

Directions of Moments and Assignments of $\pi \rightarrow \pi^*$ Transitions in Certain Biaryls from Polarized Spectroscopy on Oriented Films and from Molecular Orbital Calculations

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UV absorption spectra are reported for 2,2'-bipyridyl, 2,2'-bithienyl, 3,3'-bithienyl, 5,5'-dimethyl-3,3'-bithienyl, hexamethyl-3,3'-bithienyl, biphenyl, and *o*-phenantroline as solution spectra (cyclohexane) and as polarized spectra in oriented polyethylene films.

By comparing the experimentally obtained directions for the studied $\pi \rightarrow \pi^*$ transitions with those obtained from MO calculations, using semi-empirical parameters, conclusions have been made about the predominating conformations.

The problem of making assignments for the UV electronic transitions of bithienyls was actualized by recent investigations on the *circular dichroism* * of certain optically active bithienyls.^{15,16,30}

Although the chemistry and the optical activity of biaryls has been extensively studied¹⁻⁹ only a few theoretical treatments have been reported.¹²⁻¹⁴ One concerns the bianthryls¹³ and derives the absolute configurations *via* a one-electron theory¹⁸ and the polarization directions of the transitions in anthracene obtained from the study of the polarized spectra of an anthracene crystal.¹⁷

* The present work is part of a general attempt to understand relations between directions of electronic transitions and the corresponding circular dichroism in optically active compounds by collecting experimental information. As has been generalized by Grinter and Mason,¹³ there are mainly two types of origins of circular dichroism: 1. Electronic transitions which are allowed by selection rules in magnetic dipole radiation fields and which mix with electric dipole transitions originating from dissymmetrically positioned substituents (*e.g.* $n \rightarrow \pi^*$ transitions of the carbonyl group and the low energy $d-d$ transition of metal complexes). 2. The coupling between *non-planar* electric dipoles located in separate chromophores (*e.g.* in helical polypeptides or in sterically hindered biaryls).

It is concluded in the above mentioned investigations that of the combinations of long-axis and short-axis polarized transitions, respectively (*in anthracene*) the two transitions (in bianthryl: $A \rightarrow A$ and $A \rightarrow B$)¹³ deriving from long-axis polarization (Fig. 1a) will both have a finite dipole strength and a non-zero rotational strength.* The long-axis polarized transition should give rise to two rotational components of equal magnitude but with different signs. The observation of two CD bands with different signs and equal areas corresponding to the long-axis polarized absorption band (of the anthracene crystal) thus manifests the assignment. It is not difficult to see (Fig. 1a) that of the corresponding short-axis transitions ($A \rightarrow A$ and $A \rightarrow B$), that with A symmetry has a magnetic moment (along the z -axis) but is devoid of electric moment. The corresponding B transition has an electric moment (along the y -axis) and a parallel small magnetic moment (due to rotatory displacement of charge across the twisted internuclear bond), *i.e.* only this transition can have finite rotational strength.

In Fig. 1b we imagine a fixed twisting of the carbon-carbon bond of biphenyl. If the benzene rings retain their planes it is obvious that of the A transitions only one has non-zero rotatory strength, *viz.* (a, a) with a rotation

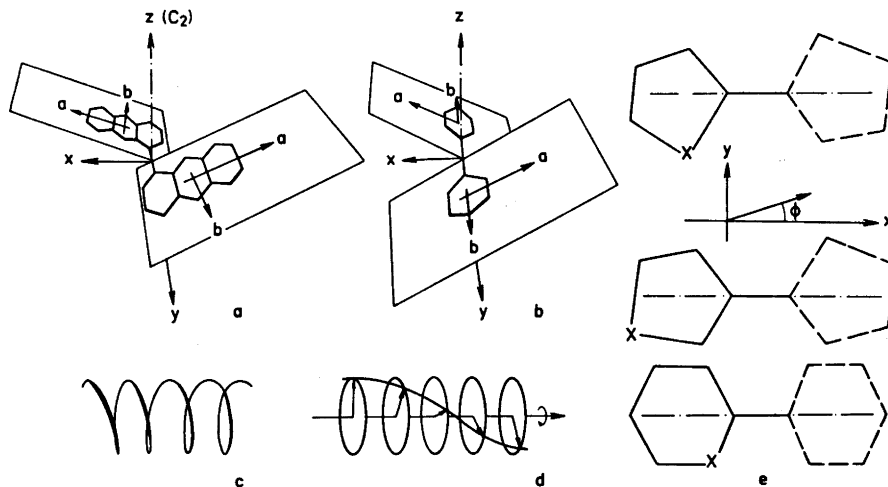


Fig. 1. (a) Coupling of the electric moments in bianthryl (a =long-axis polarized transition in anthracene, b =short-axis polarized) $A \rightarrow A$: a, a and b, b , $A \rightarrow B$: $a, -a$ and $b, -b$. (b) Coupling of moments in biphenyl, A : a, a and b, b , B : $a, -a$ and $b, -b$. (c) A right-handed helix. (d) Left circularly polarized light. (e) Directions of x and y axis used in this investigation and notation for the angle, ϕ , between the direction of the transition moment and the x axis. It should be observed that the experimental angle, α , considers the angle (without sign) between the *effective* long-axis of the molecule and the transition moment.

