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OPTICAL ROTATORY DISPERSION OF NITROBENZENE DERIVATIVES—I

o-NITROBENZOATES OF SECONDARY ALCOHOLS

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Abstract—A number of *o*-nitrobenzoates of optically active secondary alcohols were prepared and found to show Cotton effects centered at 330 nm in their optical rotatory dispersion. Most esters of *R*-configuration showed negative Cotton effects and those of *S*-configuration positive effects. The sign of these Cotton effects were rationalized in terms of conformational analysis and twisting of the nitrobenzene chromophore.

OPTICALLY active methyl *o*-nitrophenyl carbinol[1] was found to show Cotton effect centered at 330 nm in its ORD. This observation suggested that the nitrobenzene derivatives having an asymmetric center in the vicinity of the nitro group may generally show Cotton effects in this region. The ORD of dinitrobiphenyl derivatives have been reported,[2] but, there has been no general investigation on the ORD of nitrobenzene derivatives. Recently, Tsuzuki *et al.* have reported the ORD of *o*-nitrobenzylidene derivative of diethyl *dx*-tartarate.[3]

o-Nitrobenzoates of sixteen steroidal and monoterpenoid secondary alcohols were prepared and their ORD curves were measured. Their first extrema appeared at 370 nm and the second at 310 nm. Molecular amplitudes of these Cotton effects are presented in Table 1 together with $\Delta[M]_D$-values between the esters and the parent alcohols. CD curves were also measured and their molecular elipticity maxiam are listed in Table 1.

Esters of *R*-configuration show negative Cotton effects and those of *S*-configuration positive effects with a few exceptions. All these results, including the exceptional cases, can be explained on the basis of conformational analysis as follows.

An *o*-nitrobenzoyl ester can take two conformations depending on the relative positions of the nitro and ester groups (Fig. 1). Since strong repulsion is expected between the dipoles of the nitro and ester groups in the conformer **a**, the conformer **b** should be predominant. Considering the conformation around the asymmetric center (Fig. 2). Brewster explained his benzoate rule by assuming that a benzoate is a mixture of two conformers, A and B, which give contribution of opposite sign to the $[M]_D$ of the benzoate and that their relative population determines the sign of the $\Delta[M]_D$ for the benzoate.[4] While Mathieson proposed the conformation C for acetates and haloacetates from the results of X-ray analysis,[5] and Jennings *et al.* explained the ORD data of steroidal acetates depending on the conformation C.[6] The dihedral angle (θ) calculated from the X-ray data of several *p*-bromo- and *p*-iodobenzoates ranges widely between those for the Brewster's and for the Mathieson's conformation (θ = 72·7°, 76·7°, 89·0°, 107·2°, and 119·5°).[7a–e] Thus, no general con-

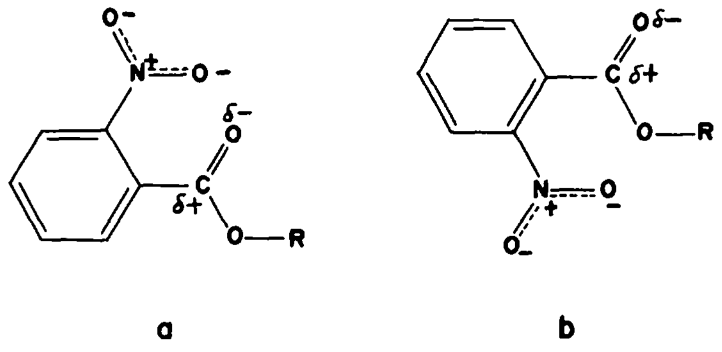
TABLE 1. THE OPTICAL ROTATORY PROPERTIES OF *o*-NITROBENZOATES(o-O_2N—C_6H_4—CO_2R)

