577. *Nitro-steroids. Part III.*[1] *Optical Rotatory Dispersion Studies*

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Optical rotatory dispersion curves of a number of nitro-steroids have been measured; the results are compared with those of circular dichroism studies.

A previous Paper in this Series[2] described the circular dichroism curves, measured in Bonn, of a range of nitro-steroids prepared in Oxford.[3] A preliminary attempt has been made [2] to rationalise the curves in terms of a Sector Rule (cf. the Octant Rule for ketones [4] and the Sector Rule for lactones [5]). The present Paper describes the optical rotatory dispersion curves which were measured in London in parallel with the circular dichroism curves. Some other recent optical rotatory dispersion measurements on nitro-compounds have been described.[6-8] These results with the two related techniques are compared for the purpose of seeing how far the theoretical relationships [9] between the two sets of results are borne out in practice, and also to compare the relative virtues of the techniques for purely structural studies. (For general reviews of both techniques, see ref. 10) The Paper also shows comparisons of the optical rotatory dispersion curves in two solvents (hexane and dioxan).

The amplitudes *a* (optical rotatory dispersion) and the $\Delta\varepsilon$ values (circular dichroism) in dioxan for the band corresponding to the $n \longrightarrow \pi^*$ absorption band of the nitro-group at 280 mμ are compared in Table 1. (Optical rotatory dispersion values in hexane are also included here.)

The ratio of $a/\Delta\varepsilon$, which should theoretically [9] be 40 for circular dichroism curves of Gaussian type, ranges in this series from 29 to 75. A significant advantage of circular dichroism over optical rotatory dispersion in this field is that in some cases [2,6] the curves of the former resolve a small band on the longer-wavelength side of the main band, which cannot be distinguished on the curves of the latter. This small longer-wavelength peak may be of the same or opposite sign to the main peak. Surprisingly, the $a/\Delta\varepsilon$ values of these two classes of compound show no significant difference from one another; this means that perhaps in practice the disadvantages of the optical rotatory dispersion technique here are less serious than theory might suggest. It may also be noted that no significant difference between the $a/\Delta\varepsilon$ values for axial and for equatorial nitro-groups is obvious on inspection.

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[1] This Paper is Part III in the Oxford Series on Nitro-steroids (Part II, J. R. Bull, Sir Ewart R. H. Jones, and G. D. Meakins, *J.*, 1965, 2601), Part XI in the Bonn series on Circular Dichroism (Part X, G. Snatzke, *Tetrahedron*, 1965, **21**, 439), and Part XVIII in the Westfield College series on Optical Rotatory Dispersion (Part XVII, A. Kjaer, W. Klyne, P. M. Scopes, and D. R. Sparrow, *Acta Chem. Scand.*, 1964, **18**, 2412.

[2] G. Snatzke, *J.*, 1965, in the press; cf. also for low-temperature measurements, G. Snatzke, D. Becher, and J. R. Bull, *Tetrahedron*, 1964, **20**, 2443.

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[4] W. Moffitt, A. Moscowitz, R. B. Woodward, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.

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TABLE 1

Comparison of optical rotatory dispersion (amplitudes, *a*) and circular dichroism ($\Delta\varepsilon$; main band at 280 mμ) results for nitro-steroids