* By resolving the electric dipole moments of the transitions in the original anthracene molecule into components parallel and perpendicular to the C_2 -axis, in bianthryl it is possible to determine a theoretical rotational strength as the scalar product between the electric dipole moment and the correspondingly generated magnetic dipole moment.

of charge around the z -axis and a small parallel electric moment. If the molecule has a fixed twisted structure according to Fig. 1b, the charge will follow a *right handed helix* (cf. Fig. 1c), *i.e.* *left* circularly polarized light (the direction of rotation is given in Fig. 1d because of general confusion in current literature^{10,19}) will render higher absorption than right, *i.e.* the transition exhibits positive circular dichroism (positive rotational strength). Of the B transitions the $(a, -a)$ transition attains negative rotational strength parallel with the x -axis while the $(b, -b)$ transition which follows the carbon-carbon bridge (long-axis polarized) will exhibit positive rotational strength.

Contrary to the case of bianthryl where the directions of transition moments were either short-axis or long-axis polarized in anthracene (D_{2h}), the discussion for biphenyl is based on two representative transitions, a and b, in the benzene nuclei which by coupling should give only short-axis and long-axis polarized transitions in biphenyl (C_{2v}).

To be able to resolve an optically active biaryl it is necessary to arrange some steric hindrance preventing rotation around the connecting bond. The substituents required to give stable enantiomers, however, will modify the polarizations discussed. Especially alkyl substituents in *ortho* position to the connecting bond confer electric moments with short-axis polarization. As the long-axis-polarized transition only renders rotational strength by the local moments along the twisted bond (which constitute only a small fraction of the total electric moment), its circular dichroism may be dominated by other bands.¹⁹ The review above is intended to (a) help the reader understand the possibilities of direct interpretation of circular dichroism spectra with a knowledge of moment directions of the corresponding transitions, (b) indicate the usefulness of a simple vector combination in a complex composed of unchanged chromophores.

The main purpose of the present investigation has been to try to determine the directions of the $\pi \rightarrow \pi^*$ transitions in certain biaryls. The best method for this is the study of the absorption of linearly polarized light in the at least partially oriented assembly of molecules obtained by stretching a polymer sheet in which the sample is dissolved. The method has been improved and extensively described by Thulstrup, Michl and Eggers (Ref. 20 and references therein). It can be assumed that the solute molecules are embedded fairly rigidly in cavities between the polymer chains. As the molecules will be separated from each other and the polymer surrounding structure will be probably irregular, the molecular state is far from the perturbed state in a crystal.

Even if the studied hetero-biaryls are assumed to be approximately planar two different possible symmetries must be considered: C_{2v} (*cis*) and C_{2h} (*trans*). A simple group-theoretical inspection shows that a transition can be expected to deflect from pure long-axis or short-axis polarization only in the *trans* case. The polarization results should thus in principle establish the conformation. As, however, the bands are broad, they will cover each other and it can be difficult to tell if a transition is both long-axis and short-axis polarized or if the studied band originates from *two* transitions with orthogonal polarization. A comparison between data for the two configurations from quantum chemical calculations and the experimental results, however, could increase the possibilities of deciding between such alternatives.

The experiments have therefore been accompanied by an SCF molecular orbital study of the $\pi \rightarrow \pi^*$ transitions for the planar *cis* and *trans* forms of bipyridyl and 5,5'-dimethyl-3,3'-bithienyl. The method used is essentially an SCF-MO-LCAO-CI method in the Pariser-Parr-Pople approximation, formally implying zero-differential overlap and semi-empirical determination of some integrals. This method has been presented in a series of papers³¹⁻⁴¹ and will not be repeated here. It has proved to be successful for the interpretation of electronic spectra of large organic molecules. Recently Skancke⁴² used this method for a molecular orbital study of 2,2'- and 3,3'-bithienyl.

The assumed structure of 2,2'-bipyridyl was chosen in accordance with the electron diffraction data of Almenningen and Bastiansen.⁴³ (See Table 3). In 5,5'-dimethyl-3,3'-bithienyl the structure was assumed the same as used by Skancke for 3,3'-bithienyl.⁴² Notations for directions of polarization are given in Fig. 1e.

EXPERIMENTAL METHOD

The preparation of the bithienyls has been reported elsewhere.^{15,16,30} 2,2'-Bipyridyl of *puriss* quality (Koch-Light) was recrystallized from hexane. All other chemicals were of *p.a.* quality and the solvents used were of spectroscopic purity.