Compound No.	R-group	Configuration	Molecular amplitude a	$\delta[M]_D$-value (°)	Max mol elipticity $[\theta]$
I	*lv*-Menthyl	*R*	−57·0	−374	−4250
II	*dx*-Neoisomenthyl	*R*	+24·3	+75	+1750
III	*lv*-Isobornyl	*R*	−12·9	−163	−1390
IV	3β-Acetoxy-5α-pergnan-12β-yl	*R*	−144·0	−629	−11,800
V	3-Methoxyestra-1,3,5(10)-trien-17α-yl	*R*	−57·3	−338	−4560
VI	3β-Acetoxypregn-5-en-20β-yl	*R*	−138·0	−558	−10,650
VII	3β-Acetoxy-5α, 22β, 25D-spirostan-12β-yl	*R*	−146·0	−1124	−11,600
VIII	*dx*-Neomenthyl	*S*	+46·9	+269	+5680
IX	*dx*-Isomenthyl	*S*	+23·8	+204	+1650
X	*dx*-Bornyl	*S*	+28·4	+184	+2050
XI	3β-Acetoxy-5α-pregnan-12α-yl	*S*	+103·7	+339	
XII	3-Methoxyestra-1,3,5(10)-trien-17β-yl	*S*	+plain	−6	
XIII	3β-Acetoxypregn-5-en-20α-yl	*S*	+40·1	+118	+3760
XIV	3β-Acetoxy-5α, 22β, 25D-spirostan-12α-yl	*S*	+96·8	+694	+8610
XV	Cholesteryl	*S*	−2·9*		
			+4·4†	+77	+815
XVI	4,4-Dimethylcholesteryl	*S*	+43·8	+399	+3703

* measured in MeOH-dioxane mixture, † measured in $CHCl_3$.

clusion can be drawn from the X-ray data. Although it is not known which conformer represents the real one in solution for general benzoates, the following discussion is based on the Brewster concept because of the convenience to explain the anomaly in the observed results.

Normally, the conformer **A** predominates and its contribution determines the sign of the Cotton effect of the *o*-nitrobenzoate as is the case with most compounds listed in Table 1. When the substituents L and S are nearly equal in bulkiness as in compound XV the populations of each conformer are also expected to be nearly equal. Then, the



a b

FIG. 1. Two possible conformations of an o-nitrobenzoate regarding the position of the nitro group to the ester group.

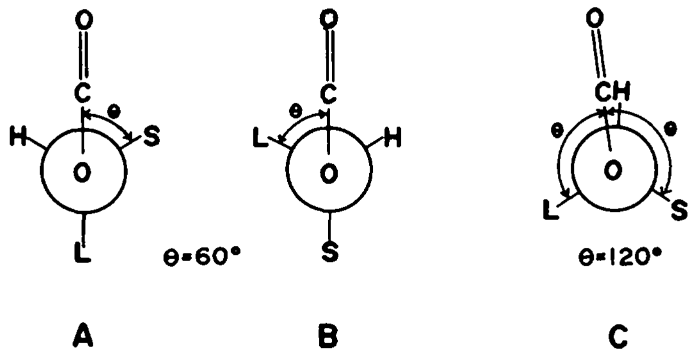


FIG. 2. Three possible conformations around the asymmetric center of an ester of S-configuration.

absolute value of the molecular amplitude would be small and the prediction of the sign of the Cotton effect is difficult because the contributions from each conformer have opposite signs as discussed below. Here, presence of the *o*-nitro group must be taken into account since it affects the stability of the conformers in some cases. When the substituent L contains a group which interacts with the nitro group repulsively, the conformer **A** becomes less stable and its population decreases. On inspection of the Dreiding model the axial isopropyl group of compound II was found to be very near the nitro group (2·5 A N—C distance) in its conformer **A** and strong repulsion is expected between them. The angular Me group of compound (XII is in a similar situation (3·5 A N—C distance) and in its conformer **A** some repulsion is expected. It is interesting to note that compound II has a positive $\Delta[M]_D$-value while *DX*-neoisomenthyl benzoate has a normal negative value ($\Delta[M]_D = -14{\cdot}8°$). Similarly, $\Delta[M]_D$ of compound XII has a sign opposite to that of the corresponding benzoate ($\Delta[M]_D = +22°$). These data suggest that the conformer **B** is predominant in such compounds and that its contribution to the Cotton effect has a sign opposite to that of the conformer **A**. Hence, it can be summarized that normal Cotton effect is observed when the conformer **A** predominates and that abnormal behaviour may be observed when the conformer **B** has a comparable or predominant population.