Configuration	Conformation of NO$_2$	*a* (Hexane)	*a* (Dioxan)	$\Delta\varepsilon$ (Dioxan)	$a/\Delta\varepsilon$ (Dioxan)
4α-NO$_2$,5α	*eq*	+22	+29	+0·63	46
4β-NO$_2$,5α	*ax*	+70	+81	+2·25 *	36 *
4β-NO$_2$,4α-Cl,5α	*ax*	+47	+58	+1·34 *	43 *
4,4-(NO$_2$)$_2$,5α	*ax* + *eq*	+81	+107	+2·52 *	42 *
4α-NO$_2$,5β	*ax*	−27	−53	−1·64	32
4β-NO$_2$,5β	*eq*	+13	+14	+0·38 *	37
6α-NO$_2$,5α	*eq*	+16	+20	+0·68	29
6β-NO$_2$,5α	*ax*	−97	−100	−2·34 *	43 *
6β-NO$_2$,6α-Cl,5α	*ax*	−53	−65	−1·37 *	47 *
6,6-(NO$_2$)$_2$,5α	*ax* + *eq*	−49	−59	−1·35 *	44 *
7α-NO$_2$,5α	*ax*	+21	+36!	+0·48	75!
7β-NO$_2$,5α	*eq*	−42	−47!	−0·84	56!
7β-NO$_2$,7α-Cl,5α	*eq*	−16	−12	−0·24	50
17β-NO$_2$ †	*eq′*	+69	+104	+2·67	39
17β-NO$_2$,17α-Cl	*eq′*	+89	+104	+2·38	44
17β-NO$_2$,17α-Br	*eq′*	+66	+80	+1·88	43
17,17-(NO$_2$)$_2$	*ax′* + *eq′*	+194	+220	+4·49	49

* Has side-band 330 mμ circular dichroism effect of opposite sign to main 280 mμ effect. For other compounds the side-band 330 mμ effect is of same sign as main band. † Substituents at C-17 are quasi-axial and quasi-equatorial (*ax′* and *eq′*).

Experimental.—Optical rotatory dispersion curves were measured on the Bellingham and Stanley–Bendix-Ericsson automatic recording spectropolarimeter "Polarmatic '62." Solvent, dioxan or hexane; $l = 0{\cdot}1$ dm.; $t = 20$—$25°$; $c = 1$ mg.$_4$ml., or less. For details of circular dichroism measurements, see ref. 2.

TABLE 2

Optical rotatory dispersion of nitro-steroids

	Cotton effect in dioxan				Cotton effect in hexane			
Cholestanes	[ϕ]	λ (mμ)	[ϕ]	λ (mμ)	[ϕ]	λ (mμ)	[ϕ]	λ (mμ)
4α-NO$_2$,5α	+880pk	337	−2005infl	268	+920pk	333	−1295infl	260
4β-NO$_2$,5α	+5750pk	303	−2360tr	262	+5210pk	304	−1770tr	264
4α-Cl,4β-NO$_2$,5α	+4080pk	310	−1710tr	267	+3860pk	308	−815	268
4,4-(NO$_2$)$_2$,5α	+5200pk	309	−5500tr	264	+4590pk	310	−3510tr	268
4α-NO$_2$,5β	−2460tr	303	+2860pk	253	−1330tr	303	+1240!	238
4β-NO$_2$,5β	+2050pk	297	+660tr	258	+1895pk	296	+580tr	260
6α-NO$_2$,5α	+1855pk	300	−165tr	265	+1820pk	300	+375tr	266
6β-NO$_2$,5α	−5050tr	306	+4950pk	258	−4530tr	305	+5120pk	261
6α-Cl,6β-NO$_2$,5α	−3050tr	311	+3480pk	264	−2620tr	310	+2655pk	261
6,6-(NO$_2$)$_2$,5α	−1885tr	310	+3980pk	276	−1520tr	313	+3395pk	276
7α-NO$_2$,5α	+120pk	312	−3510!	244	+450pk	313	−1670infl	266
7β-NO$_2$,5α	−300tr	300	+4425!	234	+130tr	306	+4300infl	261
7α-Cl,7β-NO$_2$,5α	+335infl	304	+1545infl	258	+2635!	238		
Androstanes								
17β-NO$_2$,5α	+2880pk	303	−7540tr	256	+2105pk	305	−4750	258
17α-Cl,17β-NO$_2$,5α	+2220pk	314	−8210infl	265	+2710pk	314	−9050!	238
17α-Br,17β-NO$_2$,5α	+2420pk	317	−5530tr	272	+2680pk	316	−3885tr	269
17,17(NO$_2$)$_2$,5α	+6750pk	306	−15,200tr	254	+7070pk	308	−14,960!	234

pk = peak; tr = trough; ! = lowest wavelength measured; infl = inflection.

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