Polyethylene films ("sandwich bags" and UVETEN according to Eggers *et al.*²⁰ were used, thicknesses 0.030 mm) were soaked in concentrated chloroform solutions of the substances to be studied (about 0.03 g solute/0.5 ml solvent). This was done in a sealed glass test-tube (diam. 9 mm), filled up with a glass rod (diam. 8 mm), at 60°C for one or two days. The film was then washed with ethanol, dried with a soft paper and stretched in a stretching device of the type described by Eggers *et al.*²⁰ The device fitted into the cell-compartment of a Cary 15 spectrophotometer together with a (17 × 17 mm) Glan polarizer (Bernhard Halle Nachfl., Berlin) fixed in the position which transmitted only light with the electric vector vibrating in the horizontal direction. (When speaking of linearly polarized light the old word "plane of polarization" should be avoided. The expression *direction of polarization* could instead be used for the direction (plane) of the electric vector. This direction is perpendicular to the "plane of polarization" which probably originates from the old Nörrenberg polarizer in which it equals the plane of reflexion). The film-holder could be turned around the direction of the light propagation. In figures and text the symbols \parallel and \perp will denote if the direction of stretching of the film (= direction of orientation of the effective long-axes of the molecules) is parallel or perpendicular, respectively, to the electric vector of the light.

As the cross section of the light ray is a vertical narrow rectangle, different areas of the film were exposed to the light in the two positions \parallel and \perp . Inhomogeneity in the film could thus cause erratic results. However, such errors could be ruled out by checking the absorbances at different positions of the floor of the cell-compartment.

A procedure which in several ways proved successful was to put the stretched film in a small amount of water between quartz plates. One plate (20 × 20 mm) was fixed to a square metal frame with a drilled hole (15 mm) for the light path, and which fitted into the arrangement for the ordinary stretching device in the cell-compartment, and with the possibility of different orientations (\parallel , \perp). The stretched film was removed from the stretching device and was fixed in the stretched state (clamped between metal bars and the metal frame) across the quartz plate. A drop of water was applied on both sides of the film and it was then covered with a second quartz plate. One apparent effect of this procedure was that the film turned from slightly opaque to quite clear. The transmittance increased from about 70 % to 90 %. A second and much more important advantage was the diminished evaporation (sublimation) of substance from the film. With, *e.g.*, biphenyl dissolved in an uncovered film a decrease in absorbance (*e.g.* at the long wavelength band) of almost 50 % was observed during 0.5 h, while with quartz-water-film-water-quartz the corresponding decrease was about 1 %. A third effect of this method was observed as a very small variation of absorbance when changing the

exposed area of the film. This showed that the inhomogeneity of the uncovered film was probably located to the film surface and not to concentration differences within the film.

The concentration of substance in the film was balanced to give a maximum absorbance of about 1.5 with \parallel orientation (either by varying the soaking time or the concentration of the chloroform solution). It was found that the solubility in polyethylene decreased in the sequence, hexamethyl-3,3'-bithienyl, 5,5' dimethyl-3,3'-bithienyl, 3,3'-bithienyl.

The absorbance spectra were recorded at $25 \pm 1^\circ\text{C}$ and were corrected for the absorbance of the empty film, which was approximately 0.1 for both \parallel and \perp orientation (\perp 10 % more than \parallel probably due to polarized scattering). About 15 films with each substance were studied (except in the 2,2'-bithienyl case where only two runs were performed). The stretching was varied between 2 and 3 times the original length.

EXPERIMENTAL RESULTS

In Figs. 2–6 representative absorbance spectra for the studied species are reproduced, both for the case of the electric vector being parallel with the direction of stretching ($A(\parallel)$) and perpendicular to it ($A(\perp)$), and with the substance dissolved in a polyethylene film for the case of unpolarized light

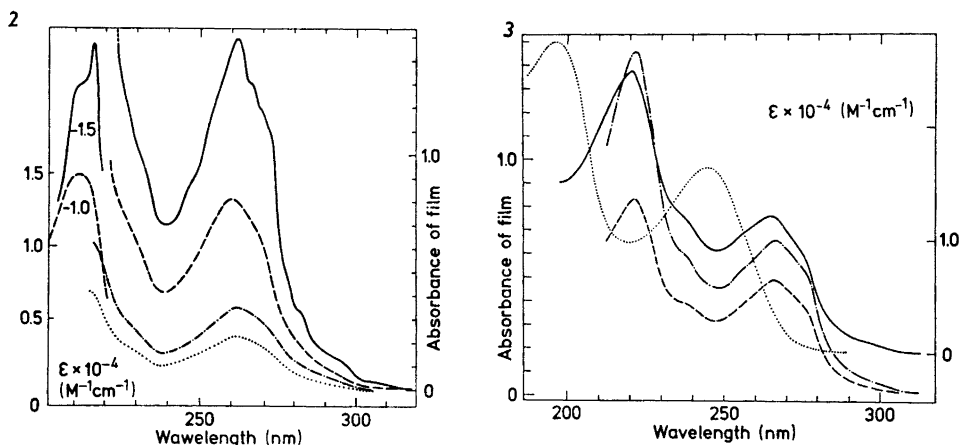


Fig. 2. Absorbance spectra of 3,3'-bithienyl, in film at -190° (right scale, —), in stretched film (right scale, \parallel - · -, \perp · · ·) and in cyclohexane (left scale, \parallel - · -, \perp · · ·) and in cyclohexane (left scale, random).

Fig. 3. Absorbance spectra of 5,5'-dimethyl-3,3'-bithienyl, in stretched film (left scale, \parallel - · -, \perp · · ·) and in cyclohexane (right scale —). Absorbance spectrum of hexamethyl-3,3'-bithienyl in stretched film (left scale \parallel or \perp · · ·) or in cyclohexane (right scale · · ·).

