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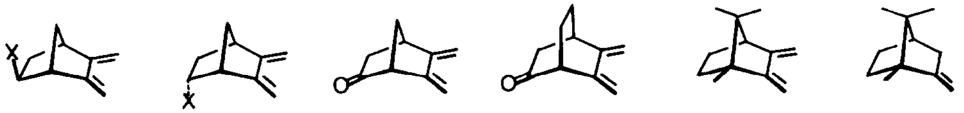
THE CIRCULAR DICHROISM OF 2,3-DIMETHYLIDENE-5-NORBORNYL DERIVATIVES

Zou Zhichen, Pierre-Alain Carrupt and Pierre Vogel*

Institut de chimie organique de l'Université de Lausanne,
2, rue de la Barre, CH-1005 Lausanne, Switzerland.

Summary. *The gas phase and solution CD spectra of (1R)-5*exo,5endo*- and (1R)-5*endo,5exo*- (epoxymethano)-2,3-dimethylidenebicyclo[2.2.1]heptanes have opposite Cotton effects for their V ← N transitions. An "extra" band is observed at ca. 215 nm for the* endo *epoxydiene only.*

The sign of the Cotton effect (CE) associated with the V ← N transition of chiral cisoïd 1,3-diene is given by its heliticity[1,2] and by contributions of allylic axial groups.[3] Chiroptical effects of more remote substitution have been little studied.[2,4] We reported[4,5] positive CE's for the exocyclic *s-cis*-butadienes 1-6 in agreement with the "allylic axial chirality rule" if one considers the C-atoms C(2,3)(see Fig. 1) of the π-system instead of the methylidene function C(3,3') as proposed by Burgstahler et al.[3] for 7 and 8.



X = OH : 1($\Delta\varepsilon_{245}$+0.33) 3($\Delta\varepsilon_{244}$+1.8) 5($\Delta\varepsilon_{248}$+10.3) 6($\Delta\varepsilon_{250}$+15) 7($\Delta\varepsilon_{252}$-0.6) 8($\Delta\varepsilon_{200}$-4.4)
X = OAc: 2($\Delta\varepsilon_{244}$+0.6) 4($\Delta\varepsilon_{243}$+2.9)

Crystallographic X-ray data of (-)-camphorquinone and derivatives[6] suggest that the norbornane skeleton can adapt for out-of-plane deformations of the exocyclic dienes grafted onto it. Considering the positive CE's observed for 1-6, all these dienes may possess some P-helicity (right-handed skew). The larger Δε values measured for the *endo* alcohol 3 and acetate 4 compared with those observed for the *exo* derivatives 1 and 2, respectively, are consistent with a larger degree of P-helicity in 3 and 4 than in 1 and 2. The latter could be attributed to a *endo*-X... C(3)=CH$_2$ repulsive effect (Fig. 2). Gauche interactions between the methyl group and the exocyclic diene might also induce a left-handed distortion (M-helicity) in 7 and thus explain the negative CE observed in the circular dichroïsm spectrum (CD) of this diene. We report CD data on the new *s-cis*-butadienes 9-11. The results are at variance with the above interpretations.

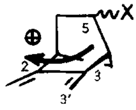


Fig. 1.

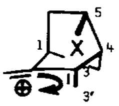
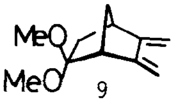


Fig. 2.



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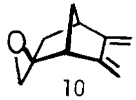

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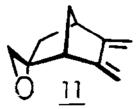

11

9	10	11	
$\Delta\varepsilon_{243}$ -1.25	$\Delta\varepsilon_{233}$-0.66 $\Delta\varepsilon_{241}$-0.50	$\Delta\varepsilon_{243}$+2.0 $\Delta\varepsilon_{212}$-1.2	(isooctane)
$\Delta\varepsilon_{241}$ -1.87	$\Delta\varepsilon_{235}$-0.61 $\Delta\varepsilon_{243}$-0.46	$\Delta\varepsilon_{244}$+0.95 $\Delta\varepsilon_{215}$-0.93	(EtOH 95%)

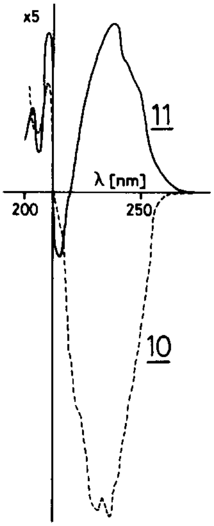

Fig. 3.

The dimethyl acetal 9 was prepared from (1R)- dienone 5 (e.e. > 98 %) whose absolute configuration was determined unambigously.[4,7] The epoxides 10 and 11 were also derived from 5.[8,9] If the *exo* and *endo* substituent contributions to the CE's observed for dienes 1-4 were additive, positive CE's would be expected for the V ← N transitions in 9-11. The negative CE's measured for 9 and 10 are a surprise. The sign inversion between *exo* and *endo* epoxy-dienes 10 and 11 was also unexpected.[10] Even more stricking is the CD spectrum of 11 which shows an "extra" band at ca. 215 nm; this is not visible in the spectra of 9-10. It was not predicted by CNDO/S calculations which included 46 singly and 45 doubly excited configuration interactions. Insignifant changes were observed between the gas phase (Fig. 3, arbitrary $\Delta\varepsilon$ scale) and solution CD spectra. We tentatively assign this "extra" band to a long-range,[11] mixed charge-transfer transition which involves components of the form n(epoxide) → π^*(diene) and π(diene) → σ^*(epoxide) in analogy with charge-transfer bands of β,γ-unsaturated ketones 5 and 6.[5]

No direct relationship can be drawn at the moment between the chiroptical properties of 10 and 11 and their Diels-Alder regioselectivities.[8] The results, however, demonstrate the role played by the relative configuration of the epoxide ring in its transannular interactions with an homoconjugated π-system. They suggest that minor modifications in the norbornane substituents can be accompanied by impredictable skeleton deformations both in solution and in the gas-phase.[12]

References and Notes.

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8. See: C. Mahaim, L. Schwager, P.-A. Carrupt & P. Vogel, preceding paper.
9. Characteristics of (1R)-9: $[\alpha]_D^{23}$+36.5°(c=0.286 g / 100 ml $CHCl_3$); (1R)-10: $[\alpha]_D^{20}$+130.5° (c=0.533 g / 100 ml $CHCl_3$); (1R)-11: $[\alpha]_D^{20}$+133.8°(c=1.167 g / 100 ml $CHCl_3$).
10. MINDO/3 as well as MNDO minimized geometries of 1-6, 9-11 show very small skew deformations for these dienes. They could not, however, be correlated with the observed CE's.
11. Since the CNDO/S calculations neglect differential overlap it is not surprising that such a transition is not predicted by this technique.
12. The racemic acetal 9 was prepared first by L. Schwager, University of Lausanne, unpublished results.

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