Chiroptical Studies. Part 96.[1] Short Wavelength (190 nm) Circular Dichroism of Ketones

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C.d. data in the region of 190 nm are analysed for 152 chiral ketones, by the empirical methods used recently in re-evaluating c.d. data for the $n \longrightarrow \pi^*$ transition (*ca.* 290 nm). The 190-nm c.d. band for compounds of either *trans*- or *cis*-decalone type is generally dominated by octant-consignate contributions of any axial alkyl substituents at the ring junction positions ' α ' or ' β ' to the carbonyl function. Group increments ($\Delta\delta\varepsilon$) derived from this analysis allow the ' prediction ' of values of $\Delta\varepsilon$, although less accurately than for the $n \longrightarrow \pi^*$ band. Compounds which include a cyclopentanone ring exhibit c.d. behaviour with signs which depend both upon the contributions of any ' α '- or ' β '-axial methyl substituents and on the conformation of the cyclopentanone ring itself. The structural information which can be obtained from the ' 190 nm ' c.d. band differs markedly in some respects from that provided by the well known $n \longrightarrow \pi^*$ c.d. band. Some applications are suggested.

THE circular dichroism of ketones in the short wavelength region (below 200 nm) has received very little study until recently, largely because of instrumental limitations. Instruments now available, however, permit the routine determination of c.d. curves to about 185 nm, opening the way for a systematic study of this part of the c.d. spectrum of ketones in solution. Apart from our own work,[2] short-wavelength c.d. appears to have been reported for only a very limited number of simple ketones.[3-8] In three cases measurements in the vapour phase were extended to *ca.* 160 nm.[4-6]

There is still much uncertainty as to assignments of carbonyl absorption bands below 200 nm. Absorption spectra for some polycyclic ketones of steroid type exhibit *apparent* maxima or inflections between 200 and 185 nm.[9-12] With strongly-rising background absorption curves, however, and the intervention of solvent absorption,[11] it has not been possible to obtain clearly defined and reliable absorption maxima below 200 nm except for some very simple ketones and aldehydes.[13-15] A recent study [15] between 200 and 167 nm, for example, has shown that acetone exhibits a distinctive absorption spectrum in the vapour phase, with vibrational fine structure; the main intensity is in a band at *ca.* 196 nm, with a progression of lower-intensity bands towards shorter wavelengths. In solution, however, the absorption maximum varies in wavelength according to the polarity of the solvent, ranging between 185 nm in hexane and 171 nm in 2,2,2-trifluoroethanol. All fine structure is lost in solution, even in hexane. Spectra for butan-2-one and pentan-2-one in solution were marginally red-shifted (*ca.* 2—3 nm) by comparison with that for acetone. The vapour-phase u.v. spectrum of (+)-3-methylcyclopentanone also showed fine structure; the first component band in the region of present interest is at *ca.* 200 nm, corresponding exactly to a peak in the c.d. spectrum.[4-6]

Most authors refer to the u.v. and/or c.d. band in the 200—185 nm region as deriving from the $n \longrightarrow \sigma^*$ transition,[2,4,9,14-16] following a proposal first advanced by McMurry [17] on the basis of calculations of intensities. Low-energy Rydberg states,[13] however, appear to mix into antibonding valence states. Evidence was recently presented [18] that the $n \longrightarrow 3s$ (Rydberg) transition appears at *ca.* 196 nm for acetone, although those authors regarded the subject of low-energy Rydberg transitions as ' a patchwork of poorly-founded assertions and shrewd guesswork.' The supposedly $n \longrightarrow \sigma^*$ bands for acetone and butan-2-one vapour show pressure sensitivity,[15] which is consistent with the promotion of an electron into a Rydberg-type orbital which extends over the whole of the molecule.[13,19] Rydberg states have also been assigned for formaldehyde.[13,20] It is generally agreed that the $n \longrightarrow 3s$ transition is the only one of Rydberg type which appears in the region between 170 and 200 nm; transitions to Rydberg $3p$ and $3d$ orbitals occur at higher energy.[13]

The location of the carbonyl $\pi \longrightarrow \pi^*$ transition is still a subject for discussion, but there is wide agreement [4,14,17,18,21] that it lies in the far ultraviolet, well beyond the region covered by the present work. A band detected at 167 nm in the spectrum of 3-methylcyclopentanone, for example, has been tentatively assigned [4] to the first vibronic component of the $\pi \longrightarrow \pi^*$ transition, although, in the case of acetone, a band at *ca.* 164 nm was considered to derive from a second Rydberg transition ($n \longrightarrow 3p$).[18]

The only other proposal found in the literature with possible relevance to the present work came from Barnes and Simpson,[21] and concerns the $n' \longrightarrow \pi^*$ transition. This transition, tentatively located by those authors at 187 nm for acetone, was considered to originate from the lower-lying of the two non-bonding orbitals on oxygen, which is believed to have substantial $2s$ character, in contrast with the higher energy $2p_x$ orbital which is formally the origin of the $n \longrightarrow \pi^*$ transition. It seems unlikely, however, that the n'-orbital would be of sufficiently high energy to contribute to a transition at *ca.* 190 nm, and the $n' \longrightarrow \pi^*$ transition has been more recently discounted by Johnson and Simpson [16] on the basis of a polarisation study. We therefore assume for the present that the ' 190 nm ' circular dichroism described in this paper is associated with the $n \longrightarrow \sigma^*$ or the $n \longrightarrow 3s$ transition, or possibly some admixture of the two.[22]

Present Work

The present c.d. study covers the range down to *ca.* 185 nm, the practical limit for routine measurements with a standard instrument. Whenever possible n-hexane was used as the solvent, because of its non-associating character, but acetonitrile was employed when necessary to overcome solubility difficulties.

The 152 ketones examined were mostly of steroid type, but included a few simpler mono-, bi-, and tri-cyclic compounds. Although the 190 nm region of the spectrum is unlikely ever to prove as useful to organic chemists as measurements of c.d. at the $n \longrightarrow \pi^*$ transition,[23] the data presented and analysed here suggest that complementary information obtained from the short-wavelength region may find applications for structural and stereochemical assignments when $n \longrightarrow \pi^*$ data alone are inconclusive. One major limitation, however, stems from the likely interference of other chromophores which have absorption bands near 190 nm. For this reason compounds containing olefinic,[24,25] aromatic, bromo, iodo, and other interfering groups,[25] were excluded from study. Acetoxy-groups at the common positions in steroids generally do not interfere, having no measurable c.d. band between 185 and 200 nm.[26] Steroidal 3-hydroxy-groups show negligible c.d.,[27] but hydroxy-groups at other positions were avoided as far as possible in view of their c.d. contributions of up to 2 units ($\Delta\varepsilon$) between 190 and 200 nm.[27] This paper includes data for a few androstan-17β-ol derivatives, which may show a weakly negative contribution to c.d. near 190 nm, attributed to the 17β-hydroxy-group.[27]

The strategy, methods, and symbolism used in this work were as described in the four recent papers [28-31] in which we reassessed c.d. data for the carbonyl $n \longrightarrow \pi^*$ transition. Measurements below 200 nm are less reproducible and contain a higher level of instrumental 'noise' than those near 290 nm (the signal : noise ratio at 190 nm is typically between 10 : 1 and 4 : 1). In cases of doubt, c.d. curves were run several times in superimposition, to average out the 'noise' as far as possible. Measured values of $\Delta\varepsilon$ are quoted to the nearest 0.1 unit (l mol^{-1} cm^{-1}) but some may contain instrumental errors of up to $\pm 10\%$. Values of $\Delta\varepsilon$ range from zero to *ca.* ± 16 units. Many c.d. curves exhibited distinct maxima near 190 nm, but in some cases the values of $\Delta\varepsilon$ were taken from shoulders at or near 190 nm on steeply rising background curves of the same sign, with the aid of a Du Pont 301 Curve Resolver.[24] The background c.d. is probably associated with unidentified transitions in the hydrocarbon framework,[32] or possibly with higher-energy transitions of the carbonyl group, with maxima below 185 nm. C.d. measurements beyond 185 nm on compounds with a hydrocarbon framework as large as that in steroids seem unlikely to yield useful information about further transitions of the carbonyl group.

The present data contain no recognisable pattern of dependence of the wavelengths of c.d. maxima on molecular structure. Tabulated wavelengths lie mainly in the rather narrow range 185—196 nm, but wavelengths given for apparent maxima below 190 nm are probably unreliable in view of the strength of background absorption.

The analysis of c.d. curves which follows is wholly empirical, its purpose being to 'map' the space around the carbonyl group in terms of perturbing effects of substituents. As with the $n \longrightarrow \pi^*$ c.d. data it has proved possible to assign increments to suitably chosen structural components which make up the dissymetric environment of the chromophore. Additivity of group contributions [28] was again assumed as a practical convenience, although the present results indicate that additivity is generally less satisfactory than for $n \longrightarrow \pi^*$ data.† A few gross departures from additivity are noted. The present conclusions differ in several important respects from those contained in the familiar Octant Rule [33] and its extensions.[28-31,34,35] These special features should have value both to organic chemists concerned with structural problems, and to spectroscopists whose aim is to locate and identify the electronic transitions of the carbonyl group which lie below 200 nm.

The terms 'consignate' and 'dissignate' [36] are used here in the same way as they were for the $n \longrightarrow \pi^*$ transition,[28-31] with reference to a three-dimensional frame of right-handed Cartesian co-ordinates, having its origin at the mid-point of the carbonyl bond (Figure 1). This is

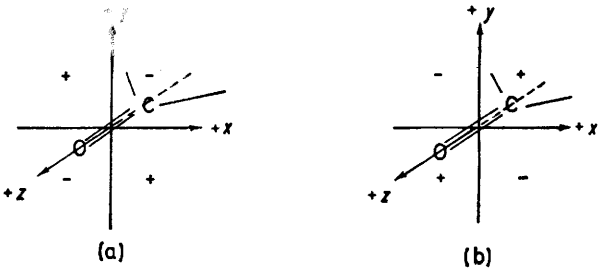


FIGURE 1 Right-handed Cartesian co-ordinate frame. 'Consignate' behaviour corresponds to the signs indicated (a) for rear octants (z negative), (b) for front octants (z positive)

the geometric framework of the normal carbonyl Octant Rule.[33] Its use in the following sections is a matter of convenience for location of substituents, and does not imply that an Octant Rule is necessarily appropriate for the 190 nm c.d. (see Discussion, p. 801).

Analysis of C.D. Data (*Tables* 1—6).—The following analysis uses data for solutions in hexane whenever these are available. Values of $\Delta\varepsilon$ often show some solvent sensitivity on changing to acetonitrile.

(A) trans-*Decalones and extended derivatives* (*Table* 1). *trans*-1-Decalone (5) itself exhibits significant c.d. [$\Delta\varepsilon$

†A referee has pointed out that the dimensionless g-factor ($\Delta\varepsilon/\varepsilon$) would provide a more reliable common scale than $\delta\Delta\varepsilon$ for group contributions. The use of $\delta\Delta\varepsilon$ is reliable only if ε is fairly constant over a group of compounds. Some measurements of ε were attempted among the present ketones, but the 190 nm absorption band at best appeared as a weak shoulder on the background absorption, so reliable values of ε could not be obtained.

