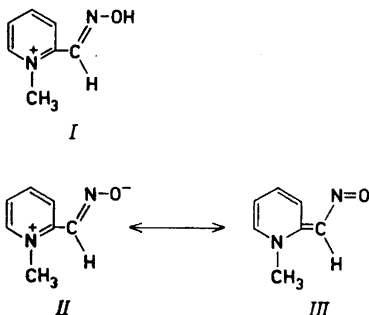


## The Structure of N-Methyl-pyridinium-2-aldoxime

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The iodide and methane sulphonate salts of N-methyl-pyridinium-2-aldoxime (I), generally denoted as 2-PAM and P2S, respectively, have been reported to be effective antidotes against poisonings caused by toxic organo-phosphorus compounds<sup>1,2</sup>. Studies on the renal excretion of P2S have shown that the excretion is markedly reduced by alkalization of the urine indicating that the dissociated, basic form (II) is more lipophilic than the acid form (I)<sup>3</sup>. Furthermore the solubility of the basic form in chloroform is about 2.5% which is unexpectedly high for a "zwitterion".



These lipophilic properties of the basic form indicate that the basic form may exist as a resonance hybrid of the structures II and III. In order to throw light on the resonance conditions in the basic form this compound has been isolated by an anion-exchange technique, and its dipole moment has been determined. Moreover its infrared spectrum has been recorded and compared with the spectrum of 2-PAM.

Presuming a coplanar configuration of the molecule, the dipole moment of the purely ionic structure (II) can approximately be calculated from the bond angles and atomic distances. The lowest moments which in this way can be predicted, are 13.0 D for the *anti* form and 20.6 D for the

Table 1. The principal absorption frequencies of 2-PAM and its basic form in the region 1 000—1 700  $\text{cm}^{-1}$ . (Figures within parentheses denote shoulders.)

Absorption frequencies in $\text{cm}^{-1}$ of		
2-PAM	Basic form	Assignments <sup>5</sup>
1003	—	N—OH
—	1140	N—O <sup>-</sup> ( $\leftrightarrow$ )N=O
1166	1179	C—H
1179	1192	C—H
1235	(1262)	
1292	1285	
1311		O—H (?)
1321	1337	
(1403)		O—H (?)
1427	1431	C—H
(1445)	1456	Pyridine nucleus and C=N (oxime group)
(1456)	1471	
1502	1499	
1575	1560	
1590	—	
1623	1634	

*syn* form. In which of these forms the compound really exists has not yet been established<sup>4</sup>. The dipole moment of the basic form was found to be 7.7 D in a chloroform solution. This value is probably 20—30% too low, because the determination was performed in a polar solvent. The found value, however, is considerably lower than the lowest calculated one, which supports that the quinoid structure (II) to a certain extent contributes to the structure of the molecule.

In a comparison between the infrared spectra of the acidic and basic forms in the region 1 000—1 700  $\text{cm}^{-1}$  two obvious differences are shown which appears from Table 1 where the principal absorption bands in this region are given. In the spectrum of the acidic form the strong absorption band originating from the N—OH bond<sup>5</sup> is found at 1 003  $\text{cm}^{-1}$  but in the spectrum of the basic form the corresponding band occurs at 1 140  $\text{cm}^{-1}$ . A large increase of the frequency is expected to occur when N—OH is changed to N—O<sup>-</sup> or N=O. The latter structure will cause the largest frequency shift, still larger than the found one, which indicates that the structure II is predominant. More remarkable is the absence of the band in the spectrum of the basic form at 1 590  $\text{cm}^{-1}$  which appears in