Effect of *p*-Substitution on the Spectroscopic Properties of 1,2-Dihydro-4*H*-2-phenyl-3,1-benzoxazines

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A series of 1,2-dihydro-4*H*-2-phenyl-3,1-benzoxazines (I) were obtained by condensation of *o*-aminobenzyl alcohol and substituted benzaldehyde. The effect of *p*-substitution on their spectroscopic properties was investigated by uv and mass spectroscopy.

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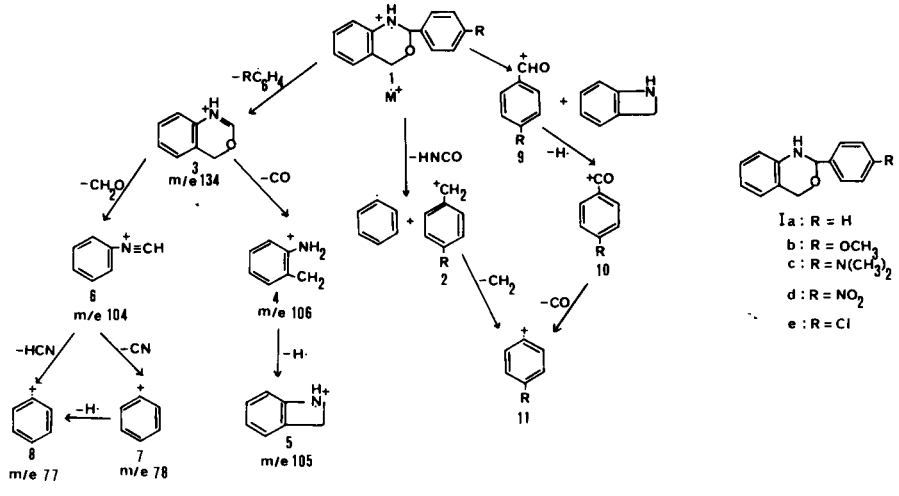
It was reported that from the condensation between γ-aminoalcohol (1) or 2-aminophenol (2a-c) and aldehydes 1,3-and 1,4-benzoxazines were obtained. The 1,2-benzoxazines were obtained by the action of nitrous gases on cinnamaldehyde or of dinitrogen tetroxide on β-nitrostyrene (1). The structure of 1,4-benzoxazines has been investigated by uv, nmr and mass spectroscopy (2c, 3-6), the synthesis and uv spectra of some *N*-aryl-2,3-dihydro-3-oxo-4*H*-1,4-oxazine have also been studied (7). A considerable work has been done on the preparation and ir, nmr and to less extent uv spectroscopy of 1,3-benzoxazines (8,9), 1,3-benzoxazinone (10-11), 1,3-benzoxazinediones (12), 2,3-benzoxazines (13,14) and 3,1-benzoxazinediones (isatoic anhydride) (15,16). One of the heterocyclic derivatives of 4*H*-3,1-benzoxazin-4-one has been studied extensively by mass spectrometry (17). In this work a new series of 1,2-dihydro-4*H*-2-phenyl-3,1-benzoxazines (I) have been prepared and the effect of *p*-substitution on the spectroscopic properties has been studied by ir, uv and mass spectroscopy. The streching frequences of NH and C-O absorption bands of (I) in nujol mull are shown in Table 1.