TABLE 1

C.d. data for the ' 190-nm ' transition of ketones: cyclohexanones, *trans*-decalones, and their polycyclic analogues

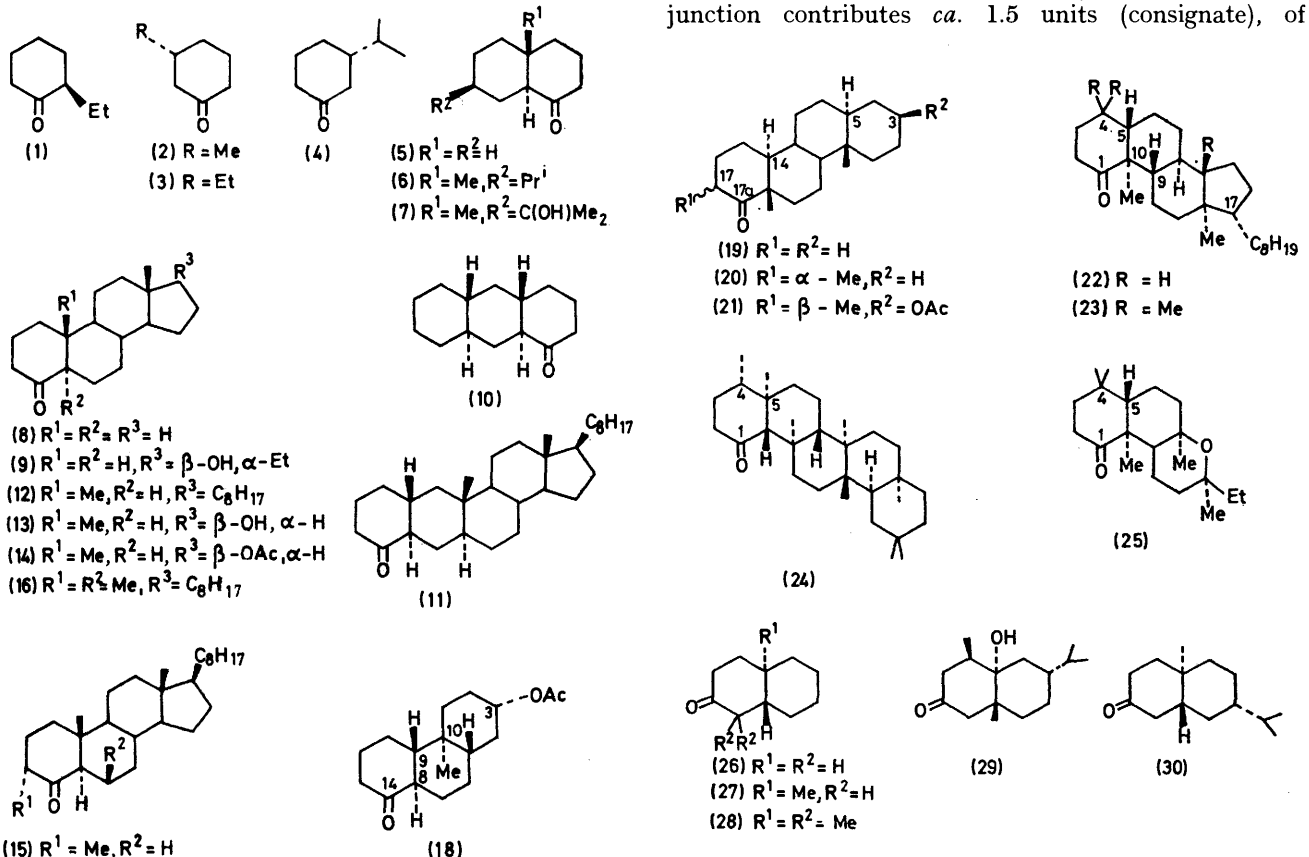
Compound	Solvent [a]	Δε (obs.) ($\lambda_{max.}$)	Δε (calc.) [b]
Cyclohexanones			
(2*R*)-2-Ethylcyclohexanone (1)	H	−1.1 (191)	−2
(3*R*)-3-Methylcyclohexanone (2)	H	+1.0 (185)	+0.5
(3*R*)-3-Ethylcyclohexanone (3)	H	+0.4 (191)	+0.5
(3*S*)-3-Isopropylcyclohexanone (4)	H	0.0	−0.5
trans-1-Decalones and extended derivatives			
(9*S*,10*R*)-*trans*-1-Decalone {(4a*R*,8a*S*)perhydronaphthalen-1-one} (5)	H	+3.6m (188)	+3.5
(7*S*,9*S*,10*S*)-10-Methyl-7-isopropyl-*trans*-1-decalone (6)	H	+5.6 (191)	+5.0
(7*S*,9*S*,10*S*)-10-Methyl-7-(1-hydroxy-1-methylethyl)-*trans*-1-decalone (7)	H	−4.8m (191)	+5.0
5α-Estran-4-one (8)	H	−4.7m (192)	−4.8
17α-Ethyl-17β-hydroxy-5α-estran-4-one (9)	H	−4.8 (189)	−4.8
	A	−3.5m (193)	
(4a*S*,8a*R*,9a*S*,10a*R*)-Perhydroanthracen-1-one (10)	H	+3.9 (187)	+3.8
4′-Oxo-2α,3β-tetramethylene-5α-cholestane (11)	H	−4.2m (194)	−4.1
5α-Cholestan-4-one (12)	H	−5.6m (191)	−6.3
	A	−2.0m (193)	
17β-Hydroxy-5α-androstan-4-one (13)	A	−3.6m (191)	−6.3
17β-Acetoxy-5α-androstan-4-one (14)	H	−5.4m (192)	−6.3
	A	−5.8m (191)	
3α-Methyl-5α-cholestan-4-one (15)	H	−1.7m (194)	−2.3
5-Methyl-5α-cholestan-4-one (16)	H	0.0	+0.2
6β-Methyl-5α-cholestan-4-one (17)	H	−5.7m (190)	−7.8
3β-Acetoxy-des-D-5α,13β(H)-androstan-14-one (18)	H	0.0	0.0
D-Homo-5α-androstan-17a-one (19)	H	−5.5m (189)	−5.2
	A	−6.0m (190)	
17α-Methyl-D-homo-5α-androstan-17a-one (20)	H	−6.1m (190)	−5.7
3β-Acetoxy-17β-methyl-D-homo-5α-androstan-17a-one (21)	H	−2.3m (190)	−3.4 [c]
5α-Cholestan-1-one (22)	H	+6.8m (189)	+6.5
	A	+7.9m (193)	
5α-Lanostan-1-one (23)	H	+2.5m (193)	+6.5
Friedelan-1-one (24)	H	+4.2 (195)	+5.0
1-Oxo-' dihydromanoyl oxide ' (25)	H	+4.6 (188)	+6.5
	A	+4.3 (195)	
trans-2-Decalones and extended derivatives			
(9*R*,10*R*)-*trans*-2-decalone (26)	H	−0.5m (190)	−0.5
(9*R*,10*R*)-10-Methyl-*trans*-2-decalone (27)	H	0.0	0.0
(9*S*,10*R*)-1,1,10-Trimethyl-*trans*-2-decalone (28)	H	−0.7 (196)	−2.5
(4*R*,6*R*,9*R*,10*S*)-10-Hydroxy-4,9-dimethyl-6-isopropyl-*trans*-2-decalone (29)	H	−4.9m (192) +1.3 (184)	(−)
(7*S*,9*R*,10*R*)-10-Methyl-7-isopropyl-*trans*-2-decalone (30)	H	+1.3 (185)	+1.5 [d]
(4a*S*,8a*R*,9a*R*,10a*R*)-Perhydroanthracen-2-one (31)	H	+1.5 (185)	+1.0
(4a*S*,5a*R*,6a*R*,10a*R*,11a*R*,12a*R*)-Perhydronaphthacen-2-one (32)	H	+2.0sh (187—190)	+1.5
		+3.0 (185)	
	A	+3.8 (189)	
(4a*R*,4b*S*,8a*R*,10a*S*)-Perhydrophenanthren-3-one (33)	H	−1.0m (195)	−0.5
	H	+1 (189)	
Des-D-5α,13β(H)-androstan-2-one (34)		+4.5m (189)	+4.5
19-Nor-5α-cholestan-2-one (35)	H	0.0	−2.5
5α-Cholestan-2-one (36)	H	+4.9m (194)	+2.5
	A	+3.2 (190)	
3β-Methyl-5α-cholestan-2-one (37)	H	−1.6m (192)	+1.0
3,3-Dimethyl-5α-cholestan-2-one (38)	H	+1.8m (184)	+0.5
(25*R*)-5α-Spirostan-2-one (39)	H	+5.3m (191)	+2.5
D-homo-5α-androstan-2-one (40)	H	+2.2 (190)	+2.5
4,4-Dimethyl-5α-androstan-2-one (41)	H	−0.5m (196)	?
	A	−0.5m (199)	
17β-Acetoxy-5α-estran-3-one (42)	H	0.0	0.0
	A	0.0	
17β-Acetoxy-4,4-dimethyl-5α-estran-3-one (43)	H	+0.3m (193) +2.1 (183)	+2.5
17α-Ethyl-17β-hydroxy-5-methyl-5α-estran-3-one (44)	H	+0.5 (190)	+5.0
5α-Cholestan-3-one (45)	H	−0.6 (192)	−0.5
	A	−2.1 (189)	
3′-Oxo-2α,3β-tetramethylene-5α-cholestane (46)	H	−0.7m (193)	−1.0
2α-Methyl-5α-cholestan-3-one (47)	H	+0.9m (190)	−2.0
2,2-Dimethyl-5α-cholestan-3-one (48)	H	−0.9 (191)	?
17β-Acetoxy-2α-methyl-5α-androstan-3-one (49)	H	−2.8 (186)	−2.0
17β-Acetoxy-4α-methyl-5α-androstan-3-one (50)	H	+1.6 (190)	+1.5
17β-Acetoxy-4β-methyl-5α-androstan-3-one (51)	H	0.0	+0.0
6α-Hydroxy-5α-cholestan-3-one (52)	H	0.0	0.0
6α-Acetoxy-5α-cholestan-3-one (53)	H	0.0	0.0
6β-Hydroxy-5α-cholestan-3-one (54)	H	−3.3m (190)	−3.5
6β-Acetoxy-5α-cholestan-3-one (55)	H	−2.6m (190)	−3.5
6β-Trifluoroacetoxy-5α-cholestan-3-one (56)	H	−3.6m (190)	−3.5
6α-Methyl-5α-cholestan-3-one (57)	H	0.0	0.0

TABLE 1 (*Continued*)

Compound	Solvent	Δε(obs.) ($\lambda_{max.}$)	Δε (Calc.)
6β-Methyl-5α-cholestan-3-one (58)	H	−2.4 (187)	−3.5
	A	−2.9 (190)	
17α-Ethyl-17β-hydroxy-6α-methyl-5α-androstan-3-one (59)	A	−2.5 (192)	0.0
17α-Ethyl-17β-hydroxy-6β-methyl-5α-androstan-3-one (60)	H	−3.5 (187)	−3.5
	A	−3.0 (195)	
4,4-Dimethyl-5α-cholestan-3-one (61)	H	+1.6m (192)	+2.0
	A	+1.4m (194)	
17β-Acetoxy-4,4-dimethyl-5α-androstan-3-one (62)	H	+1.3m (192.5)	+2.0
17β-Acetoxy-4,4-dimethyl-B-nor-5α-androstan-3-one (63)	H	−0.7 (188)	?
4,4,14-Trimethyl-5α-cholestan-3-one (64)	H	+1.1m (196)	+2.0
	A	+1.3m (195)	
Lupan-3-one (65)	H	+1.5m (193)	+2.0
	A	+1.7m (195)	
Friedelan-3-one (' Friedelin ') (66)	H	−6.3 (192)	−7.0
	A	−2.7 (194)	
5α,9β-Ergost-22-en-3-one (67)	H	0.0	0.0
17β-Hydroxy-5β,9β,10α-androstan-3-one (68)	H	−2.1 (185)	0.0
5β,8α,10α-Ergost-22-en-3-one (69)	H	0.0	0.0
3β-Acetoxy-D-homo-5α-androstan-17-one (70)	H	−5.0m (187)	−5.0
	A	−3.5m (187)	

[a] H = n-hexane, A = acetonitrile. [b] ' Calc.' values of Δε are derived from ring increments in Figure 8, and methyl substituent increments in Table 2; substituents other than methyl are allotted the increments for methyl at the same position. [c] See Appendix. [d] The isopropyl group extends a primary zig-zag, and is treated as being equivalent to the third ring in a perhydroanthracen-2-one [*cf.* compound (31)].