The 330 nm band is considered due to n—π^* transiton by analogy with nitrobenzene and corresponds to the 280 nm band of aliphatic nitro compounds. Snatzke proposed a sector rule for aliphatic nitro compounds and explained CD spectra of nitro steriods.[8] Since the nitro group in an *o*-nitrobenzoate is considered to be not coplanar with the benzene ring but twisted,[9] simple application of the Snatzke's sector rule does not seem possible. The main origin of the Cotton effects would be unsymmetrical twisting of the nitrobenzene chromophore induced by the neighbouring asymmetric center, i.e. the left- and the right-twisted conformers have unequal populations by interaction of the nitro group with the substituents on the asymmetric C atom. The conformers $\mathbf{A}_1$ and $\mathbf{B}_1$ would be more stable than $\mathbf{A}_2$ and $\mathbf{B}_2$, respectively, because the O atom (O_1) of the nitro group in $\mathbf{A}_1$ and $\mathbf{B}_1$ is situated to the less hindered side (Fig. 3). Since the conformer A is predominant normally for an *o*-nitrobenzoate of *S*-configuration the conformer $\mathbf{A}_1$ should correspond to the positive Cotton effect observed. This suggests that clockwise (counterclockwise) twisting of the nitro group

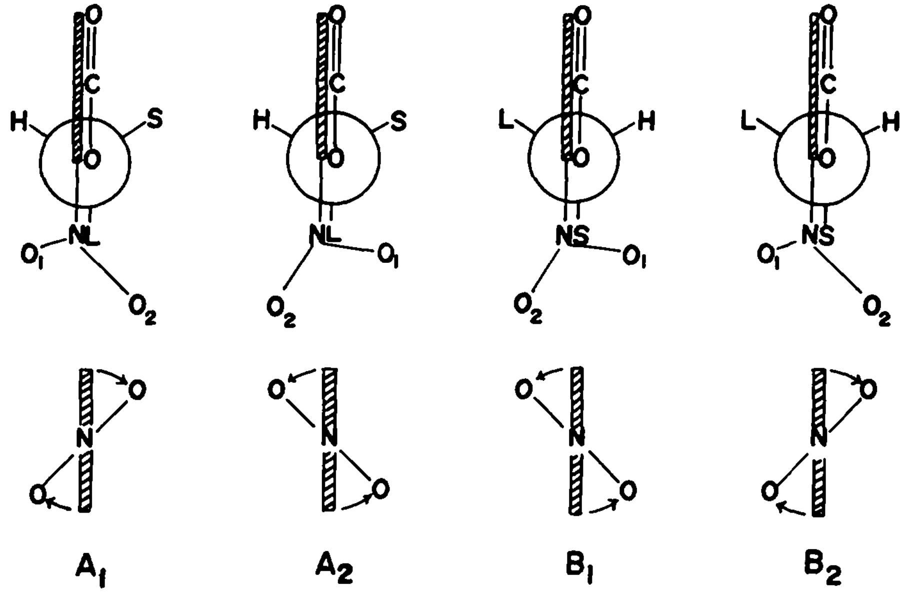


FIG. 3. Possible conformations of an *o*-nitrobenzoate of S-configuration including twist of the nitro group and the projections viewed from the nitro group side. Shaded areas mean the benzene ring.

corresponds to positive (negative) Cotton effect when viewed from the nitro group side. This relation concerning the first sphere chirality coincides formally with the Snatzke's rule that deals with the third and the fourth sphere chirality. On this tentative relation and the conformational analysis, the signs of the Cotton effects of the compounds listed in Table 1 can be rationalized without exceptions.

Hence, the Cotton effects of *o*-nitrobenzoates of secondary alcohols are useful in establishing their absolute configurations.

