

Optical Rotatory Dispersion and Circular Dichroism Data for Some Epicamphor Derivatives

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O.r.d. and c.d. data are reported for the epimeric 2-phenyl and 2-hydroxy-2-phenyl derivatives of (-)-bornan-3-one. The observed contributions of the *endo*-phenyl and the *exo*-hydroxy-group to the amplitude or the $\Delta\epsilon$ value are in an opposite sense to that predicted for alkyl groups by the Octant Rule, whereas the *exo*-phenyl and the *endo*-hydroxy-group give contributions as predicted by the Octant Rule.

THE recent reports by Thomas and Mislow¹ on the chiroptical properties of the epimeric 3-phenylbornan-2-ones and of the Westfield College group² on the 2-hydroxy- and 2-acetoxy-bornan-3-ones have prompted us to report our observations on a series of 2-phenyl- and 2-hydroxy-2-phenyl-bornan-3-ones. Cookson and Hudec³ observed that in the presence of an axial phenyl group α to a carbonyl group, the $n \rightarrow \pi^*$ transition of the carbonyl compound resulted in a Cotton effect of opposite sign to that predicted by the Octant Rule. Thomas and Mislow similarly found¹ that phenyl substitution α to a carbon group in either an *exo*- or an *endo*-configuration in some bornanones resulted in a contribution to the $n \rightarrow \pi^*$ transition (c.d. and o.r.d.) opposite to that expected from the Octant Rule. This anti-octant behaviour is probably due to electrostatic interaction between the localised transitions of the chromophores (transition moment coupling). The overlap of the carbonyl and benzene π -systems is of minor consequence in the enhancement of the u.v. absorption and optical rotatory power for the $n \rightarrow \pi^*$ transition.⁴ Hydroxy- and acetoxy-substituents α to a carbonyl group in a bornanone have been shown to effect the chiroptical properties most markedly when in an *endo*-configuration, but always in the anti-octant sense.

We now report the chiroptical effects on bornan-3-one of 2-phenyl and 2-hydroxy-2-phenyl substitution.⁵ The spectroscopic data are summarised in Tables I and 2. In contrast to the results obtained for the 3-phenyl-

bornan-2-ones,¹ no significant enhancement in the u.v. $n \rightarrow \pi^*$ absorption was observed for the *exo*-phenyl ketone (1b) compared with the *endo*-phenyl

TABLE I

O.r.d. data for 2-phenyl- and 2-hydroxy-2-phenyl-bornan-3-ones *

(1a) 2- <i>endo</i> -Phenylbornan-3-one	
$[\phi]_{250} - 4421.45$, $[\phi]_{266} - 3196.23$, $[\phi]_{258} - 3356.04$, $[\phi]_{262} - 2343.90$,	
$[\phi]_{265} - 3009.78$, $[\phi]_{268} - 1917.74$, $[\phi]_{270} - 2477.08$, $[\phi]_{288} 0$,	
$[\phi]_{297} + 585.98$, $[\phi]_{304} 0$, $[\phi]_{308} - 266.35$, $[\phi]_{314} - 2663.52$,	
$[\phi]_{320} - 2343.90$, $[\phi]_{326} - 4794.35$, $[\phi]_{350} - 1811.19$, $[\phi]_{400}$	
$- 852.33$, $[\phi]_{598} - 239.72$	
(1b) 2- <i>exo</i> -Phenylbornan-3-one	
$[\phi]_{270} + 3425.3$, $[\phi]_{272} + 3042.61$, $[\phi]_{275} + 3425.30$, $[\phi]_{280} + 3282.57$,	
$[\phi]_{300} + 1902.94$, $[\phi]_{310} 0$, $[\phi]_{314} - 1046.62$, $[\phi]_{320} - 1474.78$,	
$[\phi]_{327} - 2402.47$, $[\phi]_{340} 1665.08$, $[\phi]_{350} - 1379.63$, $[\phi]_{400} - 475.74$,	
$[\phi]_{598} - 95.5$	
(1c) 2- <i>exo</i> -Hydroxy-2- <i>endo</i> -phenylbornan-3-one	
$[\phi]_{250} - 3622.06$, $[\phi]_{260} - 1567.76$, $[\phi]_{263} - 1811.03$, $[\phi]_{268} - 864.97$,	
$[\phi]_{270} - 1135.27$, $[\phi]_{277} 0$, $[\phi]_{294} + 1324.48$, $[\phi]_{307} 0$, $[\phi]_{332}$	
$- 4838.42$, $[\phi]_{350} - 2703.03$, $[\phi]_{400} - 1675.88$, $[\phi]_{398} - 324.36$	
(1d) 2- <i>endo</i> -Hydroxy-2- <i>exo</i> -phenylbornan-3-one	
$[\phi]_{280} + 6358.19$, $[\phi]_{270} + 5485.50$, $[\phi]_{285} + 4986.81$, $[\phi]_{294} + 5236.16$,	
$[\phi]_{326} 0$, $[\phi]_{338} - 2368.74$, $[\phi]_{350} - 1090.87$, $[\phi]_{400} - 140.25$,	
$[\phi]_{598} + 124.67$	