SCHEME I



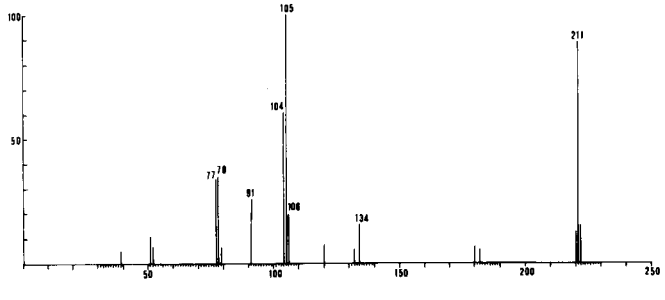


Figure 1 Mass Spectrum of Compound Ia

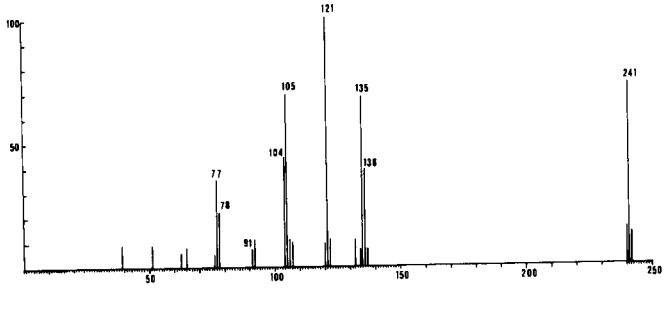


Figure 2 Mass Spectrum of Compound Ib

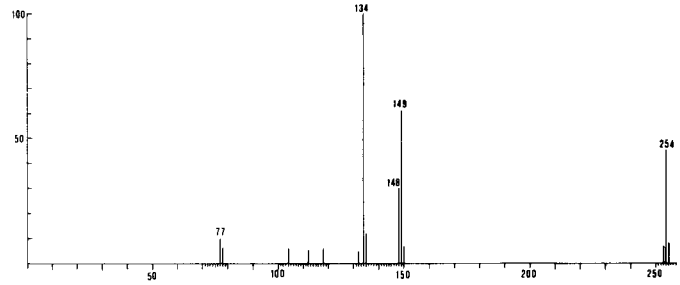


Figure 3 Mass Spectrum of Compound Ic

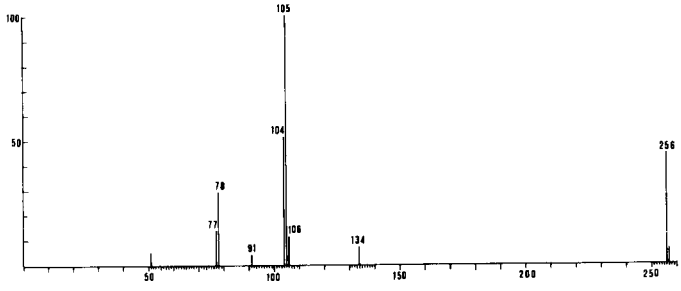


Figure 4 Mass Spectrum of Compound Id

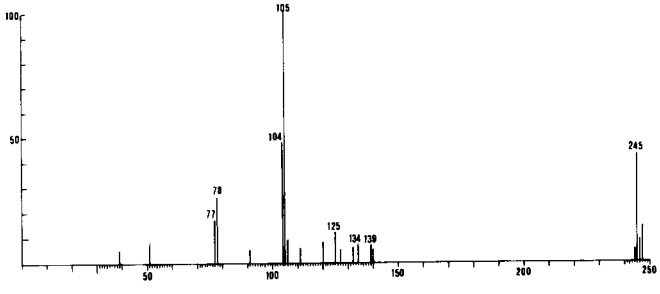


Figure 5 Mass Spectrum of Compound Ie

The ultraviolet spectrum of Ic is a special case, the spectrum of this compound shows a very high conjugation band with λ max 357 nm which contains a shoulder at 315 nm. The presence of a strong donating group such as $N(CH_3)_2$ in the *para* position may cause a high conjugation owing to charge delocalization in the direction $N(CH_3)_2$) to the other part of molecule, such high conjugation has been observed when $N(CH_3)_2$ group is introduced in the *para* position of the phenyl ring of some related molecules (19,20). In concentrated sulphuric acid complete protonation of all basic centers has occured and then charge delocalization from $N(CH_3)_2$ to the other part of molecule is prevented, therefore the ultra violet spectrum of Ic should be similar to those of Ia, Ib, Id, and Ie in this medium (Table 2). The large red shift in the spectrum of the latter molecules in concentrated sulphuric acid is attributed to high polarity of the medium. In the mass spectra of I (Figure 1-5 (21)) $M^{\cdot+}$ not represent the basic peak, the general fragmentation depends on the kind of para substituent. The preferred fragmentation pathway of these compounds is shown in Scheme I. In the presence of electron withdrawing group the compound shows a base peak m/e 105 (fragment **5**. Scheme I) which takes place from the fragmentation of oxazine ring of the ion **3** (Scheme II) by elimination of carbon monoxide and hydrogen atom, respectively. The ion **3** may originate fragment **6** which is the precursor of the fragments **7** and **8** (22,23). In the presence of $N(CH_3)_2$ and OCH_3 substituents the compounds show a base peaks m/e 134 and 121 (fragment **2**, Scheme I), respectively, which take place from the elimination of HNCO molecule from the $M^{\cdot+}$ ion followed by elimination of a phenyl radical, the mechanism of such fragmentation is illustrated in Scheme III. The mechanism of fragmentation of Ib and Ic confirms our conclusion concerning the responsibility of the 357 nm band in the uv absorption spectrum of Ic being due to the high conjugation owing to charge delocalization in the