Fig. 4. Absorbance spectra of biphenyl in stretched film (right scale \parallel - · -, \perp · · ·) and in cyclohexane (left scale, —).

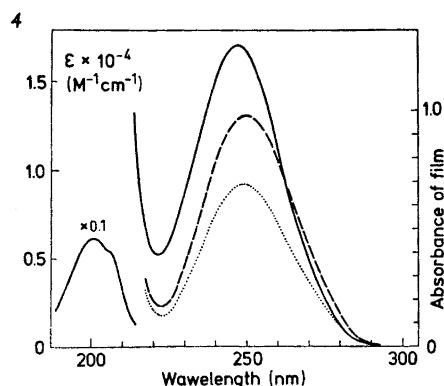


Table 1. Experimental data.

Substance	Condition	Positions of bands (wavelengths in nm) and polarizations	$\epsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)	$\frac{A(H)}{A(L)}$ (at $R = 2.0$)
3,3'-Bithienyl	- 190°C, film	309.0(a),296.0(b),282.5(c), 278.0(d),272.5(e),270.0(f) 266.5(g),262.0(h),252.5(i), 247.0(j),232.5(k),220.0(l), 216.0(m),211.5(n).		
	cyclo- hexane chloro- form film	261	1.33	
		211	2.51	
		263	1.17	
		260 x ($\alpha = 20^\circ$) 210 x ($\alpha = 0^\circ$)		1.40 1.50
5,5'-Dimethyl- 3,3'-bithienyl	cyclo- hexane	300(a),277(b),265(c), 255(d),240(e),220(f).		
		265	1.24	
	film	220	2.50	
		265 x ($\alpha = 40^\circ$) 255 x 220 x		1.25 1.75
Hexamethyl- 3,3'-bithienyl	cyclo- hexane film	244 (242) 195 244 and 197 x ?	1.63 2.73	1.02
2,2'-Bithienyl	cyclo- hexane	335(a),327(b),317(c),311(d) 302(e),290(f),275(g),254(h), 247(i),207(j),192(k).		
		302	1.23	
		247	0.71	
	film	192	1.60	
		306 x ($\alpha = 0^\circ$) 247 x and y ($\alpha = 46^\circ$)		1.50 1.10
Biphenyl	cyclo- hexane film	247	1.68	
		201 (205) ($> 250 x$) 250 x ($\alpha = 0^\circ$) ($< 200, x, y?$)	5.4	(1.6) (1.5) (1.4)
2,2'-Bipyridyl	cyclo- hexane	295(a),282(b),275(c),244(d) 237(e),232(f),190(g)		
		282	1.50	
		237	1.20	
	film	191	4.0	
		220 - 250 x 250 - 300 x		1.50 1.50
<i>o</i> -phenan- troline	film	266 x		1.3

and a random solution (cyclohexane). Fig. 2 also shows a low-temperature spectrum (-190°C) of 3,3'-bithienyl in polyethylene. Transition wavelengths and observed or concluded polarizations are collected in Table 1 together with the values of the ratio $R_D = A(\parallel)/A(\perp)$ at selected wavelengths. (The directions in the molecules are denoted as follows: *the long-axis* = the connecting carbon-carbon bond (x), *perpendicular to this direction* but in the plane of the rings (y). All transitions are assumed to be positioned in the x,y -plane; cf. Fig. 1e.)

All oriented states referred to above consider the state obtained by stretching the film exactly two times its length which we shall denote as a *stretch-factor*, R , of 2.00. In Fig. 7, however, R_D is plotted against R , for the different species (and an experimentally obtained relation between the stretch-factor, R , and the *stretch ratio* of Tanizaki,²⁵ R_S , is visualised. R_S is the ratio between the axes of the ellipse into which a circle on the film surface is changed at the stretching).

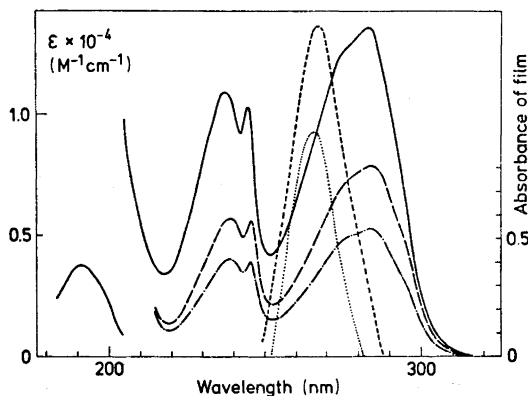


Fig. 5. Absorbance spectra of 2,2'-bipyridyl in stretched film (right scale, \parallel ---, \perp - · - ·) and in cyclohexane (left scale, ———). Absorbance spectrum of *o*-phenantroline in stretched film (left scale + 1.5, \parallel ---, \perp · · ·).

