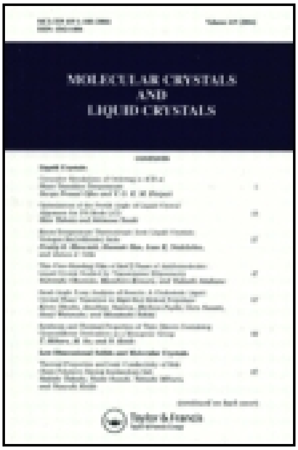

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Electronic Spectra of Thiazolo[5,4-d]Thiazole

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Electronic Spectra of Thiazolo[5, 4-*d*]Thiazole

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The uv absorption spectrum of thiazolo[5,4-*d*]thiazole has been investigated for the vapour phase and by means of the linear dichroism of single crystals and liquid crystalline solutions. Two intense $\pi^* \leftarrow \pi$ electronic transitions are observed in the region of the near uv, while a Rydberg transition occurs around 50,000 cm^{-1} in the vapour spectrum. These results are substantiated by MCD spectroscopy and a comparison with data for the parent molecule thieno[3,2-*b*]thiophen is given.

INTRODUCTION

Among five-membered condensed heterocyclic systems, a great deal of interest has centered on compounds containing sulphur atoms, because of their ability to be used as electron donors in equimolecular complexes of the donor-acceptor type.[1] In this respect, a spectroscopic investigation of appropriate materials would lead to useful information for the identification of the electronic transitions of the molecules and for a comparison with analogous aromatic compounds.

In this paper we present an experimental study of the electronic spectra of thiazolo[5,4-*d*]thiazole, sketched in Figure 1(a) and hereafter referred to as (TTZ). Uv absorption spectra for the vapour and solution phases, and single crystal spectra obtained at low temperature are reported. An analysis of the excited states involved in the electronic excitation of the molecule is given and an interpretation is offered with the aid of a corresponding study of LC-LD (Liquid Crystal-Linear Dichroism) and MCD (Magnetic Circular Dichroism) spectra. The results are also interpreted taking into account the similarities between the electronic spectra of (TTZ) and those of thieno[3,2-*b*]thiophen (TTP) [see Figure 1(b)].

To our knowledge, no experimental data on the spectroscopic properties of (TTZ) have so far been reported in the literature.

EXPERIMENTAL

(TTZ) has been synthesized following a literature method of preparation[2] and purified by repeated sublimation. Uv spectra have been obtained using conventional techniques with a Cary 15 spectrophotometer. The vapour pressure of solid (TTZ) is sufficient to achieve in a 1 cm cell, at room temperature, an optical density of about unity at the absorption maximum (250 nm). Single crystals were grown by melting and slowly recrystallizing the melt between fused silica discs, to yield a thickness of the samples of less than 1 μm. Single crystal spectra in polarized light were taken at different temperatures down to 77 K by means of a conventional glass cryostat. MCD and LD spectra were recorded by using a Jasco J 500 spectropolarimeter, equipped with an electromagnet (12 kgauss) or an LD attachment. The experimental details and the evaluation methods of the LC-LD technique have already been described elsewhere.[3,4]

FIGURE 1

RESULTS AND DISCUSSION

1. Vapour and solution spectra

The uv vapour spectrum of (TTZ), shown in Figure 2b, starts at approximately 290 nm and consists of a broad absorption centered at ~ 250 nm and a weaker absorption with some structure in the region around 200 nm. The main absorption begins with two weak shoulders at ~ 275 and at ~ 272 nm, then rises to a first intense shoulder at ~ 260 nm and a second strong maximum peaked at 248 nm with some additional structure at ~ 243 nm. From this information alone it appears difficult to discriminate whether one or more electronic transitions would occur in this region. In the region around 200 nm (see inset in Figure 2), a different electronic transition with some sharper

