Ultraviolet Spectrum and Conformation of 1-Azabicyclo[3,3,1]nonan-3-one

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Summary 1-Azabicyclo[3,3,1]nonan-3-one was synthesized; its u.v. and i.r. spectra confirm the conclusions enunciated in the preceding communication.

It has been suggested that the intensification of the $n \rightarrow \pi^*$ transition of α-axial halogeno-(Cl, Br, I)cyclohexanones is due to the overlap of the *n*-orbital of the halogen simultaneously with the carbonyl *p*- and π^*-orbitals.[1]

A similar treatment was suggested for some βγ-unsaturated ketones[2] when the *n*-orbital was replaced by the π-orbital of the double bond. Consequently the new transition that appeared at lower wavelengths (214—245 nm) was described as a $\pi \rightarrow \pi^*$ charge transfer.[2,3] Although this treatment was substantiated theoretically,[4] a later one suggested that the enhancement arises from coupling of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and that the low-wavelength band arises by splitting of the $\pi \rightarrow \pi^*$ transition, one part of which is red-shifted.[5]

Our empirical analysis of several α- and β-amino-ketones predicts that the enhancement of the $n \rightarrow \pi^*$ transition should arise when the lone pair on the α-axial N (or an equivalent position) is *trans*-diaxial to a C_α–C=O bond.[6] At the same time, we should observe a $\pi \rightarrow \pi^*$ band at lower wavelengths. In order to test these predictions we synthesized 1-azabicyclo[3,3,1]nonan-3-one (1)[7] and measured its spectra (Table).

U.v. spectra of (1)

H₂O		EtOH		n-Hexane		Vapour		CHCl₃	
λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
				344	33				
311	52	314	44	330	55	325		321	61
				317	53	313			
235[a]		225[a]		235[a]		243[b]	200[c]		
				214		215	2000[c]		

U.v. spectra of (1) *hydrochloride*

H₂O		EtOH		n-Hexane		Vapour		CHCl₃	
282	19	290	19	—		—		—	

N.m.r. spectra of (1)

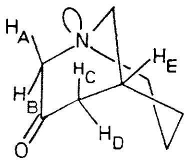
	$CDCl_3$	CCl_4	$CDCl_3 + CF_3CO_2H$
J_{AB}	17·4 Hz	17·2 Hz	17·1 Hz
J_{CD}	17·0		17·2
J_{CE}	*ca.* 5·5		*ca.* 5·5

M.p. 124—126° (uncorr.), (123—125°[7]), 1713 cm^{-1} ($CHCl_3$).

[a] Shoulder.

[b] λ_{max} is for a resolved band and not for the shoulder.

[c] These values were calculated on the assumption that the intensity of the $n \rightarrow \pi^*$ transition in vapour is 50.



(1)

It can be seen that the spectra support our expectations, even though the intensities of the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions are not as large as we expected. The reason for this can be gleaned from J_{gem} values in the n.m.r. spectra which indicate a very considerable flattening of the carbonyl-carrying ring.[8] We are currently engaged in overcoming these drawbacks.

Our work suggests that the earlier theoretical treatments[4,5] of the pertubation of the $n \rightarrow \pi^*$ transition by α-substituents are wrong as none of them would have predicted the spectral behaviour of (1). The consequence of our results to the concepts of neighbouring-group participation, and to the rates of solvolysis of the pseudo equatorial toluene-*p*-sulphonates derived from (1), will be discussed elsewhere.

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