+3.6; (9*S*,10*R*)-enantiomer]. A similar contribution, appropriately signed, is assumed for the *trans*-1-decalone component of 4-oxo-5α- and 1-oxo-5α-steroids of various types, and for 17a-oxo-D-homoandrostanes. Pairwise comparisons in the usual way,[28] and inspection of the data for this group of compounds as a whole, led to the ' best set ' of group contributions presented in Figure 2. An axial methyl group at the ' α ' ring-junction position makes a very pronounced consignate contribution (*ca.* 10 units), whereas a ' β '-axial methyl group at the ring junction contributes *ca.* 1.5 units (consignate), of opposite sign. Additivity fails, however, when both ' α '- and ' β '-axial methyl groups are present together (*e.g.* in 5-methyl-5α-cholestan-4-one): the apparent combined contributions of these substituents amounts to only *ca.* 5 units instead of 8.5 (= 10 − 1.5), although



still consignate with respect to the larger effect of the ' α '-axial methyl group. The net effect of the two methyl groups is as if the ' β '-axial group were making an extra large consignate contribution of 5 units, which would correspond to its effect in a *trans*-2-decalone (see below). Evidently ' α '- and ' β '-axial methyl groups on the same side of the carbonyl group do not act independently, perhaps because they are connected through a planar zig-zag of C–C bonds, a favourable ' coupling path ' [28,34,37] for interaction.

There is one notable exception to the consignate behaviour of an ' α '-axial methyl group: the contribution of the 3α-methyl group in 3α-methyl-5α-cholestan-4-one (15) is strongly dissignate. This apparently odd behaviour finds analogy and is discussed later (p. 796).

The ' third ' ring marked F on Figure 2 corresponds to ring C of a 1-oxo-5α-steroid, conventionally regarded as projecting into a ' front octant.' [28] The value of Δε for 5α-cholestan-1-one (+7), however, is close to that expected from rings A and B alone, with the ' α '-axial 10β-methyl group (' calc.' +6.5). It appears that rings

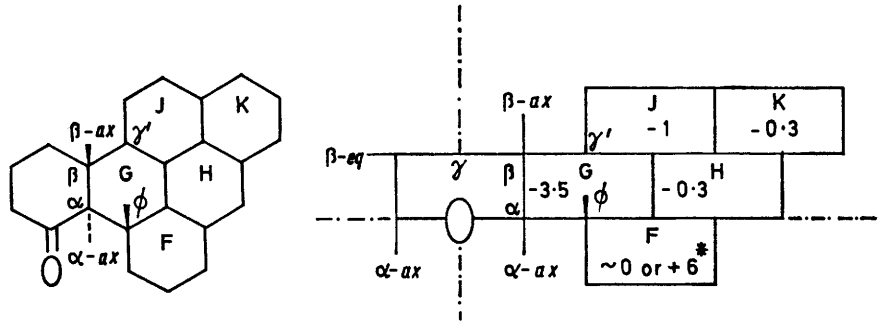
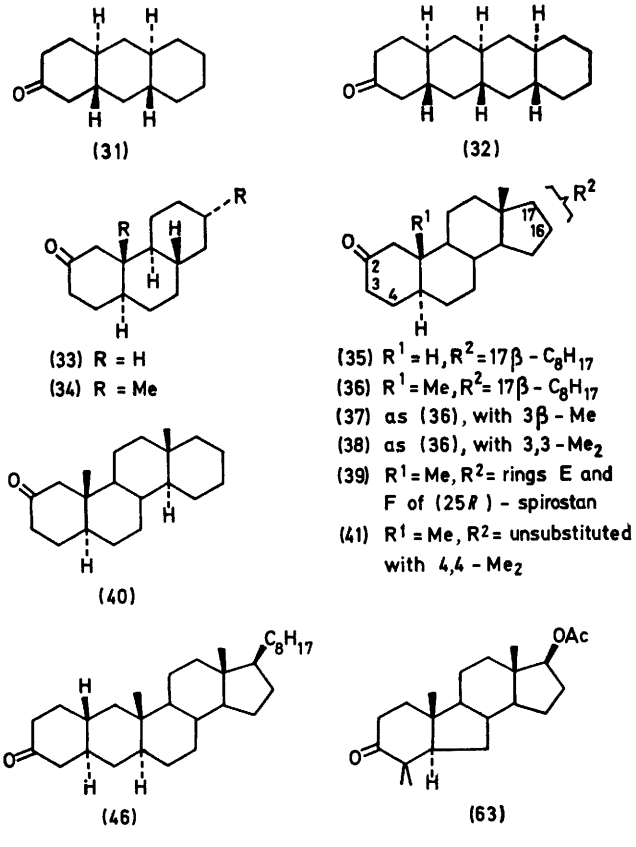
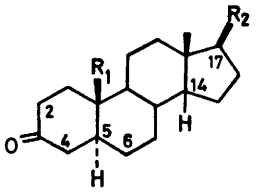


FIGURE 2 'All-*trans*' polycyclic array based on *trans*-1-decalone, with ' octant ' projection showing contributions of individual rings to Δε. (Signs are reversed for corresponding rings in octants to left of the carbonyl group)

* Ring F makes little apparent contribution in a few cases, but more commonly makes a substantial contribution—see p. 802.





	R¹	R²	other substituents
(42)	H	OAc	
(43)	H	OAc	4,4 - Me2
(44)	H	OH	17α - Et, 5 - Me
(45)	Me	C8H17	
(47)	Me	C8H17	2α - Me
(48)	Me	C8H17	2,2 - Me2
(49)	Me	OAc	2α - Me
(50)	Me	OAc	4α - Me
(51)	Me	OAc	4β - Me
(52)	Me	C8H17	6α - OH
(53)	Me	C8H17	6α - OAc
(54)	Me	C8H17	6β - OH
(55)	Me	C8H17	6β - OAc
(56)	Me	C8H17	6β - OCOCF3
(57)	Me	C8H17	6α - Me
(58)	Me	C8H17	6β - Me
(59)	Me	OH	17α - Et, 6α - Me
(60)	Me	OH	17α - Et, 6β - Me
(61)	Me	C8H17	4,4 - Me2
(62)	Me	OAc	4,4 - Me2
(64)	Me	C8H17	4,4,14 - Me3

c and D make little, if any, contribution to the c.d. of 5α-cholestan-1-one. In the quasi-enantiomeric friedelan-1-one the net contribution of rings C, D, and E is at most −2 units. These conclusions contrast sharply with those drawn from 7-oxo-steroids (p. 795),[38] where the 'front octant' ring D makes a large contribution, values of Δε dominated by a large consignate 'β'-axial methyl contribution (*ca.* 5 units). This effect is much larger than that (*ca.* 1.5) due to 'β'-axial methyl in a simple *trans*-1-decalone, but has the same value as that which results from addition of a 'β'-axial methyl substituent to a *trans*-1-decalone which already has a

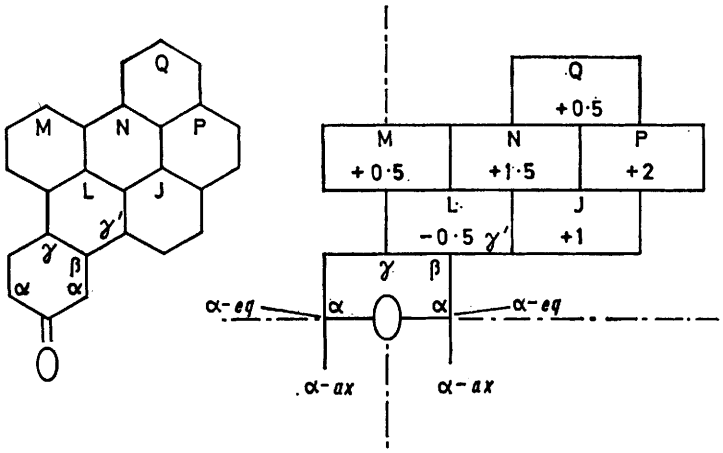
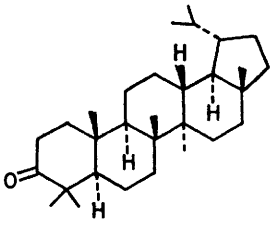


FIGURE 3 'All-*trans* polycyclic array based on *trans*-2-decalone, with 'octant' projection showing contributions of individual rings to Δε

depending upon its size (whether five- or six-membered).

trans-2-Decalone (26) and its extended derivatives of '3-oxo-5α-steroid' type give very small values of Δε (0—0.5, consignate) unless a 'β'-axial methyl substituent is present at the ring junction. Compounds of '2-oxo-perhydroanthracene' (31) and '2-oxo-perhydronaphthacene' type (32) in contrast, show apparent small



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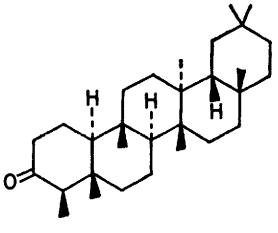

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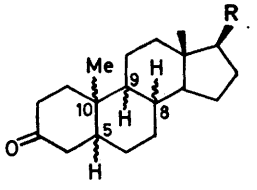
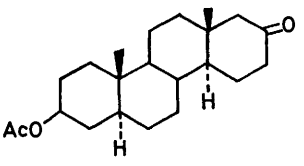


(67) 5α,8β,9β,10β, R = C_9H_{17}
(68) 5β,8β,9β,10α, R = OH
(69) 5β,8α,9α,10α, R = C_9H_{17}



(70)

dissignate contributions from the addition of the third and fourth rings in this linear type of structure. Those compounds of the *trans*-2-decalone series with a 'β'-axial methyl group at the ring junction [*e.g.* 5α-cholestan-2-one (36) and a D-homo-5α-androstan-17-one (70)] give 'β'-axial methyl substituent (see above). Variability of 'β'-axial methyl contributions has been noted previously for the $n \longrightarrow \pi^*$ transition.[28]

Rings C and D appear to contribute nothing to Δε for

TABLE 2

Summary of increments (δΔε) for methyl substituents in compounds of *trans*-1- and *trans*-2-decalone types

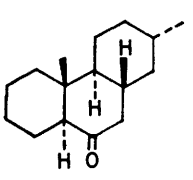
(Refer respectively to Figures 2 and 3 for locations of substituents)

Methyl group location	Compound type: *trans*-1-1-Decalone δΔε	*trans*-2-Decalone δΔε
'α'-Axial (at ring junction)	10 (con) [a]	
'α'-Axial (adjacent to 2nd ring)		0.5 (dis) [a]
'α'-Axial (remote from 2nd ring)	4 (dis)	
'α'-Equatorial (adjacent to 2nd ring)		2 (con)
'α'-Equatorial (remote from 2nd ring)	0.5 (con)	1.5 (con)
'β'-Axial (at ring junction, in *absence* of 'α'-axial Me)	1.5 [b] (con)	5 [b] (con)
'β'-Axial (at ring junction, in *presence* of 'α'-axial Me)	5 (con)	
'β'-Equatorial	0.5 (con)	
'γ'-Axial (*e.g.* 10β-Me in 3-oxo-5α-steroid)		0.5 [c]
'γ'-Axial (*e.g.* 6β-Me in 3-oxo-5α-steroid)	4 (dis)	3 (dis)
'γ'-Equatorial (*e.g.* 6α-Me in 3-oxo-5α-steroid)		0.5 (con)
φ (projecting into geometric front octant)	1.5 (con) [d]	

[a] (con) = consignate; (dis) = dissignate. [b] For ketones not belonging to either the *trans*-1- or *trans*-2-decalone class (*e.g.* *cis*-decalones) the increment of 3 units (con) approximates to the mean of the two values given here. [c] Sign determined so as to cancel the consignate contribution of 0.5 unit for the second ring of the *trans*-2-decalone. [d] (con) here means that the sign is that of the corresponding rear octant, as if a quadrant rule operates.

compounds (36) and (39), of the 2-oxo-steroid type with a five-membered ring D, but reduce the magnitude of $\Delta\varepsilon$ by some 3 units in D-homo-5α-androstan-2-one (40).

