On the Circular Dichroism Spectra of Bornane-2,3-dione[1]

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Summary (1*R*)-Bornane-2,3,dione (**1**) exhibits a negative circular dichroism Cotton effect (CE) near 470 nm in solution and in the vapour phase, but in the crystalline phase (in KBr) the CE is positive.

The chiroptical properties–molecular structure relationship of *cisoid* α-diketones has been a subject of controversy[2,3] and intensive investigation.[2–10] Most studied have been the two more accessible electronic transitions near 450 and 300 nm, which apparently originate from coupling and splitting of the two carbonyl n–π^* transitions. Both theory and experiment have been invoked to define the relative importance of contributions to the circular dichroism Cotton effect (CE) emanating from i, dissymmetry of the α-diketone chromophore and ii, extrachromophoric perturbation, *viz.* α-axial bonds. On the basis of experimental evidence, it has been argued[2,10] that for the long wavelength transition α-axial bond chirality contributions dominate dione helicity contributions, even for dione torsional angles of *ca.* 40°.[10] On the basis of molecular orbital calculations, (+)[6] or (−)[7,9] long wavelength CEs have been associated variously with the P helicity of α-diketones. The most recent complete review and theoretical treatment[9] takes into account both dione helicity and extrachromophoric contributions and ascribes the long wavelength electronic transition near 450 nm to a nearly pure $n_+ \rightarrow \pi_-^*$ transition localized on the dicarbonyl group with the next lowest transition being a less simple admixture of $n_-\pi_-^*$ (dominant contribution) and $n_+\pi_+^*$ configurational states.

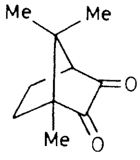
In contrast to other α-diketones studies, bornane-2,3-dione is of special interest and has been well-studied.[6–9] Its dione chromophore is expected to be nearly planar[11] and when it is planar the α-axial bond contributions are symmetrically disposed. For the planar dione, the only dissymmetric vicinal perturber is the α-pseudoequatorial C-10 methyl group, which might be expected to exercise a minimal contribution to the CE.[12]

We have obtained the room temperature cd spectrum of (1*R*)-bornane-2,3-dione (**1**) in CF_3CH_2OH (Figure) and in methylcyclohexane (Table), its variable temperature solu-

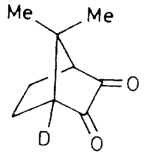
Table. Rotatory strengths of compounds (**1**)—(**3**)

Compound	Rotatory strengths, value × 10^{-41} c.g.s. units[a] (λ_{max}/nm) KBr[b]	Gas[c]	Methylcyclohexane[d]
(**1**)	+5·2(466)	(−)(475)	−9·1(483)
	+4·2(307)	(+)(289)	+8·6(293)
			−5·2(234)
(**2**)	−3·1(467)		+0·16(485)
			+0·24(284)
(**3**)	−26(457)		−6·6(477)
	+33(276)		+3·5(278)
			−1·9(238)
			+2·1(212)

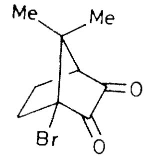
[a] To convert to S.I. units, multiply c.g.s. value by $3{\cdot}33 \times 10^{-15}$. [b] Values determined from a w/w concentration which was converted into a 1 M solution using the mol. wt. of the sample and a KBr density of 2·75 g cm^{-3} and micrometer-measured pathlength. [c] CE signs only determined. [d] The CE signs and magnitudes are essentially invariant in EPA (diethyl ether–isopentane–ethanol, 5 : 5 : 2 v/v/v) and methylcyclohexane–isopentane (4 : 1, v/v) over the range 25 to −170 °C, and the CE signs are the same as those in methylcyclohexane.



(1)