It is interesting to note that compound XV changes the sign of its Cotton effect when measured in different solvents. Since the absolute values of the molecular amplitudes in both solvents are very small, it can be explained by a slight shift in equilibrium position between the conformers A and B.

The X-ray analysis of some *o*-nitrobenzoate is now being undertaken in order to prove the assumed conformation of *o*-nitrobenzoates.

EXPERIMENTAL

The alcohols used were prepared by reducing the corresponding commercial ketones with LAH or $NaBH_4$ and by resolving the epimeric mixtures formed with preparative TLC unless otherwise stated. M.ps and specific rotations of the alcohols agreed well with that reported in literatures. M.ps are uncorrected. ORD and CD spectra were measured with JASCO Model ORD/UV-5 Optical Rotatory Dispersion Recorder at room temp ranging 10–30°. $[\phi]_{590}$-values were used to calculated $\Delta[M]_D$-values.

General procedures to prepare* o*-nitrobenzoates. The alcohol and excess of *o*-nitrobenzoyl chloride were dissolved in pyridine, sealed in a tube, and kept at room temp. Normally, the reaction was complete after 24 hr. Usual work-up and recrystallization from MeOH gave the pure ester When the ester was not crystalline it was purified by prep TLC.

lv-*Menthyl* o-*nitrobenzoate* (I). M.p. 58–59°; UV: $\varepsilon_{335} = 324$ (MeOH); ORD (*c*, 0·100, MeOH): $[\phi]_{590}$ −434°, $[\phi]_{550}$ −494°, $[\phi]_{500}$ −721°, $[\phi]_{450}$ −1060°, $[\phi]_{400}$ −2270°, $[\phi]_{370}$ −3210° (tr), $[\phi]_{310}$ +2490° (pk), $[\phi]_{300}$ +1310°; CD (*c*, 0·100, MeOH): $[\theta]_{400}$ 0, $[\theta]_{330}$ −4250, $[\theta]_{300}$ −1240. (Found: C, 67·02, H, 7·60; N, 4·51. $C_{17}H_{23}NO_4$ requires: C, 66·86; H, 7·59; N, 4·59%).

dx-*Neoisomenthyl* o-*nitrobenzoate* (II). Oil. UV: $\varepsilon_{335} = 353$ (MeOH); ORD (*c*, 0·088, MeOH): $[\phi]_{590}$ +76°, $[\phi]_{550}$ +104°, $[\phi]_{500}$ +139°, $[\phi]_{450}$ +208°, $[\phi]_{400}$ +640°. $[\phi]_{366}$ +1040° (pk), $[\phi]_{304}$ −1390° (tr), $[\phi]_{296}$ −1360°; CD (*c*, 0·088, MeOH): $[\theta]_{400}$ 0, $[\theta]_{330}$ +1750, $[\theta]_{300}$ +1065. (Found: C, 66·91, H, 7·51, N, 4·70. $C_{17}H_{23}NO_4$ requires: C, 66·86, H, 7·59, N, 4·59%).

lv-*Isobornyl* o-*nitrobenzoate* (III). M.p. 102–106°. UV: $\varepsilon_{335} = 323$ (MeOH); ORD (*c*, 0·129, MeOH): $[\phi]_{590}$ −215°, $[\phi]_{550}$ −284°, $[\phi]_{500}$ −363°, $[\phi]_{450}$ −550°, $[\phi]_{400}$ −950°, $[\phi]_{365}$ −1400° (tr), $[\phi]_{310}$ −108° (pk), $[\phi]_{300}$ −421°; CD (*c*, 0·129, MeOH): $[\theta]_{400}$ 0, $[\theta]_{330}$ −1390, $[\theta]_{320}$ −1220. (Found: C, 67·44, H, 6·95, N, 4·79. $C_{17}H_{21}NO_4$ requires: C, 67·31, H, 6·98, N, 4·62%).

