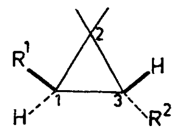
Circular Dichroism of Chrysanthemyl Derivatives; a Chiroptical Dichotomy Between 1,3-Dialkylcyclopropanes and their 2,2-Dimethyl Relatives

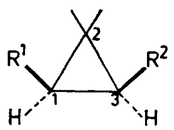
By LESLIE CROMBIE,* DAVID A. R. FINDLAY, RICHARD W. KING, IAN M. SHIRLEY, and DONALD A. WHITING*
(*Department of Chemistry, The University, Nottingham* NG7 2RD)
and P. MOLLY SCOPES and BERYL M. TRACEY
(*Westfield College, Hampstead, London* NW3 7ST)

Summary Chiroptical measurements in the chrysanthemate series show that 1,2,2,3-tetra-alkyl cyclopropanes can have the same chirality as, yet Cotton effects opposite to, those reported for the corresponding 1,3-dialkylcyclopropanes: a possible explanation is mentioned.

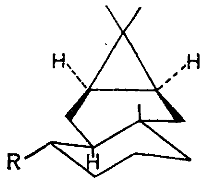
CHIROPTICAL properties of the cyclopropyl chromophore have been little studied[1,2] although cyclopropanes are structural features of important terpenoids (*e.g.* pyrethrins, cycloartenol, presqualene alcohol). The availability of both enantiomeric series of *trans*- and of *cis*-chrysanthemic esters (**1**) and (**2**), and of a series of derivatives including (**3**) and (**4**), has enabled us to study their Cotton effects (C.E.) in the region 185—230 nm. A positive C.E. is associated with the *trans*-(1*R*,3*R*)-2,2-dimethylcyclopropane, and a negative with the *cis*-(1*R*,3*S*)-2,2-dimethylcyclopropane: maxima are near 185 nm, *e.g.* (**3**), 185 (+4·6); (**4**), 185 nm (−4·0).† Such assignments agree with data[1] for tricyclic terpenoids of type (**5**), which show negative C.E.'s in the cyclopropyl region.



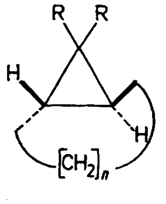
(1) $R^1 = CO_2Me$, $R^2 = CH{:}CMe_2$
(3) $R^1 = CH_2OH$, $R^2 = CH_2CHMe_2$
(8) $R^1 = CO_2Me$, $R^2 = CH_2OH$
(9) $R^1 = CH_2OH$, $R^2 = Me$
(10) $R^1 = R^2 = Me$
(11) $R^1 = R^2 = CH_2OH$



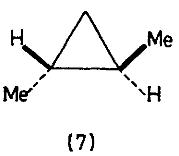
(2) $R^1 = CO_2Me$, $R^2 = CH{:}CMe_2$
(4) $R^1 = CH_2OH$, $R^2 = CH_2CHMe_2$



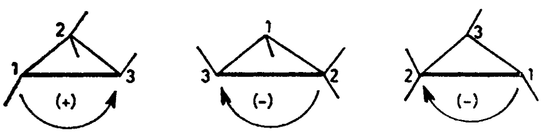
(5)



(6)
a; R = H, *n* = 5
b; R = H, *n* = 4
c; R = Br, *n* = 4



(7)



(12)

A dichotomy emerges when comparison is made with other *trans* dialkyl cyclopropanes (**6a**—**c**, and **7**) for which low-wavelength c.d. measurements have been made.[2] These all display a (+) C.E. (180—190 nm) which is *opposite* to that observed for the same chirality in the *trans*-chrysanthemyl series. To make the closest possible comparison with (1*R*,2*R*)-*trans*-dimethylcyclopropane‡ (**7**), we have synthesised (1*R*,3*R*)-*trans*-1,2,2,3-tetramethylcyclopropane (**10**) from methyl (+)-*trans*-chrysanthemate (**1**). Osmium tetroxide–sodium periodate oxidation gave the expected aldehyde,[3] selectively reduced to the hydroxy-ester (**8**) with borohydride, or fully reduced to the diol (**11**). Lithium aluminium hydride reduction of the tosylate of (**8**) gave the alcohol (**9**). Removal of the hydroxy-functions from the diol (**11**), *via* reduction of the bis-mesylate, afforded the desired tetramethylcyclopropane (**10**). The compounds displayed (+) C.E.'s as follows: (**9**) 185 (+2·9); (**10**) 187 (+6·8); (**11**) 185 nm (+0·5).†

The absolute configuration of chrysanthemic acid and its relatives is securely based both on chemical evidence[4] and two independent *X*-ray analyses.[5] The absolute stereochemistry of (**6b**) is related,[6] through *trans*-cyclo-octene and cyclo-octane-1,2-diol, to (2*R*,3*R*)-(+)-tartaric acid. That of (**7**)[7] is connected with (*S*)-(−)-2-methylbutanol and (+)-isoleucine. No ambiguities are superficially apparent in these interrelations and it appears that compounds typified by (**7**) and (**10**) are not closely analogous in chiroptical properties despite the structural similarities, the local C_2 symmetry of both systems, and the lack of conformational complication. Expectation of parallel c.d. behaviour for such systems has, indeed, been expressed in the literature.[2]

† In cyclohexane; $\Delta\epsilon$ in parentheses.

‡ We have independently confirmed the (+) C.E. (185 nm) for this cyclopropane prepared by the literature method.[7]

A possible stereochemical escape from the dilemma, in terms of an assumption that the differential bond property (*P*CMe–*P*CH) which determines the optical activity is directed (*e.g.* along the bond), has been suggested to us by Professor S. F. Mason. In (**7**) the element of chirality then resides in the asymmetric disposition of the exocyclic methyl groups and is arbitrarily designed (+). Inspection of the enantiomeric form of (**10**) shows *three* such $\alpha\beta$-dimethyl elements. That across the 1,3-bond is (+) as before, but those across the 1,2 and 2,3 bonds are, as shown in (**12**), (−): *i.e.* there is a net (−)-effect. Further study of the electronic origins of the c.d. absorption in cyclopropanes such as (**7**) and (**10**), using vacuum u.v.–c.d. methods, is now needed.

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