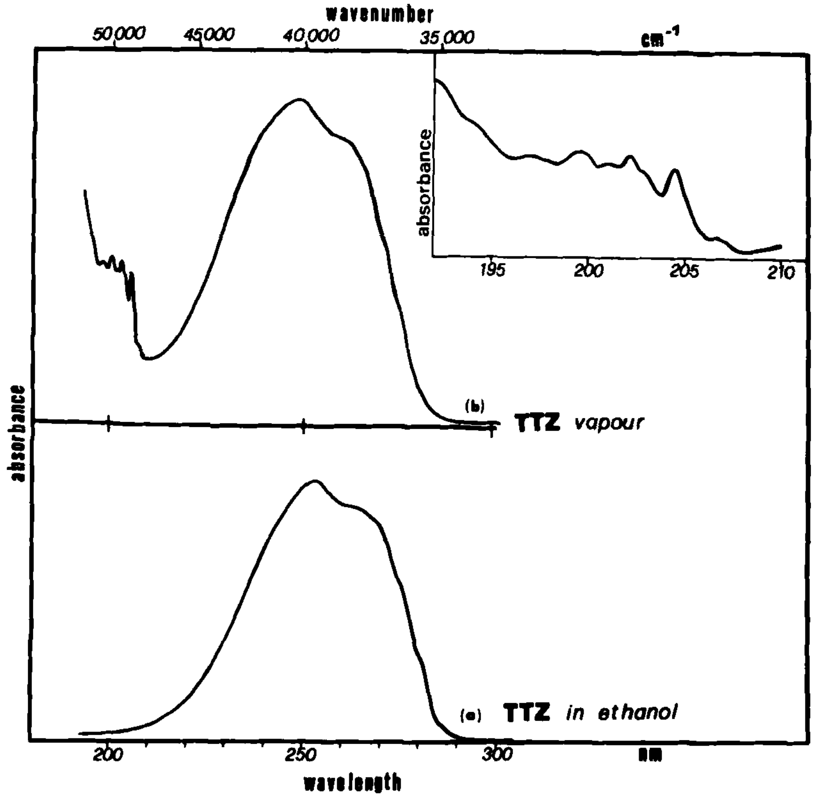

FIGURE 2 Solution (a) and vapour (b) uv spectra of (TTZ). The inset shows a closer inspection in the region of the Rydberg transition.

vibronic structure is observed. This is likely to be a Rydberg transition, as is confirmed from the spectra in the condensed phase and as expected from molecules with hetero-atoms like sulphur and nitrogen whose orbitals may give rise to allowed Rydberg states. An analysis of the nine measured bands is given in Table I. Three excited state vibronic frequencies occur at 475, 860, and 1055 cm^{-1} with respect to the origin located at 48425 cm^{-1} (206.5 nm). These vibrations compare well with totally symmetric active vibrations in Rydberg-like transitions of pyrrole[5] and thiophen.[6]

The absorption spectrum measured for the solution state (Figure 2a) corresponds in its major features to that of the vapour, except for the group of bands around 200 nm that is not now observed. In solution in *n*-hexane, again two weak shoulders appear at ~ 279 and at ~ 275 nm; then one peak is measured at 266.5 nm and a second stronger maximum is found at 252.5 nm, followed by a shoulder at ~ 243 nm. In solution in ethanol, these maxima are slightly shifted towards higher frequencies, the absorption contours being otherwise unchanged. The measured ϵ_{max} is 7600 $[m/l \cdot cm]^{-1}$ and the oscillator strength in the region 34000–48500 cm^{-1} (294–206 nm) has been estimated to be 0.236, which, corrected for solvent effect, corresponds to a value of $f \cong 0.19$ for the free molecule.

2. Crystal Spectra

At room temperature, the absorption spectrum of a polycrystalline film of (TTZ) shows a broad pattern consisting of two wide bands whose separation (~ 4000 cm^{-1}) seems too large for a vibration. This is a first indication of the possibility of two absorption systems present

TABLE I

Frequencies and vibrational assignments of the Rydberg transitions of (TTZ) vapour

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment
48425	0	0–0
48900	475	475
49285	860	860
49480	1055	1055
49750	1325	475 + 860
50125	1700	2 × 860
50530	2105	2 × 1055
50760	2335	475 + 860 + 1055
51545	3120	3 × 1055