3β-*Acetoxy-5α-pregnan-*12β*-yl* o-*nitrobenzoate* (IV). The corresponding ketone was prepared from hecogenin,[10] and the configuration of the alcohol was determined by NMR; m.p. 151–155°; UV: $\varepsilon_{335} =$ 343 (MeOH); ORD (*c*, 0·108, MeOH): $[\phi]_{590}$ −570°, $[\phi]_{550}$ −665°, $[\phi]_{500}$ −990°, $[\phi]_{450}$ −1620°, $[\phi]_{400}$ −3840°, $[\phi]_{370}$ −6400° (tr), $[\phi]_{306}$ +8000° (pk), $[\phi]_{300}$ +7100°; CD (*c*, 0·108, MeOH): $[\theta]_{410}$ 0, $[\theta]_{330}$ −11800, $[\theta]_{300}$ −4350. (Found: C, 70·35, H, 8·11, N, 2·84. $C_{30}H_{41}NO_6$ requires: C, 70·42, H, 8·08, N, 2·74%).

3-*Methyoxyestra*-1,3,5(10)-*trien*-17α*-yl* o-*nitrobenzoate* (V). M.p. 173–176°; UV: $\varepsilon_{335} = 368$ (MeOH); ORD (*c*, 0·057, MeOH:dioxan = 9:1): $[\phi]_{550}$ −306°, $[\phi]_{500}$ −459°, $[\phi]_{450}$ −915°, $[\phi]_{400}$ −2139°. $[\phi]_{370}$ −3362° (tr), $[\phi]_{306}$ +2368° (pk), $[\phi]_{300}$ +1681°; CD (*c*, 0·057, MeOH:dioxan = 9:1): $[\phi]_{410}$ 0, $[\theta]_{330}$ −4560, $[\theta]_{300}$ −2280. (Found: C, 71·62, H, 6·75, N, 3·26. $C_{26}H_{29}NO_5$ requires: C, 71·70, H, 6·71, N, 3·22%).

3β-*Acetoxypregn-5-en-20β-yl* o-*nitrobenzoate* (VI). M.p. 145–148°; UV: $\varepsilon_{335} = 348$ (MeOH); ORD (*c*, 0·092, MeOH): $[\phi]_{590}$ −775°, $[\phi]_{550}$ −942°, $[\phi]_{500}$ −1270°, $[\phi]_{450}$ −2050°, $[\phi]_{400}$ −4350°, $[\phi]_{370}$ −7550° (tr), $[\phi]_{306}$ +6250° (pk), $[\phi]_{300}$ +5150°; CD (*c*, 0·092, MeOH): $[\theta]_{410}$ 0, $[\theta]_{330}$ −10,650, $[\theta]_{300}$ −3200. (Found: C, 70·69, H, 7·75, N, 3·00. $C_{30}H_{39}NO_6$ requires: C, 70·70, H, 7·71, N, 2·75%).

3β-*Acetoxy-5α,22β,25D-spirostan-12β-yl* o-*nitrobenzoate* (VII). Amorphous powder; UV: $\varepsilon_{335} = 358$ (MeOH); ORD (*c*, 0·14, MeOH): $[\phi]_{590}$ −1330°, $[\phi]_{550}$ −1525°, $[\phi]_{500}$ −1960°, $[\phi]_{450}$ −2760°, $[\phi]_{400}$ −5600°, $[\phi]_{370}$ −8000° (tr), $[\phi]_{306}$ +6600° (pk), $[\phi]_{300}$ +4940°; CD (*c*, 0·14, MeOH): $[\theta]_{410}$ 0, $[\theta]_{330}$ −11,600, $[\theta]_{300}$ −3840. (Found: C, 69·23, H, 7·70, N, 2·23. $C_{36}H_{49}NO_8$ requires: C, 69·30, H, 7·93, N, 2·25%).