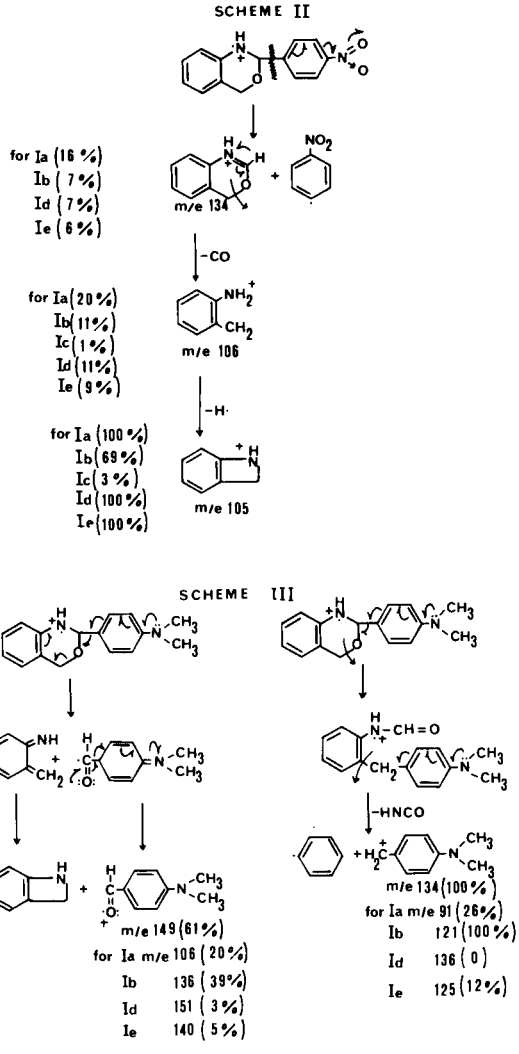
Table 1

Analyses and Infrared Absorption Bands of 1,2-Dihydro-4*H*-2-phenyl-3,1-benzoxazines

Compound No.	Mp °C	Calculated %				Found %				Infrared Bands (nujol mull)	
		C	H	N	Cl	C	H	N	Cl	$(Cm)^{-1}$	Assignment
Ia	119-120	79.6	6.2	6.6		79.4	6.3	6.7		3345	NH
										1090	C-O
Ib	135-136	74.0	6.2	5.8		73.9	6.2	6.0		3345	NH
										1095	C-O
Ic	136-137	74.0	7.1	11.0		73.9	7.0	11.1		3345	NH
										1080	C-O
Id	114-115	65.6	4.7	10.9		65.4	4.8	11.1		3350	NH
										1095	C-O
Ie	123-124	68.4	4.9	5.7	14.5	68.5	5.1	5.5	14.5	3350	NH
										1090	C-O

The ultraviolet spectra show a three $^{*}\pi \leftarrow \pi$ transitions, at 290, 248 and 212 nm for Ia. Apparently, these transitions are originating from π bands of the two phenyl ring of I (18) and their positions are only slightly affected upon *para* substitution of Cl, NO_2 and OCH_3 substituents (Table 2).

direction $N(CH_3)_2$ to the other part fo the molecule. Compounds Ia and Ic show a base peak m/e 105 and 134 which represent mostly the fragments **5** and **2** (R = $N(CH_3)_2$) with a very limited contribution from the fragments **10** (R = H) and **3**, respectively. Contribution from fragments **4** and **9** (R = H) makes the relative abundance of the ion 106 for compound Ia high relative to the other derivatives.



EXPERIMENTAL

Elemental analyses and mass spectra were preformed by the Alfred Berhardt, Mikroanalytishes Laboratorium, West Germany, melting points are uncorrected. The mass spectra were obtained on an SM 1B with data system SS 100 (Varian MAT) mass spectrometer at 70 ev and ion source temperature of 190°, the direct inlet system was used. The uv-visible and ir spectra were measured on a Pye-Unicam Sp8-200 uv-visible spectrophotometer and Pye-Unicam Sp3-300 ir spectrophotometer, respectively.

Table 2

Ultra-violet Absorption Bands of Substituted 1,2-Dihydro-4*H*-2-phenyl-3,1-benzoxazines

Compound No.	λ max (nm) (log ε) Ethanol	Concentrated Sulphuric acid
Ia	285-295 (sh) (2.29) 248 (2.77) 212 (3.22)	322 (3.44) 280 (sh) (3.33) 212 (sh) (3.36)
Ib	275-285 (3.21) 242 (2.82) 220 (3.17) 210 (3.18)	350 (3.08) 290 (sh) 212 (sh)
Ic	357 (3.35) 315 (sh) 265 (sh) 238 (3.05) 205 (3.28)	320 (3.32) 270 (3.25) 212 (sh) (3.24)
Id	295 (sh) (2.57) 255 (3.03) 207 (3.20)	320-324 (3.16) 280 (3.37) 213 (3.24)
Ie	290-300 (sh) (2.57) 250 (3.02) 217 (3.44)	324 (3.38) 280 (sh) 214 (3.15)

1,2-dihydro-4*H*-2-phenyl-3,1-benzoxazine.

This compound was prepared by direct fusion of equimolar quantities of the corresponding aldehyde and *o*-aminobenzylalcohol. On cooling, a crystalline product in every case separated and was collected and recrystallized from ethanol. Elemental analyses and infrared absorption bands are shown in Table 1.

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