A curious feature of this series of compounds lies in the pronounced effect on the c.d. of 3-oxo-5α-steroids associated with the presence of 6β-substituents ('γ'-axial), apparently irrespective of electronic type. Five such compounds [(54)—(56), (58), and (60)] in Table 1 illustrate octant-dissignate 6β-substituent effects which average −3 units, in contrast with negligible effects of the corresponding 6α-substituents. 4,4-Dimethyl substitution on a 3-ketone makes a weakly positive contribution even in the 19-nor-derivative (43), where distortion [39] is minimal. There is no evidence of the



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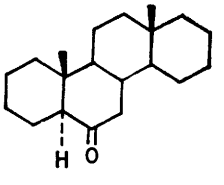

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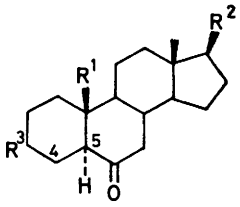
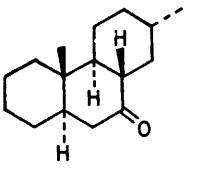


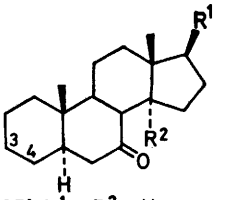
(71) $R^1 = R^2 = R^3 = H$
(73) $R^1 = Me, R^2 = R^3 = H$
(75) $R^1 = Me, R^2 = Et, R^3 = H$
(76) $R^1 = Me, R^2 = C_8H_{17}, R^3 = H$
(77) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \beta$-OAc
(78) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \alpha$-OAc
(79) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \beta$-Cl
(80) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \alpha$-Cl
(81) $R^1 = Me, R^2 = C_8H_{17}, R^3 = H$, with 4β-Me
(82) $R^1 = Me, R^2 = C_8H_{17}, R^3 = H$, with 5α-Me
(83) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \beta$-OAc, with 5α-Me
(84) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \beta$-OMe, with 5α-Me
(85) $R^1 = Me, R^2 = C_8H_{17}, R^3 = \beta$-OAc, with 5α-Cl

expected large negative contribution from the axial 4β-methyl group. 'α'-Equatorial 2α- or 4α-methyl substituents [(47), (49), and (50)], however, surprisingly make distinct contributions (*ca.* 1.5 unit).

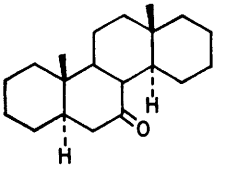
It is clear that the effects of methyl substituents do not fall into an easily recognisable pattern, like that found for the $n \longrightarrow \pi^*$ transition. Large consignate effects of 'α'-axial methyl groups are found only for ring-junction positions: 'α'-methyl substitution involving positions other than ring junctions can have weakly consignate [in compounds (49) and (50)], negligible [compound (51)], or strongly dissignate effects



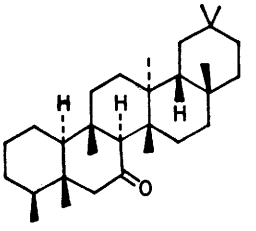
(86)



(87) $R^1 = R^2 = H$
(89) $R^1 = C_8H_{17}, R^2 = H$
(90) as (89), with 3β-OAc, 4,4-Me_2



(88)



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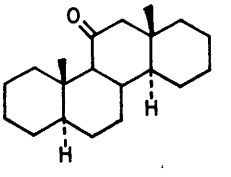
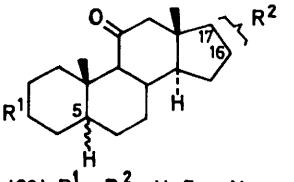


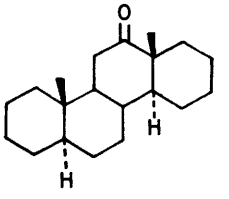
(92)

[compound (15)] depending upon the total molecular structure.

The average contributions of individual rings in



(93) $R^1 = R^2 = H$, 5α-H
(94) $R^1 = H, R^2 = 17\beta$-Et, 5α-H
(95) $R^1 = \beta$-OAc, R^2 = rings E and F of (25*R*)-spirostan, 5α-H
(96) $R^1 = H, R^2 = 17\beta$-Et, 5β-H
(97) $R^1 = \alpha$-OAc, $R^2 = 17\beta$-CHMe$(CH_2)_2CO_2Me$, 5β-H



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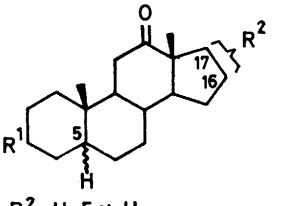


(99) $R^1 = R^2 = H$, 5α-H
(100) $R^1 = H, R^2 = 17\beta$-Et, 5α-H
(101) $R^1 = H, R^2 = 17\beta$-CHOAc-Me, 5α-H
(102) $R^1 = \beta$-OAc, R^2 = rings E and F of (20*S*,25*R*)-spirostan, 5α-H
(103) as (102), except (20*R*)
(104) $R^1 = H, R^2 = 17\beta$-CHMe$(CH_2)_2CH_3$, 5β-H
(105) $R^1 = \alpha$-OAc, $R^2 = 17\beta$-C_8H_{17}, 5β-H

compounds of extended *trans*-2-decalone type are collected in Figure 3. Table 2 lists those methyl substituent increments which appear to have sufficient validity for use in empirical calculations of the values of $\Delta\varepsilon$ to be expected for steroidal and related ketones of search for further regularities, attempts were next made to calculate $\Delta\varepsilon$ for ' middle-ring ' ketones (6-, 7-, 11-, and 12-oxo-steroids). As a first approximation, values of $\Delta\varepsilon$ were calculated on the assumption that each ' middle ring ' ketone comprises both a *trans*-1-decalone

TABLE 3

C.d. data [a] for steroid ' middle-ring ' ketones (' all-*trans* ')

Compound	Solvent	$\Delta\varepsilon$ (obs.) ($\lambda_{max.}$)	$\Delta\varepsilon$ (Calc.)
6-Oxo-5α-steroids			
5α-Estran-6-one (71)	H	+1.0m (195) −3.7 (186)	+4
Des-D-5α,13β(H)-androstan-6-one (72)	H	+4.9m (190)	+4.5
5α-Androstan-6-one (73)	H	+4.8m (192)	+5.5
D-Homo-5α-androstan-6-one (74)	H	+5.2m (192)	+5.5
5α-Pregnan-6-one (75)	H	+5.1m (194)	+5.5
	A	+5.3m (194)	
5α-Cholestan-6-one (76)	H	+5.1m (194)	+5.5
	A	+4.8m (195)	
3β-Acetoxy-5α-cholestan-6-one (77)	H	+3.9m (192)	+5.5
3α-Acetoxy-5α-cholestan-6-one (78)	H	+4.0m (192)	+5.5
3β-Chloro-5α-cholestan-6-one (79)	H	+3.8m (190)	+5.5
3α-Chloro-5α-cholestan-6-one (80)	H	+4.0m (191)	+5.5
4β-Methyl-5α-cholestan-6-one (81)	H	+7.2m (194)	+7.0
5-Methyl-5α-cholestan-6-one (82)	H	0.0	−1
3β-Acetoxy-5-methyl-5α-cholestan-6-one (83)	H	+0.6 (197)	−1
3β-Methoxy-5-methyl-5α-cholestan-6-one (84)	H	+2.4 (186)	−1
3β-Acetoxy-5-chloro-5α-cholestan-6-one (85)	H	+5.4 (190)	*b*
7-Oxo-5α-steroids			
Des-D-5α,13β(H)-androstan-7-one (86)	H	+1.0m (192)	+3
	A	0.0	
5α-Androstan-7-one (87)	H	−0.1 (188)	0.0
D-Homo-5α-androstan-7-one (88)	H	−4.3m (194)	−3
5α-Cholestan-7-one (89)	H	−0.8 (185)	0.0
3β-Acetoxy-4,4,14α-trimethyl-5α-cholestan-7-one (90)	H	0.0	+4
Friedelan-7-one (91)	H	+1.2 (190)	+2
11-Oxo-steroids			
D-Homo-5α-androstan-11-one (92)	H	+3.7m (192)	+6.5
	A	+6.1m (195)	
5α-Androstan-11-one (93)	H	+4.5m (191)	+6.5
	A	+5.3m (191)	
5α-Pregnan-11-one (94)	H	+5.9m (192)	+7
	A	+4.5m (194)	
(25*R*)-3β-Acetoxy-5α-spirostan-11-one (95)	H	+3.7 (197)	+5.5
	A	+4.5m (195)	
5β-Pregnan-11-one (96)	H	+5.6m (189)	+7
	A	+3.9m (193)	
Methyl 3α-acetoxy-11-oxo-5β-cholan-24-oate (97)	H	+5.1 (200)	+7
	A	+4.3m (196)	
12-Oxo-steroids			
D-Homo-5α-androstan-12-one (98)	H	+2.5 (192)	+3
5α-Androstan-12-one (99)	H	+3.0 (185)	+3
5α-Pregnan-12-one (100)	H	+9.3m (188)	+9 [c]
	A	+5.1 (190)	
3β,20β-Diacetoxy-5α-pregnan-12-one (101)	H	+8.8 (185)	+9 [c]
	A	+8.8 (187)	
(20*S*,25*R*)-3β-Acetoxy-5α-spirostan-12-one (102) (Hecogenin acetate)	H	+3.3sh (190) *ca.* +10 (185)	+9 [c]
(20*R*,25*R*)-3β-Acetoxy-5α-spirostan-12-one (Cyclopseudohecogenin acetate) (103)	H	+11.1 (184)	+10 [c]
	A	+7.3m (189)	
5β-Cholan-12-one (104)	H	+10.5m (188)	+10 [c]
	A	+7.6m (191)	
3α-Acetoxy-5β-cholestan-12-one (105)	H	+8.4 (191)	+10 [c]
	A	+9.4 (195)	

[a] See Table 1, footnotes *a* and *b*. [b] 5α-Cl appears to have a weakly dissignate effect (+1.5) on the 6-ketone. [c] The side-chain at C-17 is treated as equivalent to a 'front octant' cyclohexane ring.

both 1-decalone and 2-decalone types (Table 1). The four alkyl cyclohexanones (1)—(4) fall reasonably close to the expected values considering their conformational mobility.

(B) *Middle-ring ketones of ' extended* trans-*decalone ' type* (*Table* 3). To test the validity of the group increments gathered into Figures 2 and 3 and Table 2, and to component ($\delta\Delta\varepsilon$ ±3.5 units) and a *trans*-2-decalone ($\delta\Delta\varepsilon$ *ca.* 0), together with any ' α '- or ' β '-axial methyl substituents which are present (only *trans*-fused compounds are considered at this stage).

6-*Oxo*-5α-*steroids*. Agreement is generally good, with the exception of 5-methyl derivatives (82)—(84) where the 5-methyl substituent produces a smaller negative

contribution than expected. An axial 5α-chloro-substituent (85) surprisingly has very little effect. The size of ring D is unimportant (contrast the $n \longrightarrow \pi^*$ transition [31]). Polar substituents at C-3 cause a slight reduction in the magnitude of Δε. The 4β-methyl group in 4β-methyl-5α-cholestan-6-one (81) contributes *ca.* +2 units, the positive sign being consistent with a quadrant rule; according to the original octant rule [33] the 4β-methyl group projects into a front octant where it would be expected to have a negative effect.

7-*Oxo*-5α-*steroids*. The des-D-ketone (86) provides a reference value for assessing the contribution of the ' front octant ' ring D, which is found to be negative, in accordance with a quadrant rule,[38] in contrast to its positive (octant-consignate) effect at 290 nm.[28] The *magnitude* of the effect of ring D appears to depend upon the number of carbon atoms in that ring (*ca.* −6 units for a six-membered ring; −2 to −5 units for a five-membered ring). The contribution of ring D is positive for the quasi-enantiomeric friedelan-7-one. The generally large magnitudes of the effects of ring D are remarkable in view of the very small effect of the correspondingly placed ring C in 1-oxo-5α-steroids (see p. 791, and Discussion, p. 802).

11-*Oxo-steroids*. The ' calculated ' values of Δε in Table 3 are all somewhat larger than those observed. They are calculated as if rings C and D form a *trans*-2-decalone unit, since the size of ring D is evidently not a major feature in determining Δε [*cf.* compound (92)]. ' Calculated ' values assume a positive increment of +6 for the ' front octant ' ring A, which is related to the carbonyl group in a quasi-enantiomeric manner to ring D in the 7-oxo-D-homo-compound (88). The 10β-methyl group is assumed to contribute −2 units, from the value for the similarly-placed 4β-methyl group in the 6-oxo-compound (81).

