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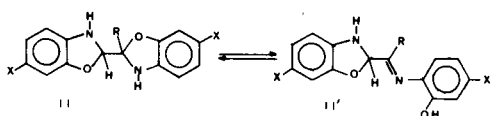
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The tautomeric structure of 2,2'-dibenzoxazolines 2'-substituted with heterocycles was investigated by ir, pmr and uv spectroscopy.

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As reported in the preceding paper (1), there was obtained, together with other products, 2,2'-dibenzoxazolines 2'-substituted with heterocycles II whose interesting tautomeric behaviour required a very careful investigation.



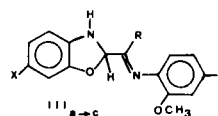
- IIa: R = 2-furyl, X = H
 IIb: R = 2-thienyl, X = H
 IIc: R = 3-thienyl, X = H
 IId: R = 2-thienyl, X = NO₂
 IIe: R = 3-thienyl, X = NO₂
 IIg: R = phenyl, X = NO₂

By ir spectroscopy the tautomeric ketimine structure II' was confirmed only for the compounds IIa and IIb; in fact in chloroform solution, together with the ν NH at 3420 cm⁻¹, the ν OH at 3590 and 3580 cm⁻¹, respectively, occurs.

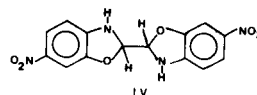
The pmr spectra of the same products, on the other hand, show a singlet at δ 9.17 for IIa, δ 9.35 for IIb, attributable to the OH proton; moreover, for the particular chemical environment, the H^a undergoes, with respect to the dibenzoxazoline form II, a down-field shift, while the H^b an up-field shift, resulting in a doublet ($J = 10$ Hz) at about δ 5.5 as found for the analogous compounds III with a blocked structure (See Experimental). Upon addition of deuterium oxide, the signals due to the OH proton and H^b disappear and the H^a results a singlet at δ 6.25 for IIa and δ 6.85 for IIb. The spectra of IIc and IIe-g, on the contrary, always show two doublets ($J = 4.5$ Hz) due to the coupling between H^a and H^b. Upon addition of deuterium oxide the NH signals are no longer present while a singlet for the methine proton H^a appears (Table 1).

Important results were obtained by the study of the ultraviolet spectra. The spectra of IIa-c in methanol solution show that IIa and IIb exist almost entirely in the ketimine form; IIc, too, partially exhibits such a tautomeric structure. Comparing these spectra with the same upon addition of alkali, displacing therefore the equilibrium towards the open chain compounds, and with the ones of the related blocked methoxy derivatives

IIIa-c in methanol, the approximate composition of the equilibrium mixture was determined.



The analysis of the spectra was performed assuming the bands to have a symmetrical shape and subtracting from the overall spectrum a symmetrical band that we fit by a Gauss function (2). It is possible in this way to split the spectrum into its presumed component bands and to calculate the approximate oscillator strength value of the chosen one, here of the band corresponding to the absorption of the ketimine system. Compounds IIa, IIb and IIc result in the tautomeric structure II' in the percentages of about 85, 100 and 40, respectively (Table 2). Otherwise the spectra in methanol solution of the compounds IIe-g were found to be unaffected by the 2'-substitution and closely similar to that of 6,6'-dinitro-2,2'-dibenzoxazoline IV, supporting, therefore, the sole tautomeric dibenzoxazoline structure II as expected from pmr data.



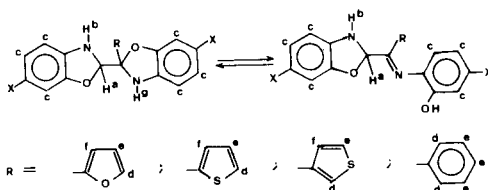
In 0.5 *N* sodium hydroxide (methanol/water) solution, moreover, there is no chain-opening reaction in the 2'-substituted benzoxazoline ring, unlike in the case of compounds IIa-c, however, a partial hydrolysis occurs. This explains why we never obtain the methoxy derivatives corresponding to the ketimine structure of these compounds. In such a solution compound IV is completely hydrolysed and its spectrum corresponds, with double absorptivity, to the one of the 2-amino-5-nitrophenate ion (3) (Table 3).