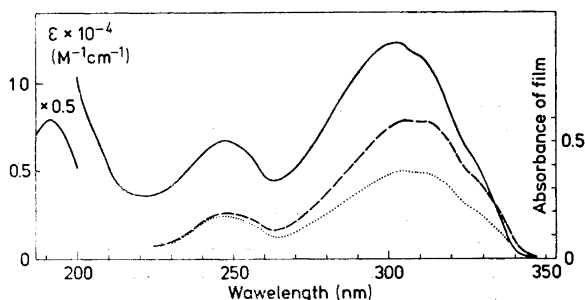


Fig. 6. Absorbance spectrum of 2,2'-bithienyl in stretched film (right scale, \parallel ---, \perp · · ·) and in cyclohexane (left scale, ———).

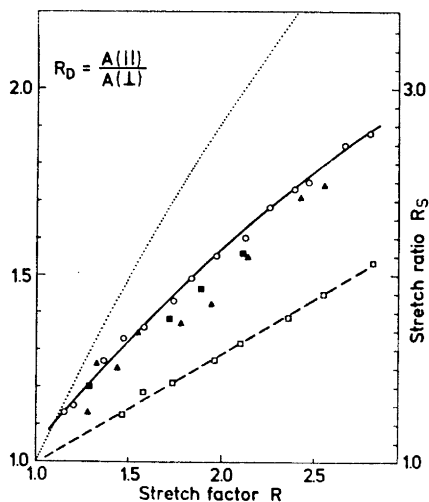


Fig. 7. Values of $R_D = A(II)/A(I)$ from the longest wavelength bands at different stretch factors (R) for 3,3'-bithienyl (Δ), 5,5'-dimethyl-3,3'-bithienyl (\square), biphenyl (\blacksquare), 2,2'-bipyridyl (\circ), and the relation between the stretch factor, R , and the stretch ratio of Tanizaki (R_S) (\cdots).

There are several slightly different methods available for treating the obtained spectra $A(II)$ and $A(I)$. Most information, however, will appear directly at an inspection of those two spectra (further treatment must often rely upon assumptions which can make the result dubious). If a band thus shows an R_D value very much larger than unity then the corresponding transition is predominantly directed towards the (effective) long axis (x) of the molecule (and with R_D less than unity the direction approaches the plane perpendicular to the long-axis).²³

One method of treating the spectra $A(II)$ and $A(I)$ which correspond to a more or less oriented assembly of molecules, is that developed by Eggers *et al.*²⁰ By forming two linear combinations, $S(II) = A(II) - c_1 A(I)$, $S(I) = A(I) - c_2 A(II)$, where the positive coefficients c_1 and c_2 are chosen to fulfill certain conditions, the "reduced spectra" $S(II)$ and $S(I)$ will represent the pure long-axis polarized and the pure short-axis polarized spectrum of the molecule, respectively. The condition can be, *e.g.*, $S(II) = 0$ at a wavelength where a separate transition is positioned which can be assumed to be perfectly short-axis polarized. If the "reduced spectra" can be obtained with correct relative intensities they will represent the long-axis and short-axis vectorial components of the transition moments, and thereby the direction of the latter.

By applying the *quasi*-statistical expression^{23,26} $R_D = (f \cos^2 \alpha + (1-f)/3) / (0.5 f \sin^2 \alpha + (1-f)/3)$, where α is the angle between the transition moment and the long-axis of the molecule and f is the *degree of orientation* (see Ref. 24, p. 2684), direct information can be obtained about the direction of the studied transition or, if this is known, a value of the orientation factor, f . (For example, by studying certain $d-d$ transitions, the symmetries of which had been established before, it has been possible to draw conclusions about the arrangement in the outer sphere of Co(III) amine complexes in oriented films.^{24,22}) The angles given in Table 1 are obtained by this method: *e.g.*, the observation that the long-axis polarized transition of biphenyl corresponds to an R_D value

of 1.5 suggests an orientation factor of 0.14 $((R_D - 1)/(R_D + 2))$,²⁴ as the transition is likely to be perfectly long-axis polarized. As the species biphenyl, bipyridyl, and bithienyl have approximately the same molecular shapes we can assume that they will render about the same orientation with a stretch factor of say 2. This means judging from the spectrum that *e.g.*, in bipyridyl the long-wavelength transitions are predominantly polarized along the long-axis ($\alpha = 0$). With 3,3'-bithienyl there can be a departure of α from 0 for the 260 nm band as $R_D = 1.4$ — the 210 band, however, is assigned a perfect long-axis polarization. Furthermore, the long-wavelength transition of 2,2'-bithienyl is consequently perfectly long-axis polarized but for the transition at 247 nm a value of $\alpha = 46^\circ$ is obtained from the expression with $f = 0.14$ ($R_D = 1.1$).

Applying this degree of orientation ($f = 0.14$) to the case of 5,5'-dimethyl-3,3'-bithienyl we obtain $\alpha = 33^\circ$ for the transition at 265 nm. As, however, the band at 220 nm exhibits an R_D of 1.75, a higher degree of order must be the case. This seems reasonable as the low R_D value of the long-wavelength transition indicates that the *trans* configuration predominates (with *cis* the symmetry is C_{2v} and any transition must be either long-axis or short-axis polarized) and with the methyl groups in *trans* positions the molecule will be longer and the orienting efficiency higher. Adopting $\alpha = 0^\circ$ for the 220 nm transition, *i.e.* $f = 0.20$, we obtain $\alpha = 40^\circ$ for the long-wavelength transition.