12-*Oxo-steroids*. Calculated values of Δε agree reasonably well with those observed. Comparison of the D-homo-compound (98) with 5α-androstan-12-one (99) shows that the size of ring D has little effect. The 17β-side-chains, in contrast, make large positive contributions in compounds (100)—(105), consistent with their location in a (geometric) front octant. A uniform contribution of +6 units is assumed, as if the side chain constituted an extra ' front octant ' ring. The 10β-methyl group is treated as a ' γ '-axial substituent. Two 5β-compounds (104) and (105) are regarded as lacking the small contribution from ring A, which is folded out of the ' all-*trans* ' position it occupies in the 5α-series.

In summary, data for middle-ring ketones demonstrate (a) somewhat poorer additivity of the group increments which reproduce Δε values for compounds with the oxo-group in a terminal ring, and (b) a general ' quadrant rule ' behaviour of any parts of the structure which project into regions of space which in the geometric sense lie in ' front octants.'

(C) cis-*Decalones* (*Table* 4). In our work on the $n \longrightarrow \pi^*$ transition,[28] the bond increments derived from *trans*-decalones were found to be directly applicable for the most part to bonds or groups in corresponding positions relative to the cyclohexanone ring in *cis*-decalones; CH_3 and $-CH_2-$ groups were treated as being equivalent for this purpose. Inspection of data for *cis*-decalone analogues at the ' 190-nm ' transition has shown a similar applicability of group increments derived from *trans*-decalones, except that even larger ' β '-axial substituent effects occur in those classes of *cis*-decalones (6*c*2*eq* and 6*c*3*ax*) [28] where a C–C bond which is ' β '-axial with respect to the cyclohexanone ring also forms part of the ' second ' ring.

Unfortunately, the number of *cis*-decalone analogues currently available for study was much more limited than the extensive list for which we previously collected $n \longrightarrow \pi^*$ data.[28] ' Calculated ' values of Δε (Table 4) are based upon increments listed for *trans*-decalones in Table 2, apart from special considerations mentioned below.

Class 6*c*3*eq* (*Figure* 4*a*). The second ring, which includes a bond ' β '-equatorial to the cyclohexanone ring, clearly makes no pronounced contribution (*cf.* Table 2). Those few compounds [(107), (113), and (115)] which show significant c.d. (Δε >1 unit) do so because they contain a ' β '-axial methyl group. The contribution of this methyl group (*ca.* 3 units, consignate) is intermediate between the values (1.5 and 5 units) found for similar methyl groups in *trans*-1- and *trans*-2-decalones, respectively.

Class 6*c*3*ax* (*Figure* 4*b*). The only two examples available show the expected consignate effects of ' β '-axial C–C bonds (' 9,8 '-; decalone numbering). The *cis*-decalone (116), although it must exist substantially in the 6*c*3*ax* conformation, may give an unreliable estimate of the value of Δε for this conformation because of the likelihood of equilibration with a small proportion of the 6*c*3*eq* form. The 2-oxo-5β-steroid (117) gives a much larger value of Δε (−8.7), which must derive largely from ' β '-axial substitution. The ' β '-axial C–C bond in this structure is part of an extended *anti*-periplanar zig-zag of bonds which begins with the C_α–C_β and ' β '-axial bonds (a ' secondary ' zig-zag; [28] bonds thickened in formula). In parallel with conclusions for the $n \longrightarrow \pi^*$ transition,[28] the existence of such a ' secondary ' zig-zag may result in a contribution to Δε which is larger than that of a simple ' β '-axial methyl substituent (*cf.* following section). Neither compound of class 6*c*3*ax* is therefore considered a perfect model for a simple rigid *cis*-2-decalone.

Class 6*c*2*eq* (*Figure* 4*c*). Here the observed values of Δε are even larger than those for class 6*c*3*ax*, and are again consignate with respect to the ' β '-axial (' 10,5 ')-bond.

It seems impossible to explain the exceptional magnitudes of Δε for compounds (118) (Δε +16) and (120) (Δε −12.7) without invoking extra large ' β '-axial effects, probably associated with the length of the ' secondary zig-zag ' especially in the 4-oxo-5β-compound (118). The other bonds expected to contribute significantly are the ' α '-equatorial and ' β' ' C–C bonds

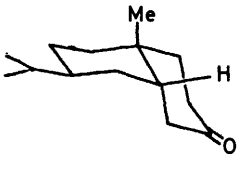
[thickened in drawings; by analogy with comparable bonds in the *trans*-decalone series (Table 2) the allotted increments are 2 units (consignate) for each of these bonds]. The 17a-oxo-13α-D-homo-steroid (119) (Δε +0.5) has an additional ' α '-methyl substituent at the ring junction which compensates for the effect of the zig-zag.

It has not been possible to correlate the c.d. contribution with the number of C–C bonds in an extended ' secondary ' (' β '-axial) zig-zag with any great accuracy from the present limited data, but values of Δε of the right order of magnitude are obtained for those compounds which contain such a zig-zag by adopting the following series of consignate increments; $n = 1$ (' β '-axial Me), $\delta\Delta\varepsilon \approx \pm 3$; $n = 2$, $\delta\Delta\varepsilon \approx \pm 6$; $n = 3$, $\delta\Delta\varepsilon = \pm 8$; $n = 4$, $\delta\Delta\varepsilon = \pm 10$; $n = 5$, $\delta\Delta\varepsilon \pm 12$ units (n is the number of bonds on the zig-zag, counting from the β-carbon atom). Values of Δε calculated on this basis are included in Table 4 (column *a*) for compounds of classes 6*c*3*ax* and 6*c*2*eq*.

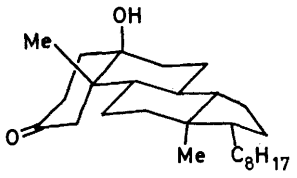
Class 6*c*2*ax* (*Figure* 4*d*). Rings A and B of a 6-oxo-5β-steroid form a structural component which belongs to the class 6*c*2*ax*. Comparison with data for 6-oxo-5α-steroids, and in Figure 2, shows that ring A makes a larger *positive* contribution in the 6-oxo-5β-compound than in the corresponding *trans*-decalone unit. The value of δΔε for ring A together with the 10β-methyl group is only *ca.* +4.5 units in the 5α-series, but *ca.* +6.5 in the 5β-series despite the fact that ring A extends into a supposedly ' negative ' octant. There appears to be a dominant *dissignate* contribution from the 4,5-bond, despite the ' α '-axial character of this bond with respect to the carbonyl group at C-6 in ring B. That this is a real dissignate effect is supported by comparison with the unexpected dissignate contribution found for the 3α-methyl group in 3α-methyl-5α-cholestan-4-one (15) (p. 791). Adoption of the 3α-Me increment ($\delta\Delta\varepsilon = 4$ units, dissignate) as appropriate also to the 4,5-bond in a 6-oxo-5β-steroid leaves +2.5 units for the ' β '-axial 10β-methyl group, agreeing well with the value of 3 units derived from other *cis*-decalones. It may be significant that each of these ' anomalous ' ketones has an ' α '-axial C–C bond at a *tertiary* position, instead of at a quaternary ring-junction site.

(−)-Valeranone (125), the only other ketone of class 6*c*2*ax* available for study, is calculated from previous data for its component bonds to have Δε +9, in fair agreement with the observed value of +7.5.

In summary, Δε values for *cis*-decalones and their extended analogues may be estimated rather crudely from the individual bond contributions, provided that additional allowance is made for all the bonds of any



(106)



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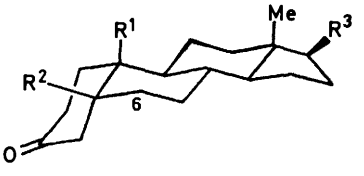
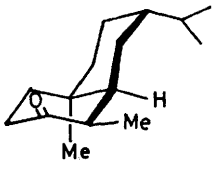
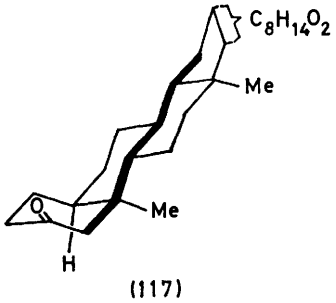


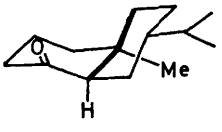
(108) $R^1 = R^2 = H, R^3 = OH$
(109) $R^1 = R^2 = H, R^3 = OAc$
(110) $R^1 = Me, R^2 = R^3 = H$
(111) $R^1 = Me, R^2 = H, R^3 = C_8H_{17}$
(112) as (111), with 6α-Me
(113) $R^1 = R^2 = Me, R^3 = C_8H_{17}$
(114) as (111), with 6β-OAc
(115) $R^1 = H, R^2 = Me, R^3 = OAc$



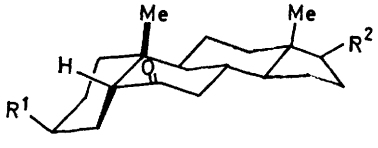
(116)



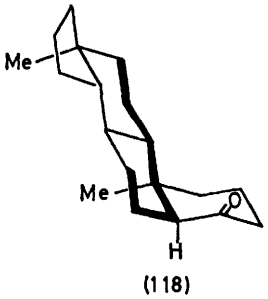
(117)



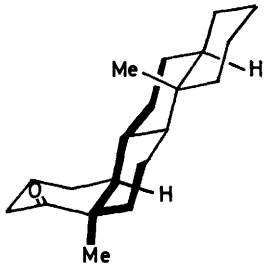
(120)



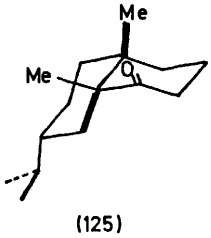
(121) $R^1 = H, R^2 = C_8H_{17}$
(122) $R^1 = OAc, R^2 = C_8H_{17}$
(123) $R^1 = H, R^2 = Et$
(124) $R^1 = R^2 = H$



(118)



(119)



(125)

TABLE 4

C.d. data for ketones of *cis*-decalone type

Compound	Solvent	Δε (obs.) ($\lambda_{max.}$)	Δε (calc.) *a*	Δε (calc.) *b*
Class 6*c*3*eq*				
(7*S*,9*S*,10*R*)-10-Methyl-7-isopropyl-*cis*-2-decalone (106)	H	+0.9m (190)	+0.5	0.0
5-Hydroxy-5α-10α-cholestan-2-one (107)	H	−2.3 (190)	−3.5	−3
17β-Hydroxy-5β-estran-3-one (108)	A	−0.4 (190)	−0.5	0.0
17β-Acetoxy-5β-estran-3-one (109)	H	0.0	−0.5	0.0
	A	0.0		
5β-Androstan-3-one (110)	H	+0.9 (190)	−0.5	0.0
	A	+1.1 (190)		
5β-Cholestan-3-one (111)	H	+1.0 (190)	−0.5	0.0
6α-Methyl-5β-cholestan-3-one (112)	H	0.0	−1	0.0
	A	0.0		
5-Methyl-5β-cholestan-3-one (113)	H	−3.5 (188)	−3.5	−3
	A	−1.5 (190)		
6β-Acetoxy-5β-cholestan-3-one (114)	H	0.0	−0.5	0.0
17β-Acetoxy-5-methyl-5β-estran-3-one (15)	H	−3.0 (187)	−3.5	−3
Class 6*c*3*ax*				
(1*R*,7*S*,9*S*,10*R*)-1,10-Dimethyl-7-isopropyl-*cis*-2-decalone (116)	H	−3.0 (185)	−8	−5
5β-Spirostan-2-one (117)	H	−8.7m (187)	−10.5	−8
Class 6*c*2*eq*				
5β-Androstan-4-one (118)	H	+16m (188)	+12	+17
	A	+12.5m (188)		
D-homo-5α,13α-androstan-17a-one (119)	H	+0.5 (194)	−1.5	−7
		−9.5 (184)		
(7*S*,9*R*,10*S*)-10-Methyl-7-isopropyl-*cis*-1-decalone (120)	H	−10sh (190)	−7	−12
		−12.7 (185)		
Class 6*c*2*ax*				
5β-Cholestan-6-one (121)	H	+8.8m (188)	+7.5	+7.5
	A	+7.7m (190)		
3β-Acetoxy-5β-cholestan-6-one (122)	H	+4.7 (192.5)	+7.5	+7.5
5β-Pregnan-6-one (123)	H	+8.2m (188)	+7.5	+7.5
	A	+6.5m (190)		
5β-Androstan-6-one (124)	H	+5.3 (191)	+7.5	+7.5
	A	+4.2 (190)		
(−)-Valeranone (125)	H	+7.5 (187)	+7	+7

[a] Calculated from bond increments derived from *trans*-decalones (Table 2), with extra allowance for extended 'β-axial zig-zags' on the basis (p. 796) that the 'β'-axial and successive C–C bonds of the zig-zag add 3,3,2,2,2 . . . . units (consignate) respectively; 'β'-axial methyl is given the value of 3 units (consignate). [b] Calculated from data summarised in Figure 5, from empirical analysis of *cis*-decalones only.