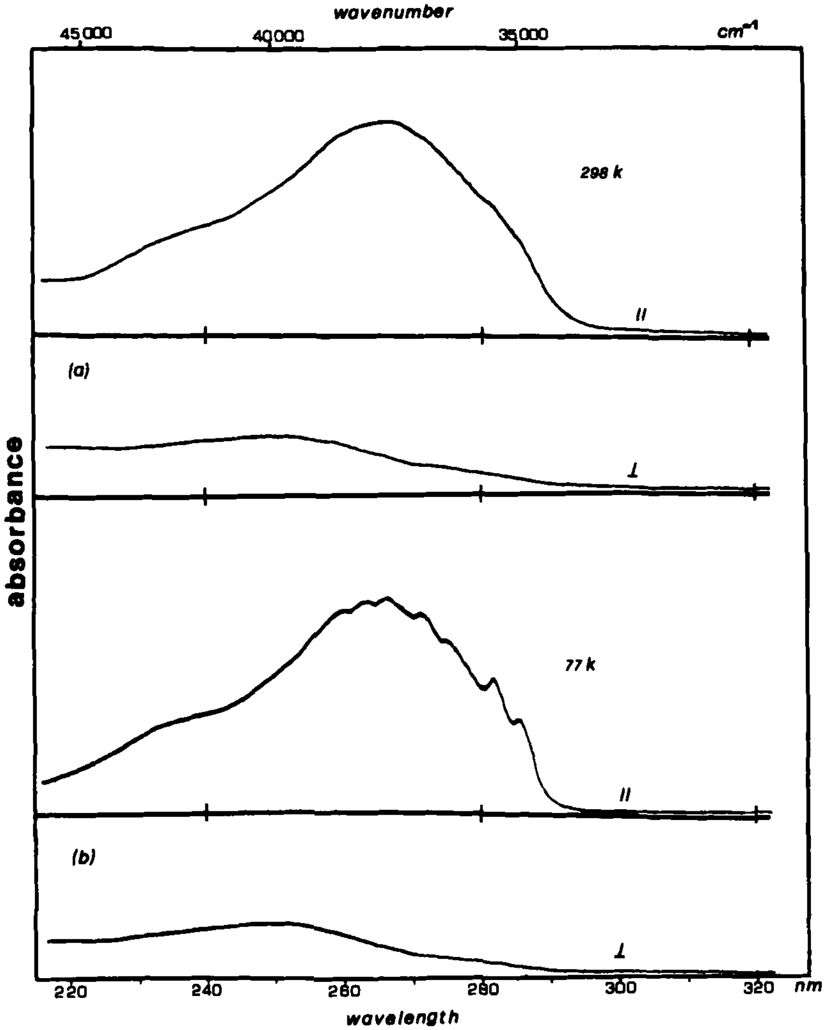

FIGURE 3 Absorption spectrum of crystalline (TTZ): (a) single crystal, room temperature; (b) single crystal 77 K.

in the region 300–220 nm, a situation which has been observed for the $\tilde{B}$ and $\tilde{C}$ system of (TTP).[7,8] The situation appears far clearer on considering spectra of the single crystal in polarized light (see Figure 3a). The spectrum has been taken along directions almost parallel and perpendicular to the cleavage lines of the most developed plane of growth. The spectrum is strongly dichroic, with most of the intensity concentrated in the parallel direction. Although the absence in the literature of any structural data and optical information does not allow a quantitative interpretation of the spectrum, it appears to be reasonable to locate two transitions with similar dichroic characteristics within the crystal. The first is weaker and is located at ~ 285 nm; the second stronger transition shows a large factor group splitting[9] with maxima of intensity at ~ 268 nm, for parallel, and at ~ 250 nm, for perpendicular, polarization. Additional information can be obtained by lowering the temperature. In Figure 3b, polarized spectra at 77 K are shown. Although at first sight the spectra appear better resolved, the absorption contours remain generally broad, particularly in the region around 250 nm. The situation does not substantially change by going to still lower temperatures with the sample immersed in liquid He or by improving the spectral resolution. In Table II, the main measured maxima of the single crystal spectrum are reported. By considering the presence of two electronic transitions, we may notice some sharper features in the first one with origin at 285.3 nm (35050 cm^{-1}). It is strongly polarized along the parallel direction and no factor group splitting is measurable. Comparison with the measured Raman frequencies (Table III) enables us to assign the observed vibronic structure to the fundamental totally symmetric ring deformation vibration and to the C—C stretching vibration. The same situation is observed in the previously mentioned crystal spectrum of (TTP),[8] where the most active vibronic progression is due simply to the totally symmetric ring deformation mode. By applying similar considerations, we may locate the second electronic transition in the crystal at 266.5 nm (37525 cm^{-1}). The excited state active frequencies are slightly changed, as expected for a different $\pi^* \leftarrow \pi$ transition. The new feature now present in the crystal spectrum is the large and

