Studies of the Circular Dichroism of the $n \rightarrow \pi^*$ Band in Cyclic Thionocarbonates

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Summary In the case of a cyclic thionocarbonate, the sign and magnitude of the Cotton effect is related to the chirality of the ring.

THE cyclic thionocarbonates of several carbohydrates have recently been prepared.[1] We report the utility of this grouping in making chromophoric derivatives of vicinal diols.

Thionocarbonates show two u.v. absorption bands, at *ca.* 315 ($\log \epsilon$ *ca.* 1·5) and *ca.* 230 nm. (*ca.* 4·2), which have been assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively.[2] The c.d. spectra of compounds (II)—(VII) have been measured for solutions in dioxan between 260 and 370 nm., and their differential dichroic absorption ($\Delta\epsilon$), rotational strengths (R) and g-factors[3] for the $n \rightarrow \pi^*$ transition are recorded in the Table, together with data on their absorption maxima in dioxan and methanol. Compounds (II), (III), (IV), and (V) are all 2,3-thionocarbonates of methyl 4,6-*O*-benzylidene-α-D-hexosides; (VI) is derived from 5α-cholestan-2β,3β-diol. The five-membered thionocarbonate ring systems in compounds (II), (III), (IV), and (VI) are attached to *trans*-decalin-type systems which may be expected to be conformationally rigid, and the chirality[†] of the five-membered ring may be deduced from Dreiding models. Compounds having an observed positive chirality exhibit positive Cotton effects and *vice versa.* These results are in accord with those of Djerassi *et al.*,[4] who measured the spectral properties of several cyclic dithionocarbonates (I; X = O and S) and trithiocarbonates (I; X = S), and who found that the chirality of the five-membered ring system was the most important factor in determining the sign of the Cotton effect of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Although compound (V) has the thionocarbonate group attached to a *cis*-decalin type of system, it is constrained to the "*O*"-inside conformation by the *trans*-nature of the fusion between the five- and six-membered rings; a positive chirality is predicted, and found.

The magnitudes of $\Delta\epsilon$ (2·3—2·8) appear to depend primarily on the chirality of the thionocarbonate ring itself. The disposition of other groups with respect to the chromophore appears to produce only second-order effects.[5] Compounds (IV) and (V) with a *trans*-five- to six-membered ring fusion have values of $\Delta\epsilon$ noticeably greater than those for the *cis*-fused isomers, (II) and (III). The formation of the five-membered ring system demands that the C(2)–O and C(3)–O bonds of the pyranose sugar derivatives move to some extent towards coplanarity. The distortion involved when these bonds occupy axial–equatorial positions as in (II), or equatorial–axial positions, as in (III), is relatively acceptable (see later), since the pyranose ring becomes slightly flattened. However, the movement together of equatorial–equatorial bonds, as in (IV) and (V), requires a greater puckering of the pyranose ring, an energetically unfavourable process.[6] Thus a greater degree of twist is maintained in the latter cases. Further evidence as to the strained nature of the thionocarbonate ring systems of (IV) and (V) is their fairly rapid decomposition in methanol solution, in contrast to the stability of (II) and (III) under identical conditions.[7]

The hypsochromic shift in the maximum of the low

[†] The chirality is defined as positive if, when the thionocarbonate ring system (I; X = O) is viewed from the thiocarbonyl sulphur atom directly along the C=S bond, the atoms C(α) and C(β) appear respectively below and above the plane containing the oxygen atoms and the thiocarbonyl group.

Spectral properties of the cyclic thionocarbonates[a]

		Absorption				Circular dichroism			
		Dioxan		Methanol		Dioxan			
Compound		λ_{max}(nm.)	ε	λ_{max}(nm.)	ϵ	λ_{max}(nm.)	$\Delta\epsilon$	$10^{40}R$[c]	g
(II	−[b]	319	26·4	311	28·3	320	−2·4	−6·5	0·068
(III)	−	319	29·4	308	35·9	317	−2·6	−6·8	0·093
(IV)	+	323	35·1	316	35·1	324	+2·8	+8·0	0·078
(V)	+	323	35·0	310	31·8	323	+2·8	+7·6	0·0716
(VI)	+	314	31·5	[d]	—	315	+2·3	+6·1	0·072
(VIIa) (VIIb)	+ −	3·8	23·6	310	25·8	320	+1·8	4·7	0·077

[a] With the exception of (VI), all new compounds gave satisfactory elemental analysis. However, the spectral properties of (VI) and an accurate mass determination on its molecular ion (found 446·3218; calculated 446·3218) fully support its expected structure.

[b] Chirality of the thionocarbonate ring, as determined by an inspection of models.

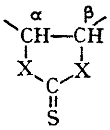
[c] Determined from the area of the c.d. band; R in c.g.s. units (*cf.* ref. 10).

[d] Insufficiently soluble for a measurable value to be obtained.