Whereas the methyl substitution in 5,5' positions on the 3,3'-bithienyl nucleus results in a more elongated symmetry, methyl groups in 2,2' and 4,4' positions will render the molecule a more spherical shape. In fact the polarized spectra $A(\parallel)$ and $A(\perp)$ of hexamethylbithienyl are practically identical (Fig. 3, Table 1). This makes impossible a direct comparison between polarized absorption spectrum and CD spectrum of the only compound with the possibility of optical activity in the substances investigated here.

It has been claimed that the degree of orientation in a polyethene film, contrary to the case with a polyvinyl alcohol film, will very rapidly reach saturation on stretching, *i.e.* the "yield point" is obtained at a very low stretch ratio.²⁶ Tanizaki has from a purely theoretical point of view deduced a relation between the stretch ratio (R_s), the absorbance ratio, R_D , and the angle (α) of the transition moment against the orientation axis.²⁵ The relation was successfully applied to cases with stretched polyvinyl alcohol films and rather high stretch ratios (4–8). The results in Fig. 7, however, do not indicate any saturation of the orientation ($f = (R - 1)/(R + 2)$ for the molecules with long-axis polarized transitions) with increasing stretch factor. However, estimates according to the Tanizaki model using the R_D variations observed, give rather high values of α (about 50° (265 nm) for 5,5'-dimethyl-3,3'-bithienyl and 40° (260 nm) for 3,3'-bithienyl).

o-Phenantroline (Table 1, Fig. 5) has C_{2v} symmetry, *i.e.* the transition studied is perfectly long-axis polarized and consequently the low R_D value must be attributed to a lower orientation factor ($f = 0.09$) than with the biaryls.

CALCULATIONS AND RESULTS

Calculated electronic singlet transitions are presented in Table 2, where also data from Skancke's calculations are quoted.

Table 2. Calculated electronic singlet transitions. The wavelengths in nm.

Compound	Symmetry	λ (nm)	f^e	Pol. ^a ϕ^c	Structure (ref.)
2,2'-Bithienyl ^b (planar <i>cis</i>)	¹ B ₂	290	0.95	0	42
	¹ B ₂	246	0.01	0	
	¹ A ₁	241	0.20	90	
	¹ A ₁	215	0.17	90	
	¹ B ₂	183	0.00	0	
2,2'-Bithienyl ^b (planar <i>trans</i>)	¹ B _u	289	0.92	1	42
	¹ B _u	250	0.25	-68	
	¹ A _g	245	0	-	
	¹ A _g	215	0	-	
	¹ B _u	176	0.74	90	
3,3'-Bithienyl ^b (planar <i>cis</i>)	¹ B ₂	259	0.43	0	42
	¹ A ₁	250	0.04	90	
	¹ B ₂	243	0.07	0	
	¹ A ₁	223	0.56	90	
	¹ B ₂	196	1.03	0	
3,3'-Bithienyl ^b (planar <i>trans</i>)	¹ B _u	261	0.54	23	42
	¹ A _g	250	0	-	
	¹ B _u	236	0.50	-76	
	¹ A _g	234	0	-	
	¹ B _u	194	1.02	-5	
5,5'-Dimethyl- 3,3'-bithienyl ^c (planar <i>cis</i>)	¹ B ₂	255	0.14	0	<i>a</i>
	¹ A ₁	246	0.09	90	
	¹ B ₂	241	0.32	0	
	¹ A ₁	228	0.52	90	
	¹ B ₂	203	1.08	0	
5,5'-Dimethyl- 3,3'-bithienyl ^c (planar <i>trans</i>)	¹ B _u	252	0.50	31	<i>a</i>
	¹ A _g	246	0	-	
	¹ B _u	239	0.57	-64	
	¹ A _g	238	0	-	
	¹ B _u	199	1.04	0	
2,2'-Bipyridyl ^c (planar <i>cis</i>)	¹ A ₁	256	0.02	90	43
	¹ B ₂	254	0.05	0	
	¹ B ₂	230	0.92	0	
	¹ A ₁	193	0.17	90	
	¹ B ₂	193	0.57	0	
	¹ B ₂	179	0.56	0	
2,2'-Bipyridyl ^c (planar <i>trans</i>)	¹ B _u	258	0.08	24	43
	¹ A _g	254	0	-	
	¹ B _u	229	0.99	-10	
	¹ A _g	198	0	-	
	¹ B _u	185	1.27	26	
	¹ A _g	183	0	-	

^a For notations: See Fig. 1e. ^b Calc. by A. Skancke.⁴² Polarization data from private communication. ^c Calc., present investigation. ^d The same structure assumed as for 3,3'-bithienyl.⁴² ^e Oscillator strength.