TABLE II

Frequencies and vibrational assignments of the (TTZ) single crystal spectrum

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment
35050	0	0–0
35510	460	460
35995	945	945
36365	1315	1315
36860	1810	460 + 1315
37525	2475	0–0
37950	2900	425
38610	3560	1085

TABLE III

Raman frequencies for the crystalline phase of thiazolo[5,4-*d*]thiazole and, for comparison, thieno[3,2-*b*]thiophen. All values are in cm^{-1}

thiazolo[5,4-*d*]thiazole		thieno[3,2-*b*]thiophen			
Freq.	Int.	Freq.	Int.	Symm. and Assign.[a]	
465	*m*	450	*w*	*Bg*	γ_{ring}
482	*w*	459	*w*	*Ag*	δ_{ring}
557	*w*	548	*m*	*Ag*	δ_{ring}
675	*w*	638	*m*	*Ag*	ν_{C-S}
		735	*w*	*Bg*	ν_{C-H}
750	*vs*	758	*vs*	*Ag*	ν_{C-S}
864	*w*				
		1066	*m*		
		1073	*m*	*Ag*	δ_{C-H}
1236	*w*	1175	*m*	*Ag*	δ_{C-H}
1371	*s*	1329	*s*	*Ag*	ν_{C-C}
1378	*s*				

[a] The measured Raman frequencies have been assigned by comparing the data with those from Ya. M. Kimmelfeld, M. A. Moskalyova, G. N. Zhizhin, V. P. Litvinov, S. A. Ozolin,and Ya. L. Goldfarb, *Opt. Spectros.*, **28** 599 (1970).

more readily measured factor group splitting (approximately 3000 cm^{-1}) by locating the perpendicular polarization component at ~ 247.5 nm (see Figure 3b). This second transition is again strongly polarized along the parallel direction. At higher energies, an additional shoulder at ~ 240 nm can be observed in the parallel direction of polarization.

It is important to note the lack of any vibronic structure in the region corresponding to that of the observed Rydberg transition of the vapour. This is expected on the basis that Rydberg states have short relaxation times in the crystal phase and are not expected to give rise to discrete absorption in the crystal spectrum, as already observed for the parent molecules of thiophen[10] and pyrrole.[5] As previously mentioned, this is one of the additional reasons to consider as safe an assignment of the absorption at ~ 200 nm in the vapour spectrum to a Rydberg transition.

3. Liquid crystal-linear dichroism (LC-LD) spectrum

Liquid crystalline solvents provide the safest and most effective way of imparting to any molecule the partial orientation required to obtain its LD spectrum. The good transparency to uv radiation assured by bicyclohexyl derivatives, like nematic ZLI-1167 (E. Merck, Darmstadt), allows LD spectra of the solute molecules to be recorded down to 200 nm. Orientation of the sample can be obtained by the usual orienting techniques such as cell-surface coating, and electric or magnetic fields.[3,4] The LC-LD $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$ and the "average absorption"[4] $[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2$ spectra of (TTZ) are reported in Figure 4 where $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are the optical densities of two perpendicularly plane polarized components, parallel ($\parallel$) and perpendicular ($\perp$) to the sample director, of a radiation of wavelength λ.

By the reduction procedure described in ref. 3, i.e., by computing the linear combinations $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] - d'/2[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]$ for $-2 \leq d' \leq 2$, only the contributions of the absorptions below 250 nm disappear in the "reduced curve" (see Figure 4 dashed line) where $d' = 0.7$: the mixed polarization of the (TTZ) spectrum in this region is thus clearly displayed. In fact, the electronic spectra of (TTZ) are actually expected to be closely related to those of (TTP) whose features in the near uv are determined by the presence of two transitions, clearly displayed and labelled $\tilde{B}$ and $\tilde{C}$ in previous papers.[3,8,9] The introduction of two hetero-atomic nitrogens at the 3 and 6 positions of (TTP) can simply be viewed as a case of inductive substitution. The treatment (see Figure 4 of ref. 3) of local perturbations (induced by methyl substituents) in the oscillating $\pi^* \leftarrow \pi$ transition charge distributions of the (TTP) chromophore fits the (TTZ) case also and the conclusions apply as well. The directions of the transition moment components induced at the 3 and 6 (TTP) positions by the nitrogens can be considered practically collinear with the (TTP) electric transition moments: the intensity, but not the polarization of the (TTP) transitions are thereafter expected to be affected by the hetero-atomic nitrogens, and $\tilde{B}$ and $\tilde{C}$-type transitions can be predicted to appear in the (TTZ) spectra also. The (TTZ) reduction curve reported in Figure 4 does not allow one to invoke the dipole-forbidden D transient observed in ref. 3 on the basis of the orientational degeneracy of the $\tilde{B}$ and $\tilde{C}$ transitions of (TTP).