* Cyclohexane used as solvent for all compounds; data obtained with a JASCO model ORD/UV-5 instrument fitted with a CD attachment.

ketone (1a). For the *exo*-phenyl ketone (1b), the absence of significant transition moment coupling is reflected in the o.r.d. and c.d. spectra, which reveal chiroptical

¹ H. T. Thomas and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 6292.

² L. Bartlett, D. N. Kirk, W. Klyne, S. R. Wallis, H. Erdtman, and S. Thoren, *J. Chem. Soc. (C)*, 1970, 2678.

³ R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 1962, 429.

⁴ A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolymer Symp.*, 1964, **1**, 75.

⁵ J. M. Coxon, M. P. Hartshorn, and A. J. Lewis, *Austral. J. Chem.*, 1971, **24**, 1009.

properties consistent with the Octant Rule. In contrast, the *endo*-phenyl group in compound (1a) makes the expected anti-octant contribution. The introduction of a 2-*exo*-hydroxy-group into the *endo*-phenyl-ketone (1a) results in a further anti-octant contribution to the

hydroxy-group and the phenyl group [whose plane will be more or less eclipsed with the C(2)-O bond], or of a change in the preferred conformation of the hydroxy-group due to steric interactions with the geminal phenyl group. Conformational constraints on the phenyl group

TABLE 2
U.v. spectra and Cotton effects of epicamphor and derivatives *

Compound	U.v.		C.d.		O.r.d.		$a/\Delta\epsilon$	$\Delta a(a_{epd} - a_{epicamphor})$
	$\lambda_{max.}/nm$	ϵ	λ/nm	$\Delta\epsilon$	Extrema	a		
Epicamphor ^{5,6} (1a)	243	85	305	-1.86				
			310	-1.44				
			317	-0.94	326, 296	(-74.11) ‡	+37.36	+20.21
			323	-1.18				
		249	120					
		253	170					
		259	219					
		265	177					
		292sh	47					
		301	53					
		311	49					
		322sh	26					
(1b)	239	187	310	-1.41	327, 294	-58.51	+41.49	+15.60
	244	192	323	-1.03				
	249	194						
	254	213						
	260	241						
	267	192						
	270infl	117						
	288br	41						
	328	9						
(1c)	252	279	312	-1.50	333, 294	-61.63	+41.07	+12.48
	259	285						
	265	239						
	268sh	137						
	282	108						
(1d)	303br	40						
	253	252		(-1.89) ‡	338, 294	-76.04		-1.93
	259	279						
	264	236						
	270	147						
	282	51						
	299	43						
340	16							

* Cyclohexane used as solvent for all compounds. † Determined with a Shimadzu MPS-50L spectrometer. ‡ Calculated by use of the relationship $\Delta\epsilon = a/40.28$.⁷

o.r.d. ($\Delta a - 7.83$). Similar introduction of a 2-*endo*-hydroxy-group into the *exo*-phenyl ketone (1b) leads to a further octant contribution ($\Delta a - 17.53$).

For the *exo*-phenyl ketone (1b) and its 2-hydroxy-derivative (1d), the absence of significant transition moment coupling is probably a consequence of the conformational constraints imposed on the phenyl group by the 1-methyl group of the bornane system. It is not clear whether the unexpected Octant Rule contribution of the 2-*endo*-hydroxy-group in compound (1d) arises as a consequence of electronic interaction between the

in compounds (1a) and (1c) are less serious and allow transition moment coupling between the phenyl and carbonyl groups, leading to anti-octant behaviour.

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⁶ C. Coulombeau and A. Rassatt, *Bull. Soc. chim. France*, 1963, 2673.

⁷ S. F. Mason, *Quart. Rev.*, 1963, 17, 20.