Before discussing the results of the MO calculations, it should be noted that the semi-empirical parameters used^{31-33,33} have been determined to fit vapour phase spectra of a series of small standard molecules. Observed spectral data for the molecules, treated here, emanate from solution spectra. It is not possible to give an accurate quantitative estimate of the solvent effect, which means that the method cannot be used for a discussion of the exact position of a single band. It can, however, be used as a basis for spectral assignments giving a realistic overall picture of the electronic energy levels.

It should also be kept in mind that Table 2 gives the calculated results for the *planar cis*- and *trans*-forms, whereas the molecules in solution or stretched polyethylene films probably have a twist of the internuclear bond as found in the vapour phase by electron diffraction studies.⁴²⁻⁴⁴

2,2'-Bithienyl. The observed band at about 190 nm can be assigned as the 1B_2 transition (183 nm) in *cis* or the 1B_u transition (176 nm) in *trans*. The *cis* band is *x*-polarized, while the *trans* band is *y*-polarized. Furthermore, the *cis* band is predicted to be very weak, while the calculated oscillator strength of the *trans* band is 0.74. The lowest singlet transition is found to be a strong *x*-polarized band for both forms.

3,3'-Bithienyl. The calculations give one strong *x*-polarized transition for both *cis* (196 nm) and *trans* (194 nm). The lowest singlet transition is *x*-polarized in *cis*, while $\phi = 23^\circ$ for *trans*.

5,5'-Dimethyl-3,3'-bithienyl. The two methyl groups only slightly affect the spectral pattern of both forms. It can be noted that the intensity of the lowest $\pi \rightarrow \pi^*$ singlet in *cis* is predicted to be lower ($f = 0.14$) than in 3,3'-bithienyl *cis* ($f = 0.43$), while in the *trans* form this band retains its strength. The intensity of the strong band in both forms is almost unchanged in comparison with 3,3'-bithienyl.

2,2'-Bipyridyl. For both *cis* and *trans* the two lowest transitions are predicted to be very close. For *cis* the lowest transition is *y*-polarized followed by a stronger *x*-polarized transition. In *trans* the lowest transition is of symmetry 1B_u with $\phi = 24^\circ$, while the adjacent transition is forbidden (1A_g).

As can be seen from Table 3, calculated bond distances (using bond order-bond length relations³³) of 2,2'-bipyridyl show that the geometry of the pyridine ring seems to be preserved in bipyridyl.

Table 3. Calculated bond distances (in Å) for 2,2'-bipyridyl. The corresponding values for pyridine^a are given for comparison.

Bond	<i>cis</i>	Bond distance <i>trans</i>	pyridine
1-2	1.3422	1.3422	1.3394
2-3	1.4037	1.4038	1.3958
3-4	1.3952	1.3952	1.3936
4-5	1.3968	1.3968	1.3936
5-6	1.3992	1.3990	1.3958
1-6	1.3367	1.3368	1.3394
2-2'	1.4694	1.4693	1.47 ^b

^a See Ref. 47.

^b Assumed value (See Ref. 43).

COMPARISON THEORY-EXPERIMENT AND DISCUSSION

2,2'-Bithienyl. The value $R_D = 1.5$ for the broad long-wavelength band is interpreted to indicate an almost perfect long-axis polarization, which satisfies both models. The observed intensity of the band at 190 nm in cyclohexane ($\epsilon_{\max} = 1.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) does not fit into the *cis* model, for which the calculations give an almost forbidden 1B_2 transition at 183 nm. It is more in accord with the *trans* model with a predicted strong allowed 1B_u transition (*y*-polarized) at 176 nm. The *trans* model is also favoured by the observed mixed polarizations of the bands at 250 nm, which cannot be explained by overlapping wings from the long-wavelength band (*x*-polarized) and the band at 190 nm (most probably *y*-polarized). For *trans* ϕ is predicted to be -68° for the 1B_u transition at 250 nm. It is true that in *cis* two transitions (one with *x* and one with *y* polarization) are predicted to be found in this region, but the value of the calculated oscillator strength for the *x*-polarized transition is very low ($f = 0.01$). These facts thus strongly favour the *trans* model, also suggested by Almendinger, Bastiansen and Svendsås⁴⁴ from electron diffraction data for the vapour phase.

3,3'-Bithienyl. The experimentally obtained value of α (20°) for the band at 260 nm indicates that the *trans* conformation predominates (*cf.* Table 2). The presence of two discrete peaks at about 210 nm in the low-temperature spectrum (Fig. 2), however, may suggest a mixture of *cis* and *trans* conformers. Recently reported electron diffraction data⁴² on vapour indicate a mixture (40 % *cis* and 60 % *trans*).

5,5'-Dimethyl-3,3'-bithienyl. The low R_D value for the long-wavelength transition band shown in Fig. 7 is striking compared with the other systems. The fact that no part of the band is purely *x* polarized makes the *trans* configuration more probable than *cis*. This conclusion is also obtained when comparing the observed intensities for the 265 and 220 nm bands with calculated oscillator strengths for the 1B_u (252 nm) and 1B_u (199 nm) transitions in *trans*. The ratio between the calculated oscillator strengths for the corresponding bands in *cis* is found to be much too low. This implies that the only possible direction for the observed transition at 265 nm is approximately the line connecting the sulphur atoms, as the alternative of *y*-polarization type is improbable (Fig. 1e). The apparent *x*-polarized transition at 255 nm may be explained by the effect of decreased intensity due to an *y*-polarized band in the neighbourhood. The calculations actually predict a strong band at 239 nm with $\phi = -64^\circ$. The methyl groups substituted at 5,5' have probably not markedly changed the angle of twist, as the observed spectrum shows the slight red shift usually found in methyl-substituted planar molecules.³² A large change of the angle of twist would radically change the spectral pattern.