4. MCD Spectra

The predicted existence of two strong $\pi^* \leftarrow \pi$ electronic transitions in the near uv spectra of chromophores like (TTZ) and (TTP) is soundly demonstrated by recording their MCD spectra. Figures 5 and 6 show MCD spectra of (TTZ) and (TTP) respectively. Here $E_l(\lambda)$ and $E_r(\lambda)$ are the optical densities of left and right circularly polarized components of the incoming radiation of wavelength λ.

With the aid of Michl's theory of MCD,[11] one can explain the strict similarity of the two spectra as well as their sign pattern. Since both

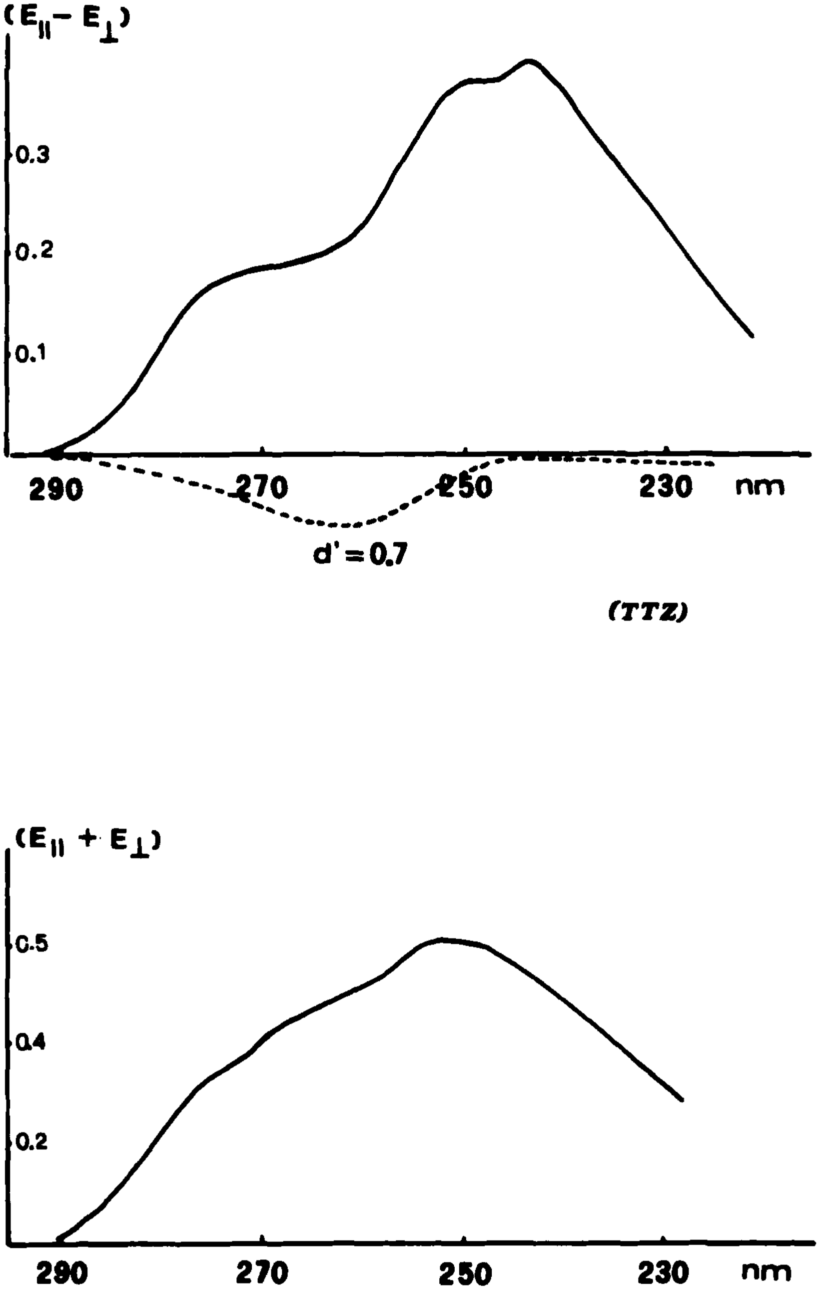

FIGURE 4 LC-LD (upper) and "average absorption" (lower) spectra of (TTZ) dissolved and oriented by the nematic phase of ZLI-1167. The reduced curve is reported in arbitrary units as a dashed line.