EXPERIMENTAL

The ir spectra were measured with a Perkin-Elmer Model 417 spectrophotometer and the pmr spectra on a Perkin-Elmer R 32 instrument at a probe temperature of 38°. The uv spectra were recorded on a Cary Model 14 spectrophotometer. Melting points are uncorrected.

Table 1

Analytical and Spectral Data of 2,2'-Dibenzoxazolines IIa-c and IIe-g



Compound	M.p. °C Solvent	Formula	Analysis (a)			Ir, ν max cm^{-1} (b)	PMR δ , ppm (c)
			C	H	N		
IIa	178-179 benzene	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3$	65.12 (65.36)	4.46 4.31	5.53 5.44	3360,1610,1500,1235,1035, 9.40,7.50. (3590,3420).	9.17 (s, OH), 7.83 (m, H^d), 7.38 (m, H^e), 6.85 (m, $\text{H}^c + \text{H}^f$), 6.25 (d, H^a , $J = 10$), 5.43 (d, H^b , $J = 10$).
IIb	176-178 ligroin	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	66.97 (67.06)	4.54 4.38	8.45 8.69	3420,3380,1610,1515,1230, 1010,955,750, (3580,3420)	9.35 (s, OH), 7.85 (m, H^d), 7.70 (m, H^e), 7.10 (m, $\text{H}^c + \text{H}^f + \text{H}^g$), 5.62 (d, H^a , $J = 10$).
IIc	169-170 chloroform	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	66.94 (67.06)	4.32 4.38	8.91 8.69	3380,1610,1500,1230,1040, 960,750. (3410).	7.43 (m, $\text{H}^d + \text{H}^e$), 7.34 (broad, H^f), 7.18 (m, $\text{H}^b + \text{H}^g$), 6.72 (m, H^c), 5.52 (d, H^a , $J = 4.5$).
IIe	205-206 benzene	$\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_6\text{S}$	52.23 (52.42)	2.89 2.93	13.40 13.59	3380,1610,1510,1320,1230, 1080,980,740.	8.80 (broad, H^f), 8.65 (d, H^b , $J = 4.5$), 7.30 (m, $\text{H}^c + \text{H}^d + \text{H}^e + \text{H}^g$), 6.20 (d, H^a , $J = 4.5$).
IIf	219-220 acetone/water	$\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_6\text{S}$	52.30 (52.42)	3.00 2.83	13.72 13.59	3410,3400,1600,1510,1320, 1230,1080,1010,750.	8.80 (s, H^f), 8.66 (d, H^b , $J = 4.5$), 7.35 (m, $\text{H}^c + \text{H}^d + \text{H}^e + \text{H}^g$), 5.97 (d, H^a , $J = 4.5$).
IIg	232-233 acetone/water	$\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_6$	58.90 (59.11)	3.45 3.47	13.56 13.79	3400,3380,1600,1510,1320, 1230,1080,1000,750.	8.80 (s, H^f), 8.65 (d, H^b , $J = 4.5$), 7.30 (m, $\text{H}^c + \text{H}^d$), 6.02 (d, H^a , $J = 4.5$).

(a) Values in parentheses refer to calculated percentages. (b) Potassium bromide; values in parentheses refer to chloroform solution. (c) DMSO- d_6 solution; TMS as internal reference; coupling constants are reported in Hz; chemical shifts quoted in the case of multiplets were measured from the approximate center.

Table 3

Ultraviolet Spectral Data of Compounds IIe-g and IV

Compound	Solvent	λ max nm, (Log ϵ)	f
IIe	MeOH	215 sh, 235 sh, 252 (4.16), 310 sh, 367 (4.47).	0.38 (374)
	NaOH 0.5 N	252 (4.22), 272 (4.28), 384 (4.41), 460 sh.	0.59 (384)
IIf	MeOH	230 sh, 258 (4.12), 310 sh, 367 (4.40).	0.37 (374)
	NaOH 0.5 N	251 (4.17), 276 (4.19), 384 (4.40), 460 sh.	0.59 (384)
IIg	MeOH	235 sh, 258 (4.14), 315 sh, 365 (4.36).	0.35 (374)
	NaOH 0.5 N	275 (4.16), 384 (4.40), 460 sh.	0.59 (384)
IV	MeOH	245 sh, 259 (4.16), 315 sh, 368 (4.40).	0.38 (374)
	NaOH 0.5 N	230 (4.23), 278 (4.30), 365 (4.05), 462 (4.26).	0.40 (462)

