtures. The results shown are based on three cytosine films and on two for each of other compounds, each stretched 3.5 times. Corrected absorbances for the separate runs were added and the totals used to evaluate the results.

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