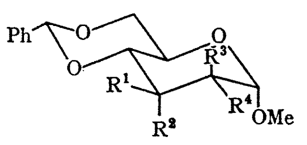
intensity band of the thionocarbonates in changing from dioxan to methanol solution supports the $n \rightarrow \pi^*$ assignment of the transition at *ca.* 315 nm. The dissymmetry factors, g, are all greater than 0·01 and indicate that this transition is magnetic-dipole allowed.[8]

Benzyl 2-*O*-benzyl-β-L-arabinopyranoside 3,4-thionocarbonate (VII) showed in dioxan a value of $\Delta\epsilon$ which was significantly lower than that which might be anticipated if the molecule existed solely in one chair conformation. Since the pyranose ring is not anchored in one form by the ring fusion, there is a possibility of conformational mobility. If only two chair forms of the pyranose ring are considered, a shift in equilibrium of the system (VIIa) ⇌ (VIIb) would be reflected in a change in magnitude and ultimately in sign of $\Delta\epsilon$, since the observed dichroic absorption band would be a superposition of the separate bands due to the individual conformers. The relatively greater stability of conformer (VIIa) would be predicted on the grounds of an axial substituent at C(1)[9] and an equatorial substituent at C(2). The values of $\Delta\epsilon$ at various temperatures (°K) for compound (VII) in methanol were: +1·5 (293); +1·6 (249); +1·75 (229); +1·9 (196) (all values at 315 nm.). Dioxan could not be used because of its relatively high freezing point. Positive rotatory power increases significantly when the temperature is lowered; this agrees with an increase in the proportion of conformers having positive Cotton effects; *e.g.* (VIIa), at the expense of conformers with negative rotatory power such as (VIIb) (or perhaps twist conformers of comparable energy). The possibility of an equilibrium between a non-solvated and a solvated species must also be considered. However, (II) in methanol solution shows a change in rotational strength of less than 5% over the same temperature range, suggesting that solvation is effectively constant over this range.

The relationship between ring chirality and sign of the Cotton effect in this type of vicinal diol derivative may have application in the assignment of configuration to polyhydroxylated natural products. These derivatives also promise to be of use in a study of the conformations of carbohydrates and thionocarbonates of acyclic *threo*-vicinal diols may yield information where n.m.r. studies have been inconclusive.[10]



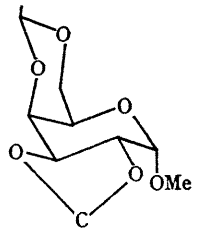
(I)



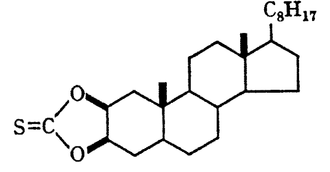
(II) $R^1, R^3 = {}^{\mathrm{O}}_{\mathrm{O}}\!>\!\mathrm{C{=}S}$; $R^2=R^4=\mathrm{H}$

(III) $R^2, R^4 = {}^{\mathrm{O}}_{\mathrm{O}}\!>\!\mathrm{C{=}S}$; $R^1=R^3=\mathrm{H}$

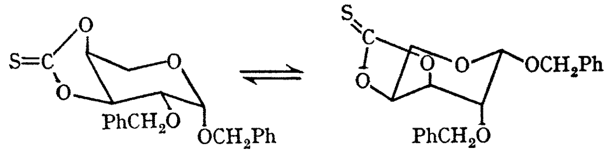
(IV) $R^1, R^4 = {}^{\mathrm{O}}_{\mathrm{O}}\!>\!\mathrm{C{=}S}$; $R^2=R^3=\mathrm{H}$



(V)



(VI)



(VIIa) (VIIb)

We thank Dr. J. MacMillan and Dr. Binks (Bristol) and Dr. J. R. Hanson and Mr. F. Bloss (Sussex) for the determination of mass spectra.

(*Received, February 3rd,* 1969; *Com.* 128.)

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[1] A. H. Haines, *Carbohydrate Research*, 1965, **1**, 214; E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell and C. E. Rist, *ibid.*, 1967, **3**, 354; D. Horton and W. N. Turner, *ibid.*, 1966, **1**, 444; and references quoted therein.

[2] M. J. Janssen, *Rec. Trav. chim.*, 1960, **79**, 464.

[3] W. Kuhn, *Trans. Faraday Soc.*, 1930, **46**, 293.

[4] (a) D. A. Lightner, C. Djerassi, K. Takeda, K. Kuriyama, and T. Komero, *Tetrahedron*, 1965, **21**, 1581; (b) "Optical Rotatory Dispersion in Organic Chemistry," ed. G. Snatzke, Heyden, London, 1967, p. 384.

[5] *Cf.* A. F. Beecham, *Tetrahedron Letters*, 1968, 3591, on γ-lactones.

[6] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformational Analysis," Wiley, New York, 1965, pp. 77, 360.

[7] E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Tetrahedron Letters*, 1967, 4481; A. H. Haines and C. S. P. Jenkins, unpublished observations. We thank Dr. E. I. Stout for a sample of (IV).

[8] S. F. Mason, *Mol. Phys.*, 1962, **5**, 343.

[9] Ref. 6, p. 375.

[10] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 743.