

## Spectroscopic Properties of 'δ'-Substituted Ketones†

By G. P. POWELL and J. HUDEC\*

(Chemistry Department, The University, Southampton SO9 5NH)

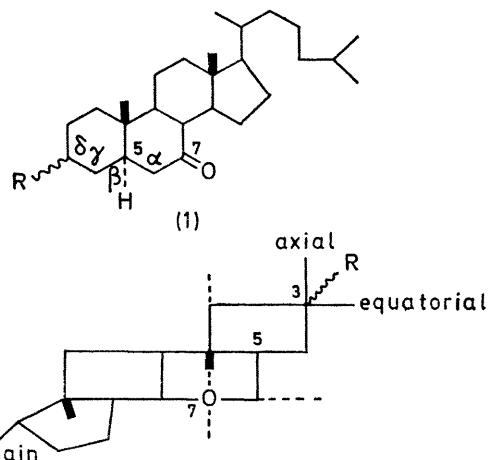
**Summary** The spectroscopic properties of pairs of epimeric 'δ'-substituted ketones show that in only one of the epimers an interaction between the substituent and the carbonyl group takes place *via* the intervening σ-bonds; c.d. spectroscopy can be used to detect this interaction, but u.v. is not sensitive.

This is in contrast to the observations on 'α' axially<sup>6</sup> and 'β' equatorially<sup>1</sup> substituted compounds, which suggests that there is no interaction between the two functional groups in the 'δ'-substituted case.

THE systematic work of Snatzke and Eckhardt<sup>1</sup> on the spectroscopic properties of 'β' equatorially and axially substituted adamantanones and the vast amount of other data in the literature<sup>2,3</sup> on 'α'-substituted ketones have led us to reappraise the various spectroscopic rules and unify them in a generalised manner.<sup>4</sup>

We have shown in the preceding communication<sup>5</sup> that 'γ'-substituents interact with the carbonyl group but to a lesser extent than the 'β'-substituents,<sup>1</sup> which show maximum interaction. We have therefore synthesised ketones with four carbon-carbon bonds between the carbonyl group and the substituent in order not only to test experimentally our rules<sup>4</sup> but also to establish the magnitude of the interaction. *A priori*, this interaction might be expected to be greater (*cf.* 'α' and 'β' series) or smaller than in the 'γ' series depending on whether a conjugative (former case) or inductive type mechanism dominates the coupling. The compounds chosen were 3-axially and 3-equatorially substituted 5α-cholestan-7-ones (**1**).

The u.v. spectra exhibit no abnormalities of the  $n \rightarrow \pi^*$  transition either in the 3-equatorial or in the 3-axial series.



However, this conclusion is negated by the  $\Delta\epsilon$  values of the equatorial substituents in comparison with the axial ones. These trends, albeit attenuated, are identical to those observed in the 'β' and 'γ' series.<sup>5</sup> The equatorial

† See footnote to preceding communication for use of 'α', 'β', 'γ', and 'δ'.

' $\delta$ '-substituted compounds show an increased "octant" trend dependent on the donating properties of the non-bonding orbital of the substituent to the  $\pi^*$  orbital of the

and ' $\delta$ ' series indicates strongly that the two functional groups interact by an inductive mechanism which shows an angular dependence.

3-Axially and 3-equatorially substituted 5 $\alpha$ -cholestan-7-ones in ethanol\*

	R	u.v.		c.d.	
		$\lambda_{\max}(\text{nm})$	$\epsilon$	$\lambda_{\max}(\text{nm})$	$\Delta\epsilon$
3-equatorial	H	289	41	291	-0.74
	F	289	35	288	-0.16
	Cl	291	42	291	-1.02
	Br	291	48	292	-1.71
	I		259(980) $\S$	291	-3.08
	OH	289	39	290	-0.71
	OAc	291	41	291	-0.33
	O·CO·CMe <sub>3</sub>	292	40	291	-0.40
	O·CO·CF <sub>3</sub>	288	34	290	-0.16
	EtS	288	68	291	-1.77
	EtSO <sub>2</sub>	290	46	290	-1.24
	N <sub>3</sub>	288	70	290	-0.76
	3-axial	F	288	44	291
Cl		291	38	291	-0.22
Br $\dagger$				291	-0.37 $\pm$ 0.09
I $\dagger$				290	-0.55 $\pm$ 0.31
OH		290	40	291	-0.72
OAc		291	40	292	-0.29
O·CO·CMe <sub>3</sub>		290	35	290	-0.26
O·CO·CF <sub>3</sub>		291	39	290	-0.21
N <sub>3</sub>	288	78	292	-0.27	

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

$\dagger$   $\Delta\epsilon$  values are calculated from measurements on a mixture of inseparable 3-axial and 3-equatorial epimers<sup>7</sup> estimated by integration of the 3-epimeric protons in n.m.r. The assumed limit of error in integration is  $\pm 6\%$ .

$\S$   $n \rightarrow \sigma^*$  of iodine.

carbonyl group *via* the extended planar **W** path.<sup>4</sup> The axial substituents show an "antioctant" trend as would be expected from the conformational-path rules for donation.<sup>4</sup> The gradual decrease in the magnitude of  $\Delta\epsilon$  in the ' $\beta$ ', ' $\gamma$ ',

These results show that c.d. is a much more sensitive tool than u.v. for probing into long-range interactions between two functional groups.

(Received, December 31st, 1970; Com. 2267.)

<sup>1</sup> G. Snatzke and G. Eckhardt, *Tetrahedron*, 1968, **24**, 4543; 1970, **26**, 1143.

<sup>2</sup> C. Djerassi, 'Optical Rotatory Dispersion,' McGraw-Hill, New York, 1960; L. Velluz, M. Legrand, and M. Grosjean, 'Optical Circular Dichroism', Verlag Chemie, Weinheim, 1965.

<sup>3</sup> P. Crabbé, 'Optical Rotatory Dispersion and Circular Dichroism,' Holden-Day, San Francisco, 1965 and Gauthier-Villars, Paris, 1968.

<sup>4</sup> J. Hudec, *Chem. Comm.*, 1970, 829; G. H. Cooper and J. Hudec, in preparation.

<sup>5</sup> M. T. Hughes and J. Hudec, preceding communication.

<sup>6</sup> S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.

<sup>7</sup> H. B. Henbest and W. R. Jackson, *J. Chem. Soc.*, 1962, 954.