chromophores do not possess threefold or higher symmetry axes, no A term can contribute to their MCD spectra, and only B terms are relevant. They arise from the mixing of $\tilde{B}$ and $\tilde{C}$ transition states, caused by the external magnetic field. The observed sigmoidal MCD spectral pattern of Figures 5 and 6 is apparently similar to that of an A term only because of the close energy locations of the two strong $\tilde{B}$ and $\tilde{C}$ transitions.

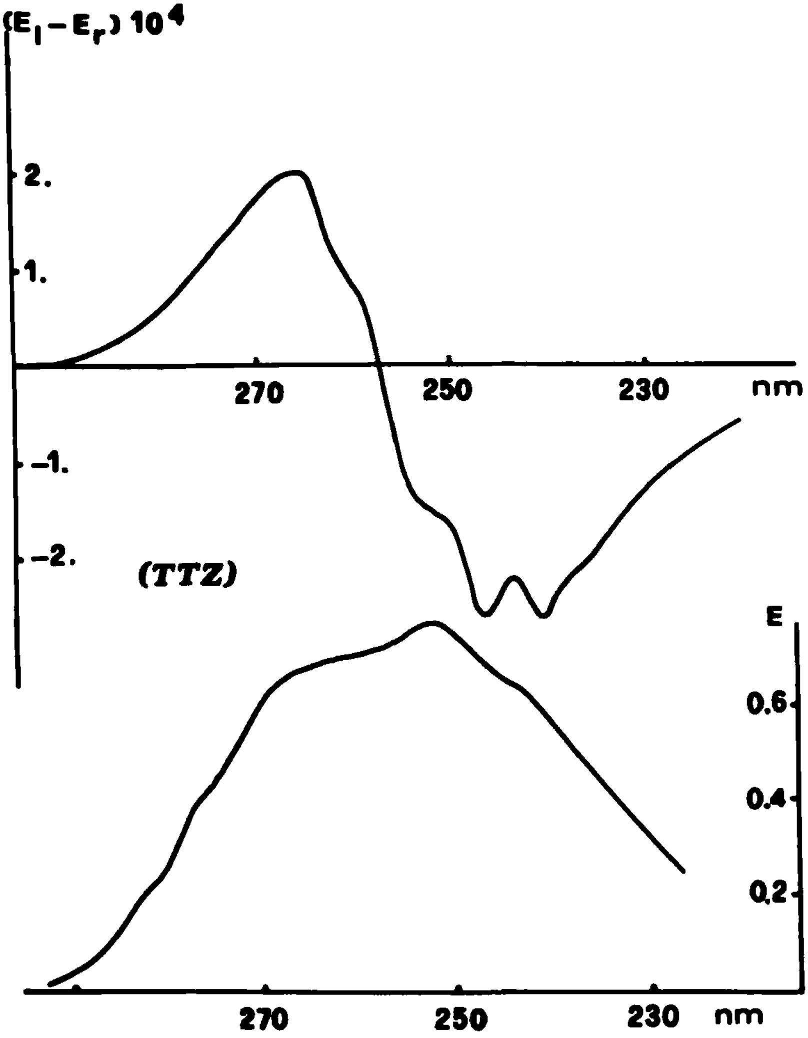

FIGURE 5 MCD (upper) and isotropic absorption (lower) spectra of an ethanolic solution of (TTZ).

