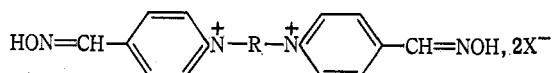


SHORT COMMUNICATIONS

THE INFRARED SPECTRA OF BISPYRIDINIUM OXIMES

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This paper describes the spectra of isomeric oximes of a number of pyridinium compounds having the general formula :



	R =	X =
(I) ;	—CH ₂ —	Br
(II) ;	—CH ₂ —CH ₂ —	Br
(III) ;	—CH ₂ —CH ₂ —CH ₂ —	Br
(IV) ;	—CH—CH—CH—CH—	I
(V) ;	—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —	Br
(VI) ;	—CH ₂ —CH ₂ —O—CH ₂ —CH ₂ —	Br
(VII) ;	—CH ₂ —CH ₂ —S—CH ₂ —CH ₂ —	Cl
(VIII) ;	—CH ₂ —CH ₂ —SO ₂ —CH ₂ —CH ₂ —	Cl

The bispyridinium oximes decompose on melting and are extremely insoluble in all solvents except water, in which they dissolve readily. The absorption frequency of the OH stretching mode in the oxime group has been found by Palm and Werbin (1953) to be characteristic of the α - and β -configurations in the case of several aromatic oximes (e.g. benzaldoxime and *p*-nitrobenzaldoxime) : α - and β -forms are those in which the H and OH groups are respectively *cis* and *trans* to one another. Palm and Werbin (1954) also found no significant correlation between structure and the OH deformation mode, except in solution. The OH stretching frequency in the solid state has therefore been used to characterize the isomers : the OH deformation has also been studied and ranges assigned to each configuration.

Experimental

Spectra were recorded on a Perkin-Elmer model 112 double-pass spectrometer equipped with lithium fluoride and rock-salt prisms. In the short-wave region samples were examined in silver iodide disks to avoid bonded OH bands in alkali halide disks but potassium bromide disks were used with the rock-salt prism. Duplicates did not differ by more than $\pm 1.5 \text{ cm}^{-1}$ in the spectral regions covered.

The oximes were prepared according to the method of Poziomek, Hackley, and Steinberg (1958).

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Results and Discussion

The bands observed in the regions of interest are given in Table 1. Palm and Werbin (1953) working with Nujol mulls, assign a medium band, sometimes broad, near 3250 cm^{-1} to the OH stretch of α -oximes and a broad, medium to weak absorption near 3115 cm^{-1} to the β -isomer.

TABLE 1
STRETCHING AND BENDING HYDROXYL FREQUENCIES IN OXIMES

Compound	ν_{OH}		δ_{OH}		Isomers Present
	α - (cm^{-1})	β - (cm^{-1})	α - (cm^{-1})	β - (cm^{-1})	
Pyridine-4-aldoxime (II) (III)	3229(s)	3125(s) 3150(s)	1314(s)	1284(s) 1295(s)	α β β
(I)	3228(m)	3132(m)	1307(m)	1293(s)	$\alpha = \beta$
(IV)	3230(s)		1324(m)	1281(s)	$\alpha > \beta$
(V)	3250(s)	3113(ms)	1309(m)	1294(s)	$\alpha = \beta$
(VI)	3214(s)	3114(ms)	1318(m)	1289(w)	$\alpha > \beta$
(VII)	3220(w)	3108(wm)	1317(w)	1300(s)	$\alpha < \beta$
(VIII)	3230(wm)	3113(m)	1310(s)	1301(w)	$\alpha > \beta$

The OH bending vibration absorbs between 1000 and 1420 cm^{-1} in a variety of compounds (Bellamy 1958): a band near 1300 cm^{-1} in α -*p*-nitro- and *p*-chloro-benzaldoximes is absent in the O and N methyl ethers (Palm and Werbin 1954) and deuteration of 1,2-cyclohexadione dioxime suppresses a strong 1300 cm^{-1} band (Voter *et al.* 1951), which is therefore assigned to the OH deformation mode.

TABLE 2
SUGGESTED ASSIGNMENTS OF STRETCHING AND BENDING FREQUENCIES IN OXIMES

Mode	Range	Mode	Range
ν_{OH}	α 3214–3250(s) β 3108–3132(ms)	δ_{OH}	α 1307–1324(m) β 1281–1301(s)

The configurations of (I), (II), and (III) were characterized by the ν_{OH} band which indicated a general assignment of the δ_{OH} vibration: α -isomers absorb above 1300 cm^{-1} and β -isomers at a lower frequency. When this assignment was applied to the remaining compounds together with the ν_{OH} criterion, the configurations could be ascertained. The use of the δ_{OH} assignment was especially useful when both isomers were present: this absorption band is sharper than that of the stretching mode and a better estimate of relative concentration is obtained. The consistency between the configurations determined by ν_{OH} and δ_{OH} is a

measure of the success of the assignment. Table 2 shows the regions in which these compounds fall; these are in agreement with the results of Palm and Werbin (1954). Although the two sets relating to the δ_{OH} almost overlap, the higher precision now attained enables them to be differentiated.

Nightingale and Wagner (1954) have shown that the N—O stretching frequency in hydroxylamine is 912 cm^{-1} . All the compounds examined have at least one band near this value but there was no correlation between *cis,trans*-isomerism and the N—O absorption frequency in the solid state. Reported frequency shifts for benzene solutions of oximes could not be verified due to insolubility.

Conclusions

The configurations of a series of bispyridinium oximes have been determined by the study of the OH stretching and bending modes. The OH deformation frequency in these oximes has been assigned to narrow distinct ranges for α - and β -isomers: earlier assignments for the OH stretching mode have been verified.

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