Circular Dichroism of the Nitrato-chromophore

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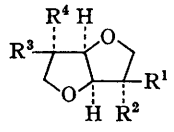
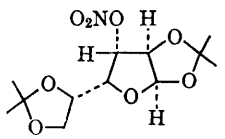
A RECENT Paper describing a circular dichroism (c.d.) band of hexose nitrates at *ca.* 270 nm.[1] prompts us to report the discovery of a second, more intense, dichromic band of the nitrato-chromophore ($-ONO_2$).

The c.d. spectra* of acetonitrile solutions of the mono- and di-nitrate esters of 1,4;3,6-dianhydro-D-mannitol (I and IV), -L-iditol (II and V), and -D-glucitol (III, VI, and VII) showed, in addition to the weak positive dichroic band at *ca.* 265 nm., a second, stronger band near 228 nm., which was positive for the compounds with *endo*-(*R*)-nitrato-groups (I, IV, VI) and negative for those with *exo*-(*S*)-nitrato-groups (II, V, VII). For compound (III) with one *endo*-(*R*)- and one *exo*-(*S*)-nitrato-group, both dichroic bands were positive, $[\theta]_{max}$ for the 225 nm. band (+7260) being approximately one-half the algebraic sum of the values for this band in compounds (I) and (II) (+6970) (Figure). As shown in the Table the signs and positions of





(VIII)

	R^1	R^2	R^3	R^4
(I)	ONO_2	H	ONO_2	H
(II)	H	ONO_2	H	ONO_2
(III)	H	ONO_2	ONO_2	H
(IV)	ONO_2	H	OH	H
(V)	H	ONO_2	H	OH
(VI)	H	OH	ONO_2	H
(VII)	H	ONO_2	OH	H

TABLE

Circular dichroism of nitrato-groups in mono- and di-nitrate esters

Compound	Configuration of nitrato-groups	Dichroic band (nm.)[a]	$[\theta]_{max} \times 10^{-3}$,[a]	$\Gamma/2$ (nm.)[a]
(I)	*endo*(*R*), *endo*(*R*)	265 (265)	+2·48 (+2·97)	20 (20)
		225 (225)	+18·4 (+16·2)	14 (14)
(II)	*exo*(*S*), *exo*(*S*)	265 (265)	+0·43 (+0·15)	19 (18)
		228 (231)	−4·46 (−1·35)	12 (12)
(III)	*endo*(*R*), *exo*(*S*)	265 (260)	+1·58 (+1·75)	19 (19)
		225 (225)	+7·26 (+8·42)	14 (12)
(IV)	*endo*(*R*)	265	+1·82	18
		228	+10·3	15
(V)	*exo*(*R*)	270	+0·40	17
		232	−2·08	9
(VI)	*endo*(*R*)	265	+2·41	19
		228	+11·0	13
(VII)	*exo*(*S*)	270	+0·10	20
		233	−1·91	10
(VIII)	*exo*(*S*)	265	+0·59[b]	21
		224	−4·13	13

[a] In acetonitrile solution. Numbers in parentheses refer to solutions in cyclohexane.
[b] The value quoted for this band at 262 nm. in chloroform solution (ref. 1) appears to have been misprinted; the value estimated from the published spectrum is *ca.* +760.

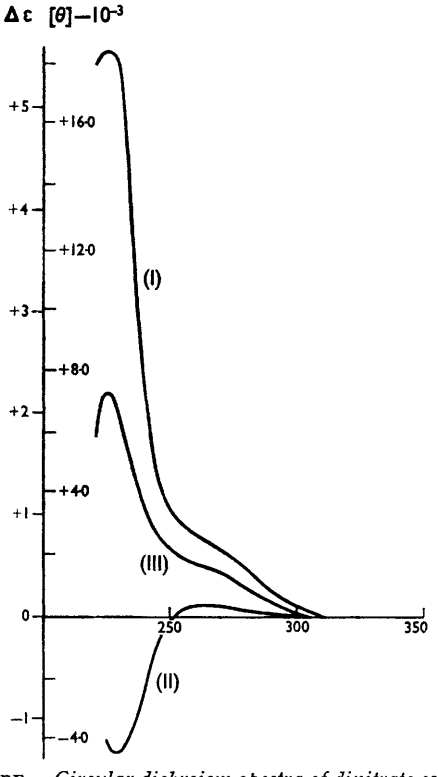


FIGURE. *Circular dichroism spectra of dinitrate esters of* 1,4:3,6-*dianhydro*-D-*mannitol* (I), -L-*iditol* (II), *and* -D-*glucitol* (III) *in acetonitrile.*

these bands were unchanged in cyclohexane solution. Acetylation of compound (VI) also did not alter the nitrato-bands significantly and this was consistent with the occurrence of a *negative* band ($[\theta]_{max}$ −1600) at *ca.* 220 nm. in the c.d. spectrum of the diacetate corresponding to compound (I) and of a *positive* band ($[\theta]_{max}$ +528) in the spectrum of the diacetate corresponding to compound (II). The occurrence of positive (265 nm.) and negative (224 nm.) bands for 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-nitrate (VIII) in acetonitrile was entirely consistent with the *S*- and *exo*-configuration of the nitrato-group. The positive band was previously reported for this compound in chloroform solution.[1] 3β-Cholesteryl nitrate in cyclohexane solution also showed both nitrato-group bands at 265 ($[\theta]_{max}$ +561) and 228 nm. ($[\theta]_{max}$ +1060) respectively.

The 265 nm. nitrato-band, the sign of which was independent of the configuration of the α-carbon atom, was identified with the $n \rightarrow \pi^*$ transition assigned[2,3] to the inflexion ($\epsilon \sim 20$) observed at this wavelength in the isotropic absorption spectra of alkyl mononitrates.[1] The new dichroic band at 228 nm. has not been observed in isotropic spectra probably being obscured by the $\pi \rightarrow \pi^*$ band (ϵ 5800) at 195 nm.[4,5] The identification of the new band, which constitutes a sensitive stereochemical probe for the configuration of optically active

* Spectra were obtained with a circular dichrometer built by the authors at Uppsala and with a JASCO UV/ORD/CD instrument at Vancouver.

alcohols, is being investigated by the Extended Hückel Molecular Orbital method.[6]

(*Received, February 13th*, 1967; *Com.* 130.)

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