'β'-axial secondary zig-zag in *cis*-decalones of classes 6*c*2*eq* and 6*c*3*ax*. Figure 5 contains the best estimates which could be made of the contributions of individual rings, considered as a whole.

(D) *Hexahydroindanones* (*Table* 5). Only a few steroids with a hexahydroindanone component were available for study. Their diversity was insufficient to permit as thorough an analysis of c.d. data as that which earlier [29] produced a consistent and comprehensive picture of $n \longrightarrow \pi^*$ c.d. behaviour. Only four of the

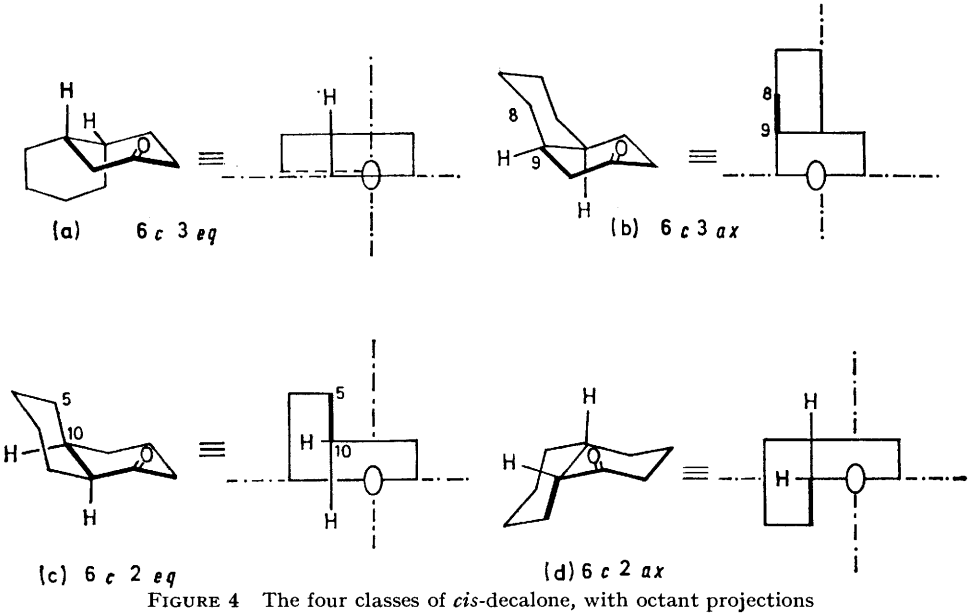


FIGURE 4 The four classes of *cis*-decalone, with octant projections

TABLE 5

C.d. data for ketones of cyclopentanone and hexahydroindanone type

Compound	Solvent	Δε (obs.) ($\lambda_{max.}$)	Δε (calc.)
Cyclopentanone			
(3*R*)-3-Methylcyclopentanone (126)	H	−5.7m (190)	−5.5
Hexahydroindanones (class 5*t*3)			
17β-Hydroxy-A-nor-5α-estran-2-one (127)	A	−6.8m (188)	−5.5 [a]
17β-Acetoxy-A-nor-5α-estran-2-one (128)	H	−5.6 (186)	−5.5
	A	−4.8m (192)	
17β-Hydroxy-A-nor-5α-androstan-2-one (129)	A	−3.6m (187)	−2 [a]
17β-Acetoxy-A-nor-5α-androstan-2-one (130)	H	−1.6 (188)	−2
	A	−5.6 (186)	
5-Methyl-A-nor-5α-cholestan-2-one (131)	H	+2.8m (190)	+1.5
3β-Hydroxy-5α-androstan-16-one (132)	A	+2.8m (193)	+2
3β-Acetoxy-5α-androstan-16-one (133)	H	+3.5m (193)	+2
	A	+2.7m (190)	
Hexahydroindanones (class 5*t*2)			
5-Methyl-A-nor-5α-androstan-3-one (134)	H	−2.1 (188)	−1
5α-Androstan-15-one (135)	H	+1.8 (195)	+2
5α-Androstan-17-one (136)	H	−8.1 (193)	−8
5β-Androstan-17-one (137)	H	−7.5m (194)	−8
	A	−6.2m (193)	
16α-Methyl-5α-androstan-17-one (138)	H	−3.0 (191)	
	A	−4.9m (193)	
3β-Hydroxy-4,4,14-trimethyl-5α-androstan-17-one (139)	H	+0.6 (201)	+1
	A	+4.0 (187)	
Hexahydroindanones (class 5*c*2*eq*)			
14-Methyl-5α,14β-androstan-15-one (140)	H	+1.2m (191) *ca.* −6 (185)	small [b]
4,4-Dimethyl-5α,14β-androstan-15-one (141)	H	−3 (186)	(—) [b]
5α,13α-Androstan-17-one (142)	H	−1.5 (185)	small [b]
	A	−1.1 (187)	
3β-Acetoxy-18-nor-5α,13α-androstan-17-one (143)	H	0.0	(—) [b]
Hexahydroindanones (class 5*c*2*ax*)			
5α,14β-Androstan-17-one (144)	H	+9.5 (185)	*ca.* +8 [c]

[a] The 17β-OH group may contribute a further −2 units. [b] See text, p. 799, and Appendix. [c] See Appendix.

five classes of hexahydroindanones [29] are represented in the present work.

Class 5*t*3 (*Figure* 6*a*). Data for compounds of 2-oxo-A-nor-5α and 16-oxo-steroid type, with a 'twisted' cyclopentanone ring, show that the *trans*-hexahydroindan-2-one unit makes a substantial contribution to Δε, averaging 5.5 units. This is close to the value for 3-methylcyclopentanone (126) which also has a 'twisted' ring. The sign is the reverse of that representing the helicity of the cyclopentanone ring, when viewed down the carbonyl bond (two-fold axis). A methyl group ('β'-axial) at the ring junction makes a consignate contribution of some 3.5 units, necessarily of sign opposite to that for the ring itself. 'Calculated' values of Δε in Table 5 use these increments. Additivity of ring and methyl contributions is rather poor, as has been found for the $n \longrightarrow \pi^*$ c.d. of similar compounds; variations of the degree of twist of the cyclopentanone ring with substitution were suggested as a possible explanation.[29]

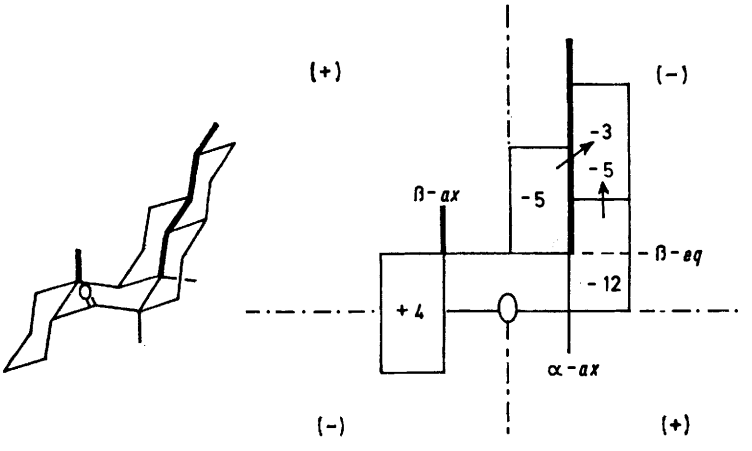


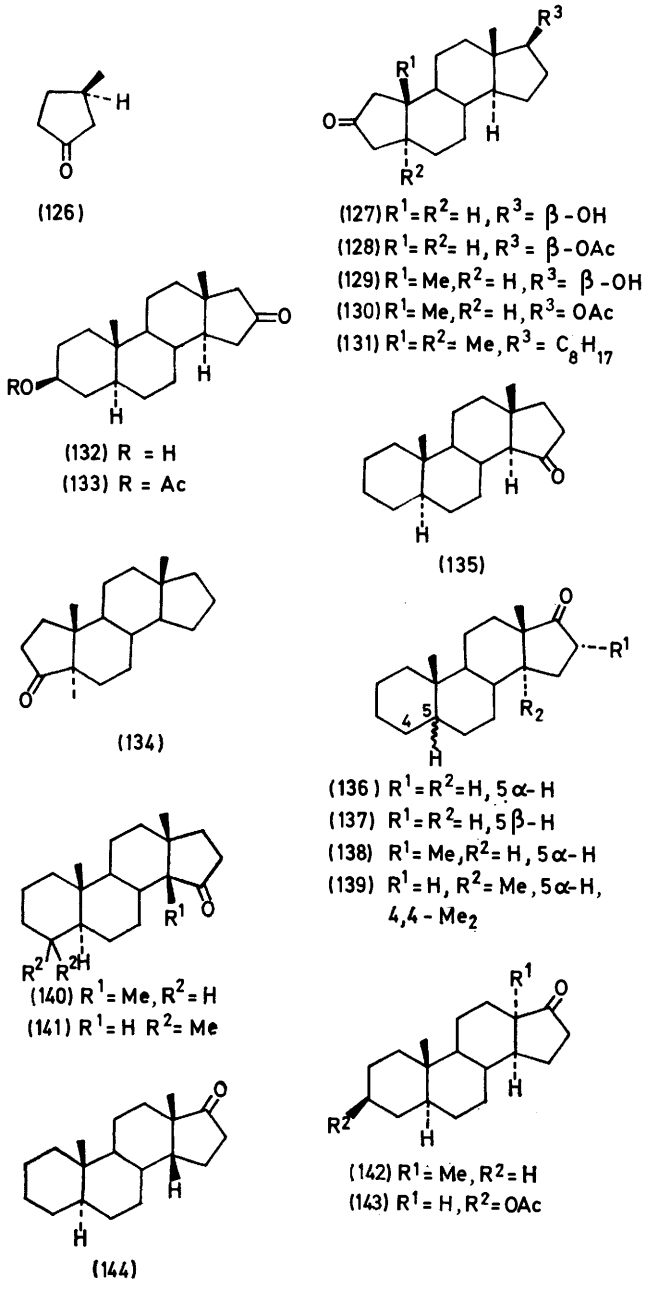
FIGURE 5 Ring contributions (δΔε) of extended *cis*-decalone structures (estimates based on analysis of data in Table 4; note alternative values for third ring, depending upon position of second ring). Increments for methyl substituents:

α-*ax* +10 (consignate)

Class 5*t*2 (*Figure* 6*b*). This class is represented by one 3-oxo-5α-A-nor- (134), one 15-oxo- (135), and four 17-oxo-steroids (136)—(139). The individual contributions of the *trans*-hexahydroindan-1-one unit and an ' α '-axial methyl substituent cannot be separated by pairwise comparison among these compounds, so estimates of group contributions are partly speculative. A ' β '-axial methyl group appears to make a very large contribution (*ca.* 9 units, consignate). [Compare the 14α-methyl-17-oxo- (139) (Δε weakly positive) with unsubstituted 17-oxo-steroids (Δε −8).] If we assume the essential invariance of ' α '-axial contributions (as was found for c.d. at the $n \longrightarrow \pi^*$ transition [29]), and adopt the ' α '-axial methyl increment of 10 units (consignate) from decalones, the effects of methyl groups at the ring junction appear to be responsible for most of the observed c.d.; the *trans*-hexahydroindan-1-one unit itself, with its ' folded ' cyclopentanone ring,[29] apparently makes a contribution of no more than *ca.* 2 units (consignate with respect to ring helicity).

