

## Long-wavelength Circular Dichroism of Dithioimides

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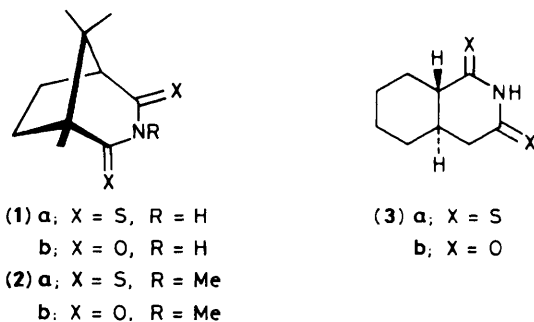
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The dithioimides (**1a**)—(**3a**) and the parent imides (**1b**)—(**3b**) exhibit similar chiroptical properties in the long-wavelength absorption regions, owing to the closely analogous nature of their  $n-\pi^*$  electronic transitions.

In recent years there has been increasing interest in chiroptical spectra of thiocarbonyl derivatives.<sup>1,2</sup> These compounds absorb at significantly longer wavelengths than the corresponding carbonyl compounds, and their c.d. spectra may serve both as a sensitive structural probe and as a useful aid to the study of electronic transitions.<sup>2</sup>

In connection with our recent c.d. studies of imides<sup>3</sup> we turned our attention to dithioimides, which show intriguing absorption in the visible region.<sup>4</sup> The optically active imides (**1b**)—(**3b**)<sup>3</sup> were smoothly converted into dithioimides (**1a**)—(**3a**) with Lawesson's reagent.<sup>5</sup> Dithiocamphorimide (**1a**) is a known compound;<sup>6</sup> its *N*-methyl derivative (**2a**) has m.p. 62 °C,  $[\alpha]_D^{20} +213^\circ$  (*c* 1.6 in  $\text{CCl}_4$ ), and (**3a**) has m.p. 131 °C,  $[\alpha]_D^{20} -46^\circ$  (*c* 1.1 in  $\text{CHCl}_3$ ).<sup>†</sup> These bright yellow or

red-orange compounds exhibit two absorption bands in the visible and three in the near u.v. region; e.g. dithioglutarimide shows  $\lambda_{\text{max}}$  482 ( $\epsilon$  72), 428 (176), 332 (31 000), 237.5 (7700), and 203 nm (7500) in cyclohexane, and 470 ( $\epsilon$  271), 419 (160), 335 (33 000), and 237 nm (7100) in methanol. By analogy with imides,<sup>3</sup> the two moderate-intensity long-wavelength bands



<sup>†</sup> All new compounds reported have satisfactory analytical figures (C, H, N, and S) and spectroscopic properties corresponding to the assigned structures.

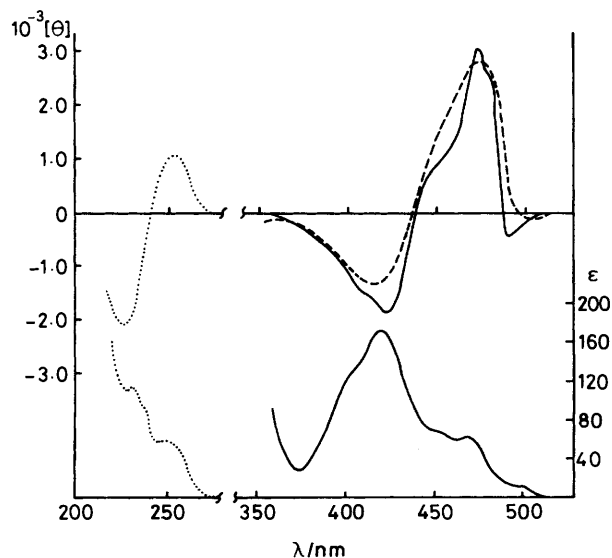


Figure 1. C.d. and u.v. (lower curves) spectra of dithiocamphorimide (**1a**) in cyclohexane and methanol, and camphorimide (**1b**) in methanol (solid, broken, and dotted lines, respectively).

**Table 1.** C.d. data of imides and dithioimides ( $\lambda$  in nm,  $[\theta]$  in deg cm<sup>2</sup> dmol<sup>-1</sup>).

Compd.	Solvent <sup>a</sup>	$\lambda$ (10 <sup>-3</sup> [θ])	Compd.	Solvent <sup>a</sup>	$\lambda$ (10 <sup>-3</sup> [θ])
<b>(1a)</b>	C	491 (-0.46), 473 (3.09), 423 (-1.88)	<b>(1b)</b>	C	268 (-0.10), 230 (-0.99)
	M	505 (-0.10), 473 (2.92), 415 (-1.34)		M	252.5 (1.03), 227 (-2.06)
<b>(2a)</b>	C	502 (4.09), 433 (-2.17)	<b>(2b)</b>	C	275 (-0.016), 259 (0.26), 235 (-1.23)
<b>(3a)</b>	C	489 (3.53), 416 (-0.37)		M	255 (1.02), 225 (-1.65)
	M	474 (3.14), 400 (0.14)	<b>(3b)</b>	C	260 (2.54), 237 (1.12)

<sup>a</sup> C = cyclohexane, M = methanol.

can be attributed to two  $n-\pi^*$  transitions and the strong absorption near 330 nm to the  $\pi-\pi^*$  excitation. The two 'non-bonding' n orbitals are symmetric and antisymmetric combinations of sulphur p orbitals. The solvent dependence of the band maxima supports their assignments. The nature of the two higher energy bands near 240 and 200 nm is unclear. They probably belong to the next  $\pi-\pi^*$  and/or  $\sigma-\pi^*$  transitions.

The c.d. data for the dithioimides (**1a**)—(**3a**) in the visible region (Table 1) show the presence of two Cotton effects with opposite signs in accordance with the opposite symmetry of the excited states involved in the two  $n-\pi^*$  transitions. The close resemblance of the c.d. curves of dithiocamphorimide (**1a**) and camphorimide (**1b**) in the long-wavelength regions (Figure 1) confirms the prior evidence that the corresponding electronic transitions are of the same character for both classes of compound. The Cotton effect is significantly larger for the dithio derivatives, and it is less solvent-dependent than for the parent imides, pointing to a greater conformational rigidity of the dithioimides.

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