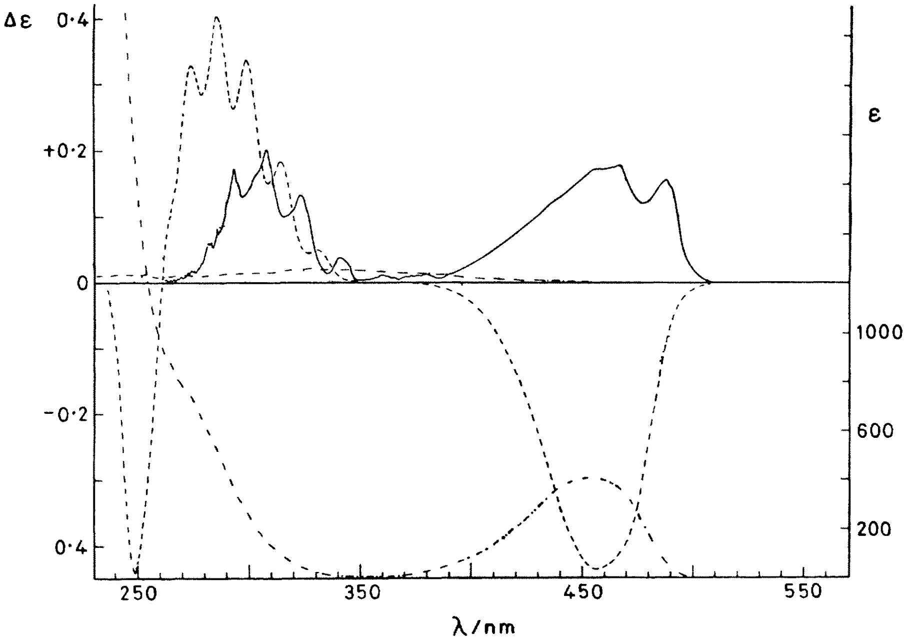


(2)



(3)

tion c.d. spectra in methylcyclohexane–isopentane and in EPA (diethyl ether–isopentane–ethanol) (Table footnote d), its gas phase c.d. spectrum (Figure), and a solid phase c d. spectrum (in KBr) (Figure, Table). Under these varied conditions, the excitation near 300 nm is unchanged in sign (+). However, the sign of the CE associated with the long wavelength transition near 450 nm does not remain invariant: it is negative in solution and in the gas phase, but positive in the crystalline phase in KBr discs (Figure, Table). If it is assumed that the CE contributions from extrachromophoric perturbers remain sign invariant through the phase changes just described, the net CE sign change observed can be explained either by a change in helicity of the dione torsional angle from P in the solid[11] to M in solution and vapour, or by exciton (Davydov) coupling between the two bornane-2,3-dione molecules in the acentric unit cell At present it is not possible for us to distinguish between these two possibilities with certainty, although the observation that the relative magnitudes of the two transitions are *ca.* 1 : 1 in solution, solid, and gas phases might make the exciton coupling argument less probable. If the change in helicity explanation is valid, then because crystalline (1*R*)-bornane-2,3-dione has been shown to have a small P dione helicity[11] it follows: i, that the observed (+) long wavelength CE is more in accordance with the predictions of Hug and Wagnière[6] than others,[7,9] and ii, that (1*R*)-bornane-2,3-dione in solution and in the vapour phase either (a) possesses a CE-dominating M dione helicity, or (b) exhibits extremely small helicity contributions, *e.g.* zero in a planar dione, relative to the predicted (−) CE contribution[9] of the vicinal dissymmetric C-10 methyl perturber. Electron diffraction or microwave studies of (1*R*)-bornane-2,3-dione vapour should reveal the sense and degree of dione helicity.



C.d. spectra of (**1**) measured on a JASCO J-40 spectrometer: (————) 1·50 mg (**1**)/200 mg KBr (density KBr = 2·75 g cm^{-3} at 25 °C); (– – – – – –) 7·34 × 10^{-3} M solution of (**1**) in CF_3CH_2OH at 25 °C; (· · · · · · ·) (**1**) at 124 °C in the gas phase; (– · – – · – – · – –) c d. spectrum of (±)-bornane-2,3-dione; (– · · – – – – – – – – · ·) u v.–vis. spectrum of (**1**) in CF_3CH_2OH (Cary 219 spectrometer). The gas phase spectrum (10 cm cell) was scanned rapidly, with concomitant loss of resolution, to circumvent deposition of solid on the windows. The KBr discs were prepared by compression in a KBr die at 16,000 lb in^{-2} following intimate mixing of the sample and Harshaw spectrograde KBr powder. This gave a translucent disc of 17 × 10^{-3} in thickness (pathlength).

C d. data were obtained similarly for the (1*R*)-1-deuterio-2,3-dione (**2**)[13] and (1*S*)-1-bromo-7,7-dimethylbicyclo-[2 2.1]heptane-2,3-dione (**3**)† (Table). The former also showed a long wavelength CE sign change [(+) to (−)] in going from solution to the crystal whereas the latter remained sign (−) invariant. The dione helicity argument suggests that the bromo-dione will have an M helicity in the crystal.

The shorter wavelength CE's near 300 nm are all (+) and CE sign invariant through the phase changes for the three

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† Prepared by SeO_2 oxidation of the corresponding 1-bromonorbornan-2-one which can be prepared as in reference 13.

compounds studied The origin of that c d transition apparently does not depend particularly on dione helicity but is governed by static extrachromophoric perturbations [9]

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