5β-Androstan-15-one (135) has ring B in a ' front octant ' location, where it appears to contribute a large negative increment (*ca.* −9) to counterbalance the positive ' β '-axial 13β-methyl effect, and account for the observed small net value of Δε (+1.8). Data are needed for further compounds, however, to test these tentative conclusions.

Class 5*c*2*eq* (*Figure* 6*c*). The four compounds of this class, which all differ in their methyl substitution at the ring junction, show remarkably small variation in Δε. Whether contributions of ' third ' and ' fourth ' rings be



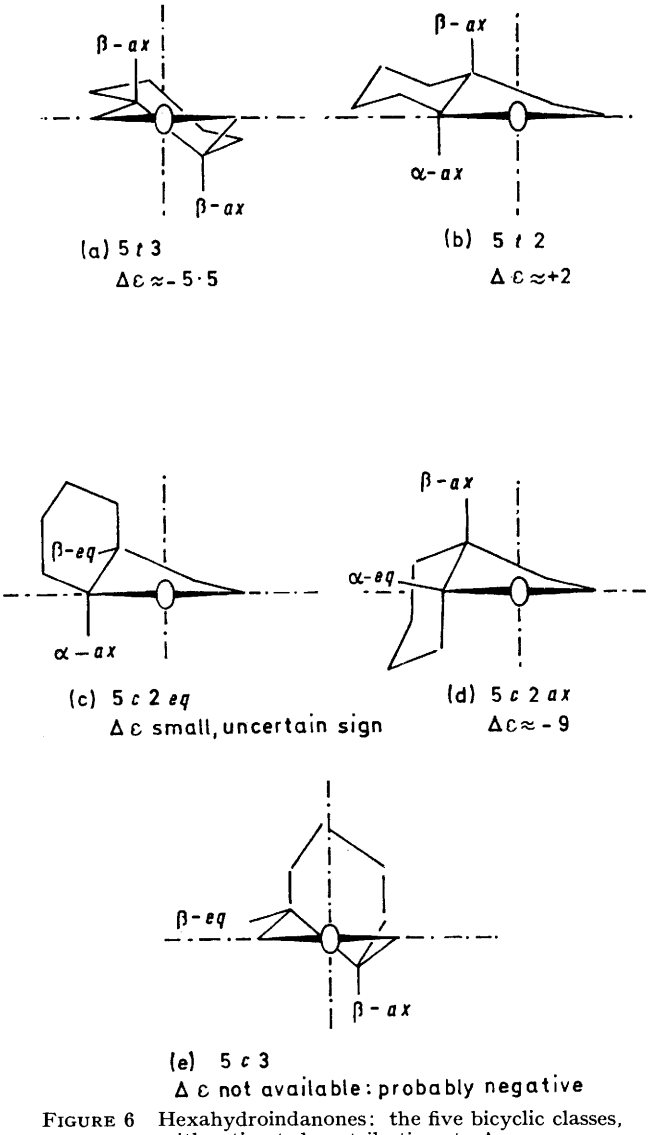


FIGURE 6 Hexahydroindanones: the five bicyclic classes, with estimated contributions to Δε

ignored or not, there is no consistency within the class between methyl group contributions. Moreover there is no clear evidence of a large consignate (negative) contribution from that C–C bond of the ' second ' ring which is ' β '-axial to the cyclopentanone. The helicity of the cyclopentanone ring suggests that its own contribution should be moderately negative. The c.d. behaviour of this class of hexahydroindanones remains unclear at present (*cf.* Appendix, p. 802).

Class 5*c*2*ax* (*Figure* 6*d*). Although 5α,14β-androstan-17-one (144) was the only such compound available, its c.d. is of special interest in providing direct support for the idea of a large consignate ' α '-axial substituent effect in a cyclopentanone of folded conformation (*cf.* class 5*t*2). The observed value of Δε (*ca.* +9.5) must derive largely from the ' α '-axial 7,8-bond of the hexahydroindanone unit.

Class 5*c*3 (*Figure* 6*e*). This class is not represented among the compounds studied. The twisted cyclopentanone ring would be expected to exhibit Δε values comparable with those for class 5*t*3, and of sign depending upon ring helicity. The ' β '-axial bond which forms part of the second ring would tend to nullify the contribution of the ring itself (*cf.* Appendix, p. 802).

(E) *Open-chain and miscellaneous ketones* (*Table* 6). The c.d.[7] of (1*R*,2*R*,4*S*)-*endo*-2-methylbicyclo[2.2.1]-heptan-7-one (145; Δε −1.2) suggests a possible weakly dissignate effect of the methyl group, which approximates to ' β '-equatorial type; distortion of the molecular framework cannot be ruled out, however. The *exo*-isomer (146) (Δε +2.8) shows the normal consignate effect of a ' β '-axial methyl group.[7] The spiro-ketone (147), chosen[8] to have its methyl group in a front octant, exhibits a weakly positive c.d. (Δε +1) at 190 nm, which matches the sign of the effect at 310 nm ($n \longrightarrow \pi^*$), and was considered[8] to indicate a ' front octant ' effect of the methyl substituent. It is difficult to predict the geometry of this compound with any certainty.

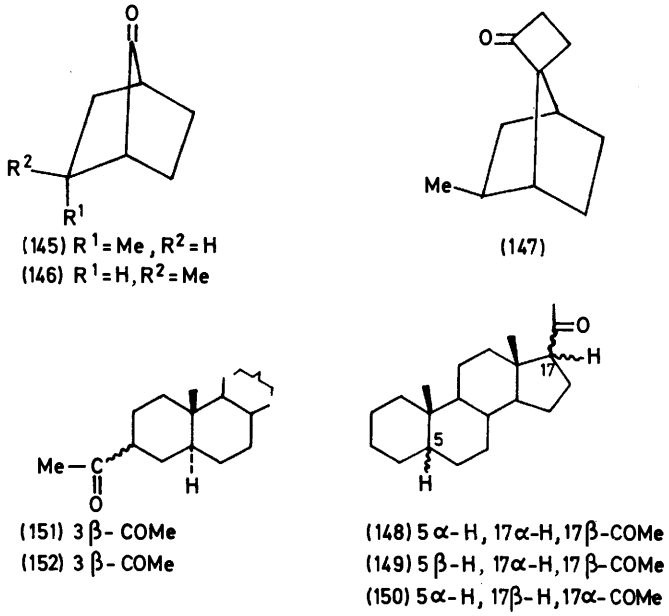
3-Acetyl-5α-cholestanes gave very weak c.d. curves at 190 nm,[40] as expected from their preferences for locally symmetric conformations. The negative sign of Δε for pregnan-20-ones is *dissignate* with respect to the location of the steroid framework and the 13β-methyl group, in the preferred conformation (Figure 7) about the 17,20-bond.[31,41] This initially surprising result may be related to the significant dissignate contributions of those parts of an extended ' primary zig-zag ' (in this case running from C-17 to C-6 [31]) which were noted above for ' all-

TABLE 6

C.d. for miscellaneous and open-chain ketones

Compound	Solvent [a]	Δε ($\lambda_{max.}$)	Δε (calc.) [b]
(1*R*,2*R*,4*S*)-*endo*-2-methylbicyclo[2.2.1]heptan-7-one (145)	H	−1.2 (190)	−0.5
(1*R*,2*S*,4*S*)-*exo*-2-methylbicyclo[2.2.1]heptan-7-one (146)	H	+2.8 (190)	+3
syn-(1′*R*)-spiro[cyclobutan-2-one-1,7′-(2′-*exo*-methylnorbornane)] (147)	H	+1.0 (190)	(−) [c]
5α-Pregnan-20-one (148)	H	−3.1m (192)	(+) [d]
	A	−2.8m (192)	
5β-Pregnan-20-one (149)	H	−1.9m (188)	(+) [d]
5α,17α-Pregnan-20-one (150)	H	−2.3m (193)	(−)
	A	−2.4m (196)	
3β-Acetyl-5α-cholestane (151)	H	+0.2m (193)	v. weak
		−0.7 (185)	
3α-Acetyl-5α-cholestane (152)	H	+1.2 (185)	v. weak

[a] H = hexane or isopentane; A = acetonitrile. [b] Using increments from Table 2, where substituents approximate to the methyl substituents listed. [c] Assuming ' quadrant ' behaviour. [d] But see text, this page.



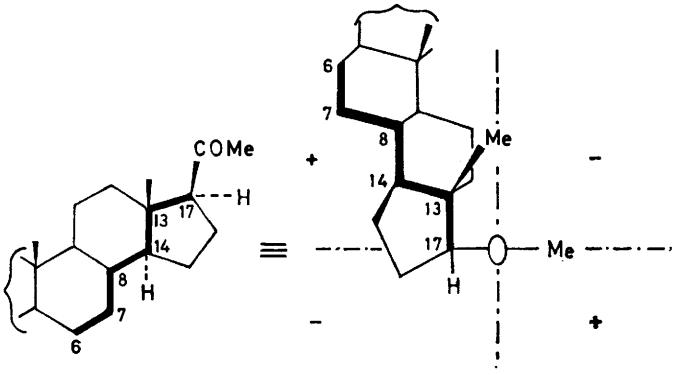


FIGURE 7 Pregnan-20-one, and octant projection of its preferred conformation

trans'-2-oxoperhydroanthracene and 2-oxoperhydronaphthacene (see Discussion). A 17α-pregnan-20-one also gave a negative sign, compatible in this case with a consignate effect of the shorter zig-zag from C-17 to C-12.[31]

C.D. Curves in Acetonitrile as Solvent.—No separate analysis was carried out for data obtained in acetonitrile, as their purpose was mainly to circumvent problems of low solubility in hexane. Numerical values of Δε often differed somewhat from those in hexane where data were available for comparison, but differences were erratic, and were considered not worthy of detailed study. A small red-shift of many of the c.d. maxima on changing from hexane to acetonitrile is discussed below.

DISCUSSION

The results of the foregoing analysis were examined in the hope that they would shed some light on the nature of the electronic transition or transitions giving rise to the observed c.d. near 190 nm.

For compounds of decalone type, the consignate effects of any ' α '-axial or ' β '-axial substituents, or of any bonds with ' α '-axial or ' β '-axial character which are part of the second ring, are generally dominant. The only rings in ' all-*trans* ' structures which make *major* contributions at 190 nm (>3 units) are the second ring of a *trans*-1-decalone unit, and any ' third ' ring which extends into a front octant region of space in the sense of a 4-oxo-perhydrophenanthrene (Figure 2; ring F).

The contributions estimated in the foregoing sections for other rings which make up an ' all-*trans* ' array cannot be ignored, however. When combined into a single diagram (Figure 8), the effects of rings show a remarkable pattern which apparently divides the space ' behind ' the carbonyl group into *eight* sectors, instead of the usual four rear octants. Figure 8 shows the projection of the ' upper ' four of these sectors onto the *xz* (horizontal) symmetry plane of the carbonyl group. The four corresponding ' lower ' sectors have the signs reversed. Put another way, the present analysis suggests the addition of a fourth boundary surface to the three which divide space into the familiar ' octants.' This new surface apparently cuts through the second row of rings, as depicted in Figure 8, dividing each rear octant into a ' near ' region of consignate effects and a ' far ' region of dissignate effects, which are by no means negligible.

As with the $n \longrightarrow \pi^*$ transition, any rings which do not lie on one side or the other of a primary zig-zag (heavy lines) make the smallest contributions, barely discernible against experimental deviations. In the present case, however, if the bonds of a primary zig-zag are assumed [28] to account for the major part of the effects of the rings in which they lie, there is a sign change from consignate to dissignate at about the third bond of the zig-zag, instead of the progressive decrease in consignate bond contributions seen for the $n \longrightarrow \pi^*$ transition.[28]

The significance of the fourth boundary surface is far from clear. It may be a real characteristic, perhaps a nodal surface of one of the molecular orbitals involved in a transition near 190 nm. Alternatively it may be merely a chance consequence of the presence of two overlapping transitions; one of these would have to show only short-range sensitivity to structure (consignate), with rapid fall-off of effects beyond 2—3 Å, while the other would need to show a more gradual diminution, with distance, of relatively smaller dissignate effects.