Table 2

Ultraviolet Spectral Data of Compounds IIa-c and IIIa-c

Compound	Solvent	λ max nm, (Log ϵ)	f (a)
IIa	MeOH	239 (4.22), 297 (4.15), 330 (4.20).	0.34 (338)
	NaOH 0.5 N	242 (4.23), 3.03 (4.27), 335 (4.27).	0.40 (338)
IIb	MeOH	240 (4.21), 285 (4.04), 295 (4.04), 343 (4.20).	0.28 (350)
	NaOH 0.5 N	249 (4.16), 304 (4.12), 347 (4.19).	0.28 (350)
IIc	MeOH	238 (4.29), 292 (4.12), 320 sh.	0.12 (335)
	NaOH 0.5 N	240 (4.33), 298 (4.28), 320 sh.	0.29 (335)
IIIa	MeOH	241 (4.29), 295 sh, 332 (4.26).	0.40 (338)
IIIb	MeOH	242 (4.29), 284 (4.02), 294 (4.02), 343 (4.20).	0.28 (350)
IIIc	MeOH	242 (4.44), 288 (4.27), 320 sh.	0.29 (335)

(a) The oscillator strength was calculated using the formula $f = 4.32 \cdot 10^{-9} \epsilon \max \sqrt{\pi \theta}$; the values in parentheses refer to the appropriate wave length found for the determination.

Methylation of compounds IIa-c to give IIIa-c. (General Procedure).

A mixture of II ($2.0 \cdot 10^{-3}$ mole), potassium carbonate ($2.0 \cdot 10^{-3}$ mole) and methyl iodide ($1.5 \cdot 10^{-2}$ mole) in methanol (70 ml.) was boiled for 10 hours. After cooling the precipitate was filtered, washed with cold methanol and recrystallized from petroleum ether (60-80°).

Compound IIIa.

This compound was obtained as a yellow powder, m.p. 181-182°; ir (potassium bromide): 3320, 1600, 1510, 1345, 1245, 755, 730 cm^{-1} ; pmr (DMSO- d_6): δ 7.93 (m, 1H), 7.45 (m, 1H), 6.96 (m, 10H), 5.75 (d, 1H, J = 10 Hz, NH), 3.65 (s, 3H, OCH₃). Upon addition of deuterium oxide the doublet at δ 5.75 disappears while a singlet at δ 6.75 appears.

Anal. Calcd. for C₁₉H₁₈N₂O₂S: C, 71.46; H, 4.73; N, 8.77. Found: C, 71.63; H, 4.93; N, 8.85.

Compound IIIb.

This compound was obtained as a pale yellow powder, m.p. 183-185°; ir (potassium bromide): 3320, 1595, 1510, 1315, 1240, 760, 730 cm^{-1} ; pmr (DMSO- d_6): 7.85 (m, 1H), 7.68 (m, 1H), 7.15 (m, 10H), 5.85 (d, 1H, J = 10 Hz, NH), 3.66 (s, 3H, OCH₃). Upon addition of deuterium oxide the doublet at δ 5.85 disappears while a singlet at δ 6.75 appears.

Anal. Calcd. for C₁₉H₁₈N₂O₂S: C, 68.04; H, 4.51; N, 8.35. Found: C, 67.95; H, 4.73; N, 8.22.

Compound IIIc.

This compound was obtained as a pale yellow powder, m.p. 144-145°; ir (potassium bromide): 3320, 1590, 1510, 1320, 1240, 760, 730 cm^{-1} ; pmr (DMSO- d_6): 8.20 (m, 1H), 7.70 (m, 2H), 7.18 (m, 9H), 5.70 (d, 1H, J = 10 Hz, NH), 3.60 (s, 3H, OCH₃). Upon addition of deuterium oxide the doublet at δ 5.70 disappears while a singlet at δ 6.80 appears.

Anal. Calcd. for C₁₉H₁₈N₂O₂S: C, 68.04; H, 4.51; N, 8.35. Found: C, 68.07; H, 4.50; N, 8.40.

REFERENCES AND NOTES

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- (3) J. F. Corbett, *Spectrochim. Acta, Part A*, **23**, 2315 (1967).