

Spectroscopic Properties of ' γ '-Substituted Ketones†

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Summary C.d. and u.v. spectra of *anti*- π -substituted (+)-camphor derivatives show that the substituent and the carbonyl group interact.

BECAUSE of the lack of suitably functionalised ' γ '-hydroxy-steroidal ketones as our substrate for studying the interaction between a carbonyl group and a substituent separated

R	anti- π -substituted camphor derivatives in ethanol*					
	U.v.		C.d.		N.m.r. coupling constant $^4J_{AX}$ (CDCl ₃)	
	λ_{max} (nm)	ϵ	λ_{max} (nm)	$\Delta\epsilon$		
H	291	33.5	295	+1.50		
OH	290	34	294	+1.68	†	
OAc	289	40	296	+1.30	†	
O·CO·CMe ₃	290.5	36	294	+1.57	0.6	
O·CO·CF ₃	288	44	294	+1.43	†	
F	292	32	298	+0.68	0	
Cl (ref. 2)	291	41	293	+3.09		
Br	291	63	293	+5.47	1.0	
I	(259 640)‡		291.5	+10.00	1.1	
CN	290	35	293	+1.73	†	
N ₃	290.5	63	292	+2.50	†	
+ NH ₃ Cl ⁻			298	+0.83		
S-Bu ^t	290	120	293	+4.07	0.85	
	236.5sh	370				
SO ₂ -Bu ^t	294.5	52	292.5	+4.50		
S- <i>anti</i> - π -Camphor	292	114	292	+10.50		
S-S- <i>anti</i> - π -Camphor	(254 360)§		293	+13.40		
SH	260inf.	110	292.5	+4.11		

* U.v. and c.d. spectra in n-hexane show the same trends in ϵ and $\Delta\epsilon$, but the values are all slightly smaller and λ_{max} show the expected small red shift and fine structure.

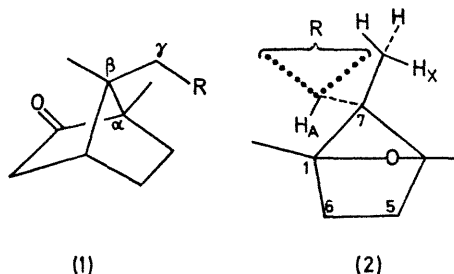
† Slight broadening of the downfield proton.

‡ $n \rightarrow \sigma^*$ of iodine.

§ $n \rightarrow \sigma^*$ of -S-S-.

† In these cyclic compounds, ' α ', ' β ', ' γ ', and ' δ ' denote the separation of the oxo-group and the substituent by 1, 2, 3, and 4 bonds respectively.

by 3 bonds, we have chosen the readily obtainable *anti*- π -substituted camphors (**1**). Although the *anti*-methyl group (**1**; R = H) is free to rotate, we felt that a substituent R would restrict its rotation (because of nonbonded interactions with *exo*-protons on C-5 and C-6) so that the substituent R would be contained between the two extreme positions [dotted lines in (**2**)] both of which are in a correct orientation for coupling with the carbonyl group through the C(1)-C(7) bond.¹



The u.v. spectra (Table) show only a slightly enhanced extinction coefficient for R=Cl² and Br³. However, the c.d. spectra show the considerable enhancements in $\Delta\epsilon$ when expected.^{1†} The λ_{\max} values are nearly constant; small red shifts are exhibited by strongly electron-withdrawing substituents only in the c.d. spectra.

The restricted rotation of the substituted methyl group is also evident in the n.m.r. spectra. The change in the magnitude of $^4J_{AX}$ (ref. 4) with the size of substituent may reflect the extent of the restriction of rotation, but it may be also equally well explained by the change in the electronegativity of the substituent.⁵

Our preliminary work on other rigid equatorially and axially ' γ ' substituted systems indicates that the magnitude of $\Delta(\Delta\epsilon) = (\Delta\epsilon_{\text{subst.}} - \Delta\epsilon_{\text{H}})$ is characteristic for a given substituent provided it is in a correct orientation for coupling.¹

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† C.d. spectra for (**1**, R = Cl and Br) have been reported.² The large changes in $\Delta\epsilon$ were then ascribed to a distortion of the bornane skeleton.

¹ J. Hudec, *Chem. Comm.*, 1970, 829; G. H. Cooper and J. Hudec, in preparation.

² D. E. Bays, G. W. Cannon, and R. C. Cookson, *J. Chem. Soc. (B)*, 1966, 885.

³ E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, 1957, **79**, 5773.

⁴ D. H. Gustafson and W. F. Erman, *J. Org. Chem.*, 1965, **30**, 1665.

⁵ C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc.*, 1962, **34**, 115.