The Circular Dichroism of the gem-Dimethylcyclopropyl Group

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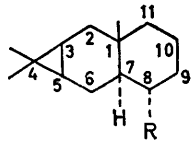
Summary Some derivatives of 1β,4,4-trimethyl-3α,5α,7α-tricyclo[5,4,0,$0^{3,5}$]undecane give very strong Cotton effects in the region 185—195 nm.

WE report the existence of strong Cotton effects in the region 185—195 nm for a series of compounds containing a tetra-substituted cyclopropane ring. The compounds listed in the Table[1] are all derived from the parent hydrocarbons (I) and (II). No absorption maximum can be detected between 200 nm (ε, 1000) and 185 nm (ε 2930), but all the compounds examined show a strong negative Cotton effect in this region. The values of Δε (*ca.* −3·5 to −7·5) are of a different order of magnitude from those which we have previously recorded for monofunctional hydroxy-steroids,[2] and are comparable to those measured for inherently dissymmetric chromophores such as αβ-unsaturated ketones. For most of the acetoxy-derivatives, a very small maximum was also observed near 220 nm, corresponding to the n–π^* absorption of the carboxy-ester group; no further dichroism is observed for acetates between 210 and 185 nm.[3] For the hydroxy compounds, any small Cotton effects due to the hydroxy chromophore, are masked by the very strong dichroism of the cyclopropyl group. The corresponding series of isopropyldecalin derivatives based upon the hydrocarbon (III), showed no dichroism apart from the relatively weak contributions of hydroxy groups.

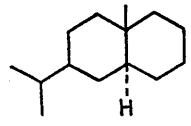
C.d. maxima of (I) *and related compounds*[a]

Substituent	Δε	λ (nm)	Substituent	Δε	λ (nm)
None	−3·9	188	—	—	—
8α-Me	−5·1	193	—	—	—
9α-OH	−6·6	185	9α-OAc	+0·05	220[b]
				−4·7	190
9α-OH,8α-Me	−5·9	197	9α-OAc,8α-Me	−0·75	222[b]
				−6·4	194
9β-OH	−4·2	193	9β-OAc	−4·2	191
9β-OH,8α-Me	−7·5	188	9β-OAc,8α-Me	+0·48	218[b]
				−6·1	190
8α-OH	−4·0	187	8α-OAc	+0·15	218[b]
				−3·3	188
8β-OH	−3·8	195	8β-OAc	−5·6	184
10α-OH,8α-Me	−5·3	190	10α-OAc,8α-Me	+0·10	216[b]
				−4·0	189
10β-OH,8α-Me	−7·1	190	10β-OAc,8α-Me	+0·12	219[b]
				−6·3	188

[a] Measured in hexane solution with a Cary 6002 c.d. attachment. [b] Acetate c.d.



(I) R = H
(II) R = Me



(III)

Cotton effects have recently been reported[4] for some *trans*-disubstituted cyclopropanes having local C_2 symmetry. The *cis*-substituted compounds discussed here have local C_s symmetry, but nonetheless exhibit pronounced dichroism due to the chirality of the rest of the molecule.

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[1] These compounds were previously described [F. Fringuelli and A. Taticchi, *J. Chem. Soc.* (*C*), 1971, 1809] and have now been shown to possess the absolute configuration, illustrated here, F. Fringuelli and A. Taticchi, submitted for publication.
[2] D. N. Kirk, W. P. Mose, and P. M. Scopes, *J.C.S. Chem. Comm.*, 1972, 81.
[3] D. N. Kirk and P. M. Scopes, unpublished observation.
[4] W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Amer. Chem. Soc.*, 1971, **93**, 4932.