dx-*Neomenthyl* o-*nitrobenzoate* (VIII). Oil; UV: $\varepsilon_{335} = 292$ (MeOH); ORD (*c*, 0·105, MeOH): $[\phi]_{590}$ +300°, $[\phi]_{550}$ +360°, $[\phi]_{500}$ +487°, $[\phi]_{450}$ +740°, $[\phi]_{400}$ +1790°, $[\phi]_{370}$ +2660° (pk), $[\phi]_{306}$ −2030° (tr), $[\phi]_{300}$ −1390°; CD (*c*, 0·105, MeOH): $[\theta]_{405}$ 0, $[\theta]_{330}$ +5680, $[\theta]_{300}$ +2240. (Found: C, 66·86, H, 7·52, N, 4·48. $C_{17}H_{23}NO_4$ requires: C, 66·86, H, 7·59, N, 4·59%).

dx-*Isomenthyl* o-*nitrobenzoate* (IX). *dx*-Isomenthol was prepared from *dx*-isomenthylamine;[11] oil; UV: $\varepsilon_{335} = 300$ (MeOH); ORD (*c*, 0·076, MeOH): $[\phi]_{590}$ +248°, $[\phi]_{550}$ +313°, $[\phi]_{500}$ +379°, $[\phi]_{450}$ +505°, $[\phi]_{400}$ +990°, $[\phi]_{370}$ +1380° (pk), $[\phi]_{308}$ −1000° (tr), $[\phi]_{300}$ −642°; CD (*c*, 0·076, MeOH): $[\theta]_{400}$ 0, $[\theta]_{330}$ +1650, $[\theta]_{300}$ +330. (Found: C, 66·74, H, 7·42, N, 4·64. $C_{17}H_{23}NO_4$ requires: C, 66·86, H, 7·59, N, 4·59%).

dx-*Bornyl* o-*nitrobenzoate* (X). M.p. 111–113°; UV: $\varepsilon_{335} = 333$ (MeOH); ORD (*c*, 0·090, MeOH): $[\phi]_{590}$ +250°, $[\phi]_{550}$ +303°, $[\phi]_{500}$ +407°, $[\phi]_{450}$ +529°, $[\phi]_{400}$ +1110°, $[\phi]_{365}$ +1660° (pk), $[\phi]_{308}$ −1180° (tr), $[\phi]_{300}$ −835°; CD (*c*, 0·090, MeOH): $[\theta]_{395}$ 0, $[\theta]_{328}$ +2050, $[\theta]_{300}$ +525. (Found: C, 67·10, H, 6·78, N, 4·42. $C_{17}H_{21}NO_4$ requires: C, 67·31, H, 6·98, N, 4·62%).

3β-*Acetoxy-5α-pregnan-*12α*-yl* o-*nitrobenzoate* (XI). See the comments for compound (IV), m.p. 162–166°; ORD (*c*, 0·071, MeOH): $[\phi]_{590}$ +432°, $[\phi]_{550}$ +563°, $[\phi]_{500}$ +860°, $[\phi]_{450}$ +1580°, $[\phi]_{400}$ +3570°, $[\phi]_{370}$ +5620° (pk), $[\phi]_{310}$ −4570° (tr), $[\phi]_{300}$ −3570°. (Found: C, 70·17, H, 8·09, N, 2·71. $C_{30}H_{41}NO_6$ requires: C, 70·42, H, 8·08, N, 2·74%).

3-*Methoxyestra*-1,3,5(10)-*trien*-17β*-yl* o-*nitrobenzoate* (XII). M.p. 164–168°; ORD (*c*, 0·129, MeOH): $[\phi]_{590}$ +202°, $[\phi]_{550}$ +253°, $[\phi]_{500}$ +303°, $[\phi]_{450}$ +388°, $[\phi]_{400}$ +557°, $[\phi]_{350}$ +810°, $[\phi]_{310}$ +1150°. (Found: C, 71·88, H, 6·73, N, 3·32. $C_{26}H_{29}NO_5$ requires: C, 71·70, H, 6·71, N, 3·22%).