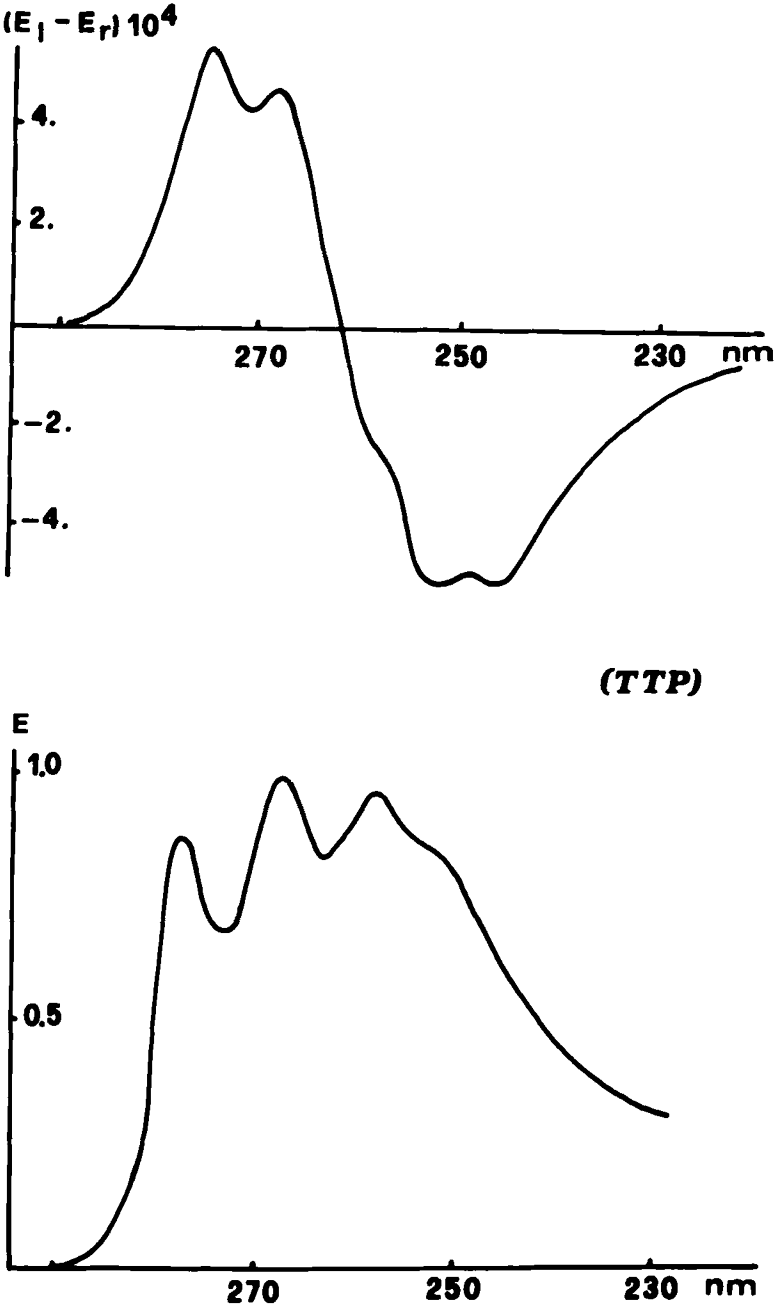

FIGURE 6 MCD (upper) and isotropic absorption (lower) spectra of an ethanolic solution of (TTP).

On the basis of the MO description of the (TTP) chromophore of ref 8, Figure 6, the $|\Delta\text{HOMO} - \Delta\text{LUMO}|$ is large; the sense-reversing excitations will thus dominate, and the MCD band-sign pattern will be governed by the sign of ($\Delta\text{HOMO} - \Delta\text{LUMO}$). Being $\Delta\text{HOMO} < \Delta\text{LUMO}$, a $+ - + -$ MCD band sign pattern with increasing energy can be predicted. The MCD pattern of the "hard" (TTP) chromophore is expected to be very little affected by the introduction of the hetero-atomic nitrogens. Hence the strict shape similarity of (TTZ) and (TTP) MCD spectra of Figures 5 and 6.

CONCLUSIONS

Vapour spectra and linear dichroism measurements of thiazolo[5, 4-*d*]thiazole single crystals and liquid crystalline solutions suggest the presence of two intense $\pi^* \leftarrow \pi$ electronic transitions overlapped in the region of the near uv, followed by a Rydberg transition in the region around 200 nm of the vapour spectrum. Further and conclusive confirmation of this interpretation has been obtained by means of MCD spectroscopy, where the results have been discussed by comparison with the parent thieno[3, 2-*b*]thiophen molecule. In this respect, some extension to this work may be obvious. It seems of interest, for instance, to study the spectroscopic properties of the charge transfer transition of an equimolecular complex of (TTZ) with a strong acceptor, such as TCNQ, in the search for new materials in the rapidly developing area of charge transfer complexes in organic quasi-one-dimensional conductors.

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