Hexamethyl-3,3'-bithienyl. The observed spectrum of hexamethyl-3,3'-bithienyl strongly resembles the spectrum of trimethylthiophene²⁹ (*cf.* that of thiophene)⁴⁵ due to steric interference between the substituents (at 2,2' and 4,4') leading to an almost perpendicular orientation of the thiophene planes. The corresponding effect of methyl substitution in biphenyl has been observed and thoroughly discussed by Suzuki.⁴⁶

2,2'-Bipyridyl. The fact that all the bands which could be studied by the film technique exhibit long-axis polarization can be understood if the double bands at about 240 and 280 nm are due to a mixture of *cis* and *trans* conformers. Both bands will be composed of a strong *x*-polarized transition and a weaker *y*-polarized (in the *cis* case) or they will be due to transitions (in the *trans* case) which deviate a little from the *x*-axis (that the deviation angles should have different signs has no importance as the considered orientation is *uni*-axial and thus only the absolute value of ϕ , *viz.* α , can be determined experimentally).

Biphenyl. The long-axis polarization of the main band at 250 nm (the *A* band) is expected from MO calculations by Suzuki.⁴⁶ It is due to a transition to the ${}^1B_{2u}$ state originating from the benzene *p* state. Transitions corresponding to that to the α state of benzene are probably made allowed along the short-axis by coupling with vibration. The H band⁴⁶ at about 270 nm is thus attributed to these transitions which can explain the lower R_D values at these wavelengths.

CONCLUDING REMARK

From theory-experiment we can conclude that the lowest strong $\pi \rightarrow \pi^*$ transitions in the biaryls studied are predominantly of long-axis (*x*) polarized character. This is of course also expected from a naïve "particle in the box" point of view.

The calculations have made it possible to identify experimental bands with theoretical transitions by comparing the measured energies, intensities and directions of polarization with the respective calculated entities. Due to large differences between the theoretically predicted spectral features of the two possible planar isomers with *trans* and *cis* conformation, it was often possible to rule out one alternative by an inspection of the polarized UV absorption spectrum.

In general the unpolarized absorption spectra of the substances investigated here in polyethylene film have been identical with those obtained in cyclohexane solution. In a few cases (Table 1) different wavelengths of the respective absorption maxima in film and solution can be observed. If the band is composed of two or more transitions at different wavelengths and with different polarizations, the band maxima of $A(\parallel)$ and $A(\perp)$ could be supposed to occur at different wavelengths but a weighted mean should still equal the unpolarized or random solution spectrum. With a high stretch-factor birefringence must be taken into consideration. However, with, *e.g.*, biphenyl, the absorption maximum in an unstretched film is situated at 250 nm while the spectrum of a cyclohexane solution has the maximum at 247 nm (*cf.* also Fig. 4). This effect must therefore be assigned as a solvent effect.

The possibilities of correlating observed directions of $\pi \rightarrow \pi^*$ transitions with optical rotatory power in dissymmetric derivatives of, *e.g.*, bithienyls which were discussed in the introduction are strongly limited by the fact that the substituents necessary for obtaining steric hindrance often perturb to a high extent (inductively or mechanically) the electronic states responsible for the observed spectrum of the pure biaryl nucleus. Of course the most natural

way is to directly investigate the species with the possibility of optical activity (with hexamethyl-3,3'-dithienyl it was impossible, however, due to a too low orientation effect) and in further investigations we hope to present results from such studies.*

However, if we adopt the direction for transition moments from 3,3'-bithienyl to, e.g., 2,2',4,4'-tetrabromo-3,3'-bithienyl (which is one of few derivatives with mainly unchanged apparent absorption spectrum from 3,3'-bithienyl) we can try to give an interpretation of the corresponding CD spectrum.³⁰ With *trans* conformation and *R*(-) configuration³⁰ the molecule will be a part of a right handed helix viewed along the internuclear bond. Theory predicts two transitions: one polarized approximately along the line connecting the sulphur atoms (261 nm), and one perpendicular to that direction (236 nm, cf. Table 2). Applying the discussion with original transition components of Fig. 1 b, we should expect one positive CD band at longer wavelength (261 nm) and two strong CD bands with different signs at shorter wavelength (the positive at longer wavelength). The reported CD spectrum reveals two bands with opposite rotational strengths at about 250 nm (the negative band at the long wavelength) but no inclination of any positive band of the long wavelength part of the absorption band. At shorter wavelengths there appears a strong positive band in harmony with the fact that the 210 nm band is perfectly parallel polarized.

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* We have recently designed a technique for measuring linear dichroism which is approximately 100 times more sensitive than the one used in this investigation.⁴⁹

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