3β-*Acetoxypregn-5-en-20α-yl* o-*nitrobenzoate* (XIII). It was prepared from the 20β-tosylate by treatment with *o*-$O_2N—C_6H_4—CO_2Na$ in acetone, m.p. 220–223°; UV: $\varepsilon_{335} = 334$ (MeOH); ORD (*c*, 0·083, MeOH:dioxan = 1:1): $[\phi]_{590}$ −123°, $[\phi]_{550}$ −92·6°, $[\phi]_{500}$ −61·6°, $[\phi]_{450}$ +61·6°, $[\phi]_{400}$ +616°, $[\phi]_{370}$ +1171° (pk), $[\phi]_{310}$ −2840° (tr), $[\phi]_{300}$ −2596°; CD (*c*, 0·083, MeOH:dioxan = 1:1): $[\theta]_{400}$ 0,

$[\theta]_{330}$ +3760, $[\theta]_{300}$ +1830. (Found: C, 70·43, H, 7·73, N, 2·69. $C_{30}H_{39}NO_6$ requires: C, 70·70, H, 7·71, N, 2·75%).

3β-*Acetoxy-5α,22β,25D-spirostan-12α-yl* o-*nitrobenzoate* (XIV). M.p. 197–199°; UV: $\varepsilon_{335} = 340$ (MeOH); ORD (*c*, 0·100, MeOH): $[\phi]_{590}$ +468°, $[\phi]_{550}$ +624°, $[\phi]_{500}$ +840°, $[\phi]_{450}$ +1310°, $[\phi]_{400}$ +3360°, $[\phi]_{370}$ +5000° (pk), $[\phi]_{310}$ −4680° (tr), $[\phi]_{300}$ −3380°; CD (*c*, 0·100, MeOH): $[\theta]_{400}$ 0, $[\theta]_{330}$ +8610, $[\theta]_{300}$ +4530. (Found: C, 69·10, H, 7·80, N, 2·32. $C_{36}H_{49}NO_8$ requires: C, 69·30, H, 7·93, N, 2·25%).

Cholesteryl o-*nitrobenzoate* (XV). M.p. 146–148°; UV: $\varepsilon_{335} = 334$ (MeOH:dioxan = 3:2); ORD (*c*, 0·202, MeOH:dioxan = 3:2): $[\phi]_{400}$ −53·6°, $[\phi]_{376}$ −75·0° (tr), $[\phi]_{315}$ +230° (pk), $[\phi]_{310}$ +185°; (*c*, 1·05, $CHCl_3$): $[\phi]_{590}$ −38·6°, $[\phi]_{550}$ −48·8°, $[\phi]_{500}$ −57·0°, $[\phi]_{450}$ −46·6°, $[\phi]_{400}$ +15·3°, $[\phi]_{376}$ +51·0° (pk), $[\phi]_{315}$ −386° (tr), $[\phi]_{310}$ −285°; CD (*c*, 1·05, $CHCl_3$): $[\theta]_{390}$ 0, $[\theta]_{335}$ +815, $[\theta]_{320}$ +285. (Found: C, 76·18, H, 9·09, N, 2·51, $C_{34}H_{49}NO_4$ requires: C, 76·22, H, 9·22, N, 2·61%).

4,4-Dimethylcholesteryl o-*nitrobezoate* (XVI). M.p. 174–176°; UV: $\varepsilon_{335} = 385$ (MeOH: dioxan = 3:2), $[\alpha]_D^{12}$ +21·4° (*c*, 0·56, $CHCl_3$); ORD (*c*, 0·100, MeOH:dioxan = 3:2): $[\phi]_{550}$ +112°, $[\phi]_{500}$ +135°, $[\phi]_{450}$ +247°, $[\phi]_{400}$ +730°, $[\phi]_{366}$ +1460° (pk), $[\phi]_{300}$ −2921° (tr), $[\phi]_{290}$ −2584°; CD (*c*, 0·100, MeOH:dioxan = 3:2): $[\theta]_{400}$ 0, $[\theta]_{325}$ +3703, $[\theta]_{300}$ +3036. (Found: C, 76·63, H, 9·75, N, 2·43. $C_{36}H_{53}NO_4$ requires: C, 76·69, H, 9·48, N, 2·48%).

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