Only the second of such an overlapping pair of bands would seem compatible with a transition which, like the carbonyl $n \longrightarrow \pi^*$, is dominated by the dissymmetry of the highly delocalised ground-state *n*-orbital [34,35] extending far along a primary zig-zag. The small red-shift of

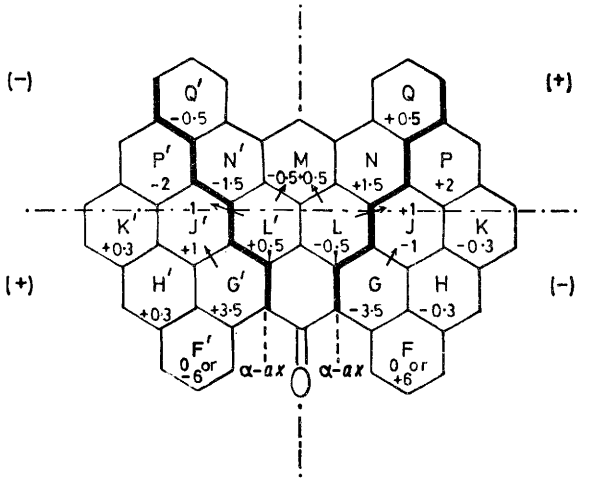


FIGURE 8 C.d. contributions of cyclohexane rings in an ' all-*trans* ' array representing extended *trans*-decalones (note different values for rings J, M, and J', according to the manner of connection to adjoining rings, indicated by arrows). — · — · — Apparent positions of sector boundaries; signs (except for rings F and F') refer to *upper* rear sectors, and are reversed in corresponding lower sectors. (Rings F and F' lie in *lower* sectors, so the apparent sign reversal compared with rings G, H, G', and H' does not imply the presence of another boundary surface separating rings in ' front ' of the carbonyl group from those ' behind ' it)

the 190-nm c.d. band on changing from hexane to acetonitrile as solvent, however, seems incompatible with any transition which originates from the oxygen *n*-orbital, for both the $n \longrightarrow \pi^*$ and the supposedly $n \longrightarrow \sigma^*$ or $n \longrightarrow 3s(R)$ transitions (p. 787) are known to be blue-shifted in polar solvents.[13,15] This is in part a consequence of stabilisation of the ground state by solvation, but also follows from the Franck–Condon principle in that the energy of the excited state is often raised by the inability of the solvation shell of a polar compound to relax in the brief time taken by the electronic transition.[42]

The very large c.d. contributions from both ' α '- and ' β '-axial substituents at 190 nm suggest that perturbation of π-type orbitals is an important feature at 190 nm, for the π and π* orbitals are favourably directed for overlap with neighbouring orbitals associated with bonds of ' axial ' type [contrast *n*-orbital perturbation as the

main contributor in the 290-nm ($n \longrightarrow \pi^*$) c.d. band].[34,35]

The foregoing considerations seem inimical to any interpretation of the c.d. data at 190 nm in terms of a single transition of either $n \longrightarrow \sigma^*$ or $n \longrightarrow 3s(R)$ type, although such a transition may be one of two which overlap. The $\pi \longrightarrow \pi^*$, $\pi \longrightarrow 3s(R)$, and other transitions originating in the π-orbital are excluded from consideration because they lie at much shorter wavelengths (p. 787). The nature of the second transition, if indeed there are two, remains uncertain.

' Front-octant Effects.'—The substantial negative contributions from ring D in 7-oxo-steroids (p. 795) suggested [38] that there is no clear basis at 190 nm for a distinction between effects of substituents behind and in front of a boundary surface bisecting the C=O bond, as there is at 290 nm. A quadrant rule was therefore proposed.[38] Present data show similar behaviour in other compounds where rings occupy the (geometric) front octant with respect to the mid-point of the carbonyl group as origin, provided that the oxo-group is in one of the ' middle ' rings of a steroid-like structure. Open chains extending into ' front octants ' have comparable effects. Examples mentioned in the foregoing discussion include side-chains in 12-oxo-steroids (p. 795), which enhance the positive c.d., and the 4β-methyl group in 4β-methyl-5α-cholestan-6-one (p. 795). Two compounds with the oxo-group in a terminal ring, however, do not fit this generalisation. 5α-Cholestan-1-one (p. 791) needs almost no allowance for rings C and D when Δε is calculated, and 5α-androstan-15-one seems to require a large negative contribution from ring B, which appears from a model to project slightly into a ' positive ' quadrant. With these exceptions, c.d. data at 190 nm seem best accommodated by an ' octant rule ' of a new type, with ' front ' separated from ' rear ' octants by a surface which lies some 4 Å to the rear of the carbon atom of the carbonyl group, as discussed above and illustrated in Figure 8. If two transitions overlap, however, such a ' rule ' has no theoretical validity, but is merely an empirical convenience.

Applications of Ketone C.D. at 190 nm.—The information provided by c.d. of ketones at 190 nm is complementary in some respects to that available from studies of the $n \longrightarrow \pi^*$ transition. The main point of distinction which seems likely to be of value for structural determinations is the relatively large magnitude of ' β '-axial substituent effects at 190 nm; ' β '-axial alkyl groups produce only second-order effects for the $n \longrightarrow \pi^*$ c.d. band.

A good illustration is provided by 6-oxo-5α-steroids.[28] The negative c.d. band (Δε *ca.* −1 to −2 according to solvent) at 290 nm reflects the strong influence of the long primary zig-zag which extends in a ' negative ' octant from C-6 to C-17. The ' β '-axial 10β-methyl group, in a ' positive ' octant, is almost without effect at 290 nm. The c.d. at 190 nm, however (Δε *ca.* +6), is dominated by the large positive contribution of the ' β '-axial 10β-methyl group (contrast 5α-estran-6-one; Δε +2). In this respect the 190-nm c.d. resembles the lowest-energy olefinic c.d. band for 6-methylene-5α-steroids, observed near 200 nm.[24] In contrast to 6-oxo-5α-steroids, a 4-oxo-5α-steroid exhibits c.d. bands of *the same* (negative) sign at both 290 and 190 nm; here both the ring system and the 10β-methyl group lie in a ' negative ' octant, and their contributions reinforce one another.

The *cis*-decalones of classes 6*c*2*eq* and 6*c*3*ax* (Table 4), which are the two types with bonds of ' β '-axial type forming part of the second ring, give characteristically very large consignate values of Δε near 190 nm which are in sharp contrast with their rather weak c.d. effects at the $n \longrightarrow \pi^*$ transition,[28] suggesting another practical application of c.d. measurements at 190 nm.

APPENDIX

Cyclopentanones and other twisted rings. In part 90 of this series [30] we presented an analysis of c.d. data ($n \longrightarrow \pi^*$) for chiral cyclopentanones, in which the value of Δε was related to the torsion angles (ω) between C_α–H and C_α–C_β bonds and the carbonyl bond by use of equation (i).

$$\Delta\delta\varepsilon = \Sigma k_H \sin^2 \omega_H + \Sigma k_C \sin^2 \omega_C \qquad \text{(i)}$$

C.d. data for cyclopentanone rings in various conformations (in hexahydroindanone analogues) were used to obtain values for the coefficients k_H and k_C (−6.2 and −1.9, respectively, corresponding to *dissignate* effects of individual C_α–H and C_α–C_β bonds).

The form of equation (i) was suggested only from considerations of symmetry, so its applicability should not be limited to any particular electronic transition. In the present work on the 190-nm c.d. it has only been possible to obtain reasonable estimates of Δε for *two* of the classes of hexahydroindanones (5*t*3, Δε ≈ −5.5; 5*t*2, Δε ≈ +2). The latter value *may* include a contribution of +2 from the ' α '-equatorial bond (Table 2) which forms part of the second ring. If this is the case, the ' folded ' cyclopentanone ring itself makes a zero contribution to the hexahydroindanone unit of class 5*t*2. From these alternative values for Δε the coefficients k_H and k_C are calculated to lie within the ranges +9 to +10 and +17 to +23, respectively, according to which value of Δε is adopted for the cyclopentanone ring in class 5*t*2 [see the previous paper [30] for torsion angles and method of calculation].

The positive signs of both coefficients imply that C_α–H and C_α–C_β bonds have consignate effects at 190 nm, in contrast with their dissignate effects at the $n \longrightarrow \pi^*$ transition. The major contribution to the c.d. of a twisted cyclopentanone again appears to come from the quasi-axial C_α–H bonds, so that a conventionally-drawn octant projection of the ring, with only C–C bonds shown, gives the impression of dissignate behaviour with respect to ring helicity which we have noted earlier.[2] The difference, $\delta k_C = k_C - k_H$, *i.e.* the effect of replacing an axial C_α–H by a C_α–C bond, has a value within the range +8 to +13 units, agreeing well with the average of +10 units found for an ' α '-axial methyl substituent at a ring junction (Table 2).

Values of $\Delta\varepsilon$ calculated for the cyclopentanone components of the five classes of hexahydroindanones [29,30] by use of equation (i) showed little sensitivity to which pair of rounded coefficients was chosen. The values are: 5*t*2, 0 or +1.5; 5*c*2*eq*, −1.5 or −2; 5*c*2*ax*, 0 or −1; 5*t*3, −5.5 [*cf.* (*R*)-3-methylcyclopentanone (126), $\Delta\varepsilon$ −5.5]; and 5*c*3, −4.5 or −5 (all values to the nearest 0.5 unit). To calculate $\Delta\varepsilon$ for the complete hexahydroindanone units of ' 1-oxo ' type it is necessary to allow also for those bonds of the second ring which are of C_α–C or C_β–C type (*cf.* Table 2): the values of $\Delta\varepsilon$ obtained for the *bicyclic* structures are: 5*t*2, +2 or +3.5 (found, +2); 5*c*2*eq*, +1.5 or +2 without making any allowance for the ' β '-axial bond (data ambiguous, $\Delta\varepsilon$ always small, p. 799); 5*c*2*ax*, −8 or −9 (found, *ca.* −9.5); 5*t*3, −5.5 (found, −5.5); 5*c*3, −1 or −1.5 (no data available).

As an independent test of the foregoing treatment of twisted rings, $\Delta\varepsilon$ was calculated by use of equation (i) for the 17β-methyl-17a-oxo-D-homosteroid (21), using the torsion angles ω estimated previously for the twisted conformation assumed to be of minimum energy,[30] with the alternative pairs of coefficients above. The ' calculated ' values of $\Delta\varepsilon$ (−3.4 or −3.1) agree quite well with that observed (−2.3), whereas an undistorted ' chair ' form, which would be destabilised by 13β-Me/17β-Me compression, is calculated to have $\Delta\varepsilon$ −10, on the basis of the data summarised in Figure 2 and Table 2 for *trans*-1-decalone derivatives.

Equation (i) in the form (ii) is proposed as the best

$$\delta\Delta\varepsilon = \Sigma 9\sin^2\omega_H + \Sigma 17\sin^2\omega_C \qquad \text{(ii)}$$

available basis at present for ' predicting ' $\Delta\varepsilon$ at 190 nm for twisted-ring ketones: increments for any ' β '-axial alkyl substituents or extended zig-zags must of course be added.

EXPERIMENTAL

Sources of most of the ketones are acknowledged in previous papers in this series.[28–31] The alkylcyclohexanones (1), (3), and (4) were provided by Professor V. Prelog, Zurich. The novel and invaluable tricyclic ketones (10) and (31), and the tetracyclic ketone (32), were synthesised by Professor F. Fernandez, Cátedra de Quimica Orgánica, Santiago de Compostela, Spain.

C.d. measurements over the range 220—185 nm were made in a 1-mm or 0.5-mm cell with a Cary 61 instrument, purged with a rapid flow of oxygen-free nitrogen. Spectroscopic grade n-hexane and acetonitrile were used to prepare solutions containing not more than 0.04% of ketone. C.d. curves and baselines were usually plotted at least twice in superimposition to average out instrument ' noise.'

Discussions with the late Professor W. Klyne made an invaluable contribution to the ideas expressed in this paper. C.d. curves were run by Mrs. M. W. Barrett.

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